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Modern Physical Chemistry for Advanced Materials

devoted to the 100th anniversary of the birth of Professor Nikolai Izmailov

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Conference “Modern Physical Chemistry for Advanced Materials” is devoted to the 100th anniversary of the birth of the outstanding physico-chemist Professor Nikolai Izmailov (1907-1961).

Kharkov University has got long-standing traditions in physical chemistry. A great Russian chemist, Professor Nikolai Beketov (1827–1911) established the physico-chemical division as early as in 1864. In 1865, Beketov delivered the first course in physical chemistry. At the end of the XIX century and beginning of the XX century, Professors P. D. Khrushchov, V. F. Timofeyev, G. E. Timofeyev, and many other scientists contributed to the field of physical chemistry, mainly in solution chemistry. A number of outstanding chemists elaborated physical chemistry in Kharkov before the World War II. Among them are G. E. Mukhin, A. N. Shchukarev, I. S. Teletov, P. P. Kosakevitch, E. N. Gapon, S. S. Urazovskiy, I. N. Frantsevich, and N. A. Izmailov.

Nikolai Arkadievich Izmailov [PhD (1937), ScD, Professor (1948), Corresponding Member of the Ukrainian Academy of Sciences (1957)] headed the Department of Physical Chemistry of Kharkov State University from 1944 to 1961. All his scientific activity was connected with Kharkov University and Kharkov Pharmaceutical Research Institute.

Two main directions of scientific interests of Nikolai Izmailov were (i) the influence of the solvent on dissociation of electrolytes; (ii) statics and dynamics of sorption from solutions. In 1938 he discovered the thin layer chromatography (together with M. Shraiber). In 1930th Izmailov investigated the possibility of application of various indicator electrodes, especially glass electrodes, in organic solvents. In 1930th – 1950th, he proposed the most detailed scheme of electrolytes dissociation in solutions, generalized the concept of unique acidity scale in different solvents, proposed several new methods for estimating Gibbs energy of ion solvation, and contributed a lot to the theory of physico-chemical analysis. Izmailov was one of the pioneers in application of radioactive indicators in physical chemistry.

Izmailov is the author of more than 270 publications; his treatise ‘Electrochemistry of Solutions’ (1959) is well known to those working in the field of solution chemistry and still is frequently cited.

31 persons got PhD degree under Izmailov’s supervision and 11 got ScD degree (A. M. Shkodin, V. N. Eremenko, V. D. Bezugliy, V. V. Aleksandrov, E. F. Ivanova, E. V. Titov, Yu. A. Krugliyak, O. M. Konovalov, V. P. Georgievskiy, V. D. Chmil, V. I. Lebed).

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PLENARY PRESENTATIONS

ULTRAMICROELECTRODES AND BIOLOGY OF THE LIVING CELLS AND LIVING TISSUES: “GOOD” AND “BAD” SIDES OF OXIDATIVE STRESS

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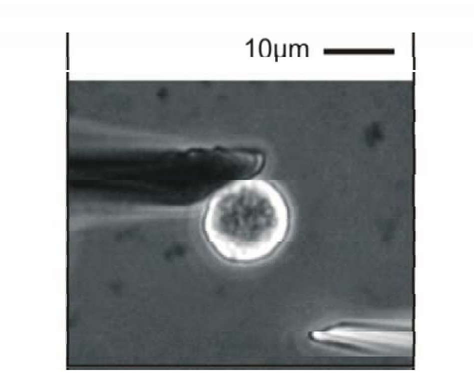
Living cells exchange informations through the emission of several chemical messengers including hormones and neurotransmitters. The importance of such messengers has been widely recognized by biologists and physicians. However what is less understood is how these chemical messengers are released by the cell in its outer-cytoplasmic fluids or in its surrounding tissues. This difficulty is easily understood when one becomes aware that most of these releases occur in the zepto- to femtomole ranges which prevents the use of classical analytical methods. We wish to show here that using the concept of artificial synapse with ultramicroelectrodes is extremely useful for monitoring such events with sufficient accuracy and precision so that the delicate physicochemical and biological mechanisms which sustain them may be revealed.

Electrochemical data obtained at ultramicroelectrodes allow to describe quantitatively the kinetics of the whole process with a precision that has never been achieved before by patch-clamp techniques or spectroscopic near-field methods. This enables to investigate finely these events and to identify the exact physicochemical nature of all the individual physicochemical and biological factors which concur to produce vesicular release.

The same methodologies allow also for the first time to characterize the nature and kinetics of functional hyperemia, viz., of the fine tuning between neuronal activity and local command of the blood flux supply in the brain. This process, investigated in rat cerebellum slices is shown to involve a timely and local release of an important flux of NO° while neurons are active.



View of the “artificial synapse” configuration showing a single chromaffin cell (center) and the ultramicroelectrode positioned above its surface, together with a micropipette (right bottom) used for eliciting the adrenaline release

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INVENTION OF THIN-LAYER CHROMATOGRAPHY BY N. A. IZMAILOV AND M. S. SHRAIBER AND MODERN PERSPECTIVES OF TLC DEVELOPMENT

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N.A.Izmailov and M.S.Shraiber published the first paper on thin-layer chromatography (TLC) in Kharkov in 1938 in Farmatsiya, №3, pp.1-7. That work presented the first description of TLC on an unfixed sorbent layer and also of the following its important variants: 1) circular TLC, 2) frontal circular TLC, 3) eluent circular TLC, and 4) frontal-eluent circular TLC.

That work has been reproduced at A.V. Topchiev Institute of Petrochemical Synthesis, Russian Acad. Sci. Results of our historical-chromatographic research practically repeated the results of the pioneering work on TLC, however, substantially better results have been obtained using up-to-date plates (Merck, Germany) with fixed adsorption layer based on Al_2O_3.

Over the last decades new non-traditional variants of TLC (NTV-TLC) with closed sorption layer have been introduced which allow to consider these variants as a flat column. This novel variant of TLC was first suggested by Hungarian researches E.Tyihak, E.Mincovics, and H.Kalasz in 1979-1981. Its use enabled to increase efficiency and to accelerate the separation process, however, a more complex equipment was needed.

Later on, simpler and more economic non-traditional variants of TLC have been suggested which either did not require external pressure for the mobile phase, or used only insignificant pressure (not exceeding 100 мм Hg.). Systematization of new "non-camera" methods of column TLC has been made and the relevant terminology has been discussed.

It appears also appropriate to consider a column micro-variant of chromatography where quarz or polymer capillaries packed with sorbent are used as columns. Apparently, such capillary columns can also be used in the same manner as a plate in TLC, i.e. after separation to scan such micro-columns in ultraviolet light or to use microdetectors. In conclusion we note that TLC is an important rapidly developing variant of chromatography playing an important role in medicine, drug manufacture, environmental protection, scientific research, and in many other fields.

PHYSICAL CHEMISTRY OF CYCLODEXTRIN COMPLEXES AND PHARMACEUTICAL APPLICATIONS

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Cyclodextrins (CDs) are doughnut-shaped molecules, formed from D(+)-glucose units linked in a cycle. Because the interior of the cavity of CD has a relative hydrophobic environment, nonpolar molecules can be trapped hereinto.

Almost all of physicochemical methods can be used to determine the binding constant between CD and guest. The NMR chemical shift method provides the binding constant as well as structural information. Each of the internal and external standards for the chemical shift has the merit and demerit. The surface tension method is based on no surface activity of CD and its complex.

The solution structure of a CD complex can estimated from the chemical shift change, the ROESY spectrum, the vicinal spin-spin coupling constant, and molecular modeling calculations. The solution and crystal structure of the complex are very close to each other for most complexes, although they are different for a few complexes. The complex is stabilized mainly by hydrophobic interactions. It is demonstrated that the binding constant is correlated to the molecular surface area change with complex formation.

For detailed analysis of the binding constant, the molar ratio of CD to guest and the solution structure of the complex are needed. The molar ratio and the solution structure depend on the size of cavity of CD. A multi-valent guest can form a few complexes with CD stepwise, where the equivalence and cooperativity of the binding sites must be investigated. For a multi-conformational guest the binding constant depends on the conformation. For these guests microscopic binding constants must be estimated.

CDs can stabilize labile drugs and can suppress the hemolytic activity and the bitter taste of drugs. These applications will be explained on the basis of complex formation.

CONTRIBUTION OF N. A. IZMAILOV TO QUALITY CONTROL AND DEVELOPMENT OF DRUGS

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SE "SSCD", the Ministry of Public Health of Ukraine

The development and quality control of drugs are impossible without analytic providing of manufacturing methods, starting with the search of bioactive compounds and finishing at quality control of prepared drugs.

Thereupon by the example of conducted studies in SSCD (earlier "Kharkov research chemical – pharmaceutical institute") – leading scientific centre at the development of drugs - under the direction of Corresponding Member of the National Academy of Sciences of Ukraine Izmailov N.A. and continuators of his school, basic works at the field of the chromatography, the theory of acid-base titration at nonaqueous media and the development at the base of this methods procedures of drugs quality control and their manufacture were examined.

In 1938 by Izmailov N.A. and Shraiber M.Ya. the article “Drop–chromatographic method of the analysis and its application in the pharmacy” at the “Pharmacy” journal was published. This article was acknowledged all over the world to be the work, which initiated the method of thin-layer chromatography. At the resume, which was done by authors at mentioned article, concretely, with no broadcast generalizations, was noticed: “Drop–chromatographic method can be used for qualitative assessment of galena drugs and their identification”.

TLC method suffered rapid development, especially in pharmacy, biology, medicine, enclosed different classes of organic and inorganic compounds. System studies at chromatographic behavior of cardiosteroids, flavonoids, coumarins, anthraquinones, alkaloids, etc. under the direction of Georgiyevskiy V.P. and Grizodub A.I. were conducted in SSCD. It was the base of efficient choice of solvents systems for effective separation of compounds of mentioned classes in aggregate drugs, raw herbal drugs and prepared drugs. It was made certain steps at the development of theoretical progress at the optimization of chromatographic separation in binar mobile phase at established sorbent and it was deduced linear equation, which connected R_m value of two chromatographic substances at the changing of the composition of one and the same solvents. Theoretical analysis also allowed to pose criteria of solvents choice for ternary mobile phase. TLC has wide application in pharmaceutical industry for the identification of drugs, the detection in them impurities and quantity assessment of the last, quantity assessment of biologically active substances in phytochemical preparations and raw herbal drug, in – process control coupled with polarography, potentiometry, spectrophotometry and fluorimetry.

Born in pharmaceutical institution – SSCD, today TLC is a part of pharmacopoeia of USSR, USA, Switzerland, Great Britain, France, Japan, International and European Pharmacopoeia and State Pharmacopoeia of independent Ukraine as general and particular monographs.

Next basic work at the field of drug quality control was the development of accelerated method of the assessment of liquid drug forms stability (1944), based on the data of hydrolysis rate from pH medium and temperature. This method, developed in the fifties–sixtieth years of last century by Izmailov N.A. followers as well as foreign researchers and got a name “ accelerated ageing testing”, allowed to forecast drugs expiry and had wide spread occurrence in the pharmacy. Today with the development of chromatographic method of TLC, HPLC, GLC, “accelerated ageing testing” allows to accelerate the development of new drug forms and it is an instrument of technologists at their work at the development of prepared drugs.

Under the direction of Izmailov N.A. basic studies at the field of the chromatography at the development of drugs on statics and dynamics of sorption of natural drugs on molecular and ion-exchange sorbent were conducted in SSCD. At the same time manufacturing methods of this substances isolation from extracts of raw herbal drugs were developed. At the base of these studies by Izmailov N.A. with Shostenko Yu.V., Mushinskaya S.M., Shein A.T. and others “Basis of adsorption technology of substances isolation from solutions” and “Plan of continued adsorption method of isolation of natural drugs from raw herbal drugs extracts” were developed and published.

Results of Izmailov N.A. and his collaborators studies at the field of theory and practice of adsorption processes of drugs production were introduced in manufactures of USSA, Bulgaria, Slovakia, Slovenia and are actual to present day. They are widely used in the development of production methods of drugs from raw herbal drugs.

Works at the use of nonaqueous solvents for acid-base titration by Izmailov N.A. at the end of the forties of the twentieth century were begun.

At the result of these studies was developed quantitative theory of the influence of nonaqueous solvents to the force of electrolytes. At that one of basic thesis of this theory was quantitative assessment of different cases of acid-base titration in nonaqueous solvents. Results of these studies in the book “Electrochemistry of solutions” in 1959 were generalized. We mast also underscore that because of this basic monograph the method of acid-base titration in analytical chemistry was developed in USSA and other countries. At a later time in SSCD by laboratory of analytical chemistry under the direction of Dzuba N.P. and Georgiyevskiy V.P. the method in the State Pharmacopoeia of USSR in IX–XI Edition and to the State Pharmacopoeia of Ukraine was introduced. This method was extended to quality control of drugs and prepared drug dosage forms, which were containing sulfanilamides, barbiturates, derivatives of pyrazolone, cardiac glycosides, alkaloids, coumarins, flavonoids and other classes of biologically active substances. It was shown that pk$_T$ value is a criterion of the possibility and the precision of the titration and is determined by two basic values: the constant of the dissociation (K_D) of the substance and the constant of solvent–ion product of the medium (K_i).

At the base of these values we can determine pk$_T$ value for concrete case and, consequently, find out the possibility of the conducting of quantitative acid-base titration in some solvent.

The selection of the solvent also can be done at the base of linear dependence between pk of acids and bases (which are in one group of chemical compounds) in the water and in nonaqueous solvents: acetone, dimethylformamide, acetic acid and acetic anhydride.

Studies, which were conducted in SSCD, promoted the conversion of nonaqueous titration to routine method of drugs analysis, widely used in their quality control.

It is significant that the discovery of the principle of the chromatography in thin layer of sorbent (Izmailov N.A., Shraiber M.S., 1938), the development of the theory of nonaqueous solvents effect on the strength of electrolytes (Izmailov N.A.), considered to be pioneer study and entered into “Chronology of most important events and discoveries in the chemistry” (Volkov V.A., Vonskiy B.V., Kuznetsova G.I. Outstanding chemists of the world. Bibliographic guide).

EXCEPTIONAL AFFINITY OF NANOSTRUCTURED ORGANIC-INORGANIC HYBRID MATERIALS TOWARDS GASES DUE TO THE CONFINEMENT OF COPPER COMPLEXES

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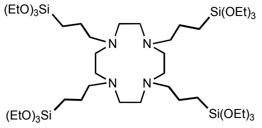
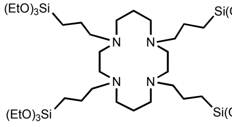
We will describe the use of tetraazacycloalcanes – mainly cyclen (1) and cyclam (2) – and tren (3) derivatives for the ultrapurification or the detection of gases. The metallic complexes of these tetra-amines are incorporated in a solid matrix to stabilize the active species after fixation of gas and to facilitate its regeneration.

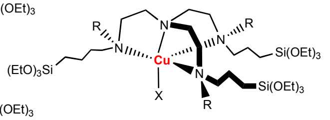
Firstly we will detail the methodologies of synthesis used to prepare the polyamine precursors of materials of xerogel or MTS types.



cyclen
1



cyclam
2



tren : R = Et or Bn ; X = Cl^- or Br^-
3

In the second section of the talk, we will describe the incorporation of copper tetraazamacrocycle or tripodal complexes within a silica matrix. The xerogels incorporating these copper derivatives exhibit a remarkable affinity towards dioxygen due to the reduction of Cu(II) complexes to Cu(I) species during the metalation and the activation step and their confinement in the silica matrix. After several adsorption-desorption cycles, a textural evolution of these materials is observed and the reactivity towards O_2 decreases. This observation prompted us to study a novel class of organic-inorganic nanocomposites named « Periodic Mesoporous Organosilicas », the PMOs, which exhibit a remarkable regularity of the structure with a homogeneous repartition of the organic moieties in the framework, a high stability of the texture and fine tuned porous diameter. These materials incorporating the above copper complexes show a similar affinity towards dioxygen but in contrast to xerogels their textural properties are almost identical after several adsorption – desorption cycles.

In the third part of the talk, we will show that copper tren complexes exhibit an exceptional affinity towards dioxygen or carbon monoxide depending on the nature of R group. The reactivity of these complexes incorporated in the walls of the silica matrix is drastically different from the one observed when they are grafted into the pores of the mesoporous material.

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SYNTHESIS AND APPLLICATIONS OF FUNCTIONALIZED SILSESQUIOXANES POLYMERS ATTACHED TO ORGANIC AND INORGANIC MATRICES

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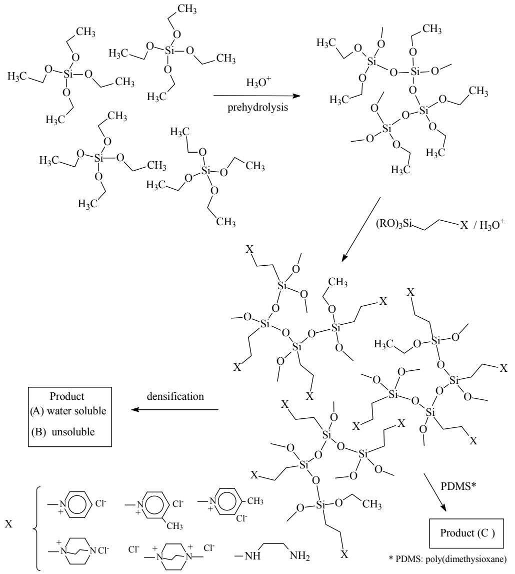
Organic functional groups attached to a silica structure have found many applications in several areas such as high capacity adsorbent materials, in pre-concentration and separation processes, as base to immobilize electroactive species viewing electrochemical applications, to prepare potentiometric sensors and adsorption of metals from non aqueous solvents. These materials normally are as water insoluble or depending on the amount of silica present in the structure, as water soluble polymers.

The silsesquioxane derivatives are obtained by the sol-gel processing method according to the following general procedure:

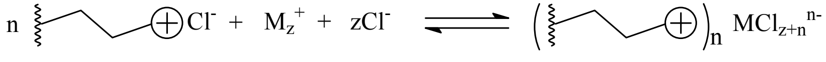


Schematic representation of silsesquioxane derivatives by sol-gel method.

The water soluble product (Product A) can be directly dispersed as a thin film of the polymer on a surface of SiO_2/Al_2O_3, Cellulose/Al_2O_3, C-graphite, Al_2O_3. The good adherence of (A) on the substrates coated with Al_2O_3 is due to the Al-O-Si bonding formation. On C-graphite surface the adherence occurs but the nature of interaction presumably is of electrostatic nature. The derivatives (B) and (C) were used as obtained.

Cationic groups attached on a solid phase surface were useful to immobilize electroactive species, such as $[Fe(CN)_6]^{4-}$ or $Co^{II}SPc^{4-}$ (TSPC: tetrasulphophthalocyanine) to study electrocatalytic oxidation of several molecules. Selective adsorption of some anions, *i.e.*, ClO_4^- or NO_2^-, allowed to construct electrodes for potentiometric or electrochemical selective determination of these anions.

Large ion exchange capacity solids have been prepared with these materials to adsorb metal ions from aqueous and non aqueous solvents. The adsorption process of metal halides MCl_z from aqueous and ethanol solutions on the solid-solution interface:



has been studied ha been studied in detail.

Acknowledgments: To FAPESP (São Paulo State Research Support Foundation) and CNPq (National Research Council) for research grants.

ELUCIDATION OF SPECIFIC ION-ASSOCIATION IN NON-AQUEOUS SOLUTION ENVIRONMENTS

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In aqueous solution, alkali metal and alkaline earth metal salts are regarded to be “indifferent salts” or supporting electrolytes, which should change the activity coefficients of ionic species. Although higher ion aggregates from 1:1 type electrolytes in low permittivity media ($\varepsilon_r < 10$) are widely accepted, only few chemists have recognized the higher ion aggregation in the higher permittivity media. However, we have clarified that the chemical interaction, such as coordination, can operate between anions and cations in non-aqueous solvents ($20 < \varepsilon_r < 65$) of low solvation ability. Acids (HA) and their conjugate base anions (A^-) may react each other to form homoconjugated species, such as $A^-(HA)_2$, in acetonitrile or benzonitrile, protophobic aprotic solvents with low hydrogen-bonding donor and acceptor abilities. After observing the direct reaction of some anions (e.g. Cl^-) and cations (e.g. Li^+) toward a certain species, we interpreted comprehensively the salt effects in chemical equilibria, on the basis of distinct chemical interaction and not mere a vague term, “medium effect.” The reaction manner similar to that in non-aqueous solution can take place even in some “aqueous” solution if the water structure of the aqueous solution is destroyed completely, because the properties of the bulk water should be arisen from the huge network of water molecules by hydrogen bonding; otherwise the properties of water must be reduced to just those of isolated H_2O molecules, in another term, “dihydrogen ether.” The chemical interaction between ions has been proved in “aqueous” solution of low water-structuredness with the addition of concentrated salts and non-aqueous solvents: a minor increase of the intermediate species which would never be observed in the chemical equilibrium sense was able to be multiplied into a measurable change in the chemical kinetic.

PHOTONICS AND MOLECULAR DESIGN OF DYE-DOPED POLYMERS FOR MODERN LIGHT-SENSITIVE MATERIALS

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The dye-doped polymers are unique photo-converters. Depending on structure, they may absorb and luminesce in the whole visible and near infrared region of the spectrum. Band shape can change from being strongly structured to being completely diffuse, from the narrow to the wide. The fluorescence quantum yield and the lifetime lie within the limits of 0.01 - 100% and 10^{-12} - 10^{-15} s respectively. Stokes shifts change from several to hundreds of nm. The dye-doped polymers are prospective materials for photoconductor sensitizers, optoelectronics, specially for devices used in quantum electronics, electroluminescence, photovoltaic solar cells, recording and storage of the information and so on. The advantage of the dye-doped matrices in comparison with the colored inorganic materials are their flexibility, lower density, products creation possibility with large working square, rather low cost and high radiative stability. These denominations in a combination to ease of the mechanical treatment make of them irreplaceable materials for the above mentioned application fields. The dye-doped polymers allow to transform a light radiation in a wide spectral range with higher efficiency, than polymers and dyes separately. However these advantages can be realized in that case, when doping of polymers by low molecular weight dyed impurities does not distort essentially spectral - luminescent and non-linear - optical properties of individual components of polymer composition. The influence of polymer nature and chemical constitution of organic dyes on photophysical and photochemical properties of these matrices is analyzed. Processes of dyes aggregation in polymers is characterized. The special attention will be given to J-aggregates, because they present the high ordered self-organized ensembles, which belong to different nanostructures. The photostability of dyed materials is discussed. The main paths of a energy degradation of electronic excitation in such materials are analyzed: internal conversion and intersystem crossing, vibronic and intermolecular interactions, an electron transfer in ion pairs of dyes and photoisomerization. The role of dyes in process of generation, recombination and carrier of charges in photoconductive polymers is considered. The prospectives of application of dyed polymer materials as passive Q-switches of solid-state lasers, active laser media with large Stokes shift, luminescent solar converters and electroluminescent emitters are demonstrated.

CALIXARENE RECEPTORS OF ENVIRONMENTALLY HAZARDOUS AND BIO-RELEVANT MOLECULES AND IONS

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Introduction

Calixarenes are versatile molecular scaffolds for design of highly efficient and selective receptors, self-assembling systems such as molecular capsules and well defined functional nanostructures. Herein we report on progress in rational design of the calixarene receptors and their supramolecular complexes with environmentally hazardous and biologically relevant cations, anions and neutral molecules. The calixarenes or their complexes can be used as materials for radionuclide extraction, construction of chemo-sensors, drug design.

Cation Receptors

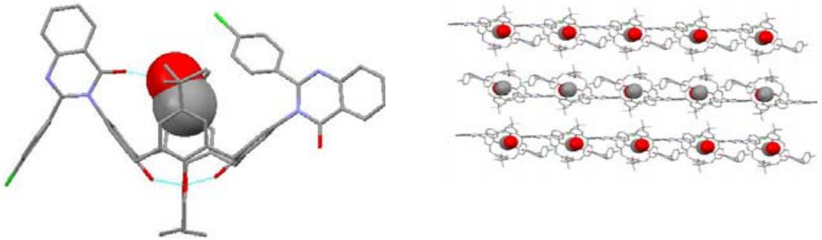
In order to obtain efficient and selective cation receptors the parent calixarenes were functionalized with phosphorus-containing legating functional groups. The calix[4]arene bearing four phosphoryl groups at the narrow rim of the macrocycle selectively binds Li^+ in the presence of Na^+, K^+, Cs^+ and NH_4^+. Calixarenes possessing phosphineoxide, carbamoylphosphineoxide and diphosphinedioxide groups at the wide rim of the macrocycle extract lanthanides as well as actinides such as Am, Cm, Pu and U [1]. The calixarenes bearing sulfur or nitrogen atoms at the wide rim form complexes with Pd(II) [2].

Anion receptors

Molecular recognition of anions is an important topic in supramolecular chemistry since anions play crucial role in many biochemical processes and in chemical technology. Several carbamide functions were attached to the narrow rim of the macrocycle in order to achieve strong and selective binding of anions through multiple and cooperative hydrogen bonding. The chiral calixarenecarbamides, bearing two fragments of *l*-Ala are capable of stereoselective binding the anion forms of racemic aminoacids. For example, *l*-phenylalanine anion is bound 4 times stronger than its *d*-enantiomer.

Receptors for organic compounds and bio-molecules

We designed new calixarene receptors which bind various organic molecules in the crystalline state, solution, and gaseous phase.



Molecular and crystal structures of the calixarene-methanol complex

The design of receptors for bio-relevant molecules is an important trend in bio-medical investigations since it allows to rationally construct the sensitive materials for diagnostic systems of biomedical application. On the basis of phosphorylated calixarenes we have obtained novel receptors for uracil and adenine derivatives, aminoacids, dipeptides [3-7].

The calixarenes functionalized at the wide rim of the macrocycle with methylenebisphosphonic or aminophosphonic acid fragments inhibit the alkali phosphatases [5, 6] with inhibition constants of 0.38 – 86 μM. The chiral calixarene-bis-aminophosphonic acids show stereoselective inhibition. Namely the *RR* isomer is about 50 times more effective than its *SS* counterpart [12].

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STRUCTURAL AND TOPOLOGICAL FACTORS OF THE CROWN ETHERS INTERACTION WITH NEUTRAL AND CHARGED "GUESTS"

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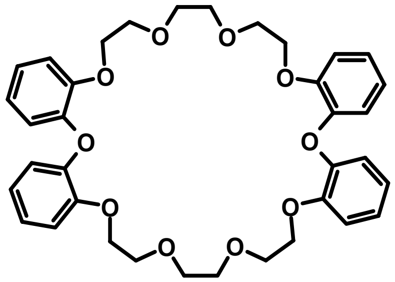
The influence of the miscellaneous crown ethers (CE) composition and structure on peculiarities of formation, stehiometry, molecular and crystalline structure as well as supramolecular organization of CE complexes (adducts) with the amidosulfuric acid zwitterion ($^+NH_3SO_3^-$), hydroxoniums (H_3O^+, $H_5O_2^+$ and $H_7O_3^+$), water and molecules containing groups H_2N-, HN< and HC<, generating hydrogen bonds with CE cavity is discussed.

In all cases, during the formation of the co-crystals, the competition of the O-containing macrocyclic H-acceptor with H-acceptor (O and S) centers in the neutral molecules leads to the substitution of the part of H-bonded supramolecular homosynthons by the supramolecular heterosynthons and change of the supramolecular architecture.

Under the $^+NH_3SO_3^-$ interaction with 15 distal and proximal dibenzo-CE (DBCE), in contrast to aliphatic, cycloaliphatic and benzo-CE (BCE), only in the case of [2.4]– and [1.5]DB18C6 as well as biphenyl-20-crown-6 (BP20C6) was a success to separate the stable complexes (1:1) in which the zwitterion, at the expense of N–H…O bonds, forms practically ideal «tripod» structure with alternant oxygen atoms of CE.

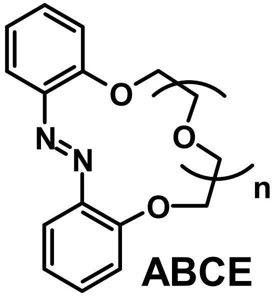


[1.4.1.4]TB30C10

The similar situation realizes in cations of complexes $[(H_3O{\cdot}BP20C6)]MF_6$ and $[(H_5O_2{\cdot}TB30C10)]MF_6$ (M = Nb and Ta), while in complexes $[(H_2O{\cdot}[1.5]DB18C6)_2(H_3O)]MF_6$ supramolecular cations are associates of two CE centralized by $H_7O_3^+$ «bridge» via H-bonds.

It was revealed that the polymeric chains in crystal of SbF_3 complex with [1.5]DB-tia-18C6 (1:1) are formed at the expense of C–H...F bonds.

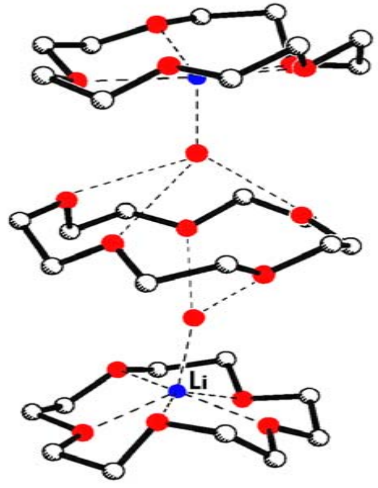
A part of transannular C-H…O interactions in stabilization of DBCE conformations and a character of macrocycle's form change as a consequence of complexation with various «guests» are considered.



ABCE

The peculiarities and possible mechanism of 5-substituted BCE, $5,5'$-disubstituted DBCE, azobenzocrown ethers (ABCE) and corresponding N-oxides (more than 60 compounds in all) interaction with the hydrated surface of non-porous aerosil (AS), γ-aminopropyl-AS and its protonated form are discussed.

The principal factors (composition and size of macrocycle, character of substituents, relative position of benzene rings etc.) determinative a binding strength of mentioned CE with surface groups are revealed.



3(15C5)·2($LiCrO_3Cl$)·2H_2O

The results of X-ray analysis of more than 30 complexes of CE with chromates $MCrO_3X$ (M = Li, Na, K, Cs and H_4N^+; X = Hal, $OCrO_3M^{/}$ and $OCr_2O_6M^{/}$; Hal = F, Cl, Br; $M^{/}$ = Na and K) including complexes containing as “extra-ligands” water molecules, determinative different variants of coordination and association of the last ones with the CE complex cations and neutral ligand, are systematized. Independently of a stehiometry of these complexes and anions nature, as well as composition, dentaty, structure and configuration of CE, the last ones assume in the most cases a “crown-like” conformation, which is more preferable for maxidentate interaction with the “guest”. At the same time the structurally "rigid" fragment which determine a form of CE in the complex and, as a consequence, a distance of the cation from the mean plane of CE oxygen atoms {$\delta(K^+–[nO]_{Crown})$}, may be not only 1,2-phenylene but 1,2-cyclohexene.

The parameter Δl (characterizing the cation translation relative to the center of CE cavity), with other conditions being equal, “responds” enough “sensitive” to a changing of “extra-ligand” composition as well as configuration of CE.

Comparison of $l(K–O_{Crown})_{av}$ and Δl parameters allowed to realize the peculiar classification (screening) of studied complexes, in crystal structure of which the cation orientation determines very largely by conformational flexibility of an initial CE. Among investigated complexes the averaged length of Cr–O bond noticeably decreasing as value of $l(K–O_{Crown})_{av}$ increases and is cymbate to changing of $\delta(K^+-[nO]_{Crown})$ and Δl values.

Interrelationships of structural factors determining a reactivity of studied complexes were revealed. Specifically, the rate of benzyl alcohol oxidation by these complexes correlates with $l(Cr–O)_{av}$ and $\delta(M^+-[nO]_{Crown})$ values.

For instance, on the range of $KCrO_3Cl$ complexes with isomeric DB18C6 the reaction rates change in the following way: [3.3] < [2.4] < [1.5]. In much the same change the $l(K–O_{Crown})_{av}$ as well as Δl values.

On the base of obtained results a possible mechanisms of alcohols oxidation by investigated complexes are proposed.

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QUANTITATIVE PHYSICO-CHEMICAL ANALYSIS OF PROCESSES AT INTERFACES OF HYBRID SILICA-ORGANIC MATERIALS

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The report is devoted to quantitative physicochemical analysis (QPCA), a powerful tool for the determination of composition and thermodynamic stability of species in different media. The modifications of the QPCA general procedures necessary to reveal and describe quantitatively features of surface modified inorganic-organic hybrid materials are presented. The main attention is paid to characterization of surface energetic heterogeneity and cooperativity effects affecting sorption and ion exchange equilibria. The calculation aspects of handling the QPCA primary experimental data are discussed too.

The results of studying processes at surfaces of chemically modified silicas and hybrid silica-organic materials obtained through sol-gel synthesis are reported. The application of the QPCA methods allows to detect and describe quantitatively factors affecting the peculiarities of immobilized reagents and properties of the near-surface layer. The conclusions made on the base of QPCA fall into line with results of independent (predominantly, spectral) methods.

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DEFECTS & THEIR PROPERTIES IN GRAPHITIC NANO-STRUCTURES

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Various decorations or defects of conjugated graphitic networks are considered, with special attention to the case that the structures are possibly extended in at least 1 dimension. This includes various polymers, their end structures, and defect side groups along the chain, or strip, or tube (as a carbon nano-tube). This approach further includes various boundary (or edge) structures on potentially semi-infinite graphite, as well as various “quasi-local” defects in what is potentially otherwise 2-dimensionally infinite graphite, these considered defects encompassing vacancy defects, selected substitutional defects, dislocations, & disclinations. In general some care is needed even to identify the possible such nano-structures, though property characterization is ultimately desired. Attention is paid to consequent occurrences of defect-localized unpaired (or weakly paired) electrons, as formulated within a resonating Valence-Bond framework, especially as regards simply applicable theorems or rules. But further within a MO-framework, attention is paid to modifications in the local density of states near the Fermi energy. Consonance of predictions from the two complementary viewpoints is taken as an indicator of a reliable prediction.

DISCOVERING NEW CRYSTAL ARCHITECTURES

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Enumeration of all possible arrangements of atoms in inorganic structures is a matter of much practical interest. A “library” of well-characterized, chemically feasible, hypothetical structures could permit us to design strategies which ultimately will lead to their synthesis. Furthermore, theoretical X-ray, neutron and X-ray diffraction patterns generated for such structures would be of great help in determining the structures of new materials: it would simply be a matter of comparing an experimentally obtained pattern with the database.

Nowhere is the construction of such a library more desirable than in the case of microporous aluminosilicate (zeolitic) and aluminophosphate (AlPO) molecular sieve catalysts, of which there are now 174 recognized structure types.[1] The problem of finding new crystal architectures is very difficult since the number of possible frameworks is infinite and until recently there was no systematic procedure for their derivation. Enumeration originates with the work of Wells.[2] Sherman and Bennett,[3] Alberti,[4] Sato,[5] Akporiaye and Price[6] Smith and collaborators,[7] O'Keeffe and collaborators,[8,9] Treacy[10] and Newsam et al.[11] found many possible new structures by combining various structural subunits. More recent work involves computer search algorithms.[9, 10, 12] The weakness of such approaches resides in their nonsystematic nature, so that one could never be certain that all the possibilities have been considered.

Our work is based on advances in combinatorial tiling theory.[13] Just as a floor can be covered with tiles of various shapes, three-dimensional space can be filled with polyhedral tiles, and the number of ways in which this can be done can be precisely calculated. The configuration of edges, faces and tiles around a given vertex can be described via the so-called vertex figure. A particular tiling can then be encoded in the form of a unique "Delaney symbol"[14] and encoded as an "inorganic gene"[15] which is then systematically permutated using computational algorithms, giving all possible structures.

Known zeolitic structures involve up to 12 inequivalent vertices (i.e. inequivalent silicon atoms), which we call *n*-nodal, where *n* is an integer between 1 and 12.[15] For example, faujasite is a 1-nodal (uninodal) structure and ZSM-5 is 12-nodal. We have so far described all possible Euclidean uni-, bi- and trinodal tilings based on "simple" vertex figures (tilings with vertex figures which are tetrahedra) and all "simple" and "quasi-simple" uninodal tilings with vertex figures containing up to six extra edges[16] (in "quasi-simple" tilings the vertex figures are derived from tetrahedra, but contain double edges). There are exactly 9 and 117 topological types of 4-connected uninodal[17] and binodal[18] nets, respectively, which are based on "simple" tilings. In addition, there are at least 157 additional uninodal nets derived from "quasi-simple" tilings.[17,19]

When our original paper[15] was published, the IZA database contained 121 recognized structure types, and the current number is 174. The 53 new structures can in principle all be obtained using our method. Among the structures synthesized since 1999 we have specifically described structure types RWY[20] (our structure 1_1)[21]; NPO[22] (our structure 1_88)[21]; BCT[23] (not registered by IZA until 14 June 2001) (our structure 1_211)[21] and UFI[24] (our structure 3_835). One would expect that only a fraction of the mathematically generated networks would be chemically feasible (there could be many "strained" frameworks requiring unrealistic bond lengths and bond angles), and that an effective filtering process is needed to identify the most plausible frameworks. In order to do this, we must inject the basics of zeolite chemistry into the problem, by replacing the mathematical points by atoms and the straight lines by chemical bonds, and calculate the energy of the resulting frameworks by slight adjustments of angles and distances. Thus, for a given chemical composition, the lower the energy, the more likely is the structure to exist. We have treated the structures as silica polymorphs with the chemical formula SiO_2. Silicon atoms were inserted at each vertex of the enumerated networks, and a 2 bridging oxygen was placed between each pair of neighbouring Si atoms, which were predefined to be separated by a typical Si—Si distance. The GULP energy minimisation program[25] was then used with interatomic potentials for SiO_2 given by Sanders et al.[26] To calculate the framework energy relative to α-quartz, the most stable form of the mineral, and the framework density (the number of tetrahedral atoms per 1000 $Å^3$) for each structure.

Enumeration of chemically realizable frameworks containing large amounts of internal space (i.e., those containing channels and/or voids) is of particular interest, because such materials can act as "microreactors" containing implanted catalytically active groups or encapsulated transition-metal complexes. The crucial structural parameters here are the amount of void volume and its accessibility (whether or not a molecule can enter the structure from the outside), which we have calculated for all the hypothetical structures. It turns out that the accessible volume for known zeolites is in the range of 0–28 $Å^3$ per Si atom and the framework energy relative to α-quartz is below 30 kJ mol^{-1}. Some of the most interesting new structures will be described.

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ORGANIZED MOLECULAR SYSTEMS AS REACTION MEDIA: A GREEN ALTERNATIVE TO THE PHASE TRANSFER CATALYSIS

A. Lattes

President of the French Chemical Society

Reactional media are one of the most important factors to realize organic synthesis in soft and non-polluting conditions, answering the conditions of sustainable development. Organized Molecular Systems (OMS) are very efficient for the application of the twelve green chemistry principles, more precisely to replace organic solvents, to realize reactions in water, in catalysis and biocatalysis, for the molecular economy (and, of course, of atoms) or to work with low energetic conditions.

These OMS possess a number of advantages: solubilization of substances that are not normally soluble in the continuous phase of OMS, localization of reactants and products, selective orientation and stabilization of the various entities in the various stage of the reaction.

Rapid and selective reactions of preparative amounts of substrate can be carried out in such media, which are also well suited for mechanistic studies.

First, we have realized organic photoreactions in microemulsions: macroscopically homogeneous and transparent media. Thus, we have been able to confirm the interfacial localization of the processes, with chemical internal sensor and infrared spectroscopy; to propose a formulation strategy for diminishing the number of substrates in the medium (molecular economy principle); to use high interfacial concentration to realize, in liquid phase, reactions which are only possible in solid state.

The most important scientific point was the demonstration of the generalization of the amphiphilicity concept, first by using polar non-aqueous solvents. In 1986, it was the end of a controversy concerning the use of formamide in place of water. With this type of solvent, we have been able to realize important reactions: the Wacker process, Diels-Alder reactions, and olefin amidations.

Then we postulated the formation of aggregates without surfactants if differential solvations were operative. All organic reactions can be influenced by the spontaneous formation of aggregates.

To finish, with such systems it is possible to orientate the reactivity of competitive reactions (e.g. cyclization and polymerization) and participate at the environment protection, for example in the synthesis of clean surfactant in clean conditions.

With the extension of these observations and results to the use of rigid objects (similar to rigid micelles) we were able to obtain very high enantioselective excess in chiral processes.

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PROTOLYTIC EQUILIBRIUM IN LYOPHYLIC NANOSIZED DISPERSIONS: DIFFERENTIATING ACTION OF THE PSEUDOPHASE AND SALT EFFECTS

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Thermodynamically stable ultramicroheterogeneous systems such as micellar solutions of colloidal surfactants, microemulsions, and other types of organized solutions are extensively applied in various fields of modern science and technology. Hence it is necessary to extend our understanding of the properties of such systems as reaction media. First of all, it is worthwhile to consider the influence of surfactant micelles and other kinds of self-assembled aggregates on protolytic reactions, which belong to the most significant ones.

Acid-base and solvatochromic indicators, including fluorescent dyes, are known to be a touchstone for examining micelles, microdroplets and related nanosized particles, including biomolecules. Indicator dyes serve as useful tools for estimating the solubilizing ability, microviscosity and interfacial polarity, for monitoring local acidity and electrical potentials, etc. Colored and fluorescent dyes embedded in organized solutions are widely used in sensor devices. The key characteristic of the acid-base indicator in micellar solutions is the so-called ‘apparent’ ionization constant, K_a^a, of the indicator acid HR^z ($\mathrm{p}K_a^a \equiv -\log K_a^a$). This quantity is typically determined by vis-spectroscopy at extremely low indicator concentration; the bulk (aqueous) ph value is checked using glass electrode. The K_a^a value is actually a constant of two-phase equilibrium. The volume of the dispersed phase (pseudophase) usually makes less than 1 % of the total volume of solution. Within the framework of the recognized electrostatic model, the following equation is valid in the case of complete binding of dyes species to the pseudophase:

$$\mathrm{p}K_a^{ac} = \mathrm{p}K_a^{w} + \log\frac{\gamma_{\mathrm{R}^{z-1}}}{\gamma_{\mathrm{HR}^{z}}} - \frac{\Psi F}{RT\ln 10} = \mathrm{p}K_a^{i} - \frac{\Psi F}{RT\ln 10}\ .$$

Here K_a^{ac} refers to complete binding of the probe, K_a^{w} is the thermodynamic ionization constant in water, K_a^{i} is the so-called 'intrinsic' ionization constant, γ are the activity coefficients of transfer of the species from water to micellar pseudophase, Ψ is the electrical potential (as a rule, regarded as the potential of Stern layer), *F* is the Faraday constant, *R* is the gas constant, *T* is the absolute temperature. Though this equation results from efforts of many authors, we find it justified to call it 'the HMFF equation', according to the names of Hartley (1940), Mukerjee (1964), Fromherz (1973,1977), and Funasaki (1976,1979).

The aim of this review is to consider the protolytic equilibria of the aforementioned molecular probes in self-assembled aggregates and related systems. Basing on more than 1500 $\mathrm{p}K_a^{a}$ values determined in this laboratory, as well as on the data published by others, the main regularities governing the protolytic equilibria of substances dissolved in organized solutions are revealed. The objects of analysis were alterations in the $\mathrm{p}K_a^{a}$ values, caused by the transfer from water to micellar solutions ($\Delta\mathrm{p}K_a^{a} = \mathrm{p}K_a^{a} - \mathrm{p}K_a^{w}$). Indicators of different structure and charge type of the conjugated acid-base couple were involved in the study, namely: sulfonephthaleins, fluoresceins, phthaleins, rhodamines, polymethines, nitrophenols, azo-dyes, and pyridine-N-phenolate solvatochromic dyes ('Reichardt's indicators'). Micellar solutions of over 20 colloidal surfactants are used, as well as mixed micellar systems. Effects caused by indifferent 'supporting' electrolytes as well as specific effects of hydrophobic counter-ions are examined. Incomplete binding of dyes, solvatochromism and tautomerism are also considered.

The differentiating influence of micellar pseudophase upon the acid-base properties of indicator couples of various charge types and nature, i.e., the disparity in their $\Delta\mathrm{p}K_a^{a}$ values, manifests itself distinctly, depending on the nature of the surfactant. This effect is caused, on the one hand, by the miscellaneous character of any micellar surface, and on the other hand – by the dissimilarity among hydrophilic portions of cationic, anionic, non-ionic (with oxyethylene chains), and zwitterionic surfactants, as well as of the Stern region of ionic micelles containing counter-ions of different hydrophobicity.

The revealed effect is compared with the concept of differentiating influence of organic solvents, developed by Izmailov (1948–1959).

A classification of the types of differentiating influence of organized solutions is proposed. This influence is demonstrated to be the main reason for limitation of the common electrostatic model of acid-base interactions and the principal hindrance to exact evaluations of the interfacial electrical potentials, Ψ, by means of acid-base indicators.

The peculiarities of protolytic equilibria in 'oil-in-water' microemulsions stabilized with various surfactants, in dispersions of phospholipids, in silica nanoparticles modified by cationic surfactants, in reversed microemulsions ('water pools') and in Langmuir-Blodgett multilayers are discussed. Aqueous solutions of some kinds of supramolecules (calixarenes, cyclodextrins, dendrimers) as media for protolytic reactions are also briefly considered.

EMERGENCE OF NON-FULLERENE NANOCARBONS NANO-ONIONS AND NANODIAMONDS

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Both are not entirely new, but have remained only partially explored behind the popular fullerenes and carbon nanotubes. Carbon nano-onions and detonation nanodiamonds are both readily formed, have a number of novel properties, and have good prospects as the low-cost industrial materials. Interests are mounting among scientists as seen by sharp increase in the number of publications. In this abstract we present short history but the lecture will focus on their latest developments.

Carbon nano-onions. This modification of graphite was first observed by Iijima in 1980 as sub-micron spherical objects having layered structure in the arc-evaporated carbon film for mounting particulate samples for TEM. During this observation he also made a historic event to watch C_{60} in the center of this object before anyone else. Later in the 1990th when fullerenes and carbon nanotubes were produced by many researchers over the world arc-evaporating graphite electrode in helium atmosphere, the nano-onions came out as well-crystallized polyhedral multi-shell fullerenes, often with void in the center, but regarded as persistent by-products than a new breed of nanocarbons.

A couple of incident events aroused interests in nano-onions. One event is the discovery by Kroto and Endo of the multi-shell formula: $C_{60}@C_{240}@C_{540}@C_{960}\bullet\bullet\bullet C_{60n^2}\bullet\bullet\bullet$, giving intershell distance identical with interlayer distance of basal planes in graphite (Fig. 1). Later we proved this formula by graph-theoretical means. The second event is Ugarte's successful transformation of crystalline polyhedral multi-shell fullerenes into crystalline carbon nano-onions by irradiation of focused electron beam in TEM. Images of perfectly spherical flawless shell structures impressed people so much that these were called ultimate fullerenes (Photo 1).

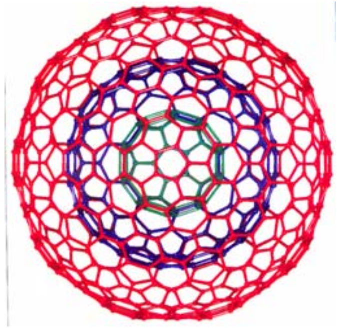

Fig. 1

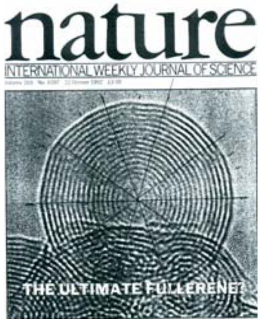

Photo1

For those who are interested in the industrial utilization of nanocarbons, we should emphasize the fact that the primary particles of soot are the defective carbon nano-onions and that each particles can be converted by continued irradiation of high-energy electron beam without thermal relaxation into spherical bucky diamonds. Thus, we have long proposed a modern alchemy, 'diamond from soot' [1].

Detonation nanodiamonds. The King of nanocarbons was discovered in Ukraine in 1963 by Danilenko and his group [2], but remained almost undeveloped for 40 years for various reasons. The long dormant King awoke in 2005 when its primary particle, single cubic crystal having coherent scattering region of 4-5 nm in size, was finally isolated (Photo 2). Surprising behaviors like discrete aggregation, absorption of strongly oriented, non-freezing layers of water onto the particle surface, and high biocompatibility are being disclosed. The first mass production of transparent, colorless and dispersed ultrananocrystalline diamond (DUNCD) particles with high-purity and controlled surface structure is underway (Fig. 2). Interesting applications are being found.

Despite the conventional definition of nanoparticles limits their range to 1-100 nm, we feel the most interesting size of nanocarbons may lie within 3-9 nm, where the surface/bulk atomic ratio starts to increase exponentially and the static as well as dynamic properties begin to change. In this regard, detonation nanodiamond appears to a good model of potentially useful nanoparticles [3].

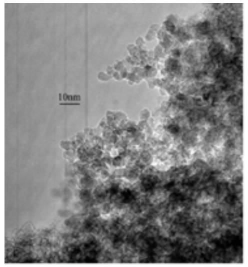

Photo 2

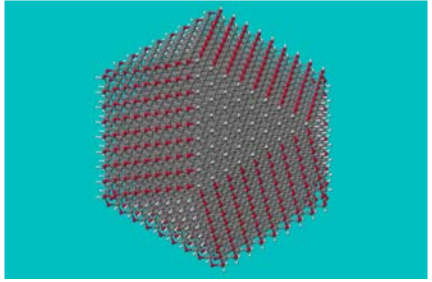

Fig. 2

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DESIGN OF GREEN MICROORGANIZED SYSTEMS FOR DECONTAMINATION OF ECOTOXICANTS

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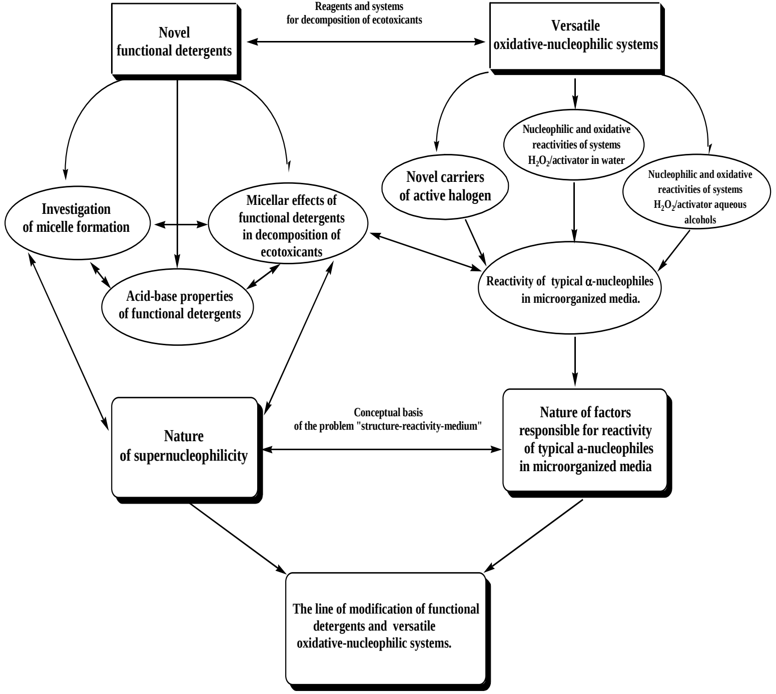
Due to population upsurge, pesticides (derivatives of organophosphorus acids included) find widespread use in agriculture. The toxicity of the compounds and long-term environmental hazard require detailed studies on decomposition mechanisms of the pesticides and development of efficient, readily available and non-expensive systems for their decontamination. Furthermore, organophosphorus compounds exhibit pronounced anticholinesterase activity and are almost identical with chemical warfare agents in their adverse effect on the human health. These compounds are easy-to-synthesize, with starting materials being ready available. The possibility of their use in terrorist acts must not be ruled out, thus increasing the significance of search and design of unique “green” reagents and versatile systems for decomposition of ecotoxicantsand.

A simple and straightforward way for decomposition of organophosphorus compounds involves their reactions with nucleophiles. Studies on reactivity of “normal” and α-nucleophiles toward electron-deficient centers allowed us to state a number of basic principles of the α-effect nature. One of the most important conclusions is: it is unlikely that the structure variations in the known α-nucleophiles will result in the compounds of a higher reactivity than that of hydroxylamine anion. As a practical matter, essential disadvantage of decomposition of organophosphorus compounds in water and organic solvents are: (i) instability of active nucleophiles and oxidizing agents, (ii) corrosiveness and (iii) extremely low solubility of organophosphorus compounds in water. The latter is especially important since the decontamination rates of the organophosphorus compounds is governed both by the reactivity of α-nucleophiles and the rate of dissolving organophosphorus compounds in aqueous formulations. This circumstance dictates the strategy of further studies, namely, carrying out the reaction in microorganized media (Scheme).

The first research line involves the development of the functional imidazole-based detergents functionalized with α-nuclephilic fragments. A number of efficient detergents was first synthesized. An examination of nucleophilicity of the functional fragments in water and in micellar phase, quantitative assessment of the factors responsible for the micellar effects showed unambiguously that the main cause of the observed accelerations is the concentrating the substrate in the micellar pseudophase. As for now, the functional detergents under consideration are the most powerful nucleophilic systems: compared to water, an increase in decomposition rates of the ecotoxicants is ~ $4 \cdot 10^3$ times for paraoxon and ~ $(1.2\text{-}7.5) \cdot 10^4$ times for 4-nitrophenyl tosylate.



The second research line consists in studies of the reactivity of versatile oxidative-nucleophilic systems involving H_2O_2/activator and polyhalide ion organocomplexes in water, aqueous alcohols and micelles of cationic detergents. Solid, stable in storage and safe-in-handle dibromobromates of bis(organoligand) hydrogen complexes as sources of the “active” bromine were first developed. Interaction between the model substrates and the bromine complexes is a stepwise process with nucleophilic attack of BrO^- ion on the electron-deficient center of the substrate and subsequent oxidation of the leaving group. Such systems make possible to carry out deep decomposition of organophosphorus compounds. In the micelles of cetyltrimethylammonium dibromobromate at a concentration << 1M, half-lives of the model substrates (paraoxon and 4-nitrophenyldiethyl phosphonate) are no more than 30 s. As a result, the novel sources of “active” halogen are highly competitive both with conventional hazardous chlorine derivatives and “green” systems involving H_2O_2/activator.

TIME-DOMAIN *AB INITIO* STUDIES OF ULTRAFAST EXCITATION DYNAMICS IN NANO-MATERIALS

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Non-adiabatic molecular dynamics techniques implemented within time-dependent density functional theory are applied to study ultrafast photoinduced processes in dye-sensitized semiconductors, quantum dots (QDs) and carbon nanotubes (CNTs). The interfacial electron injection from molecular chromophores into TiO_2 surfaces drives the Gratzel solar cell and exemplifies the molecule-bulk interface common to molecular electronics and photoelectrochemistry. The electron-vibrational and Auger relaxations of photoexcited states in QDs determine the efficiencies of hot carrier accumulation and carrier multiplication in QD solar cells. The electron-phonon scattering in CNTs affects nanotube conductivity and characterizes nanotube potential for use in nanoscale electronic devices. The real-time atomistic simulations provide detailed description of these processes.

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PYRIDINIUM N-PHENOLATE BETAINE DYES AS EMPIRICAL INDICATORS OF SOLVENT POLARITY – SOME NEW FINDINGS

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Solutions of the zwitterionic betaine dye 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate (**1**) are solvatochromic, thermochromic, piezochromic, and halochromic [1,2]. That means the position of its longest-wavelength intramolecular charge-transfer Vis absorption band depends on solvent polarity, solution temperature, external pressure, and the nature and concentration of added salts. The outstanding large negative solvatochromism of this standard betaine dye **1** has been used to establish UV/Vis spectroscopically a comprehensive empirical scale of solvent polarity, called $E_T(30)$ scale resp. E_T^N scale, meanwhile known for a great variety of molecular and ionic solvents as well as many binary and ternary solvent mixtures. In this report, Vis spectroscopic properties of betaine dye **1** as well as the definition and various applications of the solvent polarity parameters derived from **1** will be given

In addition, the negatively solvatochromic betaine dye **1** cannot only be used to measure empirically the polarity of liquids, but also that of microheterogeneous solutions (e.g. micelles [3,4), surfaces (e.g. silica [5,6], alumina [5,7], cellulose [8]), solids (e.g. polymers [9]), glasses (e.g. sol/gel systems [10]). Therefore, the term *perichromism* (from Greek peri = around and chroma = colour) has been proposed to describe all these phenomena. Some representative examples of these extended applications of **1** will be described.

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THE LIQUID-LIQUID PHASE TRANSITION OF IONIC LIQUIDS IN SOLUTION CRITICALITY AND CORRESPONDING STATES

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Ionic liquids (IL) are defined as salts with melting temperatures below 100°C. Quite recently ionic liquids became a major topic in chemistry and chemical engineering because of their potential for many applications [1]. There are ils with melting temperatures as low as -70°C. The vapour pressure of ILs is hardly measurable. In fact boiling temperatures are expected above their decomposition temperature near 300°C. The special properties of molten salts at ambient temperatures suggest applications of ils as reaction medium, catalyst and extraction medium.

From the scientific point of view the study of phase diagrams of solutions of ILs is of fundamental interest because the long range nature of the Coulomb interaction of the ions, may influence the nature of the critical point of the phase transition from the universal Ising criticality to some other critical behaviour e.g. to mean field criticality. Another interesting aspect is based on the strength of the Coulomb interactions, which enables the formation of ion-pairs and larger clusters [2,3].

For the design of separation processes it is important to know phase diagrams of the liquid-liquid phase transition in solutions of ILs. In this lecture we present a systematic study of the phase diagrams and of other critical properties as viscosity, static and dynamic light-scattering of binary solutions of ILs. The ILs considered are salts with different cations (tetra alkyl phosphonium and 1-alkyl 3-methyl imidazolium cation ($R_n mim^+$) with different lengths of the side chains). The anions are Cl^-, Br^- BF_4^-, PF_6^- and $(CF_3 \cdot SO_2)_2N^-$. The solvents considered include non-polar solvents as alkanes and arenes, weakly polar higher alcohols, and polar solvents as methanol and even water.

As the general conclusion of the measurements of viscosity, of phase diagrams, and static and dynamic light-scattering with mK accuracy it can be stated that all phase transitions belong to the Ising universality class. No difference in the nature of the critical point can be found between the phase transitions that are driven by the long-range Coulomb interactions and such driven by solvophobic interactions. Apparent mean field behaviour, which has been reported, is shown to be caused by incomplete relaxation of non-equilibrium states [4].

The concept of corresponding states has proved to be a powerful tool in order to reduce the data and also to enlighten general aspects of the systems under consideration. Corresponding states analyses are carried in order to gain insight into the systematic of the variation of the non-universal specific properties of the systems. The model-fluid of charged hard spheres in a dielectric continuum, called restricted primitive model (RPM), is taken as the basis of the analysis, because for this ionic system critical data and critical properties are known from simulation and analytical theory. With an estimate of the ion-ion distance in the ion-pair and the knowledge of the dielectric permittivity of the solvent the experimental data can be expressed in terms of reduced variables of this model. In fact this approach has been successfully used to find liquid-liquid phase transitions in ionic solutions [5]. As the first result of the analysis it can be concluded that for the non-polar solvents the critical temperatures agree with the predictions for this simple model. For solutions in non-polar solvents the critical temperatures in RPM-variables found in the experiments agree with the figures obtained by simulation of this model [6]. However, analysing the experimental data for polar solvents it is found that, in variance to the prediction of the RPM, the reduced critical temperatures depend almost linearly on the dielectric permittivity of the solvent [7,8]. This observation indicates a continuous change from phase transitions driven by Coulomb interactions in non-polar solvents to a mechanism based on solvophobic interactions in solvents of high dielectric constant.

The corresponding states approach is used also in the analysis of shape of the phase diagrams. Using the dielectric permittivity of the solvent at the critical temperature for the calculation of the reduced temperature it is found that the coexistence curves of all the different systems reduce to a master plot, which agrees with the coexistence curve of the RPM. Thus, all phase diagrams appear to satisfy the principle of corresponding states [6,7,8]. However, the situation looks quite different, when the temperature dependence of the dielectric permittivity of the solvent is taken into account in the estimates of the RPM-variables. With this choice of the corresponding state variable, the coexistence curves of solutions in

alcohols and water get a lower critical solution point, while the coexistence curves of the solutions in hydrocarbons and other aprotic solvents are unchanged. This observation indicates that in the solutions in solvents with hydrogen bonds the phase transition is driven by both, Coulomb interactions and hydrophobic interactions, while in aprotic solvents the phase transition is essentially driven by Coulomb interactions. The validity of the ising universality is not challenged by the long-range Coulomb interactions, because even in Coulomb systems the interactions become short range due to Debye shielding [9].

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SUPRAMOLECULAR DEVICES BASED ON MACROCYCLIC COMPOUNDS

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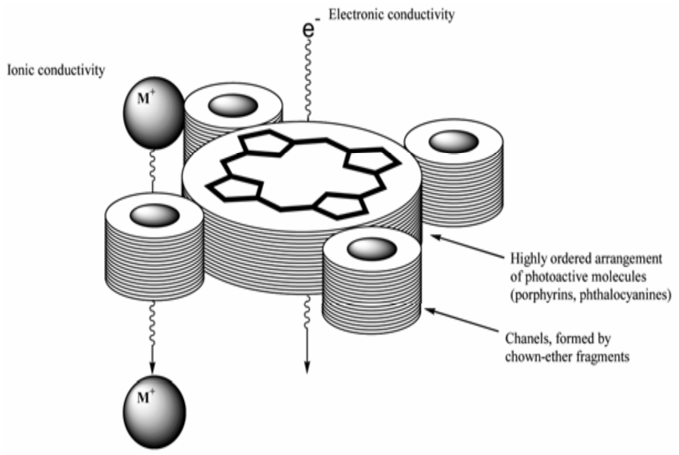
Nowadays, it is evident, that the significant increase of economic and ecological efficiency of internal-combustion engines is almost impossible. Modern technological approaches cannot lead to the further miniaturization of electronic devices. At the same time, Nature suggests the ideas of device development by examples of muscles work or photosynthesis processes. Furthermore, there have already been synthesized novel compounds, which can perform the similar functions – influence of different energy types leads to reversible transitions between the states with different properties.

Organization of stable and high-ordered supramolecular assemblies on the basis of such compounds leads to selective and efficient response towards weak energy influence. Such compounds have already been used as components of memory devices. The particular attention is paid to compounds, in which the microscopic atom rearrangements can resemble macroscopic devices. Thus, it seems to be possible to create supramolecular machines, which can perform useful work under thermal, photo- or electrochemical excitation. The structural or conformational transitions in a multistable supramolecule would correspond the mechanical “ON/OFF” switching.

The hindered intramolecular rotation and configuration rearrangements in supramolecular assemblies resembles various aspects of behavior of macroscopic mechanical systems. Various macrocyclic compounds attract much attention as components of such supramolecular machines.

When crown-substituted porphyrins and phthalocyanines act as receptors, the substrate’s role is usually played by cations. The design’s concept is the application of the mechanical switcher principle – complex formation/dissociation or ions migration.



In the present report we discuss the possible mechanisms of supramolecular building blocks cooperative arrangement and the possible disorder, which can disturb the supramolecule’s formation based on crown-substituted porphyrins and phthalocyanines.

Acknowledgements. This research was performed in the framework of European Research Association “Suprachem”.

BIOARENA: UNLIMITED POSSIBILITY OF BIOCHEMICAL INTERACTIONS IN ADSORBENT LAYER AFTER TLC/OPLC SEPARATION

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The concept of chromatography in general first became widely known through Tswett’s experimental work on complex systems as e.g. plant extracts containing dyestuffs. On the basis of this pioneer work nowadays already liquid chromatography (LC) includes two basic techniques – column LC (CLC) and layer LC (LLC). In the field of LLC after the widely applied paper chromatography (PC) (a type of partition chromatography) the first thin-layer chromatographic (TLC) experiments - by Izmailov and Schraiber in 1938 and Békésy in 1942 as well as later Kirchner et al. in 1951 and by Stahl et al. in 1956– opened a new and very prospect age in the field of LLC. Different conventional and modern versions of TLC has been used extensively for the separation, purification and qualitative and quantitative examination of virtually all types of compounds in mixtures.

Increasing the efficiency of LLC a higher mobile phase velocity was required using faster separations with an increase in zone capacity and such a velocity was necessary which is independent of the eluent front migration distance. The forced flow of eluent is a necessary requirement but not enough requirement for the efficient separation. The linear and constant development velocity over the entire separation distance is a further necessary step which gives a possibility to optimum mobile-phase velocity. One group of the forced flow planar layer liquid chromatographic techniques includes such techniques, which comply with these requirements as different linear versions of overpressured layer chromatography (OPLC). The other group includes such forced-flow techniques which are only near to these special requirements as conventional and modern versions of two planar electrochromatographic techniques (planar electrochromatography, PEC; planar dielectrochromatography, PDEC), rotation planar chromatography (RPC).

It is more and more evident that the infectious agents can be the causes or risk factors for various human diseases that were not previously thought to be caused by transmissible agents. BioArena as a complex bioautographic system integrates the up-to-date methodological and biological results of direct bioautography with capillary and forced flow techniques of LLC. This new separation and detection system exploits attractively the interaction possibilities between microbes and the dye substance as well as other small and macromolecules. All the steps of the combined method (separation of the constituents, pre-conditioning, incubation, interactions, visualisation) are performed on the same adsorbent layer. Linear technical solutions of OPLC including flowing eluent wall (FEW) arrangement are especially attractive techniques for BioArena because it generates more compact spots than TLC-HPTLC. BioArena provides more information on a given molecule separated in stationary phase than conventional direct bioautography. The

incubation time may be varied, and the changes on the adsorbent layer can be observed for 5-6 or more days. The cell proliferation promoting and/or retarding factors as well as trace elements and other co-factors can be used in the adsorbent bed and/or inoculation (culture) media. The biological systems as microbes or plants contain thousands of new biologically active constituents with beneficial and/or toxic effects. It is obvious that bioassays are the most effective solutions when they are used in conjunction with chemical screening methods so that ubiquitous and unimportant substances can be excluded from the further investigations. For chemical screening before and after inoculation, OPLC coupled with different detection methods – e.g. UV, MS, FTIR, NMR – provides a great deal of preliminary information about the composition and nature of the constituents found in special plant and microbial extracts. Although the combination of biological and chemical screening provides important information about microbial and plant constituents, it will not provide sufficient condition for the discovery of potent new drugs without suitable pharmacological-biological models. The system was applicable for studying the mechanism of action of trans-resveratrol, salicylic acid, cinnamic acid, trace elements etc. In this work, it has been established that formaldehyde (HCHO) and its reaction products play fundamental role in the antibiotic effect in general. The results of these investigations will help to explain basis of different human health risks. The inhibiting-killing/toxic effect of HCHO mobilized e.g. by means of trans-resveratrol, or trace elements can be further increased with interaction of H_2O_2. In this interaction singlet oxygen and excited HCHO can be formed. Singlet oxygen-catalyzed water oxidation results in different oxidants (e.g. ozone) which can be detected directly or indirectly in the chromatographic spots and may be important components of the plant, animal and human immune systems, alike.

KEY-NOTE AND ORAL PRESENTATIONS

CHROMATOGRAPHY

DEVELOPMENT OF N. A. IZMAILOV'S SCIENTIFIC IDEAS IN MODERN CHROMATOGRAPHIC ANALYSIS OF TOXIC ORGANIC SUBSTANCES

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Expansion of assortment and increase of scales of application of chemical substances in industry and agriculture, many of which present the real danger for a man and his surroundings, considerably increases the amount of sources of their entering in objects of environment, food raw material and food products and continues to stimulate development and use of methods of analytical chemistry of small concentrations of toxic organic substances for the aims of state sanitary-epidemiology supervision and control. To one of basic tasks of sanitary-epidemiology supervision and control after application of toxic organic matters (pesticides, substances, migrant from polymeric materials of both rubbers and other) in industry and agriculture there is a receipt of information about maintenance of toxic substances in the environment of dwelling of man. This information is needed for making a decision, directed on minimization of the unfavorable influencing of toxic substances on the organism of man, for development of prophylactic measures, warnings the further entering of these substances the controlled objects and, finally, for providing of population of high quality air, water and food products. A basic instrument for the decision of these tasks of state sanitary-epidemiology supervision and control presently is chromatography is the most effective method of separation and analysis of difficult mixtures, especially organic compounds.

By the considerable stage in world development of chromatography is became of work of outstanding Ukrainian physical-chemist and analyst, member- correspondent Academy of Sciences of Ukraine, honoured worker of science, doctor of chemical sciences, professor Nikolai Arkad'evich Izmaylov. In 1938 of N.A.

Izmaylov, working in the Ukrainian Institute of experimental pharmacy (now the State scientific center of medicaments, Kharkov), published jointly with M.S. Shrayber in a magazine «Pharmacia» by article «Dropping-Chromatographic method of analysis and his application in pharmacia». Due to work of the Ukrainian scientists exactly 1938 it is accepted to count a year in world literature by the year of birth of thin layer chromatography (TLC).

Investigations N.A. Izmaylov in area of theory of adsorption processes and development of ways of their use for practical aims TLC was not limited. The idea of N.A. Izmaylova on the use of swellings in organic solvents copolymers of styrene with divinylbenzene as spherical granules (d~0,5 mm) as «hard» (or granular) extragents and immobile phases in liquid extraction and column chromatography with the reversed phases appeared very fruitful . The use of granular methylene chloride, being in swelled copolimer of styrene with divinylbenzene, was placed in basis of dynamic sorption method of extraction of caffeine from the water extract of tea-leaf. In fact works on the use granular («hard») organic solvents in the light of modern notions it is necessary to consider as the first works on the use of method of solid phase extraction (SPE), which presently widely utillized in the analysis of organic substances for absorption and concentration from water solutions.

Development of methods of analysis of toxic organic substances in the former USSR and in Ukraine mainly determined and determined the necessity of defence of environment and man from possible influence of toxic substances through food of vegetable and animal origin stuffs, drinking-water and air, mainly as a result of application in agriculture, industry and way of life of pesticides, polymeric materials and rubbers.

In a lecture the modern state of methods of analysis of toxic organic substances (pesticides, substances, migrant from polymeric materials and rubbers, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polychlorinated biphenyls and other) and contribution of the Ukrainian scientists is examined in further development of those areas chromatography in which Nikolai Arkad'evich Izmaylov worked fruitfully.

SOME APPROACHES TO STANDARDIZATION OF LC ANALYSIS

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Some possible approaches to standardization of LC analysis are discussed. A main target was to facilitate the evolution of TLC and HPLC as routine methods of pharmaceutical analysis.

1. Standardization of binary mobile phases (BMPs)

It was proposed a BMP functional stability concept and was suggested *Stability function* (*SF*). In TLC *SF* characterizes the percent of R_f increase for a segment [0; 0.1] of active component volume fraction (m_2), referred to this BMP total R_f increase from R_{f1} (m_2 = 0) to R_{f2} (m_2 = 1.0):

$$SF = \frac{R_f(m_2 = 0.1) - R_{f1}}{R_{f2} - R_{f1}} \cdot 100\% \qquad (1)$$

Under other equal conditions, the less *SF* value, the more stable and more reproducible R_f values are in this BMP on this sorbent. The *SF* value must be taken into account when solvents for the particular BMP are chosen. Otherwise R_f values will have bad reproducibility.

2. Application of reference method for $R_M(m_2)$ curves calculation

2.1. Binary mobile phases (BMPs)

A starting presumption: different substance $R_M(m_2)$ functions are linearly dependent in the particular BMP. Assuming some substance as a reference (*st*), one gets:

$$R_M = k \cdot R_M^{st} + b \qquad (2)$$

Linear relationship (2) was experimentally confirmed in many BMPs and was applied to $R_M(m_2)$ and $R_f(m_2)$ curves calculation.

2.2. Ternary mobile phases (TMPs)

It is shown that linear relationship (2) for the BMPs is transformed into polygon for TMPs. It also gives an important theoretical result: a separation improvement in the TMP 123 in comparison with the BMPs 12, 13 and 23 may be reached in only case – when at least one R_f extreme is in these BMPs. Only in this case a range of values broadening (and separation improvement) takes place in comparison with the initial BMPs.

3. Characterization of sorbents and MPs by separation mechanism

The Unified Adsorption Center Model (UACM) and the Multi-component Mobile Phase Effective Concentration Concept were proposed. These models are based on the established Soczewinski equation for the BMPs (C – an active BMP component concentration):

$$R_M = \lg k' = a - b \cdot \lg C \,. \tag{3}$$

This equation well holds in the BMPs that include one solvent as a diluent (i.e. in this solvent $R_f \approx 0$ for substances under test). It is shown for these BMPs that the simple equation (3) is better in accord with experiment than more complex Oscik and Snyder-Jaroniec equations.

3.1. Unified Adsorption Center Model (UACM) for multi-component MPs

A starting presumption – a molecule under chromatography is concurrently adsorbed by several types of adsorption centers. The UACM results in the equation that may be considered as the generalized Soczewinski equation (C_i – MP i-th component concentration):

$$R_M = \lg k' = a - \sum_{i=1}^{n} b_i \cdot \lg C_i \tag{4}$$

It was also shown that the multidimensional planes (4) of different substances in the same multicomponent MP intersected in one point (generalized Shats equation). The equation (4) holds well for all types of sorbents in both column and thin-layer techniques in various types of MP.

b_i coefficient have a physical meaning of a partial eluent strength of the MP's i-th component, referred to the chromotographed substance on the given sorbent. The equation (4) results in conclusion: all the MP components are active (but in different extent) and concepts of "reversed-phase" and "normal-phase" mechanisms are conventional. b_i coefficient allows also to obtain a quantitative assessment of i-th adsorption center contribution into the chromatographic process and may give a new approach to sorbent standardization.

3.2. Multi-component Mobile Phase Effective Concentration Concept

If the equations (3) hold for the BMPs 12 и 13, the retention in the TMP 123 is described by the equation:

$$R_M(123) = a_2 - b_2 \cdot \lg C_{eff} \,. \tag{5}$$

The TMP effective concentration C_{eff} may be found from the relationship:

$$C_{eff} = C_2 + 10^{(a_2 - a_3)/b_2} \cdot C_3^{(b_3/b_2)} \tag{6}$$

The effective concentration concept allows to predict the TMP retention based on the BMPs data and to build unified eluotropic series for one-component and multi-component MPs.

4. R_f values reproducibility

It is shown that some TLC-plates need in standardization of R_f value uniformity within the plate. Large inter-laboratory experiment showed that R_f reproducibility is characterized by values: *SD*(in-plate) = 0.009, *SD*(inter-plate) = 0.031, *SD*(inter-laboratory) = 0.11. It is evidence of incorrectness of introduction of R_f values in pharmaceutical specifications.

HPLC INVESTIGATION OF COMPLEXATION OF CALIXARENES WITH URACIL AND ADENINE DERIVATIVES

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The cavity shaped calix[4]arenes, composed of four phenolic units connected *via* methylene links, have been investigated as a platform to design the artificial receptors capable similar to the natural enzymes to recognize a range of bio-active Guest molecules such as amino acids, dipeptides, proteines, choline or acetylcholine, nucleotides (cytidine, uridine, thymidine), nucleotides and even DNA.

In this paper we utilized the both HPLC and MD methods for investigation of the complexation of the uracil derivatives - Guests with tetrapropoxy- or dipropoxycalixarenes functionalized at the upper rim with one, two or four hydrophilic biologically relevant diisopropoxyphosphoryl groups. The stability constants of the calixarenes with uracil derivatives have been determined by HPLC method in methanol/acetonitrile/tetrahydrofuran/water (15:10:5:70 v/v) solution. The phosphoryl groups capable to change hydrophilic-hydrophobic balance of the molecule, increase the volume of the calixarene cavity as well as to be an additional binding site for the uracil-Guests due to protono-accepting properties of P=O oxygen atom. Basing on the MD trajectories atomic partition to the net molecular solvent-exposed surface was analyzed for the separated Host and Guest molecules and for the complex.

It was shown the association constants (1550 - 54300 M^{-1}) are dependent on the conformation and stereochemical mobility of the calixarene skeleton, number of the phosphoryl groups at the upper rim, as well as nature of the Guest. Hydrophobic effect, N-H-π, C-H-π interactions in the Host-Guest complexes were investigated by molecular modelling. The role of the phosphoryl groups in the binding process was discussed.

MICELLAR LIQUID CHROMATOGRAPHY IN PHARMACEUTICAL ANALYSIS

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Micellar liquid chromatography (MLC) is a new and intensively developing mode of reversed-phase chromatography. Recent reviews on MLC present its applications for separating organic and inorganic compounds, as well as for determination of distribution coefficients. Attractive to researches are MLC advantages such as high reproducibility, unique selectivity of resolution, the possibility to divide and determine simultaneously various ionic and non-ionic components, low cost and safety, and the possibility to enhance or stabilise the fluorescence. MLC has found a wide application in pharmaceutical analysis and the analysis of biological fluids due to possibility to inject a sample directly, without preliminary protein precipitation or extraction.

The general drugs contain many active ingredients. To separate these active ingredients in a single HPLC run, the gradient mode must be employed because of their quite different hydrophobicities. The gradient elution, however, is not suitable for routine analysis as a quality control method because of relatively poor reproducibility and time-consuming analysis. Sometimes for the pharmaceutical analysis in reversed-phase HPLC mode any chromatographist should use special chromatographic column.

Also for analysis of some pharmaceutical substances a normal-phase mode of HPLC and a lot of organic solvents are needed, especially if it is used in routine analysis.

MLC enables to analyse drugs and active pharmaceutical substances without using special column and large quantity of organic solvents. So, from the point of view of pharmaceutical analysis ecology and “green chemistry” conception, assay with MLC using will be better than conventional reversed-phase chromatography.

We proposed using MLC for some assay: azithromycin determination in tablets and capsules; determination of selenium (IV) as naphtylpiazselenol in multivitamin syrup; determination of pyrethroid insecticide deltamethrin in the pediculicide shampoo. As alternative conventional reversed-phase HPLC method MLC was used for analysis of Biseptol (sulfamethoxazole and trimethoprim) tablets and injection.

DESCRIPTION OF RETENTION IN MICELLAR LIQUID CHROMATOGRAPHY BASED ON MASS-ACTION CONCEPT OF MICELLE FORMATION

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The using of hybrid micellar eluents opens new field of high-performance liquid chromatography (HPLC) — micellar liquid chromatography (MLC). A main peculiarity of the micellar eluent is its microheterogeneity, as the surfactant monomers are in dynamic equilibrium with self-assembled surfactant microaggregates (micelles). The state of stationary phase in MLC is also peculiar in comparison with reversed-phase HPLC. Alkyl bonded silica stationary phase is dynamically modified by surfactant monomers and organic modifier molecules. Thus, it is of concern to develop conceptual models that take into account specificity micelle formation.

Distribution of sorbate in MLC can be presented as changing of sorbate microenvironment in transferring of sorbate from hybrid micellar eluent to modified surface of stationary phase:

$$\left\langle \mathrm{AR}_l\mathrm{S}_n \right\rangle_m \rightleftarrows \left\langle \mathrm{AR}_p\mathrm{S}_q \right\rangle_s + x\mathrm{R} + y\mathrm{S}$$

where A is a sorbate; S is a surfactant monomer; R is a modifier molecule; m and s indexes are related to mobile and stationary phases, respectively.

Application of mass-action law to distribution process and micelle formation process lead to the following description of retention:

$$\lg k = const - x\lg \mathrm{c_R} + y\beta \lg \mathrm{c_S} + x\lg(1 + (P-1)\upsilon_\mathrm{S}\left(\mathrm{c_S} - \mathrm{CMC}\right)) + y\beta\lg(1-\beta)$$

Where υ_S is the molar volume of surfactant, c_S and c_R are the total concentrations of surfactant and modifier, respectively; *P* is the partition coefficient of R between water and micellar pseudo-phase; CMC is a critical micelle concentration; β is a degree of counterion binding.

In this work the developed retention model was tested on separation of set of polyaromatic hydrocarbons and set of β-blockers. Model gives the satisfactory description of retention for all investigated compounds that allow to calculate number of molecules of modifier and surfactant which are attached/detached by sorbate transferring from a hybrid micellar eluent to a modified surface of stationary phase.

SOLID-PHASE EXTRACTION IN DETERMINATION OF ORGANIC COMPOUNDS IN WATER BY GC-MS

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Application of chlorination and oxidation agents for preparation of drinking water from natural water leads to production of chlorinated and oxidized volatile, semivolatile and nonvolatile organic compounds in low concentrations from pg/l, ng/l to µg/l. This depends on various factors: total content of organic compounds in natural water and presence amoung them of light oxidized / light chlorinated part of organic compounds, on type of oxidation agent, its doze, temperature of water etc.

Preparative isolation of nonvolatile and semivolatile organic compounds fractions (hydrophobic weak acids, hydrophobic weak bases, hydrophobic neutrals, humic and fulvic acids) from natural and drinking waters in optimal conditions was systematically investigated by solid-phase extraction method with porous polymer sorbents followed by isolation from general concentrate of antropogenic and/or toxic semivolatile compounds produced in chlorination and ozonation processes.

More than 60 classes of semivolatile organic compounds were identified by GC-MS including highest normal and isomeric alkanes, normal and isomeric aliphatic mono- and dicarboxylic acids, highest normal aliphatic monocarboxylic acids ethyl esters, unsaturated aliphatic monocarboxylic acids with one, two and three double bonds, unsaturated aliphatic dicarboxylic acids, branched (methylene attached) unsaturated aliphatic dicarboxylic acids, oxo- and hydroxyderivatives of the aliphatic mono- and dicarboxylic acids, aliphatic tricarboxylic acids, aliphatic dichlorocarboxylic acids, aromatic mono-, di- and tricarboxylic acids, phthalic acid alkyl esters, phenolcarboxylic acids, steroids, highest aliphatic alcohols, aliphatic carbonyl compounds, alkyl-, cycloalkyl- and alkenylbenzenes, alkylphenols, alkylarylureas, aryl sulfones, sulfur heterocycles, nitrogen and phosphorus compounds, surfactants etc.

Determination of C_1–C_6 carbonyl compounds, phthalic acid alkyl esters, mutagen MX and its geometric isomer E-MX, chlorophenols, organochlorine pesticides (OCPs) – α-, β-, γ-, δ-HCH, DDE, DDD, DDT, total isomeric-specific content of polychlorinated biphenyls (PCBs) (tri-, tetra-, penta-, hexa-, hepta-, octachloroisomers) in SCAN and SIM mode was carried out. MDL of procedure for OCPs makes up 0.01–0.1 and PCBs – 0.17–0.38 ng/l at enrichment factor $K=(1.50–4.00)\cdot 10^5$.

CONTROL OF RESIDUAL VOLATILE ORGANIC IMPURITIES PROFILE IN ACTIVE PHARMACEUTICAL SUBSTANCES BY GC/MS

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Control of residual volatile organic impurities (RVOI) is an important and obligatory safety test for active pharmaceutical ingredients (API). Leading world Pharmacopoeias describes various gas chromatographic (GC) techniques for RVOI determination as well as establishes limits for RVOI depending on their toxicity class or expected daily dose.

RVOI profile depends on method of API synthesis and organic solvents used in this method. Method of API synthesis is presented in open part of Drug Master File (DMF) of API manufacturer and includes in Registration Dossier for Finished Drug Product (FDP). Therefore RVOI profile can confirm method used for API synthesis.

Problem occurs when unexpected peaks of unidentified solvents are detected during routine RVOI control in API by GC with flame ionization or electron captured detectors (FID or ECD). It can testify for changes in method of API synthesis. In this case using such API for FDP manufacturing would be serious deviation from regulatory requirements.

As it was found the other reason of this phenomena is using of recycled solvents for API synthesis. It allows to decrease cost of API in the formal framework of an approved method of API synthesis. But during recycling various side organic impurities can be cumulated in basic solvent. Both levels and ranges of these impurities can be very different in various batches of recycled solvents. Additional cumulating of less volatile side organic impurities can be during evaporation basic solvents from API.

In these cases to take decision about using API batch for FDP production it's needed to know which RVOI and which their quantities are presented in API. Thus FDP manufacturers are confronted with problem of unexpected and unknown RVOI identification in API. As a rule, API manufacturers don't give information about side organic impurities in a basic solvent used. By other hand, identification of unknown RVOI in API by GC-FID or GC-ECD is very complex task requiring a lot of time and a set of large number of organic solvent reference standards.

To solve the problem of unexpected and unknown RVOI identification in API we used GC with Mass Spectrometry detecting (GC-MS). Device *Agilent 6890N* with mass selective detector *5975 Inert MSD* and head-space sampler *G1888* was applied in our investigations.

Accordingly to information of manufacturer (Sandoz Industrial Products GmbH, Germany), their sterile API *Cefotaxime sodium* can contain methanol and ethanol as RVOI. GC-MS analysis has shown presence of following RVOI in API studied sample: ethanol, ethyl acetate, methyl ethyl ketone, acetic acid (3rd toxicity class in correspondence with the European Pharmacopoeia (EP)); ethyl benzene, p- and o- xylenes (2nd toxicity class); 2-pentanone and 3-octanone. API manufacturer didn't comment these results.

Harbin Pharm. Group Co. LTD, China declared that *Benzyl Penicillin Potassium* can contain butanol and butyl acetate. Using GC-MS it was found in the API sample butanol, butyl acetate and 2-methyl propanal. Additional study confirmed that 2-methyl propanal is

API degradation product created during head-space sampling. New technique for analysis of RVOI in this API was developed.

Manufacturer Zhejiang Huahai Pharmaceutical Co., LTD, China indicated in *Captopril* DMF ethyl acetate, methylene chloride and butyl acetate as possible RVOI. GC-MS found out ethyl acetate and ethanol in API sample. Manufacturer provided an explanation for ethanol appearance in API as a result of ethyl acetate hydrolysis. Accordingly to these data new technique for analysis of RVOI was developed.

Zhejiang Kangyu Pharmaceutical Co. LTD, China declared toluene and ethanol as RVOI in API DMF of *Drotaverine hydrochloride*. Toluene, ethanol and benzene were found in API sample by GC-MS analysis. Content of benzene (1st class of toxicity) in API sample was four times more than EP limit (no more than 0.0002%). API manufacturer didn't comment this result.

Other manufacturer of *Drotaverine hydrochloride*, Salpra Pharmaceuticals & Chemicals, India declared benzene, methanol and 2-propanol as RVOS. GC-MS detected acetone, 2-propanol and toluene in the investigated sample.

In reply to our letter of inquiry manufacturer sent us the new DMF and the new sample. The new DMF indicated toluene, methanol and 2-propanol as RVOI. GC-MS showed toluene, benzene (about EP limit level) and 2-propanole (19 times more than EP limit) in the second API sample. On the base of these results it was decided to refuse collaboration with mentioned API manufacturer.

Consequently, GC-MS is a very effective tool for checking a declared method of API synthesis as well as identification of unexpected and unknown RVOI which can appear in API due to using of recycled solvents for API synthesis.

GC DETERMINATION OF *As* AND *B* LOW LEVELS IN MEDICINAL SUBSTANCES AND FORMULATED PREPARATIONS

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Impurities of arsenic (*As*) and boron (*B*) in medicinal substances and formulated preparations frequently need in control. For *As* determination, basic world pharmacopoeias recommend "classic" methods based on reduction of *As* compounds to arsine with subsequent reactions with *Hg* salts producing coloured products. For *As* determination AAS method is also used with pre-conversion *As* compounds into volatile derivatives (usually into the same arsine). For *B* low level determination, spectrophotometric methods are used, based on reactions with curcumin, benzoin and other reagents. All these methods are widely used in pharmaceutical industry, their performance don't produce any trouble, especially for single assays. Laboriousness and need in permanent laboratory assistance may be considered among shortcomings of these methods.

For automation of *As* and *B* low level determination it is proposed a gas chromatographic method with use of an electron-capture detector (ECD) for *As* and a flame-ionization detector (FID) for *B* derivatives detection. For inversion *B* and *As* compounds into volatile substances it is proposed to use an automation device for preparation and injecting of equilibrium head space (EHS) into a chromatograph. Such devices may be in complete of many gas chromatographs.

As impurity determination. The method is based on production of volatile arsine in hermetically sealed vial by reduction of *As* compounds in an acid medium by sodium borohydride or zinc granules in presence of $SnCl_2$ with subsequent sampling and injecting of gas samples into a chromatograph. Arsine production and gas samples chromotographing are carried out on a gas chromatograph GC-14B equipped with a HSS-2B device for preparation, sampling and injecting of EHS and "standard" ESD-14 (Shimadzu, Japan). Chromatographic conditions: a capillary column 30 m x 0.53 mm coated with poly[methyl(95)phenyl(5)]siloxane (5 µm), column temperature - 45°C, detector temperature – 120°C, carrier gas (nitrogen) flow – 5 ml/min, injection volume 0.4 ml.

B impurity determination. Method is based on easy production of volatile trimethyl borate in methanol medium in presence of sulphuric acid and thermostating of sample vial during 30 min at 70°C. The same chromatograph is used but the temperature column is 130°C and the detector is the FID with 527 nm filter.

Detection limits: 0.2 µm of *As* and 10 µm of *B*.

LUMINESCENCE DECAY OF POLY(P-PHENYLENE VINYLENE) NANOWIRES AND NANOCOMPOSITES

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Luminescent conjugated polymers such as poly-(p-phenylene vinylene) (PPV) and its derivatives have been extensively studied for their potential applications in organic light-emitting diodes and photovoltaic cells. On the other hand, single-walled carbon nanotubes (SWNT) are materials with remarkable mechanical and electrical properties. Polymer composites containing SWNT are thus of considerable technological interest, because they may combine the best electrical, mechanical, and optical properties of each of the components. So far, research on PPV-based materials has been mainly directed at understanding the bulk properties of thin films which can be easily fabricated at low cost over large areas. A very interesting challenge concerns the elaboration of nanotubes and nanowires from organic conducting polymers and composites with the aim to design novel nanoelectronic devices for sensors, addressable displays, and for biomedical applications. In this context, PPV/SWNT composites have been prepared in Nantes from PPV-precursor solutions thermally converted with SWNT concentrations up to 64 % in weight. Synthesis of PPV nanowires was achieved with a template method by filling nanopores of polycarbonate membranes with precursor solutions at various concentrations. The materials were investigated by steady-state optical techniques combined to time-resolved photoluminescence spectroscopy. In PPV/SWNT composites a blue shift and a quenching of the luminescence are observed when the SWNT concentration increases. These modifications proceed from structural disorder and shortening of effective conjugation lengths induced by SWNT during synthesis. PPV nanowires exhibit a remarkably quasi-exponential long-lived and blue-shifted photolumine-scence ascribed to a confinement effect of intra-chain singlet excitons. Additionally, these nano-objects show an increase in the quantum yield with respect to bulk samples. The acquired optical data confirm that PPV-based nanomaterials may be suitable for nanotechnologies.

AN ALGORITHM FOR THE SIMULATION OF ECL INTENSITY MEASURED USING CONFOCAL MICROSCOPY IN DOUBLE BAND MICROELECTRODE SYSTEM

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As has been shown recently [1] the local intensity of electrogenerated chemiluminescence (ECL) emission registered by a confocal microscope in the system with two band microelectrodes imbedded into an infinite planar insulator does not follow the theoretically predicted behavior. This occurs due to specific features of confocal microscopy such as finite size of the sampling volume so that the measured light intensity represents the flux of photons through its surface instead of pointwise values. Another reason for distortions appearing in the registered ECL intensity is reflection of light from the electrode surfaces which amounts to the appearance of side peaks and/or smearing of the main peak depending on the distance between the electrode/insulator plane and the scanning plane [1].

In this work, we model the process of ECL emission in the system with two band microelectrodes taking into account the influences of finite sampling volume size and reflection from the electrode surfaces as it was predicted in work [1]. The concentration distributions were accurately calculated using the conformal mapping of spatial coordinates suggested in [2]. This conformal mapping gives highest grid resolution in the area between the electrodes (gap) where the recombination and emission relaxation reactions take place, i.e. where the ECL emission is localized. The simulation algorithm developed here is not bound to a particular chemical substance and may be easily extended and adapted to other reaction schemes leading to ECL or to other geometrical configurations.

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THE ELECTROCHEMICALLY ACTIVE COMPLEXES FORMATION IN THE ION DISCHARGE FROM AQUEOUS ELECTROLYTES

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The usual methods for determining the composition of electrochemically active complexes are based on the fact that only one complex in equilibrium with the complex that is dominant in the bulk of the electrolyte is discharge on the electrode. It is evident that the overwhelming majority of electrochemical systems are characterized by quite a number of complex compounds in the bulk of the electrolyte and in the electrode layer. It is also quite logical to think that metal ions are discharged from all or several ionic species that are present in the bulk of the electrolyte or are formed in the cathode layer and on the electrode surface in a particular case, a single species may be such an electroactive species.

We have developed methods for determining electroactive ionic species on the basis of the method developed earlier for determining all concentrations on the electrode surface. New electrochemical functions are proposed: "discharging ion complexity", which relates formation constants to electrode reaction parameters, and "average coordination number of discharging ion", which indicates the composition of discharging complexes.

The study of equilibriums in the bulk electrolyte and in the cathode layer as a function of the ratio of the main solution components, pH and polarizing current density in conjunction with electrochemical parameters makes it possible to establish, by using the proposed theory, the composition of EAC's that are directly involved in the electrode reaction during the reduction of complexes and hence to control electrochemical processes.

The proposed theory and methods permit one, unlike conventional ones, to investigate electrochemical systems containing no excess ligand (ligands) when several complex metal compounds are present in the electrolyte in comparable amounts and one or several electroactive complexes are directly involved in the electrode process.

Method for determining electrochemically active and electrochemically inactive ions are shown for the discharge of cadmium, zinc, silver and cooper coordination compounds with complexones and halide ions.

CONSTRUCTION OF OPTIMAL QUASI-CONFORMAL MAPPINGS FOR THE 2D NUMERICAL SIMULATION OF DIFFUSION AT MICROELECTRODES. APPLICATION TO RECESSED DISKS AND BANDS AND THEIR ARRAYS

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Unique and wonderful properties of quasi-conformal and conformal mappings allow efficient and elegant solutions of problems from various areas of science and engineering. In particular, their application to the numerical solution of physicochemical problems involving protruding/recessed micro- and nanoelectrodes, active three-phase boundaries, nanotubes, etc., with singularities which pose important challenges that cannot be resolved easily with conventional methods is undoubtedly a very important approach. Singularities in such problems occur due to local large or infinite concentration gradients or due to sharp fronts of very fast reactions which cannot be described with sufficient accuracy on sparse discrete meshes.

We propose a new method of constructing quasi-conformal mappings for obtaining optimal spaces for the numerical simulation of stationary and quasi-stationary diffusion-reaction problems at microelectrodes. The method performance is demonstrated in full details at a particular example of pure diffusion at the microdisk electrode. The method scope is then further expanded by introducing compression functions (in the form of a spline function) to adjust the properties of the quasi-conformal mapping to the problem at hand. This generalized approach has also been applied to the microdisk electrode and the resulting spline-function and the analytical compression function have been compared [1]. The method has also been applied for the numerical solution of 2D-diffusion problems in systems with recessed disk and band microelectrodes. The obtained optimal quasi-conformal mappings allow for effective resolution of singularities present at the electrode edge and at that of the hollow in which the electrode is deposited. This enables fast and precise simulations of single recessed/protruding microdisk (microband) electrodes with arbitrary inclination angles as well as their arrays [2].

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WATER FLOW ADJACENT TO A POLARIZED COATED ELECTRODE

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A novel approach to pipe flow improvement is presented on the basis of applied positive electric potentials to the pipe. For all forms of transport of fluids in pipes, there is loss of pressure due to friction, which is of electrical origin. The question is whether it is possible to decrease the friction at the pipe wall by controlling the electrical potential between the fluid and the surface of pipe wall (electrode). This was studied by measuring the pressure drop over the whole length of a 13.1 m slanting epoxy coated pipe (coated electrode) made of black steel, through which water was flowing under constant flow conditions. Sections of the top and the bottom parts of the pipe were substituted by uncoated inserts made of stainless steel and were electric isolated from the pipe. The inserts were electrical connected and acted as a counter electrode. The potentials were applied between the counter electrode and the pipe itself by a constant potential source. Positive end on the pipe. The results show a decrease in the pressure drop (up to 2%) when positive electric DC-potentials in the range 0.6 – 1.6 V were applied to pipe. The positive polarization of the pipes was noticeable throughout the whole length of the pipe though decreasing with the increase in a distance from the counter electrode. However, no significant changes in the pressure drop were observed when the applied potentials were within the ranges 0 to 0.6 V, 1.6 to 2.0 V or 0 to -2.0 V.

Upscaling to field-scale pipelines in a hydroelectric power plant (12.5 MW, 85 GWh) has also been done. Water flows through the single turbine pipe (length 1562 m, mean diameter 1 m, total fall 380 m) made of carbon steel and coated inside with an epoxy polymer. The positive DC-potential (1.1 V) has been applied between the pipe and the manlock (made of stainless steel and electric isolated from the pipe), located 54 m from the pipe inlet. Results from the experiments show that the head loss decreased from 45 m to 39 m at maximum flow rate (4.68 m^3s^{-1}) after 2.5 years of exposure to the potential. That means a 13% reduction in the head loss, which corresponds to a 1.8% increase in the electricity production. The experiments are still in progress.

KINETICS AND CATALYSIS

DETERMINATION OF ACTIVATION PARAMETERS IN REACTION OF OXIDATION OF AZID BY IODINE IN THE PRESENCE OF THIOSULPHATE AS A CATALYST IN BUFFER SOLUTION

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Reaction of oxidation of azid by Iodine in the presence of thiosulphate has been studied spectrophotometrically by monitoring the absorbance of Iodine at 349 nm.

The parameters affecting the rate of reaction such as pH, Iodine concentration, sodium azid concentration and time of measuring absorbance changes were investigated and the optimized conditions were obtained. In this investigation all parameters were kept constant except the ones to be optimized.

Then by using the Eyring theory of transition state, the activation parameters were also calculated for catalyzed and uncatalyzed reactions.

N-ACYLONIUM SALTS AS DRIVING FORCE IN THE INVERSE PHASE TRANSFER CATALYSIS REACTIONS

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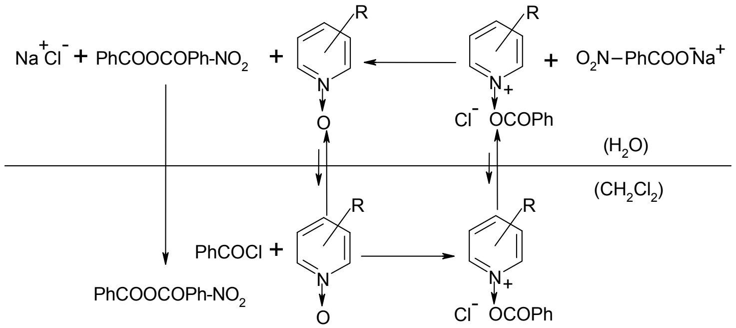
Phase-transfer catalysis (PTC) is considered an effective tool for synthesis of organic chemicals from two immiscible reactants. In the PTC process, the mechanism of the main reaction is that a nucleophilic agent is transferred to the organic phase through the quaternary cation soluble therein. However, a few examples exist of synthetic procedures in which a reagent soluble in an organic solvent is activated by conversion to an ionic intermediate and transported to the aqueous phase for reaction. Such processes described as inverse phase-transfer catalysis (IPTC). In fact, only pyridine 1-oxide (PNO) is commonly used as inverse phase-transfer catalyst [1].

We investigated the reaction of benzoyl chloride and sodium *p*-nitrobenzoate in a system of dichloromethane and water using pyridine 1-oxides as the inverse phase-transfer catalysts:



Our main purpose is to evaluate the effects of the catalyst structure on the reaction rate, the yield of the main product benzoic *p*-nitrobenzoic anhydride and the conversion of benzoyl chloride.

The rate was determined by measuring anhydride concentration in the organic phase. The apparent coefficient for the rate of consumption of benzoyl chloride was used to express the reaction rate,

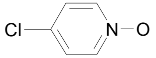
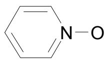
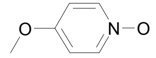
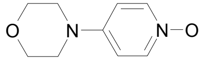
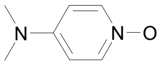
$$-\frac{d[PhCOCl]_{org}}{dt} = k_{obs}[PhCOCl]_{org}$$

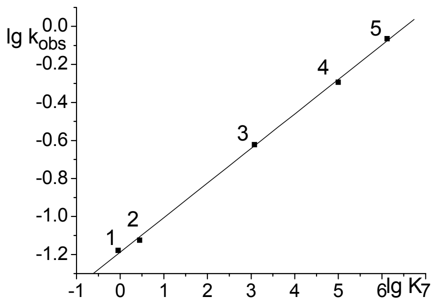
in which $[PhCOCl]_{org}$ is the concentration of benzoylchloride in the organic phase and k_{obs} is a linear function of the initial concentration of pyridine 1-oxide in the aqueous phase, i.e.,

$$k_{obs} = k_h + k_c[PyO]_{aq}$$

where $[PyO]_{aq}$ is the initial concentration of pyridine 1-oxide in the aqueous phase and k_h and k_c are uncatalyzed and catalysed rate coefficients, respectively.

Table. Effect of pyridine 1-oxide structure on the benzoyl chloride- *p*-nitrobenzoate ion reaction in H_2O/CH_2Cl_2 medium (293 K)

№	Catalyst	Yield, %	Reaction time, min	k_{obs}, min^{-1}
1		80.0-	25	0,066
2		59.0	10	0,075
		80.8	20	
3		81,4	10	0,239
4		84.2	10	0.508
5		74,7	10	0,862



As shown in Table, the obtained values of k_{obs} are strongly affected by the catalyst structure. Presumably this result indicates that the reaction rates depend on the catalyst ability to form reactive intermediate – 1-benzoyloxy- pyridinium chloride. This conclusion is supported by the data shown in Figure, which shows that the values of k_{obs} increased with increased of equilibrium constants (K) of formation of appropriate 1-benzoyloxypyri- dinium chlorides in dichloromethane (298 K) [2].

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MECHANISTIC STUDY OF RUTHENIUM(VIII) CATALYSED OXIDATION OF SOME POLYHYDRIC ALCOHOLS BY ALKALINE SODIUM PERIODATE

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Kinetic investigations on Ru(VIII) catalyzed oxidation of polyhydric alcohols (viz. ethylene glycol, glycerol and erythritol) by alkaline solution of sodium periodate in the presence of mercury(II) acetate as a scavenger have been made in the temperature range of 30-45°C. The rate shows zero order kinetics in substrate i.e. ethylene glycol, glycerol and erythritol and order of reaction is one with respect to sodium periodate and Ru(VIII). Addition of $[OH^-]$ shows zero effect. Negligible effect of addition of mercury(II) acetate, acetic acid and sodium perchlorate was observed. A suitable mechanism in conformity with the kinetic observations has been proposed and the thermodynamic parameters computed. Following rate law has been obtained.

$$\frac{-\,d[NaIO_4]}{dt} = K_1K_2k_3[RuO_4][IO_4^-]$$

GEOMETRICAL APPROACH FOR APPLICATION OF NANOMATERIALS IN CATALYSIS

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The chemical and physical properties of solid surfaces play a key role in many industrial processes, particularly in heterogeneous catalysis. New materials based on molecular structures on the nanometer scale are of great importance for improving catalytic performance of various solids. Metal and metal oxides nanoparticle composites play a key role in this issue. Changing precisely a size of nanoparticles or nanopores of composite may drastically change the catalytic properties of material. Simple theoretical consideration shows that dependence between catalytic activity and size of nanoparticles may be monotonically increasing or decreasing. It also may be bell-shaped indicating maximum of catalytic activity of nanoparticles in some range of their size. Quantum mechanical analysis shows a possibility for appearance of jumps in dependence between catalytic activity and size. All these considerations take into account only geometry of nanoparticles or nanopores.

These theoretical predictions are confirmed by our experimental studies of the dependence between catalytic activity of nanocomposites and their characteristic size (size of nanoparticles or nanopores). Comprehensive study of the CO oxidation on nanoparticles with controllable size for various metal oxides (iron, copper, zinc, cobalt, chromium, tungsten, zirconium) shows that catalytic activity of these solids shows either monotonic or bell-shaped dependence on the size of nanoparticles. Those finding give a hint to improve a catalyst for the CO preferential oxidation for hydrogen purification to use it in fuel cells. Similar experimental results obtained for hydrogen production by catalytic steam reforming of bioethanol, for the Fischer-Tropsch synthesis, methane partial oxidation producing formaldehyde, cyclohaxanole dehydrogenation, and some acid-base catalytic processes. We also show that geometrical approach allows synthesizing nanomaterials, such as carbon nanotubes, with controllable size by heterogeneous catalytic synthesis.

Finally we discuss briefly two main restrictions for the geometrical approach resulting from either nanoparticles aggregation or surface modification caused by change of the nanoparticles size.

KINETICS OF THE PROCESSES WITH THE PARTICIPATION OF SILVER AND GOLD NANOPARTICLES IN MICELLAR SOLUTIONS

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Reverse micelles of surfactants in nonpolar organic solvents are known to be convenient systems for synthesis of nanodispersed metal particles with a narrow size distribution. Micelles consist of aqueous droplets (aqueous cores) of small size that are separated from the balk organic phase by a surfactant layer. They act as nanoreactors in which the size of the core and hence the size and the shape of the forming metal particles are controlled by varying solubylization degree V_s/V_o (dispersed water phase volume / micellar solution volume). Reverse micelles collide continuously due to Brownian motion. The forming short-lived dimers exchange their water phase content and after a short time separate into two micelles again. So nanoparticles can be obtained by mixing micells with dispersed aqueous solutions of ionic metal and a reducing agent, or one can investigate the reactions of metal particles with dispersed aqueous solutions of different reagents. We have studied the formation processes for gold and silver nanoparticles (reduction of Au^{III} and Ag^{I} by sodium citrate) and their dissolution (oxidizing agents $HCl+H_2O_2$ and HNO_3 respectively) in micellar solutions of sodium bis-(2-ethylhexyl) sulphosuccinate and Triton N-42 as surfactants. The processes kinetics is well described by autocatalytic models (in pseudo first order conditions, M^+, M^0 — ionic and metallic gold or silver):

growth $M^+ \rightarrow M^0$, k'_{1g} (in dispersed aqueous phase)
$M^0 + M^+ \rightarrow 2\,M^0$, k'_{2g} (on particle surface)
dissolution $M^0 \rightarrow M^+$, k'_{1d} (on particle surface)
$M^0 + M^+ \rightarrow 2\,M^+$, k'_{2d} (on particle surface)

Both models take into account a changing of the surface area (k'_{2g}, k'_{1d}, $k'_{2d} \sim n_s$) and of the effective charge density (k'_{2g}, k'_{1d}, $k'_{2d} \sim z \cdot n_g / n_s$) of the particles in the reaction process, k'_{1g}, k'_{2g}, k'_{1d}, k'_{2d} — observed velocity constants, n_g, n_s — general number of atoms and number of surface atoms in the particle, z — number of valent electrons for metal. Models lead to kinetic equations $d\,[M^0]_t / d\,t = a_0 + a_1 \cdot [M^0]_t + a_2 \cdot [M^0]_t^2$ that correspond with experimental data ($[M^0]_t$ — current concentration of metal in micellar solution, in the case of dissolution parameter $a_0 = 0$).

This work was supported by the Russian Foundation for Basic Research, project No. 05-03-32308.

MATERIAL SCIENCE

DETERMINATION OF REACTIVITY RATIOS FOR AM AND NVP MONOMERS IN COPOLYMERIZATION AND STUDY EFFECT OF PH ON REACTIVITY RATIOS OF MONOMERS

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Copolymers have been extensively used in industry and everyday they are used in new dimensions with new characteristics. As a result, the study of the reactions leading to their formation would be of significant importance.

Therefore, the investigation and the study of types and structure of copolymers and determination of their reactivity ratios of monomers involved in copolymerization seems to be essential.

According to different application of AM-NVP copolymer in this research, copolymerization reaction between AM and NVP in water and ethanol (4:1) with redox system ($FeSO_4$-H_2O_2) in 30±0.1°C temperature in pH= 2 and pH= 6 is studied.

Copolymerization reaction is stopped by hydroquinone inhibitor for measuring remaining of monomers in the end of specific periods.

Dieing out monomers depend to the times specified by bromometry and gas chromatography methods.

Also by applying graphic solution of Mayo-Lewis equation by computer, the reactivity ratios of monomers are calculated as they are shown here:

pH=6	$r_{AM}=4.12$	$r_{NVP}=0.059$
pH=2	$r_{AM}=3.48$	$r_{NVP}=0.074$

THE EFFECTS OF CHEMICAL MODIFICATION OF STYRENIC POLYMERS BY BULKY ORGANOSILYL GROUPS ON STRUCTURE AND THERMAL PROPERTIES

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Chemical modification of polymer structures is an important route for modification of polymer properties such as mechanical, thermal and surface properties. In recently years, modification of polymer properties has been studied by attachment of various groups to macromolecular chains. 4-Chloromethyl styrene (CMS) is an important dual functional monomer that can be polymerized before or after chemical functionality reactions on the benzyl chloride group. The functionalized CMS polymers have been widely used in different processes as bactericide polymers, photo-sensitizers, solar energy storages, photo-resists, non-linear optics and polymeric prodrugs in drug delivery systems. The very bulky tris(trimethylsilyl)methyl group, $(Me_3Si)_3C$-, in which three organosilyl groups are attached to the central carbon atom, is one of the largest substituents and referred to as the 'trisyl' ligand. In this research work, CMS was copolymerized with various molar ratios of methyl methacrylate or ethyl methacrylate monomer by solution free radical polymerization method. The molar compositions and average molecular weights of the copolymers were determined using ^1H NMR spectra and gel permeation chromatography, respectively. Then, very highly sterically hindered $(Me_3Si)_3C$- group was covalently linked to the obtained copolymers as side chains by reacting trisyllithium with benzyl chloride bonds of polymers. FT-IR, ^1H and ^{13}C NMR spectroscopy techniques were confirmed the structure of the obtained trisyl-based polymers. Study of differential scanning calorimetry curves showed that chemical modification of CMS copolymers with $(Me_3Si)_3C$- ligand leads to an increase in the chain rigidity of polymers with decreasing free volume. Also, incorporation of $(Me_3Si)_3C$- groups in polymer structures increases the glass transition temperature of polymers and creates new styrenic macromolecules with novel modified properties.

SYNTHESIS OF MESOPOROUS SILICA MATRICES WITH SPHERICAL MORPHOLOGY OF PARTICLES

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Mesoporous silicas with high specific surface area and ordered pore structure are perspective adsorbents and carriers of catalysts. Particles morphology is one of the primary factors for their application in separation processes and heterogeneous catalysis. That is why the ability of macroscopically control with improving of pore structure is an important trend in the field of ordered mesoporous silicas studies. In present investigation the influence of media type on pore structure and particle morphology of mesoporous silicas was established.

Syntheses of ordered silicas under alkaline conditions were carried out from tetraethoxysilane (TEOS) and cetyltrimethylammonium bromide (CTAB) in alcohol-ammonia media with different molar ratios of TEOS/CTAB using both ethanol and isopropanol (ROH). Molar ratios of components were 1TEOS : XCTAB : $11NH_3$: $144H_2O$: 58ROH, where X were 0.1, 0.2, and 0.3. Synthesis of silica under acidic conditions was held in hydrochloride acid solution with use TEOS as a silica precursor and CTAB was applied as a cationic surfactant. Molar ratio of reactants was 0.1TEOS : 0.1CTAB : 0.45HCl : $100H_2O$.

The synthesized silicas were characterized by adsorption-desorption of nitrogen at 77 K (ASAP-2000) to determine the specific surface area, pore volume and pore size distributions. The structure of samples was investigated using the small-angle X-ray diffraction (automated diffractometer DRON-4-07, CuK_{α}-radiation) and transmission electronic microscopy (JEM-100CXII). Method of scanning electronic microscopy (Superprobe-733, JEOL) was applied to study the form and size of the obtained silica particles.

In alcohol-ammonia media mesoporous silicas with pore diameter about 25-35 Å and specific surface area of 450-1200 m^2/g have been obtained. It was established that silicas with monodisperse spherical granulation of particles were formed with use ethanol under molar ratios of CTAB/TEOS=0.2 and 0.3. Mesoporous silicas with disordered pore arrangements and less uniformity of spherical particles were obtained in isopropanol. In acidic media uniform spherical particles of microporous silicas of 10 µm size have been synthesized, they characterized by less value of specific surface area (600 m^2/g) and weakly ordered pore structure.

DESIGN AND FUNCTIONAL PROPERTIES OF NEW NANOSTRUCTURE MAGNETIC MATERIALS ON THE BASE OF POLYNUCLEAR METAL COMPLEXES

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The past decade is characterized by continuously growing interest to the polynuclear coordination compounds. This is mostly connected with vigorous development of such directions of modern chemistry as bioinorganic modeling, molecular magnetism, metallocomplex catalysis and crystal engineering. Nano-sized exchange clusters of high nuclearity represent a special interest as such systems can be regarded as original nanoobjects exhibiting unique functional properties and thus can be considered as perspective substances for creation of magnetic material of new generation. Presently one of the most important problems in this field is development of rational synthetic pathways for creation of nano-sized exchange clusters of high nuclearity. In the report the

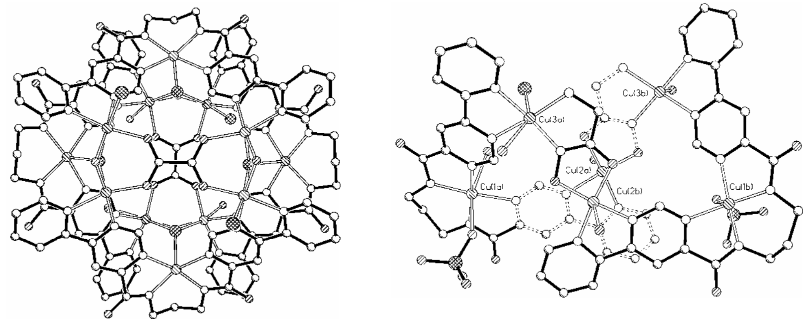

Fig 1. Molecular structure of 12- and 6-nuclear copper(II)-containing exchange clusters obtained by hierarchical self-assembly in solution.

possibilities of application of different preparative approaches for such objects are reviewed. A special attention is paid to the use of one of the most perspective methods for creation of multinuclear exchange clusters – use of processes of hierarchical self-assembly in solution. In the report a series of examples of successful use of this approach by the authors is presented (Fig. 1). The peculiarities of molecular structure of the multinuclear assemblies are discussed together with their magnetic, spectral and other important functional properties.

NANOPARTICLES OF METALS IN SURFACE LAYER OF SILICA MATRICES

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Nanoparticles of noble metals have potential applications in catalysis, optics, optoelectronics, and biology. However, in a majority of cases obtained nanoparticles are unstable. Immobilization of such nanoparticles on the supports, such as polymer latex particles, alumina, zeolite, carbon cages, and silica, to form appropriate nanocomposites is of great interest.

One of possible approaches of controlled synthesis of silver and gold nanoparticles is use of porous matrices that confine growth of nanoparticles. For preparation of supported metal nanoparticles the chemically modified ordered mesoporous silica of MCM-41 type was applied in this work. Reducing reagents immobilized on the external surface of ordered mesoporous silicas were used for *in situ* reduction of nanoparticles of gold and silver at the interaction with chloroauric acid or silver nitrate solutions in the mild conditions. For this silica matrices were modified with triethoxysilane in the presence of acetic acid with the object of producing grafted silicon hydride groups on the silica surface. Absorption bands at 2240 cm^{-1} in the IR spectrum of the modified silica could provide evidence for the fact that attachment of silicon hydride groups occurred.

The x-ray powder diffractograms of the prepared samples confirm formation nanoparticles of gold or silver with a face-centered cubic arrangement. The electron microscopy data provided evidence for formation of nanoparticles of gold (diameter 20–30 nm) and silver (diameter 25–28 nm).

Another possible route of metal nanoparticles stabilization is reduction of metal ions in time of silica particles formation using sol-gel transformations. We have observed silver nanoparticles formation in the mixtures of silver nitrate and triethoxysilane solutions. The formation process and the optical properties of the silver nanoparticles can also be identified from both the color change and the UV-Vis spectra of the solutions. After stirring the color of obtained solution became yellow immediately. This observation is supported by the UV/vis-spectra of the coatings, which show a clear minimum in reflection around λ=420 nm due to the plasmon resonance of colloidal silver. The change of peak position and the shape of the absorption spectra were obvious during the whole reaction process. After keeping under quiescent conditions for 8 h the color of the solution was changed from yellow to light grey as the reaction progressed. The Ag-colloid formation was monitored by UV-VIS spectroscopy as a function of time. Changing of color was accompanied with appearance of another high-frequency peak at λ=600 nm, that can be explained by fractal aggregates formation.

GROWTH OF SiO_X NANOWIRES USING METAL LAYERS

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Since the discovery of carbon nanotubes, much interest has been drawn towards the one-dimensional nanomaterials because of their special characteristics. In this communication, we have demonstrated the synthesis of SiOx nanowires using the thermal reaction between Si-containing materials and predeposited metal layers. We have characterized samples by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We have discussed the possible growth mechanisms, with respect to the role of metal layer.

MATERIALS SCIENCE OF RADIATION STABILITY: THE CRYSTAL-CHEMICAL APPROACH

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Contemporary nuclear power application in the world power engineering is significant. Its prognostic level is still more grandiose, taking into account the technology of fusion and fission nuclear reactors of the future as well as the perspectives of future space technologies. Along with special problems of these directions of world energetic there is one, being general for all of them: people with physicochemical education have to provide materials which would endure tortures of ionizing irradiation of extremely high doses more than 10^{22} of fast neutrons per cm^2 (for example) during a year of exploitation. The same problem arisen is the nuclear waste containerization for a long term like thousands of years.

It is the great challenge for scientists: the ionizing irradiation caused the damages in solids, which spoil their exploitation parameters. Some of these damages can be removed by annealing at high temperatures, but it is not a suitable method for nuclear power industry. Thus one has to propose any idea to avoid the damages *in statu nascendi.* Is it possible?

This is the review of present state of the problem.

In 1969 we had discovered the group of inorganic compounds of In_2Te_3 type with extremely high radiation stability. Then it had been shown that the semiconductor and insulator compounds of such type preserve all their properties during and after action of great doses of gamma-quanta, of electrons of high energy (from 10 to 300 Mev), and of fast neutrons as well. The maximum dose achieved (for fast neutrons, for instance) is 10^{18} cm^{-2}. The "classical" crystals like Ge, Si, InAs, CdTe etc. are spoiled completely under doses less for some orders of value. We had investigated different parameters of In_2Te_3 type compounds: electrical conductivity, Hall-effect, thermoelectric coefficient (all at wide range of temperature); optical absorption in visible and infrared region; mechanical parameters (microhardness). All these parameters appeared to be unchanged for the compounds of the family named along and after irradiation by fluencies of such large scales.

The theory developed showed that this unusual effect is determined by the peculiarities of crystal structure of pure chemical compounds. It is the result of two reasons. First is the existence of so called zones of absolute instability of complementary as well as similar defects in a definite vicinity of other defects. This value can be calculated beforehand. The second precondition of radiation stability is the suppression of the effect of so called focusing of atomic collisions – simple (by Silsby) or "additional".

being really more effective (Tompson, Nelson). We had showed that the presence and content of regular structural voids, which existence in the crystal lattice of a given inorganic compound is determined by valence interrelations exclusively, provide the formulation of the criterion of presence or absence of atomic collisions focusing, which appears to be a factor of producing stable radiation defects. The criterion of radiation is as following: if the radius of instability zones of defects in more than the free path length in a given compound crystal lattice, all radiation defects are annihilate at the same point in which they were born within a term of order of 10^{-11} s. Using the crystal-chemical approach we were able to predict crystal materials with extremely high radiation stability. These are semiconductor or insulator compounds as well as metal alloys of definite compositions, but all of them have the loose crystal structure, which predetermines the absence of focusing atomic lenses and existence of defocusing ones.

The radiation stable semiconductor and insulating materials can be used for measurements in cosmos as well as in inter-reactors' measurements. The radiation stable metal alloys can be used as construction materials for nuclear power industry. Reviews [1-3] are devoted mostly to the theory of radiation stability. The technical applications of radiation stable materials one may find in the recent review [4]. One may find in it the complete description of radiation stable resistors, thermoresistors, photo-resistors, measures of extremely high intensities and doses of ionizing radiation of different origin. The possibilities for radiation stable electronics based at the chemical compounds with loose crystal structure are presented as well.

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ELECTROCHEMICAL FORMATION OF COPPER GAS-SENSITIVE NANOSTRUCTURES IN SOLID ELECTROLYTE

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The point-contact gas-sensitive effect discovered recently [1] can be arranged among the most modern achievements in the field of sensor activity. The general metrological parameters of point-contact sensitive elements such as speed of response, amplitude of response signal, recovery time, etc. surpass those of all the known for today nanostructure-based analogs. These advantages are provided with unique physical properties of point contact [2]. At the same time there are several problems on the way to creation of the commercial samples of such sensor caused by specificity of point contact structures. Mechanical stability of point contacts during their transportation and replacement in the media under investigation is among these problems.

In the present work we studied the opportunity of creation of stable gas-sensitive dendrite point contacts in solid copper-sulphidic electrolytes. Point contacts in the form of prolonged copper channel were synthesized electrochemically through thin (10 nanometers) layer of copper sulphide situated between two copper electrodes. As a key parameter of process control resistance of point contact was used. It is connected both with linear dimensions of samples under study [2] and state of the sample surface on which the certain gas agent is adsorbed. Responses of copper dendrite point contacts to the action of several wide-spreading gases (NH_3, NO_X, H_2S) and complex gas mixture exhaled by a human were registered. The relative correlations of parameters which are significant for the process of point contact formation were determined. The method is developed and the electrochemical synthesis of necessary nanostructure is optimized.

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PHYSICOCHEMICAL INVESTIGATION OF MATERIALS BASED ON POLYACRILONITRILE DERIVATIVES AND HETEROMETALLIC COMPLEXES OF SOME D-ELEMENTS

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The general principle of the synthesis of fibrous inorganic ion-exchanging composites, containing the combination of polymer analogous conversion reactions of the fibres and cycles of ion-molecular layering is advanced. The synthesis of thin nanomolecular layers of the Cu(II) and Fe(III) hexacyanoferrates (II) was performed by the method of the chemosorption layering on a matrix which represented the derivatives of polyacrylonitrile fibres containing **$HO{-}N{=}\dot{C}{-}NH_2$** groups with the degree of substitution of **CN**-groups about 50%. The synthesized materials were studied while using methods for chemical and X-ray analyses, electronic-microscopy, IR-spectroscopy and sorption investigations. According to the data from the X-ray studying of the synthesized pellicular hexacyanoferrates, their composition is described by the formulas **$K_x Cu_{(2-x)} [Fe(CN)_6] \cdot 4H_2O$** and **$K_x Fe_{(4-x)} [Fe(CN)_6]_3$** (compounds I and II respectively). By the methods of IR-spectroscopy, formation of heteroatomic cycles by polyacrylonitrile derivatives (with participation of strong **H**-bonds) was shown. They were capable to disintegrate under the effect of the ions of **d**-metals. It is suggested that strong adhesion of the layers with the matrix is caused by formation of linkage between **$[Fe(CN)_6]^{4-}$**-ions and the ions in chelates' composition through **CN**-bridges. The equilibrium ion-exchange capacity on the Rubidium, Cesium, Strontium and Thallium ions linearly depends on the layer's thickness, which is determined by the number of layering cycles **(n)** and reach maximum when n = 8. The ion-exchange property testing of the synthesized compositions was carried out by sorption from water solutions of the strontium ions and stable and radioactive Cesium isotopes. The investigation of ion-exchange kinetics of $^{137}Cs^+$-ions into K^+-ions was carried out by the method of limited volume while using of a semiconductor multichannel gamma-spectrometer for measurement of solution specific activity. The full ion-exchange capacity of ionites on the basis Cu(II) and Fe(III) ferrocyanides reaches 1,0 mmol-equ/g. Ion-exchange equilibrium on synthesized ionites is reached approximately 30 times faster, than on corresponding powdery crystalline ferrocyanides. Conclusion about prospect of the synthesized material usage in ion-exchange technology, including for extraction of radionuclides is made.

STIMULI-RESPONSIVE HYDROGELS FROM ACRYLAMIDE WITH N-[3-(DIMETHYLAMINE)PROPYL]METACRYLAMIDE. SYNTHESIS AND PROPERTIES

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Polymeric hydrogels derived from poly(acrylamide), crosslinked by a small amount of a bifunctional compound, have found wide applications in the fields of agriculture and medicine (1-2). Among water-containing polymeric gels, and hydrogels derived from

polyacrylamide are among the most widely investigated.

Hydrogels are now recognized as a well established class of polymers with widespread applications in agriculture, medicine, food industry, biotechnology, environmental sciences, among others. The structural feature of these materials dominates its surface properties, permeselectivity and permeability, giving hydrogels their unique, interesting properties and the similarity of their physical properties to those of living tissue (3).

Hydrogel properties mainly depend on the degree of crosslinking, the chemical composition of the polymeric chains, and the interaction between the network and surrounding liquids. Hydrophilicity or high water retention in hydrogels is attributed to the presence of hydrophilic groups, such as carboxylic acids, amides, alcohols and so on.

The aim of this work is synthesize copolymers of acrylamide with N-(3-dimethylamine)propylmetacrylamide at different initial comonomer ratios with different degrees of crosslinking, and to study the swelling effects of these hydrogel systems in twice-distilled water at different pH, temperature, time, and salt concentration.

Cross-linked copolymers of acrylamide (AAm) with N-[3-(dimethyl amine)propyl]metacrylamide (NDAPM) were prepared by solution radical polymerization at different feed molar ratios. In this reaction, ammonium persulfate (APS) and N,N´-methylene bis (acrylamide) (MBA) were used as initiator and cross-linking reagents respectively. The effects of reaction parameters, including the concentration of crosslinking reagent and initiator, the monomer concentration, the pH, temperature, the various salt solutions and solvent polarity, on the water absorption have been investigated. Some results are shown in figures 1 and 2.

The effects of pH on the absorbency were studied. It was found that the absorbency of poly(AAm-*co*-NDAPM) increases as the pH increases from 1 to 2, and then decrease abruptly at higher pH. It was found that the absorbencies increase until 50 ºC in the three copolymers, and then remains constant up to 70 ºC. These results implies that poly(AAm-*co*-NDAPM) can be used in a wide temperature range. The influence of the salt solutions on the absorbency was investigated, and the results indicate that absorbency is a decreasing function of the rising salt concentration.

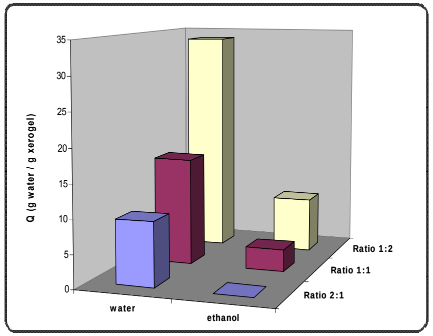

Figure 1. Absorption (Q) of poly(AAm-co-NDAPM) co-NDAPM) 1:1; 1:2; 2:1 / 4 % MBA in bidistilled water and ethanol at room temperature.

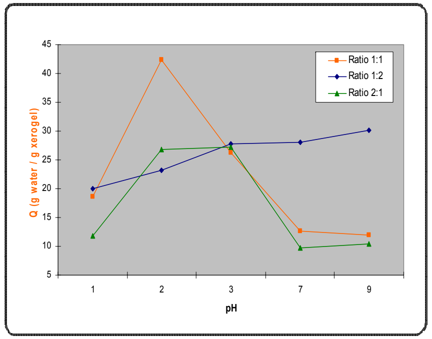

Figure 2. Absorption (Q) of poly(AAm- co-NDAPM) 1:1; 1:2; 2:1 / 4 % MBA in water to pH 1; 2; 3; 7 and 9 at room temperature.

The results indicate that the copolymers obtained are stimuli-responsive hydrogels that change their volume and elasticity in depending on the properties of the liquid phase.

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FUNCTIONAL POLYMER MATERIALS TO REMOVE IONS IN CONJUNCTION WITH ULTRAFILTRATION MEMBRANES

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Water-soluble polymer-ions interactions take place in a homogeneous medium. To face the problem of separation of ions bound to the polymer and non-bound, one of the most promising techniques used is the application of separation methods based on membrane process (1-3). Membrane filtration easily allows this separation by means of the method known as the *liquid-phase polymer-based retention (LPR)* technique.

The present work is related with the synthesis and characterization of water-soluble polymers containing carboxylic acid, sulfonic acid, and ammonium as groups as well as the study of the ion ability retention properties through the LPR technique.

The water-soluble polymers were characterized by FT-IR and ^{1}H-NMR spectroscopy.

The ion retention properties are investigated by LPR technique (washing method) (see figure 1). This is a batch-like method where a solution containing the polymer and the metal ions to be separated is placed in the ultrafiltration cell at a given pH and ionic strength. Interactions of metal cations: Co(II), Ni(II), Ca(II), Mg(II), Pb(II), Cd(II), Zn(II), and Cu(II), and As(V) as anionic specie with water-soluble polymers were studied at different pH and filtration factor, Z.

It is useful to quantify the separation process by plotting the retention of the metal species versus the filtration factor. The filtration factor (Z) is defined as the volume ratio of the filtrate (V_f) versus volume in the cell (V_o). Retention (R) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration.

Metal ion (M) remaining in the cell during filtration consists of the sum of the metal ion bound to the polymer chain and the metal ion free in the solution.

To obtain the retention profiles a polychelatogen : ion 40:1.0 relationship is used. It corresponds to 0.2 mmol : 0.005 mmol. This ratio obeys to ensure an excess of the ligand groups respect to the ion specie.

The metal ion retention ability of the water-soluble polymer depends strongly on the pH. As the pH increases the metal ion retention increases. It is due to at higher pH, the majority of carboxylic acid groups are non-protonated. Therefore, the carboxylate group is more available to bind metal ions. Particularly at pH>5, which is above to the pKa value for an acrylic acid. The interactions between the polymer and the metal ions are mainly due to electrostatic forces and to formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase. Respect to the removal of metal ions, at higher pH, as pH 5 and pH 7, increased the ability to bind metal ions and there is not an important decrease on the retention as increases Z. That means that the sulfonic/sulfonate-metal ion interaction is strong. The polymer-metal ion interaction may be intramolecular, intermolecular or both. As(V) species are removed by polymers containing ammonium groups. The highest retention ability was observed at higher pH (6 and 8). The retention of arsenic occurs basically by ion-exchange through the exchange of the counter ion of the polycation and the anionic specie of the arsenic.

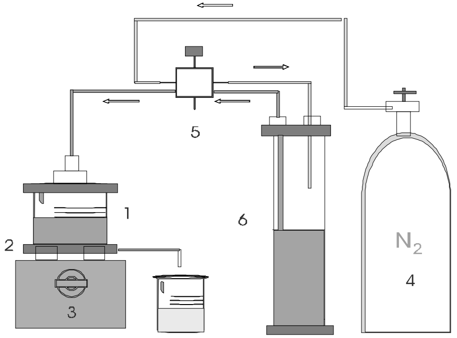

Figure 1. Instrumental arrangement: (1) filtration cell with polymeric and metal ion solution; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with water.

In addition, water soluble polymers containing carboxylic acid and sulfonic acid groups showed a high affinity for metal ions. It depends on the structure of the polymers and on the pH, and filtration factor, Z. The functional polymer group-metal ion interaction would occur through different mechanisms. For carboxylate groups should be by complexing process and for sulfonic acid it should be by electrostatic process.

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NANOSCALE LANGMUIR-BLODGETT FILMS BASED ON CALIX[4]RESORCINARENES: PREPARATION, PROPERTIES AND APPLICATION IN CHEMICAL SENSORS

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Calix[4]resorcinarenes (CRA) are well known macrocyclic compounds which are noted for their size-related selectivity in binding cations as well as organic guests molecules [1]. Thin films can be constracted from CRA for sensing applications using various deposition techniques. We used Langmuir-Blodgett (LB) technique that allows obtaining high-ordered nanosized film of amphyphilic molecules with precisely controllable thickness and directional spatial orientation [2]. Amphiphilic calix[4]resorcinarenes with hydrocarbon chains have been specially synthesized for the application to LB technique.

Preliminary the behavior of CRA monolayers on the liquid aqueous subphase (bidistilled water and metal-containing aqueous solution) by surface pressure – area per molecule isotherms measurement has been investigated. The characteristics of CRA monolayers (the limited area per molecule, collapse surface pressure and compressibility) have been obtained. It has been shown that CRA molecules forming monolayer interact with metal ions (Cu^{2+}, Ni^{2+}, Tb^{3+}, Eu^{3+}, La^{3+}) from the aqueous subphase.

LB-films have been built up by transferring CRA and CRA-Me monolayers on quartz, GaAs and silicon substrates. Transfer ratio measurements, ellipsometry data, UV-visible optical absorption spectra and mass-spectra were used for information about the structure, molecular arrangement and composition of the CRA LB films. The information obtained was used for design of optimal conditions for sensor layer preparation.

The films were applied as modifiers of piezoresonance sensor for the organic solvent (benzene, toluene, acetone and etc.) vapor detection. The important features of the sensors are reversibility, fast response and long lifetime.

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PRIDINE-2-CARBALDEHYIDE-OXIME N, N' METAL(MERCURY): SYNTHESIS AND STRUCTURAL CHARACTERIZATION

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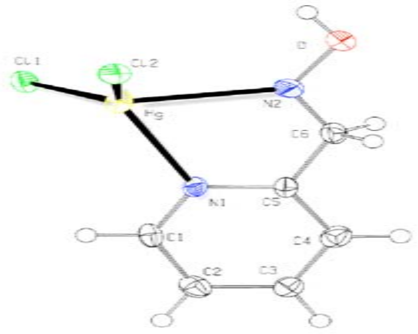
The solid state structure of $C_6H_7N_2OHgCl_2$ was determined by using X-ray diffraction and appropriate assignment of N-Hg binding by FT-IR spectrum was made. The monomeric mercury(II) complex crystallize in the triclinic system, $P1^{-}$, a=3.875(10) Å, b=8.724(3) Å, c=13.942(5) Å, α=107.06(5)º, β=95.90(5)º, γ=95.22(5)º, V=444.54 Å$_3$, Z=2, , T=173 k. The structure has been refined to a final value of the conventional R-factor of 0.0441 based on 2370 observed independent reflections and wR(F2) is equal 0.1298. The coordination number around mercury(II) atom is four.



Pridine-2-carbaldoxime mercury (II), was obtained by reacting of pridine-2-carbaldoxime as ligand (L; 0.34 gr, 2.7 mmol) with mercury(II) chloride (0.4 gr, 1.4mmol) in methanol (4ml) at 45ºc temperature after a week crystallized as colorless crystals. Melting point is 210.1ºc.

In the compound, $Cl_2Hg[C_5NH_4]CH_2NOH$, the Hg atom linked by bridging N atoms. Our attention was drown to potentially coordinating ligand pridine-2-carbaldoxime, recorded initially as forming complexes with manganese(II) and zinc(II) salt [1], seemingly mononuclear. In this research synthesis of 1:1 mercury(II) chloride pridine-2-carbaldoxime was followed. The pridine-2-carbaldoxime ions in this complex are coordinated via N atoms (figure **1**). There is a significant difference between Hg-N$_1$ [2.364(6) Å] and Hg-N$_2$ [2.525(8) Å] bond length. It is nearly the same as the sum of single-bond covalent radii of Hg-N, 2.51 Å [2], which indicates that a strong single- bond covalent interaction is formed between Hg and N. But Hg-N bond length has been reported between (2.106-2.800) [2-5]. The valence bond angles around the metal atom are 101.40(18)º , 92.94(18)º 67.50(2)º and 134.10(7) respected to N$_1$-Hg-Cl$_1$, N$_2$-Hg-Cl$_2$, N$_1$-Hg-N$_2$ and Cl$_1$-Hg-Cl$_2$. The complex is insoluble in dichloromethane, chloroform, water, aston and asetonytril, it can be a good idea for omiting mercury from industrial residual.

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ELECTROCHEMISTRY OF MESOPOROUS SILICA FILMS

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Sol-gel electrochemistry has gained great popularity in the past decade, mostly because of the ease of formation of silica and organosilica films with tailor-made properties that can be advantageously exploited for several applications when coated on a suitable electrode surface [1-3]. The usual way to get such films involves either dip- or spin-coating a sol-gel medium containing the appropriate (organo)alkoxysilane precursor(s), which are hydrolyzed and (co)condensed on the electrode surface. Such film-modified electrodes have found applications in various fields including electroanalysis and sensors, electrocatalysis, or bioelectrochemistry [2, 3]. More recently, silica-based materials displaying a regular structure at the mesoporous level have been found very promising electrode modifiers [4] because they ensure fast mass transport processes, which are often rate-determining in electrochemistry.

The aim of this lecture is to highlight and discuss some recent achievements performed with such new materials in electroanalytical chemistry. Three complementary directions will be considered. The first one relies on the usefulness of electrochemical techniques to get information on mass transport through ordered mesoporous films, with special emphasis on the influence of the mesostructure type and the nature of the redox probe on these processes [5]. The second aspect concerns a feedback of materials science to electroanalysis, by exploiting the attractive and sometimes unique properties of mesoporous (organo)silica films on electrodes to improve their sensitivity in comparison to the non-ordered ones, when applied as voltammetric sensing devices [6, 7]. The third domain is related to the use of electrochemistry to prepare thin films of sol-gel-derived (organo)silica films, via a rather novel electrochemically-driven deposition method [8]. This involves basically the formation of a self-assembled monolayer of mercaptopropyltrimethoxysilane on a gold electrode, which is then transferred to a silica sol containing the hydrolyzed precursors where a cathodic potential is applied to increase pH locally at the electrode/solution interface and to induce co-condensation of the precursors [9]. Special attention will be given to highlight the effect of the electrodeposition conditions (applied potential and duration) on the film formation mechanism and on its properties [10]. Preliminary results on the possibility to prepare ordered and oriented mesoporous films by this method will be also discussed.

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POROUS SILICON AS A SUPPORT FOR DEVELOPMENT OF MINIATURE ANALYTICAL DEVISES

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Potential application as lab-on-chip devises was studied for porous silicon produced electrochemically on silicon wafer. To develop solid phase extraction (SPE) cartridge, silicon wafer was etched all the way through and porous membrane with thickness of 200 um and $1cm^2$ surface was created. Up to 3 pl/min of liquid can be pumped through. It was found that such membrane has weak chemical stability hydrophilic properties and small (less them 10 nm) average pore size. Hydrosilylation of porous silicon improve its chemical stability. Size of pores can be increased by controlled stain-etching. Upon optimization covalent immobilization of ligand was performed to develop micro SPE. To develop microfluidic system suitable for LC silicon wafer was etched along its surface to create silicon micro (50 um) channels filled with porous silicon. Silanisation and hydrosilylation reaction were used to modify porous silicon surface. It was demonstrated that surface of the channel after such treatment may have hydrophobic, complexing, ion-exchange and activated groups. In order to integrate in one devise separation and analytical block, ability of porous silicon to be used as support for surface-induced Raman spectroscopy was studied. For this silicon wafer were electrochemically treated to obtain porous silicon membrane with 50 um thickness and 1 cm diameter. The membrane was treated by silver compounds and optimal conditions for chemical/thermal reduction of the metal were investigated. Formation of Ag metal clusters through all membrane thickness was proved by SIMS. Raman spectra were detected for 20 ul of 0.1 mM solution of imidazole after it was absorbed on Ag-treated membrane. Using silicon with different porosity of adjacent layers Bragg mirrors was prepared. Under chemical treatment hydrophilic properties of this material can be varied and so chemical sensor to volatile compounds can be developed. Linear relationship between solvent reflection index (I_r) and adsorption maximum in the sensor reflection spectra was found as next: ($\lambda=1.655+0.229\cdot I_r$). Hydrophobisation of porous silicon surface improve its stability and increase selectivity towards more ecologically important volatile compounds.

USE OF VIBRATION AND SOLID-STATE NMR SPECTROSCOPY, MALDI AND METAL MICROPROBE METHOD FOR ESTABLISHMENT OF THE SURFACE LAYER STRUCTURE IN FUNCTIONALIZED MESOPOROUS SILICAS

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Application of sol-gel and template methods, which are based on hydrolytic polycondensation reactions, has allowed to obtain the whole scale of new hybrid organic-inorganic materials, which contain various functional groups in their surface layer, including complexing

groups. It is known, that advantages of sol-gel method are both an opportunity to use the multicomponent systems and variations of synthesis conditions in a wide range. It allows not only to enter necessary functional groups (or their combinations) into a surface layer, but also to influence on the structural–adsorption characteristics of final products – xerogels. The use of various surfactants during synthesis causes the formation of structures with porous of the identical size and form. In another words, the template method allows to conduct fine tuning of porous structure of functionalized mesoporous silicas according the solving problems requirements.

However during such researches not enough attention was payed to determination of composition and, especially, structure of the surface layer. It is obvious, that transformation of complexing groups (at least, their parts) is possible during hydrolytic polycondensation reaction, especially in the case of acid or basic catalysts application. The questions connected with studying of conformational mobility of functional groups in a surface layer, their possible display of cooperative effects etc. also have dropped out of from researchers field of vision. However such data is necessary for purposeful synthesis of new effective adsorbents, selective catalysts, carriers for chromatography, etc. Therefore, the given report is an attempt to summary the results of composition and structure studying of functionalized mesoporous silicas surface, which were obtained previously in our laboratory. These results have been received with the help of a number of physical methods (electronic microscopy, the thermal analysis, IR and Raman spectroscopy, solid-state (CP/MAS) NMR spectroscopy (on such nucleus as ^{1}H, ^{13}C, ^{29}Si, ^{31}P), MALDI, metal microprobe method) and also quantum chemistry.

Thus by example of aminocontaining polysiloxane xerogels it was shown that the state of 3–aminopropyl groups, which are located in a surface layer, depends on quantity of water molecules which are contained in it. At the composition of xerogels, which can shown in the following formula $(SiO_2)_{2.6}\cdot[O_{3/2}Si(CH_2)_3NH_2]\cdot H_2O$, the amino group is not protoned and forms - through a molecule of water - hydrogen bound with silanol group. Protoning of an amino group becomes energetically favorable only in case of more than one molecule of water occurrence in a surface layer, i.e. when the wetting of samples takes place. The similar picture is observed in the bifunctional surface layer, which consists of amino- and mercaptogroups. In other words, the thiolgroup shows certain inertness. At some ratios of these groups the essential increase of surface layer thermal stability in such xerogels is observed.

Differently, the synergism effect is shown.

During the studying of phosphineoxidecontaining nonporous xerogels it was revealed that their treatment by a hydrochloric acid leads not only to porous structure occurrence, but also to the following transformation of functional groups: $\equiv Si(CH_2)_2P(O)(OEt)_2 \rightarrow \equiv Si(CH_2)_2P(O)(OH)_2$. Thus during vacuum drying of xerogels about a quarter of new groups forms bound with silanol groups as $\equiv Si–O–P(O)(OH)(CH_2)_2Si\equiv$. This bound is hydrolytic unstable, however its formation should be taken into account during the application of such xerogels, for example, in nonaqueous mediums and gas chromatography.

The increase of content of the alkoxysilanes with ligand group in an initial reaction solution - in comparison with structure-forming agents - frequently conducts to formation of xerogels with the polymeric surface layer. It causes not only the various morphology of final products, but also leads to occurrence of distinctions at complex formation with metal ions. The similar effect appears also in the case of the use of xerogels with a bifunctional surface layer (for example, at composition $\equiv Si(CH_2)_3SH/\equiv SiCH_3$; $\equiv Si(CH_2)_3SH/\equiv Si(CH_2)_2CH_3$, etc.), which contains a different ratio of functional groups.

Hence, in case of functionalized mesoporous silicas study only the use of a number of physical methods and also quantum chemistry allows to obtain data of structure and behavior of their superficial layer.

The partial financial support of the NATO (SfP-978006) and Ministry of Education and Science of Ukraine is gratefully acknowledged.

PHOTOCHEMISTRY AND FLUORESCENCE

EFFECT OF METAL CATIONS ON THE PHOTOCHROMISM OF SPIROOXAZINES

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Spironaphtoxazines (SNO) are among the most prospective types of photochromic compounds because of their potential application as optical sensors for metal ions and elements of photoswitchable molecular devices. Introduction of crown-containing moieties into SNO structure opens a possibility to control their spectral and kinetic properties by addition of metal cations [1].

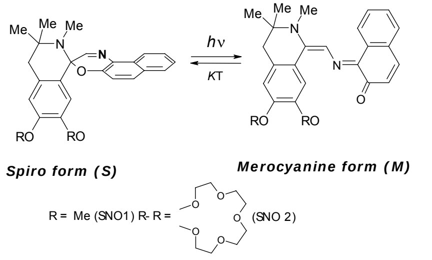


Figure 1. Structure of SNO

Photochromism of SNO is determined by the transitions of a spiro (S) form and a merocyanine (M) form (Fig. 1). For crown-containing SNO (marked as 2) the formation of complexes between S-form and metal cations was observed. The structure of SNO 2 complexes with Met^{2+} (Fig. 2) was studied by UV, NMR and ESI-MASS spectrometry. Equilibrium constants were determined.

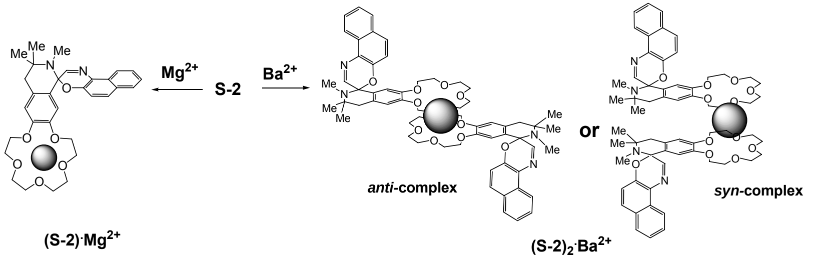
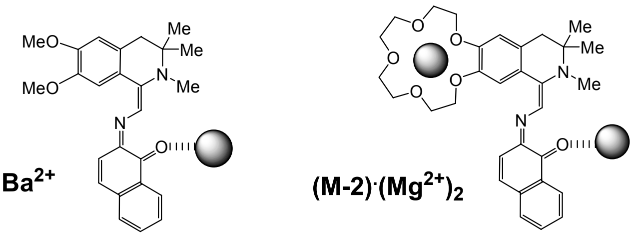


Figure 2. Structure of SNO complexes with metal cations in CH_3CN

Irradiation of a spiro form of SNO in the near UV region leads to the formation of a merocyanine (M) form (Fig. 1), which has a very intensive absorption in the region of ca. 600 nm. The characteristic times of the back M→S transitions at a room temperature are about several seconds. The values of activation energies are always in the range of 65-90 kJ/mole, which is typical for all the SNO. Crown-containing SNO 2 demonstrate a significant effect of metal cations on the stability of the M-form. When the concentrations of SNO and Met^{2+} are comparable, the rate constants of M→S transitions for (M-2)-Mg^{2+} and $(M\text{-}2)_2$-Ba^{2+} complexes are 16 and 4 times higher than for free M-2. The reason of the decrease in the stability of merocyanine form is the Coulomb repulsion between the metal cation and the partial positive charge of M-form, which is located on the nitrogen atom of the indoline ring (Fig. 1).

When the concentration of metal cations is much higher than that of SNO, both crownless and crown-containing SNO demonstrate a significant increase in the stability of M-form. This effect compensates and surpasses the initial increase in M → S rate constants. For crown free SNO 1, the effect of M-form stabilization due to Ba^{2+} cations is about an order of magnitude in comparison with free spironaphtoxazine. For crown-containing SNO 2, the effect is not so large, but also sufficient. The stabilization of M-form is accompanied by a hypsochromic shift (ca. 50 nm) of the maxima of M-form absorption band. Complexes of M-forms with metal cations are shown in Fig. 3. The stabilization of M-form of SNO could be explained by the cation binding by an oxygen atom of the oxazine moiety of merocyanine with the formation of (M-1)-Ba^{2+} and (M-2)-$(Mg^{2+})_2$ complexes. For the Ba^{2+} complex with M-2 the increase in the metal ions concentration could lead both to the conservation of the sandwich structure characteristic for $(S\text{-}2)_2$-Ba^{2+} and to the transition to the structure of (S-2)-Ba^{2+}.



(M-1)·Ba^{2+} **(M-2)·$(Mg^{2+})_2$**

Figure 3. M-form complexes with metal cations

Finally, this study could be considered as a necessary step in the development of photochromic systems with the controlled spectral and kinetic properties.

The work was supported by RFBR (grants No. 05-03-32474, 05-03-32268 and 04-03-96045) and the Program of Integration Projects of Siberian Branch of Russian Academy of Sciences (grant No. 77).

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SYNTHESIS, THERMAL, OPTICAL, ELECTROCHEMICAL, ELECTROCHROMIC AND PROTONATION CHARACTERIZATION OF NOVEL ADVANCED POLYIMIDE MATERIALS

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A new diamine containing pyridine heterocyclic and naphthalene substituents, 4-(2-naphthyl)-2,6-bis(4-aminophenyl) pyridine (NBAPP), was synthesized using Chichibabin reaction and used in preparation of poly(pyridine-imide) by direct polycondensation with 4,4'-hexafluoroisopropylidenediphathalic anhydride (6FDA) in *N*-methyl-2-pyrrolidinone (NMP). The poly(pyridine-imide) derived from diamine (NBAPP) with naphthalene substituents is highly organosoluble, such as soluable in tetrahydrofuran (THF), *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), γ-butyrolactone at room temperature, and pyridine, dimethyl sulfoxide (DMSO) and cyclohexanone upon heating at 70°C. The poly(pyridine-imide) was converted into color lightness, optically transparent, flexible and tough polyimide film by casting on glass from DMAc solution. This polymer exhibited good thermal stability (T_d^{10}=527°C) in air and high dielectric constant as high as 4.39 at 1KHz. The polyimide film has a tensile strength of 102 MPa and a tensile modulus of 1.8 GPa. The optical properties exhibit the UV-vis absorption bands at the region of 223÷400 nm and possess strong green-yellow fluorescent (500 nm) after protonated with acid.

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SPECTROSCOPIC STUDY OF SQUARAINE DYES AGGREGATION IN SOLUTIONS

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Among the variety of organic dyes squaraine dyes gain more and more scientifical and practical value lately. Squaraines, dyes of polymethine group, are luminescent dyes for red and near infra-red spectral range, that's why they are well-suited for medical-biological researches as fluorescent probes and labels.

Concentration dependence of absorption and luminescence spectra's of several squaraine dyes in water solutions were studied. Absorption and luminescence spectra's for all of them remain almost invariable in 10^{-6}-10^{-5} M concentration range and they were associated to monomer form of dyes. Quantum yield, frequency of pure electronic transition and other spectral-luminescent properties were determined for them.

With concentration increase till concentrations 10^{-3} M we observed invariability of absorption and luminescence spectra's for one group of dyes, while other group of dyes revealed the appearance of new shortwave and longwave (relative to band of monomer molecules) bands in absorption spectra. At the same time, shape of luminescence spectra does not change, only decrease of emission intensity (i.e. concentration luminescence quenching) was observed.

Observed spectral changes are explained by formation of non-luminescent associates of different structure. Correlation between spatial structure of dye molecules (calculated using quantum-mechanical methods) and observed concentration effects was found, expected structure of associates is proposed.

The study was carried out within international STCU grant (project UZB-111, 2004-2006)

STRUCTURE AND PHOTOCONDUCTIVITY OF MIXED PHTHALOCYANINE LAYERS

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Intentional doping of metallophthalocyanines, PcMet with molecular electron acceptors (*e.g.*, TCNQ, C60, chloranil (CA) *etc.*) is widely known to modify optical and/or electrical properties of the bulk doped material or its interfaces. At least three factors will affect conductivity of the mixed solid (recently called as “bulk heterojunctions”): i) formation of supramolecular structures (*e.g.*, weak contact complexes, charge transfer complexes (CTC), or ion-radical salts), ii) violation of molecular order in PcMet, since quite dissimilar dopant molecules enter the original packing, and iii) change of situation at the interfaces (such as concentrating or reaction of admixture with contacts).

Herein we report on alteration of the lateral conductivity in two model systems: PcCu\$Cl_{16}$PcCu and PcPb\CA. For the surface cells, changes in the thin mixed films obtained by simultaneous vacuum co-deposition of components with various ratios are compared with those in thin two-layer films of components (*i.e.*, sequentially deposited). In the latter case, the bottom (basic) layer contacting the electrodes covers the dielectric gap, whereas the upper layer does not have direct electrical connection. It was found out that for the PcCu films thinner than 100 nm the conductivity is severely affected by deposition of the second top Cl_{16}PcCu layer: a decrease in the film resistance is accompanied by the change of the I/V plot profile to the non-ohmic type.

In the PcPb\CA system, the interaction with strong donor CA leads to the CTC formation, which is responsible for appearance of new (or shift of existing) bands in the visible and IR domains of optical spectrum In the two-layer PcPb\CA structure, enhancement of sensitivity of the in-plane conductivity in the basic PcPb film to the white light illumination was observed. In the mixed films, the structural factor itself (*i.e.*, changes in crystalline packing) may inhibit or promote the acceptor effect, as revealed by comparison with analogous free base-Pc/CA systems.

The results can be useful for design of sensors or photovoltaic cells based on PcMet.

ADVANCED FLUORESCENT MATERIALS FOR BIOMEDICAL APPLICATIONS

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We have developed novel fluorescence-based materials for use in biological, pharmaceutical and biomedical research, clinical diagnostics, and high-throughput screening: Reactive Red and Near-infrared (NIR) Fluorescent Labels of Square and Seta series for covalent attachment to biomolecules such as proteins, amino-acids, peptides, oligonucleotides, DNA, RNA, and drugs; Fluorescent Probes for proteins, lipids and cells; Fluorescence Lifetime (FLT) Probes and Labels of SeTau series for FLT based and polarization based applications; Dark quenchers of SQ series for Fluorescence Resonance Energy Transfer (FRET) applications; Classification Dyes for single or multiple encoding of microspheres used in High-throughput Screening (HTS). The Square and Seta dyes absorb and emit in the 500–900 nm spectral range. Unlike dyes of the Cy and Alexa series, these red and NIR emitting markers can be excited not only with the red, 635-nm and 670-nm diode lasers but also with the blue, 380-nm or 405-nm lasers or light emitting diodes (LEDs). These dyes have high extinction coefficients (up to 265,000 $M^{-1}cm^{-1}$) and protein conjugates of these labels are extremely bright (quantum yields up to 70%). The microenvironment sensitive lifetimes of these dyes are in the range of 500 ps to 3 ns. Selected probes exhibit high affinity for proteins, biomembranes and lipoproteins and can be used to detect and quantitate these species. A series of pH-sensitive markers for pH 5.5–12.0 was also developed. In general the new dyes exhibit higher photostability as compared to Cy or Alexa dyes. Our new SeTau tracers that fluoresce in blue and green spectral region have the FLT in the order of up to 40 ns in water. The newly developed reactive Dark Quenchers of SQ series that absorb in the 600–800 nm spectral range have several times higher extinction coefficients as Black Hole Quenchers, do not exhibit any residual fluorescence and are perfectly suited for covalent labelling of proteins, peptides and oligonucleotides for use in FRET and real-time PCR based applications.

The work was supported by the STCU grants No. U111, 3804, and P313.

PHOTOCATALYTIC ACTIVITY OF NANOSTRUCTURED TiO_2 FILMS MODIFIED BY BIMETALLIC PARTICLES

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An application of heterogeneous photocatalytic reactions with TiO_2 to environmental purification has been widely reported and is becoming more and more promising. In these investigations the emphasis is traditionally done on the photocatalysis in the aqueous suspensions of titania. However, highly efficient photodegradation of organics adsorbed at the titania surface can occur under UV illumination in contact with a humid air via the mechanisms much similar to the conventional photocatalytic one. Here we report the preliminary results concerning the modification of the thin-film nanostructured titania photocatalyst with fine metallic and bimetallic particles to enhance the photocatalyst performance in air conditions.

The nanostructured films of titanium dioxide were prepared by a pulverization of aqueous colloid of TiO_2 on the glazed ceramic tile with the following heating at the temperature 450°C. The thickness of the films was of 200 nm. The SiO_2 sublayer has been introduced to prevent the thermodiffusion of glaze components during an annealing. The photocatalytic activities of the samples were evaluated by the photodegradation of Rhodamine 6G (Rh6G) under the irradiation with 365 nm line of medium-pressure Hg lamp and with the air humidity control. The relative change in the Rh6G concentration was evaluated from reflectance measurements sing the Kubelka-Munk formula [1]. The sulphate and chloride solutions of silver and palladium ($C_{Ag_2SO_4}=10^{-5}$ M, $C_{PdCl2}=5\cdot10^{-4}$ M were used for the photodeposition of fine metal particles. Hypophosphite and formaldehyde solutions were used for further electroless nickel and copper depositions. The surface concentration of a deposited metal was determined using Rutherford backscattering spectroscopy, in atoms per square centimeter. The size of the particles was evaluated using electron microscopy in combination with extractive replica technique).

The figure 1 shows that the deposition of fine silver particles results in drastic increase in the efficiency of the photodestruction of the probing dye deposited on the surface of the metal-modified coating. This effect, however, manifests itself only in a rather narrow range of metal loading, namely several monolayers, that corresponds to the metal particles 2.5-3.5 nm in size. Similar results were obtained for other noble metals (Pd, Pt) but not for copper. The growth of bimetallic particles using the electroless deposition of different metals allows us to enlarge the number of metals which can be deposited on the surface of TiO_2, and even greater increase the photocatalytic activity of the films (the growth of Ag/Ni). The chemical depositions of copper and cobalt over the photodeposited silver centers result in decrease of photocatalytic activity (fig.1).

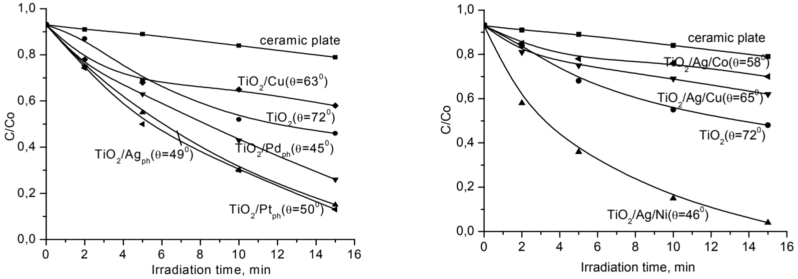

Figure 1. The kinetic curves of the photodegradation of Rh6G (there are the meaning of contact angles in the brackets).

The observed enhancement in the photoactivity can be attributed first of all to a lower level of recombination losses as it was evidenced by a higher efficiency of the photocurrent generation in the photoelectrochemical cell in the case of titanium dioxide modified by noble metals, whereas modification with base metals results in higher recombination level. Moreover, the chemoluminescent measurements with luminol have evidenced that Ni(Ag)-modified TiO_2 photocatalysts under UV illumination exhibit much higher yield of a superoxide generation as compared to the bare and Ag-modified titania, with the photoproduced superoxide ions together with hydroxyl radicals being involved in the photodegragations on the photocatalyst surface. Simultaneously the enhanced hydrophlicity of the metal modified coating provides better conditions for running surface photoreactions according to the conventional mechanism of photocatalysis, leading to the sharp rise of photoactivity with the humidity of the surrounding medium. The atomic force microscopic images evidence that this films possess more rough surface in nanoscale. This permits to attribute the observed nonadditive increase in the hydrophilicity to the fact that more developed mosaic surface is formed in the this case.

The modification of titania with bimetallic particles thus permits to suppress the surface recombination, to improve the hydrophilicity and to attain high superoxide yield that permits one to radically enhance the photocatalyst performance.

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EQUILIBRIUM AND TRANSPORT PROPERTIES OF HYDROGENHALIDES IN NON-AQUEOUS SOLUTIONS

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Investigations of liquid non-aqueous solutions containing proton are especially actual, so their application in chemical technology is increasing continuously.

Results of studying equilibrium (ionization, solvation) and transport (electric conductivity (EC)) properties of ionogens HCl, HBr, HI (HHal) in a number of primary alcohols methanol - nonanol over the temperature range 278,15 K - 328,15 K using EC and e.m.f methods are submitted.

Ionization constants (K_{gen}) and values of limiting molar conductance (λ_0) for HHal have been calculated from conductance dependency on concentration. Changes of K_{gen} and λ_0 values have been analyzed in terms of solvent influence on system properties taking into account possible ionic equilibria.

The effective short-range ion-ion potential (d_{ij}) at 278,15 - 328,15 K has been calculated using experimental data on ionization constants of ionogens. It is shown that d_{ij} values decrease with growth of temperature and increase of carbon atoms number in alcohol molecule.

Entropies ($\Delta_c S^o_i$), enthalpies ($\Delta_c H^o_i$) and free Gibbs energies ($\Delta_c G^o_i$) changes for HHal, H^+ and Cl^-, Br^-, I^- (Hal^-) solvation in a number of alcohols from methanol to nonanol over the temperature range 278,15 K - 328,15 K have been calculated as described in [1]. This method allows solvated ions effective radii (ER) estimating in various solvents as well as electrostatic and noncoulombic parts in $\Delta_s G$ for cations and anions (including proton). Calculations error does not exceed 1 %. ER values of H^+ and Hal^- have practically insignificant dependency on temperature and alcohol number. It is shown that non-coulombic part of free Gibbs energy promotes proton solvation, but counteracts halide-ion solvation in this number of alcohols.

The single null activity coefficients of (γ_0) proton in a number of alcohols methanol - nonanol over the temperature range 278,15 K - 328,15 K and primary effect of (lg γ_0 (H^+)) medium have been calculated. This data shows that alcohol acidity (in comparison with water) increases with both temperature and alcohol molar mass growth.

Solvation numbers (n_s) of halogenide-ions and proton have also been determined. They have been calculated using three different methods in the alcohols investigated. n_s values for halogenide-ions change from 1 in higher alcohols to 5 in methanol. n_s values for proton exceed 5.

Results of quantum-chemical *ab initio* calculations using DFT method in 6-31+G* basis, thermodynamic and structural characteristics of solvation process for HCl, proton and chloride-ion in methanol have been determined. Equilibrium geometry of $(MeOH)_m$ molecular clusters and $(MeOH)_m{\cdot}H^+$, $(MeOH)_m{\cdot}Cl^-$, $(MeOH)_m{\cdot}HCl$ solvated complex structures with number of alcohol molecules (m) from 1 up to 4 have been calculated. Calculated IR-spectra for clusters and solvated complexes have been investigated.

The most general scheme of equilibria which takes into account interparticle interactions in electrolyte solutions was offered by N.A. Izmajlov. We have added two stages to this scheme: contact ion pair (CIP) conversion to solvent-separated ion pair (SSIP) and SSIP dissociation into ions. The scheme we offer includes 10 mutually related equilibria. Each equilibrium is quantitatively characterized by its own constant:

– formation of $HHalM_n$ solvate complex containing n molecules of solvent M;

– transformation of this complex in a contact ion pair (CIP);

– formation of CIP from covalent molecules of HHal and solvent (alcohol);

– CIP conversion to solvent-separated ion pair (SSIP) containing one solvent molecule;

– transformation of $HHalM_n$ solvate complex in SSIP;

– SSIP formation from covalent molecules of HHal and solvent;

– dissociation of SSIP;

– CIP dissociation;

– ionization of ($HHalM_n$) solvate complex;

– overall process of electrolyte ionization.

It has been shown that at the temperatures investigated, concentration of $HHalM_n$ solvate complex prevails in all alcohols. Stages of CIP and SSIP formation are the most probable. Thus, probability of such equilibrium processes decreases with growth of hydrocarbon radical length.

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EFFECTS OF DYE-SURFACTANT IONPAIR FORMATION ON EFFICIENCY AND EFFECTIVENESS OF AQUEOUS CATIONIC SURFACTANTS

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The hydrophobicity-induced deprotonation[1] of three sulfonephthalein dyes in dye-surfactant closed-packed ionpairs formed in submicellar aqueous solutions of different cationic surfactants has been investigated in buffered aqueous solutions by tensiometric and spectroscopic methods to gain information on hydrophobic interaction. The dyes used, viz., phenol red (PR), cresol red (CR) and cresol purple (CP), were all anionic. The cationic surfactants used were hexadecyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB), hexadecylpyridinium bromide (CPB) and hexadecylpyridinium chloride (CPC). The observed surface tension of the aqueous solutions as a function of surfactant concentration in absence and in the presence of the dyes indicate a cooperative role of the dye and the surfactant in the surface activity, which increases the efficiency and decreases the critical micelle concentration (CMC) of the surfactant without significantly affecting the effectiveness of the surfactant. The surface excess concentrations of the surfactants have been determined. The cooperative role has been suggested to be through closed-packed dye-surfactant ionpair formation at submicellar concentration ranges of the surfactants and occupation of the solution interface with air by the dye-surfactant ionpairs in the presence of the dye in place of the surfactants alone as occurs in the absence of the dye. The equilibrium constants of the interactions have been determined spectrophotometrically and computed assuming the interaction to be formation of deprotonated ionpair from the dye and the surfactants in the aqueous solutions. The plots of logarithm of the equilibrium constants *vs.* pH have been found to be linear with a negative slope in all cases. Such linearity has been reported in the cases of other phenomena or interactions driven by hydrophobic force, which supports the assumption of closed-packed ionpair formation and that the subsequent deprotonation of the dye in the dye-surfactant ionpair is driven by hydrophobic interaction where the electrostatic attraction between the dye and the surfactant ions is a primary requirement. The interaction has been found to increase in the order CP<CR<PR in the case of the dyes and DTAB<TTAB<CPB<CTAB in the case of the surfacytants. As the concentration of the surfactant increases and micelles are formed, the ionpairs are broken and the dye molecules are solubilized in the micelles.

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EXPERIMENTAL AND THEORETICAL STUDIES ON THE INTERACTIONS BETWEEN PROTON OR THE LITHIUM ION AND THE 4-ISOPROPYLTROPOLONATE ION IN APROTIC SOLVENTS

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By means of voltammetry, conductometry, and UV-visible and NMR spectroscopies, we have certainly demonstrated that alkali metal (M^+) and alkaline earth metal ions (M^{2+}) have "weak" but unexpectedly distinct chemical (i.e., covalent bonding or coordinating) as well as Coulombic interactions with many simple anions, not only in low permittivity media ($\varepsilon_r < 10$) but also in higher permittivity media ($20 < \varepsilon_r < 65$) with poor solvating ability; where the simple anions include halides, carboxylates, phosphates, sulfonates, etc.[1] Stable carbocations can be produced from trityl halides by the addition of the perchlorates salts of Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in acetonitrile; the carbocations have been detected by UV-visible, ^1H and ^{13}C NMR spectroscopies. The concentrated salt effects on solvolysis reaction rates of typical S_N1 substrates, such as *t*-butyl chloride and 1-adamantyl halides (RX), have been elucidated based on the (chemical) interaction between M^+ or M^{2+} and the halide ions (X^-) from the substrates in organic solvents and water mixtures. We have proposed that the properties of bulk water are altered into those of "dihydrogen ether" (R[H]-O-[H]R) if the huge network of bulk water is distorted by added organic solvents and concentrated salts. In a previous paper,[2] the specific interaction between lithium ions and the tropolonate ion ($C_7H_5O_2^-$: L^-) in acetonitrile and other solvents, was examined by means of UV-visible and ^1H or ^{13}C NMR spectroscopy.

In the present paper, we have experimentally and theoretically examined the interaction between 4-isopropyltropolonate ion (L'^-) and proton or lithium ion by means of ^{13}C NMR chemical shifts. The results indicate that two C atoms bonding to O atoms show higher magnetic-field shifts as cations are added to L'^-, although the other C atoms in the seven-membered ring show lower magnetic-field shifts. We have decomposed the shielding constants into diamagnetic and paramagnetic terms, and further analyzed them based on the perturbation theory.

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PRECISE DILATOMETRY OF 2-HYDROXYPROPYL-β-CYCLODEXTRIN AQUA SOLUTIONS

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Cyclodextrins (CDs) are typical natural oligosaccharide receptor molecules composed of D(+)-glucopyranose units linked via 1,4-α-glycoside bonds. The most common representatives of CDs are α-, β-, and γ-cyclodextrins, that contain six, seven, and eight units, respectively. Having a hydrophobic cavity, their molecules are capable to form “host- guest” inclusion complexes with a wide variety of organic and inorganic hydrophobic or ionic species in aqueous or aqua-organic solutions. The crucial factor for this unique type of complexation is the ratio between the size of the guest and the cavity of the CD molecule. Owing to this feature, natural CDs found numerous applications in many fields of pharmaceutical, food, cosmetic industries, analytical chemistry and other sciences [1].

The driving forces for guest incorporation into the CD cavity are hydrophobic interactions, hydrogen bonding and steric effect. The formation of inclusion complex in aqueous solutions results in a substantial rearrangement and removal of the water molecules originally hydrated to both the CD and guest molecules. Moreover, this process also induces the release of “high-energy” water molecules from the CD cavity into the bulk water. The cavity water molecules are entropically unfavorable because of an incomplete intermolecular hydrogen-bonding network and hence they have another properties then molecules in the bulk water [2].

It is well-known that volumetric and compressibility studies can contribute to our understanding of the intermolecular forces which govern the properties of aqua solutions as well as solute-solute, solute-solvent interactions and influence of solute molecules on the structure of water network. Traditionally, these investigations have been focused on a small organic molecules dissolved in water and practically no publications devoted to receptor molecules like cyclodextrins and their inclusion complexes.

The aim of this work – a precise dilatometric study of the aqua solutions of 2-hydroxypropyl-β-cyclodextrin (2-HP-β-CD). Density (ρ), isothermal compressibility (β_T), and thermal volumetric expansion coefficient (α) [3] were measured with high accuracy at the several temperatures for 2-HP-β-CD aqua solutions with errors $1x10^{-2}$%, 1%, and 2%, respectively. The pressure drop ΔP and temperature drop ΔT amounted to 4×10^5 Pa and 0.4 K, respectively. The results of experiment are listed in Tables 1-3. It was found that the hydrogen bond network does not change in the presence of 2-HP-β-CD molecules up the concentration of 20.30 mass %. The hydration type of 2-HP-β-CD was discussed.

Table 1. Density (ρ, g/cm^3) of 2-HP-β-CD aqua solution.

W* t,°C	0.51	1.01	5.61	9.02	15.24	20.30
25	0.99851	0.99998	1.01742	1.03130	1.05036	1.06900
50	0.98950	0.99094	1.00795	1.02161	1.04022	1.05859

W* - mass % units concentration of 2-HP-β-CD aqua solution.

Table 2. Thermal volumetric expansion coefficient ($\alpha\cdot10^5$, K^{-1}) of 2-HP-β-CD aqua solution.

t,°C W*	10	15	20	25	30	35	40	45	50
0.51	9.8	15.7	21.1	25.8	30.5	34.8	38.6	42.4	45.9
1.01	11.6	16.6	21.6	26.0	30.8	35.2	38.8	42.6	46.0
5.61	12.2	17.8	22.4	26.8	31.3	35.8	39.4	43.2	46.2
9.02	14.2	19.2	23.8	28.2	32.4	36.6	40.1	43.9	46.6
15.24	16.4	21.2	25.6	29.7	33.7	37.4	40.8	44.5	47.8
20.30	18.6	22.8	27.2	31.1	34.8	38.5	42.2	45.2	48.7

Table 3. Isothermal compressibility ($\beta_T\cdot10^{11}$, Pa^{-1}) of 2-HP-β-CD aqua solution.

t,°C W*	10	15	20	25	30	35	40	45	50
0.51	47.0	46.2	45.0	44.8	44.4	44.0	43.5	43.8	43.5
1.01	46.5	45.8	45.0	44.4	44.1	43.9	43.7	43.6	43.6
5.61	45.2	44.4	43.8	43.3	42.9	42.7	42.6	42.6	42.6
9.02	44.1	43.4	42.7	42.3	42.0	41.9	41.8	41.9	41.9
15.24	42.4	41.7	41.1	40.6	40.3	40.3	40.2	40.3	40.4
20.30	40.8	40.1	39.7	39.4	39.3	39.4	39.5	39.7	39.8

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SPECTROSCOPIC MANIFESTATION OF THE AGIBA (ANGULAR GROUP INDUCED BOND ALTERATION) EFFECT IN LIQUIDS

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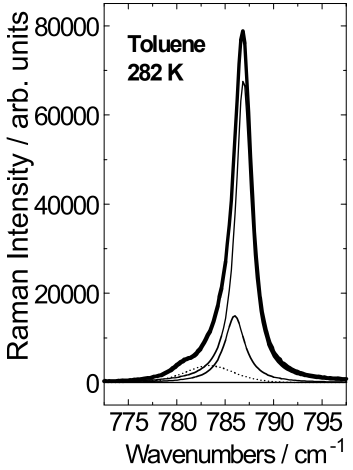
During more than one and a half century aromaticity serves as one of the most important concepts in organic chemistry. The most obvious consequence of this concept is the common confidence that in aromatic compounds, bond lengths do not alternate and are between typical to the single and double ones. However, in 1994, performing crystal structure investigations of substituted pyridines and their salts, Krygowski and co-workers have discovered a very surprising effect [1]: It appears that some substituents can induce bond alternation in aromatic rings.



Continuing Raman investigations of the liquid toluene [2], we have noticed that under the envelope of the line corresponding to the ring vibration, a signature of two spectroscopic features is present [3] (see figure), possibly corresponding to two AGIBA isomers. The energy difference between these two distinct isomers estimated in temperature dependent Raman studies appears equal to 6.68 kJ/mol.

Similar intriguing splittings have been already noticed in the spectra of other methyl substituted benzenes (xylenes, mesitylene). In this presentation, differences between AGIBA, staggered and eclipsed conformers will be considered, and a discussion of possible spectroscopic manifestations of the AGIBA effect in liquids will be given.

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DETERMINATION OF SOLVENT AND IONS MOBILITY IN NONAQUEOUS ELECTROLYTE SOLUTIONS BY MEANS OF MULTINUCLEAR NMR

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The first part of the report includes a brief survey of NMR application for detection of the composition of the first coordination sphere of various metal cations, both paramagnetic and diamagnetic. In particular, using as the tools (i) the paramagnetic shifts under conditions of slow and/or fast exchange and (ii) the relaxation times/rates, NMR allows a direct determination of a cation *CN,* an evaluation of the nearest environment of cations in mixed solvents, a testing of *rotational* dynamics of solvated ions, etc. A huge array of the results is available to the moment. It is briefly summarized in the report, and a number of examples – mostly for non aqueous solutions – are shown. A comparison with the data of X-ray and neutron experiments is provided for some cases. As a separate item we discussed an applicability and usefulness of this approach to the solutions in (nano)porous matrices.

The second part of the report describes main features of pulse-NMR method widely used for investigation of the _translational_ mobility (self—diffusion) in liquids. The adventures of NMR method are as follows

No special labels need, i.e. the method is of non-invasive type;

Wide range of self-diffusion coefficients is available for measurements, especially under application of so-called PGSE method, i.e. under using pulse gradients of magnetic field.

Based on the PGSE method it begins possible to study so-called restricted diffusion, i.e. mobility of molecules and ions in porous media including porous nanostructures. An analysis is given for NMR potentiality to estimate the type of self-diffusion on different time scales depending on nanostructure geometry.

Both parts include literature data as well as the authors' original results.

SOLVATION OF $[Ni(en)_3]^{2+}$ ION IN WATER AND METHANOL

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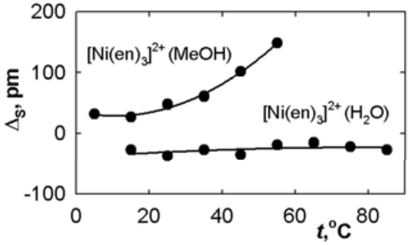

Fig. 1 Temperature dependence of dynamic solvation shell thickness of $[Ni(en)_3]^{2+}$ in water and methanol.

The results of conductometric investigation of $[Ni(en)_3]^{2+}$ solvation in methanol and water solutions are present in this work. The conductance experiment was performed over the temperature ranges 5–55 °C in methanol and 15–85 °C in water.

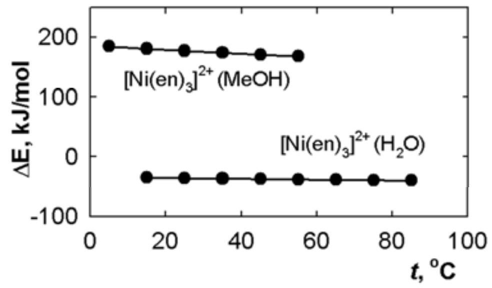

Fig. 2. Temperature dependence of ΔE parameter of $[Ni(en)_3]^{2+}$ in water and methanol.

The quantitative characteristics of ion solvation were obtained by applying Lee-Wheaton conductance equation for unsymmetrical electrolytes [1] along with author's methodology [2,3] for experimental data processing.

The thickness of dynamic solvation shell (Fig.1) and ΔE parameter in terms of Samoylov's kinetic theory of solvation (Fig. 2) were calculated.

The analysis of these quantities showed structure-making influence of $[Ni(en)_3]^{2+}$ on surrounding solvent in methanol and structure-breaking one in water.

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AZO HYDRAZONE TAUTOMERISM OF BENZIMIDAZOLE RED DYE IN IONIC SURFACTANTS

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Spectral behavior of benzimidazole red dye was studied by differential spectroscopy. The spectral changes produced by varying amounts of ionic surfactants are attributed to the shifting of azo hydrazone tautomeric equilibrium. Alterations in absorption patterns lead to the conclusion that dye occupies more than one residence sites within the micelles. The phenomenon was portrayed by utilizing micelle-water partition coefficients determined for dye-SDS and dye-CTAB systems. The thermodynamic data was used to high light the energy efficiency of the process.

ASSOCIATION OF IONIC FORMS OF DYES IN SOLUTION: FROM MEASURING SPECTRAL DATA TO FORECASTING THE ASSOCIATES STABILITY

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The results of modern investigations served as a powerful incentive to a more detailed study of the phenomenon of association of different classes of dyes in solutions. The interest in this phenomenon has recently increased due to the advent of new types of machinery, perfection of technologies, and creation of devices. The association of organic dyes exerts a substantial influence on their photophysical and photochemical properties that determine the application of dyes as converters of light energy in laser technology, the photographic industry, solar power engineering, optoelectronics, biochemistry, biology and medicine [1].

One of the most "sensitive" methods of studying association of dyes remains electronic spectroscopy (absorptive and luminescent), which makes it possible to investigate associateformation in both aqueous and nonaqueous media at a sufficiently low level of contents and in a rather broad concentration range (10^{-7}–10^{-4} mol/l). It is not accidental that the processes of associate-formation of intensely absorbing and (or) luminescing amino- and oxyxanthene, cyanine, acridine, sulfophthalein, and thiazine dyes are studied most widely.

For example, it has recently been found that the formation and dissociation of association species between the cyanine dye pinacyanol [2] and the oxyxanthene tetrabromophenylfluorone [3] provide a means for quantitative determination of ionic surfactants in aqueous solutions. In this connection, it is of particular interest to investigate the properties of association species formed by cyanine dye cations, including pinacyanol (1-ethyl-2 -[3 -(1 -ethyl -1H -quinoline -2 -ylidene) -propenyl] -quinolinium, PC^+), Quinaldine Red (2-[2-(4-dimethylamino)phenyl]-ethenyl-1-ethylquinolinium), astraphloxine, etc.

It is noteworthy that not only dissociation but also association (e.g., the association of a dye cation and the dodecyl sulfate (DS^-) anion as a surfactant ions) is kinetically controlled. However, there is a fundamental difference between these processes. While PC^+ and DS^- react completely within a fraction of a second (k~30 s^{-1}), dissociation may last for tens or hundreds of seconds, particularly at IS concentrations well below CMC. In this case, the interaction between the association species and the surfactant can be represented as

$$Ct^+{\cdot}An^-+DS^- \rightleftharpoons Ct^+{\cdot}DS^-+An^-, \quad Ct^+{\cdot}An^-+CP^+ \rightleftharpoons Ct^++CP^+{\cdot}An^-,$$

where CP^+ is the colorless cation of CPB. The difference between the association and dissociation rates is due to the difference in the type of reaction: the addition reaction between the cyanine and the surfactant is much more rapid than the anion substitution reaction. This kinetic study of the decomposing effect of ionic surfactants confirms that the association of cations and anions in aqueous solution is an equilibrium process.

The following conclusion can be drawn from our numerous experimental data: the statistically important difference in the values of association constant K_{as} is indicative of the fact that the stability depends substantially on the structure of counterions that enter into the composition of heterogeneous associates.

To determine the structural properties of dyes, classical quantum-mechanical methods are used, which make it possible, on the basis of molecular diagrams, to draw conclusions concerning the reactability of one or another fragment of a molecule. Each method gives its set (often different from other sets) of molecular parameters. However, it is important that the results of calculations (electron density, length and order of bonds, valence angles, etc.) of dyes and associates may differ substantially because of the noncoincidence of the initial calculation bases, assumptions, and approximations [4].

The influence of the temperature (range 292–329 K) on the stoichiometry of the associates being formed is considered using as an example the PC^+ associates. With increase in the temperature, the isobestic point is blurred in the spectral series, which may point to the presence in the system of associates with a different relationship between the stoichiometric coefficients. Moreover, calculation of the characteristics on the assumption of the existence of associates of only one composition leads to a situation where only negative values of K_{as}. Thus, in the indicated range of temperatures the coexistence of the PC^+ associates of different stoichiometry has been established.

The high values of K_{as} may indicate the formation of contact ionic associates. However, in aqueous solutions, electrostatic interactions between counterions are weakened and π-electronic, Van der Waals (predominantly dispersion), and hydrophobic interactions play a considerable part in the formation of heterogeneous associates with the participation of large organic dyes.

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ORGANIZED MEDIA – A STRATEGY OF CHEMICAL ANALYSIS BASED ON THE PRINCIPLES AND EFFECTS OF NANO AND SUPRAMOLECULAR CHEMISTRY

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Nano and supramolecular chemistry are the most popular and fastest growing areas of experimental and theoretical chemistry. Their interdisciplinary nature has brought about wide-ranging collaborations between inorganic, organic, solid-state chemists, biochemists, biologists, physicists, computational specialists etc. Analytical chemistry being a highly interdisciplinary too cannot set aside the attractive power and advances of supramolecular chemistry – “the chemistry of molecular assemblies and of intermolecular bonds” as defined by Jean-Marie Lehn. Recognition, reactivity, and transport, as well as self-assembly, self-organization and self-replication are the basic functional features of supramolecular chemistry that attract the attention of analysts.

The most known and wide used representatives of supramolecular species in analytical chemistry are so-called organized systems and molecules-receptors forming organized media in solution and on the surface [1]. At the same time, the supramolecular assemblies serve as the examples of nanosize objects. The properties of the interface or the medium inside of such liquid nanoassemblies or molecules-receptors differ significantly from those at the large scale; more importantly, these microscopic properties and analytical properties respectively can be regulated easily by many ways [1]. The main supramolecular self-assembled species involved in analytical chemistry are micelles, microemulsions, liposomes, vesicles, bilayer membranes, dendrimers, Langmuir-Blodgett films composed of diphilic surfactant molecules or ions as well as molecules-receptors such as calixarenes, cyclodextrins, cyclophanes, cyclopeptides, crown ethers etc.

The presentation will focus on the peculiarities of organized media including differences and similarities, their effect on spectroscopic, electrochemical and chromatographic methods of analysis, sensor properties in respect of selectivity and sensitivity problems as well as methods of control over their efficiency in the context of nano- and supramolecular chemistry principles will be considered.

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THERMODYNAMIC DESCRIPTION OF CONTRIBUTIONS DUE TO SOLUTE AND SOLVENT PARAMETERS INTO SOLVATION AND ASSOCIATION OF ALIPHATIC AMINO ACIDS IN MIXED SOLVENTS

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New approachs in biological thermodynamics of ligand binding and regulation of proteins, DNA and polysaccharids, experimental and theoretical description of interaction in these systems must concern the biomolecule solvation and the role of the solvent in methabolism. The extraordinary complexity of biological structures and functions requires the limitation of analysis firstly only on the macroscopic aspects of phenomena.

Experimental thermodynamic properties are free of assumptions on molecular nature and structure of a system and are the key for the understanding of interaction in biological active substance solutions [1]. For the description of biological system functions it is necessary to know the biochemical reactions features on the basis of analysis and elaboration of quantitative prognosis methods for chemical reactions in biological systems.

On the basis of our experimental thermodynamic function values on dissociation with carboxylic ($\Delta G^0_{d,1}$, $\Delta H^0_{d,1}$, $\Delta S^0_{d,1}$) and amino groups ($\Delta G^0_{d,2}$, $\Delta H^0_{d,2}$, $\Delta S^0_{d,2}$) of glycine and β-alanine in methanol-water (0, 20, 40, 60, 80, 95 % wt) at 278.15-318.15 K (with step of 5 K), α- alanine and valine in methanol-water (0, 20, 40, 60, 80 % wt) at 278.15-318.15 K (with step of 5 K), for glycine (0, 20, 40, 60, 80% wt) at 278.15-318.15 K (with step of 5 K) and α-alanine, β-alanine and valine in propan-2-ol-water (0, 20, 40, 60, 80 % wt) at 278.15-328.15 K (with step of 10 K) obtained by potentiometric method in galvanic cells without liquid junction:

$$\text{Gl. el. } (H^+) / Z^{\pm} (m_1), \text{ HCl } (m_2) / \text{AgCl, Ag} \qquad (I)$$

for the determination of dissociation constants of amino acid ($Z^{\pm}$) with carboxylic groups, K_1, and:

$$\text{Gl.el. } (H^+) / Z^{\pm} (m_1), \text{ NaOH } (m_2), \text{ NaCl } (m_3) / \text{AgCl, Ag} \qquad (II)$$

for the determination of dissociation constants of amino acid with amino groups, K_2, and the literature data on glycine and α-alanine in ethanol-water system at 298.15 K at I = 0.1 mol/l (0-60% wt and 0-80% wt accordingly) the multiple correlation analysis of the aqueous-organic solvents′ (water-methanol, water-ethanol, water-propan-2-ol) and solute effect on the strength of amino acids has been provided. The meaningful not linearly connected descriptors stipulated the change of amino acid dissociation Gibbs energy for solvent (E_T^N, δ_N^2, $1/\varepsilon_N$, Z) and solute ($M_{r,i}$, μ) have been founded. Dissociation Gibbs energy with carboxylic groups $\Delta G^0_{d,1}$ has been shown to stipulate by E_T^N, δ_N^2 and dissociation Gibbs energy with amino groups $\Delta G^0_{d,2}$: by E_T^N , δ_N^2 and $1/\varepsilon_N$. Both the decrease of amino acid strength with carboxylic groups and the increase of amino acid strength with amino groups with increase of non-aqueous component content in the system – in both cases - are determined by cohesion part $\Delta G^0_{d,1,2}(\delta_N^2)$. This fact reflects prevailing contribution of structural reorganization of water-organic solvent at formation of cationic and anionic amino acid forms. The short-range interaction part of dissociation Gibbs energy, $\Delta G^{0}_{d,1,2}{}^{*}$ has been obtained assuming the borders of ionic association area, it dependence from $M_{r,i}$,$1/r_i$, μ of amino acid and from solvent properties has been analyzed.

Study of solvation in amino acid, olygopeptide and protein solutions facilitates the revealing of connection between structure and energetics of individual chemical components of vital matter. From the point of view of the unified quantitative electrolyte dissociation theory proposed by Ismailov [2] (dissociation Gibbs energy of electrolyte (ΔG_d^0) is stipulated by solvation energy of ions ($\Sigma\Delta G_{S,i}^0$) and that one of molecules ($\Delta G_{S,\ mol}^0$)) the splitting of standard Gibbs energy of transfer of α-amino acids from water into alcohol-water mixtures into ionic contributions (molal scale) has been provided with the use of the data on dissociation Gibbs energy and Gibbs energy of transfer of amino acid zwitterionic form. The analysis from solvent and solute descriptors is provided.

The theoretical modeling of concentration dependence of experimental osmotic coefficients of amino acids and their salts has been provided. Simple one-parametric approach with correlation function in MSA form has been founded to describe satisfactory the thermodynamic properties of amino acid salts up to 0.6-0.7 mol/kg. At the same time the distance parameter has been shown to be not sufficient adjustable parameter as hard-sphere parameter.

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SPECTROSCOPIC STUDY OF ACID-BASE IONIZATION AND TAUTOMERISM OF FLUORESCEIN DYES IN DIRECT MICROEMULSIONS AT HIGH BULK IONIC STRENGTH

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Ultramicroheterogeneous dispersions in water are widely used in photochemistry, chromatography, chemical analysis, catalysis, in nanotechnology, etc. The Stern region of ionic surfactant micelles and microemulsions represents a unique combination of water, high concentration of organic and inorganic electrolytes, hydrocarbon chains and relatively high electrical charge. Variety of properties of micellar pseudophase can be reached by modification of self-assembled surfactant aggregates by various additives. In particular, cationic surfactant-based microemulsions at high ionic strength (*I*) of the bulk phase created by potassium (sodium) chloride possess unique solvation properties: 1) the electrostatic potential value becomes extremely low; 2) the differentiating action of cationic surfactant on the acid-base properties of the substances bound in the Stern region is retained; 3) the Cl^- concentrations in the bulk and in the Stern region are coming closer; 4) ion exchange of Cl^- with components of buffer solutions is negligible. In present work, we report the results of vis-spectroscopic study of prototropic equilibria of hydroxyxanthene dyes ($H_3R^+ \rightleftarrows H_2R \rightleftarrows HR^- \rightleftarrows R^{2-}$) in direct microemulsion benzene-pentanol-1-cetyltrimethylammonium bromide (CTAB)-water, at high bulk ionic strength. Volume fraction of the organic phase, φ , equals 1.3%.

Table. The apparent ionization constants of fluorescein dyes in water and direct microemulsion, 25°C

Dye[a]	Water[c]	direct microemulsion, φ =1.3% benzene-pentanol-1-CTAB-water, *I* = 1 M KCl		
	K_{a1}/K_{a2}	pK_{a1}^{a}	pK_{a2}^{a}	K_{a1}^{a}/K_{a2}^{a}
Fluorescein[b]	224	5.84	6.50	4.57
2,7-Dichlorofluorescein	15.5	5.21	5.12	0.81
2,4,5,7-Tetrabromofluorescein	8.7	1.74	5.27	$3.4{\cdot}10^3$
2,4,5,7-Tetraiodofluorescein	–	1.68	5.04	$2.3{\cdot}10^3$
2,4,5,7-Tetrabromothiofluorescein	–	1.28	5.21	$8.5{\cdot}10^3$
2,4,5,7-Tetranitrofluorescein	–	0.07	0.87	6.31
$3',4',5',6'$-Tetrachlorofluorescein	794	5.30	6.47	14.8
4,5-Dinitro-2,7-dibromofluorescein	–	0.50	6.52	$1.0{\cdot}10^6$
4,5-Dibromo -2,7-dinitrofluorescein	–	1.73	5.88	$1.4{\cdot}10^4$
$3',4',5',6'$-Tetrabromofluorescein	–	5.64	6.49	7.08

[a] dyes concentration was within the range $(0.8\text{-}2.0)\times10^{-5}$ M;

[b] pK_{a0}^{a} = –0.07 and 2.14 in the investigated microemulsion and in dilute aqueous solution, respectively;

[c] $I \rightarrow 0$.

Hydroxyxanthene dyes exhibit a lot of valuable photophysical and photochemical properties. Therefore they were studied in various kinds of liquid media. Hence, it is worthwhile to examine the influence of self-assembled aggregates on the interconversions of various prototropic forms of hydroxyxanthenes. In the table, the indices of "apparent" stepwise ionization constants of the aforementioned dyes are presented ($\mathrm{p}K^a_{a0}$, $\mathrm{p}K^a_{a1}$, $\mathrm{p}K^a_{a2}$ (±0.05)). The spectral data confirm the assumption of complete binding of dye species to the microdroplets.

The comparison of $\mathrm{p}K^a_a$s of solutes in the investigated systems with those in water revealed the strong differentiating action of the media under study on the acid-base properties. The inspection of the table also allows to state the variations of the ratio of stepwise ionization constants of dyes, which are actually polyprotic acids. Note, that we define the differentiating action not only as that resulting in increase of the ratio of stepwise ionization constants, but also in approaching each other in some cases.

Differentiating of acidic strength of the reagents is caused by the charge type of acid-base couples, nature of ionizing groups and the character of substituents.

Neutral and (in some cases) mono- and dianionic forms are actually equilibrium mixtures of several tautomeric species. Vis-spectroscopic study allowed to identify them and to estimate their fractions. This, in turn, allowed to single out the so-called microscopic ionization constants and thus to rationalize the medium effects.

QUASI-LATTICE MODEL IN THE THEORY OF ACTIVITIES OF STRONG ELECTROLYTES AND ITS USE FOR THE SOLUTION OF VARIOUS PROBLEMS IN PHYSICAL CHEMISTRY

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1. For the quasi-lattice model a correlation of ln$\gamma_\pm$ with the term containing the factor $C^{1/3}$ is characteristic. This term is single in the description of dilute solutions and is a component in the description of concentrated solutions.

For the first time the dependence ln$\gamma_\pm = -AC^{1/3}$ was formulated in 1910 upon the analysis of the experimental results.

It received a theoretical justification in the works of Ghosh (1918) by taking into account the Coulomb interactions and the type of crystal structure. The concentration limit of the equation applicability for 1,1-electrolytes was 0.1 M.

The model of ion atmospheres proposed by Debye and Hückel (1923-1924) displaced the quasi-lattice model for a considerable period of time. The quasi-lattice model was reverted to in the second half of the 20th century.

Glueckauf (1968–1969) ascertained the practical relevance of ln$\gamma_\pm$, $C^{1/3}$, but was not ready to reject the term $C^{1/2}$, and proposed their combination. Using two variable parameters, he described $\gamma_\pm$ for LiCl and NaCl solutions in a wide concentration range. He did not consider the multiple-charge electrolytes.

Bach (1972–1975), taking into account the Coulomb interactions and the gradient of the dielectric permittivity of the solvent in the vicinity of the ion, proposed the approximation solution in the form ln$\gamma_\pm = -AC^{1/3} + BC$, where A depends on the Madelung constant, B is a variable parameter. Due to a specific dependence of A only 1,1- и 2,1-electrolytes were considered. The upper limit of the description of 1,1-electrolytes was 4 M.

2. In 1982 one of the authors of the present communication proposed a new variant of the quasi-lattice model, in which apart from the usual Coulomb interactions, the polarization effect was taken into account and an effective parameter of the type of Madelung constant was introduced. The conditional character of this parameter allowed not only to describe the properties of salts of any structural type, including such complex ones as $Al_2(SO_4)_3$, but to extend the analysis to the description of acids.

Since simple thermodynamic relations exist between $\gamma_\pm$, the osmotic coefficient ϕ, and the activity of water a_w, any of these properties can be easily described. In the terms of $\gamma_\pm$ for an aqueous solution at 298.15 K the analyzed dependence has the form:

$$\ln\gamma_\pm = z_+ z_- q\left[-\frac{0.89565}{\nu^{2/3}}m^{1/3} + 0.0095806\left(d_0^2 - \frac{\Phi}{d_0}\right)m + 0.00094395\nu^{1/3}\Phi m^{4/3}\right],$$

where d_0 (Å) is the distance of the closest approach of the ions (generally a variable parameter), ν is the number of ions in the formula composition of the electrolyte, $\Phi = \frac{\alpha_+\nu_+}{\nu_-} + \frac{\alpha_-\nu_-}{\nu_+}$, α (Å^3) is the ion polarizability (taken from reference books), m is the concentration in moles per kilogram of the solvent, $q = \left(\frac{z_+^2 \nu_+ + z_-^2 \nu_-}{2} \right)^{1/2}$, z_i is the charge number of the ion. The proposed formula allows the description of $\gamma_\pm$, ϕ, and a_w in a wide concentration range.

3. The effectiveness of the aforementioned model in the description of $\gamma_\pm$ of individual electrolytes allowed to solve the problem of its description also in multicomponent mixtures, which led to the possibility of theoretical description of concentration equilibrium constants of ion exchange on strong-acid ion exchangers and the prediction of the influence of the third component on the exchange of lithium and sodium isotopes on these ion exchangers.

The use of this model allows in principle to reconsider the solution of the problems of concentration description of diffusion coefficients, the electrical conduction of electrolytes in solutions, and also the surface tension in these solutions.

In the present communication a new method of the description of the concentration dependence of the diffusion coefficients of electrolytes in aqueous solutions at 298.15 K both for dilute and for concentrated solutions is presented.

In the case of dilute solutions the sought-for formula is derived by simultaneous solution of the Nernst-Hartley equation and the quasi-lattice model of the description of $\gamma_\pm$ according to Kuznetsova (the 1st approximation). In the case of concentrated solutions the formula of the description of $D(C)$ is the result of the simultaneous solution of the Hartley-Krank equation and the aforecited equation upon averaging of $\frac{d \ln \gamma_\pm}{d \ln m}$.

MODIFIED ACTION OF REAGENTS ON THE STRUCTURE AND PROPERTIES OF SURFACTANT-BASED MICROHETEROGENEOUS REACTION MEDIA

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The use of micellar solutions and microemulsions as a reaction medium has awakened great interest due to a growing number of scientific and technological applications, connected mainly with highly-organized microheterogeneity of structure and intrinsic properties of these systems. A satisfactory quantitative explanation of reaction kinetics in such media is made on the base of pseudophase model in which every of microphases (water, oil and phase boundary) is combined into volumetric one. The main shortcoming of this approach, which is frequently left behind, lies in the requirement for properties of each pseudophase to be unchanged under experimental conditions, when either concentration of reagents, ratio between system constituents, temperature, etc. is under alteration.

In the present work different examples of modified action of reagents on the structure of micellar solutions and microemulsion are shown. To control the structure of microheterogeneous systems (the size and shape of aggregates, packing of surfactant molecules and polarity of different zones of surfactant films, redistribution of components between phases, shift of percolation threshold) the complementary methods NMR-diffusometry, ESR spine-probe and conductometry were used. We analyze changes in widespread systems and show how they can modify chemical kinetics and disturb regularity of pseudophase model.

As an examples the action of inorganic and organic ions, alkylamines, alkylphenols, esters and proteins on the structure and properties of micellar solutions and microemulsions are shown. Possible effects of such modification on reaction kinetics are displayed by the examples of basic, general basic and enzyme-catalyzed disintegration of ester bonds.

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THEORETICAL MODELS FOR THE ELECTRON FLUX AND THE QUANTUM EFFICIENCY CHARACTERISTICS OF NANOSTRUCTURED TiO_2 THIN FILMS IN PHOTOELECTROCHEMICAL CELLS

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Nanostructured TiO_2 thin films are the basis of both nanostructured solar cells and photocatalytic devices. Due to these important and wide ranged of applications, there is continually a great deal of research focused on producing higher activity TiO_2 thin film electrodes. However, the fundamental principles of charge transport and transfer mechanisms in such films are not fully understood. The difficulty is gathering all affecting parameters into a unified quantitative model, which can consider the competitive processes involved in such systems together. Generation of the electron-hole pairs, trapping and recombination pathways, transfer and transport mechanisms of both electron and hole through the semiconductor and at the interface are the fundamental interested processes in this respect. In nanostructured photocatalytic thin films, the main approach to obtain higher performances is to minimize the recombination rates, and control the charge transfer reactions at the same time.

Applying a bias potential was the well known approach in minimizing electron hole recombination in conventional bulk semiconductors. This potential regulates the band bending across the space charge region in order to, typically, minimize electron hole recombination processes. In contrast, when a nanostructured semiconductor comes in contact with an aqueous media, there is no substantial junction or band bending, formed within the extremely small semiconductor particles, because the electrolyte is able to penetrate the film all the way to the back contact, and every colloid will be in contact with the electrolyte. This will totally deplete all charge carriers, and there will be no band bending. In other word, the bands within semiconductor nanoparticles are almost flat, and consequently, there is no space charge layer formed across the thin film. So, in this case, the spatial separation of the photo generated charge carrier pairs can be achieved only by removal of at least one type of charge carriers through interfacial reactions. Therefore optimization of the interfacial charge transfer is essential for photocatalytic electrodes.

A theoretical model for describing the photo electrochemical behavior of nanostructured TiO_2 thin-film electrodes in contact with aqueous electrolytes containing dissolved pollutant species have been used.

The model is based on: (i) the electron transport in the semiconductor occur via diffusion. (ii) The diffusion length of the electrons in the semiconductor through the nanostructured film is constant. (iii) Recombination processes are assumed to be of first order.

Analytical expressions are derived to theoretically analyze the effect of different structural and operational parameters on the electron concentration at the back contact and the quantum efficiency of the nanostructured TiO_2 photocatalytic electrodes in contact with aqueous electrolytes. The influence of film thickness, light absorption coefficient and electron diffusion coefficient are considered cumulatively to find the optimal fabrication conditions. Light intensity, concentration of the dissolved pollutant and the recombination rate constants are also analyzed, as the main affective parameters during the operation of the photocatalytic device. Finally the competitive behavior of generation and recombination rates of photogenerated charge carriers are considered together along with the quantum efficiency. The results indicate that for any given condition there is always an optimal film thickness, at which the quantum yield of the overall processes has its highest amount. So if a thinner nano particulate TiO_2 electrode is preferred, the synthetic method should be modified to obtain the particles with higher extinction coefficients, to compensate the efficiency drop from the thickness. The results from analyzing the operational parameters indicate the light intensity as the most important operational factor, for which, the optimal amount should also be determined for any specific films and operational conditions. The concentration of the dissolved pollutant and the kinetic rate constants are also other matters of importance. There seems to be a saturation concentration, below which, due to the high recombination rate and diffusion limitation, system can not reach its highest efficiency.

On the whole, because of the complex behavior of the affecting parameters on the efficiency of indirect photooxidation of pollutant molecules on the surface of photocatalytic TiO_2 electrodes, it is should always recommended to optimize these amounts before fabrication and utilization processes.

CARBON NANOTUBES WITH ACETONITRILE ELECTROLYTE SOLUTIONS AS PROMISING MATERIALS FOR SUPERCAPACITORS

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Single-walled carbon nanotube (SWCNT) is a cylindrical nanoscale object formed by a single atomic layer of carbon atoms. It was demonstrated that carbon nanotubes can be used as materials for constructing high performance supercapacitors due to a high degree of structure symmetry and great surface inside.

This work is a part of our broad research programme involving investigation of carbon nanotube influence on structure and transport properties of ions and molecules of non-aqueous electrolyte solutions (NAES) inside. A set of molecular dynamics simulations of acetonitrile (AN) and solutions of Li^+, BF_4^-, Me_4N^+, Et_4N^+ based on it by the author's programme package MDCNT [1] was carried out.

Both pure AN and ionic solutions were located in parallelepipedic MD cells which contained armchair SWCNTs of fixed length (3.07 nm) and various diameters (from 1.0 up to 4.0 nm with a step of 0.5 nm). The simulation were performed in NVT ensemble at 298 K, the number of solvent molecules varied from 216 up to 800 in different systems.

The result of our analysis has shown that carbon nanotube greatly reinforces liquid structure and slows down particle diffusion coefficients, and this effect is more pronounced as SWCNT diameter decreases. It was determined that average transport properties of electrolyte solutions based on AN confined by SWCNT approach to bulk ones if the diameter of SWCNT hastens to 4 nm.

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MAGNETIC PROPERTIES OF ANISOTROPIC SPIN LADDERS

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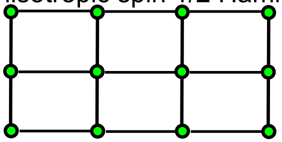
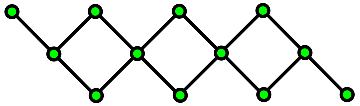
We performed exact diagonalization study of temperature and field dependence of magnetization *M*, magnetic susceptibility χ and specific heat C_v of finite clusters formed by 10-12 spins of 3-leg and necklace anisotropic spin ladders (Figure 1), which are described by anisotropic spin 1/2 Hamiltonians.





These calculations show the existence of magnetization plateau at $M = M_s/3$ (M_s is the saturation magnetization) and the appearance of additional peaks in temperature dependence of specific heat in comparison with corresponding isotropic spin ladders. Anisotropic necklace spin ladder may have the magnetization plateau even in case of zero value of ground state magnetization. In case of zero temperature the plateau may appears at zero magnetic field.

To explain the effects of spin anisotropy we performed numerical simulation of the lowest part of energy spectra of ladder clusters consisting up to 18 spins (Davidson method) and the corresponding density renormalization group (DMRG) study for different values of model parameters. In case of strong coupling in rungs (unit cells) we gave perturbative analyses and proposed approximate partition function of infinite ladder which takes into account only exact energies of low lying states with one inverted spin and approximate energies of the bound states with two and three inverted spins without dispersion.

MULIT-SCALE DENSITY FUNCTIONAL THEORY OF SOLVATION: FROM SIMPLE SOLUTES TO SELF-ASSEMBLED NANOSTRUCTURES

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Solvation gives rise to diverse specific effects revealing multi-scale character. Current studies of solvated biomolecules apply distinct procedures to model solutes at various scales, moreover, the data obtained at one scale are used as input parameters for another scale.

The state-of-art multi-scale density functional theory (DFT) is considered within the context of current approaches to solvation effects. The key concept and numerical scheme of multi-scale DFT is outlined. The schemes, based on the correlation function formalism and the integral equation method, are described. The main attention is focused on the application of the DFT to solvated quantum solutes, molecular complexes, and self-assembled nanostructures. The main idea of the proposed method is to approximate inter- and intra-molecular distribution functions in a unique wavelet basis set consisting of compactly supported wavelike functions, which can be shifted and scaled. Wavelets is a powerful and mathematical tool in physics and chemistry, they are useful in those cases when the result of the analysis of function should contain not only the list of its typical scales, but also the list of the local coordinates where these scales are important. Wavelets are very effective to treat smooth functions as well as complicated distributions in both the real and the reciprocal spaces in contrast to plane waves or gaussians, which are typically used as basis sets in computational chemistry. Using wavelets, I have approximated with high accuracy the radial distribution functions (RDF) for liquid water, for coil and globular homopolymers, even the electron density distribution for solvated electrons. Within this approach I have reduced the DFT to the evaluation of the approximating coefficients by the minimization of the density functional. As a result, I have constructed an efficient algorithm for solving integral equations of simple and molecular liquids. Due to the fast multi-level wavelet procedure I have developed a hybrid method based on combination of the integral equation theory (IET) and quantum chemical calculations. The multi-scale DFT and the IET based on wavelets can reduce sufficiently the computational costs due to the compact representation of any signals including RDF. The examples of the applications of the multi-scale DFT at various scales starting from simple molecular solutes up to self-assembled nanostructures are given.

MULTIREFERENCE STATE-SPECIFIC COUPLED CLUSTER APPROACHES

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It is well known that the coupled cluster (CC) theory is an excellent theoretical tool for the high accuracy prediction of molecular properties. The CC wave operator transforming the reference wave function $\left|0\right\rangle$ into the exact wave function has the exponential form:

$$\left|\Psi_{CC}\right\rangle = \exp(\hat{T})\left|0\right\rangle \qquad (1)$$

In the standard CC approach the operator $\hat{T}$ is truncated and includes single and double excitations (CCSD method). Among other desirable properties of the CC method, the size extensivity is most important one. However, there are some problems with application of the standard CCSD method to certain classes of important chemical problems (open-shell systems, electronically excited states, dissociative curves, *etc*). The major source of errors of standard CC theory is the use of the single determinant $\left|0\right\rangle$ as the reference function and truncating the exponential operator to the certain level of excitation (typically to the double excitation level). The effective way to handle this problem is using *multiconfigurational* reference function (multireference, MR). In our resent works for excited and quasi-degenerate states we have considered several MR approaches based on calculation of selected state (*state-specific* or *state-selective,* SS) ideology. The general SSMRCC method has been implemented as *complete active space,* CAS(n,m)CCSD approach. The wave function of CAS(n,m)CCSD can be described as:

$$\left|\Psi_{\mathrm{CAS(n,m)CCSD}}\right\rangle = \exp(\hat{T}_1 + \hat{T}_2)\left(1 + \hat{C}^{(\mathrm{int})}\right)\left|0\right\rangle \qquad (2)$$

In this wave function the *internal* operator $\hat{C}^{(\mathrm{int})}$ generates the reference function by acting on the "formal reference" determinant $\left|0\right\rangle$. The *external* operators $\hat{T}_1$ and $\hat{T}_2$ generate single- and double- excitations from all reference determinants. All the reference determinants arise by distribution of n electrons among m CASSCF orbitals. In a calculation of an open-shell excited state one can notices that for spin (and/or spatial) symmetry reasons, the closed shell determinant $\left|0\right\rangle$ may not contribute to the wave function of the considered state. To accomplish this and to have the CASCCSD wave function include the most important configurations and corresponding excitations (in exponential form) from these configurations we use the following *ansatz*:

$$\left|\Psi_{\mathrm{SSMRCC}}\right\rangle = \exp(\hat{T})\left(\frac{\hat{E}_{\mathrm{AI}}}{\sqrt{2\left(1+\delta_{\mathrm{AI}}\right)}} + \hat{C}^{(\mathrm{int})}\right)\left|0\right\rangle \qquad (3)$$

where the unitary group generator $\hat{E}_{\mathrm{AI}}$ generates the most important singly-excited configuration of the reference wave function. In calculation of triplet states we use unitary group generator in the form:

$$\tilde{\hat{E}}_{\mathrm{rs}} = a^{+}_{r_\alpha} a_{s_\alpha} - a^{+}_{r_\beta} a_{s_\beta} \qquad (4)$$

For an open-shell singlet excited states the CC ansatz can be derived also by removing the formal reference determinant ($\left|0\right\rangle$):

$$\left|\Psi\right\rangle = \left(\exp(\hat{T})\exp(\hat{T}') - 1\right)\left|0\right\rangle, \qquad (5)$$

where operator the $\exp(\hat{T}')$ generates the reference function of excited state. Also for an open-shell excited state the SSMRCC approach can be represented in the following form:

$$\left|\Psi_{\mathrm{CAS(2,2)CCSD-x}}\right\rangle = \exp(\hat{T}_1 + \hat{T}_2)\left(\left|\mathrm{I\bar{J}}\right\rangle \pm \left|\mathrm{\bar{I}J}\right\rangle\right) \qquad (6)$$

(only open-shell spin-orbitals designated in (6)). One can chose one of the two open-shell determinants ($\left|\mathrm{I\bar{J}}\right\rangle$, $\left|\mathrm{I\bar{J}}\right\rangle$) as formal reference.

Another possibility to describe an open-shell singlet or triplet state is based on two formal reference determinants (*double origin approach, DOA*):

$$\left|\Psi_{\mathrm{DOA(2,2)CCSD}}\right\rangle = c_1 \exp(\hat{T}_1^{(1)} + \hat{T}_2^{(1)})\left|\mathrm{I\bar{J}}\right\rangle + c_2 \exp(\hat{T}_1^{(2)} + \hat{T}_2^{(2)})\left|\mathrm{\bar{I}J}\right\rangle, \qquad (7)$$

where $\hat{T}_1^{(1)}, \hat{T}_2^{(1)}, \hat{T}_1^{(2)}, \hat{T}_2^{(2)}$ are independent CC operators which are defined on their respective reference determinants $\left|\mathrm{I\bar{J}}\right\rangle$ and $\left|\mathrm{I\bar{J}}\right\rangle$.

The test results have been obtained for some model systems (molecules with two- and three- atoms, dimeres).

DYNAMIC STRUCTURE OF NON-AQUEOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

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This work is a continuation of our broader research programme involving the joint application of a multi-technique approach to explain the microscopic structure, particle dynamics and transport phenomena in non-aqueous electrolyte solutions with particular goal to promote their practical applications in modern electrochemical technology.

The object of this work is to present a new view on the microscopic structure and particle dynamics in several chosen non-aqueous solvent and non-aqueous electrolyte solutions. Nowadays it is commonly adopted to use the technique of space-time correlations functions as the most powerful tool in elucidation of fluid structure and its time evaluation at a molecular level [1]. Among the different kinds of correlation functions the space-time van Hove correlation function defined by

$$G(\mathbf{r},t) = 1/N\left\langle \sum_i \sum_j \delta\left[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)\right]\right\rangle \qquad (1)$$

plays a key role in theoretical description and experimental analysis of dense fluids.

The interest to G(r,t) is fourfold. First, van Hove correlation function separates into two parts, the self G_s(r,t) and distinct G_d(r,t) correlations functions that allows one to analyse separately a single particle dynamics and cooperative effects in particle dynamics due to intense interactions in polar liquid and ion-molecular systems. Secondly, the Fourier transforms of proton G_s(r,t), intermediate scattering function F_s(r,t) and self (incoherent) dynamic structure factors $S_s(\mathrm{r},t) \equiv S_{inc}(\mathrm{r},t)$ are the quantities that can be directly measured by using quasi-elastic neutron scattering (QENS) technique on hydrogenated liquids. Thirdly, the van Hove space time correlation function is characterized by well understandable limits. At the initial time the static function $G_d(r,0)$ is proportional to the radial distribution function, $G_d(r,0) = \rho g_{ij}(\mathrm{r})$. Also G_s(r,t) have has a rather direct relation to the self diffusion coefficients D of a tagged particle

$$D = \frac{1}{2}\lim_{\omega\to 0}\lim_{k\to 0}\left(\frac{\omega}{k}\right)^2 S_s(k,\omega) \qquad (2)$$

And finally, the space Fourier transforms of van Hove correlation functions, namely self part of intermediate scattering function of ion F_s(r,t) and distinct part of this function F_d(r,t) of solvent molecules consist of a basis of the mode coupling theory applied to description of the ion friction coefficient in electrolyte solutions [2].

In this research the information about different kind of space and time correlations functions were obtained by using both, the high-resolution quasi-elastic neutron scattering technique and molecular dynamics (MD) simulations. QENS technique has been applied to study the translational and rotational diffusive motion of methanol (MeOH) molecules in pure liquid and $NiCl_2$ solutions in wide temperature and concentration ranges. MD simulations have been carried out in the NVT ensemble to explore the static and dynamic behaviour of the experimentally investigated systems as well as a set of electrolyte solutions of single charged ions in methanol, acetonitrile (AN) and dimethyl sulphoxide (DMSO). An example of the distinct part of the van Hove functions for the pairs of ion-interacting site of the solvent molecule are shown in Fig. 1.

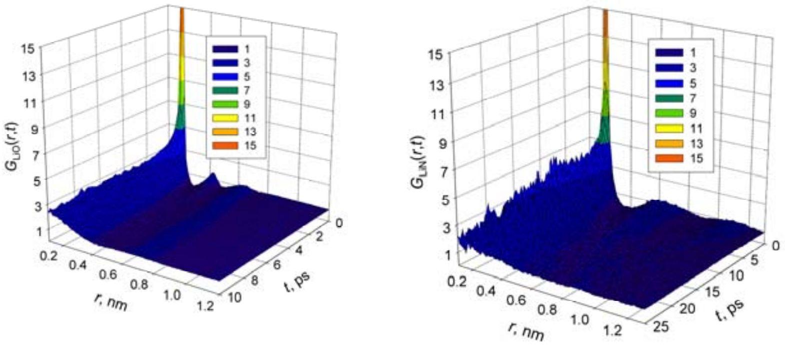

Fig 1. Time-space correlations in Li^+ - MeOH and Li^+ - AN solutions.

The microscopic structural and dynamic characteristics of the ion-molecular systems under consideration are discussed in connection with the results of experimental investigation of transport coefficients at phenomenological level (electrical conductivity, viscosity and translation self diffusion coefficients).

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CHEMISTRY OF FORM IN UNDERSTANDING SOLID STATE REACTIONS

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The comprehension of the form is becoming more and more relevant in various fields of contemporary chemistry. This includes such apparently different brunches as photosynthesis and heterogeneous catalysis, high-tech materials and genetic engineering, biominerals etc. Also, the issue of form gave birth to an intriguing interdisciplinary area of knowledge that links chemistry with biology, physics, geology and, widely speaking, aesthetics via sculpture and architecture. Nature surely opens the lists of most outstanding sculptures and architectures of all times.

The three-dimensional periodicity of atoms or their groups in crystals is the simplest and straightforward structural basis for understanding the form. In spite of very long history, the study of crystal habits still remains one of topical directions of present-day chemistry. But side by side with this cold beauty of equilibrium crystals we face completely different beauty of biominerals that Nature has produced of the same materials but forms of which are absolutely incompatible with basic principles of crystal chemistry. Together with a number of other issues this determines the transition from structural to process-based description of form. In a sense, this approach goes back to D'Arcy Thompson who combined words "form" and "growth" in the title of his seminal book "On Growth and Form" (1917).

Then, what is a simple example of a non-equilibrium form capable of exploring and illustrating spatial-temporal interrelations of elementary events comprising the growth process? One of possible answers is thermal decomposition figures of single crystals. When the crystal growth is concerned, the medium for this process is an isotropic liquid. In the case of thermal decomposition, the crystal itself is an anisotropic medium for the reaction. Two essential distinctions in describing these processes are non-Euclidean metrics and inherent discreteness determined by the crystal structure. In these terms, all three levels of the micro-macro hierarchy – elementary events, crystal structure, and macroscopic form – may be integrated into a unified model providing a deeper insight into the nature of solid state reactions.

PHYSICAL CHEMISTRY OF AQUEOUS SOLUTIONS OF MACROMOLECULES: THE EMERGENCE OF SELF-ORGANISED STRUCTURES

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The dynamics of self-organizing molecular structures is complex. Nano-scale sized agglomerates of complicated shape are spontaneously formed in aqueous solutions. The driving forces behind this process are still largely unknown. Because of the system's high dimensionality and non-linear equations of motions the dynamics of individual atoms is usually assumed to be chaotic and their short time fluctuations at the picoseconds time scale are treated as noise. However, the local dynamics completely determines the evolution of the molecular system over long time scales including the appearance of highly reproducible self-organised molecular structures, such as folded proteins and oligopeptide ribbons. Non-trivial long term behaviour implies complicated spatio-temporal structures of the system's trajectory over short time scales. Discovering and quantifying this intrinsic complexity can therefore shed light on the origin of such emergent molecular behaviour, and is the subject of the present work.

In this paper we give an overview of the methods used, systems studied, and representative results obtained in applications of the complexity approach to self-assembling nano-scale oligopeptide structures.

In our approach the phase-space of a complex molecular system is first partitioned into regions labelled by symbols from a finite alphabet, the trajectory is converted into a symbolic sequence according to the partitioning, and, finally, the symbolic sequence is analysed using the apparatus of Computational Mechanics [1]. The latter quantifies the complexity of the dynamical system by detecting and quantifying dynamical patterns present in the signal. Because of determinism, the patterns in the trajectory must contain regularities inherent in the complex behaviour of the system as a whole and using this approach they can be quantified.

The trajectories for the analysis were obtained using classical molecular dynamics technique. For large scale simulations of poly-L-Glu based assemblies we used GROMACS and NAMD Molecular dynamics software. The details of our simulation set-up are described in [2].

We have found that the hydrogen velocities of MD simulated bulk water form a dynamical pattern of causal histories of length up to at least ~0.45 ps. The pattern has a non-zero value of complexity [3] and surprisingly remains statistically separated from the rest of the histories for tens of nanoseconds. However, over the same long time scale the pattern is gradually destroyed as unstructured trajectories fill the velocity space. This is the first suggestion of the existence of dynamical structures that survive in bulk water for such long times.

Computational Mechanics analyses symbolic dynamics. In order to convert the continuous molecular trajectory into a sequence of symbols from a finite alphabet, an appropriate partitioning of the continuous space is required. A natural choice for such partitioning is the generating partition [4] that has the property of a one-to-one correspondence between the continuous trajectory and the generated symbolic sequence. However, there is no algorithm for finding a generating partition for a general high-dimensional system.

It is also possible to use physically reasonable criteria for partitioning the phase-space, for example, natural clustering of the dihedral angles of peptides. We have found that the results substantially depend on the way the trajectory is clustered. Thus, conformation separations of the macromolecules should be done with great care.

With the use of the described techniques we investigated complex structural transitions of the nanoclusters formed in the aqueous solutions of several *de-novo* poly–L-Glu based oligopeptides. It is known from experiments that these rationally designed oligomeric peptides (10-30 residues) undergo one-dimensional self-assembly into regular nanostructures (beta-tapes, ribbons and multiribbons: figure 1) at appropriate solvent conditions [5]. These new self-assembling bio-materials have novel rheological properties controllable by external chemical (pH, ionic strength) and physical (high shear flow) triggers. These properties, together with their high temperature stability, bio-compatibility, smart bio-processing and reprocessing options make these materials quite attractive for a wide range of biological and medical applications.

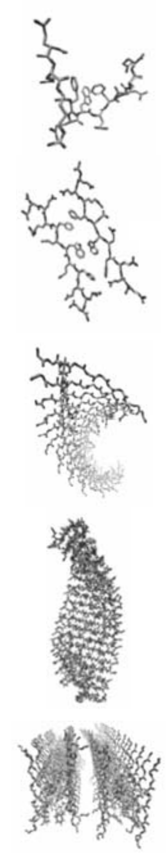

Figure 1. Structures formed by synthetic de-novo oligopeptides in aqueous solutions.

Our study revealed that the dynamics of water and cosolvent molecules in the vicinity of the oligopeptides strongly influences the formation of nanostructures. Moreover, we have shown that changes in the solvent properties (temperature, pH level, salt concentration) lead to essential changes in the self-assembly pathways. Therefore, one could rationally design the structures of the oligopeptide aggregates simply by varying the solvent conditions.

We believe that this theoretical study would lead to a better understanding of how to control the properties of the oligopeptide nanostructures. This, in turn, would lead one to the foundations for the production of a new class of soft-solid nanostructured materials with high biocompatibility and biodegrability.

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POLARIZABLE CONTRIBUTIONS TO THE SURFACE TENSION OF LIQUID WATER

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Surface tension, γ, strongly affects interfacial properties in fluids. The degree to which polarizability affects γ in water is thus far not well established. To address this situation, we carry out molecular dynamics (MD) simulations to study the interfacial forces acting on a slab of liquid water surrounded by vacuum using the Gaussian Charge Polarizable (GCP) model at 298.15 K. The GCP model incorporates both a fixed dipole due to Gaussian distributed charges and a polarizable dipole. We find a well-defined bulk-like region forms with a width of ≈31 Å. The average density of the bulk-like region agrees with the experimental value of 0.997 g/cm^3. However, we find that the orientation of the molecules in the bulk-like region is strongly influenced by the interfaces, even at a distance 5 molecular diameters from the interface. Specifically, the orientation of both the permanent and induced dipoles show a preferred orientation parallel to the interface. Near the interface, the preferred orientation of the dipoles becomes more pronounced and the average magnitude of the induced dipoles decreases monotonically. To quantify the degree to which molecular orientation affects γ, we calculate the contributions to γ from permanent dipolar interactions, induced dipolar interactions, and dispersion forces. We find that the induced dipole interactions and the permanent dipole interactions, as well as the cross interactions, have positive contributions to γ, and therefore contribute stability to the interface. The repulsive core interactions result in a negative contribution to γ, which nearly cancels the positive contributions from the dipoles. The large negative core contributions to γ are the result of small oxygen–oxygen separation between molecules. These small separations occur due to the strong attractions between hydrogen and oxygen atoms. The final predicted value for γ (68.65 mN/m) shows a deviation of ≈ 4 % of the experimental value of 71.972 mN/m. The inclusion of polarization is critical for this model to produce an accurate value.

FEATURES OF LIQUID Al-Ni AND Al-Co ALLOYS' STRUCTURES IN THE RANGE OF EXISTENCE OF QUASICRYSTALLINE PHASES

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Particular interest to research of structure binary and ternary alloys of aluminum with 3d - transition metals is caused by quasicrystalline phases found which receive at upon melt quenching or prolonged anneal from a solid state. Analysis of the literature data has shown that correlation between local atomic structure of liquid alloys and their susceptibility to formation of quasicrystalline phases has not been understood to the present day.

The structure of liquid Al-Ni with 0, 10, 18, 25, 28, 32, 40, 75, 90, 100 at % Ni and Al-Co alloys with atomic percentage of Co 10, 18, 23.5, 26 80.7 и 100 have been studied by X-ray diffraction method using MoKα - radiation at temperatures about 50 ^{0} above liquidus. The Reverse Monte-Carlo method was employed for reconstruction of structural models of investigated alloys from experimental structural factor curves. The initial basic cell contained 5000 atoms different type in the stoichiometric ratio. Coordinates of particles were set as random distribution. The size of basic cell was consistent with the melts' density at the temperature of studying.

The Voronoi–Delaunay method was used for analysis of atomic ordering in received model configurations of binary liquid alloys. The concentration dependences of the metric and topological parameters of the Voronoi polyhedron show a peculiarity in the ranges with content 20-40 at % Ni for Al-Ni alloys and 18–26 at % Co for Al-Co alloys, which correlates with the range of melt-quenched quasicrystalline phases [1-2]. Percolation analysis of the Delaunay simplexes' network has shown that in quasicrystalline concentration region specific ordering atoms 3d - transition metals in polytetrahedral clusters is observed. These cluster form icosahedral ordering of atoms in liquid alloys and determine of prepeak's existance on structural factor curves. Pentagonal rings predominantly contain Ni and Co atoms, which are located at an average distance about 4.1-4.2 Å, alternating with aluminum atoms.

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ACID-BASE EQUILIBRIUM ON THE ACTIVE CARBON SURFACE: QUANTUM-CHEMICAL POINT OF VIEW

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The nature of the active carbon amphoteric properties were under active investigations a long term. While the acid properties of active carbon were identified a long time ago as a properties of the functional groups like phenolic, carboxylic and similar oxygen-containing groups, but the origin for basic groups are not completely clear up this time. There is not common model for the basic groups fro oxygen-free active carbon, but this basic property is well known experimentally.

Using graphite-like and amorphous models we have quantum chemically (QC) simulated the acid-base properties of of active carbon with respect to water and aqueous acids and bases. The attention has been focused on the oxygen-containing and oxygen-free structures with basic properties. The graphite-like pyron-type clusters with different mutual positions of two oxygen atoms have been considered. The interaction of the clusters in differential multiplicity states with proton and hydroxonium ions as well as HBF_4 has been examined. The QC simulated data show that the distance between oxygen atoms in the considered clusters does not significantly influence on the energy of protonization if they are included into conjugated system. Therefore, the carbonic system with the spatially spased oxygen atoms may still posses the properties of the pyron-type structure. Such fragments may be responsible for the basic properties of the partially oxidized carbon materials. The basicity of all investigated systems (more 800) has the same interaction energetics in respect to each acid, namely H^+, H_3O^+ and HBF_4. Nonclassic condenced conjugated systems, e.g. azulen, incorporated into graphite-like clusters, have a bit less basic properties in comparison with the above mentioned pyron-like systems. The protonization of the considered systems is reversible.

Contrary, the amorphous-like carbon clusters may react with the protons and hydroxyd ions irreversibly. Results of the QC simulations are compared along with the experimental data of vibrational spectroscopy and potentiometry.

POSTER PRESENTATIONS

CONDUCTANCE AND ASSOCIATION OF $M(ClO_4)_2$ (M=Mg, Ca, Ba) IN ACETONITRILE

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For the mean time a little attention either practical or theoretical is paid to investigation of unsymmetrical electrolytes in non-aqueous solvents.

In this work the results of experimental research of conductivity and ion association in dilute solutions of perchlorates of alkali earth metals $M(ClO_4)_2$ in acetonitrile in the temperature range from 5 °C to 55 °C are presented.

From experimental conductometric data the limiting molar conductivity $\lambda_0(1/2M^{2+})$ and $\lambda_0(ClO_4^-)$ and ion association constant K_A of ion pair $[MClO_4]^+$ formation are calculated by using the extended Lee-Wheaton equation.

Microscopic interpretation of K_A is carried out in terms of the Rasaiah-Friedman potential of model for ion-ion interactions. It is established that difference in absolute values and temperature dependence of short-range non-Coulombic part of inter-ion potential for $[MClO_4]^+$ can be explained by different ion-molecular interaction patterns in solvation shell of M^{2+} . In case of $[MgClO_4]^+$ the potential is positive. This fact indicates that solvation shells of ions prevent their associations. For $[BaClO_4]^+$ the potential is close to zero in the whole temperature range. It can be explained by the equal probability of formation of contact and solvent shared ion pairs.

Limiting molar conductivities $\lambda_0(1/2M^{2+})$ and $\lambda_0(ClO_4^-)$ are interpreted in terms of Stokes radii of ions. On the basis of analyses of temperature dependence of Stokes radii it is determined that dynamic solvate shells are stable enough. Their thickness is proportional to charge density on ions surfaces.

A THERMODYNAMIC APPROACH TO CHOOSING PERVAPORATIVE MEMBRANES

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This work refers to the separation of a mixture of several components obtained as product of thermo degradation of the methyl poly(méthacrylate) (PMMA).we wish to purify the methyl methacrylate monomer (MMA) obtained by thermal degradation with 95% in mass to reach the maximum concentration of 99.5% using the pervaporation process. This work aims to study the theory of pervaporation and to apply the principal thermodynamic criteria for the choice of the suitable polymer membranes to the separation of MMA/PRP/ISB mixture. These thermodynamic criteria are based on the interaction parameters and solubilities of the monomers in the membrane. The advantage of the use of this technique of separation lies mainly on the fact that this method has low energy consumption compared with the other processes such: distillation or crystallization.

THERMODYNAMICS OF CONDUCTIVITY AND VISCOUS FLOW OF THE SOLUTIONS 1-BUTYL-2,3-DIMETHYLIMIDAZOLIUM TETRAFLUOROBORATE – PROPYLENE CARBONATE

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The necessity of developing new technologies for electroplating, creating new chemical energy sources and nanotechnologies, led in the past years to a steep increase of the interest to experimental and theoretical studies of water free electrolytes based on organic salts, e.g. ionic liquids. Investigations of the quantitative correlation of water free electrolytes’ physico-chemical properties form the basis for choosing specifically the media for different technological processes.

Very important properties of this class of substances, influencing the electrochemical processes, are conductivity and viscosity.

For this reason we investigated viscosity and conductivity in a wide temperature range with addition of propylene carbonate up to 20%.

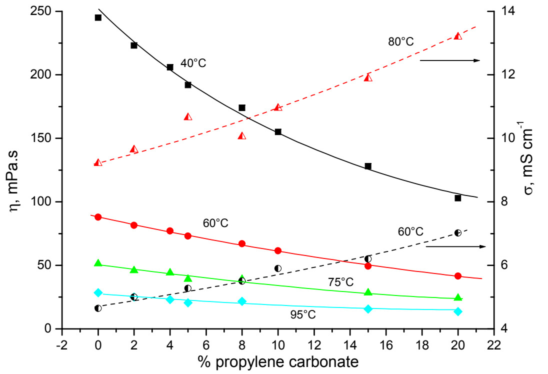

Fig.1 Viscosity and conductivity dependences on composition at selected temperatures.

The change of values of ion migration processes and viscous flow were calculated and analysed. On the basis of the measured viscosity and conductivity at different temperatures, it was discovered, that enthalpies of the activation processes of ion migration and viscous flow are almost equal in the systems studied. This fact evidences, that the main contribution to the conductivity change with temperature of the propylene carbonat - 1-butyl-2,3-dimethylimidazolium tetrafluoroborate mixtures makes a corresponding viscosity change.

The analysis of the thermodynamic characteristics of ion migration and viscous flow processes showed that ion migration in the solution is determined by the viscosity value.

In conclusion, the aspects of the solvent influence on the ion migration were justified and the physical interpretation to isokinetic effect in the systems studied has been done.

The financial support within the K*plus*-programme sponsored by the FFG (Austrian Research Promotion Agency) and the government of Lower Austria is gratefully acknowledged.

DETERMINATION OF LIPOPHILICITY PARAMETER OF SIROLIMUS AND ITS ANALYTICAL CONCENTRATION IN BLOOD BY HPLC

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Sirolimus (rapamycin) is a hydrophobic, temperature, pH and light sensitive compound which is an anti-rejection drug used in renal transplant. It suppresses cytokine-mediated T-lymphocyte proliferation. In human blood sirolimus is extensively distributed in red blood cells. As a first step of his action, the penetration through the cellular membrane of these cells is considered. An important indication of this process is the lipophilicity parameter of the compound investigated.

As method for determination of the lipophilicity parameter in last years, high performance liquid chromatography (HPLC) is suggested in the literature. This technique has been used mostly due to the identity of the lipophilicity parameter to the capacity factor *K*. The capacity factor is easily determined using the method of reversed phase HPLC applying the following equation:

$$K = \frac{(R_t - R_0)}{R_0}$$

where *K* is the capacity factor, R_t is the retention time of the compound investigated, and R_0 is the retention time of the non-retained compound.

Very often, the pH is a key factor for the value of R_t (respectively *K*). Investigating the pH dependency of the capacity factor of rapamicin, and drawing the curves of this dependency, important information about the strength of the processes of protonation and deprotonation for the sirolimus can be obtained.

LOW-TEMPERATURE SYNTHESIS OF NANOCRYSTALLINE $Ca_{10}(PO_4)_6F_2$ AND $GdPO_4$ DOPED WITH RARE EARTH ELEMENTS

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Impurity-doped apatite-like compounds ($Me_{10}(ZO_4)_6X_2$) and lanthanide phosphates ($LnPO_4$) are widely used as materials for laser techniques, high-quality optical ceramics and light converting coatings. Creation of «core-shell» nanostructures on the base of metal (Au or Ag) shell and phosphate luminescent core with improved luminescent characteristics and optical size effects seems to be very promising. "Soft" chemistry processes allow obtaining nanocrystals controlling their diameter, shape, and providing narrow particle size distribution. Therefore the influence of peculiarities of synthesis procedure on physical and chemical properties of nanocrystalline phosphors belongs to the topical problems of modern material science.

Nanocrystalline phosphates (FAP and $GdPO_4$) doped with Eu^{3+} ($C_{Eu(III)}$ = 1-5 %), have been synthesized in aqueous solution under different conditions. Polyacrylic acid (PAA) was used as stabilizer. The samples were studied by XRD, SEM, TEM and XPS methods.

Amorphous spherical particles 10-80 nm in diameter with elemental composition of $GdPO_4:Eu^{3+}$ are formed at 20 °C and pH = 4, whereas X-ray diffraction of product obtained at 90 °C, corresponded to monazite structure, that is characteristic for $GdPO_4$.

It was demonstrated that initial stage of FAP structure formation at pH = 4.7 and t = 90 °C is nucleation of CaF_2 (particles with diameter of 10-20 nm). Grown $FAP:Eu^{3+}$ nanoparticles have complex rod-like structure with 50-200 nm in length and 30 nm in width.

Effective segregation coefficients of Eu^{3+} in $GdPO_4$ and $Ca_{10}(PO_4)_6F_2$ structures, obtained under various conditions, were determined. The influence of rare earth elements concentration, temperature, and annealing duration on luminescence intensity were studied.

IONIZATION OF LONG-CHAIN FATTY ACIDS IN MICELLAR SOLUTIONS OF SURFACTANTS

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The interfacial electrostatic potential, Ψ, of surfactant micelles is an important quantity for the description and interpretation of acid-base equilibria in organized media. As a rule, dyes or indicators are used as molecular probes for the determination of Ψ. However, this approach of Ψ value estimation may lead to some errors coused by two reasons: 1) such probes are not always located precisely at the micellar interface, and 2) rather bulky molecular probes can distort the micellar structure. Molecules of long-chain fatty acids are seemingly preferable for this purpose because their size is close to that of surfactant molecules (ions) and their hydrophobic tails have properties similar to those of majority of surfactants.

The apparent ionization constant, K_a^a, of any acid localized on a charged surface is connected with the ψ value

$$\mathrm{p}K_a^a = \mathrm{p}K_a^i - \frac{F\Psi}{2.303RT},$$

where K_a^i is the so-called intrinsic ionization constant; it equals to the apparent ionization constant if $\Psi \to 0$. Usually the K_a^a value of an acid in nonionic micelles is used as an estimate of K_a^i in ionic ones.

Ionization constants of some fatty acids (hendecanoic, myristic and palmitic) solubilized in surfactant micelles of different types – anionic (sodium dodecyl sulfate), cationic (cetyltrimethilammonium bromide), nonionic (brij-35) and zwitterionic (cetyldimehtylammoniumpropane sulfonate) have been determined at 25 °C. The potentiometric titration method based on the measurement of electromotive force of the cell with liquid junction consisting of glass electrode and silver/silver chloride electrode have been used for the determination of K_a^a values.

Titrations were carried out in aqueous solutions with acid concentration of 5×10^{-3} mole/l in the presence of NaCl or KCl (2.0, 0.4 or 0.05 mole/l) as inert salt as well as in salt-free solutions. The concentration of surfactants was adjusted so that each micelle contained 1-3 molecules of the acid. The error of the determination of $\mathrm{p}K_a^a$ values was near ± 0.1.

It has been found the $\mathrm{p}K_a^a$ values do not depend on the hydrocarbon chain length of the acid and are practically identical for micelles of the same type. The $\mathrm{p}K_a^a$ values in solutions containing cationic micelles are smaller than in the presence of anionic micelles, the $\mathrm{p}K_a^a$s in nonionic micelles have values mediate between those in cationic and anionic ones, while the $\mathrm{p}K_a^a$s in zwitterionic micelles are close to those in anionic micelles. The increase in ionic strength of solution leads to approaching of $\mathrm{p}K_a^a$ values in micelles of different type to each other. The electrostatic potentials of micellar interfaces calculated by using the experimental $\mathrm{p}K_a^a$ values agree qualitatively with those determined by using spectrophotometric technique with acid-base indicators as probes.

QUANTUM-CHEMICAL MODELING DOPED CONDUCTING POLYMERS AND THEIR MOLECULAR COMPLEXES WITH OXYGEN

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Electron-conducting polymers (ECPs) are a relatively new class of polymer materials that gain electron conductivity after doping – insertion of ions from solutions into their structure. It was taken as an example for detailed experimental investigations into electric [1, 2], electrochemical [3] and other properties of ECPs. Polyaniline (PANI) is one of the most stable representatives of this class. However, in spite of abundant experimental studies of ECPs there is lack of theoretical studies which would enable one to explain the nature of the appearance of electron conductivity in doping, the mechanism of electrochemical and electrocatalytic reactions involving ECPs.

This work is aimed at carrying out a detailed chemical analysis of the electronic structure of PANI-type ECPs before and after doping of cations and anions (using H^+ and Cl^- as the examples) into their structure, and estimating the influence of these dopants on electric conductance, mechanical flexibility of the polymer chain and electrocatalytic activity of PANI toward the reaction of oxygen reduction.

The clusters model a geometrical and electronic structure of completely oxidized form of PANI (MC-I), emeraldine (MC-II) and completely proton-doped and anion-doped forms of emeraldine (MC-III).

Monoatomic anions of chlorine were tested as dopants. The calculation of the electronic structure of the molecular clusters with full optimization of their geometrical parameters was carried out by using semi-empirical quantum-chemical MO LCAO method in the PM3 approximation.

The calculations show that considerable weakening and extension of the initial N–C bonds occur during the processes of doping by protons and anions. The nitrogen atoms lose a considerable part of the electronic density (of about 0.42 e) and go into the cationic form. The anions as dopants not only destabilize the electron shell of nitrogen, but also contribute more than 50 % of electronic energy to forming the highest occupied molecular orbital (HOMO), whose electrons pass to the conduction band upon applying an external electric field.

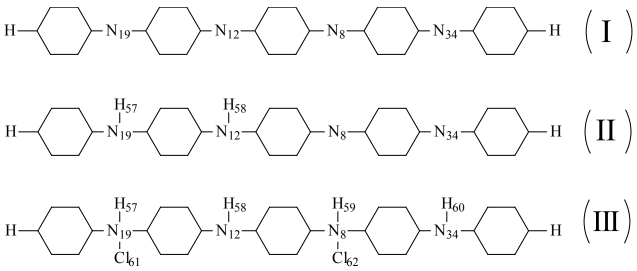

Fig.1. Molecular clusters of PANI: completely oxidized form (I), half-reduced form (II) and the form completely doped with two molecules of HCl (III)

The weakening of bonding between the electrons of the valence shell of nitrogen and nuclear skeleton quantitatively reveals itself in a considerable rise of the HOMO energy. Due to the increase of ionicity and weakening of bonding in the N–C coordination centre the PANI polymer chain becomes more flexible. Thus, the doping anions play the main role in increasing the conductivity and mechanical flexibility of the polymer chain.

To study possible reasons and mechanisms of the catalytic activity of PANI, we modeled the electronic structure of adsorption complexes of doped PANI with oxygen. The results of calculations showed that molecular oxygen is reversibly chemisorbed on the PAN surface so that both atoms form bonds to molecular-cluster atoms (so-called “bridge” model of adsorption – Fig. 2).

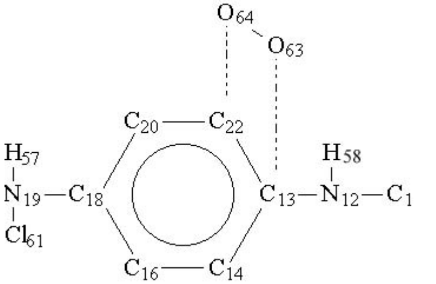

Fig. 2. A “bridge” model of oxygen adsorption at doped PANI

In the adsorption complex “PANI-O_2”, the PANI surface is an electron density donor. In adsorbed O_2 molecules, the bond orders decrease by about 30%, and the bond lengths L increase by more than 20 %. Thus, adsorbed O_2 molecules have a fairly high degree of activation and can be easily reduced.

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ELECTROPLATING OF NOBLE METALS FOR ADVANCED MICROELECTRONICS AND MICROTECHNICS

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The operational characteristics of coatings of noble metals and their alloys are defined by bath composition and conditions of their reception. In paper the composition of the modern electrolytes for deposition of noble metals, particular of reception and property of separate kinds of coatings by noble metals with reference to cases of integral microscheme are analyzed. It is shown that electrolytes on a basis of phosphates are perspective. The structures of the electrodeposited coatings are considered in connection with their corrosion properties. The ways of the structure control hence from electrolytes composition and electrolyse condition are considered. The ways of economy of noble metals for technical application are analysed.

The microstructure of silver films electrodeposited from different types of baths had been studied. The principal formulations of baths were following (Table 1):

Table 1. Composition of bath for silver electrodeposition.

№	Bath	Composition of bath
1	cyanide	0.75M $KAg(CN)_2$ + 1.5M KCN+0.2M KOH
2	dicyanoargentate-thiocyanate (DCAT)	0.75M $KAg(CN)_2$ + 6M KCNS + 1M K_2CO_3
3	dicyanoargentate-borate-phosphate-carbonate (BPC)	0.75M $KAg(CN)_2$ +0.82M KH_2PO_4+ 0.41M H_3BO_3 + 0.15M K_2CO_3 + 0.69M KOH
4	thiocyanate	0.75M $AgNO_3$ + 6M KCNS

XRD patterns and intensities of peaks obtained for silver films depend on the current density applied for electrodeposition as well bath type used for films electrodeposition. Regardless on the type of bath utilized for silver films electrodeposition, the obtained silver films are polycrystalline. There is no evident dependency of interplanar distance on the current density applied for Ag films electrodeposition from various baths. However, these distances obtained for Ag films are higher than that obtained for metallurgically prepared silver.

The electrodeposited silver films and metallurgic silver are nanocrystalline. The smallest values of grain size as ~60 nm could be obtained at certain current densities (15 - 40 mA cm^{-2}) for films electrodeposited from cyanide baths, and highest values of grain size (100 -120 nm) are obtained for films electrodeposited from thiocyanate and BPC baths.

The deposits obtained from the baths in which thiocyanate or sulphite Ag(I) complexes are a source of silver contain all possible textures like in metallurgic silver, whereas deposits obtained from the cyanide, DCAT and BPC baths does not contain texture (220) or corresponding peak is negligibly low. Moreover, the textures (311) and (222) almost are absent in deposits, obtained from the BPC bath.

The minimal roughness is observed on the deposits obtained from cyanide and DCAT baths and highest was found for deposits obtained from BPC baths

The obtained corrosion current density for bulk silver in 0.2M H_2SO_4 solution is ~2 10^{-5} A cm^{-2} whereas the Ag films electrodeposited from various baths exhibit higher corrosion current densities. The corrosion current density could be correlated with grain size of Ag films that trends to increase in corrosion current density when values of grain size exceed 80 nm. The corrosion properties was determined by impedance spectroscopy and voltammetry (AUTOLAB system).

The EDX analysis was performed using SEM. The composition of the corrosion products was determined. The formation of Ag_2SO_4 was fixed as most probable.

The corrosion behavior of silver coatings electrodeposited from the borate-phosphate-carbonate (BPC) bath on copper and nickel substrates at varying current densities was studied.

The corrosion behavior of silver coatings was strongly related to their morphology. A higher corrosion resistance was found for silver coatings obtained on copper substrate at lower current densities: 0.3 – 0.5 A dm^{-2}. These coatings were fine-crystalline, smooth and compact. A higher corrosion resistance was found for silver coatings obtained on nickel substrate at current density: 0.75 A dm^{-2}. However silver coatings deposited at all range of current densities on copper substrate was possess of the higher corrosion stability than coatings obtained on nickel substrates.

The silver coatings electrodeposited from BPC bath on the copper substrate may be using for microelectronic industry.

DYE-CONTAINING POLYAMIC ACID-BASED LANGMUIR-BLODGETT MULTILAYER FILMS AS FUNCTIONAL MATERIALS

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Ordered liquid-crystal films prepared by the Langmuir – Blodgett (LB) technology find application in designing the elemental base of electronic devices, for using in nanotechnology, in optical chemical sensors, for instance, containing immobilized acid-base indicators, etc. Among other substances, high-molecular-weight compounds are extensively used for creating LB films due to their high thermal, mechanical, and chemical stability.

The purpose of the present work was to find optimal conditions for obtaining the stable monolayers of polyamic acid (PA) with one carboxylic group per repeating unit on the aqueous lead-containing subphase, to prepare dye-containing LB films based on such kind of PA monolayers and to investigate the pH-dependence of their absorption and luminescence spectra.

The conditions for the preparation of stable PA monolayers on Pb^{2+}- containing aqueous subphase were described. The influence of *N*-octadecylpyridinium bromide on the character of isotherms and stability of monolayers is studied.

Basing on these polymeric monolayers, LB films containing various dyes (Quinaldine Red, Bromothymol Blue, Rose Bengal B, Decylfluorescein, Decyleosine, *N,N´*-Dioctadecylrhodamine) are fabricated. Films with these dyes demonstrate distinct pH-response after soaking in aqueous buffer solutions. The spectral properties of the films and the pH-dependence of absorption spectra of multilayers containing these dyes are studied. The values of the ‘apparent’ ionization constants of the dyes in the films were estimated using the standard vis-spectroscopic procedure and compared with those determined in aqueous micellar solutions of colloidal surfactants.

LB films with aforementioned dyes appeared to be most suitable for monitoring acidity within an extremely wide pH range, including the ‘physiological’ region. Such stable dye-containing polymeric LB films with reproducible spectral and acid-base properties can be used in optical sensors and related devices.

ENVIRONMENTALLY SAFE OXIDATIVE-NUCLEOPHILIC SYSTEMS FOR DECOMPOSITION OF ECOTOXICANTS

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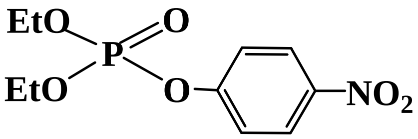
Studies on the kinetics of paraoxon (I) decomposition and oxidation of thioanisol (II) by hydrogen peroxide in water and aqueous alcohols at pH 8-10 showed that H_2O_2 is a versatile decontaminant.

This agent in the form of HOO^- anion is a powerful α-nucleophile ($k = 0.5\ M^{-1}s^{-1}$) and can be used in decontamination of nerve gases.

Being a soft oxidizing agent, hydrogen peroxide converts substrate **II** in the corresponding sulfoxide ($k = 0.0014\ M^{-1}s^{-1}$) and can be recommended for decontamination of mustard gas and its analogues.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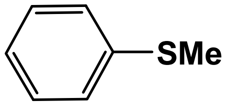
II

An addition of activators of hydrogen peroxide (NH_4HCO_3 and $B(OH)_3$) gives rise to more than 100-fold increase in oxidation rates and accelerates nucleophilic substitution considerably. The observed effects result from the formation of active ions – peroxyhydrocarbonate HCO_4^- and peroxoborates $[B(OH)_3HOO]^-$ and $[B(OH)_2(HOO)_2]^-$, which are both powerful nucleophiles and strong oxidizing agents.

Carrying out the reactions of oxidation and nucleophilic decomposition in the cationic micellar systems (CTABr) in the presence of activators gives rise to considerable increase in solubility of substrates I and II (K_s(I) = 500 M^{-1} and K_s(II) = 900 M^{-1}), thus increasing the rates of oxidation-nucleophilic interactions.

To summarize, the findings suggest that the system H_2O_2/HCO_3^- ($B(OH)_3$)/cationic detergent are promising “green” component part of the versatile systems efficient in decomposition of a great variety of ecotoxic substrates.

APPLICATION OF CHEMOMETRICS IN REVERSED-PHASE LIQUID CHROMATOGRAPHY AND RELATED TECHNIQUES

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Chemometrics is a powerful tool of analytical chemistry that can be applied to any part of analytical systems, experiments and instrumental signals [1]. Signal enhancement, de-noising, elimination of background, chromatograms warping, peak deconvolution is the commonly used methods for chromatograms treatment in software programs for high-performance liquid chromatography (HPLC). However, main problem of method development in HPLC and related techniques such as ion-pair, micellar and microemulsion liquid chromatography is a finding of optimal conditions for fine separation of complex mixtures. Several optimization strategies have been proposed to assists the resolution of problems, but slow and insufficient trial-and-error methods are still frequent [2].

Thus, main topic of this presentation is focused on new ideas and results of optimization of separation conditions by sequential and interpretative schemes, mainly in micellar liquid chromatography. Earlier developed retention models based on mass action concept of micelle formation has been applied for retention modeling [3]. Another previously solved problem of unknown uncertainty of retention factor [4,5] has been used in this work for adequate using of interpretative optimization strategy.

In MLC micelle concentration and content of organic modifier in micellar eluent both influence on separation selectivity, which is controlled by two main factors: hydrophobic and electrostatic interactions of solute with dynamically modified stationary phase and hybrid mobile phase [3].

Due to different types of interactions and the competing equilibria in MLC, one can expect any form of the selectivity behavior (i.e. peak convergence, divergence, and crossover), especially for ionized compounds. In this work sequential optimization strategy based on simplex algorithm and Berridge critical response function for estimation overall resolution has been used for finding region with good separation of 13 2,4-dinitrophenyl amino acids. The three main factors have been varied: concentration of sodium dodecylsulfate, content of 1-propanol and pH.

However, it is difficult to find optimal separation conditions for non-ionized compounds, which retention is controlled mainly by hydrophobic interactions, without peak modeling and estimation of overall resolution in each point of factorial space. The interpretative optimization strategy has been used for data processing of retention of set of food preservatives in MLC. Optimal separation conditions were achieved only by careful investigation of response surface, because only somewhat small differences in influence of surfactant concentration and organic modifier concentration on retention of preservatives with similar physicochemical properties provide resolution of 14 components of mixture. The using of earlier proposed simple three-parameter retention model [3] and obtained results of dependence of retention factor uncertainty on value of retention factor [4,5] lead to more reliable results of selectivity optimization for set of preservatives.

Thus, it could be concluded that two chemometrics approaches of optimization of separation in HPLC (sequential and interpretative) are helpful and give good results by their adequate exploration for each special case.

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EFFECT OF SILICA FILLER FUNCTIONALIZATION ON STRUCTURE OF POROUS POLYMER SPHERES

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High-disperse silica is effective filler that allow considerably improving properties of polymeric material. The filler surface fuctionalization by chemically inert or/and active organic groups increases its compatibility with polymer and leads to formation of cross-linked structure.

We revealed [1-2] that the uniform distribution of inorganic particles in the polymer during the suspension-emulsion polymerization is obtained at filling with partially methylated silica. It was also found that in the presence of surface silicon-hydride groups the cross-linked structure is achieved due to formation of hydrolytically stable polymer – silica bonds during hydrosilylation of unsaturated monomer groups [3]. Thus, the presence of methyl and hydride groups on silica surface presumably will allow one to obtain high filler dispersion and chemical structuring of a nanocomposite. The effect of surface hydrophobization with the possibility of polymer – filler chemical interaction is also achieved via vinyl groups grafting. The intensity of interfacial bonds network may be varied by the quantity of surface functional groups.

The aim of the present work is to investigate the effect of grafted groups and its concentration on specific surface area, porosity and size of the copolymer spheres. The system copolymer divinylbenzene with di(methacryloyloxymethyl)naphthalene – silica filler with varied surface functionality was studied. The filler samples with varied concentration of surface vinyl, methyl or hydride, as well as methyl and hydride groups were obtained. Porous spheres were obtained via suspension-emulsion polymerization [4] at filler presence or absence. The filling degree was 15% of monomer weight. Nanocomposites obtained were studied by means of low-temperature adsorption-desorption of nitrogen and AFM spectroscopy. Size of polymer spheres was found by bolting.

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RADIATION-CHEMICAL SYNTHESIS OF NANO-SCALED POLYELECTROLYTE BRUSHES ONTO PLANAR POLYMER SURFACES

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Polymer brushes are assemblies of macromolecules that are tethered by one end to a surface or interface. Attachment of the polymer chains in close proximity to one another forces the polymers to adopt a stretched conformation. As a result of these densely packed polymer topologies, the synthesis of polymer brushes has attracted increasing attention for applications in areas such as surface property tailoring, chemical gating and nanolithographic patterning. Polymer brushes can be prepared by either physical adsorption or covalent attachment, achieved by the “grafting to” and “grafting from” techniques. In the “grafting to” technique, preformed end-functionalized polymer molecules react with an appropriate substrate to form polymer brushes, while in the “grafting from” one the surface immobilized initiator causes in-situ polymerization with polymer brush formation.

Among some variants of “grafting from” technique the radiation-chemical method of initiation has some preferences. Highly reactive radicals formed on the polymer surface (or entire volume) after electron beam or γ-rays irradiation initiate graft polymerization and extension of long polymer brushes over a range of tens of nanometers to the micrometer scale.

For the purpose of synthesis chemically active polymer brushes acted as a chemical gate for the purpose of separation (adsorption) and biotechnological processes the radiation-induced graft polymerization of poly(glycidyl methracrylate) (poly-GMA) brushes onto planar polyethylene and polypropylene films using electron beam irradiation have been carried out.

The utilization of this method allowed us to control both the density and length of the (poly-GMA brushes varying the absorbed dose and grafting conditions (time and temperature of grafting). The following modification of the reactive epoxy-groups of poly-GMA chains provided the basis for a versatile functionalization of the grafted brushes that allowed us to synthesize a wide range of bio-chemically active solid polyelectrolytes acting as a chemical gate.

THERMODYNAMICS OF CHEMICAL EQUILIBRIA. METHODOLOGICAL AND PRACTICAL ASPECTS

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The equation interconnecting chemical affinity ($\Delta_r G$, Gibbs energy of reaction $\nu_A A + \nu_B B = \nu_C C + \nu_D D$) in the different solvents, thermodynamic characteristics of reagent resolvation ($\Delta_{\mathrm{tr}} G_i^0$), concentration activity coefficients of reagents (γ_i^*), and the concentration of solutions (X_i) has been proposed

$$\Delta_r G^{S-W} - \Delta_r G^{W} = \sum_i \nu_i \Delta_{\mathrm{tr}} G_i^0 + RT \ln \left(\frac{\prod_i (X_i \gamma_i^*)^{\nu_i}_{(S-W)}}{\prod_i (X_i \gamma_i^*)^{\nu_i}_{(W)}} \right)_{nonequilibr}$$

The thermodynamic parameters of complex formation ($K_{i,\mathrm{ML}}$), ligand dissociation ($K_{i,\mathrm{dis}}$), ion association ($K_{i,\mathrm{ass}}$), and reagent resolvation ($\sum \Delta_{tr} G_i^{\mathrm{o}}$) equilibria in solution at standard state are interrelated by the general equation

$$\prod K_i^{SW} = \prod K_i^{W} exp \left\{ \frac{\sum \Delta_{tr} G_i^{\mathrm{o}}}{RT} \right\}$$

The complex formation between cations and crown ethers in pure water, methanol, propan-2-ol, acetonitrile and in methanol–water, propan-2-ol–water mixed solvents (18-crown-6 (18C6) with Na^+, K^+, NH_4^+, Ag^+); dioxane–water, acetone–water, acetonitrile–water mixed solvents (18C6 with Na^+, K^+, NH_4^+); propan-2-ol–water mixed solvents (dicyclohexyl-18-crown-6 (DCH18C6) with Na^+, K^+, NH_4^+); acetonitrile–water mixed solvents (dibenzo-18-crown-6 (DB18C6 with Na^+, K^+) and the complex formation of Ag^+ with acetate and benzoate ligands in methanol–water and propan-2-ol–water mixed solvents over the whole composition range and at various temperatures (from 278.15 to 318.15 K at 5 K intervals) have been systematically studied at the standard state with the use of the methods of potentiometry, conductometry, UV spectrometry, radiometry, isothermal calorimetry.

Methodological questions of thermodynamics of chemical equilibria have been discussed: normalizing of the standard state for reagents in solution; choice of concentration units for the equilibria constants; the comparative quantitative analysis of chemical equilibria thermodynamics of in different solvents; media effect on thermodynamics of chemical equilibria.

The influence of reagent concentrations and water-alcohol solvents composition on complex formation chemical yield have been considered.

A comparative quantitative analysis of contributions of aqueous organic solvent (water-methanol, water-propan-2-ol) effects (standard Gibbs energy of resolvation of reagents, $\Delta_{tr}G^{o}$), of reagent concentration and of the deviations from ideality (γ) in the change of the concentration stability constants of sodium and potassium coronates ($K'_{\mathrm{MLA}} = K_{\mathrm{MLA}}\dfrac{[\mathrm{MA}]}{[\mathrm{MLA}]}\dfrac{\gamma^{2}_{\pm\mathrm{MA}}}{\gamma^{2}_{\pm\mathrm{MLA}}\gamma_{\mathrm{L}}}$) in mixed solvents are provided in comparison with water:

$$RT\ln\frac{K'^{W}_{\mathrm{MLA}}}{K'^{SW}_{\mathrm{MLA}}} = \left(\Delta_{tr}G^{o}_{\mathrm{MLA}} - \Delta_{tr}G^{o}_{\mathrm{MA}} - \Delta_{tr}G^{o}_{\mathrm{L}}\right) +$$

$$+RT\left(\ln\frac{[\mathrm{MLA}]^{SW}}{[\mathrm{MLA}]^{W}} - \ln\frac{[\mathrm{MA}]^{SW}}{[\mathrm{MA}]^{W}}\right) + 2RT\left(\ln\frac{\gamma^{SW}_{\pm\mathrm{MLA}}}{\gamma^{W}_{\pm\mathrm{MLA}}} - \ln\frac{\gamma^{SW}_{\pm\mathrm{MA}}}{\gamma^{W}_{\pm\mathrm{MA}}} - \frac{1}{2}\ln\frac{\gamma^{SW}_{\mathrm{L}}}{\gamma^{W}_{\mathrm{L}}}\right)$$

An empirical “enthalpy–entropy compensation” of complex formation thermodynamics of crown ethers with cations in aqueous organic solution has been discussed: $T\Delta S(\mathrm{ML}^{+}) = \alpha\Delta H(\mathrm{ML}^{+}) + (T\Delta S)_{o}$, $\delta\Delta G(\mathrm{ML}^{+}) = (1-\alpha)\delta\Delta H(\mathrm{ML}^{+})$.

Thermodynamic classification of crown-ether complexes stability on the basis of reagent resolvation contributions into a change of the monocoronate stability $\Delta\Delta_{r}G(\mathrm{ML}^{+}) = RT\ln(K^{w}/K^{sw}) = \Delta_{tr}G(\mathrm{ML}^{+}) - \Delta_{tr}G(\mathrm{M}^{+}) - \Delta_{tr}G(\mathrm{L})$: 1) $\Delta_{tr}G(\mathrm{ML}^{+}) > 0$, $\Delta_{tr}G(\mathrm{M}^{+}) > 0$, $\Delta_{tr}G(\mathrm{L}) > 0$; $|\Delta_{tr}G(\mathrm{M}^{+}) + 0,\Delta_{tr}G(\mathrm{L})| > \Delta_{tr}G(\mathrm{ML}^{+})$, 2) $\Delta_{tr}G(\mathrm{ML}^{+}) < 0$, $\Delta_{tr}G(\mathrm{M}^{+}) < 0$, $\Delta_{tr}G(\mathrm{L}) < 0$; $|\Delta_{tr}G(\mathrm{ML}^{+})| > |\Delta_{tr}G(\mathrm{M}^{+}) + 0,\Delta_{tr}G(\mathrm{L})|$, 3) $\Delta_{tr}G(\mathrm{ML}^{+}) < 0$, $\Delta_{tr}G(\mathrm{M}^{+}) > 0$, $\Delta_{tr}G(\mathrm{L}) > 0$, 4) $\Delta_{tr}G(\mathrm{ML}^{+}) < 0$, $\Delta_{tr}G(\mathrm{M}^{+}) < 0$, $\Delta_{tr}G(\mathrm{L}) > 0$, 5) $\Delta_{tr}G(\mathrm{ML}^{+}) < 0$, $\Delta_{tr}G(\mathrm{M}^{+}) > 0$, $\Delta_{tr}G(\mathrm{L}) < 0$ has been proposed. Effects of aqueous organic solvents on the complexation between cations and crown ethers were interrelated in terms of additivity, antagonism and synergism of reagent resolvation.

Quantitative analysis of the effects of aqueous organic solvents on the cation selectivity of crown-ethers at standard state $\left(K_{\mathrm{ML}^{+}} / K_{\mathrm{NaL}^{+}}\right)$ has been performed.

The general equation that describes primary medium effect (γ_{o}) and solution ionic strength (γ^{*}) influence on the acid-base equilibria of dyes ($\mathrm{p}K$, BH = B^{-} + H^{+}) in a pseudo-phase and on the Galvani-potential (φ) on the border aqueous solution (*w*) - pseudo-phase (*m*) has been developed on the basis of N.A. Izmailov thermodynamical approach

$$\mathrm{p}K^{m}_{a} = \mathrm{p}K^{w}_{a} - \frac{\varphi F}{2.303RT} + \lg\frac{[\mathrm{B}^{-}]^{m}}{[\mathrm{B}^{-}]^{w}} - \lg\frac{[\mathrm{BH}]^{m}}{[\mathrm{BH}]^{w}} + \lg\frac{\gamma^{*,m}_{\mathrm{B}^{-}}\gamma_{\mathrm{o,B}^{-}}}{\gamma^{*,w}_{\mathrm{B}^{-}}} - \lg\frac{\gamma^{*,m}_{\mathrm{BH}}\gamma_{\mathrm{o,BH}}}{\gamma^{*,w}_{\mathrm{BH}}}$$

ELECTROCHEMICAL INVESTIGATION OF NEW 9-FURYLNAPHTOPHURANES DERIVATIVES

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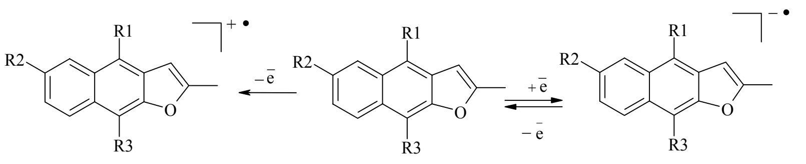
Redox properties of 9-furylnaphthofurans were studied in order to determine general principles of their redox behavior and observation of stable intermediate radical-ions

The Derivatives of napthofuran were studied by the method of cyclic voltamerometry on platinum disk micro and ultramicroelectrodes in acetonitrile and dimethylformamide. All compounds were oxidized in two steps via unstable radical-cations at the first stage. In the case of compounds b and d, their transformation leads to the corresponding diketones.

Reduction of the studied compounds is two stage process for compounds a-d and one stage for e-j. For the radical-anions of compounds h, g at the first stage ESR spectra were recorded .



a-j

R_1= H, R_2=H, R_3= 2-Methyl-fur-5-yl **a** R_1= O(CO)CH_3, R_2=Cl, R_3= 2-Methyl-fur-5-yl **e**
R_1= H, R_2=Cl, R_3= 2-Methyl-fur-5-yl **b** R_1= O(CO)CH_3, R_2=Br, R_3=2-Methyl-fur-5-yl **f**
R_1= H, R_2=Br, R_3= 2-Methyl-fur-5-yl **c** R_1= CHO, R_2=Cl, R_3= 2-Methyl-fur-5-yl **g**
R_1= O(CO)CH_3, R_2=H, R_3= 2-Methyl-fur-5-yl **d** R_1= NO_2, R_2=Cl, R_3= 2-Methyl-fur-5-yl **h**
R_1= H, R_2=Cl, R_3=-pent-2-ene-1,4-dione-2-yl **i**
R_1= O(CO)CH_3, R_2=H, R_3= -pent-2-ene-1,4-dione-2-yl **j**

The work was supported by projects of the ministry of education and science of Russian Federation RNP 2.2.2.2.5592 and RNP 2.1.4939 and within the Project Y4-C04-04 of the program “Fundamental research and high education” (ministry of education and science of Russian Federation and CRDF).

SPECTROSCOPIC INVESTIGATION OF PHYSICAL-CHEMICAL PROPERTIES OF FUROCOUMARINS

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Furocoumarins (psoralens) are planar, tricyclic compounds, consisting of a furan ring fused to a coumarin moiety.

At present, the administration of psoralen in combination with longwave ultraviolet A (UVA) radiation (320–400 nm) is the most widely used form of the drug-plus-light therapy referred to as PUVA [1, 2, 3]. Psoralens are tricyclic aromatic compounds in which the furan ring is fused with a coumarin moiety (hence the name furocoumarin) [4].

Originally, PUVA was used to treat psoriasis, i.e., a hyperproliferative skin disesase, and vitiligo, i.e., an acquired pigmentary alteration in the skin [5]. Now, PUVA is used for treatment of a wide variety of skin diseases, such as psoriasis, vitiligo, lichen planus, persisitent palmoplantar pustulosis, and solar urticaria [2, 3].

Two new substituted coumarins are investigated. The examined molecules are unique from the viewpoint of their electronic structure. They have been synthesized at Taras Shevchenko Kiev National University. A theoretical and experimental study of these compounds is carried out. The absorption spectra, rate constants are determined using the INDO method. The experimental absorption spectra of the examined molecules are registered using a CM-2203 spectrofluorimeter (Solar, Byelorussia). A very good agreement between the calculated and experimental data is established.

The work is supported by the Russian Basic Research Foundation (Project № 06-08-01380-a).

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AQUEOUS SUSPENSION OF SILICA NANOPARTICLES MODIFIED WITH CATIONIC SURFACTANT: EQUILIBRIA OF ACID-BASE INDICATORS

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Functionalized nanosized silica is widely used as a component of biomarkers,sensors, etc. Addition of cationic surfactant is often used for modification of their surface properties. In present work, uniform silica nanoparticles with diameter of 40±5 or 85±5 nm, with surfactant adlayer, have been studied by using indicator dyes as probes. The goal of the investigation is to compare the properties of surfactant-coated silica with those of common surfactant micelles. Namely, the influence on the acid-base equilibrium of different indicators was compared.

The system composition was chosen to be as a rule 0.35 g per dm^3 of SiO$_2$ and 3×10^{-4} M cationic surfactant cetyltrimethylammonium bromide (CTAB) in the case of nanoparticles with diameter of 40 nm and 0.28 g per dm^3 of SiO$_2$ and 3×10^{-4} M CTAB for suspension containing nanoparticles of 85 nm in diameter. This was done in order to avoid possible coexistence of usual surfactant micelles and surfactant-modified silica particles: under aforementioned conditions this phenomenon is not likely to occur. Both pure silica nanoparticles aqueous sol and sol with surfactant has been characterized by measuring electrokinetic potential (ζ). It was shown that when surfactant is stepwise added into the suspension, the ζ-potential value gradually alters from ca. –34±5 to ca +37±5 mV. This points on silica surface recharge and formation of surfactant adlayer. The system of chosen composition remains stable due to formation of lyophilized particles.

Table. The pK_a values of indicator dyes in different media

Indicator	pK_a^w, $I\to0$	pK_a^a		
		0.35 g per dm^3 SiO$_2$ (d=40 nm) + 3×10^{-4} M CTAB, I = 0.03 M (NaCl)	0.28 g per dm^3 SiO$_2$ (d=85 nm) + 3×10^{-4} M CTAB, I = 0.03 M (NaCl)	Cationic surfactant micelles, I = 0.05 M
Bromophenol blue[a], pK_{a2}	4.20	–	2.38 ± 0.07	2.04
Bromocresol green[a], pK_{a2}	4.90	–	3.39 ± 0.02	3.22
Bromocresol purple[a], pK_{a2}	6.40	–	5.10 ± 0.04	5.08
Phenol red[a], pK_{a2}	8.00	7.34 ± 0.05	–	7.08
Bromothymol blue[a], pK_{a2}	7.30	6.51 ± 0.03	–	6.36
Thymol blue[a], pK_{a2}	9.20	–	8.85 ± 0.01	8.83
Fluorescein				
pK_{a0} ($H_3R^+ \rightleftarrows H_2R + H^+$)	2.14	–	0.94 ± 0.03	0.98
pK_{a1} ($H_2R \rightleftarrows HR^- + H^+$)	4.45	4.70 ± 0.05	4.08 ± 0.05	3.60
pK_{a2} ($HR^- \rightleftarrows R^{2-} + H^+$)	6.80	5.81 ± 0.08	5.68 ± 0.08	5.54
Decylfluorescein				
pK_{a0} ($H_2R^+ \rightleftarrows HR + H^+$)	3.10[b]	–	0.89 ± 0.02	0.82
pK_{a1} ($HR \rightleftarrows R^- + H^+$)	6.28[b]	–	4.70 ± 0.02	4.94

[a] $HR^- \rightleftarrows R^{2-} + H^+$; [b] as decylfluorescein is insoluble in water, the pK_a^w values of ethylfluorescein are given here.

Using spectrophotometry with potentiometric determination of the bulk phase pH, we have estimated the “apparent” ionization constants, K_a^a, of sulfonephthalein dyes, fluorescein, and decylfluorescein in investigated systems at constant bulk ionic strength (*I*). The obtained $\mathrm{p}K_a^a$ values are presented in the table; the $\mathrm{p}K_a^w$ values refer to aqueous solutions.

Obviously, surfactant-covered silica nanoparticles resemble cationic surfactant micelles in general trend of affecting the protolytic equilibria of indicators. Though, some differences in $\mathrm{p}K_a^a$ values point on specificity of surfactant adlayer structure. The experiments on kinetics of bromophenol blue fading ($R^{2-} + OH^- \rightarrow ROH^{3-}$), as well as the spectral properties of methyl orange and solvatochromic Reichardt’s indicator and some other data revealed the specificity of surfactant-coated silica nanoparticles, presumably, originating from their surface morphology.

THE NATURE OF CATIONIC POLY(PROPYLENE IMINE) DENDRIMERS IN AQUEOUS SOLUTIONS AS STUDIED USING VERSATILE INDICATOR DYES

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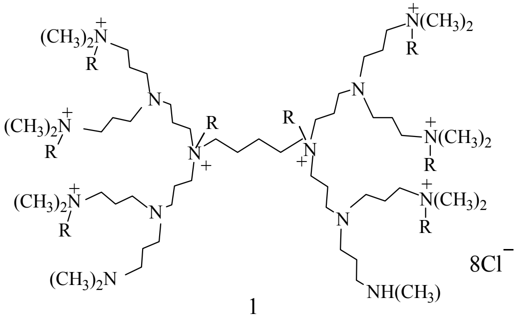
Dendrimers of various types are currently the objects of intensive investigations. The “host – guest” interaction between dendrimers and different molecules and ions as well as their self-assembly properties are of great importance in creating sensors, light-harvesting systems, in drug delivery, in homogeneous catalysis, etc.

In present work, the protolytic behavior of indicator dyes in aqueous solutions of two cationic poly(propylene imine) dendrimers, **1** and **2**, was studied. These dendrimers, being modified by hydrophobic hydrocarbon tails (R = *n*-$C_{12}H_{25}$), behave in aqueous solutions like cationic surfactants: their critical aggregation concentrations are 9×10^{-5} M and 3.8×10^{-4} M, respectively [1].



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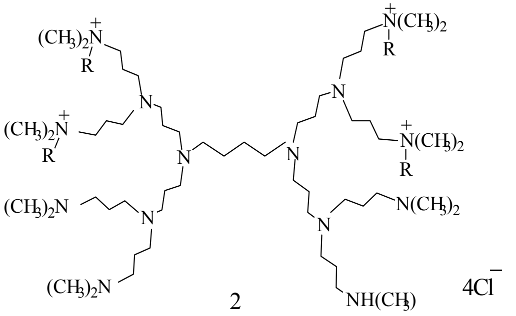

2

We have obtained the ‘apparent’ $\mathrm{p}K_\mathrm{a}^\mathrm{a}$ values of sulfonephthalein and hydroxyxanthene dyes, and methyl orange in dendrimer solutions by vis-spectroscopy, as a rule at 25 °C; the pH values of solutions were determined using glass electrode. The obtained results are presented in the table. The positions of absorption maxima of dyes species are shifted as compared with those in dendrimer-free aqueous medium. These displacements are similar to those registered earlier in micellar solutions of cetyltrimethylammonium bromide (CTAB) and of other cationic surfactants. The dendrimers under study cause changes in emission and excitation spectra of fluorescein dianion, R^{2-}, similar to those observed in CTAB solutions. The medium effects for the apparent ionization constants, $\Delta\mathrm{p}K_\mathrm{a}^\mathrm{a} = \mathrm{p}K_\mathrm{a}^\mathrm{a} - \mathrm{p}K_\mathrm{a}^\mathrm{w}$, are compared in the table with those obtained in CTAB micellar solutions; here K_a^w is the thermodynamic ionization constant in water.

Table. The pK_a^a values in solutions of dendrimers (ionic strength $\approx$0.01 M) and in CTAB micellar solutions (Br^- bulk concentration: 0.01 M)

Dye (pK_a^w)	pK_a^a		CTAB ΔpK_a^a	
	In **1** solutions[a]	In **2** solutions[b]	In dendrimer solutions	In CTAB solutions
Bromophenol blue (4.20)	2.19 ± 0.04	1.81 ± 0.06	–2.0	–1.94
Bromothymol blue (7.30)	6.42 ± 0.04	—	–0.88	–0.71
Thymol blue (9.20)	8.50 ± 0.03	—	–0.70	–0.30
Decylfluorescein (6.31)	4.92 ± 0.03	—	–1.39	–1.37 [c]
Methyl orange (3.40)	2.40 ± 0.15	—	–1.07	–2.40 [d]
Fluorescein, pK_{a1} (4.45)	—	3.07 ± 0.17	–1.38	+0.03 [e]
Fluorescein, pK_{a2} (6.80)	—	4.85 ± 0.07	–1.95	–0.99 [e]

[a] Dendrimer **1** conc.: 1.2×10^{-4} M; [b] dendrimer **2** conc.: 5.09×10^{-4} M; [c] Bulk Cl^- conc. 0.05 M. [d] total Br^- concentration: 0.126 M; [e] bulk ionic strength: 0.03 M (buffer + NaCl).

Though the numerical values did not coincide exactly, the general picture is rather similar. The decrease in the pK_a^a values reflects the location of the dyes in the region with positive electrical charge, while the spectral data indicate the non-aqueous character of microenvironments.

The relatively high fluorescein pK_{a1}^a value in CTAB micelles is caused by the strong shift of the tautomeric equilibrium of the molecular form toward the colorless lactone [2]. Indeed, in **2** solutions the decolorization of fluorescein neutral species is expressed to a less degree, and hence ΔpK_{a1}^a is more negative.

In these report, we also communicate some results of kinetic studies in dendrimer solutions.

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CONCENTRATION OF NOBLE METAL NANOPARTICLES IN MICELLAR SOLUTIONS OF TRITON N-42 AND AOT

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In current variety of physical and chemical methods for the nanoparticles obtaining, a «solution» synthesis is the most often used. Particularly perspective for nanoparticle synthesis has liquid organized solutions on the base of reverse micelles. The polar cavity of reverse micelles is an advanced chemical nanoreactor, providing reagents exchange and interaction; source clusters formation and growth. Besides, nonpolar part of micelles is a factor, limiting nanoparticles growth. As a result micellar syntheses is the most intellectual, since it allows getting nanoparticles with the given size. Except creation of varied materials, the perspective direction of nanotechnology is the use of nanoparticles for metals concentrating. This will allow to use solutions with low contents of the precious metals for new material obtaining.

Essential of the proposed approach is concluded as following. On the first stage metal ions are extracted into micellar phase from dilute water solution with high contents of the background electrolytes (salts and acids). Triton N-42 and AOT were used as micelles forming surfactants. The gold (III) distribution coefficients have values ~10^3 for Triton N-42 and ~10 for AOT.

On the second stage gold ions are reduced to gold nanoparticles by hydrazine. Stable systems with nanoparticles are gotten under high concentration of the hydrazine and low solubilization capacities (<1 vol.%). The electrophoretic mobilities for gold nanoparticles are determined with the modified border motion method. Calculated electrokinetic potential reaches 13 mV for gold nanoparticles in Triton N-42 micelles and 43 mV in AOT micelles. High values of electrophoretic mobility of gold nanoparticles in AOT reverse micelles allow to realize additional electrophoretic concentrating in organic phase. Its essential is concluded in separation of micelles with nanoparticles from "empty" ones. The high limiting gold content in concentrated solution (~1mol/l), factors of concentrating as function of micelles parameters are calculated and model for electrophoretic concentrating is proposed. Experimental enrichment factor with value about 1.5×10^3 was obtained, greater values are limited by the electrolysis.

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SPECTROSCOPIC STUDY OF INTERACTION OF PORPHYRIN DYES WITH REPRESENTATIVE LAYERED SILICATES

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Organic/inorganic hybrid compounds have been widely investigated due to their unique properties, resulting from the combinations of characteristics of both the organic and inorganic components. Embedding organic molecules in inorganic hosts often provides novel properties due to specific interactions with inorganic surface, chemical and thermal stability of the guest molecules, self-assembling structural properties, control of the molecular orientations and highly functional surface activities (Ogawa and Kuroda, 1995). One type of such materials, based on layered inorganics and organic dyes could provide unique photofunctional and optical properties. (Yui and Takagi, 2003). Generally, dye molecules tend to aggregate on the clay surface or in the interlayer spaces. The layer charge of layered silicates controls the molecular aggregation of the dyes of various structural types (Bujdák and Iyi, 2002).

The objective of this study is to investigate the interaction of three representative cationic porphyrin dyes with layered silicates (layered-silicate/porphyrin systems, LSP). As layered silicate matrices the series of reduced-charge montmorillonites Nanocore was used. These were prepared from one parent material by Li-saturation and thermal treatment. The effect of the layer charge is investigated in detail. In case of those with higher layer charge, molecular aggregation is expected to be suppressed due to high electrostatic repulsion forces between the dye cations. This paper studies in detail, if the molecular aggregation is sufficiently suppressed regardless the properties of silicate template. The study is based on the investigations of spectral characteristics of layered silicate-porphyrine systems (LSP) using UV-VIS and fluorescence spectroscopy.

We found out that adsorption of studied porphyrin dyes leads to the significant changes of their optical properties. The changes in absorption spectra in a visible spectral region partially reflect the layer charge characteristics of layered silicate templates. The position of a main Soret band is generally shifted to lower energies, even more significant changes are observed in the spectral range of Q-bands. Judging from these data, spectral analysis indicates the formation of J-aggregates of the dye on the silicate surfaces, characterised with side-by-side intermolecular association.

Formation of non-luminescent “pure” H-aggregates was not confirmed in any reaction systems. This fact confirms the systems based on porphyrin/layered silicates composites as perspective materials for photochemical applications.

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MICROSCOPIC DESCRIPTION OF ION ASSOCIATION CONSTANS OF 1-1 ELECTROLYTES IN PROPYLENE CARBONATE AND GAMMA-BUTYROLACTONE

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In the present work an investigation of ionic association for 1-1 electrolytes solutions in propylene carbonate (PC) and gamma-butyrolactone (γ-BL) at 5 – 125 °C is presented. Association constants were obtained from our own and literature conductance experiments.

The values of ion association constants were used for calculation of Gurney parameters A_{+-} in the framework of Ramanathan-Friedman model of inter ion potential by using the method proposed early [1].

Analysis of Gurney parameters for 1-1 electrolytes shows that in PC A_{+-} values are negative and decrease with increasing anion's radius for given cation. One can conclude that overlapping of ion's solvation shells and formation of contact ionic pairs is energetically favorable for the majority of single charged ions in PC and γ-BL solutions.

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RESEARCH OF PHYSICAL AND CHEMICAL PROPERTIES OF GEL-FORMING FIRE EXTINGUISHING AND FIRE-RESISTANT COMPOSITIONS

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Today for increasing the efficiency of fire extinguishment it is offered to use fire extinguishing and fire-resistant gel-forming systems [1-3]. These systems represent two separately stored and simultaneously submitted compositions. The first composition is a solution of gel-forming agent. The second composition is - a solution of the catalyst forming of gel. While simultaneously submitting two solutions they mix up on the burning or protected surfaces. Between components of solutions there is an interaction resulting in formation of a proof gel. On the surface a gel forms non-fluid fire-resistant layer easily kept on vertical and inclined surfaces.

Advantage of gel-forming fire extinguishing and fire-resistant compositions comparing with water is in substantial reduction of losses in fire extinguishing substances due to absence of water flowing down inclined and vertical surfaces. It allows not only to reduce the charge of fire extinguishing substances, but also to reduce fire losses usually resulting in flood of floors. Another advantage of gel-forming fire extinguishing composition is their high fireproof action. They protect the treated surfaces from ignition, for the period of time of 10-20 minutes.

The major component of fire extinguishing actions is its cooling action. Because of complexity of multi-componential gel-forming systems theoretical calculation of cooling action is difficult to conduct. Therefore cooling action of such systems has been determined experimentally. As a gel-forming systems has been chosen the substance with the best results at fire tests - $CaCl_2 + Na_2O{\cdot}2{,}7SiO_2$. It has been investigated by the method of differential calorimetric scanning (DCS) at various concentrations of system components.

DCS-thermograms have shown presence of great endothermic effects in the field of temperatures 25-250°C. The maximum of endothermic effects was observed at temperatures 100-150°C. In this temperature field there was a removal of the basic part of water from a solution. Apparently at the high temperatures the water connected in crystalline hydrate and water adsorbed by silica gel was removed.

With increase in concentration of components of gel-forming systems some reduction of total endothermic effect was observed. The cooling action of gel-forming fire extinguishing systems has some deficiencies comparing with water, but in view of reduction of losses for fire extinguishing means due to reduction of flowing down they considerably surpass water in total cooling action.

With the definition of cooling action it was determined the loss of weight for samples of gels in conditions of open flame exposure. Thermograms researches have been conducted together with the chemical analysis of products produced by heating of the gel. It is established, that by the basic product produced is water. Besides water in case of presence of excessive quantity in system calcium chloride when heating gels HCl is produced.

IMPURITY-VACANCY PAIR STABILITY IN $Ge_{1-x}C_x$

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Ab initio simulation techniques have been used to study the binding energies of a range of substitutional phosphorous-vacancy (P-V), arsenic-vacancy (As-V) and aluminium-vacancy (Al-V) pairs in germanium carbide (GeC) and for comparison, in germanium. The calculations used a plane-wave basis set and pseudo-potentials within the generalized gradient approximation (GGA) of density functional theory (DFT). Plane-wave pseudopotential DFT has been used extensively to predict defect behaviour in Si, SiGe and Ge to aid experimental investigations.

GeC is being considered as a promising alternative material for photovoltaic and other electro-optic applications. This is because the addition of carbon in germanium results to the increase of the band gap and reduces the lattice parameters thus allowing the ordered growth on silicon substrates. The incorporation of dopants such as aluminium in GeC decreases the crystallinity but enhances the photon absorption and therefore is important for the optoelectronic properties of the material. In previous theoretical and experimental studies in germanium it has been demonstrated that dopants such as phosphorus and arsenic associate with vacancies forming pairs.

In the present work the impurity-vacancy pairs in GeC have been studied in detail. The calculations for GeC indicate important differences in the binding energies of the impurity-vacancy and related complexes in GeC compared to Ge.

THERMODYNAMIC CHARACTERISTICS OF ASYMMETRICAL ELECTROLYTES IN NON-AQUEOUS MEDIA

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The thermodynamic characteristic analysis of ionic association processes of aprotonic Lewis acids makes it possible to evaluate their relative force and, as sequence, their catalytic activity. The most reliable criteria of acid force are the constant of ionic association or free Gibbs' energy as well as enthalpy and entropy of the process. The majority of Lewis' acids are asymmetrical electrolytes, so receiving correct data encounters difficulties dealing with finding the constants of stage association..

The present work deals with conductometric investigation of $CuCl_2$, $[Cu(en)_2]Cl_2$, $FeCl_3$, $SnCl_4$ and $ZrCl_4$ solutions in binary mixed solvent dimethylsulfoxide-chlorobenzene (DMSO-CB) in a wide range of electrolyte concentrations (10^{-6}–10^{-2} mol/dm^3). Investigations were carried out at the temperature interval 298,15 –323,15 K. Ionic association constants (K_{ai}) for investigated asymmetrical electrolytes were calculated only for two stages of association according to schemes:

for 2-1 electrolyte ($CuCl_2$, $[Cu(en)_2]Cl_2$)

$$MCl_2 \underset{K_{a2}}{\rightleftarrows} MCl^+ + Cl^- \underset{K_{a1}}{\rightleftarrows} M^{2+} + 2Cl^-$$

for 3-1 electrolyte ($FeCl_3$)

$$MCl_3 \underset{K_{a2}}{\rightleftarrows} MCl_2^{+}+Cl^{-} \underset{K_{a1}}{\rightleftarrows} MCl^{2+}+2Cl^{-}$$

for 4-1 electrolyte ($SnCl_4$, $ZrCl_4$)

$$MCl_4 \underset{K_{a2}}{\rightleftarrows} MCl_3^{+}+Cl^{-} \underset{K_{a1}}{\rightleftarrows} MCl_2^{2+}+2Cl^{-}$$

The solvent influence on ionic association constants is convenient to examine by analyzing dependences of corresponding $\ln K_{ai}$ on inverse permittivity. In conventionally-universal solvent DMSO-CB where the nature of solvation remains practically unchanged at all range of compositions of binary solvent linear dependences $\ln K_{ai}=f(1/\varepsilon)$ for all investigated electrolytes have been obtained. This confirms our preceding assumption that in this binary solvent the solvation is realized only by one solvatoactive component – dimethylsulfoxide.

Integral thermodynamic characteristics (ΔG_{ai}, ΔH_{ai}, ΔS_{ai}) only superficially describe the process of ionic association. It's because the stage association constants depend not only on temperature but also on solvent permittivity which in its turn depends on temperature, e.g. $K_{ai} = f(T, \varepsilon(T))$. The permittivity changing with temperature variation is not the same for different solvents most of all for mixed.

So for correct analysis and thermodynamic characteristics comparison it is necessary to exclude the influence of solvent permittivity changing with temperature variation on ionic association constants. That's why the division of integral thermodynamic characteristics in two components was carried out. Temperature one was caused only by temperature variation but not by the temperature influence on the values of solvent permittivity. The thermodynamic characteristics determination exhibited an error no more than 3 %.

For all investigated electrolytes enthalpy ($\Delta H_{ai,T}$) and entropy ($\Delta S_{ai,T}$) temperature components dependences on inverse permittivity are linear at both stages of association. This fact proves the invariation of the solvation nature at all range of compositions of conventionally-universal solvent DMSO-CB. Experimental data give the approximate equations for $\Delta H_{ai,T}$ (kJ/mol) and $\Delta S_{ai,T}$ (J/(mol$\cdot$ K) dependences on inverse permittivity:

for $CuCl_2$ solutions

$\Delta H_{a1,T} = 38{,}6 - 3044{,}0/\varepsilon$; $\Delta S_{a1,T} = 162{,}5 - 7287{,}0/\varepsilon$;

$\Delta H_{a2,T} = 26{,}7 - 1117{,}0/\varepsilon$; $\Delta S_{a2,T} = 111{,}1 - 2197{,}0/\varepsilon$;

for $[Cu(en)_2]Cl_2$ solutions

$\Delta H_{a1,T} = 25{,}1 - 2163{,}0/\varepsilon$; $\Delta S_{a1,T} = 145{,}1 - 5347{,}0/\varepsilon$;

$\Delta H_{a2,T} = 31{,}9 - 1622{,}0/\varepsilon$; $\Delta S_{a2,T} = 128{,}6 - 3867{,}0/\varepsilon$;

for $FeCl_3$ solutions

$\Delta H_{a1,T} = 25{,}1 - 1104{,}0/\varepsilon$; $\Delta S_{a1,T} = 116{,}0 - 1876{,}0/\varepsilon$;

$\Delta H_{a2,T} = 38{,}1 - 678{,}0/\varepsilon$; $\Delta S_{a2,T} = 127{,}0 - 702{,}0/\varepsilon$;

for $ZrCl_4$ solutions

$\Delta H_{a1,T} = 52{,}5 - 1114{,}0/\varepsilon$; $\Delta S_{a1,T} = 215{,}0 - 2555{,}0/\varepsilon$;

$\Delta H_{a2,T} = 40{,}6 - 427{,}0/\varepsilon$; $\Delta S_{a2,T} = 151{,}0 - 434{,}0/\varepsilon$;

for $SnCl_4$ solutions

$\Delta H_{a1,T} \approx 0$; $\Delta S_{a1,T} = 47{,}8 - 2539{,}0/\varepsilon$;

$\Delta H_{a2,T} \approx 0$; $\Delta S_{a2,T} = 66{,}7 - 1378{,}0/\varepsilon$.

According to the model of ideal ionic association (the process that has neither changes of ionic radii of associating ions nor the absence of covalent interactions) this process should be exothermic in the dielectric medium. Endothermicity of the process established at the first stage of association for zirconium chloride and at the second stage for zirconium and ferrum chlorides probably is stipulated by the ion desolvation during the ion associate formation. Ion desolvation also takes place in the cases when $\Delta H_{ai,T} < 0$ but exothermicity of ion-ion interactions compensates the endothermicity of the process of lossing the solvatoactive component molecules of binary solvent.

NEW APPROACHES IN PLANAR DIELECTROCHROMATOGRAPHY USING THE VERTICAL CHAMBER

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In the conventional thin-layer chromatography (TLC) the migration of solvent through the layer is controlled by capillary forces, thus its velocity at which the front moves is dependent on the distance of the front from the solvent entry position. We showed that in porous media the velocity and the migration distance of the solvent front could be increased by the application of an external alternating electric field. Combining this type of electric forced flow and the classical diffusion we demonstrated that the separation of compounds by TLC might be improved. As it was shown in our previous papers [1-4], we proposed a new approach of planar electrochromatography (PEC), namely planar dielectrochromatography (PDEC). In this technique, the armatures are not applied at the ends of TLC plates like in PEC, the electric field is applied on the both sides of TLC plates.

In this paper we use vertical PDEC technique (V-PDEC) in order to improve the eluent distribution on the TLC plate and to increase the selectivity of the separated compounds.

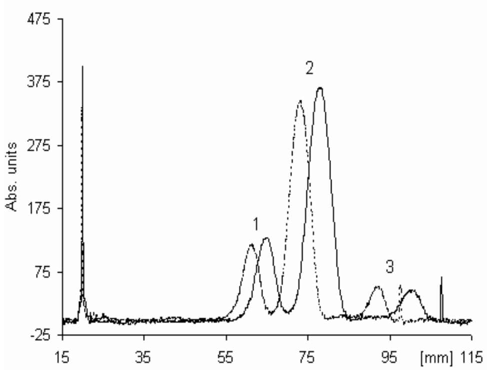
Our experiments showed the following effects in comparison with the conventional TLC: *(i)* the electric field influences the chromato-graphic process; *(ii)* the distribution and the movement of solvent vapours lengthways of the TLC plate is influenced by the arrangement of armatures, namely: in equi-current (tops of the electrodes in the direction of solvent diffusion) and counter-current (tops of the electrodes reversed) (see figures from text).

The achieved PDEC experiments using the vertical chamber present some specific elements *versus* those performed by horizontal PDEC technique (O-PDEC) [4]: *(i)* the elimination of the wicks that transport the solvent to the TLC plate offers a better reproducibility of the chromatographic process; *(ii)* the modification of the angle between armatures can lead us to obtain better results.

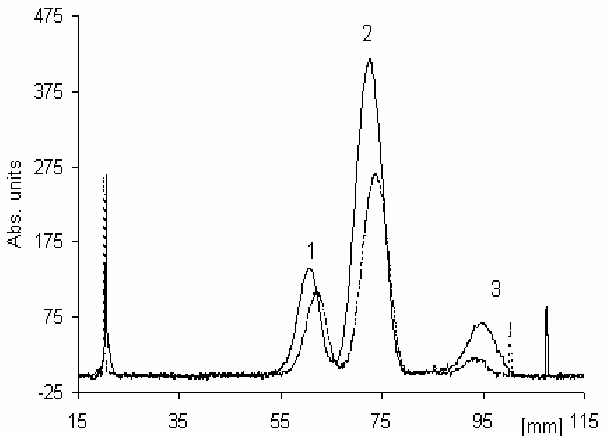
The separation quality was evaluated by the relative Rx value:

$$Rx = \frac{\textit{Migration distance of solute in electric field}}{\textit{Migration distance of solute without electric field}}$$

V-PDEC chromatograms (λ = 506 nm) obtained from lipophilic test dye mixture on alumina plates: with electric field (3 kV, 50 Hz) (—) and without electric field (- - -). Dyes: indophenol blue (1), Sudan red G (2), 4-dimethylaminoazobenzene (3). Eluent: benzene.



Equi-current
Rx values:
1.125 (1);
1.093 (2);
1.084 (3);
1.128 (solvent front).



Counter-current
Rx values:
0.953 (1);
0.981 (2);
1.000 (3);
1.113 (solvent front).

In conclusion, the V-PDEC technique offers the possibility of optimization of separation conditions by adjusting the flow rate of the solvent. The best results were obtained using the equi-current arrangement of armatures.

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INTERMOLECULAR INTERACTIONS IN SOLUTIONS STUDIED BY INFRARED SPECTROSCOPY

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The parameters of a vibrational band (frequency, half bandwidth, intensity) are sensitive to the environment created by solvents. Studies on the solvent dependence of these parameters can provide useful information on the intermolecular interactions between the solute and the solvent molecules.

The interaction of 2-bromopropane and *trans* and *gauche* conformational isomers of 1-bromopropane (abbreviated bromopropanes) with solvents evidenced by the change of stretching C–Br band parameters is non-specific and is dominated by the dielectric properties of the solvents [1, 2]. The Onsager reaction field [3] is a suitable model to describe the interaction of bromopropanes with solvents.

The mentioned compounds have interesting properties under electric field action. To obtain more information on bromopropanes behaviour in media with special dielectric properties we studied the effect of two binary solvent mixtures [cyclohexane/tetrahydrofurane (CH/THF) and carbon tetrachloride/acetonitrile (CCl_4/ACN)] measuring the changes of the ν(C–Br) infrared band parameters.

In the case of a homogeneous mixture of a nonpolar (N) and a polar (P) solvent, the effective Onsager function $f(\varepsilon) = (\varepsilon-1) / (2\varepsilon+1)$ should be a simple linear combination of the Onsager functions of both considered solvents according to the molar fractions x_N and x_P of the two solvent components:

$$f(\varepsilon)_{mixture} = x_N\, f(\varepsilon_N) + x_P\, f(\varepsilon_P) \qquad (1)$$

From the dielectric measurements it is known that CH/THF mixture follows the relation (1) and could be considered as the ideal one. When the probe solute disturbs the solvent structure, the frequency shift of the absorption band varies linearly *vs.* x_P, the polar solvent molar fraction. A behaviour was noticed for bromopropanes under the effect of CH/THF mixture.

The deviation from the linear dependence of ν(C–Br) frequency *vs.* molar fraction x_P of acetonitrile observed under the effect of CCl_4/ACN mixture is due to the different interactions of the solute with the two solvent components. The magnitude of deviation is a measure of the strength of the "preferential solvation", that is of the increase of the molar fraction of the polar solvent around the solute. The *Z* index of "preferential solvation" [4] expresses the relation between the $X = x_N/x_P$ and $Y = y_N/y_P$ molar ratios:

$$Y = X\, e^{-Z} \qquad (2)$$

where by x are noted the molar fractions in the undisturbed bulk of the mixture and by *y* the molar fractions close to the solute.

The index *Z* of "preferential solvation" of bromopropanes in CCl_4/ACN mixture and the molar fractions y_P of acetonitrile in the solvation shell calculated assuming a linear dependence of ν(C–Br) frequency on the molar fraction y_P of acetonitrile are given in the following table (c is the concentration of bromopropanes).

x_P	y_P					
	2-bromopropane		*gauche* 1-bromopropane		*trans* 1-bromopropane	
	c=0.11M	c=1M	c=0.22M	c=2.2M	c=0.22M	c=2.2M
0.058	0.149	0.120	0.125	0.097	0.106	0.090
0.084	0.208	0.169	0.176	0.138	0.150	0.129
0.155	0.344	0.289	0.300	0.243	0.260	0.228
0.269	0.512	0.450	0.461	0.392	0.414	0.372
0.479	0.724	0.671	0.691	0.617	0.639	0.597
0.648	0.840	0.804	0.811	0.763	0.780	0.748
0.786	0.913	0.891	0.895	0.866	0.876	0.856
0.846	0.940	0.924	0.927	0.906	0.913	0.898
1.000	1.000	1.000	1.000	1.000	1.000	1.000
Z	*1.05*	*0.80*	*0.84*	*0.55*	*0.65*	*0.48*

It can be noticed that *Z* value increases in the order *trans* 1-bromo-propane < *gauche* 1-bromopropane < 2-bromopropane. The decrease of solute concentration in CCl_4/ACN mixture determines also an increase of *Z.* For all studied molecular systems, the y_P–x_P difference has a maximum value for CCl_4:ACN volume ratio of 2:1. At this value, that corresponds to x_P ~ 0.4, the dependence of half bandwidth *vs.* the molar fraction x_P of acetonitrile has a maximum. Because the "preferential solvation" process determines a change of the local concentration of the solute, the theory of concentration fluctuations developed for binary mixtures [5] was extended to explain the effect of solvent mixtures on the parameters of ν(C–Br) infrared band.

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ELECTRICAL CONDUCTIVITY AND INTERION ASSOCIATION WITH THE FORMATION OF THE ION PAIRS AND TRIPLE ION OF $LiClO_4$ AND $NaClO_4$ IN THE TETRAHYDROFURAN AT $5\div45\ ^{O}C$

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The results of a conductometric investigation on $LiClO_4$ and $NaClO_4$ solutions in tetrahydrofuran in the temperature range 5-45 ºC are presented. The ion association constants and limiting molar conductivities of single and triple ions are determined by using Lee-Wheaton conductance equation. The conductivity of single and triple ions and constants of ion association up to the ion pairs (K_a) increases with temperature increasing, while the constants of ion association up to the triple ions (K_t) changes a little.

Using the data of K_a values the non-Coulombic short-range interionic potentials have been calculated. The positive values of short-range potentials indicates the presence of repulsion when ions solvation shells intersects. With temperature increasing the values of non-Coulombic potentials decrease, that is short-range repulsion weakens.

The values of distance parameter (a_3) of triple ions have been determined. They exceed 1.5 (r_++r_-) what accertaines the formation of solvent-shared ionic aggregates.

The attraction friction coefficients of single and triple ions as the quantitative characteristics of ions solvation dynamics were calculated in terms of Wolynes theory by using the values of limiting molar conductivities. It was determined that influence of positively charged single and triple ions on dynamics of tetrahydrofuran molecules is more pronounced as compare with negatively charged single and triple ions. It was established considerable temperature change of attraction coefficients of lithium and sodium cations.

STUDY OF SPECTROSCOPIC AND PHOTOPHYSICAL PROPERTIES OF STILBENS BY XeCl* LASER EXCITATION

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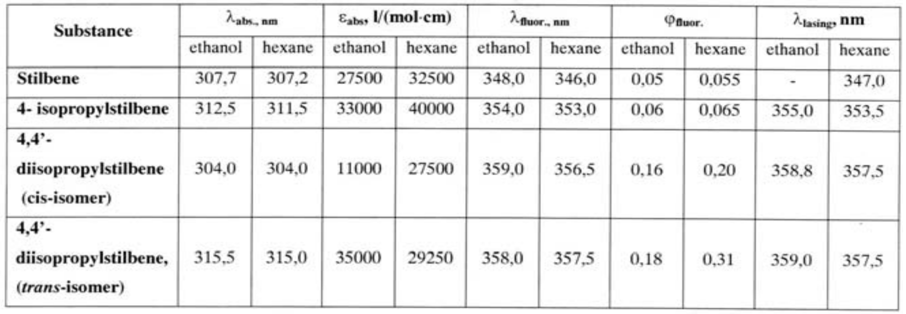
In the field of spectroscopy stilbene is certanly one of most extensively investigated organic compounds. At present time the photophysical and spectroscopic properties of stilbene attract a much attention due to the fact that super fast isomerization occurs in these systems by excitation. It is known that isomerization reaction has two ways: *singlet* and *triplet* mechanism. As far as *trans*→cis reaction is concerned, it proceeds during femtosecond interval time scale in liquid phase depending on solvent. In this case it is necessary to get over a small potential barrier about 3-4 kcal/mol for stilbene to occur isomerization reaction. But *cis*→*trans* reaction proceeds barrierless practically during ~ 0.3 - 2 ps time scale. The quantum yield of fluorescence for *trans* - stilbene at room temperature is 0.03 - 0.05 and the lifetime of it ~ 100 ps time scale. The main reason of very low quantum yield is photoisomerization reaction of molecule, which occurs at excitation more probably.

That's way, lasing of *trans* - stilbene was obtained only recently in our research institute. As a source of excitation was used XeCl* laser with the wavelength of lasing 308 nm, in conditions of experiment the lowest exited vibration levels of the S^*_1 state was populated. Also the experimental research of fast and super fast competing processes of generation and photoisomerization in stilbene's substituted (4-isopropylstilbene, 4,4'-diisopropylstilbene) have been done by excitation XeCl* laser. Spectral characteristics obtaining by excitation XeCl* laser are presented in table 1.

The theoretical study of spectroscopic and photophysical properties of stilbene and its substituted forms has been carried out by semiempirical quantum-chemistry method INDO/S. The structure molecules has been studied; the energy levels diagrams, rate constants of photophysical processes have obtained by this method. The influence of structural changes of geometry of molecule stilbene on the spectroscopic properties has been considered.

Table 1



Substance	$\lambda_{abs.}$, nm		ε_{abs}, l/(mol·cm)		$\lambda_{fluor.}$, nm		$\varphi_{fluor.}$		λ_{lasing}, nm	
	ethanol	hexane	ethanol	hexane	ethanol	hexane	ethanol	hexane	ethanol	hexane
Stilbene	307,7	307,2	27500	32500	348,0	346,0	0,05	0,055	-	347,0
4- isopropylstilbene	312,5	311,5	33000	40000	354,0	353,0	0,06	0,065	355,0	353,5
4,4'-diisopropylstilbene (cis-isomer)	304,0	304,0	11000	27500	359,0	356,5	0,16	0,20	358,8	357,5
4,4'-diisopropylstilbene, (*trans*-isomer)	315,5	315,0	35000	29250	358,0	357,5	0,18	0,31	359,0	357,5

MICELLE-FORMATING TRIHALIDE ION ORGANOCOMPLEXES AS A BASIS FOR SYSTEMS EFFICIENT IN DECOMPOSITION OF ORGANOPHOSPHORUS COMPOUNDS

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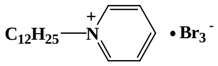
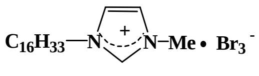
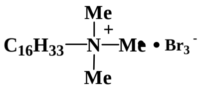
Development of effective decontaminants for decomposition and utilization of ecotoxicants (pesticides, etc.) requires search and design of wide-spectrum reagents. Novel oxidative-nucleophilic systems I and II that generate in water BrO^-, HOBr or BrO^-/HOBr (depending on pH) are proposed.



I

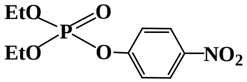


II

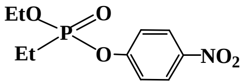


III

An undoubted advantage of compounds I and II is their ability to form micelles that allow to solubilize almost completely water-insoluble substrates. By the example of reaction of cationic surfactant III with NPDEP and NPDEPN it has been shown unambiguously that micelles of III accelerate both the nucleophilic substitution and subsequent oxidation of 4-nitrophenoxide released.



NPDEP



NPDEPN

The role of microenvironment and concentrating effects in "micellar catalysis" of cleavage of organophosphorus compounds has been estimated using pseudophase partitioning approach. The main factors responsible for increasing of observed rate constants in the presence of surfactant tribromide salts are the effects of concentrating of reactants. In weak alkaline media the half-life of NPDEPN in the presence of III at $[BrO^-] = 0.02$ M does not exceed 6 s, an increase in the observed rate constant is ~ *40* times as compared with water.

THE REGULARITIES OF THE INTERPHASE DISTRIBUTION IN THE CLOUD-POINT EXTRACTION SYSTEMS: THE INFLUENCE OF THE SUBSTRATES' NATURE, STRUCTURE, HYDROPHOBICITY AND CHARGE

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Micellar extraction based on the phase separation at cloud point temperature in the non-ionic surfactants solutions is considered lately as a convenient and environmentally safe alternative to extraction with organic solvents. The effectiveness of the cloud point extraction is due to its high selectivity and the possibility to obtain high coefficients of absolute preconcentrating while analyzing small volumes of the sample. However, despite the availability of extensive evidence in this area, the problem of substrates hydrophobicity, charge and structure influence on the distribution between nonionic surfactant-rich and water phases remains open.

The distinction in a kind of substrate interphase transfer in the traditional extraction systems and the cloud point extraction was shown in the work present. The specificity of the micellar extraction is determined by the appearance of the host-guest phenomenon at molecular level and the high level of structural organization of the micellar phase itself. Such specificity of the surfactant-rich phases is evinced by their ability to extract high charged ions of organic reagents. Here the tendency of the distribution coefficient decrease with the ion charge increasing was established and observed in the investigation of the cloud point extraction of the different type reagents. Another appearance of the specificity of interphase transfer in the micellar-extraction systems is the independent and cooperative influence of the substrate molecular structure and hydrophobicy on its distribution between the water and the surfactant-rich phases. On the basis of data obtained the possibility of substrates distribution and their D-values prediction using regressions which consider the log P and $^1\chi$ values in the cloud point extraction systems was shown. The recommendations for the selection of optimal complex formation ligands for the effective metal extraction and for the optimization of micellar-extraction system has been developed.

On the basis of investigations it was proposed the procedures for atomic-absorption and spectrophotometric determination of metal ions in the tap and natural waters with cloud point extraction preconcentrating.

ANALYSIS OF LOW MOLECULAR WEIGHT CRYOPROTECTANTS INTERACTION WITH MICROSOMAL MEMBRANE SURFACE USING THE SQUARAINE FLUORESCENT PROBE

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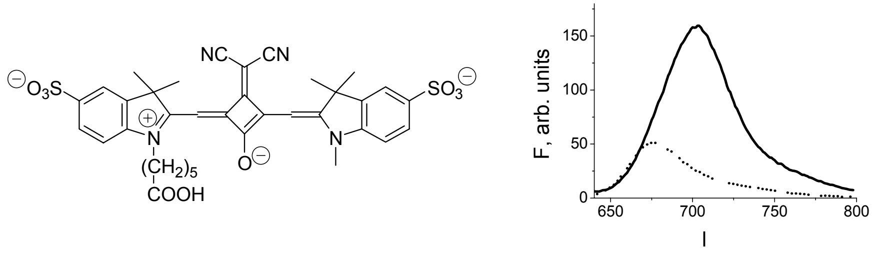
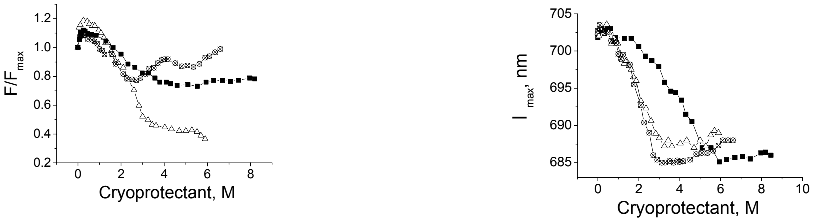
The long-term storage of the human and animal cells at low temperatures now finds wide applications in biology, transplantation medicine, biotechnology and other spheres of human activity. Thus, successful choice and optimal requirements to artificial cryopreserved materials introduced into cell suspensions (cryoprotectants, CP's) in many respects define the outcome of cryoconservation process. The important problem thus is maintenance of structural and functional wholeness of one of the most cryolabile cell structures, which are cell membranes. However, the molecular mechanism of CP protective action is not established well. One of the approaches to study this mechanism is based on observation of fluorescent probe interaction with cell membranes in presence of CP. This work investigates mechanism of interaction of CP's such as ethylene glycol, 1,2-propanediol and dimethyl sulfoxide (DMSO) with surfaces of natural membranes by using fluorescent dicyanomethylene-squaraine probe (Fig. 1, a). This probe was recently found to be very sensitive to a change of structure and hydratation of lipid bilayer polar region [1]. Chicken liver microsomes were utilized as the model of natural membranes.



a) b)

Fig. 1. Dicyanomethylene-squaraine probe (a) and its fluorescence spectra (b) in buffer (1) and chicken liver microsomes (2)



a) b)

Fig. 2. Relative fluorescence intensity (a) and spectra maxima (b) of the dicyanomethylene-squaraine probe in chicken liver microsomes *vs.* concentration of cryoprotectants PD, EG and DMSO ($\lambda_{excit.}$ 650 nm)

Association of dicyanomethylene-squaraine probe with microsomal membranes results in more than 3-fold increase of fluorescence intensity, while emission maximum (λ_{max}) was shifted from 675 nm in buffer to about 702 nm in chicken liver microsomes (Fig. 1, b). It was established that the CP interaction with biomembranes is found to depend on the CP nature. The fluorescence maximum and intensity of the probe bound to microsomal membranes change non-linearly *vs.* CPs concentrations (Fig. 2). The observed changes of fluorescence spectra of the stained microsomes are conditioned by processes of CP sorption at the membrane surface followed by competitive replacement of the dye molecules with CP. DMSO causes more pronounced decrease of fluorescence intensity compared to EG and PD, which is an evidence of its stronger interaction with membrane binding sites. High performance of DMSO interaction with microsomal membranes is supposed to be connected with diphilic nature of its molecule. DMSO molecule can form H-bound with microsome surface area but also has a nonspecific hydrophobic attraction to the non-polar frontier area of lipid bilayer. At the same time, the smaller displacement efficiency of the dye molecules with PD and EG evidences that these CPs interact predominantly with microsomes surfaces. Apparently, specific H-binding predominates in this interaction. We found a good correlation between the displacement rate (substitution of dye molecules with CP in surface area of natural lipid-protein membranes) and the cryopreservation efficiency of cryoprotectants applied to low-temperature storage of cells. The data obtained demonstrate also that the dicyanometylene-squaraine dye allows obtaining useful information on molecular mechanism of biomembranes and cells cryoprotection.

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INVESTIGATION OF INORGANIC ION-EXCHANGE NANOMATERIALS WITH SMALL-ANGLE X-RAY SCATTERING AND IMPEDANCE SPECTROSCOPY

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Usage of granulated inorganic ion-exchange phosphate-containing nanomaterials of amorphous modification in electromembrane processes like electrodeionization [1] is complicated by particle fragmentation under the influence of electrochemically stimulated acidic-basic reactions. These reactions occur not only on the surface of ion-exchange particles, but directly on the ion-exchanger particles. Chemical instability of amorphous inorganic nanomaterials is probably caused by a multi-level structure, which is formed during synthesis [2]. The investigation of ion-exchanger morphology and the search of methods, which influences the structure in the synthesis stage, is the actual task.

Structure of phosphate-containing nanomaterials was investigated with a SAXS technique. In order to simulate the curves obtained, the unified exponential function method was used. Such structure parameters as type of fractal aggregates, fractal dimension, aggregate size and a number of particles of the lowest level in fractal aggregates of higher level were determined. Based on results obtained, the synthesis conditions, which provide formation of mass fractals, were determined. It was shown, that the materials with this morphology are characterized by higher chemical stability comparing with multi-level ones.

Real part of electrical conductivity ($\sigma^{/}$) of multi-level ion-exchangers was found to be characterized with dispersion in the diapason of 10^{-2}-10^{6} Hz. This complicates the identification of *dc* conductivity (σ_{dc}) and conductivity of grain contacts. Nevertheless the diapasons of preferable influence of bulk, grain contacts and polarization were determined by means of analysis of frequency dependencies of real and imaginary parts of impedance, complex dielectric permittivity and complex electric module. The σ_{dc} values were found using simulation of frequency dependencies of $\sigma^{/}$ according to Joncher equation.

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IONIC MOBILITY IN NON-AQUEOUS AND MIXED SOLVENTS

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The models of solvated ion, which taking into account structure of the ion first solvation shell are proposed. Models are based on hydrodynamical approach. They are taking into account changes of local viscosity near to an ion, the effective sizes of solvated ions and boundary conditions on a surface of moving sphere.

Within the framework of some models it is possible to obtain rather simple equations which allow to calculate limiting ionic electric conductances. The calculated values were compared with experimental data for the most investigated ions in 18 solvents. It is shown, that the proposed approach allows to describe well limiting mobilities of alkaline metals ions. A number of regularities of influence of solvation shell structure on ionic mobility were revealed. Within the framework of the suggested models it is possible to explain:

a) an increasing of ionic mobility with growth of radius for monoatomic ions;

b) infringement of sequence of change of mobility in a number of ions (for example, for alkaline metals ions in dimethylacetamide);

c) phenomenon of "negative" solvation;

d) temperature dependence of ionic mobility .

Within the framework of the proposed models it is shown, that cubed effective Stokes radii of ions are additive for solutions in mixed solvents. Comparison of calculated and experimental values for binary solvents shows the good agreement for mixtures of aprotic solvents.

With minor assumptions the proposed approach can be generalized for calculation of other transport and thermodynamic properties of ions in solutions. Comparison of the calculated values with experimental data for ionic Jones-Dole B coefficients, Gibbs free energies of ion solvation and partial molar volumes of ions shows their satisfactory convergence. An effective values of some parameters for calculation can be obtained from experimental data on limiting ionic mobility, that improves the results of calculations

THE PHASE BEHAVIOUR OF THE POLYOXYETHYLATED NON-IONIC SURFACTANTS IN THE PRESENCE OF PHENOL

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The cloud point of nonionic surfactant solutions is sensitive to additives, which may raise or lower it. The relation between cloud point temperature and additive concentration is nonlinear and highly variable in form in different system. The most effective hydrotrope additive is phenol. The data of micellar phases nature formed at a presence of additives of phenol and others hydroxy-derivatives, are limited. Therefore the purpose of the work was studying of the influence of the nature of non-ionic surfactants, concentration conditions and solutions acidity on the clouding and phase separation at the presence of phenol.

Phases formed in solutions of non-ionic surfactants of various types (polyoxyethylated alkylphenol, alcohols and sorbitol ethers) were investigated. It was established that adding of 0,1-1,0 % of phenol into 0,5% solution of non-ionic surfactant OP-10 decreases the cloud point temperature (CP) up to 3ºC. Thus, concentration dependences of the cloud point temperature have two fragments: close to linear falling branch and the bottom plateau. The point of crossing of these curves CP=f($C_{Ph\text{-}OH}/C_{surf}$) with an abscissa axis corresponds to the bottom plateau beginning. This parameter characterizes some critical point of the system - $(C_{Ph\text{-}OH}/C_{surf})_{cr}$, - in which the change of its' nature is observed. Thus, received by extrapolation on zero surfactant concentration $(C_{Ph\text{-}OH}/C_{surf})_{cr}$ value correlates with the oxyethylation degree (m) of surfactant molecule. On the basis of data received the dependence of $(C_{Ph\text{-}OH}/C_{surf})_{cr}$ via oxyethylation degree for various surfactants has been gotten. The dependence $(C_{Ph\text{-}OH}/C_{surf})_{cr}=f(m)$ is close to linear (r=0,98) and is described by the equation $(C_{Ph\text{-}OH}/C_{surf})_{cr}=-3,2 + 1,4\cdot m$. The nearness of the slope of the dependence discussed to one unit shows that the interaction of phenol with one oxyethylene fragment of surfactants occurs with 1:1 stoichiometric ratio. It was shown, that the change of the pH-value in the interval 0,5 - 9 do not influence the cloud point of the OP-10 solutions. At that, the increase of the pH above 9 units leads to the increase of the CP temperature which become close to CP for pure surfactant solutions. This phenomenon can be explained by the destruction of polyoxyethylene chains of surfactant molecules. It is established, that molecular form of phenol is responsible for hydrotropic action. At that it is possible to explain the cloud point decrease by the formation of hydrogen bonds between oxygen atoms of polyoxyethylene chain of surfactant and hydroxy-group of phenol molecule.

STRUCTURAL FEATURES OF SUPERCRITICAL AQUEOUS NaCl SOLUTION

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Active interest to the investigation of supercritical water-salt systems is caused by their significant role in many natural processes and engineerings. Nevertheless, till now there is not clearness in many structural aspects of ion hydration and ionic association under extreme conditions, and also in the molecular mechanism of the structural changes induced by external influences.

The structure formation features of aqueous NaCl solution (21 wt. %) at sub- and supercritical conditions (T = 450−750 K, p = 25 MPa) studied by the extended RISM integral equation theory are considered in this report. Sodium chloride is a usual co-product of processing of chlorine waste treatment by means of Supercritical Water Oxidation Technology (SCWO). This technology used for destruction of different toxic substances successfully is one of the most perspectives because of the economic efficiency and ecological safety. The investigated supercritical region corresponds to technological conditions of carrying out of SCWO process (T = 700−1000 K, p = 25 MPa [1]).

On the base of obtained results it has been established that in the subcritical region (T = 450−625 K) thermal ion dehydration and increasing of ionic association are taking place in aqueous NaCl solution. Transition of investigated system into supercritical state is accompanied by significant reorganizations in local structural fragments, having hydrogen bonds, and as well as a nearest environment of ions. It has been determined that the transformation of solution structure is observed from state with hydrated ions and ion pairs (subcritical region) to structure with not H-bonded molecules and low-dimension clasters (supercritical region).

This work was supported by the Russian Foundation for Basic Research (grant No. 06-03-96317-r_centre_a).

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AN INVESTIGATION OF ASSOCIATIVE ABILITY OF THE SUB- AND SUPERCRITICAL CARBON DIOXIDE MOLECULES UNDER ISOTHERMAL COMPRESSION AND ISOBARIC HEATING

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Special interest to the investigation of sub- and supercritical carbon dioxide is caused by the originality of its physical and chemical properties. Use of $scCO_2$ as alternative solvent in many industrial branches is the most perspective from the ecological point of view.

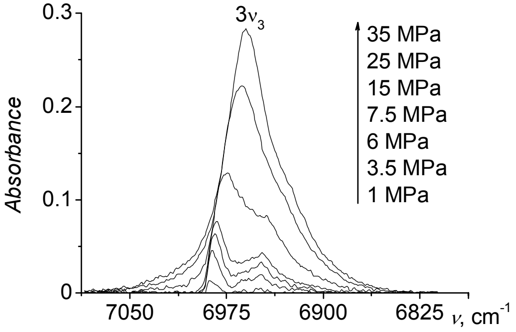

Fig. 1.

The results of investigation of neat CO_2 under compression (p = 1−35 MPa, T = 383 K) and heating (T = 313−653 K, p = 25 MPa) on the base of the NIR-spectroscopy data and MD-simulation results are presented in the report. The aim of present study is the investigation of associative ability of the sub- and supercritical carbon dioxide molecules under extreme conditions and the establishment of the types of its cluster structures under conditions of high- and low-density fluid.

The details of spectroscopic data treatment.

Under conditions of isothermal compression the changes of the spectral band in the frequency range 7100-6800 cm^{-1} (overtone $3\nu_3$) were analyzed (Fig.1). In the frequency range 5175-4800 cm^{-1} the analysis of the changes of combination modes $4\nu_2+\nu_3$, $\nu_1+2\nu_2+\nu_3$, and $2\nu_1+\nu_3$ under highest pressures investigated is impossible because in this area the strong absorption caused by the big optical length of the sample takes place.

Under isobaric heating the changes of the combination modes $4\nu_2+\nu_3$, $\nu_1+2\nu_2+\nu_3$, and $2\nu_1+\nu_3$ were analyzed (Fig. 2). An analysis of overtone $3\nu_3$ behavior is not effective because of its low intensity at the temperature above 473K.

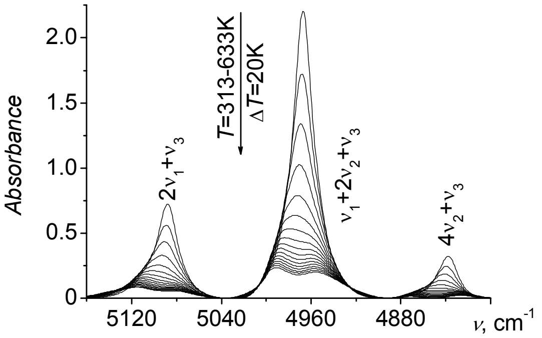

Fig. 2.

The details of MD-simulation.

The simulation have been performed in *NPT*-ensemble with periodic boundary conditions and time step 0.01ps. The cubic box contained 512 particles. The three site polarizable model of CO_2 based on classical Drude oscillators was used.

On the base of obtained experimental results and simulation data it has been established that:

Under isothermal compression (T=383 K) in the pressure range 1-7.5 MPa there are not significant modifications in the CO_2 structure. With further increasing of pressure from 7.5 MPa up to 35 MPa at the transition into the state of high-density $scCO_2$ (p_c=7.38 MPa) the probability of formation of the cluster structures (dimer CO_2) increases noticeably.

With the temperature increase up to 633 K accompanied by drastic decreasing (almost in five times) of the fluid density, the significant decrease of fraction of dimer, which were the main structural unit of high-density carbon dioxide at T=313 K and p=25 MPa takes place. At highest temperatures investigated (T > 550 K) the CO_2 molecules do not practically form intermolecular bonds and exist preferably under monomeric form.

The analysis, comparison and summarizing of the data obtained by two methods allow making a few important conclusions about self-organization of structure of sub- and supercritical carbon dioxide:

In subcritical region (p < 7.38 МПа) carbon dioxide has relatively stable structure with predominant fraction of monomers.

At transition into the state of high-density fluid (p > 25 MPa) in the structure of $scCO_2$ the cluster structures in the dimeric form start to prevail.

At transition of the supercritical carbon dioxide from high-density into low-density state (T > 550 K) the destruction of the dimeric cluster structures takes place. As the result, low-density $scCO_2$ become similar to the dense gas the structure of which is defined mainly by monomeric molecules.

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SELF-ORGANIZATION OF NaCl-H_2O SYSTEM AT HIGH PRESSURES

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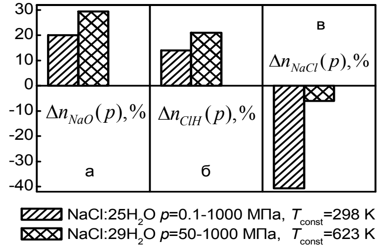
Studying of physical and chemical properties of water-salt systems under pressure influence has fundamental value in a wide spectrum of applications as from understanding of behaviour of water solutions in Earth mantle before determination of pressure effect up to the rates and mechanisms of many chemical and geological processes. Despite of the different conducted a long time experimental researches at high pressures, while no clearness in a question about what effect of compression renders on structure of aqueous electrolyte solutions especially on ion hydration.

High pressure effect (0.1-1000 MPa) on structure of (aq) NaCl solutions (1.91-3.08*m*) is considered at two fixed temperatures 298 K and 623 K in this work. Structural characteristics have been computed by the site-site Ornstein-Zernike integral equation.

According to the received data, the largest structural changes are shown in a range of 200-1000 MPa. At T_1=298 K structure formation of solutions is determined by failure of tetrahedral network of the water molecules, resulting to increase in ion hydration. In this case disordering effect of pressure dominates of its limiting factor. At T_2=623 K tetrahedral structure of water is destroyed, and at high pressures the partially dehydrated ions restore its hydration spheres which they had in ambient conditions. The pressure increasing up to 1000 MPa leads to decreasing of ion ability to association in ~2-3*m* NaCl solutions. Domination of the packing factor at high pressures is the reason of the detected feature.



Relative pressure change of particle coordination numbers in *aq*. NaCl solutions at different constant temperatures.

This work was supported by the Russian Foundation for Basic Research (grant No. 06-03-96317-r_centre_a).

IONIZATION CONSTANTS OF ORGANIC ACIDS OF DIFFERENT NATURE IN ACETONE CONTAINING 5 mol. % of DMSO

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Acetone is widely used in analytical, physical, and organic chemistry, as well as in technology as a useful medium for many reactions, including acid-base ones. However, the state of protolytic equilibria in this solvent are strongly influenced by traces of moisture, because of extremely low basicity of acetone. Even if very small amounts of water are present in acetone, the lyonium ion in various buffer mixtures can exist as H_3O^+, $H_5O_2^+$, etc. This phenomenon hinders quantitative studies of properties of a lot of organic acids in acetone. This also makes somewhat doubtful the data on $\mathrm{p}K_\mathrm{a}$ values reported in a set of early studies.

Therefore we decided to introduce a kind of mixed acetone-based solvent, namely, acetone + dimethyl sulfoxide (DMSO), with molar fraction of the latter equal to 0.05. Taking into account the high basicity of DMSO, even in the presence of moisture the state of the proton-exchange equilibrium

$$H_3O^+ + (CH_3)_2SO \Leftrightarrow H_2O + [(CH_3)_2SOH]^+$$

will be strongly shifted toward the right. Therefore, lyonium ion in such a system must be the protonated DMSO molecule.

Such DMSO-containing acetone is expected to possess, like pure acetone, strong differentiating influence on acidic strength of solutes of various nature and can serve as a medium for reproducible determination of $\mathrm{p}K_\mathrm{a}$ values. The difference between the $\mathrm{p}K_\mathrm{a}$ values of the given organic acid in two dipolar non-hydrogen bond donor (or ‘aprotic’) solvents is, as first approximation, governed by the difference between the corresponding $\log {}^{w}\gamma^{s}(\mathrm{H}^{+})$ values. Hence, the ionization constants in DMSO-containing acetone must differ strongly from those in acetone, taking into account the dramatic difference of the transfer activity coefficients of proton in these two solvents: $\log {}^{w}\gamma^{s}(\mathrm{H}^{+}) = -3.4$ (S = DMSO) and $> + 7$ (S = acetone).

The density, viscosity, and relative permittivity of this solvent are 800.7 kg m^{-3}, 3.28×10^{-4} Pa s, and 22.19, respectively (at 298.15 K).

In this work, we studied the ionization of some organic acids and acid-base indicators in acetone containing 5 mol. % of DMSO. The acidity of solutions was created using $HClO_4$, HCl, and five buffer systems: picrate, 2,4-dinitrophenolate, salicylate, benzoate, and 5,5-diethylbarbiturate. Following indicators were examined: ortho-, meta-, and para-nitroanilines, methyl yellow, methyl red, quinaldine red, thymol blue (‘cation to neutral’ transition), neutral red, bromophenol blue, bromocresol green, and bromothymol blue (‘neutral to anion’ transition), ethyl eosin, 2,4- and 2,6-dinitrophenols, rhodamine B, bromophenol blue and bromocresol green (‘anion to dianion’ transition). Both UV-Vis spectroscopy and potentiometry were used for determination of acidity constants. The incompleteness of dissociation of buffer salts (sodium salicylate, tetraethylammonium picrate, tetramethylammonium 2,4-dinitrophenolate, etc.) was taken into account, and the corresponding dissociation constants were estimated using conductivity measurements.

ELECTRO-OPTICAL AND ELECTROCHEMICAL PROPERTIES OF AN IONIC CONJUGATED POLYMER: POLY(2-ETHYNYLPYRIDINIUM-N-BENZOYLSULFONATE)

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For more than 40 years, electric conduction in organic solids has been one of the most fascinating topics for synthetic chemists and solid-state physics. Various polyacetylene-based conjugated polymers have been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems.[1] Conjugated polyelectrolytes are charged conjugated macromolecules containing a large number of ionizable or ionic groups. The conjugated polyelectrolytes such as poly(propiolic salt)s, triethylammonium salt of poly(6-bromo-1-hexyne), and poly(ethynylpyridine)s were reported.[1-3] We have also reported on the preparation of various ionic conjugated polymers having different functionalities.[4,5] Due to their extensive conjugation and ionic nature, these ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, light-emitting devices.[2] We prepared a novel self-dopable ionic conjugated polymer, poly(2-ethynylpyridinium-N-benzoylsulfonate) (PEPBS), by the activated polymerization of 2-ethynylpyridine with the ring-opening of 2-sulfobenzoic acid cyclic anhydride without any additional initiator or catalyst.

The spectral analyses on polymer structure revealed that the PEPBS has a ionic conjugated polymer system bearing the N-benzoylpyridinium sulfonate moieties. The inherent viscosity of PEPBS was 0.21 dL/g at 25 ^{o}C in DMF. The electrical conductivity (σ) of undoped PEPBS was 5.7×10^{-9} S/cm. The photoluminescence

(PL) spectra of polymer showed that the photoluminescence peak is located at 545 nm corresponding to the photon energy of 2.28 eV. The cyclic voltamograms of the polymer exhibited the reversible electrochemical behaviors between the doped and undoped peaks. It was found that the kinetics of the redox process of the present polymer is controlled by the diffusion process mixed with the electron transfer process from the experiment of the oxidation current density of polymer versus the scan rate.

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STRUCTURE OF Al-Cu MELTS IN REGION OF 0-40 at. % Cu

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Structure of Al-Cu liquid alloys with 0, 14, 25, 30, 40 and 100 at. % Cu has been studied by X-ray diffraction using MoK_{α}-radiation monochromatized with Zr-Y differential filters in a diffracted beam at temperatures near liquidus. The analysis of experimental structure factor's curves (SF) showed presence of prepeak in the area of 1-2 $Å^{-1}$ for all investigated alloys. It is necessary to note, that intensity of prepeak in alloys Al-Cu is less than in other binary melts of aluminium with 3d - transition metals (Al-Co, Al-Ni). The most pronounced changes in the SF and pair distribution function of atoms are observed on going from pure aluminum to a melt with *14* Cu at %, indicating a noticeable influence of small copper additions on the structure of melted aluminum.

Obtained SF experimental curves were used for reconstruction of three-dimensional models of studied melts by means of Reverse Monte-Carlo method. The initial basic cell contained 5000 atoms different type in the stoichiometric ratio. Local atomic structures were analyzed using partial structure factor's curves, partial radial distribution functions of atoms and the nearest neighbor distances calculated from the models obtained. The statistical-geometrical Voronoi-Delaunay method has been applied for the detailed analysis of atomic ordering at Al-Cu melts.

It have been established, that the prepeak on the experimental SF curves is caused by a correlation in arrangement of copper atoms in polytetrahedral clusters at a distances of about 4.7 Å. It is showed that the contents of copper atoms in clusters of this type are much higher (twice as high) than stoichiometric ratio of atoms in alloys. As appears from the above the chemical ordering in liquid Al-Cu alloys in areas with the higher dense of packing of particles is exist. Angles' distribution curves in the atom-atom-atom bonds calculated from the models points to more strong ordering copper's atoms among themselves and with respect to aluminum atoms than ordering of aluminum's atoms among themselves. The significant decreasing of interatomic distances correlates with concentration dependence of thermodynamic properties of melts, that points on deviations from ideality.

THE SYNTHESIS AND PROPERTIES OF NANOMATERIALS BASED ON TITANIUM PHOSPHATE

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Synthesis of one-dimensional (1D) nanostructured materials has received increasing attention over the past decade. This is related to some unusual and often unique chemical and physical properties associated with this class of materials. Various preparative methods have been developed and successfully utilized for the preparation of nanostructured compounds. Among them are vapor-liquid-solid and solution-liquid-solid processes, surfactant capping and hydro(solvo)thermal methods, template-directed synthesis, self assembly of smaller nanocrystallites as well as utilization of crystal intrinsic structural anisotropy. However, the ability to shape the morphology of inorganic nanocrystals in a predicted and controlled manner still remains a challenge and important goal of modern materials chemistry.

Titanium phosphates (TiP), as compounds possessing properties valuable for a broad range of applications (ion exchange, intercalation, catalysis, ionic conductivity etc.), have been studied extensively during the last century. Synthesis of over two dozens of titanium phosphates with different compositions and structures have been reported, but none of them was made as nanostructured compound so far.

The controlled synthesis of titanium phosphates nanoparticles with different morphologies, such as rod-like, whisker-like, tubular, and platelet, was successfully achieved by authors using microemulsion-mediated solvothermal and microwave-assisted methods. Possible routes and mechanisms for the formation of different TiP compounds, including nano-materials, in microemulsion systems were proposed and discussed. It was found that the reaction temperature, concentration of reagents and molar ratio of the reactants have significant effect on the structure, shape and size of the nanocrystals formed. X-ray powder diffraction, transmission electron microscopy, selected area electron diffraction, infrared spectroscopy, thermogravimetric analysis and nitrogen adsorption/desorption isotherm measurements were used to characterize the obtained products. Interlayer structure of some compounds at molecular level and their layering behavior was probed by molecular dynamics simulation.

THERMODYNAMICS OF CETYLTRIMETHYLAMMONIUM AND N-CETYLPYRIDINIUM PERCHLORATES SOLUBILITY IN WATER – ORGANIC MIXTURES

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In order to elucidate the solvation character of surface-active cations we studied the thermodynamics of dissolution of cetyltrimethylammonium and *N*-cetylpyridinium perchlorates (CTAP and CPP, respectively) in water-organic mixed solvents. Utilization of perchlorates allows preventing the micelle formation in solutions.

The solubility of CTAP and CPP was determined in mixtures of water with methanol, 2-propanol, acetone, and acetic acid within the whole range of compositions, at 278.15–308.15 K, by the procedure of isothermical saturation. The gravimetrical, potentiometrical, and spectrophotometrical methods were used for determination of concentrations.

The ion association in the systems studied was examined using conductivity. The $\log K_{\mathrm{ASS}}$ values were calculated by Lee – Wheaton equation. It must be pointed out, that the analysis of conductivity data confirms the “simple“ association mechanism, without micelle formation.

The solubility products of electrolytes and standard thermodynamic functions of transfer of (cation + $\mathrm{ClO_4^-}$) pairs from water to mixed solvents, ΔG_{tr}^0, ΔH_{tr}^0, and $T\Delta S_{\mathrm{tr}}^0$, were calculated taking into account incomplete dissociation of salts in some of non-aqueous solutions. The non-linear increase in solubilities of both CTAP and CPP along with temperature rise was registered. The solubility of salts in water on adding organic solvents (up to pure solvents) increases in accord with the following sequence:

2-propanol < methanol < acetic acid < acetone

Interestingly, the solubility in H_2O-CH_3OH system increases gradually, while in all the other systems solubility maximum was revealed. Such effects are known to be typical for heterosolvation of electrolytes in mixed solvent systems.

Introducing of organic co-solvents results in expressed strengthening of solvation of the amphiphilic cations, $n-\mathrm{C_{16}H_{33}N(CH_3)_3^+}$ and $n-\mathrm{C_{16}H_{33}NC_5H_5{}^+}$, while the weakening of $\mathrm{ClO_4^-}$ solvation is smaller. This assumption is in accord with negative values of Gibbs energies of transfer ($\sum \Delta G_{\mathrm{tr}}^0$ < 0) within the whole range of mixed solvents composition. The $T\Delta S_{\mathrm{tr}}^0$ contribution is always more significant than that of ΔH_{tr}^0.

Hence, the solubility alterations along with temperature variations are caused mainly by structural effects.

The solubility of CPP in solvents studied is somewhat higher as compared with that of CTAP. And really, in the last-named salt, the positive charge in the cation is evidently more shielded from solvation.

The comparison of the solubilities and $\sum \Delta G^0_{\mathrm{tr}}$ values of CTAP and CPP with those of the perchlorates of short-tailed tetraalkylammonium cations, (*n*-butyl, ethyl, and methyl) demonstrates, that the $\sum \Delta G^0_{\mathrm{tr}}$ values drop more strongly for the smaller cations at first additions of organic co-solvents ($0 < x_2 < 0.2$). At $x_2 > 0.2$, the solvation of the symmetrical tetraalkylammonium perchlorates becomes poorer, manifesting itself in rise in $\sum \Delta G^0_{\mathrm{tr}}$ even to positive values, whereas in the case of CTAP and CPP $\sum \Delta G^0_{\mathrm{tr}}$ is always negative. The reason for such difference are solvophilic effects, which become more significant along with the size increase of the organic cation.

CLOUDING AND THE PHASE SEPARATION IN NON-IONIC SURFACTANT TRITON X-100 MICELLAR SOLUTIONS

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As the temperature of an aqueous nonionic surfactant solution is increased or some additives are added, the solution turns cloudy and phase separation occurs. The solution may separate into a surfactant – rich phase and a dilute phase. A solute that originally exists will unevenly partition into those two phases. This technique is known as cloud point extraction. Recently great attention has been attracted for its great potential in preconcentrating and separation of metal ions and biological material, removal of toxic solutes from polluted water, etc. Cloud point extraction as a preconcentrating method offers many advantages, such as low cost, safety, and a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentrating factors.

For concentrating and separation of biological materials it is convenient to use systems with a low clouding temperature. The most effective depressant of cloud point temperature of water solutions of nonionic surfactants is phenol. However the phase separation in solutions of nonionic surfactants at presence of phenol practically is not investigated. So the influence of main factors: concentration conditions, acidity of solutions on the cloud point, volume and lyophilic properties of the formed micellar phase of nonionic surfactant Triton X-100 in the presence of phenol has been investigated in the work. It is established that the adding of small amounts of phenol decreases the cloud point of 0,5% solutions Triton X-100 by 10°C. At phenol concentration increase up to 0,8 % the cloud point decreases to 18°C.

In this study the hydration values (Hv) of non-ionic surfactants are estimated for Triton X-100 surfactant-rich phases. At that the measured and calculated Hv values actually denotes the ratio of the total number of water molecules (bonded and free) to the one oxygen atom of polyoxyethylene chain of surfactant in the surfactant-rich phase. The distribution of phenol and Triton X-100 between the water and surfactant-rich phases was investigated. On the basis of data obtained the mole fractions of water, phenol and Triton X-100 in the non-ionic surfactant- rich phases formed at different concentration conditions were calculated. Recommendations for the creation of effective phenol-induced cloud point extraction systems for preconcentrating of organic substrates of different nature were suggested.

TEMPERATURE AND ELECTRIC FIELD INFLUENCE ON THE NATURAL PHENOLS OXIDATION PROCESS IN AN AQUEOUS MEDIUM

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The development of effective methods of natural phenol antioxidants (AO) obtaining will allow to decide the problem of antioxidative stabilization of fats, oils, fat-containing products, pharmaceuticals etc. Effective and accessible way of obtaining of natural Phenol is their extraction from vegetative raw material.

The extraction in an electric field is one of the methods of extraction process intensification used on practice both for increase of total of the substances, extracted from plants, and for the obtaining separated groups of biological - active substances. The authors designed extraction method of obtaining of phenol antioxidants from medicinal vegetative raw material by a maceration in a constant electric field (at voltage U=35 V and current direct I=250 mA) by a principle of an electrodialysis. The caring of the extracted substances in to the ionization form is going under the operation of an electric current through a semipermeable membrane, i.e. the wall of a vegetative cell. Extraction was realized during 2 hours at T=293K, constantly intermixing. As extraction agent was used 1-% aqueous solution of acetic acid with addition the Twin - 80 ($C=8{,}8\cdot10^{-4}$ mol / l) as a surfactant substance. The extract increases the stability of sunflower oil to an oxidizing more than in 4 times.

During electroextraction the extracted phenol compounds can be oxidized by air molecular Oxygen in an aqueous medium under the operation of temperature, electric field etc., that can reduce in lowering of a native part of extracted Phenols in a finished stock. The influence of the main physical factors of extraction to the oxidation rate of natural Phenol solutions by molecular Oxygen at their obtaining from vegetative raw material is not investigated practically. Such researches will allow to identify the differences in stability of the different groups of natural Phenols to an oxidizing, to spot the optimal conditions for their extraction extract, and also to receive the data for the simulation of the process of extraction from the plants of the most effective phenol antioxidants.

The main purpose of this investigation is the research of oxidation rate of different groups of natural Phenols by the molecular Oxygen in an aqueous medium, and learning the influence temperature and electric field on this process.

In this investigation the most spread natural Phenol – representatives were used: hydroxybenzols, flavonols, phenolcarbons acids and hydroxy-cinnamic acids. An oxidizing of Phenol in water (pH=6,5) was conducted in two modes: at the temperature 373 K without effect of an electric field in a glass reactor and at the temperature 293 K under the constant electric field in a specially manufactured liquid junction cell with graphite electrodes. A loss of Phenol in the system as a result of an oxidizing was

determined on its speed reaction with a radical diphenilpikrilgidrazil (DPPG) in a solution ethanol at room temperature (T=293 K) by a photocolorimetric method at λ_{max}=520 nm. The less was the reaction rate of Phenol with DPPG, the was low the concentration of the reduced form of Phenol in a researched aqueous solution and, so, its oxidized part was higher. As the speed of researched response depends not only on concentration of Phenol, but also from its chemical nature, it is necessary to use by the ratio of speeds of interaction not oxidized (V_{aq}) and oxidized ($V_{aq,T(I)}$) of aqueous solutions of Phenol with a radical DPPG - $\frac{V_{aq}}{V_{aq,T(I)}}$. The more the parameter $\frac{V_{aq}}{V_{aq,T(I)}}$, the activity of Phenol in oxidizing reaction is above. The results on an oxidizing of aqueous solutions of investigated natural Phenol in a constant electric field at room temperature have shown, that at low current modes (at voltage U=35 V and current direct I=250 mA) the parameter of an oxidizing of Phenol is small, comparing with the higher current modes. With highing U and I it is observed the increase of a rate of oxidation of Phenols, that corresponds the decreasing of reaction rate of a solution of Phenol with a radical DPPG ($V_{aq,I}$). It is stimulated by derivation in aqueous mediums of the fissile forms of Oxygen ($^1O_2$), including radical ($O_2^{\bullet-}$, $HO^\bullet$, $HOO^\bullet$) of more strong oxidizing agents of Phenol:

It was determined, that the electric field with the small current mode (U=35 V, I = 250 mA) in a smaller measure will activate the process of an oxidizing of Phenol in water, in comparison with the operation of heightened temperatures (368 - 373 K). The link of chemical constitution of molecules of natural Phenol (PI) with their ability to an oxidizing $\left(\frac{V_{aq}}{V_{aq,T(I)}}\right)$ was placed as the correlation equations. Irrespective of the accelerating processes factors of an oxidizing the representatives hydroxy-cinnamic and phenolcarbons acids of acids which molecules having low potentials of ionization (a Gallic and a Coffee acids, Anther ethylic of Gallic acid) are most subject to these processes.

MOLECULAR SIMULATION OF METHANE PHYSISORPTION ON SINGLE WALLED CARBON NANOTUBE

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Methane adsorbed on porous materials is a promising alternative to compressed natural gas as a clean vehicular fuel and for bulk transportation [1]. Because of being mostly "surface", carbon nanotubes has become the most promising candidate for this purpose [2,3]. Although, there are many comprehensive experimental and theoretical reports on the hydrogen adsorption and storage on CNTs, it seems that this area has not been fully considered for the other gaseous fuels like methane. Molecular dynamic simulations, among the common computational methods used to model the adsorption phenomenon, is often preferred due to its more realistic and less time consuming procedure. In this study, using this method, we present the results of the physisorption of methane on open ended single walled carbon nanotubes. Since it has been investigated that the chirality of the nanotubes has no significance effect on the adsorption [4], an armchair (3,3) nanotube has been chosen to be examined in this paper. The applied intermolecular potential is modified Lennard-Jones, which is based on the curvature of the nanotube. Using this curvature dependent fore field, we have carried out our equilibrium MD simulations in the constant NVT canonical ensemble applying the Berendsen thermostat, at different tempretures, 77, 300 and 600 K at higher than ambient pressure, i.e. 7.5 Kbar.

Time averaged short range energies calculation over 130 ps., shows that the system at 600 K is significantly more thermodynamically favorable, and as deduced from the relevant radial distribution functions, remarkably shows the highest amount of adsorption (Table 1).

The magnitude and range of nanotube distortions during our MD simulations are also represented quantitatively using analysis of the angle between three selected longitudinally oriented carbon atoms of the SWNTs. The effect of temperature on SWNT deformations is clearly observed. The maximal longitudinal distortion is occurred at 600 K and in the presence of methane. It worth nothing to add that due to the small diameter of the here considered nanotube, and the large repulsive lateral interactions between the methane molecules, there is no insertion of methanes into the nanotube, and therefore no endohedral adsorption is observed.

Table 1. The energies and the amount of adsorption of Methane on SWNTs.

Tempreture (K)	77	300	600
Energy (Kcal mol^{-1})	-9.87	-10.84	-20.83
Amount Adsorbed (mmol gr^{-1})	6.253	11.118	11.811

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IONIC LIQUID BASED ON POLYHEDRAL SILSESQUIOXANE

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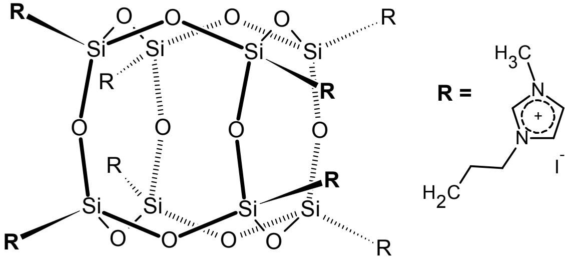
Imidazolium ionic liquids (ILs) bearing iodide anion have been extensively considered as non-volatile substitutes for liquid electrolytes employed in dye-sensitised photoelectrochemical (DSPEC) cells. But the use of ILs has not overcome the leakage problems in DSPEC cells. In order to avoid this, the ILs has been solidified to a quasi solid-state consistency by using various gellators [1], nanoparticles [2] and by the incorporation of ILs in various polymers. Recently, we synthesized a new imidazolium iodide type ionic liquid [3,4,5] namely MTMSPI$^+$I$^-$ (1-methyl-3-[3-(trimethoxy-λ^4-silyl)propyl]imidazolium iodide), which due to the trimethoxysilane group, exhibits condensation reactions after the addition of acidified water and the completely cross-linked system has been attained after long ageing times (few days) or accelerated by heat-treatment at 180°C.

Here we report about the one step synthesis leading to a fully condensed MTMSPI$^+$I$^-$. This was achieved by long time mixing (72 h at room temperature) the hydrolysed (25 % NH_3 solution) MTMSPI$^+$I$^-$. The results show that after the removal of volatile components under reduced pressure, the MTMSPI$^+$I$^-$ was in a form of the polyhedral silsesquioxane (PSS-MTMSPI$^+$I$^-$), having imidazolium cation attached to each corner of the silsesquioxane cube. PSS-MTMSPI$^+$I$^-$ condensation species were formed in-situ during the synthesis therefore representing a more efficient solidification agent with respect to other additives such as nanocrystalline TiO_2, SiO_2 or nanosized carbon, added to the ILs. The greatest advantage of the PSS-MTMSPI$^+$I$^-$ ionic liquid is – besides its small size and the quasi solid-state consistency – its optical transparency combined with moderate ionic conductivity.

The structure of the synthesized compound was determined with ^{29}Si NMR and infrared spectroscopy. Results confirmed the presence of condensation products characterized by the T^3 silicon environment. These results showed that under the synthesis conditions used, the ionic liquid could be in-situ solidified into a quasi-solid state. Results of the conductivity measurements of the PSS-MTMSPI$^+$I$^-$ will be presented and the possibility of using the PSS-MTMSPI$^+$I$^-$ in DSPEC cell will be discussed.



Structure of PSS-MTMSPI$^+$I$^-$

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APPLICATION OF FRACTAL THEORY TO SOL-GEL SYNTHESIS OF NANOCOMPOSITE POLYMER-SILICA MATERIALS

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For surface chemistry and material-proofing particles as same powders, surfaces of porous carries, such as hybride polymeric composite materials, using as sorbents are important examples. The use of fractal theory by sol-gel process gives the possibility to determine quantitative characteristics of grafted and adsorbed molecules, grafting density intermolecular space and other characteristics.

Properties of nanocomposite polymer silica materials are determine mainly by structure and nature of aggregated particles, forming as a result of sol-gel process development of disperse system. Aggregates generating in the process of primary particles coagulation, possess with self-similar or fractal structure. The bases of fractal theory of disperse particles aggregations allow to propose two types of aggregation process structural models. In the first type of models aggregates firming in the space are ansidered as disperse formations and in the second type they form space (percolation) structure.

Percolation model proposes formation of accidental bonds between the separate elements of system, terminating by appearance of extended spatial network. Process of sol-gel transition is considered as percolation transitions when between the discrete isolated particles (clusters) or particle aggregates bridges formation and endless aggregate (cluster) building takes place.

According to common presentations framework of silica-gel is formed by spherical particles touching in the places of their contacts. Pores are empty spaces between these particles. Primary sphere-like particles with size 1-10 nm are formed on the early stages of polycondensation before hydrogel formation. On this stage material interpenetration in hydrogel of additives determining silica functionalization takes place. The concepts on fractal structures we applied under obtaining composite nanohybride polymer-silica sorbents by sol-gel technology the sorbents were obtained with various functionality is the cost of polymeric additives use (polycaproamide, polyacrilonitril, chitosan, cellulose). Nanohybride polymer-silica materials synthesized were successfully used as sorbents for HELC and HETLC for separation of various compounds.

DESIGN OF POLYMER-SILICA OF NANOCOMPOSITION MATERIALS

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Nanostructures synthesis and treatment are corrected to various material types (organic, inorganic, and biological), which are used in different spheres of science, medicine and technologies. These processes have the special importance, because the possibility of materials practical use depends just of them. Molecular design allows deceasing the questions, connected with regulation of shape, size, structure and morphology as well to investigate the questions of molecules, supermolecular formations nanoobjects and nanostructural materials connection with various properties.

The structural investigation of hybrid sorbent samples on the base of polyetoxysiloxane (PES) and chitosan of various origins (crabs, silk warn chrysalis) have been carried out. X-ray investigations have shown that all hybrid sorbents on PES and chitosan base have amorphous diffract grams, though the initial chitosan has clearly expressed reflexes due to its crystalline structure. However, chitosan crystal lining does not manifested evidently at the expense of interaction between the hybrid sorbent components.

On the example of some nanohybrid sorbents with various functionality, obtained by sol-gel technology the possibility to obtain a new generation of sorption materials for HPLC and HPTLC has been shown. The data on investigation of nanohybrid sorbents properties (polycaproamide, polyacrylonitrile, chitosan and zirconil) are quested as well as the examples of the their practical use for chromatography.

As the experiments showed, this process differing by simplicing of equipment design, proceeds in soft conditions, well controlled and allows to get selective nanohybride sorbents with different functional groups at low temperatures to use these in high effective liquid and thin-layer chromatography.

MOLECULAR SELF-ASSEMBLY ON NaCl/Au(111) SUBSTRATE

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The fabrication of nanostructures or nano-objects for potential applications in sensors, molecular electronics, and solar cells is one of the essential challenges of nanotechnologies. Self-assembly of organic molecules by spontaneous ordered adsorption onto specific surfaces can lead to complex 1D or 2D architectures. Molecular self-assembly has been widely studied on metallic substrates. However, the adsorption of an organic molecule directly to a metal surface implies that the electrons in the molecule can interact with the electrons of the metal, which may have drawbacks for specific applications. Therefore, the adsorption, dynamics and self-assembly of organic molecules on non-metallic substrates such as oxides or thin dielectric films is highly desirable for “molecular electronics”. It was recently demonstrated by adsorbing organic molecules on a thin dielectric film of NaCl, grown on a metal substrate, that the molecular electronic structure can be decoupled from that of the metal, while still allowing Scanning Tunneling Microscopy (STM) imaging[1]. This work was initially focused on the growth of ultrathin dielectric film consisting of a few atom layers, by UHV thermal evaporation of NaCl onto metallic surfaces Au (111) cleaned by sputtering and annealing cycles. The sample temperature was kept between 300 and 350 K, in order that defect-free NaCl islands of up to three atomic layers can be formed. A particular challenge in this respect is that molecules are highly mobile on such dielectric surfaces due to a low molecule-substrate interaction. In the iNANO SPM group, a molecular self-assembly has recently been investigated by deposition and co-deposition of melamine (M) and cyanuric acid (CA) on a Au(111) surface[2]. Thus, once NaCl substrates were grown with confidence, we extended the ongoing studies of melamine/cyanuric acid to these thin films in order to investigate the effects of a reduced molecule-substrate interaction by comparing to the results for Au(111). An important goal of the present work has therefore been to synthesize molecular structures that are stable at higher temperatures by optimizing the molecule-molecule interactions (in practice T>120K).

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FLUORIMETRIC DETERMINATION OF SOME 4-FLUOROQUINOLONE AND TETRACYCLINE ANTIBACTERIALS BASED ON THE ENERGY-TRANSFER IN MICELLES OF SURFACTANTS

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Tetracyclines (TC) and 4-fluoroquinolone (FQ) are bacteriostatic and antibiotic drugs widely used in veterinary practice to control disease and promote growth of animals and fish. Their representatives, such as norfloxacin, ciprofloxacin, enrofloxacin, flumequine, and tetracycline, doxycycline, oxytetracycline exhibit activity against of nearly all gram-positive and gram-negative bacteria. Intensive use of this antibiotic in animal husbandry and poultry or fish farming for prophylactic control of bacteria infections and at subtherapeutic levels as feed additives to enhance growth of food producing animals and fish farming has led to a wide expansion of antibiotic resistance among bacterial species.

Among different methods have been applied to the determination of FQ and TC, fluorescent spectroscopy has considerable opportunity based on the use of highly sensitive and selective lanthanide-sensitized fluorescence which originates from an intramolecular energy transfer from the excited ligand through its triplet state to the chelated europium or terbium ions and allows as a result to provide an indirect determination of FQ and TC. Detailed investigation of the fluorescence enhancement of Eu^{3+} (Tb^{3+}) complexes with antibiotics mentioned by different organic bases (Phen and its derivatives, TOPO) as co-ligands and by micelles of different surfactants has been performed in this work.

It was found that in the presence of Phen as co-ligand the fluorescence intensity of Eu^{3+} and Tb^{3+} mixed ligand complexes with FQ (TC) and Phen increased on the average by a factor of 3. The fluorescence intensity increased additionally by 2 – 5 times as a result of solubilization of the complexes in micelles of surfactants. Finally, the joint action of the both factors (co-ligand and micelles) provided to enhancement of fluorescence of chelates by a factor of 6-10. The dynamic concentration range of TC and FQ determination was found to be $5\times10^{-8} – 5\times10^{-4}$ M. Simple, selective and sensitive procedures for sensitized-fluorimetric determination of the antibiotics were developed and applied to their determination in blood plasma and poultry.

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ELECTROCHEMICAL REDUCTION OF ALIFATIC ALCOHOLS CONTAINING WATER ADDITIVES

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Possible electric reduction of aliphatic alcohols - $R(OH)_n$ (methanol, ethylene glycol, glycerin)of various valence (n) firstly was presented in paper [1] regarding finding-out the reasons of very low outputs of electrical current of germanium (BT(Ge)≈3-4%) in alcohol solutions of germaniumisation. The assumption about possible current consumption for non-basic Faraday's process - electric reduction of molecules of solvent - is based on the phenomena of alcohol dissociation (as pH <7) [2, 3] and possible autoionization of molecules $R(OH)_n$ [4]. Possibility of reduction of autoionization of alcohol molecules on the cathode have not been considered before because at dissolution of strong electrolytes ($GeCl_4$, LiCl, KCl) compositions like $GeCl_{4-m}\bullet R(O_n(H_{n-m}))$ and molecules HCl are formed in aliphatic alcohols. It was traditionally supposed, that almost all electrical power is consumed for electric reduction of HCl (as $\Delta E(H_2/2H^+) << \Delta E(Ge^0/Ge^{+4})$). To state the fact of electric reduction of $R(OH)_n$ voltamperameter researches were conducted both in pure alcohol, and with additives of water (H_2O is protonating solvent to $R(OH)_n$, as $pK_{ai}(R(OH)_n) > pK_{ai}(H_2O)$). It is established, that the current limits (j_c) of diffusion cathodic reduction auto protating molecules of pure alcohols decreases with increase of n while concentration of H^+ ions is increasing with increase of n (as values of pK_{ai} in a number: methanol, ethylene glycol, glycerin decrease from 16,7 to 15,00). While introducing the additives H_2O opposite character of a course of dependences ″j_c-$\omega(H_2O)$″ and ″pK_{ai}-$\omega(H_2O)$″ is unchangeable due to appearance of additional effect of protonation of molecules $R(OH)_n$ by molecules H_2O or own autoprotoning of molecules H_2O (to H_3O^+).

The reasons of inverse relationship between j_c and $C(H^+)$ or $C(R(OH)_n \cdot H^+)$ are in significant distinction of dynamic viscosity (η) of alcohols [4] with the increase in their valence, and consequently, with rapid decrease in factors of diffusion (D) discharged particles. It is known [5], that $j_c = zFD^{2/3} \cdot V_0^{1/2} \cdot C_0/\eta^{1/6} \cdot l^{1/2}$ (1). Thus, with η solutions the value j_c should decrease, as it is observed in experiment.

Wile introducing $\eta \approx const$ for all three alcohols factors of diffusion D will differ a little and consequently j_c will be determined only by concentration of H^+-ions. Hypothetically dependences j_c for alcohols can be corrected considering viscosity correction for $\eta \approx 1$, for what in calculations it should be used the ratios of diffusion current limits: $j_{c2}(R(OH)_2)/j_{c1}(R(OH)_1)$ (2) and $j_{c3}(R(OH)_3)/j_{c1}R(OH)_1)$ (3). Using the ratios (2) and (3) for researched number of alcohols it is stated that character of corrected to $\eta \approx 11$ dependence j_c-$\omega(H_2O)$ is directly proportionally connected with concentration of H^+-ions and grows with increase of valence of alcohols and water additives.

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NOVEL SUPERNUCLEOPHILIC SYSTEMS INVOLVING FUNCTIONAL DETERGENT FOR DECOMPOSITION OF ORGANOPHOSPHORUS COMPOUNDS

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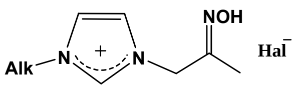
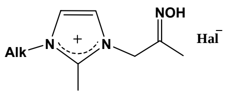
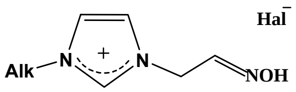
Search and design of the reagents for efficient decomposition of organophosphorus compounds, mainly, ecotoxic substrates (pesticides, chemical warfare agents, etc.) is an acute problem now. It is important to achieve both high reaction rates and solubilization of the organophosphorus compounds which are only scarcely soluble in water. Development of novel detergent with the imidazolium ring and specific moiety of α-nucleophile – oximate group (I - III) – is the most promising approach in this line.



I (Ia)

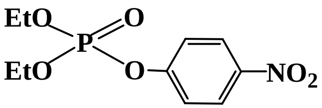


II (IIa)

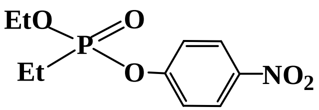


III (IIIa)

Alk = $C_{16}H_{33}$, Hal^- = Cl^- or Br^- (I-III); Alk = CH_3, Hal^- = Cl^- or Br^- (Ia-IIIa)



IV



V

It was first shown that the reactivity of α-nucleophilic moiety of the functional detergents (I - III) in decomposition of 4-nitrophenyl esters of diethylphosphoric (IV) and diethylphosphonic (V) acids can be related to that of their methyl analogues (Ia - IIIa). This enables one to design supernucleophilic microheterogeneous systems of tailored reactivity. Half-lives of the organophosphorus substrates for the most efficient detergent (III) do not exceed 14 s and 2 s for IV and V, respectively. In this case the micellar effects of the functional detergents I - III are considerably higher than those for conventional pyridine- and iodosobenzoate-based systems.

STRUCTURE ELUCIDATION FOR FRAME AMINOALCOHOLS USING MODERN HIGH-RESOLUTION NMR METHODS

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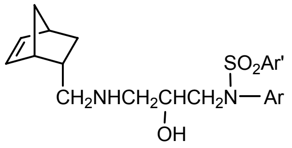
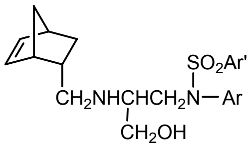
Taking into account discovered during last years high neurotropic activity of derivatives of amines with norbornene, norbornane and adamantane frames containing sulfonamide or aminoalcohol fragments we studied the reactions of stereochemically homogeneous *endo*-5-aminobicyclo[2.2.1]hept-2-ene with several glycidylsulfonamides. Studying of the structures of the chromatografically cleared products by the ^{1}H- and ^{13}C-NMR method, the DEPT spectrum, and also COSY, NOESY, HMBC and HMQC spectra. Taking of signals in proton spectra was made by homonuclear correlations, but it was impossible to choose between two structures containing secondary or primary alcohol fragment (CHOH and CH_2OH) – products of epoxide cycle opening in multispin systems in accordance or against the Krasusky rule only on their basis.



I



II

The reliable taking of signals of all methylene groups was done on the basis of the geteronuclear correlations HMQC and HMBC. Thus, the joint analysis of the spectra confirmed a structure (I) and completed preparation for neurotropic activity testing of perspective group of substances containing a bicyclyc frame fragment, aminoalcohol and sulfonamide groups in one structure.

NANOPARTICLES OF METALS IN SURFACE LAYER OF SILICA MATRICES

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Nanoparticles of noble metals have potential applications in catalysis, optics, optoelectronics, and biology. However, in a majority of cases obtained nanoparticles are unstable. Immobilization of such nanoparticles on the supports, such as polymer latex particles, alumina, zeolite, carbon cages, and silica, to form appropriate nanocomposites is of great interest.

One of possible approaches of controlled synthesis of silver and gold nanoparticles is use of porous matrices that confine growth of nanoparticles. For preparation of supported metal nanoparticles the chemically modified ordered mesoporous silica of MCM-41 type was applied in this work. Reducing reagents immobilized on the external surface of ordered mesoporous silicas were used for *in situ* reduction of nanoparticles of gold and silver at the interaction with chloroauric acid or silver nitrate solutions in the mild conditions. For this silica matrices were modified with triethoxysilane in the presence of acetic acid with the object of producing grafted silicon hydride groups on the silica surface. Absorption bands at 2240 cm^{-1} in the IR spectrum of the modified silica could provide evidence for the fact that attachment of silicon hydride groups occurred.

The x-ray powder diffractograms of the prepared samples confirm formation nanoparticles of gold or silver with a face-centered cubic arrangement. The electron microscopy data provided evidence for formation of nanoparticles of gold (diameter 20–30 nm) and silver (diameter 25–28 nm).

Another possible route of metal nanoparticles stabilization is reduction of metal ions in time of silica particles formation using sol-gel transformations. We have observed silver nanoparticles formation in the mixtures of silver nitrate and triethoxysilane solutions. The formation process and the optical properties of the silver nanoparticles can also be identified from both the color change and the UV-Vis spectra of the solutions. After stirring the color of obtained solution became yellow immediately. This observation is supported by the UV/vis-spectra of the coatings, which show a clear minimum in reflection around λ=420 nm due to the plasmon resonance of colloidal silver. The change of peak position and the shape of the absorption spectra were obvious during the whole reaction process. After keeping under quiescent conditions for 8 h the color of the solution was changed from yellow to light grey as the reaction progressed. The Ag-colloid formation was monitored by UV-VIS spectroscopy as a function of time. Changing of color was accompanied with appearance of another high-frequency peak at λ=600 nm, that can be explained by fractal aggregates formation.

SILICA MATRICES WITH ORDERED MESOPOROUS STRUCTURE, UNIFORM PARTICLES MORPHOLOGY AND DESIRED CHEMICAL SPECIFICITY

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Template synthesis of silicas with controlled porosity and adjusted morphology of particles has been intensively investigated because of their applications in separation processes, catalysis and sensoric technologies. Peculiarities of template synthesis of ordered porous silicas with spherical morphology of particles were investigated in the alkaline and acidic media. Mesoporous silica matrices with high specific surface area (450-1200 m^2/g), ordered pore structure and spherical particles granulation with size about 0.5 µm were synthesized in alcohol-ammonia media. Silica spheres with average diameter about 10 µm, slightly ordered porous structure and less value of specific surface area (600 m^2/g) were obtained in the acidic medium.

The approaches employed for imparting desired specific properties to the silica surface under chemical modification depend on character of a task in question and may involve such major methods as weakening of intermolecular interactions of surrounding molecules with sites of the surface, or, conversely, enhancement of these interactions with a view to lend specificity and chemical activity to the surface. In many cases functionalization of a surface is also effected to immobilize diverse compounds on silica surfaces to make them heterogeneous. We have developed efficient and versatile enough methods for activation of surfaces of functional organosilicas with amino-, vinyl-, mercapto- and silicon hydride groups in modifying layer. These methods were used for immobilization of oxygen-, nitrogen-, sulfur-containing complexing ligands, some analytical reagents and enzymes.

Mesoporous silicas with chemically modified surfaces have been applied in synthesis of different nanostructures. Results concerning using of silica matrices in the carbon nanotubes preparation are summarized. Porous silicas with grafted layer of hydridepolysiloxane were used for *in situ* preparation of supported nanoparticles of gold and silver by reduction of metal ions from chloroauric acid and silver nitrate solutions, respectively. Nitrogen adsorption-desorption, X-ray powder diffraction analysis, scanning and transmission electron microscopies, IR-, UV-Visible and laser correlation spectroscopies were applied for characterization of adsorbents and nanostructures obtained.

SPECTRAL- FLUORESCENT PROPERTIES OF OXYCOUMARINE DYES IN SOLUTIONS

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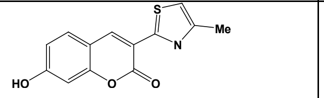
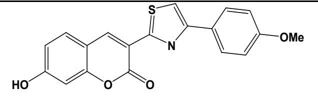
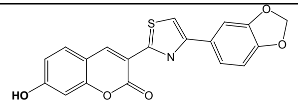
Coumarine dyes are widely used as active media for lasers, luminescent solar concentrators, as well as fluorescent probes and labels for investigation of proteins and nucleic asides in medicine and biology. Therefore, the synthesis of a new compounds of this class with regularly changing structure and the study of their spectral-fluorescent properties represents both scientific and practical interest.

Structural formula's of oxycoumarine dyes, studied in this paper, are shown in Table.

The concentration dependence of these dyes electronic absorption spectra in dimethylformamide were studied. Absorption spectra of dyes I-III in wide concentrations range ($5\times10^{-6}\div2\times10^{-3}$M) remain constant and correspond to monomer dye molecules. For monomer molecules of dyes followings were determined from obtained experimental results (see Table): molar extinction coefficient (ε), oscillator strength (f_e), excited state lifetime (τ), quantum yield of fluorescence (B) were determined.

№	Structural of dye molecules	$\lambda_{\max}^{abs}$	$\lambda_{\max}^{flu}$	B	ε (M^{-1}* см$^{-1}$)	τ, (ns)	f_e	$\nu_{0\text{-}0}$, (sm^{-1})
I		387	498	0,14	25800	4,3	0,58	23100
II		399	525	0,13	21100	5,1	0,51	21400
III		400	510	0,11	25300	3,1	0,85	20700

The dependence of spectral-fluorescent properties of synthesized oxycoumarines on their structure is also discussed.

THE MATHEMATICAL MODELLING OF EQUILIBRIA PROCESSES OF HEXAFLUOROSILICA ACID – AMINE AQUEOUS SOLUTIONS BY POTENTIOMETRIC RESULTS

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In the work [1] the interaction of hexafluorosilica acid with rather strong and weak nitrogen-containing organic bases (Am) of a different nature has been investigated. The character of the acid-base interaction in the stated components aqueous solutions depending on their concentration and mole ratio has been determined by titrations in the pH- and pF-potentiometry variants.

In this work the mathematical model of equilibrium processes in system "water – hexafluorosilica acid – amine" is presented. Its adequacy has been checked up with the use of the earlier experimental data. With the use of the model investigated the presence of equilibrium processes with the participation of various ionic - molecular forms of the hexafluorosilicate ion has been proved and their component structure has been established. On the basis of the obtained data the diagrams of the investigated systems component structure have been plotted and the equilibrium processes constants have been calculated with their use.

It is stated that at the potentiometric titration of hexafluorosilica acid aqueous solutions by the organic bases the protolytic interaction process was accompanied by the appreciable hydrolysis of complex anion SiF_6^{2-} to form such fluorosilica compounds as $SiF_5(H_2O)^-$, $SiF_4(H_2O)_2$, and by the presence of HF molecules, as well as by the presence of ion pairs $\{(AmH^+)_2SiF_6^{2-}\}$, $\{(AmH^+)\ SiF_5(H_2O)^-\}$, $\{AmH^+F^-\}$, anion complex $SiF_5(Am)^-$, and the intermolecular compound {HF·Am} being the products of nitrogen-containing organic bases interactions.

The analysis of the researches carried out has allowed to ground the variant of hexafluorosilica acid aqueous solutions potentiometric titration and to choose the nitrogen-containing organic base as a titrant.

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VIBRATIONAL STATES OF THE DIATOMIC HYDRIDES IN THE STATE-SPECIFIC COUPLED CLUSTER THEORY WITH CAS REFERENCE

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The wave function in the multireference state-specific coupled cluster theory based on the complete active space (CAS) reference has the following form:

$$\left|\Psi_{\mathrm{CASCCSD}}\right\rangle = \exp\left(\hat{T}_1 + \hat{T}_2\right)\left|\mathrm{Ref}\right\rangle . \qquad (1)$$

Operators $\hat{T}_1$, $\hat{T}_2$ generate all necessary one- and two-electron excitations from the reference function $\left|\mathrm{Ref}\right\rangle$. The smallest active space involves two orbitals and two electrons. In this case the reference is a superposition of one- and two-electron excitations from the “formal reference” determinant $\left|0\right\rangle$:

$$\left|\mathrm{Ref}\right\rangle = \left[\delta + \lambda\left(a_A^+ a_I \pm a_{\bar{A}}^+ a_{\bar{I}}\right) + \gamma\, a_A^+ a_I a_{\bar{A}}^+ a_{\bar{I}}\right]\left|0\right\rangle , \qquad (2)$$

where a_A^+ and a_I denote creation and annihilation operators, respectively, and δ, λ and γ are configurational coefficients derived from a CASSCF calculation and adjusted in the subsequent CAS coupled-cluster (CASCC) calculation. These numbers depended from the spatial and spin symmetry of the target state. As we have demonstrated the CASCCSD ansatz (1) has an excellent ability to describe the potential energy surface (PES) for ground [1] and excited [2] states as compared to the full configuration interaction (FCI) results. In the present work we have used the CASCCSD method to calculate PES’s for several diatomic hydrides (LiH, BH, HF, *etc*) in the lowest energy states with different spatial and spin symmetries ($^{1,3}\Sigma^{\pm}$, $^{1,3}\Pi$ and $^{1,3}\Delta$). The calculated potential curves were fitted using generalized Morse functions:

$$V(\rho) = \sum_{i=2}^{q} \alpha_i \left(1 - \exp(-\beta_i \rho)\right)^i , \qquad (3)$$

where parameters α_i and β_i are determined using the nonlinear least-squares method. In (3), $\rho = r - R_e$ is displacement from the equilibrium internuclear distance, R_e. $q = 3 \div 5$ was usually enough for an almost exact description of PES’s obtained in the CASCCSD calculations in this work. The one-dimensional vibrational Schrödinger equation with potential $V(\rho)$ was solved using a new variant of the Numerov method. Energies of the vibrational states

($G(\nu)$) and Frank-Condon factors have been calculated and compared with the experimental data and the theoretical results obtained by others.

The efficiency of different numerical approaches for the vibrational calculations has been investigated in the evaluation of molecular constants (ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, $\overline{D}_e$). Also, static dipole-dipole polarizabilities and hyperpolarizabilities in the ground and electronically excited states have been calculated for the diatomic molecules considered in this work.

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THE USAGE OF ORGANIC Sn(II) CONTAINING SOLS IN CONDUCTIVE METAL PATTERN PRODUCTIN

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The production of conductive metal patterns with the demanded thickness and micron size of elements needed in solid-state electronics. It can be achieved by using the photoresist free technique of photochemical dielectric substrate activation followed by selective electroless metal plating and subsequent film growth up to a required thickness (0.1–25 μm).

The negative patterns on dielectrics can be manufactured using semiconductive photosensitive films such as TiO_2, ZnO, PbI_2 and others. Photo electrons are generated under the action of actinic irradiation and than they are captured by the adsorbed noble metal ions with the production of metal catalytic particles which initiate electroless nickel or copper plating on the irradiated parts of samples. The positive patterns are manufactured in a process of palladium catalyst formation when Pd(II) is reduced with Sn(II) compounds absorbed from $SnCl_2$ water solutions on the non-irradiated parts of the dielectric substrate. Palladium does not appear on the irradiated sites because UV irradiation stimulates oxidizing of Sn(II) by oxygen with the formation of a positive pattern [1, 2]. So, the materials and the nature of processes responsible for negative and positive pattern formation are different.

The quality of the positive metal patterns depends much on the $SnCl_2$ solution composition which in its turn varies with the ageing of a solution in the result of Sn(II) hydrolyses and oxidation [3]. Stabilization of $SnCl_2$ solutions with the acids, ligands and surfactants could help a little according to our previous data [3] but it does not solve the problem.

The purpose of this work is to use organic solvents for preparation of Sn(II) containing sols stable to coagulation and oxidizing and to try them in a process of photoselective electroless metal pattern plating.

The ethanol and propanol $SnCl_2$ solutions were prepared which enclude not more than 6 mol/l of water and 0.05–0.44 mol/l of HCl necessary to prevent $SnCl_2$ hydrolysis. These sols were stable for more than 25 days. TEM investigation has shown that solutions contain particles 3–10 nm in size and only a small quota of them are larger (up to 15–20 nm). Thin films (less than 50 nm in thickness) were obtained on the glass by spin coating of sols. This films consist of the nanoparticles and contain $(7–60)\cdot10^{-3}$ mol/m^2 of Sn(II) compounds.

The traditional operations which include UV irradiation, treatment in $PdCl_2$ solution and nickel electroless plating allowed us to obtain negative patterns on the glass covered by these films. This effect differs from the usual positive patterning and it means that palladium is reduced under UV irradiation of Sn(II) hydroxy compounds nanoparticles. The nature of such a reduction may be connected with generation of photoelectrons in these particles which reduce the adsorbed Pd(II). The absence of palladium catalyst on the non irradiated sites of the film can be connected with the disappearance of a hydrophilicity and Sn(II) oxidizing with the oxygen. The both reasons are stimulated by the heating of Sn(II) containing film on the sites covered by dark and nontransparent to UV irradiation parts of a photomask. This heating promotes evacuation of alcohol molecules covering Sn(II) containing nanoparticles and the following Sn(II) oxidation with the oxygen on the freshly naked surface of nanoparticles. The most probable product of oxidation is α-stannic acid that at a fast storage transfers into β-form and loses the ability for wetting and dissolution. It is interesting to note that the presence of alcohol shell on Sn(II) containing nanoparticles prevents oxidation of tin(II) in air. The facts that confirm such a core-shell structure are the retardation of hydrolysis, coagulation and especially Sn(II) oxidation by oxygen in the bulk of colloidal solutions and in films on a glass in the darkness and under UV irradiation. The loss of alcohol is observed after 2-4 hours of the film storage or at its heating for some minutes. It is important to note that the aged Sn(II) containing films deposited from organic sols are identical to the films obtained from the acid $SnCl_2$ water solutions. After their UV irradiation, palladium activation and electroless nickel plating positive metal patterns are obtained owing to photostimulated Sn(II) oxidation with the oxygen and photoelectrons either do not appear or are captured by oxygen after generation.

The experimental results have shown that Sn(II) containing organic sols can be used for deposition of UV sensitive films on a dielectric surface and for production of negative or positive conductive metal patters depending on their storage. It is shown that alcohol adsorbed on Sn(II) containing nanoparticles protects tin from oxidation.

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PROCESSING OF LIQUID HYDROCARBONS BY MEANS OF OZONIZATION

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When evaluating various methods of soil decontamination, polluted by hydrocarbons it is possible to use various criteria. For example time of full decontamination percent of decontamination per a unit of time an output of by-products (and their "ecological compatibility") etc. Considering the problems, which exist in the particular case at planning liquidation of environmental contamination and on the basis of comparison of methods by the certain criteria, the choice of the most optimum method is made. One of the research tasks of choice and optimization of the method is the analysis of the information about cleanout process kinetics grounding the expediency of application of the method of cleanout, and also determination of the most effective direction for the further researches.

Scientists before have considered kinetics of oxidations of hydrocarbons by ozone in organized fluidized layer of soil [1] and peculiarities of kinetics in this process when a soil contains organic substance (humus) [2]. The determined distinctions in changing speed of chemical reaction with contents of organic substance in initial soil allow to conclude that humus of soil can influence greatly on specificity of process of soil decontamination from hydrocarbons.

Later the objects of the researches were a soil and gasoline (pollutant), similar by composition to those ones, which were used in research of oxidation kinetics peculiarities in the samples of soil with organic substance (humus) [2]. Time intervals through which analyzed presence of organic substances in tests of soils [3] were similar also.

Oxidation of gasoline by ozone was conducted in the device with organized fluidized layer (suspended in stream of O_3 particles of soil impregnated by gasoline). It allows to provide the fullest interaction of two phases and to conduct the reaction even in the field of explosive concentrations. As a source of ozone the ozone generator on the basis of corona discharge was used. To evaluate the level of soil pollution by gasoline the method of IR-spectroscopy was used.

As a result of experiments it has been established, that in system "soil + humus + pollutant (gasoline)" dependence of quantity of initial organic products (IOP) from time of processing has quite complex character: firstly IOP content in test varies slightly, and only then after half of time of full cleanout this dependence gains character of a flowing straight line with transition to equilibrium concentration of humus (4,9 % weights of test).

Experiment data processing in coordinates Fig.1 shows that with increase of gasoline content in tests the expenses of ozone and time of full oxidation (t_{proc}) of gasoline in soil grow according to the linear law. On the basis of linear character of dependence $m(O_3)$ - $m(C_8H_{18})$ and t_{proc} - $m(C_8H_{18})$ it is possible to state, that speed of oxidation C_8H_{18} is not influenced with diffusion, speed of mixing in fluidized layer, i.e. the factors having crucial influence on delivery of oxidizer’s molecules to octane molecules adsorbed on microparticles of soil. Results of these researches allow to plan possible ways for intensification of oxidation process of oil products (decrease t_{proc} and $m(O_3)$), for example by additional dispersion of particles of soil.

Experiments have shown, that in system "soil + humus + C_8H_{18}" it is observed full decomposition of hydrocarbons and humus remains as a buffer, inhibiting process of oxidation additive in tests of soil.

The important recommendations for designing hardware system of oxidation of hydrocarbons in suspended (fluidized) layer are stated on the basis of the results of conducted researches.

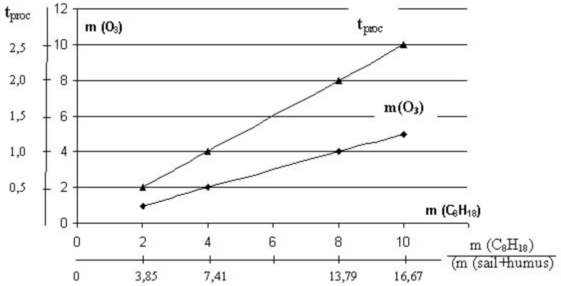

Figure 1. Dependence of the ozone expenses ($m(O_3)$) and time of processing (t_{proc}) from weight of gasoline in samples ($m(C_8H_{18})$) or relative concentration of gasoline in samples (($m(C_8H_{18})$) / (m(soil+humus))).

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CONDUCTOMETRIC INVESTIGATION OF TRILUOROACETIC ACID SOLUTIONS IN NON-AQUEOUS MEDIA

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The trifluoroacetic acid – aliphatic alcohol – ethylene glycol systems have been studied by conductometry for the purpose of investigation into the influence of the nature of solvent on the current transfer mechanism and thermodynamic characteristics of ion migration and viscous flow processes. Ethanol, butanol and hexanol were taken as aliphatic alcohols.

The systems were studied within the 273,15 – 323,15 K temperature range on changing the content of ethylene glycol from 0 to 100 mole percent. The concentration of trifluoroacetic acid was varied from 10^{-4} to 10^{-3} mole/l.

To investigate the processes of association, migration and oversolvation of trifluoroacetic acid in double mixed solvents physical-chemical analysis of mixed monobasic aliphatic alcohol – ethylene glycol solvents was carried out over the whole temperature and concentration range.

On forming a mixed solvents from monobasic and polyatomic alcohols the nature of distribution of hydrogen bond changes, due to which there appear nonuniform-energy zones broken through by protons in prototropic mechanism of current transfer. The number of protons taking part in the mechanism at the given composition of mixed solvents is determined, in particular, from the association constants of heteromolecular complexes formed. This is why the association constants and products of Walden were calculated from the values of limiting equivalent conductivities found out in the study. A decrease in dielectric permeability of the mixed solvents observed with increasing the concentration of aliphatic alcohol promotes electrostatic interactions, changes the contribution of prototropic mechanism of current transfer, which causes increase in the association constants and decrease in products of Walden.

Free activation energies of ion migration and viscous flow were calculated by modified equation of Eyring. The enthalpy and entropy of ion migration and viscous flow were found out by differentiating temperature dependences.

THE INVESTIGATION OF MICELLE FORMATION IN AQUEOUS SOLUTIONS OF MONOALKYLSULFOSUCCINATES

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Numerous experimental data concerning parameters of micellization in various ionic surfactants solutions are available. The most part of them concerns surfactants with singly charged both surface active ion and counterion, for instance alkyl sulfates, alkyltrimethylammonium bromides and chlorides, alkyldimethylbenzylammonium chlorides, acyl isethionates and others. However, data for multiheaded surfactants are limited.

The aim of the work is to study the micellization in solutions of disodium monoalkylsulfosuccinates of the general formula $ROOCCH_2CH(COONa)SO_3Na$, where R is a long chain hydrocarbon radical from C_{10} to C_{15}, by methods of conductometry and viscosimetry. Surface active anions of these salts contain two ionic groups – carboxylate and sulfonate ones. The surfactants were synthesized from individual long-chain primary alcohols by esterification by maleic anhydride following by sulfonation with aqueous solution of sodium sulfite, then isolated from a reaction mixture and purified according to known procedure. To obtain the double-charged form of the surfactants recrystallization from aqueous solution should be carried out at pH 6,5-7. At lower pH values the product is obtained as a mixture of double and single-charged forms of monoalkylsulfosuccinates. This fact is confirmed by results of conductometric measurements, namely by the shape of specific conductivity polytherms which are characteristic for surfactant mixtures and slopes of specific conductivity isotherms before and after CMC.

Using the conductometric method critical micellization concentrations (CMC) and Krafft points of the surfactants have been determined. The influence of NaCl additives on CMC also has been studied. Values of degree of Na^+ counterion binding are calculated by the Evans' and Fram's methods as well as from the Corrin-Harkins' dependence. The dependence of viscosity of monoalkylsulfosuccinates solutions on surfactant concentration and NaCl additives has been studied and form-factor is estimated. As it was supposed near CMC the micelles of monoalkylsulfosuccinates are of spherical form. On the base of data obtained the thermodynamic parameters of micellization for monoalkylsulfosuccinates homologues are calculated.

PHOTOPHYSICAL PROPERTIES OF NEW SQUARAINE-BASED pH-SENSITIVE FLUORESCENT DYES FOR RED AND NEAR-INFRARED SPECTRAL REGION

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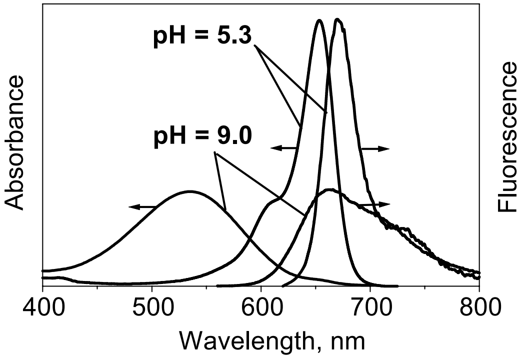
pH-Sensitive fluorescent dyes are widely used for intracellular and biomedical studies among other applications. Most of the existing pH-sensitive dyes are known to emit between 350 and 550 nm and they also do not contain any functionality for covalent biolabeling. We developed and investigated a series of new squaraine-based pH-sensitive fluorescent dyes currently available from SETA Biomedicals (www.setabiomedicals.com) as free carboxylic acids, amine-reactive N-hydroxysuccinimidyl (NHS) esters and thiol-reactive maleimides. Their absorption and emission spectra, extinction coefficients, quantum yields, fluorescence lifetimes and polarization were measured in aqueous media, free in solution and after binding to albumin (BSA) and immunoglobulin (IgG). Protonated forms of the free dyes absorb between 634 – 693 nm with extinction coefficients (ε) 87,000–188,000 $M^{-1}cm^{-1}$ and fluoresce between 646 – 714 nm. The excitation of these labels with a 635 or 670-nm diode laser results in improved signal-to-noise ratios due to reduced background from the biological sample.



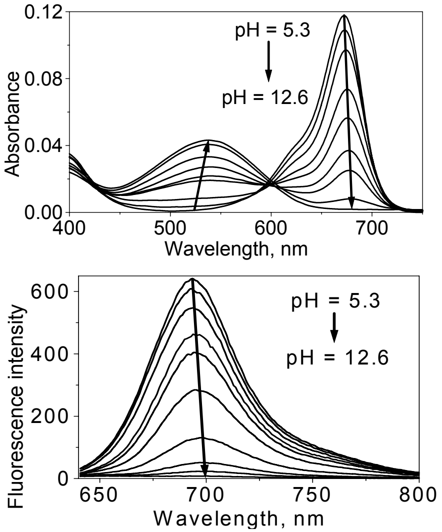
Absorption and emission spectra of K8-1405 at pH 5.3 and 9.0

The additional short-wavelength absorption band (ε 12,000–30,000 $M^{-1}cm^{-1}$) in the spectra of these dyes allows excitation with a 380-nm, 405-nm or 436-nm diode laser. Importantly the quantum yields are independent of the excitation wavelength. These new dyes exhibit adequate quantum yields in aqueous media and when covalently bound to protein.

Characteristics of New pH-Sensitive Labels

Label	pKa	pH Range	Absorption max, nm	Fluorescence max., nm
K8-1405	7.17	5.2–9.0	653/535	671/663
K8-1675	8.65	7.8–9.5	662/543	679
K8-1365	8.86	6.5–11.0	672/537	694
K8-1765	9.37	7.3–11.1	641/514	668
K8-1375	9.56	8.8–11.5	693/557	714
K8-1775	9.92	8.2–11.6	662/539	684
K8-1665	10.29	8.4–11.8	640/519	656
K8-1610	10.65	9.4–12.8	634/520	646

In basic environment the long-wavelength absorption band of these dyes decreases and a new absorption band at 520–560 nm appears whereby the fluorescence of almost all the investigated dyes is totally quenched. An exception is K8-1405, where both forms, the protonated as well as the deprotonated, are fluorescent. The Stocke's shift of deprotonated form of K8-1405 is extremely large — more than 3,600 cm^{-1}, which is one of the largest Stokes' shifts that have been observed in a cyanine-based dye. The pKa values of the dyes are in the range between 7.17 and 10.65. The pKa values of the IgG and BSA-conjugates are similar as those for the free dyes.



Absorption and emission spectra of K8-1365 *vs.* pH

These pH-probes are easily coupled to antibodies and other proteins using standard procedures.

Applications are in biological, pharmaceutical and biomedical research, clinical diagnostics, and high-throughput screening for the investigation of biological cells, membranes, and the role of intracellular pH in diverse physiological and pathological processes.

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SILICA BASED MATERIALS WITH IMMOBILIZED CALCEIN

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Silica-based hybrid organomineral materials are widely used as sorbents, for preparation of heterogeneous metallocomplex catalysts, development of new analytical procedures, etc. Calcein, 2´,7´-bis-[N,N-bis(carboxymethyl)aminomethyl]-fluorescein forms stable and coloured complexes with many metal ions, and fluorescence of dye is quenched in the presence of Cu(II) and Fe(III). This inspires interest to hybrid silica-calcein materials with a potential to be used in analysis.

In this work calcein was immobilized by a non-covalent immobilization from aqueous solutions and a sol-gel process. The diffusion coefficient of calcein in the near-surface layer is equal to $7{\cdot}10^{-10}$ m^2 s^{-1}. The characteristics of equilibrium of calcein adsorption on silica gel at pH 3.2 were determined too, and the distribution of active adsorption centers in respect to their affinities to calcein was found. Dependently on the calcein specific concentration, 1-3% of the dye are washed out. The dye included into the material via a sol-gel process is held strongly, and washing out is practically absent. Complexation of immobilized calcein with Ni(II), Cu(II), Zn(II) and Pb(II) was studied, the conditional heterogeneous stability constants $\beta > 10^5$. The complexation chromogenic reaction was proved to be prospective for visual detection of transition and heavy metal ions in solutions. At the same time, the quenching of calcein fluorescence in presence of Cu(II) enabled to develop the visual test procedure for the Cu(II) detection at its concentrations higher than 0.02 mg l^{-1}.

QUANTUM-CHEMICAL STUDY OF ADSORPTION OF CHLORIDE IONS FROM AQUEOUS SOLUTIONS AT INTERMETALLICS $CuAl_2$ AND $CuAl_2Mg$ SURFACE

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The modern molecular approaches to theoretical study of electrochemical corrosion consider a metallic surface as an aggregate of atoms one or different types which allocated in definite positions of crystalline lattice. In relation to an electrode these atoms have different values of electronic density and the system of local centers of anode–cathode is created on a surface. It determines corrosive destruction of metal. Consequently, the estimation of corrosion dissolution of metals and alloys can be made by study of influence of water molecules and solution ions on durability of metallic bond. The quantum-chemical methods and cluster model of metals are used for this purpose.

We calculated of the interaction of aggressive chloride-ions with the surface of $CuAl_2$ and $CuAl_2Mg$ intermetallics, which are contained in duralumin alloys and have a considerable influence on their corrosion resistance. The semiempirical PM5 method of MOPAC calculation package [1] was used for the quantum-chemical estimation of interaction of chloride-ions with the intermetallics surface. This method includes parameters for atoms of copper, aluminium, magnesium, oxygen, chlorine and hydrogen, which take part in formation of chemical bonds in the system water environment – intermetallics.

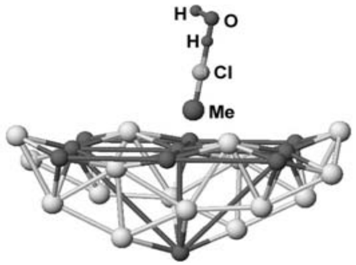

Fig. Formation of metal complex on surface (110) cluster of intermetallic

We studied of the surface (110) of the $CuAl_2$ intermetallics. The cluster which models the surface (110) of the $CuAl_2$ intermetallics, contained 10 atoms of copper and 16 atoms of aluminium, and in the cluster of $CuAl_2Mg$ 4 atoms of magnesium were substituted for the aluminium atoms. The surface (110) of clusters has a stepped structure. Distance between the atoms of aluminium and copper on the surface was 2,67 Å. The interatomic distances in both clusters in the process of calculation were not optimized.

We calculated of the gas adsorption of chloride-ions. Such results are necessary for establishment of places of adsorption of chloride-ions on the surface (110) of $CuAl_2$ and $CuAl_2Mg$ clusters (tabl.).

Table. The calculated parameters of gas adsorption of chloride-ions on the clusters of $CuAl_2$ and $CuAl_2Mg$

Cluster	Adsorption distance (Me-Cl^-), Å	Charge (Cl^-), e	Adsorption heat, eB
$CuAl_2Mg$	1,756	-0,258	2,689
$CuAl_2$	1,983	-0,276	2,467

On both clusters the most power advantageous position of chloride-ions is hollow. At adsorption of chloride-ions there is a considerable transfer of electronic density on the metal surface. Thus reaction ability of chloride-ions is higher on the surface of $CuAl_2Mg$ cluster, which is confirmed by greater adsorption heat and transfer of electronic density on this surface.

Chloride-ions sharply lower potential of ionization, that testifies about decline of thermodynamic resistance and consequently an output of atoms from metal in water solution is possible.

The water molecule was replaced by $Cl^-(H_2O)$ during adsorption at the intermetallics surface and complex $MeCl^-(H_2O)$ was formed (fig.).

We calculated interaction potential curves of molecular complex $Cl^-(H_2O)$ with the surface atoms of intermetallics clusters, which are preliminary, covered with molecules of water in top positions. In this case only bonds of Me-Cl^- and Cl^--H were optimized. A molecular complex was oriented athwart to the cluster surface. The water molecules adsorbed on a cluster were not optimized. Within the framework of such model adsorption heats of molecular complex $Cl^-(H_2O)$ on the surface (110) of clusters of $CuAl_2$ and $CuAl_2Mg$ are equal 2,013 eB and 2,345 eB accordingly. Obtained results correlate with information of gas adsorption of chloride ions on these clusters. The presence of water environment determines the 20% decline of adsorbability of chloride ions on intermetallics clusters. These results testify about greater adsorbtivity of the $CuAl_2Mg$ intermetallics surface concerning chloride ions, and consequently the surface of $CuAl_2Mg$ is subject of localized corrosion.

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QUANTUM MOLECULAR DYNAMICS SIMULATION OF LiBr IN ACETONITRILE

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The solvation dynamics of ions in polar solvent is a topic of current interest in chemical physics, with implications in biochemical, medical, and technological research. In present work, the solvation of Li^+ and Br^- in liquid acetonitrile will be analyzed by *ab initio* molecular dynamics within Car-Parrinello (CPMD) program code [1, 2].

The simulation have been performed in cubic box with periodic boundary conditions. Two systems, one containing Li^+ and several AN molecules and other with Br^-, have been studied. Martins-Troullier pseudopotentials have been used along with Kleinman-Bylander decomposition angular moments projectors. Density functional calculations in the generalized gradient approximation (GGA) have been performed by using BLYP exchange correlation functional.

To validate the computational strategy adopted, the structure and some of electronic properties of the acetonitrile complex with both Li^+ and Br^- ions have been calculated and compared with correlation consist quantum-chemical calculations with a localized Gaussian basis set. The results show that the BLYP functional in conjunction with the plane wave basis set satisfactory reproduce the structure parameters of both complexes.

The lithium cation interacts primarily with the nitrogens and the chloride anion with hydrogens of the solvent molecules. The first peak position in the radial distribution functions is in a good satisfactory with experiment.

The authors would like to thank Prof. O.V. Prezhdo for a help in usage of computer resources of Department of Chemistry, University of Washington, USA.

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***AB INITIO* CALCULATION OF GEOMETRY, SPECTRA AND THERMODYNAMIC PARAMETERS OF FORMATION FOR PROTONATED CLUSTERS IN METHANOL AND ETHANOL.**

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The traditional theoretical description of electrolyte solutions is based on the continuum models, with solvent as unstructured continuum with macro properties (relative permittivity, density, viscosity). The molecular dynamics computation methods are based on simulation of interparticular interactions.

But neither traditional theories, nor MD methods can give exact estimation for electrolyte solvation energy in H-bonded solvents. Properties of such systems can be simulated well by *ab initio* methods, taking into account configuration interactions.

In present work we have trying to estimate enthalpy and entropy of cluster formation for ions (H^+, Cl^-, Br^-, I^-) and molecules (HCl, HBr, HI using *ab initio* methods. IR-spectra of clusters have been calculated too. Here are the clusters we optimized:

$(CH_3OH)_n$; $(CH_3OH_2^+)\cdot(CH_3OH)_{n-1}$; $(CH_3OH)_n\cdot Hal^-$; $(CH_3OH)_n\cdot HHal$
$(C_2H_5OH)_n$; $(C_2H_5OH_2^+)\cdot(C_2H_5OH)_{n-1}$; $(C_2H_5OH)_n\cdot Hal^-$; $(C_2H_5OH)_n\cdot HHal$,

Calculation stages:

Initial geometry optimization using semi-empirical PM-3 method. Optimized coordinate matrix has been used as initial approach for the next stage;

More exact geometry optimization (with MP2 method in basis 6-311++G(d,p)) with Gaussian'03 and PC GAMESS program.

Normal vibration modes calculation for cluster. Then we estimated full cluster enthalpy and free Gibbs energy of system formation by nuclei and free electrons.

The changes of thermodynamic functions have been found as a difference between their values on initial and final stages of cluster formation:

$\Delta_f G(H^+\cdot(ROH)_n) = G(H^+\cdot(ROH)_n) - G((ROH)_n)$
$\Delta_f H(H^+\cdot(ROH)_n) = H(H^+\cdot(ROH)_n) - H((ROH)_n)$
$\Delta_f S(H^+\cdot(ROH)_n) = (\Delta_f H(H^+\cdot(ROH)_n) - \Delta_f G(H^+\cdot(ROH)_n)) / T$

Our results are in a good accordance with experimental data.

PHYSICO-CHEMICAL PROPERTIES OF NAPHTALENE IN THE INDIVIDUAL AND MIXED SOLVENTS

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The results on measurement of solubility, density and viscosity of naphthalene in organic solvents and their mixes are discussed. Aliphatic alcohols, alkanes and their mixes have been chosen as solvents. A choice of solvent follows from two reasons. First, preliminary studies, both theoretical and experimental, have revealed a number of structural and thermodynamic features in alcohol-alkane mixtures due to solvophobic effects. In this connection, influence of addition of polycyclic aromatic hydrocarbon (PAH) on the mentioned features of these mixed solvents has been studied. Second, studying of solubility PAH is of practical importance for extraction technologies.

The data on solubility of naphthalene in ethanol-heptane and ethanol-octane mixes at 298.15 K are presented. The largest solubility of PAH is observed in octane and the least one – in ethanol. It is connected with properties of solvents, namely with solvophobic effects. It is interesting to note that naphthalene solubility is increased as even small amount of alkane is added to alcohol. Viscosity was measured by means of Ubellode's viscosimeter with a trailing level and photo-electonical scheme of the flowing time fixing at 298.15 K. Density of naphthalene solutions was measured by means of vibrating densimeter. Experimental data with the accuracy of $\pm 2\cdot 10^{-6}$ $g\cdot sm^{-3}$ were obtained. Values of apparent and partial volumes have been calculated and discussed in the report. The density of solutions increases with growth of naphthalene concentration and its values for the mixed solvents are in an interval between densities of double systems: ethanol-naphthalene and alkane-naphthalene. The other picture can be seen on dependences of volumetric testimonials from of concentration. In particular, dependences apparent molar volume from concentration of the dissolved substance passes through a maximum. It is safe to say it relevant as pure solvents as their mixes. At mole fraction 0.98 and 0.96 ethanol apparent molar volumes of naphthalene at its small concentration are less than in ethanol-naphthalene mixture, i.e. small additives alkanes render very strong influence on structure of a solution. It does not observe for the ethanol-octane mixes.

EFFECT OF STRONG FINITE ELECTRON REPULSION ON FERROMAGNETIC ORDERING IN HUBBARD MODEL

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Magnetic properties of transition metal compounds of low-dimensional structure attract much interest in context of the design of electronic nanoscale devices. These compounds are described well by strongly correlated electron models such as Hubbard model with strong electron repulsion.

We studied magnetic ordering in quasi-one dimensional compounds of ladder structure like $(C_5H_{12}N)_2CuBr_4$, described by this model. It is known that in the case of infinite electron repulsion for weak coupling between unit cells and partial filling of the electron band this system may have ferromagnetic ground state. The question is how this picture would change if strong but finite repulsion will take into account.

Using the perturbation theory in weak interaction between unit cells of the ladder, we have shown that the ferromagnetic ordering is suppressed totally if

$$U\left|t_2\right| < 4t_1^2 .$$

Here U is a parameter of electron repulsion; t_1 and t_2 are resonance integrals, describing electron hops inside of unit cells and between neighbor cells.

If this condition is failed under big values of U, the ferromagnetic ordering is possible. With the help of polaron hypotesis and perturbation theory we have found the interval of the electron concentrations under which the ferromagnetic ground state of the ladder take place.

$$1+\left(\frac{3\ln 2}{2\pi^2}\alpha_1\right)^{1/3} \le \rho \le 2-\left(\frac{6\alpha_2}{\pi^2\alpha_1}\right)^{1/3}, \alpha_1 = \left|\frac{t_2}{t_1}\right|, \alpha_2 = \left|\frac{t_1}{U}\right|$$

This analysis had been checked up by direct numerical calculations of the exact energy spectra of finite lattice clusters formed by 5 and 7 unit cells with 9 and 8 electrons respectively for different values of anisotropy parameters α_1, α_2 and electron repulsion U. The results of numerical calculations agree well with perturbative predictions.

COMBINED MICROCALORIMETRIC AND SORPTION-ANALYTIC STUDIES OF ION EXCHANGE THERMODYNAMICS ON MORDENITE

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Combined sorption-analytic studies of ion exchange equilibria and direct microcalorimetric measurements of ion exchange heats of K^+ and Ca^{2+} cations were performed on Na-forms of two natural mordenites (M): mainly calcium mordenite from Vodica deposit (Transcarpathia) and mostly sodium mordenite from Karadag deposit (Crimea). The ion exchange was studied in static conditions (S:L = 100) in aqueous solutions of Na^+, K^+ and Ca^{2+} chlorides at constant ionic force I = 0.1 and various proportions (10 variants) of exchange cations. The integral heats of ion exchange were measured in similar conditions using the Calve microcalorimeter (Setaram, France) equipped with specially designed measuring cell.

The ion exchange isotherms exhibit high selectivity of the two mordenite samples with respect to K^+ cations. For the exchange systems involving Ca^{2+} ions, the ion exchange isotherms exhibit the change of selectivity at certain degree of exchange.

At low concentrations of Ca^{2+} ions in the solution, the two samples exhibit pronounced selectivity with respect to these ions; at higher concentrations the zeolites become more selective to Na^+ cations. It is to be noted that the amount of Ca^{2+} ions sorbed by Vodica mordenite (which possesses large number of extraframework cations) is by a factor of two higher than that adsorbed by Karadag mordenite. This fact can be explained from structural considerations: by the memory effect of mordenite with respect to the extraframework cations which were present during the natural crystallisation of the mineral.

The exchange of K^+ ions on both samples is accompanied by the release of heat in the entire occupation range. For the Ca^{2+}–NaM system of Vodica deposit the exothermal exchange was observed only at $\theta \le 0.2$. The Karadag mordenite is characterised mainly by negative exchange heats ($\Delta H > 0$).

From the experimental data, the variations of integral molal free energies ΔG_m and entropies ΔS were calculated in the entire range of solid phase occupation θ by sorbed cation. It was shown that the free energy of exchange in the K^+–NaM system is determined by the enthalpy constituent, and in the Ca^{2+}–NaM system – by the entropy constituent.

MOLECULAR AND ELECTROLYTE SOLUTION SYSTEMS IN FIRE SUPPRESSION

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Among solvents existing on the Earth water is the cheapest and accessible fire extinguishing substance, but it has insufficient extinguishing ability, which is lower then calculated. For increase of extinguishing properties of water it is offered to add substance of the different nature in water. There is too much information on the given problem in scientific literature, but in many cases it is rather difficult for the analysis. Therefore in work it is made on attempt of generalization of this information for establishment of interrelation between physical and chemical properties of solutions and time of extinguishing (τ).

Typical for fires in residence sector is a burning of wood and cellulose products (class A fires). According to the analysis of existing papers about extinguishing efficiency of water it is more often offered to use solutions of electrolytes and high-molecular compositions. The action of different by the nature additives is different. Addition of polymeric impurities essentially influence on the period of extinguishing of the fire at small concentration [1]. At concentration more than 2-3 $\%_{weight}$ the time of extinguishing increases, therefore the mixture with concentration more than $5\%_{weight}$ is not expedient for extinguishing. Addition of electrolytes is effective only at the high concentration (10-20 $\%_{weight}$). The last is caused by the fact that electrolytes in two-componental mixture influence on a superficial tension (σ) and viscosity (η) insignificantly, and at the high concentration the dominating role is got with effect of inhibition of cathalatik centers of a flame.

Optimum concentration of surface-active substances (SAS) in solutions makes 0,25-0,5 $\%_{weight}$. The superficial tension essentially decreases only at concentration of impurity up to 1 $\%_{weight}$. In two-componental mixture (the second component - SAS) σ does not decrease below for $(27\text{-}30)10^{-3}$ N/m. It is caused by gradual growth of amount of SAS molecules on surface split of phases. Time of extinguishing essentially depends on viscosity of a solution so at increase η on $(2\text{-}3)10^{6}$ m^2/s time of extinguishing decreases in 3-4 times. Optimum for extinguishing of wood by two-componental mixture is η $(4\text{-}5)10^{6}$ m^2/s [2]. The indicated optimum viscosity is achieved at concentration of a thickener up to 2 $\%_{weight}$. Use of such widespread thickeners as polysilicate and polyakril acid is non-expedient because optimum viscosity is achieved only at - 6-7 $\%_{weight}$. The most effective thickeners are polyoks and methylcellulose.

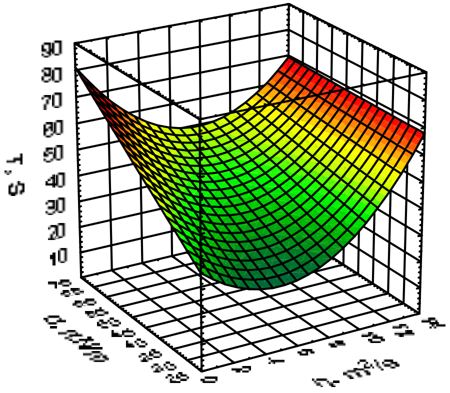

Fig. 1 Dependence of extinguishing time on physical and chemical properties of extinguishing compositions (σ, η).

Using the additive of one nature, corrects only one parameter of extinguishing composition. Only use of the combined additives (polymeric substance + low-molecular SAS + electrolyte) gives optimum values the basic physical and chemical properties of a composition (fig. 1). From figures it is obviously, that during extinguishing in which effect of inhibition is absent, to achieve time of extinguishing class A fire less than ~ 20 s is impossible at any concentration of additives.

However it is necessary to take into account, that the given dependence is submitted for temperature 20^0C. At ingress extinguishing substances in a zone of burning viscosity of solutions is reduced in 2-3 times whereas the superficial tension decreases insignificantly - on $(10\text{-}15)10^{-3}$ N/m.

For decrease of extinguishing time it is effective to use homogeneous solutions - emulsion. Halogenhydrocarbons with temperature of boiling <373K, which at ingress in a zone of burning boil and increase dispersiveness of a stream of extinguishing solution are as a disperse phase. At extinguishing by means of emulsion efficiency increases by means of inhibition by halogenhydrocarbons and the large heat-conducting surface.

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FAVORABLE BINDING SITES AND LOCALIZATION OF PYRROLOQUINOLINE ANALOGUES IN A DPPC BILAYER FROM MOLECULAR DYNAMICS SIMULATIONS

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A series of heteroazaaromatic compounds, composed of pyrrolo- and quinoline moieties has revealed an interesting phenomenon of solvent-catalyzed excited-state tautomerization [1]. The electronic excitation of such a system induces significant intramolecular transfer of electron density from an H-bond donor (pyrrole) to an acceptor (quinoline) parts of a chromophoric system. The remarkable and cooperative acid-base changes, which occur on opposite parts of the excited chromophore, introduce also a driving force for the proton transfer reaction. In the presence of some appropriate protic solvents, H-bond donor-acceptor bifunctional compounds are able to form cyclic intermolecular H-bonded complexes, in which solvent molecules act as an H-bonded wire connecting the proton donor and acceptor atoms. In such an H-bonded solute-solvent complex, the solvent-assisted excited-state proton transfer becomes therefore possible [2]. This feature makes this class of fluorescent compounds to be very promising candidates for fluorescent probing of water content and a penetration depth of water molecules in lipid membranes.

Molecular dynamics (MD) simulation has been used to investigate the partitioning behavior of 1*H*-pyrrolo[3,2-*h*]quinoline (PQ), 11*H*-dipyrido[2,3-*a*]carbazole (PC) and 7-azaindole (7AI) at a water/membrane interface. The MD study has been focused on the distribution and favorable binding sites of these probes inside a model membrane. Our simulations have shown that the probes are preferentially found mostly in the upper acyl chain and headgroup regions of membranes. The favorable localization of the studied heteroazaaromatic compounds within the DPPC bilayer are determined by a number of electrostatic interactions, including hydrogen bonding to the phospholipid carbonyl group, and vad der Waals probe-lipid interactions.

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PHYSICAL-CHEMICAL REGULARITIES OF CHEMICAL AND ELECTROCHEMICAL DISSOLUTION OF COPPER AND ITS ALLOYS IN CHLORIDE SOLUTIONS

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V.V. Datsenko

The investigation of copper and its alloys dissolution in chloride solutions of different compositions is an actual problem. With the help of different electrochemical methods the main regularities of copper dissolution in water and water-organic solutions were determined, the catalytic mechanism of process was proved. The forms of catalytic and inhibiting complexes of copper (II) were defined. The catalytic complexes are $[Cu(H_2O)_2(NH_3)_4]^{2+}$, $[Cu(H_2O)_3(NH_3)_3]^{2+}$ in ammonia solutions, $[Cu(H_2O)_4Cl_2]$, $[Cu(H_2O)_3Cl_3]^-$ - in chloride solutions and $\{(CuClFe)Cl_{j-1}{}^{5-j}\}$- in $FeCl_3$ – $CuCl_2$ solutions, the inhibiting complexes are
$[Cu(OH)_n(H_2O)_{6-n}]^{2-n}$. The principles of copper dissolution process intensification were formulated. The new compositions of ammonium and hydrochloric solutions of $CuCl_2$ were developed on the basis of this principles. The character of organic amines influence on copper dissolution was defined.

The theory of multilayer anodic copper passivation in chloride solutions of different acidity was developed. The scheme of stage copper passivation in ammonia solution was proposed. The mechanisms of surface copper compounds modification under of the different factors were discovered. The means of operating of its properties were showed. The increase of surface layer conduction as a result of grain boundary diffusion of Cu(II) ions and its concentration in polycrystalline precipitates has been registered. The effect becomes stronger under the increase of layer porosity degree, the repeated potential scanning and possibility of processing of Cu(II) contrary diffusion. The strongest effect for the $CuCl_2 \cdot 3Cu(OH)_2$ compound.

For copper alloys Brass-62, Fe-Cu, Cu-Ni the selectivity, main process stages, causes of its limitation and influence of alloy's component correlation on kinetics and mechanism of active dissolution and surface passivation under corrosion and anodic dissolution were determined. Complexantes inputted into nitrate copper electrolyte, their copper complexes as well as NO_3^- -ion reduction products have been established to include into electrolytic copper precipitates. The change in copper electroprecipitation kinetics in electrolyte contained small additions of ligand has been revealed. The formation of mixed copper complexes through the electrolysis and their participation in precipitation process of glittering copper layers has been confirmed experimentally.

ACID-BASE AND COMPLEXATION PROPERTIES OF AMINOPROPYLIDENEDIPHOSPHONIC ACIDS IN AQUEOUS AND MICELLAR MEDIA

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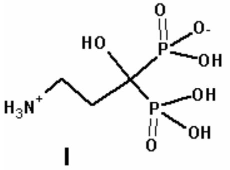
Aminopropylidenediphosphonic acids (APDPA) are effective complexons and perspective in medical and biological investigations as regulators of calcium metabolism in human organism. It is interesting to establish the specific behavior of APDPA in biomimetic systems such as solutions of surfactants.

The aim of the work is to characterize the effect of self-organized solutions of surfactants on acid-base properties of APDPA and complexation with ions of bioactive metal (Ca^{2+}). The solutions of cationic surfactant cetylpyridinium chloride (CPC) were used for investigations. The dissociation constants of APDPA (I – III) and the stability constants of complexes with Ca^{2+} in aqueous media and micellar media of CPC were studied by potentiometric titrations (CPC 0.1 mol L^{-1}; 25°C; Ionic strength 0.1 mol L^{-1} (KCl); solutions of KOH as titrant).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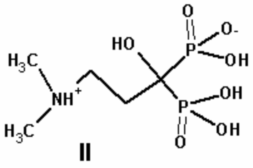
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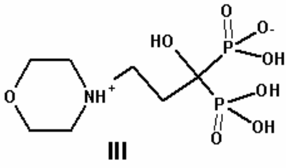
III

Micellar media of CPC solutions is practically not influence on dissociation of APDP at the first dissociation step, others dissociation constants increase in the presence of CPC micelles in comparison with aqueous media.

The Ca^{2+} ions form complexes CaL^{2-}, $CaHL^{-}$, CaH_2L with APDPA (I – III) in aqueous as well as in micellar media. The stability constants of Ca^{2+} – APDPA (II – III) decrease in the micellar media of CPC in comparison with aqueous solutions, especially for complexes with APDPA (III). Stability of complexes CaL^{2-} CaH_2L where L^{4-} is an ion of APDPA (I) is somewhat higher than in aqueous media.

DISTRIBUTION OF CATIONIC SURFACTANTS AND THEIR ASSOCIATES BETWEEN THE WATER AND NONIONIC SURFACTANT-RICH PHASES AT CLOUD POINT TEMPERATURE

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Associates formed by large organic and inorganic counterions are used for extraction and determination of many substances. Methods of determination of amines, hydrophobic organic acids and cationic surfactants based on extraction of coloured associates with dyes with subsequent photometric determination are described in the literature. The disadvantages of such methods are their labouriousness, low sensitivity and selectivity. The cloud point extraction of microcomponents by the non-ionic surfactant-rich phases is the convenient alternative of the traditional extraction with the organic solvents. Micellar extraction is characterized by increased selectivity, provides high coefficients of preconcentrating and is easily combined with different analytical methods of determination.

The regularities of the micellar extraction of cationic surfactants - alkylpyridinium chlorides with n=10-16, and their associates with dodecylsulphate-anion into the surfactant-rich phases of the non-ionic surfactant OP-7 were investigated in the work. Individual cationic surfactants are extracted into the micellar phase in a wide range of acidity. Thus, in the optimum conditions (pH=7,5) the maximum of the extraction degree (R>99%) of cationic surfactants is observed for dodecylpyridinium chloride with n=12. The increase and decrease of the hydrocarbon chain length of cationic surfactants reduces the efficiency of the extraction of substrate into the micellar phase. From another hand the most effective extraction of associates of cationic surfactants with dodecylsulphate-anion is observed for three- and tetradecylpyridiniums with n=13, 14 (pH 2,5-7,2 and 4,5-8 respectively). Such character of distribution of individual cationic surfactants and their associates is explained in the work by appearance of the “host-guest” phenomenon, which is typical for surfactant based organized media, and the lyophilic compliance between substrate and surfactant-rich phase for the optimal extraction systems.

On the basis of data obtained recommendations for creation of the conditions for extraction of cationic surfactants and their spectrophotometrical determination with Mo-brompirogallol red complex were suggested.

SURFACE TENSION OF POTASSIUM PHOSPHOTUNGSTATE MELTS

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For optimization of refractory metals electrolytic deposition from molten salt comprehensive knowledge about the physical properties of melts is required. The KF–KPO_3–WO_3 melts are found to be suitable for electrodeposition of W [1]. However, properties (e.g. conductivity, surface tension, etc.) of these melts were not studied that makes industrial adaptation impossible. The objective of this work is to measure the surface tension for the melts of the binary KPO_3–WO_3 system as the KF–KPO_3–WO_3 system constituent. The liquidus temperatures of the $(1–x)KPO_3+xWO_3$ mixtures with molar content x = 0-0.60 were determined by differential thermal analysis. Two compounds: $K_2WO_2P_2O_7$ and $KPO_3{\cdot}2WO_3$, two eutectics located at x = 0.16 (965K) and at x = 0.47 (956K), and dystectics at x = 0.53 (1022K) were determined in the KPO_3-WO_3 system according to DTA, X-ray diffraction and microstructure analysis. Polymorphic transformations in the KPO_3 and $KPO_3{\cdot}2WO_3$ were found at 723K and 823K, respectively. $K_2WO_2P_2O_7$ melts congruently at 1023±5 K with Δ_mH = 11.85 kJ mol^{-1}. $KPO_3 \cdot 2WO_3$ melts incongruently at 1022±10K. The surface tension of the $(1–x)KPO_3 + xWO_3$ melts with x = 0-0.5 was measured by interfacial tensiometry from temperature 10-20 K above melting up to 1373K. Obtained data for pure KPO_3 were fitted by a linear dependence *vs.* temperature and compared with literature data. The surface tension of the $(1–x)KPO_3 + xWO_3$ melts was found to be decreased non-monotonously with decreasing WO_3/KPO_3 ratio. Two broad bends at x~0.16 and x~0.33 were observed on the surface tension concentration dependence. These bends correspond to the eutectic and dystectics, the last refers to formation of $K_2WO_2P_2O_7$. Temperature factor affects significantly the melts reducing the surface-tension. The temperature coefficient of surface tension for the melts reaches $(0.01–0.06){\cdot}10^{-4}$ mN/m K. Equations describing T_{liq}, temperature and concentration dependences of the surface tension of these melts were proposed.

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STATISTICAL THERMODYNAMICS OF MODEL POLAR LIQUIDS AND THEIR MIXTURES

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For the description of liquids with electric multipole interaction between particles in works [1,2] proposed model of the hindered rotation of molecules. In this model the liquid represents as a "macromolecular ball" – quasi-one-dimensional chain of the molecules connected among themselves by electrostatic forces. The opportunity of "one-dimensional" representation of a liquid is caused by anisotropy of multipole potentials – presence of the picked out direction in which intermolecular potential has a minimal value. Thermodynamic functions of liquids are received in approaches of interaction of the nearest neighbors in which statistical sum of the chain is expressed through statistical sum of pair of nearest particles in liquid.

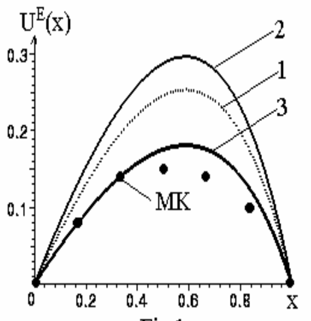

Fig.1

Within the framework of this model the approximate analytical expressions for thermodynamic and dielectric functions of model liquids dipolar (DHS), quadrupolar and a dipole-quadrupolar hard spheres are received and are in a good agreement with machine experiment data.

For example, internal energy of DHS liquid are:

$$\beta U_d/N = 1 - z\coth(z),$$

where $\beta = 1/kT$; d – dipole moment; $\rho = N/V$ – density of liquid and

$z = 2\beta d^2\rho$ – dimensionless interaction parameter.

Application of this model for the description of thermodynamics of DHS mixtures demands take into account interaction with next nearest neighbors. These interactions represent “packing effects” in liquids and are responsible for deviations from approach of a casual mixture.

In fig. 1 we present concentration dependence of excess internal energy of mixture of DHS differing in size ($\sigma_2/\sigma_1 = 1.26$) and dipole moments ($d_2/d_1 = 1.09$). Curves 1 and 2 – first and second approximation of the model of hindered rotation of molecules in a “casual mixture” approximation and curve 3 – at the account of packing effects; points (MK) – the data of Monte-Carlo method [3].

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HYDROPHOBICITY-RETENTION AND RETENTION-HYDROPHOBICITY RELATIONSHIPS IN MICELLAR LIQUID CHROMATOGRAPHY

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Owing to lack of generally accepted methodology, the retention-hydrophobicity relationships in liquid chromatography are constructed on the basis of physical-chemical models as well as by using of empirical equations. However, disembodied data do not allow recognizing clearly the advantages of one of the approaches.

In this work the quality of modeling of retention-hydrophobicity relationships was tested on the unified experimental data. It was observed that composition of mobile phase influence considerably on quality of retention-hydrophobicity relationships. As a result it is necessary to search unified method for estimation of hydrophobicity by micellar liquid chromatography.

Systematic investigation of influence of mobile phase composition on quality of relationships between k/log k and log K_{ow} for parabens (log K_{ow} from 1.96 to 3.57) leads to consequence of inadequacy of both models.

Parameters of Arunyanart and Cline-Love model (binding constants of analytes by micelles in mobile phase) are calculated with high uncertainty and as sequence could not provide high quality of modeling. Parameters of another physical-chemical model that based on quasi-chemical model of micelle formation have been used for derivation of new model for hydrophobicity estimation. However, quality of new model could not be evaluated on the basis of available data.

At present time more universal and adequate is a methodology of hydrophobicity evaluation that based on the using of relationships between log k_{mw} and log K_{ow}, where log k_{mw} is obtained by extrapolation of logarithm of retention factor on zero concentrations of surfactant and organic modifier in micellar eluent.

It was demonstrated that the deviations from linearity for first members of homologous series or congeneric substances is nonrandom. Thus, it is appropriate using of micellar liquid chromatography for estimation of hydrophobicity of compounds with log K_{ow} not less than 3.

SOLUBILITY AND FLUORESCENCE LIFETIME OF 2,5-DIPHENYLOXAZOLE AND 1,4-BIS(5-PHENYL-OXAZOLYL-2) BENZENE IN WATER-ETHANOL AND WATER-ACETONE SOLVENT SYSTEMS

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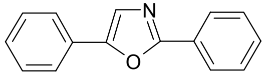
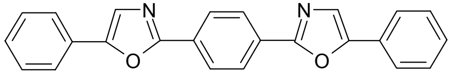
The solubility and the excited state lifetimes of 2,5-diphenyl-1,3-oxazole (PPO) and 1,4-bis(5-phenyl-oxazolyl-2) benzene (POPOP) luminophores have been studied in mixed water-acetone and water-ethanol solvent systems at 298.15 K.



2,5-diphenyl-1,3-oxazole (PPO)



1,4-bis(5-phenyl-oxazolyl-2) benzene (POPOP)

The solubility (s) of PPO increases from 7.50×10^{-6} mol/l in water to 6.08×10^{-1} in ethanol and to 2.17 mol/l in acetone. The s values of POPOP vary from 4.02×10^{-8} mol/l in water to 1.44×10^{-4} mol/l and 1.77×10^{-3} mol/l in ethanol and acetone respectively. It has been found that the most expressed changes in solubility occur at the very first additions of an organic solvent to water. If molar fraction of cosolvent is more than 0.3, the further change in solubility is much less significant. The lifetimes (τ) of PPO and POPOP excited state range from 1.75 to 1.03 nanoseconds. The τ values smoothly decreases with organic solvent mole fraction.

According to the linear solvation energy relationships (LSER), the experimentally measured solvent-dependent quantity (Y) can be represented as a function of solvent properties:

$$Y = Y_o + A_1 \delta_H^2 + A_2 E_T^N + A_3 \frac{n^2 - 1}{n^2 + 2} + A_4 \frac{\varepsilon - 1}{2\varepsilon + 1} \qquad (1)$$

where Y_o is the value of Y in inert solvent, δ_H^2 is square of Hildebrand solubility parameter, E_T^N – is the normalized Reichardt's parameter, n – refractive index, ε – solvent dielectric constant; $A_1..A_4$ – correlation coefficients. The multiparameter correlation analysis has been carried out in accordance with equation (1). The Gibbs energy of dissolution ($\Delta G_S = -RT \ln s$) and the value of $\ln(1/\tau)$ have been used as Y quantity. It has been revealed that ΔG_S values of PPO and POPOP in each solvent systems are in good correlation with solvent properties, but the correlation becomes better if points for pure water are excluded. Hildebrand solubility parameter is found to be the principal parameter that determine solubility. The analysis of data for both luminophores solubility in each solvent systems shows that correlation decreases in comparison with single solute but remains satisfactory, while the integrated data for both luminofores and solvent systems is characterized by a lack of correlation. The result of solution of the equation (1) for the $\ln(1/\tau)$ dependence on solvents properties shows good correlation for POPOP, while for PPO correlation is not satisfactorily.

CONDUCTIVITY AND INTERPARTICLE INTERACTIONS IN SOLUTIONS OF Bu_4NBr IN ACETONITRILE

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The tetraalkylammonium salts solutions in acetonitrile (AN) are widely used as electrolytes for supercapacitors. For such application the possibly highest conductivity of electrolyte solution is needed. But literature survey shows that an existing theoretical basis is too poor in adequate prediction of the properties of these solutions in a wide concentration range.

In this work the results of conductometric investigations of Bu_4NBr in AN at temperatures 278.15, 288.15, 298.15, 308.15, 318.15K over the concentration range from $2 \cdot 10^{-4}$ up to 0.9 mol/dm^3 are presented.

The concentration interval was divided into three parts: dilute, moderate and highly concentrated once. It was established that Lee-Wheaton equation describes well conductance of investigated solutions up to $5 \cdot 10^{-3}$ mol/dm^3 (dilute region). At moderate concentrations ($5 \cdot 10^{-3}$ – $2 \cdot 10^{-1}$ mol/dm^3) the best results in treatment of conductance data of Bu_4NBr in AN was obtained by using quasilattice theory of electrolyte solutions [1]. The values of limit molar conductivity obtained by using quasilattice model equation for moderately concentrated solutions are agreed with ones obtained by using Lee-Wheaton equation in the dilute solutions. It was determined that moderately concentrated and dilute solutions are characterized by small association. Unfortunately, for the mean time there is no adequate model for description of conductivity of highly concentrated solutions.

On the basis of the present investigation an idea how to expand the quasilattice model for concentrated solutions was formulated.

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NITROGEN MOLECULE DISSOCIATION IN THE COUPLED CLUSTER THEORY

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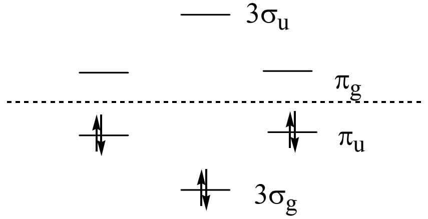
Dissociation of the triple bond (especially in the case of the nitrogen molecule) is one of difficult tasks in quantum chemistry. So called *non-variational collapse* at stretched internuclear distances is observed in the perturbation theory and standard coupled cluster (CC) approaches. Essential interest in this problem is connected with an extension of the CC theory by inclusion of higher excitations in someway. In our recent works we have considered and tested so called CASCCSD approach. The goal of the present work is comparison of the CASCCSD results for the nitrogen molecule with the results of other recently developed theoretical approaches (CR-CCSD(TQ), MMCC, QECCSD, RMR-CCSD *etc.*)

The CASCCSD wave function as applied to the nitrogen molecule dissociation problem takes the following form:

$$\left|\Psi_{CAS(6,6)CCSD}\right\rangle = \exp(\hat{T}_1+\hat{T}_2)\left(1+\hat{C}_1+...+\hat{C}_6\right)\left|0\right\rangle \quad (1)$$

Here the operators $\hat{C}_1,...,\hat{C}_6$ generate the *reference function* by acting on the “formal reference determinant” $\left|0\right\rangle$. The reference function is a superposition of determinants, which guarantees qualitatively correct description of dissociation. All reference determinants arise by distribution of six electrons among six orbitals (active space). The scheme of active orbital occupation in the formal reference determinant $\left|0\right\rangle$ is:



The operators $\hat{T}_1$, $\hat{T}_2$ generate a superposition of the one- and two- particle excitations from *all reference* determinants. Such excitations can be interpreted as higher order excitations from $\left|0\right\rangle$. Useful detailed information about the structure of the wave function (1) has been obtained by analysis of CI coefficients of the most important configurations:

$$\left\langle \begin{matrix} a_1a_2...a_k \\ i_1i_2\,...\,i_k \end{matrix} \middle| \Psi_{CAS(6,6)CCSD} \right\rangle, \quad (2)$$

where $\left\langle \begin{matrix} a_1a_2...a_k \\ i_1i_2\,...\,i_k \end{matrix} \right|$ – k-electron excited determinant. Corresponding total weights of all k-electron excited configurations were calculated in the following way:

$$W_k = \sum_{\substack{i_1>i_2>...>i_k \\ a_1>a_2>...>a_k}} \left| \left\langle \begin{matrix} a_1a_2...a_k \\ i_1i_2...i_k \end{matrix} \middle| \Psi_{CAS(6,6)CCSD} \right\rangle \right|^2 \quad (3)$$

Appropriate diagrammatic representation of the CC equations and the computer code capable for *parallel execution* have been derived automatically using our program package CLUSTER.

The calculations were performed in different basis sets and compared with the full configuration interaction (FCI) results. Mean deviation of CAS(6,6)CCSD results from FCI along the entire potential energy curve (PEC) is 0.66 mHartree (mH) for DZV basis set and 1.81 mH for the cc-pVDZ. In order to evaluate the similarity of the FCI PEC and PEC obtained with CAS(6,6)CCSD method the “non-parallelity” indices were calculated. The structure of the wave function (1) at different internuclear separations has been studied. For example at R = 8 a.u. (triple zeta basis set) the reference function is:

$$\left|\mathrm{Ref}\right\rangle \approx \left|0\right\rangle - 0.977\left|\begin{matrix}3\sigma_u 3\sigma_u\\ 3\sigma_g 3\sigma_g\end{matrix}\right\rangle - 0.997\left|\begin{matrix}3\sigma_u 3\sigma_u\\ 3\sigma_g 3\sigma_g\end{matrix}\right\rangle + 0.994\left|\begin{matrix}\pi_g\pi_g\pi_g\pi_g\\ \pi_u\pi_u\pi_u\pi_u\end{matrix}\right\rangle \tag{4}$$
$$+ 0.974\left|\begin{matrix}\pi_g\pi_g 3\sigma_u 3\sigma_u\\ 3\sigma_g 3\sigma_g \pi_u\pi_u\end{matrix}\right\rangle - 0.971\left|\begin{matrix}\pi_g\pi_g\pi_g\pi_g 3\sigma_u 3\sigma_u\\ 3\sigma_g 3\sigma_g \pi_u\pi_u\pi_u\pi_u\end{matrix}\right\rangle$$

Corresponding excitations from (4) give noticeably smaller contributions to the wave function. For example, among the most important one-electron excitations from the reference there are the following excitations from $\left|0\right\rangle$:

$$....0.121\left|\begin{matrix}(20)\\ 3\sigma_g\end{matrix}\right\rangle - 0.112\left|\begin{matrix}\pi_g\pi_g(21)\\ 3\sigma_g\pi_u\pi_u\end{matrix}\right\rangle + 0.119\left|\begin{matrix}\pi_g\pi_g\pi_g\pi_g(20)\\ 3\sigma_g\pi_u\pi_u\pi_u\pi_u\end{matrix}\right\rangle + ...$$

(the number of orbital outside the active space is shown in the parentheses).

The authors would like to thank the Alumni Association of Karazin Kharkiv National University for partial support of this work.

THE INFLUENSION OF PHYSICAL AND CHEMICAL CONDITIONS ON THE CHROMATHOGRAPHYC DETERMINATION OF DERIVATES OF HYDROPHILIC ORGANIC COMPOUNDS

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The wide spread of organic compounds use in industry and agriculture resulted in global problems connected with their remnants extraction from food, agricultural lands, environment.

The pesticides and herbicides and their remnants could be toxic for human, animals and plants. It is necessary to clean the surroundings of human and animals from residues of the chemicals.

The literature analysis provides the data about the pesticides destruction with development of chloramine, one atoms phenols, substituted indoles etc.

Direct estimation of these compounds has several methodological problems.

In this work we suggest to use of some derivate reactions for better estimation of the residues of pesticides and herbicides. The п-nitrodiazophenile was used as reagent.

The reaction of the reagent with prime amines resulted in development of triazenes.

The indole and its derivates provide the reaction of azolinking in position 1 with development of diazocompounds. Phenoles and their derivates develop diazocompounds with this reagent also, however joining take place mainly in the para-position to OH-group.

The effect of media pH on reaction was studied. The development of azoderivates of phenols is better in slightly alkaline and creation of amines is better in acidic media. The maximum of the derivates yield was observed at 10 – 20 fold excess of diazonium cations. The kinetics of the reactions is studied. The optimum time of derivates production is from 20 to 60 min. The obtained compounds are well extracted by chloroform and dichlormethane. Some of them, particularly, azoderivates of 1-naphtylamine, indole, o-cresole are well soluble in diethyl ether. The compounds were isolated separately from the reaction mixture. The method of the IR-spectrometry revealed the –N=N- and =NH groups. The active proton presence in =NH group of triazenes was proved by the method of spectrophotometry (the change of the absorption spectra in dependence from the solution pH). The dissociation constants of the protone (pK_a) were estimated in the range 8-10. The absorption spectra of the molecular and anionic forms of triazenes were obtained and molar coefficients (ε) of absorption were calculated in different solutions.

The analytical HPLC studies were carried out on “Perkin-Elmer” chromatograph coupled with spectrophotometric detector by isocratic elution. The stainless steel column 25 × 4.6 mm was filed by “Silasorb C18”. The elution agent was the mixture of CH_3CH + 0,05 M KH_2PO_4, v/v = 2:1. The velocity of elution agent flow was 1-1,2 ml/min.

The dependence of height and area of the chromathographic peack from the concentration of derivate is studied. This dependence is linear in the range of 0.1 – 10 μg/ml.

The methods for the determination of some pesticides residues in sewage and soils were developed on the basis of this study.

EFFECT OF OLEFINS ON CATALYTIC DECOMPOSITION OF *TRET*-BUTYL HYDROPEROXIDE

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Organic hydroperoxides are valuable intermediates and in some case are final products of many chemical and biological oxidation processes. Hydroperoxides are useful reagents both as oxidants for catalytic processes and as radical-chain initiators in catalytic autooxidations and polymerization processes. Therefore investigation of reactions of hydroperoxide especially reaction of decomposition and oxidation are very actual and important.

The main aim of this work is investigation of the effect of concentration and nature of unsaturated compounds containing a double bond, 1-octene and cyclooctene, on the reaction of *tert*-butyl hydroperoxide (TBHP) decomposition in the presence of molybdenum disilicides $MoSi_2$.

The addition of olefins in low concentration into the reaction system of catalytic decomposition process containing TBHP, solvent and catalyst results in the decrease of the rate of hydroperoxide consumption. It indicates the inhibitory effect of olefin at its low concentrations on the decomposition of TBHP. The higher olefin content in the reaction mixture leads to increase of the process rate. In the case of cyclooctene the minimum value of hydroperoxide consumption rate is observed at lower olefin concentration than for 1-octene.

The investigated catalytic process of hydroperoxide consumption in the presence of olefins in the reaction mixture involves two competitive catalytic reactions: TBHP decomposition and olefin epoxidation by TBHP. At the higher olefins concentration increasing of the rate of hydroperoxide consumption is connected with increase of contribution of catalytic interaction between olefin and hydroperoxide with epoxide formation.

On the base of obtained results the kinetic scheme of process is proposed which includes the formation of intermediates: catalyst–hydroperoxide complex in *tert*-butyl hydroperoxide decomposition reaction and catalyst–olefin complex in olefins epoxidation process. The rate equation is obtained and kinetic parameters of process are determined.

The work is supported by the Ukrainian Fundamental Researches State Fund.

A ROLE OF SILANOL GROUPS IN SORPTION PROCESSES ON SILICA SURFACES

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High-disperse silica surface contains both free (non-bonded) and hydrogen-bonded silanol groups. The first type of them shows a narrow intensive absorbance band with a maximum at 3750 cm^{-1}, yielding wider absorbance bands at 3680 and 3550 cm^{-1}.

The question on the participation of silanol groups in the processes of adsorption and chemisorption on high-disperse silica surface is still of great interest.

The interaction of hexamethyldisilazane (HMDS) with high-disperse silica surface was studied by IR spectroscopy method. The absorbance bands of both types of silanol groups were obtained due to graphical decomposition of IR spectra.

The intensity of absorbance band at 3750 cm^{-1} was found to reduce as a result of interaction between HMDS and silica surface, the rest absorbance bands remaining unchanged. This is an evidence of participation of free silanol groups in chemical reaction with HMDS. Another types of silanol groups do not participate in processes of chemisorption.

Earlier we studied the interaction of polyvinylpyrrolidone (PVP) with silica surface. Free silanol groups were shown to play the main role in adsorption processes such as interaction with water-soluble polymers. Adsorption of poly(vinylpyrrolidone) on high-disperse silica surface occurs with formation of hydrogen bounds between carbonilyc oxygen atoms of macromolecules and hydrogen atoms of free silanol groups of silica surface. The absorbance band with a maximum at 3750 cm^{-1} is shifted to the region of lower frequency for 400 cm^{-1} as a result of polymer adsorption. The relative bonding energy is about 48 kJ/mol. Absorbance bands corresponding to silanol groups forming mutual hydrogen bond (3680 и 3550 cm^{-1}) remained unchanged.

Partial substitution of trimethylsilyl groups for silanol ones as a result of interaction of HMDS with silica surface was found to effect on the accessibility of surface OH groups to polymer macromolecules. That is caused by the structural particularities of polymer adsorption layer on silica surface.

ELECTROCHEMICAL REFINING OF COBALT TO HIGH PURITY

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In the present work some approaches were used to improve the effectiveness of electrochemical refining as a cobalt purification method. Such approaches were: choice of the optimal electrolyte composition and electrolysis conditions on the basis of investigations of electrode processes, application of the reactive electrolysis method, development and use of a system for the deep purification of electrolyte and creation of most suitable electrolyzer.

The investigations carried out showed that halide electrolytes are better suitable for obtaining high purity cobalt than sulfate ones because cobalt free from sulfur can be extracted from halide electrolytes at higher current density and with higher current efficiency.

The method of reactive electrolysis is based on using crude metal alloyed with certain additives, generally nonmetals, forming in crude metal matrix strong, electrochemically inactive compounds, preferably with impurities. By this way impurities are removed from electrolysis process and concentrated in anode slime.

For deep continuous purification of the electrolyte we used a two-step system, including cementation of more electropositive impurities on crushed high purity cobalt and sorptive extraction of remaining impurities by means of specially developed sorbents. The sorbents consisted of synthetic activated carbon used as a carrier and organic reagents immobilized on the carbon surface. Chosen organic reagents selectively form strong, as a rule, chelate complexes with impurity cations in a certain interval of electrolyte pH-value. It was found that a series of columns filled with sorbents containing different complexing reagents allow one to extract many impurities from electrolyte solution.

By electrochemical refining using the above approaches, the cobalt with a total percentage of 14 controlled impurities of $1.38{\cdot}10^{-4}$ % was obtained.

The electrolyzer used was made from acrylic plastic. Its anode and cathode chambers were separated by an anion-exchange membrane. The electrolyte continuously circulates between the anode chamber, electrolyte purification compartment and cathode chamber.

ELECTROCHEMICAL PRODUCTION OF HIGH PURITY MANGANESE

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High purity manganese is a promising material for the production of semimagnetic semiconductors such as $Cd_{1-x}Mn_xTe$, $Cd_{1-x}Mn_xSe$, $MnGa_2Se_4$, magneto-optic ($Zn_{1-x}Mn_xTe$, $Hg_{1-x}Mn_xTe$, etc.) and other valuable materials. For production of a high purity metal the more practical is the electrochemical method. This work is devoted to increasing the efficiency of the method.

The purity of manganese-containing electrolyte is one of the determining factors in the process of high purity metal production. For impurity extraction from solutions sorbents based on of synthetic activated carbons with immobilized on their surface organic reagents were developed. Such sorbents allow selective extraction of impurity metal ions due to formation by the latter of strong complex compounds with organic ligands.

For choosing the optimal conditions of electrolysis, the laws governing joint discharge and ionization of manganese and accompanying impurities have been studied. Based on the results obtained the electrolysis conditions: pH, temperature, current density were chosen. Thus, the carrying out of the process at high cathode current density, which is possible in halide electrolytes, allows one to significantly reduce impurity amount in the cathode deposit as the impurity ion discharge takes place, as a rule, at the limit diffusion current.

The results of investigation of kinetics and mechanism of manganese discharge and ionization in ammonium chloride, bromide and mixed electrolytes are presented; the optimal compositions of electrolytes, the metal current efficiency in which is 85 – 93 %, have been chosen.

A design of electrolyzer, in which the cathode and anode chambers are separated by an anion-exchange membrane, with continuous electrolyte circulation has been proposed.

On the basis of the investigation carried out, a technology has been developed for the production of high-purity manganese (99,99 – 99,999 %) by electrolysis.

APPLICATION OF ^{31}P NMR SPECTROSCOPY FOR STUDYING IONIC EQUILIBRIA IN SOLUTIONS OF LANTANIDE NITRATES COMPLEXES WITH PHOSPHORYL-CONTAINING LIGANDS

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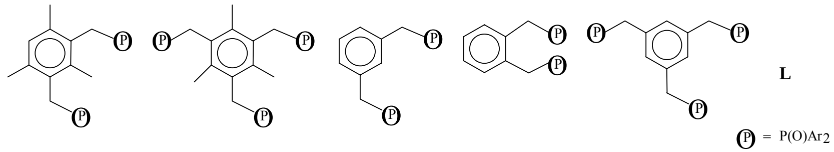
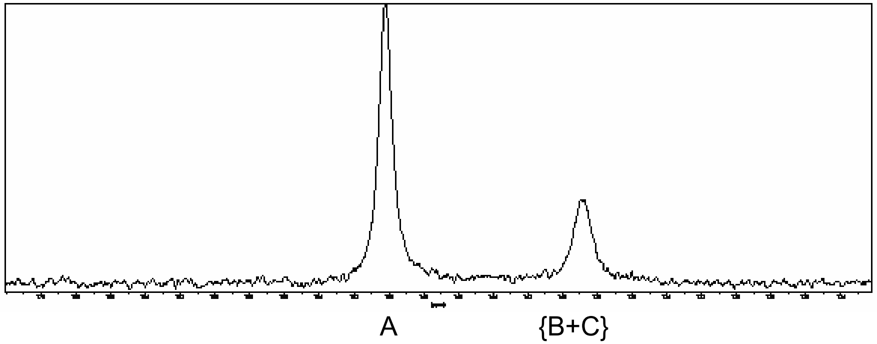
We established that ^{31}P NMR spectroscopy allows studying ionic equilibria in solutions of lanthanide nitrate complexes with phosphoryl-containing ligands (L) due to separate detection of the molecular complexes (A) and cationic species within ion pairs (B) and free ions (C). This approach is likely to have general character and practical importance for investigation of extraction processes and optimization of extraction conditions.



$$\underset{A}{[Ln(L)_n(NO_3)_3]^0} \leftrightarrow \underset{B}{[Ln(L)_n(NO_3)_2]^+ \bullet (NO_3)^-} \leftrightarrow \underset{C}{[Ln(L)_n(NO_3)_2]^+ + (NO_3)^-}$$

n = 1,2;

Ln = La, Ce, Nd, Er



Methods used in the study:

^{31}P NMR spectroscopy (including temperature evolution), IR and Raman spectroscopy, X-ray diffraction (5 structures), sedimentation analysis (MW determination), conformation analysis (molecular mechanics), conductivity measurements.

OBTAINING OF ENSEMBLES PLATINUM AND PALLADIUM NANOCRYSTALS ON SILICIUM DIOXIDE NANOPARTICLES

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Creation of new materials on the basis of nanodimensional structures is one of the actual problems of modern materials science in connection with the prospects of the wide use of such materials for infrared radiation detection, creation on the basis of them high-selective biological and chemical sensors, new high-selective catalysts.

In this work we have studied the conditions of forming heteronanoparticles like “core – shell” on the basis of silicon dioxide with the shell from metallic platinum and palladium for creation a new types of selective catalysts.

By the method of colloid synthesis in solution monodisperse spherical form nanoparticles with the diameter of spheres in the range of 40 – 500 nm has been obtained. The degree of dispersion of SiO_2 nanoparticles does not exceed 10%. The colloid Pt and Pd nanoclusters of controlled sizes (2-6 nm) have been received with small dispersion in the sizes (< 15 %).

Possibility of controlled concentration of nanoclusters on the surface of nanotemplates from silicon dioxide is shown. On the surface of nanotemplate from silicon dioxide (40, 120 and 350 nm) is formed ensembles of Pt and Pd nanocrystals in the form of isolated nanoclusters or shells with an effective thickness 2, 3, 7 nm. The concentration of nanocrystals on the surface of template enables to avoid the undesirable processes of nanoparticles agglomeration with diminishing of specific surface of catalyst and multiply probability of flowing of all stages of catalytic process.

It is experimentally demonstrated that on the surface of dielectric core from silicon dioxide polycrystalline coverage is formed from the Pt and Pd nanocrystals with face-centered structure. The nanocrystals of metal in heteronanoparticles are fastened on the dielectric core surface as clusters that stipulate their high reactionary ability.

THE PHYSICO-CHEMICAL CONFORMITIES OF A REACTION OF HIGH-MOLECULAR COMPLEX COMPOUNDS FORMATION OF METAL IONS WITH POLYMERIC FIBRES IN MIXED SOLVENTS

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Reaction of metal ions with functional groups of complex forming cross-linked polymers-complexites results in formation of high-molecular complex compounds (HMCC). This reaction proceeds in a heterogeneous system, in which case along with protolytic ion-exchange and complex formation equilibria it is accompanied by mass transfer phenomena - distribution of solvent molecules and other solvent components between phases. Thus, complexite is specific medium for reactions of HMMC formation; reactivity of functional groups, composition, stereochemistry and thermodynamical HMCC stability being dependent upon its properties. Despite the peculiarities of the systems stated the shift of chemical equilibrium in them when nature and composition of mixed solvent are changed as in analogous low-molecular systems has to do with reaction constants of formation and dissociation of complexes, differences in rates being the consequence of reagents salvation changes and reaction products. Due to the peculiarities stated above polymer matrix solvation effect in polymeric systems. This effect may be quite appreciable for matrices of fibrous nature.

In the present paper we tried to reveal the role of solvation factor when protolytic properties of complex forming polyfunctional cellulose fibre with hydroxamic acid groups and amidoxime by the reaction of HMCC formation of Cu^{2+} ions with its presence in water mixtures dimethylsulfoxide mole fraction (x) x=0,06; 0,13; 0,26; 0,48; water with methanol at x=0,19; 0,36; 0,83 and 1,0 are studied. Data of sorbtion degree by fibre and HMMC components of mixed solvent, swelling, polymers specific volume in pH 2,0-6,0 region were used as solvation characteristics; methods of pH-meter titration, microcalorimetry, refractometry being applied. Then distribution coefficients of mixed solvent components between polymer, HMCC and solvent were calculated that were used for determination of Gibbs energy of swelling (ΔG_S, kJ/mole) of the samples studied. Values of dissociation constants of polymer groups – K_0 (pK_0=-lgK_0) in mixtures were determined according to the results of potentiometric studies, Katchalsky equation being applied. Then these values were used in calculations of HMCC stability constants of the composition metal:ligand=M:L=1:1 – K_{st_1} and M:L=1:2 - $\beta_{st.}$ Hydroxamic group of fibra being ligand. Diagrams of equilibrium compositions of polymer protonised, mono- and bis- complex forms were calculated according to K_0, K_{st_1}, and β_{st}. Kinetics of complex formation reactions in mixtures was studied by the method of limited volume of a solvent. The mechanism was stated using mixed diffusion model, according to which corresponding kinetic parameters and effective diffusion coefficients of water molecules $\overline{D_{H_2O}}$ and Cu^{2+} ions $\overline{D_{Cu^{2+}}}$ in a polymer were calculated. The experimental results obtained allowed to give the following generalizations:

1. The increase of K_0 values with the increase of mole fraction of mixtures non-aqueous component coincides with the sorbtion degree of non-aqueous solvent by a fibre and is accompanied by the decrease of

polymer specific volume, its swelling, $\overline{D_{H_2O}}$ value. Polymer ΔG_S dependence upon the reverse value of solvent dielectric permeability ($1/\varepsilon$) is non-linear. This testifies to the predominant influence of solvation effects upon protolytic properties of complex forming fibries.

2. HMCC formation in the range of pH 2,0-6,0 in mixtures with dimethylsulfoxide (x=0,06; 0,13) and with methanol (x=0,19; 0,36) is accompanied predominantly by sorbtion of water molecules with polymer (pH 3,5-5,5). Maximum sorbtion of non-aqueous component of a mixture occurs at x=0,26, 0,48 of dimethylsulfoxide and at 0,83; 1,0 of methanol (pH 2,0-6,0). Sorbtion rate of metal ion in water, mixtures, water molecules and non-aqueous solvent decreases sharply with the increase of its composition on the boundary of pH 3,0-3,5 values. Accordingly, swelling, $\overline{D_{H_2O}}$, and $\overline{D_{Cu^{2+}}}$ values decrease in fibre. $\overline{D_{H_2O}}$, and $\overline{D_{Cu^{2+}}}$ values are quite comparable in mixtures, but they are essentially less than analogous values in the polymer-aqueous solution-metal salt system. ΔG_S values are <0 in a polymer and HMCC. Their values are lower in HMCC and become less negative or change their sign when non-aqueous component composition is high, e.g., when x=0,83 and x=1,0 of methanol. This may be due to differences between the energy of specific reagents solvation, reaction products and strength of mixed solvent H-bonds that increase with x growth.

3. Mono- and biscomplexes of Cu^{2+} with fibre are formed both in aqueous medium and in mixtures. Maximum monocomplexes composition corresponds to pH ranges with minimum concentration of polymer protonized forms. The character of the dependencies of $\lg K_{st_1}$, $\lg\beta_{st}$.and ($\lg\beta_{st}$-$\lg K_{st_1}$) – the second stage of complex formation of $\lg[H_2O]$ excludes the effect of the dilution factor, and non-linearity of isotherms of $\lg K_{st_1}$, $\lg\beta_{st}=f(1/\varepsilon)$ dependencies is indication of solvation effects influence upon formation and reconstruction of HMCC coordination sphere when molecules of non-aqueous component that create definite medium in a fibre at the expense of their concentration by a polymer at selective sorbtion participate.

4. Mixed diffusion mechanism of complex formation kinetics is characterized by increasing contribution of inner diffusion with the increase of x in mixtures. This is linked with the development of chemical stage that is a two-stage one owing to the formation of mono- and biscomplexes. Analysis of kinetic characteristics, rate, $\overline{D_{H_2O}}$, $\overline{D_{Cu^{2+}}}$, sorbtion degree at pH 2,0-6,0 range in different stages of the reaction, equilibrium parameters being accounted, suggests that HMCC thermodynamical stability is determined by the rate of exchange of mixed solvent non-aqueous component between polymer phase and solution.

PHISICOCHEMICAL INVESTIGATION OF IRON-YTTRIUM GARNET SOLUTIONS IN THE PbO-B_2O_3-BaO-BaF_2 MELT

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The solutions-melts on the basis of solvent PbO-B_2O_3-BaO-BaF_2 can be used for obtaining of single crystal films of ferrite-garnets on the gadolinium-gallium garnet substrate by the method of liquid phase epitaxy with application of the solution-melt moistening film technology. Solutions of the garnet-forming oxides and iron-yttrium garnet in this solvent were studied.

The basic physicochemical properties of iron-yttrium garnet solutions-melts were studied experimentally. It was found that at temperature range 1050-1350K the dependencies of viscosity, surface tension and the density on temperature are symbate. The values of these parameters are decreased with increasing temperature and are increased with growing garnet concentration under isothermal conditions. The values of conductance of studied solutions-melts allow to refer them to systems with ionic structure, where basic carriers of charges are the ionic products of dissociation of solvent and ionic oxygen complex of iron and yttrium. The interrelations of viscosity, specific volume and conductance of melts were investigated. Temperature and concentration range for obtaining film and bulk single crystals of the ferrite-garnet were defined.

The restricted pseudo-binary phase diagrams of systems consisting from solvent PbO-B_2O_3-BaO-BaF_2 and yttrium oxide, iron(III) oxide and iron-yttrium garnet were built. At studied temperature and concentration range the pseudo-binary solutions-melts are represented as simple eutectic systems. The main products of the solution-melt crystallization were identified by the Roentgen phase analysis. In garnet solutions-melts the basic product of crystallization is iron-yttrium garnet. The calculated values of iron-yttrium garnet elementary lattice cell parameters have the good agreement with the literature data. At crystallization of iron oxide solutions-melts the single crystals of hexaferrite with composition $Ba_{1-x}Pb_x Fe_{12}O_{19}$ were obtained.

Enthalpies and entropies of melting of solvent and garnet-forming oxides in solutions-melts on the basis PbO-B_2O_3-BaO-BaF_2 were calculated. The cryoscopic analysis of the phase diagrams was fulfilled.

PROTONATION CONSTANTS INVERSION IN 4',4''-BIS-(DIMETYLAMINO)-DIFLAVONOL IN EXCITED STATE

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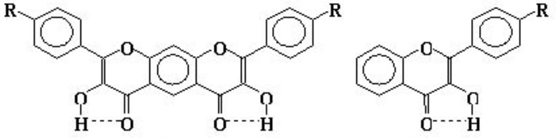
As it was shown earlier [1] diflavonols have symmetrical electronic structure in the ground state. Under light excitation, these molecules undergo asymmetrical electron density redistribution, which leads to asymmetrical intramolecular charge (ICT) and proton transfer. Driving force of excited state intramolecular proton transfer (ESIPT) is difference in changes of acid-base properties of *ortho*-oxycarbonilic fragments of the molecule under excitation. That is why, the investigation of acid-base properties of presented objects is important to understand proton transfer mechanism.



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Diflavonols (Scheme 1) are perspective dyes for design of fluorescent probes which may be used in biological objects study.

Scheme 1. Structures of diflavonols (***1***) and flavonols (***2***): ***a*** – R = H, ***b*** – R = $N(CH_3)_2$.

Present work is devoted to study of *1b* protonation in the ground and excited states. As *1b* has four centers of protonation, compounds *1a* and *2a-2b* were used as models.

Basicity constants of all compounds were calculated using results of spectrophotometric titrations. It was also estimated excited state protonation constants using Förster method.

Analysis of the obtained values for *1b* showed that the consequence of the protonation constants in the ground state is $K_{b1(N)} > K_{b2(N)} > K_{b1(O)} > K_{b2(O)}$. In the excited state, the inversion of this consequence takes place. It was found to be $K_{b2(N)} > K_{b1(O)} > K_{b1(N)} > K_{b2(O)}$. These results demonstrate another order of protonation of the basic centers upon excitation.

Based on analysis of spectral parameters of the model compounds and quantum chemical calculations of their optimazed geometries, the conclusions about protonation consequence and structure of *1b* protolytic forms were made.

Reference:

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KINETIC RESEARCH OF THERMAL DECOMPOSITION OF PRIMARY– TERTIARY PEROXIDE GROUPS IN OCTEN–CO-MALEIC ANHYDRIDE-CO-TERT-BUTYLPEROXYMETHYLMALEATE

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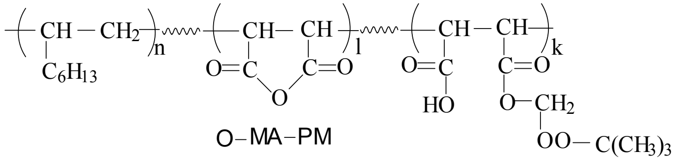
One of the efficient ways to create new composite materials is the interface modification of colloidal systems. Polymer surface modification was carried out via its activation and further radical and polymeranalogic reactions at the interface. The interface could be activated by γ-and IR - rays, ozonation, plazma treatment, different reactants.

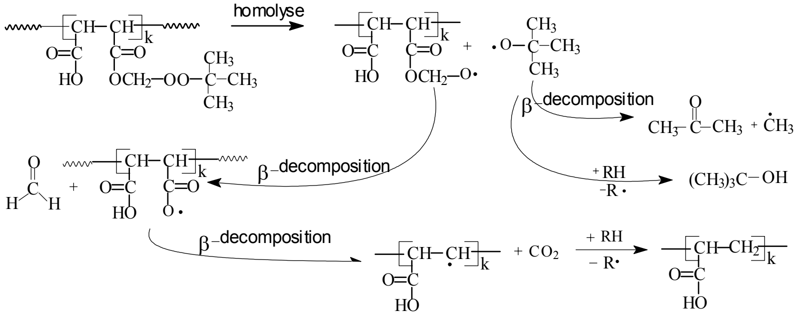
Perspective way of polymer surface modification is grafting of heterofunctional polymers and oligomers containing peroxide fragments to it. Such polyperoxides with thermal stable ditertial peroxide fragments were used for the compatibilization of polymer mixtures, for the modification of polyolefin surface in order to made them hemocompatible and antibacterial, and to get core - shell latex polymer [1]. The synthesis of polyperoxides with primary - tertiary peroxide fragments and their application for interface modification are also of great interrest. Primary – tertial peroxide fragments have lower thermal stability than of the known ditertial ones. This gives us the opportunity to modify polymer surfaces at 333 - 393K.

For application of heterofunctional polymers as interface modifiers we shoud have information about their thermal stability, mechanism and kinetic parameters of thermolysis.

In this report the result of kinetic research of thermal decomposition of primary-tertial peroxide fragments in copolymer octen-co-maleic anhydride-co-tert-butylperoxymethylmaleate (O-MA-PM), which has the following structure:


O–MA–PM

Thermal decomposition of polyperoxide was carried out in dioxane solution and in inert atmosphere with the presense of ionol. The ionol guantity was equvivalent to the quantity of peroxide fragments in O-MA-PM. Thermolysis low-molecular products were determined by gaseous-liquid chromatography. According to the analysis of the low-molecular thermolysis products the following decomposition scheme was proposed:



The kinetics of O-MA-PM thermolysis was controlled by measuring quantity of low-molecular thermolysis products: propanon and 2-methyl-2-propanol. The linear character of half-logarithm anamorphoses confirm monomolecular peroxide decomposition at the experimental conditions and allows to determine the decomposition rate constants. From Arrhenius plot the decomposition activation parameters of prime - tertiary peroxide fragments were calculated: activation energy (E_a) 127 kJ/mol and the coefficient A - 1,6•1013. This values are related to the analogical parameters of tert-butylperoxymethanol in the cumene solution with the concentration 1,2•10-3 mol/l (E_a = 134 kJ/mol, A = 6,3•1013)[2]. Thus thermolysis kinetic parameters of tert-butylperoxide fragments in the structure of copolymer O-MA-PM are similar to decomposition kinetic parameters of low-molecular tert-butylperoxymethanol.

References.

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ELECTROCHEMICAL SYNTHESIS OF CATALYTIC ACTIVE ALLOYS

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Development of the electronic techniques, the PC and communication systems production requires the improvement of coating deposition technologies. Deficiency of noble metals in Ukraine has caused necessity of their replacement with alloys. Increase of reliability, accuracy and universality of technical devices toughens requirements to galvanic coatings; therefore the problem of their controlled synthesis is an actual. Electrochemical synthesized composite materials with catalytic properties allow replacing both noble metals and alloys. The decision of the given problem is impossible only by new electrolytes elaboration. Therefore, electrochemical deposition of coatings in non-stationary modes is one of the most effective methods. Use of a pulse and nonsymmetrical electrolysis modes is capable to provide an opportunity for efficient control of content, structure, physical-mechanical properties, corrosion resistance and catalytic activity of metal and composite coatings. Non-stationary electrolysis also allows intensifying deposition process, to simplify and optimize electrolyte composition. Application of the program electrochemical updating of the worn out details sizes allows to receive coatings with the set properties and considerably to speed up process.

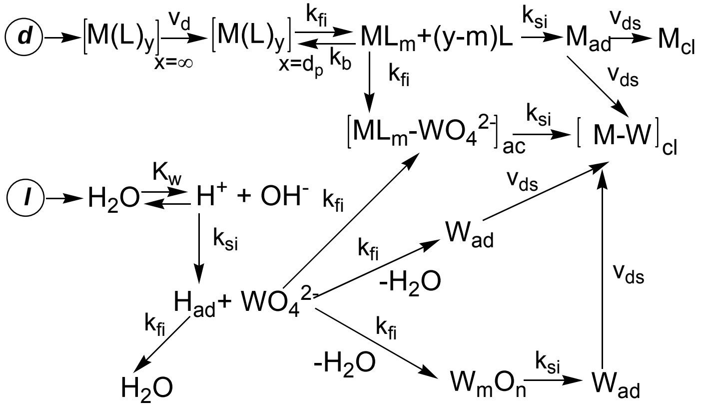
New electrode and catalytic materials development requires formation of a roughness surface (for a catalytic neutralization of gas emissions, surface pretreatment before a coating deposition, high porosity constructional materials, filtering membranes etc). That demands application of methods of the previous form-building processing.

Increase in a catalytic activity of alloys is possible to expect in application of metals with vacant d-shells (IV-VI groups) and d-metals (VIII group) with significant amount filled d-shells. The nickel alloys with W, Fe, Cu, Co, Pd etc electrochemical formation mechanism was investigated and the processes kinetic parameters were determined. Ionic equilibrium in the electrolytes based on the Pd(II)-$P_2O_7^{4-}$ and Pd(II)-$P_2O_7^{4-}$-NH_3 systems was investigated. The pyrophosphate and mixed pyrophosphate-ammonium palladium complexes composition as well as their electrochemical behavior and dissociation constants ($PdP_2O_7^{2-}$ – $2{,}2{\cdot}10^{-18}$; $Pd(P_2O_7)_2^{6-}$ – $2{,}6{\cdot}10^{-20}$; $Pd(NH_3)P_2O_7^{2-}$ – $5{\cdot}10^{-29}$) were studied using potentiometry, linear and cyclic voltammetry. The ligand and central ion concentration effect on the complexes red-ox reactions kinetic parameters were estimated. The chemical reaction of the palladium complex dissociation exhibits before the charge transfer step:

$$Pd(NH_3)P_2O_7^{\ 2-} \leftrightarrow PdP_2O_7^{\ 2-} + NH_3\,,$$

$$PdP_2O_7^{\ 2-} \leftrightarrow Pd^{2+} + P_2O_7^{4-}\,.$$

If the electrolyte composition is *a* – {M(L)Y, Kt^{z+}, A^{z-}, L, WO_4^{2-}, H_2O,…} ,
where M – {Ni, Co}, Kt^{z+} – cation, A^{z-} – anion, L – ligand (L – {OH^-, Cit^-, NH_3, $H_mP_2O_7^{m-4}$…}), we can present the number of partial reactions (*d* and *l*)under alloy electrochemical deposition by scheme



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where v_d and v_{ds} – bulk and surface diffusion rate of *a* components from electrolyte bulk (x=∞) to the electrode surface (x=0) or reaction layer (x=δ_p); rate constants of the electrochemical k_{si} and chemical k_{fi} reactions, water equilibrium constant K_w, ad-atoms $()_{ad}$ or crystal lattice atoms $()_{cl}$ formation. Optimization of electrolytes and electrolysis regimes for reception of coatings with the set content was carried out.

Definition of the received alloys catalytic activity in modeling hydrogen reduction reaction dependence on the alloy components content is established. The numerical optimization methods based on the theory of fuzzy sets were applied for alloys structure optimization. Uses of artificial intellect elements, in particular artificial neural networks (ANN), for modeling of complex electrochemical systems behavior will allow to purposefully create new and to estimate a condition of existing electrode materials.

Kinetic laws of composite coatings synthesis by non-stationary electrolysis regimes are revealed. Models of materials electrochemical synthesis are created. Electrode and constructional composition which meet the set requirements (corrosion resistance, catalytic activity etc) are optimized using the most modern information technologies (ANN).

ABSORPTION SPECTRA OF REICHARDT BETAINE INDICATORS, IMMOBILIZED IN GELATINE AND ON PHOTOGRAPHIC FILM

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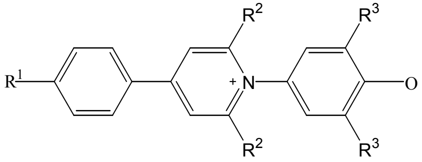
The search of new supporting materials is important way of new test-tools elaboration. Transparent materials such as polymethacrylate, nitrocellulose and others polymers are the most interesting among them. Gelatinous gel is a promising media for analytical reagents immobilization and for development of test-tools. Ready-made gelatinous layers of commercial photographic films are convenient to use. Application of gelatinous layers of photographic films as reaction media for spectrophotometric investigations [1,2] and for study of dyes state in gelatinous gel [3,4] has been reported. Purpose of work is investigation of properties of gelatinous layers of photographic films as reaction media for development of new test-tools. Properties of gelatinous gel and photographic film were investigated by Reichardt solvatochromic betaine indicators of different hydrophobicity, the structure of which is cause of the strong dependence of absorption spectra in UV- and visible ranges from polarity of media:



R^1: H (II, VIII, IX, XI), $C(CH_3)_3$ (III), $CO_2^-Na^+$ (V), C_6F_{13} (VII);
R^2: C_6H_5 (II, V, VIII, IX), 4-$C(CH_3)_3$-C_6H_4 (III), 4-C_6F_{13}-C_6H_4 (VII), 3-pyridyl (XI);
R^3: C_6H_5 (II, V, VII), 4-$C(CH_3)_3$-C_6H_4 (III), $(-CH_2-)_9$ (VIII), $(-CH_2-)_{12}$ (IX), 3-pyridyl (XI).

Absorption spectra of Reichardt indicators, immobilized on photographic film, triacetylcellulose carrier and in gelatinous gel, obtained on glass carrier in laboratory conditions were studied. The most hydrophobic indicators (III, VII, IX) and hydrophilic indicator (XI) were not absorbed by photographic film. Hydrophilic indicator (V) was absorbed by photographic film very faintly. Indicators (II) and (VIII) were absorbed both photographic film and triacetylcellulose carrier. Indicator (II) and the most hydrophilic indicators (V), (XI) were absorbed in gelatinous gel on glass carrier.

The polarity of media was evaluated by empirical parameters of solvent polarity $E_T(30)$ and normalized E_T^N values and by shift of absorption maximum (λ_{max}) in comparison to water-alcohol solution ($\Delta\lambda$) (table).

Media	Characteristics	Reichardt betaine indicators			
		II	V	VIII	XI
$\frac{C_2H_5OH}{H_2O}$	λ_{max}, nm	505	510	525	490
Photographic film	λ_{max}, nm	615	540-550	605	—
	$\Delta\lambda$	110	30-40	80	—
	$E_T(30)$(kkal·mol^{-1})	46.5	52.2-53.2	—	—
	E_T^N	0.487	0.664-0.694	—	—
Triacetylcellulose carrier	λ_{max}, nm	625	—	610	—
	$\Delta\lambda$	120	—	85	—
	$E_T(30)$(kkal·mol^{-1})	45.8	—	—	—
	E_T^N	0.465	—	—	—
Gelatine on glass	λ_{max}, nm	500	480	—	490
	$\Delta\lambda$	-5	-30	—	0
	$E_T(30)$(kkal·mol^{-1})	57.2	60.3	—	56.4
	E_T^N	0.817	0.915	—	0.792
Gelatine on glass over 2 day after contact with solution of indicator	λ_{max}, nm	520	520	—	515
	$\Delta\lambda$	15	10	—	25
	$E_T(30)$(kkal·mol^{-1})	54.9	55.4	—	53.5
	E_T^N	0.749	0.763	—	0.703

Experimental dates testify that Reichardt indicators are absorbed both by carrier and by gelatinous layer of photographic film.

Polarity of microenvironment of indicators immobilized in photographic film is like to polarity of nitromethane, pentanol-2, and acetonitrile according to Reichardt polarity scale. Hence moderately hydrophobic analytical reagents, solubility of which is higher in these solvents then in water, are suitable for immobilization in photographic film. It was confirmed by spectral shifts that freshly-prepared gelatinous gel is more polar media then gelatinous layer of photographic film and slowly becomes more hydrophobic under drying during long time. Thus, it is difficult to standardize preparation of gelatinous films by precipitation on glass in laboratory conditions.

We are grateful to Professor C. Reichardt, University of Marburg, for putting the betaine dyes and valuable information about it properties at our disposal.

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ASSOCIATION OF SOME COMPLEX ORGANIC IONS IN MIXED AND NON-AQUEOUS MEDIA. THE INFLUENCE OF SOLVENT AND CATION NATURE

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Ion association plays important role in media with moderate and low polarity, where electrostatic interactions are quite essential. The number of experimental data on association constants reported in literature is huge. Also, several theories of ion association are also developed. Nevertheless, there is lack of accurate data on ion association in non-aqueous and mixed solvents for solutes formed by large charged organic species, such as dye and surfactant ions. For such systems, theoretical predictions of ionic association constants are usually failing because the contribution of specific interactions is significant. Thus, experimental investigation of ion association in such systems is still necessary.

In order to elucidate the significance of selective solvation (including hydration) in isodielectric solvents, we studied the association of sodium and tetra-*n*-butylammonium (Bu_4N^+) cations with perchlorate anion in *n*-butanol, *iso*-butanol and *iso*-butanol – water mixtures (with water content of 5 mass% and 10 mass%) at 298.15 K by conductometric method. Conductance data were analyzed by non-linear least-square method using Lee-Wheaton conductance equation to calculate limiting molar conductivities Λ_0 / Sm·cm^2 mol^{-1} and association constants K_A. The results are presented in Table1.

Table 1. Association constants and limiting molar conductivities in alcoholic media

		Bu_4NClO_4		$NaClO_4$	
Solvent	ε	log K_A	Λ_0	log K_A	Λ_0
n-Butanol	17.49	3.36±0.01	18.39±0.09	—	—
iso-Butanol	17.53	3.38±0.01	13.93±0.15	3.35±0.02	13.48±0.18
iso-Butanol-water (5%)	17.01	3.18±0.01	17.97±0.09	2.83±0.01	18.18±0.06
iso-Butanol-water (10 %)	17.58	2.92±0.01	19.97±0.09	2.48±0.02	19.85±0.11

These data clearly demonstrate, that water content in mixed solvents causes much more influence on the K_A values than dielectric constant.

We have also studied the association of perchlorate anion with more complex organic cations, namely cetylpyridinium (CP^+) and cetyltrimethylammonium ($CTMA^+$), in *n*-butanol and acetone-water (10 mass %) mixture. Recently, attention of investigators is often attracted to the interaction between ionic surfactants and dyes. These species are widely used to obtain various complexes, multilayers, Langmuir-Blodgett films, etc. Therefore, we have studied the association of tetramethylammonium (Me_4N^+), CP^+, $CTMA^+$, and phenpiverinium (PP^+) cations with methyl orange (MO^-) and rhodamine 200 B ($R200B^-$) anions. For these systems conductance and vis-spectroscopy measurements were carried out in *n*-butanol and acetone-water mixture. Unfortunately, it was impossible to calculate reliable values of association constants using spectroscopic data because the changes in spectra were very small. The results of conductance data analysis are compiled in Table 2. The standard deviation of $\log K_A$ values was as a rule ± (0.01–0.03), while that of Λ_0: ± 0.5 Sm·cm^2 mol^{-1}.

Table 2. The $\log K_A$ and Λ_0 values at 298.15 K.

Electrolyte	Acetone – water (9 : 1)		*n*-Butanol	
	$\log K_A$	Λ_0	$\log K_A$	Λ_0
$CTMA^+$ $R200B^-$	2.26	78.9	4.06	12.10
CP^+ MO^-	2.06	85.1	3.39	12.9
$CTMA^+$ MO^-	2.19	84.6	3.47	12.38
Me_4N^+ MO^-	2.28	200	3.53	22.9
PP^+ MO^-	1.88	79.7	—	—
CP^+ ClO_4^-	1.77	125.7	3.39	18.26
$CTMA^+$ ClO_4^-	1.72	121.5	3.43	17.36
Bu_4N^+ ClO_4^-	1.9	154	3.36	18.39

Basing on the literature value of single ionic limiting mobility of Bu_4N^+ in *n*-butanol we have calculated the single ionic mobilities of some studied ions in *n*-butanol at 298 K. The results are listed below.

ion:	Bu_4N^+	CP^+	$CTMA^+$	ClO_4^-	MO^-
Λ_0^i / Sm·cm^2 mol^{-1}	8.0	7.8	7.0	10.4	5.3

These data can be used for prediction of association of the above large and complex ions, as well as for separation of experimental Λ_0 values into ionic contributions.

THE PROTOLYTIC PROPERTIES OF INDICATORS EMBEDDED IN THE GELATINOUS GEL

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The search of new materials and media for analytical reagents immobilization and the study of their properties are of importance for chemical analysis. In this work, we propose to use gelatinous films with immobilized indicators, bromophenol blue (BPB), bromocresol green (BCG), neutral red (NR), malachite green (MG), eosin (EO), ethyleosin (EEO), decyleosin (DEO), and decylfluorescein (DF), for pH monitoring in aqueous media. Commercial gelatinous layers of “AGFA” photographic films were used after removing silver halogenides. The films specimens were transparent and colorless. They were previously modified by soaking into aqueous or water-alcohol solutions of indicators and then dried on air.

The ranges of indicators color transitions were both below and above the isoelectric point of gelatin (pH ca. 5). Anionic indicators BPB, BCG, EO, EEO were used at pH < 4.9, where the net charge of gelatin macromolecules is positive. In the case of negative net charge (pH > 4.9), the cationic indicators NR and MG were used. The positions of absorption bands of indicator species in gelatin films appeared to be shifted as compared with those in aqueous solutions (see the $\lambda_{\max}$ values in Table 1).

Acid-base equilibrium in two-phase water/gelatin film system was described by equation (1) and characterized by the indices of “apparent” ionization constants of indicators, pK_a^a. The line above formula denotes the gelatin phase, the charges are omitted for simplicity.

$$\overline{\mathrm{HR}} \Leftrightarrow \overline{\mathrm{R}} + \mathrm{H}^+ ,\ K_a^a . \qquad (1)$$

Table 1. The $\lambda_{\max}$/nm and pK_a^a values of indicators and medium effects

Indicator (acid form)	$\lambda_{\max}^{gelatin}$ ($\lambda_{\max}^{water}$)		pK_a^a (gelatin)	ΔpK_a		
	acidic form	basic form		Gelatin	Surfactant micelles	
					anionic	cationic
BPB (HR^-)	416 (440)	604 (590)	2.22 ± 0.17	–1.98	–	–2.21
BCG (HR^-)	433 (443)	634 (616)	3.54 ± 0.12	–1.36	–	–1.71
NR (HR^+)	505 (534)	462 (450)	8.83 ± 0.08	2.30	2.42	–
MG (R^+)	630 (613)	–	12.44 ± 0.10	0.4	0.4	–
EO (HR^-)	–	534 (518)	4.48 ± 0.16	0.84	–	–0.82
EO (H_2R)	–	–	2.54 ± 0.17	–0.23	–	–2.17
EEO (HR)	482 (492)	543 (520)	1.66 ± 0.09	–0.24	–	–1.9
DEO (HR)	–	545 (520)	2.23 ± 0.08	0.3	2.6	–
DF (HR)	460 (445)	515 (495)	3.7–8.9	see text	2.65	–1.39

The pK_a^a values were determined by the standard vis-spectroscopical procedure at bulk ionic strength 0.05 mol/l; the pH values of aqueous phase were checked with glass electrode.

The calculated pK_a^a and medium effects ($\Delta pK_a = pK_a^a - pK_a^w$) are presented in Table 1; pK_a^w is the thermodynamic value in water.

The alterations of acid-base and spectral properties of indicators reflect the influence of gelatinous microenvironment. The influence of gelatinous gel medium on indicators protolytic properties depends on the charge of gelatin molecules and is qualitatively similar to medium effects in micellar solutions of corresponding ionic surfactants, microemulsions, and liposome suspension [1]. The decrease in the second ionization constant of EO, instead of its increase, can be explained by proximity of the working pH range to the isoelectric point of gelatin. In this case, the net charge of gelatin matrix is close to zero, and the observed effect is analogous to those in micelles of nonionic surfactants.

The behavior of DEO and DF is quite interesting. In contrast with other indicators, these dyes remained in gelatinous matrix on the whole pH range owing to their long hydrophobic radical. The influence of gelatin on protolytic properties of DF could be compared with that of micellar solutions of cationic and anionic surfactants below pH 5 and above the isoelectric point, respectively. Thus, within the pH range from 2.9 to 9.2, the pK_a^a value of DF vary from 3.7 to 8.9.

The systems studied can be used in sensor devices for pH monitoring.

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NONCONTINUUM MODELS OF VAN DER WAALS INTERACTIONS FOR DESCRIBING THE PHYSICOCHEMICAL PROPERTIES OF PURE MOLECULAR LIQUIDS AND BINARY SOLUTIONS OF NONELECTROLYTES

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A noncontinuum model based on the use of such molecular characteristics as molecular refraction (MR), dipole moment (μ), and molar volume (M/d) is suggested for quantitatively describing the physicochemical properties Q (surface tension, enthalpy of vaporization, boiling temperature, viscosity, etc.) of pure molecular liquids. The ratio between the coefficients of correlation equations relating electrostatic and dispersion contributions to all the properties analyzed was found to be invariant.

Description of the physicochemical constants of pure liquids [1]. The experimental data on the enthalpies of vaporization $\Delta_{VAP}H$, boiling points t_b , surface tension σ , and viscosities η of pure nonelectrolytes were treated using the general correlation equation

$$Q = A + B\,\mu^2\,(d/M) + C\,MR^2\,(d/M), \qquad (1)$$

where Q is some molar physicochemical property (or a property reduced to molar) of a pure liquid. Equation (1) explicitly describes the contributions of only pair dispersion and orientation (dipole–dipole) interactions between two molecules. The introduction of the term describing the contribution of dipole–induction interactions virtually does not change the correlation coefficient, and the coefficient of the dipole–induction parameter itself proves to be statistically insignificant. The presence of the free term A in (1) (this term should be equal to RT for the enthalpies of vaporization) is likely related to certain ignored factors, possibly such as anisomerism of molecules (especially when homologous series are analyzed), which changes synchronously with the dispersion parameter, or inaccuracy of the representation (or selection) of the molar property Q.

A model of competing van der Waals (universal) interactions was suggested for describing the excess physicochemical properties of binary systems and excess thermodynamic functions of solvation [2]. As distinct from the Redlich–Kister and Hwang polynomials, the coefficients of this model (2) are functionally significant and related to various mechanisms of van der Waals, in particular, electrostatic interaction manifestations as the composition of the binary solvent changes. The suggested model was used to estimate the contributions of electrostatic nonstoichiometric interactions and mutual component destructuring effects to the observed physicochemical properties of binary systems. The empirical Dimroth–Reichardt solvatochromic scale of solvent polarities for binary systems was shown to be related to the electrostatic contribution of the model.

In the model under consideration, the variable distance between the interacting dipoles was as a first approximation measured by the polar component concentration f_P raised to the first power (the molar concentration c_P , which is inversely proportional to the cube of the distance between dipoles, could possibly be used to advantage for this purpose). The second factor that should be included in the description of two competing electrostatic interaction mechanisms is the transition of part of the dipoles from free rotation to an energetically (electrostatically) balanced state. This was done with the use of the inverse exponential weighting of the interaction energy of freely rotating dipoles to decrease the exponential function value when its argument reached a certain value comparable with kT . Analytically, this corresponds to the transition from dipole–dipole interactions to the mutually balanced state. Based on these considerations, we suggest the equation

$$F^E = a\, f_P \exp(b\, f_P) + c\, f_P\, f_N + d\, f_N \exp(e\, f_N), \qquad (2)$$

as a first approximation of the model of competing van der Waals (universal) interactions. In (2), F^E is an excess thermodynamic function or some excess physicochemical property of the binary system, $af_P\exp(bf_P)$ is the electrostatic contribution with an extremum at $f_P = -1/b$, and cf_Pf_N is the classic term symmetrical with respect to the equimolar binary solvent composition. The latter is usually introduced to describe deviations of the excess functions of binary systems comprising nonpolar components. It is related to dispersion interactions determined by the polarizabilities and volume characteristics of molecules interacting in solution. Lastly, $df_N\exp(ef_N)$ is the contribution related to the destructuring action of the nonpolar binary mixture component N on the electrostatically structured polar component P. This contribution is written analytically similarly to the electrostatic contribution but describes the special features of the dependence of excess functions or properties close to $f_P = 1 - f_N = 0.8$. The extremum of the destructuring contribution is situated at $f_P = 1 + (1/e)$. The destructuring character of this contribution is sometimes substantiated by the opposite signs of the a and d coefficients.

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THE INVESTIGATION OF SOME DISTYRYL DYES INTERACTION WITH BOVINE SERUM ALBUMIN

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Styryl dyes are widely used as fluorescent probes in medicine and biology investigations. The study of experimental results on styryl dyes interaction with bovine serum albumin (BSA) is presented in this paper.

Distyryl dyes Dst-5 and Dst-10 dyes consist of two monostyril dye F molecules coupled by alcyl chain with 5 and 10 sections respectively. The coupling by chain leads to the 3 and 260 times increase of dye aqueous solution fluorescence intensity in the presence of BSA, at the same time, the binding constant of dye molecules to BSA is also increased compared to F. The increase of fluorescence intensity by one order of magnitude in solutions with BSA is observed also for Dbt-5 and Dbt-10 dimer dyes, as compared to monomer dye Sbt. However, the increase of coupling chain length for these distyryl dyes do not lead to the change of binding constant of dye molecules with BSA. Distyryl Dil-10 and Dbo-10 dyes have also on one order magnitude larger fluorescence intensity increase as compared to monomer Sil and Sbo dyes.

The lengthening of distyryl dyes coupling chain leads to the decrease of dye molecules aggregation probability among themselves. It was also established that homodimer styryl dyes with longer coupling chain are better fluorescent probes for quantitative study of proteins.

The nature of observed phenomena is discussed in paper.

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MAXIMUM HARDNESS, MINIMUM POLARIZABILITY AND MINIMUM ELECTROPHILICITY PRINCIPLES IN TAUTOMERIZATION OF THIOSEMICARBAZONES

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Seeking new concepts, rules, laws, principles and theories is the major aim of computational chemistry. Such key properties as chemical hardness and polarizability and their related principles (Maximum Hardness and Minimum Polarizability Principles) have been applied in chemistry [1,2]. Electrophilicity defined as

$$\omega = \mu^2 / (2\eta)$$

is another parameter, which can be used successfully as a reactivity descriptor in chemical reactions. In this relation μ and η are the chemical potential and hardness of system, respectively. It seems that the nature of a chemical reaction is toward the molecules with less electrophilicity. This is called Minimum Electrophilicity Principle, MEP [3].

Hardness, polarizability and electrophilicity values for more than 40 tautomers of different thiosemicarbazones were calculated by using HF and DFT methods, with different basis sets (3-21G**, 6-31G**, 6-311G** and 6-311++G**). These values show that although in all cases the stable tautomer has less electrophilicity and the Minimum Electrophilicity Principle (MEP) is valid, but Maximum Hardness and Minimum Polarizability Principle are failed in more cases.

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PROTOLYTIC PROPERTIES OF XANTHENE DYES

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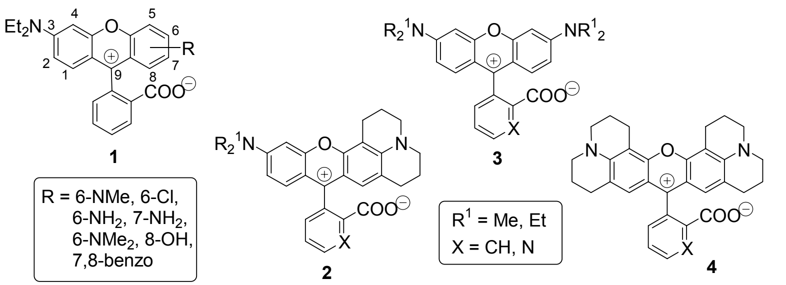
A series of symmetrical and unsymmetrical xanthene dyes 1–4 was synthesized and their spectral and protolytic properties in solutions were studied. The tautomerization constants, K_T, describing the equilibrium between two species, the deeply colored zwitter-ionic tautomer and the colorless lactone one were determined spectrophotometrically. An acetone-water mixture (mass ratio 9 : 1) was used as a solvent. The K_T values are found to vary in a wide range of 0.12 to 29.8, depending on the dyes structure. Decrease in K_T correlates with increase of electron donor ability of substituents in the 3 and 6 positions of xanthene moiety. Thus K_T decreases in the sequence: Cl > NH_2 > NEt_2 > NMe_2 > julolidine. Replacement of phenyl ring in position 9 with pyridyl also results in K_T decrease, i.e. the tautomeric equilibrium is shifted toward the colored and brightly fluorescent zwitter-ionic form.

Using xanthene dye 2 (R^1 = Et, X = CH) as a representative substance, we examined the influence of the solvent nature on the state of tautomeric equilibrium. The K_T values were found to increase in the following sequence: methanol < (benzene – ethanol – water; mass ratio 47 : 47 : 6) < *n*-butanol < *iso*-butanol < *iso*-propanol < acetone-water (mass ratio 9 : 1) < *tert*-butanol < acetone-water (mass ratio 95 : 5) < acetonitrile < DMF < DMSO. Thus the K_T can be changed from 0.095 in methanol up to 17.67 in DMSO.



INHIBITION ACTIVITY OF LIPASES BY LOW-MOLECULAR-WEIGHT CHITOSAN FROM THE GREAT WAX MOTH, GALLERIA MELLONELLA

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A procedure of isolation chitin, chitosan and water-soluble low-molecular-weight chitosan from Great Wax Moth has been developed. This procedure includes deproteinization of larvae of the Great Wax Moth, discoloration of the chitin-melanin complex, deacetylation, and enzymatic hydrolysis of chitosan.

The inhibition of *Candida rugosa* lipase and wheat germ lipase by low-molecular-weight chitosan (5.7 kD) at reactions of p-nitrophenyl palmitate splitting have been studied. Using the preincubation of enzyme and inhibitor before an addition of substrate it was show that the equilibrium of complex formation between every lipase and chitosan are achieved during 30 minutes. It necessitates that in solution lipases have two conformations with closed and opened active sites. Measured inhibition constants of *C.rugosa* lipase and wheat germ lipase by chitosan are equal to 1.4 и 0.9 mM, respectively. It was observed that contribution of electrostatic interaction to complex formation of chitosan and lipases is insignificant

IONIC EQUILIBRIUM IN SOLVENTS WITH LOW RELATIVE PERMITTIVITY: ION PAIRS, TRIPLETS, AND QUADRUPOLES FORMED BY TETRA-*n*-BUTYLAMMONIUM PICRATE AS STUDIED BY CONDUCTIVITY

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Ion association between cations (Ct^+) and anions (An^-) is known to control all the processes in media of low polarity (low relative permitivity, ε). Conductance studies serve as a universal method of determination of corresponding equilibrium constants.

In media with extremely low ε values ($\varepsilon < 10$), two general problems arise. The first one is that the possibility of stepwise ionic association is to be taken into account, even in the absence of specific interactions. Fuoss and Kraus introduced the model of ion triplets formation. Moreover, at high concentrations of the electrolyte, formation of quadruples or even more complicated species is possible:

$$Ct^+ + An^- \rightleftarrows Ct^+An^-,\ K_A \qquad (1)$$

$$Ct^+ + Ct^+An^- \rightleftarrows Ct^+An^-Ct^+,\quad K_{T+} \qquad (2a)$$

$$An^- + Ct^+An^- \rightleftarrows An^-Ct^+An^-,\quad K_{T-} \qquad (2b)$$

$$2\,Ct^+An^- \rightleftarrows (Ct^+An^-)_2,\quad K_Q \qquad (3)$$

The second problem consists in estimation of limiting molar conductivities of charged species (or some of them). One way is to calculate these values as optimized parameters together with equilibrium constants during fitting procedure, but there are many mathematical difficulties in this way. Otherwise, it is possible to obtain these values by some additional approaches (for instance, using Walden rule). In this case, only the equilibrium constants are parameters to be calculated.

Consequently, one must take into account the multiplicity of possible approaches to processing of conductance data.

Contrary to the concept developed by Fuoss and Kraus, Sukhotin demonstrated that in some cases the experimental data could be fitted using the simple association scheme (1) only. On the other hand, Hojo and co-workers recently demonstrated that using some reasonable assumptions it is possible to evaluate all the above constants (K_A, K_T, and K_Q).

Finally, at high concentrations of the electrolyte or/and high temperature, the term ‘ion association’ in low-permitivity media is somewhat conventional.

Taking into account the multiplicity of ion associates (not only contact and solvent-separated, but also penetrated ones, as well as with H-bond, etc.), we decided to consider the behavior of tetra-*n*-butylammonium picrate (Bu_4NPi). In this case, specific interactions between cation and anion seem to be less probable.

Electronic absorption spectra and electrical conductivities were measured for Bu_4NPi solutions in acetone, *n*-butylacetate (BA) and acetone-BA mixtures with acetone content of 12.5, 25, and 40 mass %. The concentration range was 5×10^{-6} to 5×10^{-3} mol dm^{-3}.

Some differences between spectral curves of free ions and ionic associates were revealed, but only in several cases it was possible to roughly estimate the association constants (by contrast, the association of picrate with metal ions distinctly manifests itself in UV-vis spectra).

Conductance data were analyzed by non-linear least-square method using Onsager or extended Lee–Wheaton conductance equation.

The results of calculations made by using Hojo's algorithm are compiled in the Table.

Table. The equilibrium constants of tetra-*n*-butylammonium picrate in acetone – *n*-butylacetate system (298.15 K)

Solvent	ε	log K_A	log K_T	log K_Q
Acetone	20.56	1.97±0.01	–	–
Acetone (40 mass %) – BA	10.97	3.46±0.04	–	–
Acetone (25 mass %) – BA	9.065	4.05±0.02	–	–
Acetone (12.5 mass %) – BA	6.68	5.34±0.01	2.6±0.1	–
BA	5.105	7.25 to 7.7	3.3 to 5.1	2.65 to 3.8

In our calculations, the assumption $K_{T+} = K_{T-} = K_T$ was made. The results are dependent on the concentration range and method of calculation used. Note that the DLS method does not indicate any large-sized particles in Bu_4NPi solutions in pure BA.

The results in systems with $\varepsilon < 9$ must be considered as preliminary ones. However, the calculations for pure BA for simple association scheme (1) results in unlikely low log K_A value of 5.17±0.05, while the extrapolation of the linear (log K_A vs. $1/\varepsilon$) plot to $\varepsilon = 5.105$ leads to the value 6.9, which is much closer to that given in the Table.

CHEMOMETRIC TOOLS AT BUILDING MODELS OF EQUILIBRIA ON SURFACES OF HYBRID SILICA-ORGANIC MATERIALS

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Many hybrid silica-organic materials with immobilized functional groups demonstrate sorption or ion-exchange properties. To characterize quantitatively the sorption (ion-exchange) equilibria, one has to handle the sorption (ion-exchange) isotherm and to determine the stoichiometric compositions of immobilized complexes and the corresponding equilibrium constants (β_i). Often not only these parameters, but also the effective sorption (ion-exchange) capacity (t_Q) should be determined too. The last requirement follows from the well known fact that the effective capacity may differ significantly from the theoretic one found by elemental analysis.

We disjoined the determination of β_i and t_Q. At the first stage the borders of possible t_Q variation are searched (all t_Q values varying within this interval allow to construct the adequate models), and the corresponding confident regions $R_{\left|\beta_i\right\rangle}$ are determined. Then the array of adequate models is reduced to the final model with only one set of parameters $\left|\beta_i^{\text{final}};t_Q^{\text{final}}\right\rangle$. For this the confident regions of fitting parameters are handled as multidimensional fuzzy numbers, and the θ^{final} estimations are found with the application of the centroid defuzzification technique.

For each tested t_Q values the fitting parameters $\theta = \left|\theta_j\right\rangle$, $j = 1, 2, \ldots, Y$, are calculated through the minimization of functional

$$M(\theta) = \sum_{k=1}^{N} \rho(\xi_k), \qquad (1)$$

where k is the number of the experimental points; N is the total number of measurements; ρ is a certain "loss function"; weighed discrepancy $\xi_k = \Delta_k \cdot w_k$; discrepancy $\Delta_k = N_f^{\text{calculation}} - N_f^{\text{experiment}}$; N_f is the value of adsorption, and w_k is the statistical weight of the k^{th} measurement. The maximum likelihood method prescribes to assign the loss function as ξ^2 (least squares metrics, LS) if ξ obey the Gauss law. But this hypothesis is frequently disturbed due to the presence of outliers in data. Instead of the least squares estimations, the robust Huber's *M*-estimates were employed. By postulating the certain fraction of outliers δ, the Huber's estimates establish a compromise between the methods of least squares and least modules (LM). As the δ value can be assigned neither a priori nor a posteriori, the minimization of criterion (1) is repeated several times for δ values varying from 0 (corresponds to LS) to 1 (LM)). Simultaneously with estimations θ^* corresponding to the minimum of functional (1), their dispersion-covariance matrix $D(\theta^*)$ and the confidence region R_θ are found. The adequacy of fitting is judged with the use of the χ^2 criterion.

Different sets of experimental data were handled with the application of the proposed approach. First, curves of pH-metric titration of aqueous glycine solutions by alkaline solutions were used to calculate the dissociation constants of glycine. The concentrations of glycine were considered as rough, and the dissociation constants were determined with the aid of the procedure described above. The calculated values were found to coincide with ones included into the "Critical Stability Constants" reference book. Second, the elaborated method was successfully applied for characterization of a new hybrid material, 3-n-propylpyridiniumsilsesquioxane chloride ion exchanger. The equilibria of Fe(III), Cu(II), Zn(II), Cd(II), and Hg(II) chlorides sorption by this material from ethanol solutions were simulated [1].

The sorption capacities of the material and the constants of sorption equilibria were successfully determined.

Authors are deeply grateful to Professor Yoshitaka Gushikem for the experimental data on the metal chlorides adsorption and helpful discussions.

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ENHANCEMENT AND QUENCHING OF FLUORESCENCE OF RED AND NEAR-INFRARED POLYMETHINE DYES ON SILVER AND GOLD NANOPARTICLES

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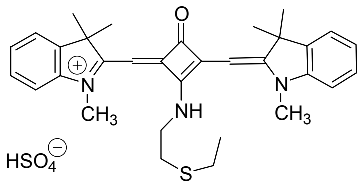
Biological matter displays auto-absorbance and auto-fluorescence, which can severely compromise the sensitivity and specificity of fluorescence-based assays and measurements in biomedical and pharmaceutical research and clinical diagnostics. The auto-absorbance and auto-fluorescence decreases at longer wavelengths and is negligible beyond 600 nm. Therefore, red and ner-infrared (NIR) dyes are perfectly suited as fluorophores for sensing applications in biological systems. However it is very difficult to develop organic dyes with high fluorescence quantum yields in the red and NIR region, especially in aqueous solutions, due to a strong quenching effect. But it is even more difficult to obtain the long-wavelength quenchers — real dark dyes for the Fluorescence Resonance Energy Transfer (FRET) applications — which have no readable fluorescence.

In this work we explore a novel, recently reported approach to improve spectral properties of a series of polymethine dyes in order to synthesize high bright fluorophores but also real dark quenchers. This approach is based on the interaction of light with small, sub-wavelength nanoparticles, which can result in a significant increase in the local electromagnetic field. If a fluorescent molecule is exposed to the enhanced local field of such a metallic nanoparticle a substantial increase in the fluorescence intensity can be observed. In contrast at small distances of 50 Å or less the fluorescence intensity can be totally quenched.

We investigated the spectral properties of water-soluble squaraines 1 and 2 and the bis-polymethine dye 3 free in solutions and in presence of such metallic nanoparticles both in solutions and being immobilized onto a solid slide. The fluorescence of dyes 1 and 2 that contain metal-reactive ethylthio-groups was found to be significantly decreased (up to 13 times) in aqueous solutions in presence of 20-nm gold nanoparticles. Dyes of similar structure lacking the ethylthio-group did not exhibit any fluorescence quenching in presence of the same gold nanoparticles.



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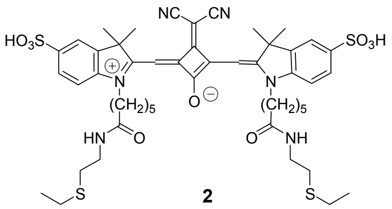

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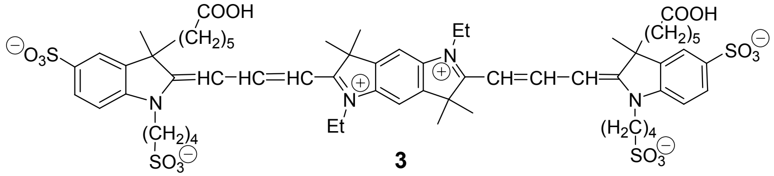

3

We also investigated the surface plasmon enhancement effect known as "radiative decay engineering". For that purpose we coated one part of a quartz slide surface with a silver island film while the other one remained untreated. 10–15-nm silver islands were prepared by chemical deposition. To obtain the required distance between the silver nanoparticles and the dye a 15-nm spacer layer was deposited onto the plate. The spacer covering both, the silver nanoparticles and the free quartz surface was formed by cryolite ($AlF_3 \cdot 3NaF$) thermal vacuum evaporation. Dye 3 having 5% fluorescence quantum yield was deposited on the spacer surface layer by spin-coating its aqueous solution. In this way a two- or three-layer coating was obtained on the quartz plate surface: spacer–dye and nanosilver–spacer–dye. Subsequently the fluorescence emission spectrum was measured for both layers at excitation wavelength 600 nm. The fluorescence intensity of dye 3 located at a certain distance from the silver nanoparticles was found to be 2.3 times higher as compared to the dye deposited directly to the quartz slide. The size of silver islands and the spacer layer were not optimized and we expect to obtain even a higher enhancement of the spectral response after optimization of these parameters.

The aforementioned experiments show the potential of these dyes to be used for the development of biomedical assays that are based on the enhancement of the fluorescence intensity of such dyes in proximity of the metal-island surfaces.

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SOME PHYSICO-CHEMICAL PROPERTIES OF THE PARAFFIN INTERFACE MODIFIED BY SURFACTANTS

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Now the large attention is given to studying of the solid surfaces modified by surfactants. Surfactant molecules fixed on a surface are able to change wettability, adhesive, electrosuperficial, rheological and sorption properties of the system. The paraffin interface modified by surfactants represents a reagent possessing a paraffin hydrophoby and a surfactant ability to interact with metal ions. Physical and chemical properties of such reagents are investigated insufficiently. These reagents are perspective for adsorption and floatation treatment of the sewage containing toxic components (for example, radioactive nuclide and heavy metal ions).

In the given work ionogenic (ltrialkylamine (TAA), dialkyl phosphinic acids (DAFA), palmitic acid) and nonionic (tributyl phosphate (TBP)) surfactants were used as the modifiers of the paraffin surface. For preparation of the modified paraffin at first we dissolved necessary quantity of a surfactant in the melted paraffin. A mixture was cooled and placed in a hot distilled water (60 - 70^0C) and then the ultrasonic dispergation was carried out. The preparated emulsion was cooled up to a room temperature. At the emulsification of a system the surfactant molecules were guided on the paraffin particles surface in such mode that their polar groups were inverted to a water (a polar liquid) whereas hydrocarbonic radicals to a paraffin phase (nonpolar liquid). After cooling emulsion was turned to suspension.

Our experiments have shown that the physico-chemical properties of the modified paraffin suspensions by studied surfactants depended on the surfactants nature. All suspensions were stable aggregately and sedimentationly owing to significant value of the disperse phase particles electrokinetic potential and their high dispersity degree. The way to calculate the surfactants optimum quantity necessary for the formation of the surfactants monolayer on the carrier surface is offered. It is shown that this quantity depends on the surface area occupied with the surfactant polar group in limiting packed layer. The theoretically calculated quantities of the surfactants to 1 kg of paraffin (0,5 mole TAA, 0,33 mole DAFA, 0,25 mole palmitic acid) coincide with the values determined experimentally. In this work for this purpose the methods of direct adsorption definitions, adsorption conductometric titration, electrophoresis, viscosimetry, a limiting wetting angle of surface measurements and particles average radius measurements were used. However in the case of the paraffin modified by TBP, packing of a surface by polar groups was not observed because TBP bi- and trimolecular layers on the paraffin surface were formed.

It is experimentally established that the investigated water suspensions of the modified paraffin well adsorb metal ions. This fact can be used at sewage treatment.

OXYGEN REDUCTION ELECTROCATALYSTS BASED ON PYROLYSIS PRODUCTS OF HETEROBIMETALLIC Cu(II)-Mn(II) COMPLEXES

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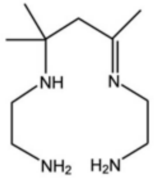
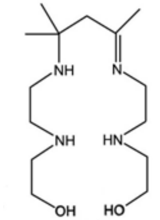
Heteropolynuclear complexes as precursors for the production of oxygen reduction electrocatalysts can form, in comparison with mononuclear complex compounds, more active catalysts [1,2] for fuel cells and electrochemical power sources.

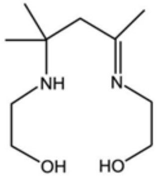
The investigations were carried out with heterobimetallic complexes Cu(L1)$MnCl_4$, Cu(L2)$MnCl_4$, Cu(L3)$MnCl_3$ (where L1 = 4,6,6-trimethyl-1,9-diamino-3,7-diazanon-3-ene; L2 = 1,15-dihydroxy-7,9,9-trimethyl-3,6,10,13-tetraazapentadec-6-ene; L3 = 1-hydroxy-9-oxy-4,6,6-trimethyl-3,7-diazanon-3-ene), which were prepared by direct template synthesis [3]. The structure of the ligands were as follows:



L1



L2



L3

The catalysts were synthesized by the adsorption of complexes on the surface of the support, activated carbon SIT-1, and subsequent heat treatment of it in an inert argon atmosphere at 200, 400, 600 and 800°C.

The thermal properties of the complexes have been studied and their pyrolysis products established by thermogravimetric analysis and by the method of thermal desorption with mass spectrometric analysis of desorbing particles. The electrochemical characteristics of catalysts were studied with the aid of a floating gas-diffusion electrode in 1M KOH by taking stationary polarization curves.

The change in the stationary potential of oxygen reduction electrocatalysts with respect to the support is about 0.01 V. The shift of the stationary polarization curves towards positive potential values in comparison with SIT-1 for copper-manganese catalysts prepared from complexes with L1 was 0.115 V, with L2 0.125 V, with L3 0.100 V. The slopes of the stationary polarization curves are within the ranges: $b_1 = 0.053–0.063$ V, $b_2 = 0.115–0.126$ V.

It has been shown that the electrocatalysts prepared by the thermodestruction of the heterobimetallic complexes Cu(L1)$MnCl_4$ and Cu(L2)$MnCl_4$ at 800°C have the maximum activity. On the basis of electrochemical measurements and results of a thermal analysis it is suggested that the active sites of these oxygen reduction electrocatalysts are complex pyrolysis products bonded through nitrogen to the support surface.

Cu(L3)$MnCl_3$ complex pyrolysis products form active sites in the form of oxide compounds on the support surface at 600°C.

Thus, the pyrolysis of complexes with L1 and L2, which have in their structure ligands coordinated through nitrogen to the central atom, yields electrocatalysts which form on the carbon support surface active sites in the form of organometallic remnants of complexes bonded to the carbon surface through nitrogen atoms; the mechanism of active site formation is similar to that for phthalocyanine or porphyrin N_4 complexes. Complexes with L3, whose ligands are coordinated to metals through oxygen atoms, form as a result of pyrolysis active sites of oxide structure.

The catalytic activity of the oxygen reduction catalysts synthesized decreases in the order of heterobimetallic copper-manganese complexes:

$$\mathrm{Cu(L2)MnCl_4} > \mathrm{Cu(L1)MnCl_4} > \mathrm{Cu(L3)MnCl_3}$$

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N-PROPYLPYRIDINIUM CHLORIDE - MODIFIED POLY(DIMETHYLSILOXANE) ELASTOMERIC NETWORK: PREPARATION, CHARACTERIZATION AND STUDY OF METAL ION ADSORPTION FROM ETHANOL SOLUTION

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Silicone-based materials have been studied on many different areas, mostly because of the singular characteristics of these polymers. The poly(dimetilsiloxane) is the most studied on academic researches and technological processes. This work has the objective to combine the properties of poly(dimethylsiloxane), PDMS, and an electrolyte (3-n-propylpyridinium chloride),ClPy, to obtain an elastomeric polyelectrolitic material with high adsorption potential and chemical stability.

PDMS/ClPy elastomeric network was prepared by mixing PDMS, 3-chloropropyltrimethoxysilane and ethanol, 1:1:1 weight ratio. Tin dibutil acetate was used as catalyst (1 wt% in relation to PDMS). The mixture was stirred for ~30 min at 298 K. The resulting solution was cast onto Teflon® Petri dishes and left to produce a mechanically stable, transparent, crack-free, self-supported film. This film was ground as fine powder and immersed in pure pyridine and heated at reflux temperature for 4h. The resulting product was heated at 373 K to evaporate the pyridine excess, washed with 0.1 mol L^{-1} HCl solution, followed with water and dried at low pressure (10^{-4} mmHg).

Infrared spectrum (IR) shows characteristic bands of the pyridine ion at 1630 and 1487 cm^{-1},[1] of PDMS at 1261 and 804 cm^{-1} ($Si(CH_3)_2$), and 1100-1020 cm^{-1} (Si-O-Si). In addition, the absorption at 469 cm^{-1}, associated to siloxane ring breath (D_1 mode)[2] was also observed.

Thermogravimetric analysis of the product showed an initial weight loss temperature in the 300-500 K range, associated to water and ethanol volatilization, due to the thermal induced condensation. From 500 to 600 K the pyridine ion is eliminated. The organic segments of chloropropyl are degraded from 600 to 700 K; the PDMS rearrangements and the mineralization process occur in the range of 700 to 1000 K, remaining the SiC_xO_y. Using the weight loss for pyridine ions, was estimated the exchange capacity of the PDMS/ClPy (0.65 mmol g^{-1}). The solid state HPDEC ^{13}C NMR spectra evidenced the signals showed in Figure 1.[3]

Adsorption isotherms for Fe^{+3}, Cu^{+2} and Co^{+2} chlorides are obtained and presented in Figure 2. The amount of adsorbed metal on PDMS/ClPy was 0.25, 0.29 and 0.45 mmol g^{-1} for Co^{+2}, Cu^{+2} and Fe^{+3}, respectively.

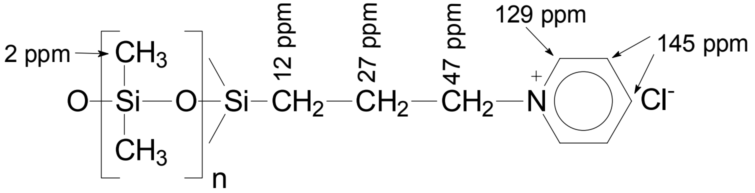

Fig. 1. Illustration of the PDMS/ClPy structure and respective chemical shift for ^{13}C NMR.

The nature of the anionic complex structure was proposed by the UV-Vis diffuse reflectance spectra of the metal adsorbed. Absorption bands corresponded to $(PDMS/Py^+)_2MCl_4^{2-}$ (M= Co and Cu) and $(PDMS/Py^+)FeCl_4^-$ adsorbed on the polymeric chains, where observed.[4]

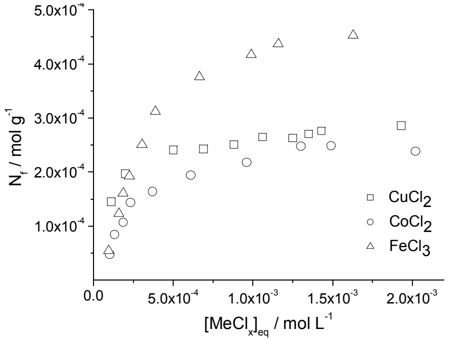

Fig. 2. Adsorption isotherms on PDMS/ClPy of MeClx from anhydrous ethanol solution at 298 K.

Equilibrium constants of metal halides on the surface of modified PDMS network were determined. Analyzing the obtained results, it was possible to see that the Langmuir equation in its linearized form allows to fit well the $CoCl_2$ and $CuCl_2$ adsorption on the PDMS material. However, the fit obtained to $FeCl_3$ was not adequate. A simulation using the model of fixed bidentade binding centers allows revealing the positive cooperative effects of $FeCl_3$ adsorption and adequately describes the adsorption process.[5]

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QUANTUM-CHEMICAL ANALYSIS OF INTERACTION BETWEEN VEGETABLE POLYPHENOLS AND COLLAGEN

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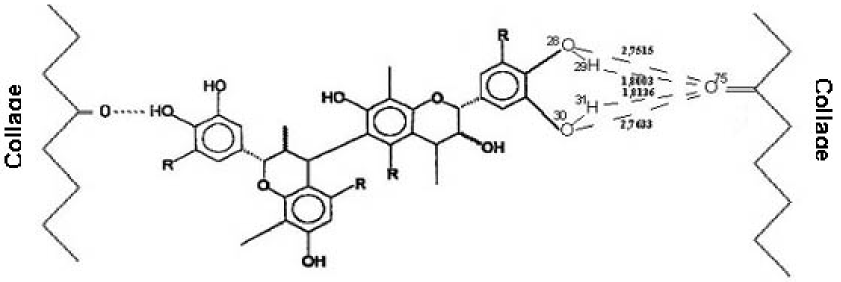
A profound understanding of the chemical structure and structural transformations of derma collagen is necessary for developing new technologies of animal skin processing as well as improving the existing ones. The multilevel structure of collagen, as a protein base of hides, makes the technological process of manufacturing leather difficult and labor-intensive. Though the technologies of hides processing have been known for many years, development of new, low-waste and more eco-friendly technologies is still a problem of current concern. Combined tanning with the use of vegetable polyphenols (tannides) [1] is one of alternative ecologically safe tanning technologies. For thousands of years substances of vegetable origin have been used as tannages. The generally accepted classification of vegetable tannages takes into account the nature of links between several parts in their molecules [2]. According to the classification, all the vegetable tannages can be divided into two groups: 1) hydrolysable (tannides of mirabolan, oak, divi-dibi etc.); 2) condensed (tannides of quebracho, mimosa, gambire etc.).

In the present work the chemical and electronic structure peculiarities of the condensed tannides of mimosa, quebracho and hydrolysable tannides of mirabolan have been studied with the help of semi-empirical MO LCAO method with a PM3 approximation using the MOPAC computer system to model their interaction with the derma collagen during combined tanning.

It should be noted that the molecules of tannides contain the atoms of carbon, hydrogen and oxygen, which differ considerably in their electronegativity. This causes non-uniform distribution of electron density among the functional groups, polarity and ionicity of chemical bonds in the molecules. Thus, the non-uniform distribution of electron density among the atoms will promote polarization of the molecule and formation of a molecular electrostatic field around the molecules of tannides. This will first cause electrostatic attraction between the molecules of tannides and functional groups of collagen, and then result in formation of hydrogen bonds. Besides, chemical bonds polarization in the tannides molecules at the some conditions contributes to making the coordinating bonds between the tannides molecules and metal atoms during combined tanning [3].

For electrostatic attraction between phenolic hydroxyls of tannides and peptide groups of collagen to occur the distance between them should be no more than 5 Å [2]. It has been established that for initial distances fitting the range 2.5-3.0 Å the oxygen atom of collagen is likely to form a split-type hydrogen bond with two OH-groups of tannides. One hydrogen bond is possibly formed between the tannage and collagen at initial distances 3.0 Å and 4.0 Å [4].



The functional groups of polypeptide side chains are the most available for interaction with tannides from the spatial point of view. During the vegetable tanning the amino-group of lysine and guanidine group of arginine are fully ionized and more preferred for interaction on this reason. It is confirmed by quantum-chemical calculations that the penta-nominal cycles with a high durability have arise during the interaction between the side chains of arginine and tannides oxy-groups. Such interaction leads to the increasing the collagen hydrothermal stability.

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MOLECULAR DYNAMICS SIMULATION OF LIQUID PROPYLENE CARBONATE

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Classical force field molecular dynamics simulations of liquid propylene carbonate (PC) at 298 K were performed in order to investigate its structure. All simulations were performed using the MDNAES package for the system consisting of 54 L + 54 D isomers in an NVT ensemble and at experimental density.

At the first stage the force field model of propylene carbonate molecules which reproduces the experimental properties, such as heat of vaporization, viscosity and dielectric permittivity was developed. The rigid and unpolarisable model of the PC molecule has been adopted. This model consists of 7 sites: 3 O atoms and 1 C atom, CH_3, CH_2 and CH groups as united sites. The geometry of the molecule was optimized by *ab initio* quantum chemical calculations at the RHF/6-31G(d) level of theory. The positions of CH_3, CH_2 and CH sites were assumed to coincide with the positions of the corresponding carbon atoms. Another isomer was obtained by coordinate inversion. The charges on all 13 atoms were calculated using the Breneman CHELPG method at the B3LYP/6-31G(d) level of theory and then recalculated to 7 model atomic charges with constraint of the total charge, Cartesian components of dipole momentum, charges on the carbonyl oxygen, and carbon and the sum of the charges on another two oxygens. Lennard-Jones parameters for all sites were taken from the GROMOS96 force field model as recommended in the manual for the GROMACS package.

Results of the simulations show that in the liquid phase PC molecules associate mainly through the carbonyl oxygen of one molecule and the CH_3 and CH groups (partially with CH_2 group) of another molecule. This is confirmed by an analysis of molecular orientation correlations which shows preferable parallel orientation of nearby molecules. Only for very small interatomic distances does an antiparallel orientation predominate. Analysis of spatial molecular correlations allows one to conclude that a racemic mixture of L and D isomers possesses the properties of an ideal mixture.

REDOX PROPERTIES AND CONDUCTIVITY OF AMIDINYLCYCLOPENTADIENE METAL COMPLEXES

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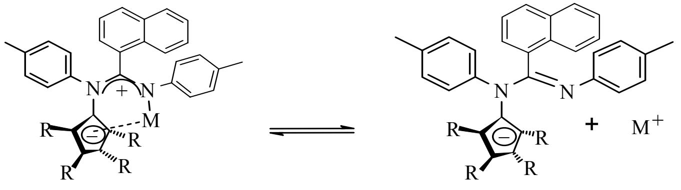
Dissociation of amidinnylcyclopentadiene metal complexes was found in different temperatures by NMR of H, C:



I a-e **II a-e** **(1)**

R = CO_2Me, M = Li (Ia), Na (Ib), K (Ic), Rb (Id), Cs (Ie).

The estimation complexes I a-e dissociation was made by measuring specific electrical conductivity in the range of 1.0-1.3 M. Results of the measurements treated by the methods of R.M.Fuoss e.a. [2] are shown. The dissociation constants are increased from Ia to Ie due to weakening coordination interactions (coordinated action) metal–ligand that takes place at increasing the metal-ion radius and the power of field. Methods of cyclic voltammetry and ESR allowed to detect stable radical after oxidation of anions IIa-e.

The work was supported by the project of the Ministry of Education and Science of the Russian Federation RNP 2.2.2.2.5592, RNP 2.14939, RFBR (grant № 06-03-32158a) and is a part of the program "Fundamental Research and Higher Education" (Ministry of Education and Science of the Russian Federation and CRDF Y4-C04-04).

SEMI-CONDUCTOR SENSORS OF GAS FIRE DETECTORS FOR DETECTION OF MIDGET CONCENTRATION OF GASEOUS PYROLYSIS PRODUCTS

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There are many scientific articles in which significant attention is given to the problem of use of semi-conductor sensors (SCS) as sensors for gas fire detector (GFD) due to their high sensitivity (a low activation point) and short activation time [1]. The GFDs detect the beginning of smouldering by change of air composition in a room, i.e. by appearing the gaseous products of smouldering of fuel in air and increase of their contents. The question of expediency of application of SCS as sensitive elements (SE) for GFD has not been investigated in any articles considering chemical stability of sensitive weight (SW) to the products of paralysis of fuel (F).

It is known, that at an initial stage of a fire - during smouldering - the basic products of pyrolysis, peculiar for all F, - CO, CO_2, H_2, CH_4 are produced. Therefore to prove an opportunity of application of SCS on basis of SnO_2 as gauge of GFD, in work according to the algorithm resulted in [2] we have carried out thermodynamic calculations of an opportunity of corrosion and chemical processes on a surface and in volume of sensitive weight of the SCS at temperatures of the maximal adsorption - desorption of gas molecules which are the basic products of smouldering of F [3]. As to the table 1 it is clear, that in case of the basic component of sensitive weight - SnO_2 (95-97 % SW) process of all chemical reactions (with H_2, CO - variants 1 and 2) at different temperature conditions it is thermodynamically allowed at T≥843 K for (H_2), at T≥623 K for (CO - a variant 1), at T=573 K for (CO - a variant 2). By all means it leads to irreversible processes of destruction of SW of the SCS, formation of new by functional properties compositions in SW ($SnO_{(f)}$, $Sn_{(f)}$), that will be reflected in basic characteristics (BC) of GFD based on such SCS.

Results of behavior of TiO_2 are especially important. They allow to ascertain, that films TiO_2 (corrosion and chemical proof component SnO_2 and In_2O_3 the SCS) [2] do not react with products of pyrolitic decay. Absence of decomposition processes of SW (see tab. 1) prevents to decrease in the BC of GFD and in the automatic fire detection and alarm systems as a whole during all time of its operation.

Table 1 - Values of Gibbs energy (ΔG) for different reactions of chemical interaction a component of sensitive weight of SCS (SnO_2, TiO_2) in the environment: hydrogen $(H_2)_{(g)}$; $(CO)_{(g)}$.

N	Nature of a gas component of pyrolitic decay	Equation of thermochemical reactions	$\Delta G^0_{(298\ K)}$, kJ/mol	$\Delta G_{(573\ K)}$, kJ/mol	Opportunity of reaction
Hydrogen $(H_2)_{(g)}$.					
1).	$(H_2)_{(g)}$.	$2H_{2(g)}+SnO_{2(f)} = Sn_{(f)}+2H_2O_{(p)}$	63,2	30,98	impossible
				-0,2 (at T≥843K)	Probably
2).	$(H_2)_{(g)}$.	$2H_{2(g)}+TiO_{2(f)}=Ti_{(f)}+2H_2O_{(p)}$	431,6	385,95	impossible
$(CO)_{(g)}$ - a variant 1.					
1).	$(CO)_{(g)}$.	$CO_{(g)}+SnO_{2(f)} = SnO_{(f)}+CO_{2(g)}$	5,48	0,07	Impossible
				-0,95 (at T≥623K)	Probably
2).	$(CO)_{(g)}$.	$CO_{(g)}+TiO_{2(f)} = TiO_{(f)}+CO_{2(g)}$	136,58	132,32	Impossible
$(CO)_{(g)}$ - a variant 2.					
1).	$(CO)_{(g)}$.	$2CO_{(g)}+SnO_{2(f)}=Sn_{(f)}+2CO_{2(g)}$	5,96	-3,16	Probably
2).	$(CO)_{(g)}$.	$2CO_{(g)}+TiO_{2(f)} = Ti_{(f)}+2CO_{2(g)}$	374,36	351,8	Impossible

On the basis of conducted thermodynamic calculations the substantiation of an opportunity of use of suggested chemical compound of sensitive weight of a semi-conductor sensor control of helicoid type as sensitive element of the GFD of system of fire detection at an initial stage is made.

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PERFORMING TASKS OF CHEMICAL KINETIC IN MICROREACTOR SYSTEMS BY THE DEVELOPED PROGRAM “KINETIC 1.0”

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In research of heterogeneous catalytic reactions the major place borrows kinetic studies. At the same time as one of the major factors of finding-out of the mechanism of reaction, kinetic studies open a way for a prediction of optimum parameters for process conducting. Knowing these parameters, it is possible to plan conditions of practical realization of the process.

The characteristic tendency of new technological developing in last decade was the origin of microsystem technologies. One of the directions of development in microsystem technologies are microreactors. The smaller devices need less space, materials and energy. Reactions with toxic substances or at high pressures, are carried out more safely in microreactors. Also the emissions of harmful substances in environment are decreased.

High complexity of a microreactor is caused by the complex set of the separate processes occurring in it.

The aim of the work is to create a program which could help chemists to plan the experiment, to solve direct and return kinetic problems in microreactors and carry out kinetical calculations for the heterogeneous reaction systems.

The work is executed with the developed software product "KINETIC 1.0", the obtained experimental data was analyzed for the purpose of construction, the modeling representations for a microreactor and research of processes occurring in it.

In the "KINETIC 1.0" finding and extraction of mathematical model parameters on experimental data is carried out. The choice of a model means a choice of hypothesis, and record the differential equations system of a direct kinetic problem for each hypothesis.

The suggested technique allows forming automatically on the basis of records of differential equations system, to calculate the sum of absolute squares of relative deviations of experimental and calculated values, and also to solve a direct and a return problem as an optimization task with restrictions. At the return problem decision, it is possible to find constants of reaction rate, parameters of degrees of the kinetic equations as well as missing initial values on some concentration in conditions of the data incompleteness.

For finding a decision of a problem the search minimization method of chosen functional decisions deviations of system from experimentally found values is used. The efficiency criterion of constants estimation can be received on the basis of a Fisher's maximum plausibility principle.

By a variation of model parameters there is a minimum of chosen function. Then it is possible to accept or reject a checked hypothesis by mathematical statistics, i.e. to solve the problem of adequacy of model. If the hypothesis should be rejected, it is necessary to choose another model. After the hypothesis about adequacy is checked up, it is necessary to carry out research of uniqueness of the found model.

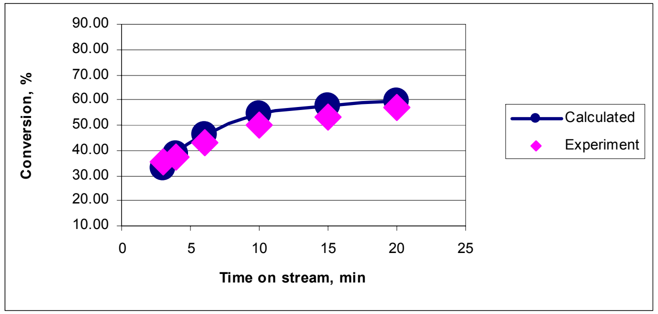

Figure 1 – Comparison of the experimental and calculated data

The results of the calculations are represented by means of graphics. The error is being calculated in every point. The results of finding constants of reaction rate for one of the experiments for process of alkylation of phelylacetonitrile are shown in figure 1. The results of the experiment and concentrations calculation with found constants are compared.

Work is made within a framework of the joint project between the St.-Petersburg State Technological Institute (Technical University) and TU Dresden.

DEVELOPMENT OF NANOSENSORS BASED ON THE FUNCTIONALISED CYCLODEXTRINS AND CALIXARENES

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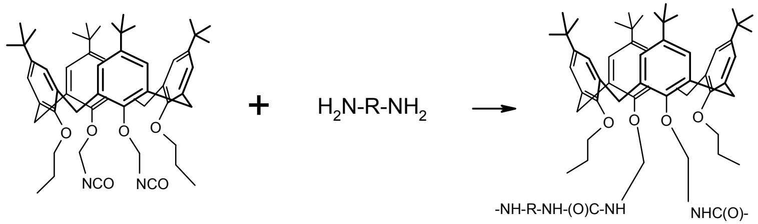
In this work we present the results dealing with the design and fabrication of novel cyclodextrin and calixarene based receptors ("Hosts") highly selective for recognition and binding of different sorts of organic substrates ("Guests") and elaboration of nanoscale support layers and thin films based on functionalized cyclodextrines and calixarenes for sensor technologies [1, 2], capable for deposition on the solid surfaces through different nano-technologies.

Cyclodextrins derivatives have been synthesized using silylation protection with thexyldimethylchlorosilane of the lower rim (6-position), then product obtained being treated with bromoacetylbromide involving the upper rim (2-position), followed by subsequent reaction of bromide group with appropriate amines fragments, which are capable of binding a range of organic species.

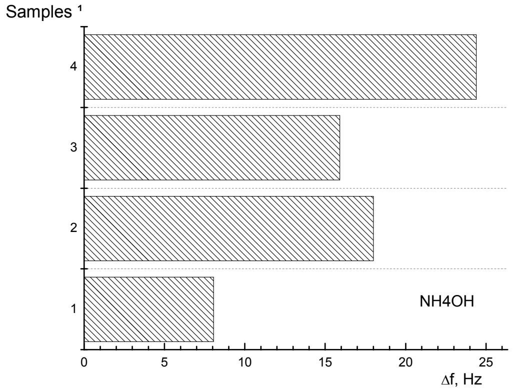
Calixarene based polymers were obtained as follows:



The polymers elaborated and functionalised cyclodextrins are identified by IR-spectroscopy, elemental analysis, size exclusion chromatography (SEC), DSC, WAXS and SAXS methods and MALDI-TOF.

Characteristics of thin films as sensitive support layers towards to a different organic vapors are determined using 8-channel QCM (Quartz crystal microbalance resonator) based sensor array.

According to the results obtained, the analytes analyzed (standard concentration 1000 ppm) regarding their ability to be detected on the surface of calixarene containing polymer sensors are arranged in the following range: ammonia > chloroform > ethanol and for the cyclodextrins synthesized: hexane > acetone > chloroform > benzene (toluene) > chlorobenzene > p-xylene.



This work is supported by the Science and Technology Center in Ukraine, STCU Project № 3643.

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TAUTOMERISM OF SOME 9-AMINOACRIDINE DERIVATIVES: RELATIVE STABILITY OF TAUTOMERS AND THEIR SPECTRAL PROPERTIES

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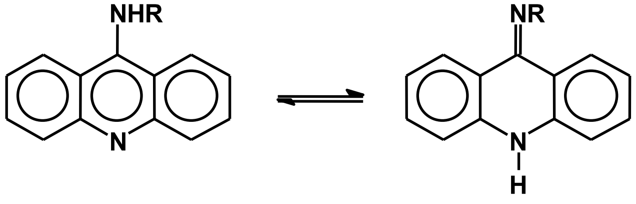
The tautomerism of some 9-aminoacridine derivatives has been investigated earlier using electronic and IR spectroscopy, ^{1}H NMR, X-ray diffractometry [1,2]. Depending on electron donating or accepting ability of substituents at exocyclic nitrogen atom, amino-, imino-tautomers, as well as their mixtures have been found.

In present work, 9-aminoacridines with various alkyl and phenyl substituents at exocyclic nitrogen atom (see Figure) have been investigated.

RM1 quantum chemical calculations of enthalpies of formation (ΔH_f) of investigated compounds in the ground state showed that the imino tautomers are more stable that the amino ones. Depending on the electron donating ability of the substituents, the presence of mixtures with a different ratio of tautomers may be expected. In the excited state, ΔH_f values of amino forms *Ia* - *Ie* and *Ig* are lower then those of imino forms. Therefore, the equilibrium shifts to amino tautomer upon excitation. In the case of *If* derivatives, imino tautomer is the predominant form in both the ground and excited states.



amino form imino form

Ia - R = methyl
Ib - R = n-hexyl
Ic - R = cyclohexyl
Id - R = tert-butyl
Ie - R = benzyl
If - R = phenyl
Ig - R = trichloracetyl

Spectral characteristics of the compounds have been obtained in six solvents of different polarity, polarizability and nucleophilicity. It has been found that *Ia* - *Ie* and *Ig* demonstrate intense emission of the amino form (480-500 nm) in all the media. The emission band of *If* strongly depends on solvent polarity (510- 580 nm). The fluorescence quantum yields of *If* are very low. Analysis of spectral characteristics of *If* and comparison with pyridine substituted compound studied earlier [2] permitted to attribute *If* emission to this of imino tautomer.

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DEFINITION OF PARAMETERS OF DISTRIBUTION OF PHASES IN THE MATRIX OF HETEROGENEOUS ALLOYS THE METHOD OF THE LOCAL ELECTROCHEMICAL ANALYSIS

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The equation of gradual curve $i_{\phi_i} = f(C_{\phi_i})$ for the local electrochemical analysis of heterogeneous alloys is offered

$$i_{\phi_i} = \frac{I^{max}_{\phi_1}}{1+\frac{C_{\phi_2}}{C_{\phi_1}}\cdot\frac{\gamma_{\phi_1}}{\gamma_{\phi_2}}\cdot\left(a\cdot C_{\phi_1}+b\right)} \qquad (1)$$

where a and b - parameters of distribution of dissolution phases in a matrix of an ingot of an alloy.

The algorithm of calculation of the specified parameters is developed.

Step 1. Data input: $I^{max}_{\phi_i}$, i_{ϕ_i}, C_{ϕ_i}, γ_{ϕ_i}.

Step 2. Calculation of value of function

$$f_{\phi_i} = \frac{i_{\phi_i}}{I^{max}_{\phi_i}},\ i=\overline{1,2}$$

Step 3. Calculation of factor of distribution of a phase

$$K_{\phi_i} = \frac{1-f_{\phi_i}}{f_{\phi_i}\cdot\frac{C_{\phi_2}}{C_{\phi_1}}\cdot\frac{\gamma_{\phi_1}}{\gamma_{\phi_2}}}$$

Step 4. Find the equation of a straight line $d: Ax+By+C=0$, the sum of distances from which up to a point with coordinates $M_i\left(C_{\phi_i}, K_{\phi_i}\right)$ - it is minimal:

$$\rho\left(M_i, d\right) = \frac{\left|A \cdot C_{\phi_i} + B \cdot K_{\phi_i} + C\right|}{\sqrt{A^2 + B^2}} \rightarrow min$$

Step 5. Definition of parameters of distribution

$$a = \frac{A}{B}; b = \frac{C}{B}$$

The given algorithm of the program is realized in the environment of visual programming *Delphi*.

ADSORPTION OF MIXED ACID ORANGE AND SODIUM DODECYLSULFATE ON THE BIRCH ACTIVATED CARBON

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Most of the literature works on adsorption of dyes and surfactants from aqueous solutions are devoted to the study of their adsorption from individual solutions on different solid adsorbents (active carbon, silica gels, montmorillonite, aluminium and iron hydroxides). As a rule, regularities established in these works can not be applied at the description of adsorption of dyes and surfactants from their multicomponent solutions inasmuch as an non-ideal behaviour of components, resulting in an increase (synergism) or decrease (antagonism) of adsorption, shows up in the last case. Recently scarce information about adsorption of surfactants mixtures and dyes mixtures from aqueous solutions on solid adsorbents has appeared. At the same time, common adsorption of dyes and surfactants from aqueous solutions had not been explored up to the present time.

The study of adsorption of dyes and surfactants mixtures on the boundary phase “solid adsorbent – aqueous solution” is of great importance for further development of modern adsorption theory from solutions, and also for the practical tasks, related to the problems of industrial wastewaters rendering safe.

In the present work the research results, directed on finding out the influence of mixture composition of acid dye and anionic surfactant either on the total adsorption value of removed components or on the adsorption value of each component, have been shown.

The Acid Orange and sodium dodecylsulfate chosen for the investigation were chemically pure. The total concentration of mixture components was $1,4 \cdot 10^{-4}$M. Granulated activated carbon BAC-A was chosen as an adsorbent. It has a BET specific surface area of 820 m^2/g, total pore volume 1,29 cm^3/g and particle size 1-1,5 mm. Active carbon was preliminary prepared: it was dust-removed on the sieve with 0,25 mm holes during 3 min, threefold boiled in aqueous distillate. Then adsorbent was dried at 110 ^{0}C and sieved to get required fraction.

The adsorption of dye and surfactant mixtures was performed under static conditions by shaking 0,15 g of adsorbent in 100 cm^3 of the solutions, containing individual components or their mixtures, at 115 rpm in rotary shaker for 8 hours at 20 ± 1^0C. The preliminary analysis showed that this time was sufficient to set the adsorption equilibrium in the system. Then the water phase was separated from the adsorbent by means of decanting, and samples equilibrium concentration was determined spectrophotometrically (for dye) and extraction-photometrically (for surfactant). Spectrophotometric researches showed that methods chosen for surfactant and dye analysis were possible to apply for their quantitative determination from aqueous solutions of mixtures, because neither sodium dodecylsulfate nor Acid Orange in their mixtures have influence on absorbance of each other. The ionic strength was kept at 0,01 M with sodium chloride. Dyes and surfactant adsorption was obtained at the pH values 3, 6, 10 of solutions.

For the explanation of the influence of composition of dye and surfactant mixture on the adsorption process adsorption properties of the explored systems were compared with the similar properties of the hypothetical ideal systems, where energy and entropy of each component depend on its nature and solution temperature, but do not depend on the other components presence. For the ideal systems rectilineal dependence of dye or surfactant adsorption on solution composition is to be observed.

It was stated in this work, that for all investigated mixtures of Acid Orange and sodium dodecylsulfate their total adsorption, found experimentally, exceeded theoretically calculated (for the ideal system), so synergism of adsorption was observed. Comparison of the experimentally found adsorption values of each component with theoretically calculated ones showed that at adsorption of Acid Orange from mixture synergism showed up in the cant of adsorption values for all studied pH values areas. In the case of sodium dodecylsulfate adsorption from mixture in acid and alkaline areas the experimentally found values of sodium dodecylsulfate adsorption closely agree with theoretically calculated, so additivity of adsorption has been found out (correlation coefficient R^2=0,99). At pH=6 the experimentally found values of sodium dodecylsulfate adsorption insignificantly deviate from theoretically calculated (correlation coefficient R^2=0,96). Therefore, regardless of solution pH value the adsorbent surface is equally saturated by sodium dodecylsulfate at its adsorption both from individual and from binary solutions, containing the dye.

Thus, the carried out investigations have shown that at adsorption of the acid dye and anionic surfactant from their mixture the component with higher adsorption activity in individual solutions (surfactant) is adsorbed from binary solutions on the carbon surface irrespective of less active component (dye) content. Substance with lower adsorption activity in individual solutions (dye) shows synergism of adsorption in the presence of a more active component.

AGGREGATION-INDUCED EMISSION FROM DERIVATIVES OF BARBITURIC ACID

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A decreasing fluorescence efficiency in the solid state is quite general and is mainly attributed to the intermolecular vibronic interactions which induce the nonradiative deactivation processes, such as excitonic coupling, excimer formations, excitation energy migration to the impurity traps, etc. However, the cases when compounds under their aggregation, on the contrary, show an increasing of luminescence intensity (the so-called phenomenon of the aggregation-induced emission) are known also. The nature of the given phenomenon is not enough studied. In particular, some derivatives of barbituric acid show an example of such spectral manifestations.

In the present work, 5-(4-dimethylaminobenzylidene)-barbituric acid (compound I) and 5-(4-methoxybenzylidene)-barbituric acid (compound II) were synthesized and their spectral-luminescent properties were studied. The drop of fluorescence intensity for a solution of compound I in water-ethanol mixture as function of the content of ethanol is shown in Fig.1. Also, quantum-chemical calculations of structures and electronic transitions for the molecular and aggregated forms of compounds I and II are carried out. The factors causing their aggregation-induced emission are discussed.

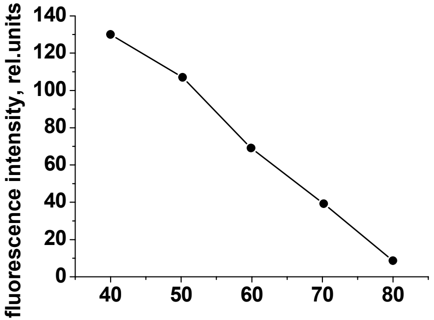

Fig.1. Dependence of fluorescence intensity at 644 nm of compound I on ethanol content in water-ethanol mixture.

CHEMICAL CORRELATION EQUATIONS

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Chemical correlation equations of the Hammett-Taft type etc. are grounded on the phenomenon of linear free-energy relationship, LFER, which, in turn, is also possible to express in the form of the correlation equation. In this work, new type of correlation dependence for energy parameters of a system, special case of which is the LFER phenomenon, is considered. It is shown that this type of correlation is more universal than linear free-energy relationship. Examples of the specified correlation for energy

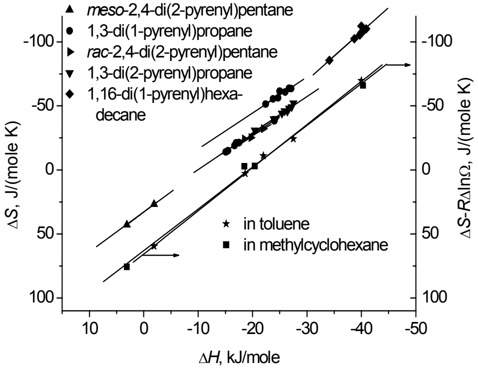

Fig.1. Results of correlation ana-lysis for bichro-mophores. Re-gression para-meters are r= 0,9992, sd= 2.1756, n=5 (to-luene, T_i=296.6 K) and r=0,9978, sd=4.7244, n=4 (methylcyclohe-xane, T_i=306.5 K).

parameters of excimers forming in different dipyrenylalkanes are demonstrated (see Fig.1).

It is shown that there are two types of linear energy relationships: LFER takes place under constant phase volume, whereas the second type holds in the case of variable phase volume. The connection of linear relationships with the correlation equations of the Hammett-Taft type is discussed. Both dependences are characterized by corresponding iso-temperatures, T_i, $T_{i1,2}$. These temperatures, in particular, define the ρ-parameter figuring in correlation equations of the Hammett-Taft type,

$$\rho = \frac{T_{i2} - T_i}{T_{i1} - T_i} \frac{T_{i1} - T}{T_{i2} - T}.$$

EMPIRICAL METHOD OF THE ACCOUNT OF INFLUENCE OF SOLVENT DISSOCIATION CONSTANTS OF SOME CARBOXYLIC ACIDS

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Existing methods of quantitative of media effect on dissociation constants of organic compounds are based on the complex,

resource-consuming methods of quantum chemistry, thus the error of calculations remains at rather appreciable level.

The empirical method for calculation of dissociation constants of organic acids in various solvents that use exclusively experimental data about physical properties of these acids and solvents is proposed. The method based on the well known LFER principle, but the sum of atomic contributions to the considered molecular parameter is taken in account. The key idea of this approach is the assumption that for some pair of physical properties of one substance may exist a linear correlation between deviations δX_j of experimental molecular properties X_j^{ex} from the sum of atomic contributions to these properties $\sum_i g_{ij} X_i$:

$$\delta X_j = X_j^{ex} - X_k \sum_i g_{ij} X_i \ , \tag{1}$$

where g_{ij} – quantity of *i*-th atoms in *j*-th molecule, X_i – the contribution of *i*-th atom to the physical property. X_k - dimensionless scaling factor.

The proposed method is the modification of our earlier approach [1-3] applied for establishment of correlation between and molecular volume and polarizability [1], two different thermodynamic values [2], proton affinity and molecular volume [3] and calculation of these values one from other. The main difference of current approach from our previous work consists in application of linearity principle to establish correlation between physical properties of two substances instead of two properties of one substance.

Thus in order to calculate of *k*-th acid in *j*-th solvent (pK_a^{jk}) the formal equation representing the above mentioned linear correlation is used:

$$\delta pK_a^{jk} = a_k \cdot \delta X_{jk} + b_k \ , \tag{2}$$

where a_k and b_k – parameters. The value of δpK_a^{jk} is connected with a dissociation constants linearly by equation:

$$\delta pK_a^{jk} = pK_a^{jk} - Y_j \quad (3)$$

by means of constant factor Y_j. δX_{jk} deviation of solvent molecular parameter X_j^{ex} from the sum of atomic contributions by analogy to eq. (1).

To find the parameters a_k, b_k, X_k minimization of the sum of squares of relative deviations between experimental and calculated values of dissociation constants of *k*-th acid in a series of the chosen solvents is performed. The condition of a minimality of this sum represented by the system of equations:

$$\frac{\partial \mathrm{E}_k}{\partial a_k} = \frac{\partial \mathrm{E}_k}{\partial b_k} = \frac{\partial \mathrm{E}_k}{\partial X_k} = 0 \quad (4)$$

and numerical solution of this system yields all required parameters.

Optimum values of atomic contributions X_i and constants Y*j* of solvent selected manually due to impossibility to solve general system of equations concerning parameters for all chosen acids in all solvents together.

The proton affinity in gas phase (PA) and Dimroth-Riechardt solvatochromic parameter (E_T^{30}) was selected for pK_a calculations as the molecular properties of solvent because they provided better results. One may expect that atomic PA values may be good approximation for the atomic contribution to molecular PA but in fact it was not correct. Although physical meaning of atomic contributions to the *a priori* non-additive value E_T^{30} is not clear, equal values of X_i for both E_T^{30} and PA are obtained.

Atomic contributions	X_C	X_H	X_O	X_N	X_S
X_i	-1.97	1.75	-2.30	-2.85	-0.76

The resulting equation to calculate of dissociation constantt for *k*-th acid in j-th solvent (pK_a^{jk}) was:

$$pK_a^{jk} = a_k \left(X_j^{ex} - X_k \sum_i g_{ij} X_i \right) + b_k + Y_j , \quad (5)$$

363 values of dissociation constants for 33 derivatives of benzoic and acetic acids in 11 solvents of are calculated by the given method. The reached relative error of calculation less than 9.5 %. Only 4 pKa values from 173 calculated in the literature for last 7 years have deviations relative to experiment data lower, than the results obtained by the offered method.

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EFFECTIVENESS OF MODELING LIQUID METALS' STRUCTURES BY MOLECULAR DYNAMICS AND REVERSE MONTE-CARLO METHODS

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There are certain problems with a technique of interpretation of the diffraction experimental data for disordered systems using curves of the structural factor (SF) and radial distribution function (RDF) of atoms. Therefore at the analysis of the received experimental data statistical methods of structure modeling, such as reverse Monte-Carlo (RMC) and molecular dynamic (MD), are widely used. As both methods are intensively applied to interpretation of liquid metals' structure, we had been undertook attempt to analyze adequacy of the received models on the example of liquid Na, K and Al.

Modeling of structure of liquid metals by RMC-method was carried out for melts of sodium (373K, 473K), potassium (338K, 508K) and aluminum (973K, 1073K, 1173K). SF's curves for alkaline metals were taken from the literature, for liquid aluminum - were determined by X-ray diffraction method. MD-modeling was carried out for NTV ensemble of particles, at same temperatures as RMC-modeling, for the systems containing 5832 (18^3), 10648 (22^3) and 15625 (25^3) atoms of metal. Modeling was carried out during 75000 steps (150 ps.). The pair potentials of interaction *U (R)* for all liquid metals were calculated by the pseudopotential's method. Modeling curves are well coincided with experimental curves.

Received MD and RMC-models were analyzed by a statistical - geometrical Voronoi-Delauney method. For liquid alkaline metals values of the metrical and topological parameters for Voronoi polyhedrons (VP) well coincide for both methods of modeling. Some difference in values of a root-mean-square deviation of factor of sphericity (σ) for MD-models point on higher local ordering of atoms in the given models in comparison with RMC-models, that also is observed in the increasing of contents of VP with topological indexes $n_4n_5n_6$ and shares of atoms (X_a), included in polytetrahedron clusters. Other situation is observed for models of liquid aluminum. Different methods of modeling give value of parameters which essentially enough differ among themselves. For the MD-models values of factor of sphericity and the contents of polyhedrons with topological indexes $n_4n_5n_6$ are more less than for RMC-models, that indicated to less dense packing atoms in MD-models. MD-method gives more ordered picture of atoms' distribution for liquid aluminum than RMC-method.

NONLINEAR CONDUCTIVITY OF POINT-CONTACT SENSORS UNDER GAS ACTION

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The field of sensors has undergone a rapid progress during the past years and is currently subject to world-wide research investigations combining physics, chemistry and material sciences. Drastic efforts are made to improve the crucial parameters of these devices. One of the most prospective directions in this activity is creation of sensors based on different nanoobjects. These structures offer unprecedented prospects for improving sensory characteristics which cannot be achieved with bulk samples. Undoubtedly, the breakthrough towards nano-object technologies yields unvalued opportunities to improve considerably the techniques of sensors. But absolutely new sensor characteristics can be discovered by using advanced fundamental benchmarks which were not applied up to now. Taking this into consideration recently a novel approach in this field was proposed [1]. As a result point contacts have been discovered to present excellent and unprecedented characteristics when used as gas sensors.

Following this approach we created new sensitive elements based on single-walled carbon nanotubes' point contacts to combine both advantages of the new method and new materials. Upon exposure to gaseous molecules such as NH_3 and NO_x these samples demonstrated dramatic nonlinear behavior of their conductivity on time. The parameters of point-contact sensors under study such as recovery time or limit of detection exceeded essentially those of existing sensor analogs. Thus new point-contact sensors have been shown to be prospective objects for further development and investigation.

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SUPERNUCLEOPHILIC REACTIVITY OF PEROXYHYDRO- AND PEROXOCARBONATE IONS

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Search and design of ready available and efficient oxidative-nucleophilic systems for decomposition of ecotoxicants is one of the acute problems now.

The systems involving hydrogen peroxide and its activators, particularly, hydrocarbonate ions, are promising for this purpose. Here we report studies on the decomposition kinetics of 4-nitrophenyldiethyl phosphonate (I) - an analogue of some chemical warfare agents - in system $H_2O_2/NH_4HCO_3/NH_4OH$ (μ 2M, 25°C). In this system an interaction of (I) with peroxide anions, HCO_4^- and CO_4^{2-}, formed gives rise to *ca.* 2.5-fold increase in the observed pseudo-first order rate constants.

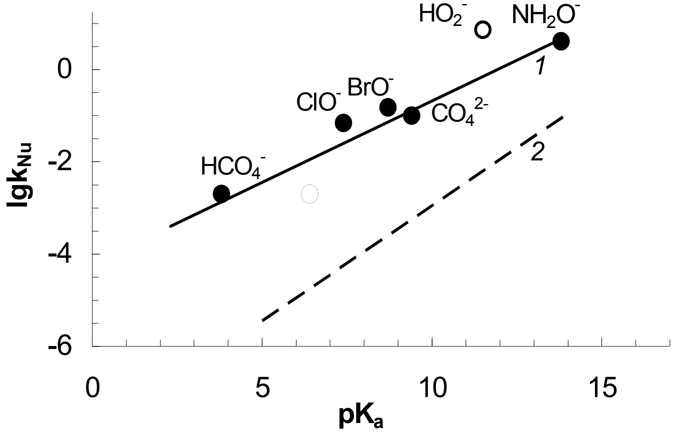

Figure. Bronsted plots for reactions of inorganic α-nucleophiles (*1*) and arylate (alcoholate) ions (*2*) with 4-nitrophenyldiethyl phosphonate.

A comparison of decomposition rates of (I) in this system with those in system H_2O_2/NH_4Cl allowed us to assess quantitatively the nucleophilic reactivity of HCO_4^- and CO_4^{2-} ions toward (I): $k_{HCO_4^-}$ =0.0046 l·mol^{-1}·s^{-1} and $k_{CO_4^{2-}}$ =0.095 l·mol^{-1}·s^{-1}.

Comparison Bronsted plots for the reaction (I) with inorganic ionic nucleophiles is given in the Figure. The points for HCO_4^- and CO_4^{2-} fall considerably higher than the line *2* for standard reaction series of arylate (alcoholate) ions [1], and form a separate Bronsted plot with known (See ref. [2]) α-nucleophiles ClO^-, BrO^-, NH_2O^- (line *1*, solid points):

$$lgk_{Nu}=-(3.48\pm0.27)+(0.29\pm0.03)\ pK_a$$
$$r\ 0.986,\ s_o\ 0.20,\ n\ 5.$$

It should be noted that HCO_4^- anion is the least basic (pK_a 3.8) from inorganic α-nucleophiles on record. To summarize, HCO_4^- and CO_4^{2-} anions should be classified as supernuclephiles.

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THE INTERACTIONS OF SOLVATOCHROMIC PYRIDINIUM *N*-PHENOLATES WITH L- AND H-ACIDS IN SOLUTIONS. VIS- AND NMR-SPECTROSCOPIC STUDIES

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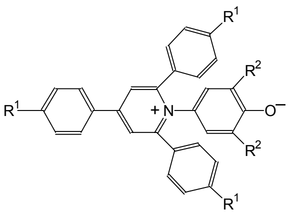
The charge-transfer (CT) band of pyridinium *N*-phenolate betaine dyes, $D^{\pm}$, exhibits the largest range of solvatochromism among other solvatochromic probes known up till now. These substances are therefore used for polarity estimation of various pure and mixed solvents, salt solutions, micellar media, etc.

The highly dipolar (zwitterionic) $D^{\pm}$ species are known to interact with both H- and L-acids in solutions. While in the first case completely colorless species, HD^+, appear, the second type of interactions, though described in some publications, is still not so clearly understood. We examined the interactions of four pyridinium *N*-phenolates (1-4)



No	R^1	R^2
1	H	H
2	H	C_6H_5
3	H	$C(CH_3)_3$
4	H	Cl
5	$C(CH_3)_3$	$4\text{-}C(CH_3)_3\text{–}C_6H_4$

with Li^+, Na^+, Mg^+, La^{3+}, and cations of some other lanthanides in DMSO, acetonitrile, acetone, *n*-butylacetate, trichloromethane, and 1-butanol. Metal ions were introduced into the solutions as a rule in form of perchlorates. Vis-spectral data reflect strong interactions caused by association of metal cations, being actually L-acids, with the negative (phenolate) part of the dye dipole. Numerously reproduced experiments allowed to rationalize such interactions by assuming two principle kinds of cation–dipole associates: (i) loose (or solvent separated, or solvent-shared) pairs, with blue shift of the CT band and (ii) colorless tight (or contact, or maybe even penetrated) pairs. The latter are very similar to the HD^+ species, which is proved using ^1H NMR spectra in $DMSO_{d6}$ solutions. The conversion of colored loose associates into the colorless tight ones occurs relatively slowly, more quickly with multi-charged cations, less quickly in DMSO, where the cations are strongly solvated. In all the cases, dye 4 is not completely decolorized in DMSO. Maybe, two Cl atoms participate in the interactions. For (4 + Li^+) system in DMSO, K_A = 6.2 ± 0.4 (loose cation-dipole associates). The association constants for tight associates are too high to be determined accurately. The decolorization is reversible: addition of basic agents or metal-complexing ligands restores the CT band.

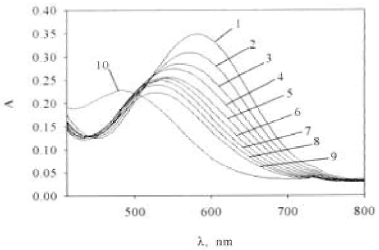


Fig. 1. Abs. spectra of dye **1** (2×10^{-4} M) in DMSO; conc. $LiClO_4$: 0 (1); 1×10^{-3} M (2); 2×10^{-3} M (3); 3×10^{-3} M (4); 4×10^{-3} M (5); 6×10^{-3} M (6); 8×10^{-3} M (7); 0.01 M (8); 0.012 M (9); 0.5 M (10).

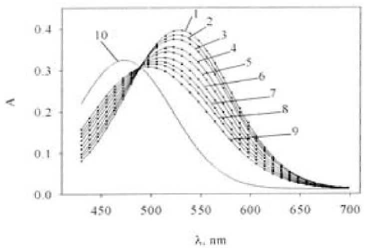


Fig. 2. Abs. spectra of dye **4** (1×10^{-4} M) in DMSO; conc. $LiClO_4$: 0 (1); 0.01 M (2); 0.02 M (3); 0.04 M (4); 0.06 M (5); 0.09 M (6); 0.12 M (7); 0.15 M (8); 0.2 M (9); calculated spectrum of (**4 +** Li^+.) associate (10).

Furthermore, the introduction of crown ethers and other ligands allows obtaining ligand-separated cation-dipole associates. In solvents with low polarity, where the inorganic salts, e.g., $NaClO_4$, are practically not dissociated, the aforementioned vis-spectral changes are to be explained in terms of loose, tight, solvent- and ligand-separated associates of ion pair with dye dipole.

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PRECISE DILATOMETRY OF 2-HYDROXYPROPYL-β-CYCLODEXTRIN AQUA SOLUTIONS

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Cyclodextrins (CDs) are typical natural oligosaccharide receptor molecules composed of D(+)-glucopyranose units linked via 1,4-α-glycoside bonds. The most common representatives of CDs are α-, β-, and γ-cyclodextrins, that contain six, seven, and eight units, respectively. Having a hydrophobic cavity, their molecules are capable to form “host- guest” inclusion complexes with a wide variety of organic and inorganic hydrophobic or ionic species in aqueous or aqua-organic solutions. The crucial factor for this unique type of complexation is the ratio between the size of the guest and the cavity of the CD molecule. Owing to this feature, natural CDs found numerous applications in many fields of pharmaceutical, food, cosmetic industries, analytical chemistry and other sciences [1].

The driving forces for guest incorporation into the CD cavity are hydrophobic interactions, hydrogen bonding and steric effect. The formation of inclusion complex in aqueous solutions results in a substantial rearrangement and removal of the water molecules originally hydrated to both the CD and guest molecules. Moreover, this process also induces the release of “high-energy” water molecules from the CD cavity into the bulk water. The cavity water molecules are entropically unfavorable because of an incomplete intermolecular hydrogen-bonding network and hence they have another properties then molecules in the bulk water [2].

It is well-known that volumetric and compressibility studies can contribute to our understanding of the intermolecular forces which govern the properties of aqua solutions as well as solute-solute, solute-solvent interactions and influence of solute molecules on the structure of water network. Traditionally, these investigations have been focused on a small organic molecules dissolved in water and practically no publications devoted to receptor molecules like cyclodextrins and their inclusion complexes.

The aim of this work – a precise dilatometric study of the aqua solutions of 2-hydroxypropyl-β-cyclodextrin (2-HP-β-CD). Density (ρ), isothermal compressibility (β_T), and thermal volumetric expansion coefficient (α) [3] were measured with high accuracy at the several temperatures for 2-HP-β-CD aqua solutions with errors $1x10^{-2}$%, 1%, and 2%, respectively. The pressure drop ΔP and temperature drop ΔT amounted to 4×10^5 Pa and 0.4 K, respectively. The results of experiment are listed in Tables 1-3. It was found that the hydrogen bond network does not change in the presence of 2-HP-β-CD molecules up the concentration of 20.30 mass %. The hydration type of 2-HP-β-CD was discussed.

Table 1. Density (ρ, g/cm^3) of 2-HP-β-CD aqua solution.

W* t,°C	0.51	1.01	5.61	9.02	15.24	20.30
25	0.99851	0.99998	1.01742	1.03130	1.05036	1.06900
50	0.98950	0.99094	1.00795	1.02161	1.04022	1.05859

W* - mass % units concentration of 2-HP-β-CD aqua solution.

Table 2. Thermal volumetric expansion coefficient ($\alpha\cdot 10^5$, K^{-1}) of 2-HP-β-CD aqua solution.

t,°C W*	10	15	20	25	30	35	40	45	50
0.51	9.8	15.7	21.1	25.8	30.5	34.8	38.6	42.4	45.9
1.01	11.6	16.6	21.6	26.0	30.8	35.2	38.8	42.6	46.0
5.61	12.2	17.8	22.4	26.8	31.3	35.8	39.4	43.2	46.2
9.02	14.2	19.2	23.8	28.2	32.4	36.6	40.1	43.9	46.6
15.24	16.4	21.2	25.6	29.7	33.7	37.4	40.8	44.5	47.8
20.30	18.6	22.8	27.2	31.1	34.8	38.5	42.2	45.2	48.7

Table 3. Isothermal compressibility ($\beta_T\cdot 10^{11}$, Pa^{-1}) of 2-HP-β-CD aqua solution.

t,°C W*	10	15	20	25	30	35	40	45	50
0.51	47.0	46.2	45.0	44.8	44.4	44.0	43.5	43.8	43.5
1.01	46.5	45.8	45.0	44.4	44.1	43.9	43.7	43.6	43.6
5.61	45.2	44.4	43.8	43.3	42.9	42.7	42.6	42.6	42.6
9.02	44.1	43.4	42.7	42.3	42.0	41.9	41.8	41.9	41.9
15.24	42.4	41.7	41.1	40.6	40.3	40.3	40.2	40.3	40.4
20.30	40.8	40.1	39.7	39.4	39.3	39.4	39.5	39.7	39.8

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FLASH PHOTOLYSIS AND PULSE RADIOLYSIS STUDIES ON ELASTIN HYDROLYSATES IN WATER SOLUTION

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Elastin is the abundant biopolymer in animals where it provides the principal structural and mechanical support. The main amino acids in elastin are: glycine, proline, hydroxyproline and alanine. Elastin is readily available, non-toxic and has got the fibril architecture that is inherent in natural tissues. As a component of a skin elastin is often exposed to UV irradiation. The aim of our work was to study the photochemistry and radiation chemistry of elastin hydrolysates solution in water. The main point of the work is to show what kind of radicals and short living species are involved in photochemical reaction in elastin. The paper deals with photoionization and photodecomposition measurements of elastin hydrolysates in aqueous solution at pH 7.2 in the absence and presence of oxygen or N_2O as electron scavengers. The investigation of the photochemical properties of elastin hydrolisates in water was carried out using nanosecond laser irradiation. The transient spectra of elastin hydrolysates solution excited at 266 nm show two bands. One of them with maximum at 295 nm and the second one with maximum at 400 nm. The peak at 400 nm is due to tyrosyl radicals. The first peak at the transient absorption spectra at 295 nm is probably due to phenylalalanine radical. The reactions of hydrated electrons and $^{\cdot}$OH radicals with elastin have been studied by pulse radiolysis. In the absorption spectra of products resulting from the reaction of elastin with e_{aq}^- no characteristic maximum absorption in UV and visible light has been observed. In the absorption spectra of products resulting from the reaction of the hydroxyl radicals with elastin two bands have been observed. The first one at 320 nm and the second one at 405 nm. Reaction of $^{\cdot}$OH radicals with tyrosine residues in collagen chains gives rise to Tyr phenoxyl radicals (absorption at 400 nm).

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COLLAGEN- SYNTHETIC POLYMER INTERACTIONS IN SOLUTION AND IN THIN FILMS

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During the past two decades there has been great scientific and commercial progress in the area of polymer bends. According to the theory of Flory-Huggins the miscibility and compatibility of two polymers depend on their ability to form specific interaction between them, which contributes to diminish or make negative the mixing enthalpy. Blends of synthetic and natural polymers represent a new class of materials with better mechanical properties and biocompatibility than those of the single components. Collagen is the most abundant biopolymer in animals where it provides the principal structural and mechanical support. Collagen is readily available, non-toxic and it provides an excellent basis for biomaterials. The aim of this work was to study the interactions between collagen and selected synthetic polymers. Blends of collagen and synthetic polymer have been prepared mainly in the form of films using the solution casting method. The interactions between two polymers and physico-chemical properties of the blends were investigated by FTIR, UV-VIS spectroscopy, differential scanning calorimetry and viscosimetry measurements.

The FTIR, DSC and viscosimetry results show that collagen macromolecule could form different types of hydrogen bonds with synthetic polymer macromolecule:

between two hydroxyl groups (OH······OH),

between the hydrogen of the amide group and oxygen of the hydroxyl group (NH····OH),

between the hydrogen of heteroatoms and the carbonyl group of the amide (C=O····HO, C=O····HN).

The above specific interactions between two polymers can modify their physico-chemical properties.

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CREATION OF CHITOSAN NANOLAYERS AT THE SURFACE OF LATEXES PARTICLES

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Perspective hi - tech branch of the design of the new materials is interface modification of disperse systems and planar surfaces.

One of the effective ways of interface modification of disperse systems is grafting of heterofunctional polyperoxides to the surface [1].

Recently a close interest is paid to the natural polymer of chitosane (Chi) - β-1,4-(2-deoxy-2-amino-D-glucopyranoside) and its derivaties due to such unique properties as biodegradability, bio- and hemocompatibility, has antibacterial properties, is not toxic, etc.

Via radical grafted copolymerization of Chi and 5-tert-butylperoxy-5-methyl-1-hexen-3-in (VEP) were synthesized Chi derivative surfactants with ditertial peroxide fragments in grafted side chaines poly-tert-butylperoxy-5-methyl-1-hexen-3-in (polyVEP). Chi-VEP was used as macroinitiator and co-emulsifier for emulsion polymerization of vinyl monomers. Polystyrene (polySt) and polybutylacrylate (polyBA) latexes with particles, which suface was covalent modified by grafted Chi-VEP. During the emulsion polymerization Chi-VEP and trimethylcetylammonium bromide (MCAB) were used as coemulsifiers. The initiators were the radicals formed by thermal decomposition of ditertial peroxide groups of Chi-VEP. Emulsion polymerization of styrene at 343K and styrene – water phase ratio 1:9 lasted for 1 – 3 hours until the conversion value of 98 – 99%.

It was discovered, that the stabilization of disperse system during the emulsion polymerization is accompanied by synergism when both Chi – VEP and MCAB are used, which is a charactical feature of Chi and its derivatives [2]. Under similar conditions if Chi-VEP and MCAB were used separately they can provide the stabilization and emulsion polymerization of styrene.

Immobilization of Chi – VEP surfactant initiator at the surface of polymer–monomer particles (PMP) occures via its adsorption due to hydrophobic–hydrophobic interactions between the grafted polyVEP chaines and polySt at particles surface. It is obvious that the initiative radical formation occures in the adsorptive layers of PMP [3].

Thus the general dependence can be represented by the following equation:

$$W \sim k\,[\text{Chi-VEP}\ ]^{n}\,[\text{MCAB}]^{m}\,[\text{styrene}]^{1}$$

It was determined that the order of emulsion polymerization with respect to the initiator Chi-VEP over the 343-353K is close to 0,5, order with respect to the coemulsifier MCAB is close to 0,5, order with respect to the monomer is close to 1,0. This allows to consider emulsion polymerization with the presence of Chi-VEP and MCAB within the Medvedev theory.

It was discovered that during the emulsion polymerization occures the covalent grafting of Chi-VEP to the latex particles surface. Using thermogravimetric analysis and chromatography was determined that the quantity of chemicaly grafted Chi-VEP in latex polySt is 5-12%.

It was proved that synthesized polySt and polyBA released from the latexes via freezing and separated from the ungrafted Chi-VEP depress the growth of bacterial culture of Sarcina flava and bacillus culture of Bacillus.

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PHASE SEPARATION IN THE ORGANIZED SYSTEMS BASED ON THE ANIONIC SURFACTANTS FOR PRECONCENTRATING MICROCOMPONENTS

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Micellar extraction based on the phase separation at cloud point temperature in the non-ionic surfactants solutions is often used as an alternative to the extraction with organic solvents. When compare with liquid-liquid extraction micellar extraction has some advantages such as increased selectivity and the possibility to get high absolute preconcentrating coefficients while analyzing small sample volumes. However, traditional micellar extraction based on heating of the non-ionic surfactant aqueous solutions to high temperature can not be used for preconcentrating of some biologically-active, volatile and hydrolyzable substances. From another hand the phase separation in the solutions of ionic surfactants can be observed at the low temperatures, which are convenient for extraction of organic substances. Therefore, the phase separation in the organized systems based on the anionic surfactant

- sodium dodecylsulphate (SDS) - for the preconcentrating of the organic microcomponents was studied in the work.

Aqueous solutions containing ionic surfactants exhibit the property of being separated into two phases by cooling to under Krafft point temperature or an addition of salts or hydrotropes (such as phenol). The optimal conditions for phase separation in the organized systems based on the SDS were found. Systems of four types were investigated: aqueous solutions of SDS; solutions of SDS-NaCl mixtures, solutions of SDS-phenol mixtures and ternary systems which contained SDS, phenol and NaCl simultaneously. Two main parameters were studied: the phase transformation temperature and the volume of surfactant-rich phase. The ability to concentrate the organic substances by the SDS phases was investigated using model compounds - basic triphenylmethane dyes and aliphatic carboxylic acids. It was shown the high effectiveness of dyes preconcentrating by SDS-NaCl phases. From another hand, phases formed from SDS-NaCl-phenol solutions showed good characteristics at carboxylic acids preconcentrating. At that, both NaCl containing SDS phases were able effectively extract positively charged substrates. Corresponding recommendations for the optimal phase choice for the preconcentrating of substrates of different nature were formulated.

PHASE EQUILIBRIUM IN MULTI-COMPONENT AQUEOUS SYSTEMS BASED ON Na_2SO_4 AND POLYETHYLENEGLYCOLS

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Ability of polyethyleneglycols aqueous solutions to form two-phase aqueous systems when large concentrations of some salts are present has been long enough used in biotechnology of biologically active compounds division.

Recently such systems have been applied in extraction, concentration and separation of various metals, radionuclides being among them.

The important fact that determines the possibility of preparation of two-phase system with inorganic salt is high solubility of salt in water and low one in glycols. However, from the data presented in literature it is impossible to draw a single conclusion what salts and at which concentrations can form heterogeneous systems with PEG.

Phase equilibria in PEG water-salt solutions of different molecular weights (400, 600, 1000, 1500) have been studied in the given paper in order to choose conditions necessary for obtaining heterogeneous systems.

Sodium sulphate whose solubility was 1-2 orders higher in water than in studied glycols was used as saline agent.

Phase equilibria have been studied by titration method of aqueous PEG solution with the help of the studied salt solution till the point of opacity.

We found sodium sulphate to be a good saline agent and minimum Na_2SO_4 concentration in aqueous polyethyleneglycole solution necessary for appearance of heterogeneous system to be frequently less than minimum concentration that causes division for electrolytes used traditionally in such systems. Phase diagrams of aqueous-polyethyleneglycole systems with Na_2SO_4 have the form traditional for such systems where the field of two phase equilibrium occupies the greater part of Gibbs-Rosenbone triangle.

When glycole molar mass increases the equilibrium region of two liquid phase expands: the higher the degree of PEG, the lower is its concentration necessary for the preparation of extraction system, minimum concentration of salt necessary for obtaining heterogeneous system being also decreased.

PHOTO-INDUCED HYDROLYSIS OF THIOSQUARYLIUM DYES

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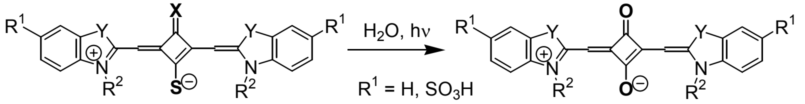
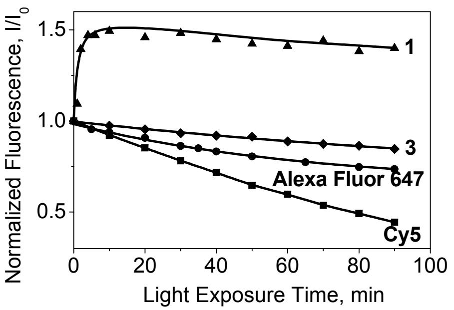
Next to extinction coefficient and quantum yield the photostability of dyes plays an important role for their use in biomedical applications. While the conventional cyanine dyes and conventional squarylium dyes photobleach upon exposure to light, the absorbance (*A*) and emission intensity (*I*) of the thio-squaraines **1** and **2** were found to increase. This effect can be attributed to a photo-induced hydrolysis of the thio-squarylium C–S group whereby the thionated dyes **1** and **2** are transformed into oxo-squarylium dyes **3.** Because the photodecomposition of **3** is much slower than the hydrolysis rate of **1** and **2**, and because **3** has a higher extinction coefficient and higher quantum yield than **1** and **2**, the absorption and fluorescence intensity increases until **1** and **2** is totally transformed to **3**.



1 X = O; **2** X = S R^2 = Me, $(CH_2)_5COOH$, $(CH_2)_4SO_3H$ **3**

During this process only a small blue-shift of the absorption and emission (no more than 16 nm) is observed. Neither squaraine **1** nor **2** hydrolyze in the absence of light.



Due to their photophysical properties and high photostability as compared to cyanines Cy5 and Alexa Fluor 647, thio-squarylium dyes **1** and **2** show potential for use in biological imaging to investigate the structure and function of cells.

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SPECTRAL PROPERTIES OF LONG-WAVELENGTH DICYANOMETHYLENE-SQUARYLIUM DYES

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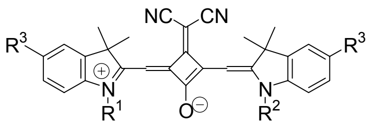
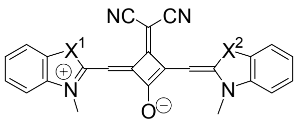
Spectral properties of dicyanomethylene-squarylium dyes **1–9** free in solutions and after interaction with Bovine Serum Albumin (BSA) and cells such as human fibroblasts and *Saccharomyces Cerevisiae* yeast were investigated.





1 R^1, R^2 = Me, R^3 = H; **2** R^1, R^2 = $(CH_2)_2OH$, R^3 = H; **6** X^1 = CMe_2, X^2 = O; **7** X^1 = CMe_2, X^2 = S;
3 R^1 = Me, R^2 = $(CH_2)_2OH$, R^3 = H; **8** X^1 = O, X^2 = S; **9** X^1 = S, X^2 = S;
4 R^1 = Me, R^2 = $(CH_2)_5COOH$, R^3 = H;
5 R^1 = R^2 = Me, R^3 = NO_2

These dyes absorb and emit in a wide spectral range depending on the nature of the terminal heterocyclic moiety. They have long-wavelength absorption and emission maxima in chloroform (647–757 nm), very high extinction coefficients (104,000–208,000 M^{-1}·cm^{-1}) and quantum yields as high as 80%. The terminal heterocyclic moieties cause a red-shift of the absorption and emission maxima in the order: benzoxazole < indolenine < benzothiazole < 5-nitro-indolenine. All the dyes exhibit additional absorption bands in the 378–396 nm range with extinction coefficients of about 29,000–44,000 M^{-1}·cm^{-1} while dye **5** absorbs not only in the red and UV but also in blue spectral region (468 nm) with extinction of 32,000 M^{-1}·cm^{-1}. This makes dicyanomethylene-squaraines also suitable for use with the blue (380, 405 and 470-nm) diode lasers excitation. Absorption and emission spectra in methanol are blue-shifted by 10–30 nm compared to chloroform and the quantum yields are somewhat lower. These dyes form non-fluorescent aggregates in aqueous media. As a result the long-wavelength absorption band becomes broader and a new band appears. The fluorescence intensity of dyes **1–4** and **6** substantially increases in presence of BSA with quantum yields as high as 95%. Therefore these dyes are perfectly suited for fluorescence-based quantification of proteins and *in-situ* biological imaging because they readily stain cells of different nature.

ADSORPTION PROPERTIES OF POLYIONENE-MODIFIED SILICAS

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As known. polymeric ion-exchangers for the solid-phase extraction and preconcentration of metal-containing anions have relatively high sorption capacity, but they are characterized by swelling and low adsorption rate. At the same time, inorganic adsorbents possess good kinetic properties and practically do not swell, but they have lower sorption capacity. Introducing polymers with quaternary nitrogen atoms into the surface layer permits one to combine properties of inorganic matrix and functional polymer and to obtain adsorbents with well expressed anion-exchanging properties.

In present work the water-soluble 1,4-MePh polyionene having quaternary nitrogen atoms in the main chain of polymer was applied for modification of silica gel with a specific surface area of 256 m^2/g. Silicas with polyionene adsorbed from water solutions and the samples obtained by *in situ* ionene polymerization in the presence of silica particles have been prepared. The concentrations of adsorbed and bound polymer were monitored thermogravimetrically and spectrophotometrically using bromphenol blue as an indicator (λ=600 nm). Such modified silicas were applied for separation and solid-phase preconcentration of metal-containing anions, namely MoO_4^{2-}, WO_4^{2-}, $Cr_2O_7^{2-}$, VO_3^- from the solutions of ammonium salts and $AuCl_4^-$ from chloroauric acid solutions.

Silicas modified with polyionene was found to remove molybdate- and dichromate-ions (95 and 67% accordingly) in the acidic media at pH=1-2, and tungstate- and vanadate-anions (95 and 73% accordingly) at pH=4. Silicas with adsorbed and immobilized polyionene was shown to display the same adsorption properties towards anions studied. From X-ray fluorescence data, silica with immobilized polyionene practically quntitatively removes $AuCl_4^-$ ions over a wide concentration range (from 1 up to 100 mg/L) at pH=2. Reduction of $AuCl_4^-$ ions to metallic gold (at the surface concentrations of 10-100 μg/g) was observed at interaction with immobilized polyionene and characteristic violet coloration of silica (λ=640 nm) was detected. This observation may be applied for elaboration of adsorption-photometric method analysis of Au(III) traces in solutions using silica modified with polyionene.

THE ELECTRODE PROCESSES ON PASSIVE METALS (Fe, Ni, Co, Cr) AND THEIR ALLOYS

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Nowadays all kinds of corrosion-resistant alloys are used in various areas of science and engineering, for example in medicine and jewelry industry.

Such alloys are: stainless steel, chromium-cobalt and chromium- nickel alloys. The main components of these alloys are chromium, nickel, and cobalt, which determine their good anticorrosive properties.

These alloys are electrochemically worked in order to obtain certain capabilities or properties the alloys don’t have: improvements of decorative properties, increasing of surface conductivity, solder ability, or biological resistance. Electrochemical coatings plated on these alloys can be made from copper, silver, and gold.

Electrochemical coatings on such alloys obtained by usual methods don’t show excellent results, since the passive surface film prevents obtaining coating with strong bonding. Thus, it is necessary to activate the surface, i.e. to remove an oxide film.

The research of electrode processes on passive metals and alloys is an actual problem of modern electroplating.

Chromium-cobalt and chromium-nickel alloys are widely used in dentistry. In domestic stomatological practice they use the chromium-cobalt alloys of which the demountable and fixed dentures are made. It is known that there are corrosion processes occurring on these metals because of contact with a saliva, mineral and organic compounds in a oral cavity of the patients. Therefore in order to add bioaesthetic properties for dentures the alloys are usually electroplated with gold. Only complex gold cyanide electrolytes are used for this purpose. The alternative to these electrolytes is chloride electrolytes of gilding which makes possible the deposition of thick (up to 100 microns) gold layers. Application of the anodic processing of chromium-cobalt and chromium-nickel alloys by means of etching with solutions of hydrochloric acid and its mixture with sulfuric acid significantly increases the adhesive properties of gold coatings.

By means of analysis of dynamic and static polarization measures, the kinetics mechanism of anodic processes on chromium-cobalt and chromium-nickel alloys has been investigated. The polarization of alloys by constant currents is characterized by transferring into transpassive state, and prevents obtaining an active surface. However, potentiodynamic method with maintenance of fixed polarization potential (0,2±0,05V) promotes the selective dissolution of an alloy with etching of chrome, as the most electronegative component. At small densities of anodic current (up to $5\cdot 10^{-3}$ A/cm^2) formation of an active microrough surface is observed.

The electrode processes on stainless steel (mark 08X18H10T) are investigated in solutions based on chlorides. It is established that the passive state of steel is disturbed in mixture of sodium chloride and sulfanic acid under the conditions of anodic polarization. The anodic process runs under the mixed control. The processing of steel at small anodic current densities $(0,2 - 0,6)\cdot 10^{-3}$ A/cm^2 is accompanied by even dissolution of steel with the formation of active surface. Obtaining of such surface allows precipitating copper coating from acidic copper chloride electrolyte on steel. The main components of this electrolyte are copper chloride (II) and hydrochloric acid. This coating is characterized by high adhesion to a substrate as well as by compactness and fine crystallinity. The ability to form depositions is determined by reactions on cathode:

$Cu^{2+} + Cl^- + e \rightarrow CuCl \qquad E^0 = +0{,}538\ V;$ (1)
$Cu^{2+} + 2e \rightarrow Cu \qquad E^0 = +0{,}137\ V;$ (2)
$2H^+ + 2e \rightarrow H_2 \qquad E^0 = 0\ V.$ (3)
$mH_2O + nM \leftrightarrow M_nO_m + mH^+$ (4)

The reactions # 1 - 3 describe the reduction of copper, and reaction #4 describe the chemical formation and reduction of metal oxide. High speed of reduction reaction compared to the reaction of oxidization allows us to get high quality of deposits.

Studying of acidic chloride solutions of electrolytes has the practical interest for implementation of anodic and cathodic processes on metal susceptible to passivation. The application of the new nontoxic solution and optimal conditions of electrolysis with original technological decisions and methods positively influence the electrochemical quality of deposits and increase the environmental safety of electrochemical treatment of alloys.

CATALYTIC OXIDATION OF CYCLOOCTENE BY MOLECULAR OXYGEN IN THE PRESENCE OF VANADIUM DIBORIDE

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The liquid-phase oxidation reaction of hydrocarbons by molecular oxygen is important reaction of organic synthesis because it allows to obtain various oxygencontaining compounds – epoxides, acids, alcohols, etc., using ecologically clean oxidant - molecular oxygen. Use of catalysts in this process allows to increase reaction rate and to turn process in the necessary direction and in such way carry out the process with high selectivity of main product.

In the present work the initial stages of the liquid-phase oxidation of cyclooctene by molecular oxygen in the presence of vanadium diboride as a catalyst at 353 K are investigated. At partial pressure of oxygen higher than 0,05 mPa the rate of both catalytic and noncatalytic oxidation process does not depend on the pressure of oxygen.

It has been established that vanadium diboride influences on the oxidation process in the presence of *tert*-butyl hydroperoxide in the reaction system and does not influence on the process in the presence of azodiizobutyronitrile. In the area of independence of the oxidation rate from the partial pressure of oxygen the increasing of *tert*-butyl hydroperoxide concentration leads to the linear increase of the oxidation rate of cyclooctene. It indicates that the reaction is first order in hydroperoxide. The process rate nonlinearly depends on the olefin concentration and catalyst content and the reaction is smaller than first order with respect to this components.

The radical formation in the investigation system are result of proceeding of two processes – noncatalytic and catalyzed by vanadium diboride bimolecular decomposition of *tert*-butyl hydroperoxide.

From the obtained results the kinetic scheme of the initial stages of oxidation reaction of cyclooctene by molecular oxygen in the presence of vanadium diboride is proposed. The kinetic model includes processes of complex formation between components of reaction system. The rate equation of oxidation process is obtained and kinetic constants are determined. The theoretical dependences of the oxidation rate on concentrations of olefin, hydroperoxide and catalyst content are calculated and they coincide with experimental data.

The work is supported by the Ukrainian Fundamental Researches State Fund.

PHASE DIAGRAMS OF POLYCOMPONENT SYSTEMS

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The determination of crystallization conditions and solubility of salts in salt-water-systems with more than three components has an exceptional importance for synthesis of multiple-state (complex) inorganic materials and for production them from natural poly-mineral and industrial raw materials.

Liquid waste materials consisting partially of sodium and potassium sulphates, carbonates, bicarbonates and fluorides are produced at the industrial production of aluminum. Their utilization is necessary to solve the ecological problems and to improve the industrial economy. It is very difficult to identify each of the produced solid phases that restricts the experimental study of this kind of systems with many components. We need the preliminary forecast of phase equilibria in such systems. We investigated the common crystallization of phases in equilibrium on structure with four components consisting of simple hydrated double types and mixed types of salts of sulphate, carbonate, bicarbonate and fluoride by the method translation. Translation method derives from the possibility of combining structural characteristics of diagrams on composition with *n* and *n*+1 components and depends on the state rules of Gibbs. We built the simultaneous (balanced) phase crystallization of systems with four components at 25 °C. For system Na,K//CO_3,SO_4-H_2O:C.10 + C.7 + Gz; Mb + Gz + C.10; Na.K.6 + K.1,5 +Ar; C.7 + Na.K.6 + Gz; Ar + Gz + Na.K.6. For system Na, K//CO_3,HCO_3 - H_2O: C.10 + C.7 + Tr; $NaHCO_3$ + $KHCO_3$ +Tr; C.7 + Tr + Na.K.6 Na.K.6+K.1,5+Tr; $KHCO_3$ + S + N + K.1,5 ; $KHCO_3$ +N + Tr; K.1,5 + N + Tr. For system Na, K//SO_4, HCO_3 - H_2O: Mb + Gz + $NaHCO_3$; Mb + Gz + KHCO3; $KHCO_3$ + $NaHCO_3$ + Gz. For system Na, K//CO_3,F-H_2O: Na.10 + Na.7 + NaF ; Na.K.6 + K.1,5 + KF ; Na.7 + Na.K.6 + NaF; NaF + KF + Na.K.6. Also the closed phase diagram of system Na,K//CO_3,HCO_3,SO_4-H_2O with five components at 25 °C was constructed. The following conventional signs of phase equilibriums were used: C.10 – $Na_2CO_3\cdot10H_2O$; C.7 – $Na_2CO_3\cdot7H_2O$; Mb – mirabilite $Na_2SO_4\cdot10H_2O$; Gz – glazerite $3K_2SO_4.Na_2SO_4$; Na.K.6 – $Na_2CO_3\cdot K_2CO_3\cdot6H_2O$; K.1,5 –$K_2CO_3\cdot1{,}5H_2O$; Ar – arkanite K_2SO_4; Tr – Trona $NaHCO_3\cdot Na_2CO_3\cdot2H_2O$; S – $2KHCO_3\cdot K_2CO_3\cdot1{,}5H_2O$; N – $NaHCO_3\cdot K_2CO_3\cdot2H_2O$.

CRYSTAL STRUCTURE AND ELECTRICAL PROPERTIES OF ANION-RADICAL TCNQ SALTS (N-Me-2,5-di-Me-Pz)$(TCNQ)_2$ AND (N-Me-2,6-di-Me-Pz)$(TCNQ)_2$, (Pz is pyrazine)

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Anion-radical salts (ARS) of 7,7,8,8-tetracyanoquinodimethane (TCNQ) containings N-methyl-2,5-dimethyl-pyrazinium (N-Me-2,5-di-MePz)$^+$ and N-methyl-2,6-dimethyl-pyrazinium (N-Me-2,6-di-MePz)$^+$ cations have been first synthesized.

These compounds have been investigated by several methods: IR-spectroscopy, X-ray structure analysis and electrical conductivity measurements in a wide temperature range [1].

Crystal structure of (N-Me-2,5-di-Me-Pz)$(TCNQ)_2$ (I) formed by N-methyl-2,5-dimethyl-pyrazinium (N-Me-2,5-di-MePz)$^+$ cations in a special position and TCNQ anions in a general position. The salt has layered structure, where cations layers alternates with TCNQ layers along *c* axis. Anions forms stacks along *a* axis, where they are shifted with respect to each other in pairs. TCNQ particles have a charge equal to –0.44. Crystal structure of (N-Me-2,6-di-Me-Pz)$(TCNQ)_2$ (II) formed by N-methyl-2,6-dimethyl-pyrazinium (N-Me-2,6-di-MePz)$^+$ cations situated in a general position and three TCNQ anions (A, B, C). One of them (A) takes a general position, but B and the C anions are situated in special center-symmetrical positions. This salt has layered structure, where cation layers alternates with TCNQ anion-radical layers along *c* axis.

Electrical conductivities of these ARS at room temperature differs by three decimal orders: σ_{RT}(I) = $3.9\cdot10^{-5}\Omega^{-1}cm^{-1}$, and σ_{RT}(II) = $2.4\cdot10^{-2}\Omega^{-1}cm^{-1}$. A simple activation model can describe temperature dependence of electrical resistance for both ARS.

Reference:

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AQUEOUS SOLUTIONS OF CALIX[4]ARENE CHOLINE AS MEDIA FOR ACID-BASE REACTIONS

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Solvatochromic dyes and acid-base indicators are widely used for examination of organized solutions [1]. Spectral and protolytic properties of many dyes are rather sensitive to the solvation properties of the microenvironment, to local electrical charges, etc. The "calixarene + dye" systems, as well as other "calixarene +

substrate" systems, are usually considered in terms of "Host-Guest" interactions, resulting in formation of inclusion complexes with 1:1 stoichiometry. On the other hand, the formation of calixarene micelles in the process, cannot be also excluded. Therefore, the changes in the protolytic properties of the dyes, caused by water-soluble calixarenes, can evidently result not only from interaction with the molecular cavity, but also from indicator adsorption on the surface of the aforementioned aggregates. In the present study, the average particle size, size distribution and ζ-potential of dispersion of tetrapropoxycalix[4]arene **(I)** bearing four hydrophilic choline groups at the upper rim [2] (Figure 1) were determined by Dynamic and Electrophoretic Light Scattering methods. In pure water, without additional electrolytic background, aggregates appear at calix[4]arene concentration $\geq 6 \times 10^{-3}$ M. The rough estimate of their diameter is 3-4 nm, while the zeta–potential value is $\xi \approx +66 \pm 5$ mV. Hence the properties of such calix[4]arene solutions must be studied thoroughly in terms of micellar effects on versatile dissolved substrates.

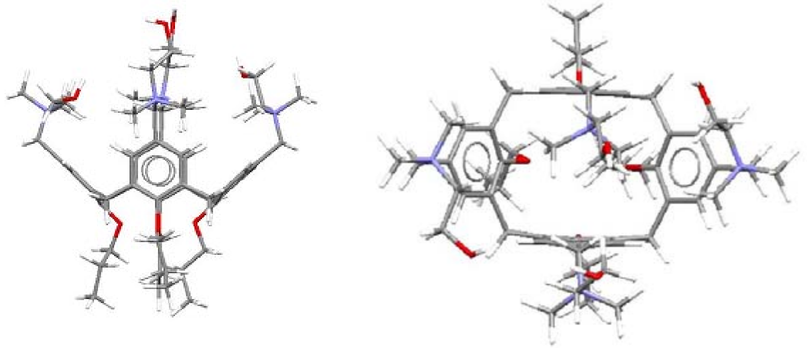

Figure 1. The molecular structure of tetrakis(N,N-dimethyl-N-hydroxyethylammonium-methylene)-tetrapropoxycalix[4]arene tetrachloride **(I)** (HyperChem 6. MM+), (Cl^- are omitted).

The so-called "apparent" ionization constant, K_a^a, of fifteen indicator dyes of different structure and molecular size were determined in aqueous solutions of the cationic calix[4]arene (concentration range of 1×10^{-5} to 0.01 M) by means of vis spectroscopy with potentiometric determination of pH. Dyes concentration was approximately 1×10^{-5} M. The pK_a values of dyes in water and in aqueous of solutions calix[4]arene (2.5×10^{-3} M) at ionic strength 0.05 M (NaCl + buffer solution) are compiled in Table 1. The majority of the dye species are completely bound by macrocyclic compound at this calixarene concentration.

Table 1. The pK_a values of dyes in water and in aqueous of solutions calix[4]arene, 25°C

Indicator	Charge type	pK_a^w	pK_a^a
Thymol blue	A^+B^0	1.49 ± 0.01	0.29 ± 0.13^a
Methyl orange	$A^{\pm}B^-$	3.14±0.05	1.38 ± 0.08
Methyl yellow	$A^{\pm}B^-$	3.06±0.05	2.57±0.04
Bromophenol blue	A^-B^{2-}	4.05±0.02	2.59±0.02 [2]
Bromocresol green	A^-B^{2-}	4.85±0.01	4.14±0.05
Bromocresol purple	A^-B^{2-}	6.30±0.02	5.51±0.10
Bromothymol blue	A^-B^{2-}	7.26±0.09	6.82±0.03
Phenol red	A^-B^{2-}	7.97±0.02	7.40±0.06
o-Cresol red	A^-B^{2-}	8.25±0.01	7.58±0.04
m-Cresol purple	A^-B^{2-}	8.55±0.01	8.28±0.05
Thymol blue	A^-B^{2-}	9.07±0.02	9.14±0.02
2,4-Dinitrophenol	A^0B^-	3.81±0.02	2.88±0.05 [2]
2,6-Dinitrophenol	A^0B^-	3.58±0.01	3.24±0.01
2,5-Dinitrophenol	A^0B^-	5.08±0.02	4.52±0.05
4-Nitrophenol	A^0B^-	7.07±0.04	7.08 ± 0.12
N,N'-dioctadecylrhodamine	$A^+B^{\pm}$	3.22^b	2.58±0.03[2]

[a] ionic strength > 0.05 M; [b] the pK_a^w value of rhodamine B, ionic strength → 0

The "calixarene + dye" interactions manifest themselves in shifts of pK_a^a and λ_{max} values as compared with the values in pure water. Medium effects for investigated dyes in aqueous solutions of cationic calixarene ($\Delta pK_a^a = pK_a^a - pK_a^w$; $\Delta\lambda_{max} = \lambda_{max}^{Calix} - \lambda_{max}^{H_2O}$) are very similar to those in micellar solutions of cationic surfactant [2].

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BINDING CONSTANTS OF THE 4-HYDROXYBENZOIC ASID ESTERS WITH MICELLAR PSEUDOPHASE OF SURFACTANTS

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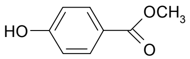
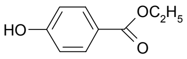
The most employed descriptors of organic substances hydrophobicity are partition coefficients in 1-octanol–water system ($P_{o/w}$) and in water–micellar pseudophase biomimetic system ($P_{m/w}$). There are several methods of hydrophobicity parameters determination, indirect methods are among them. Biopartitioning micellar chromatography (BMC) is one of indirect methods and it was suggested as in vitro model for studying of drug partitioning process in biological systems.

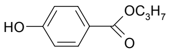
The objects of investigation were homologous series of 4-hydroxybenzoic acid (4-HBA) esters:



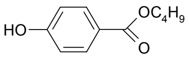
4-HBA methyl ester



4-HBA ethyl ester



4-HBA propyl ester



4-HBA butyl ester

The aim of our investigation is to determine the binding constants of substances with the micellar pseudophase. Brij 35 and sodium dodecylsulfate (SDS) were used as surfactants. The solutions of these surfactants are used as micellar eluents in BMC and in micellar liquid chromatography, respectively.

Binding constants of these substances were determined from change of substances apparent ionization constants, pK_a^a, in Brij 35 and SDS micellar medium.

Apparent ionization constants of the 4-HBA esters were determined by UV-spectrophotometry. The ionic strength 0.1 mol/l has been generated by NaCl. For the methyl and ethyl esters of 4-HBA the pK_a values in water solutions and in micellar solutions of 0.01 and 0.005 mol/l Brij 35 respectively, essentially are the same. This fact indicates that these esters are slightly bonded with micellar pseudophase of Brij 35. For the other esters the pK_a^a values raise with increase of Brij 35 concentration and range up to 9.06 for the propyl ester and 9.48 for the butyl ester in 0.01 mol/l Brij 35 micellar solutions. At that time the pK_a value in water solution for the propyl ester is 8.45 and for the butyl ester is 8.37. In SDS micellar solutions dependence of the pK_a^a values vs. SDS concentration reach a limiting value in 0.1 mol/l SDS solution.

The binding constants of esters protolitic forms by SDS and Brij 35 micellar pseudophase were calculated from obtained dependences. The partition coefficient values have been also obtained. The 4-HBA esters anionic forms don’t bind with SDS and Brij 35 micellar pseudophase.

EFFECT OF HYDROGEN TUNGSTEN (MOLYBDENUM) BRONZES ON CATALYTIC ACTIVITY OF PALLADIUM COMPOSITE CATALYSTS IN REACTIONS OF H_2, CO and CH_4 OXIDATION

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In this work the results of examination of catalytic activity in the reactions of complete oxidization of H_2, CO and CH_4 on WO_3 and MoO_3 partly-reduced with H_2 in presence of Pd and/or Cs^+ are reported. Catalysts were prepared by the impregnation on moisture capacity and further were reduced with hydrogen. The WO_3 and MoO_3 were saturated with solutions of $PdCl_2$ in order to obtain 0.5 % mass. of metal in the sample composition. The catalysts samples were dried out at 393 K and were reduced with hydrogen (mixture 10 % H_2 in Ar) during 1 h at 673 K. For the joint introduction of Pd and Cs^+ catalysts were saturated with solution of $CsJO_3$ accounting on 0.05% mass. Cs^+ in the catalyst. These samples were dried at 393 K and reduced in a stream of hydrogen-argon mixture (10% H_2) during

1 h at 673 K. To compare the catalysts with standards, Pd/γ-Al_2O_3 with 0.5% mass. of metals were prepared. H_2 treatment of these catalysts was conducted for the standards just as for the Pd composite catalysts. Composition and temperature of achieving certain conversion degree ($T_{20\%}$, $T_{40\%}$, $T_{100\%}$), are listed in a table.

Table. Temperatures of certain conversion degree of H_2, CO and CH_4 ($T_{\%}$) in K on the catalysts of oxidation.

Sample	H_2 oxidation		CO oxidation			CH_4 oxidation		
	T_{20}	T_{80}	T_{10}	T_{30}	T_{100}	T_{10}	T_{20}	T_{40}
0.5%Pd/Al_2O_3	310	336	448	470	478	750	770	785
WO_3	475	-	660	768	-	-	-	-
MoO_3	526	-	715	805	-	-	-	-
0.05%Cs^+/WO_3	408	550	628	685	-	-	-	-
0.05%Cs^+/MoO_3	486	-	625	738	-	-	-	-
0.5%Pd/WO_3	273	310	383	425	442	623	642	670
0.5%Pd/MoO_3	273	310	400	442	455	634	645	680
0.5%Pd·0.05%Cs^+/WO_3	-	288	360	418	430			
0.5%Pd·0.05%Cs^+/MoO_3	273*	297	388	435	442			

In the reactions of gas-phase oxidization for reaction mixtures (1% H_2 (CO, CH_4) and 20% O_2 in inert an gas (Ar, He)) observes that introduction of Pd in TO_3 (T = Mo, W) results in increasing of *S* in 5-6 times, addition of Cs^+ to these catalytic systems results in the further *S* increase. The trioxides posses low activity in oxidization of H_2 and CO, but in methane complete oxidation they are quite inactive. Hence after reduction with H_2, the catalytic activity of systems containing Pd in these reactions increases considerably as compared to Pd/γ-Al_2O_3. For the reaction of CO oxidation considerable extent of temperature region of low-active state of catalyst with $X<20\%$ and lowering of the temperatures of reaction beginning on 100–120 K as compared with Pd/γ-Al_2O_3. the synergetic phenomenon are characteristic for the complex catalytic systems, *i.e.* non-additivity of catalytic activity at introduction of Pd or pair of Pd and Cs^+ in the trioxides. The temperature of beginning of CH_4 complete oxidation shifts approximately on 140 K lower as compared with Pd/γ-Al_2O_3, but at temperature increase to 700 K the activity decreases and becomes equal to one of standard catalysts. In the XRPD spectra of catalysts containing 0.5 mass.% Pd was observed intensive diffraction peaks of $WO_{2.9}$, H_xWO_3 and Mo_4O_{11} and H_xWO_3, the catalysts with Cs^+ contain Cs_xWO_3 and Cs_xMoO_3. Study of surface layer composition of catalyst by XPS was conducted for WO_3 samples supported with Pd and Cs^+. It was shown by XPS that the binding energy of W 4$f_{7/2}$ is of 35.9–36.0 eV, and degree of W oxidization are <+6. Correlation of W:O in the surface layer of catalysts is ranged from 1:3 to 1:2.7, that confirms existence of oxygen vacancies on the catalysts surface, and also well co-ordinates with results of XRPD. The binding energy of electrons of Pd 3$d_{5/2}$ shows that Pd degree of oxidization is near to 0. The binding energy of Cs corresponds to the charge state of cesium (+1) and testifies formation of Cs_xWO_3. XRPD and XPS studies of the catalysts worked in H_2 oxidation showed that phase composition and valence of catalysts components did not change in a surface layer. According to XRPD results, the catalysts worked in CO oxidation does not contain evident quantities of H_xTO_3 (T = Mo, W). Thus in a line with $WO_{2.9}$ and Mo_4O_{11}, that were registered in the catalysts before the reaction, the phases of WO_{3-x} ($0.1<x<0.28$) and MoO_{3-x} compositions are appeared (x = 0.12–0.2). Treatment of the catalysts in the O_2 excess reaction mixture at temperatures higher 700 K results in 1) oxidation of active in the catalysis hydrogen oxide bronzes and in 2) formation of $WO_{2.9}$ and Mo_4O_{11} containing vacancies on oxygen the latest originate high catalytic activity. Thus, it was determined that hydrogen bronzes as H_xTO_3 (T = Mo, W), formed at H_2 reduction of the trioxides in presence of Pd, are active not only in the mixtures containing H_2 excess, but also in the O_2 excess mixtures used for complete oxidization of small molecules. However, operational temperatures of these processes are limited by a range from r.t. to 700 K where the systems work the best.

THE INFLUENCE OF FORMATION CONDITIONS OF Co- AND Ag-CONTAINING ZEOLITE SYSTEMS ON THE CATALYTIC ACTIVITY IN CO OXIDATION

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Metal-containing (Pt, Pd, Ag, Au, Co, Cu, Mn and other *d*-metals) catalysts on supports of various chemical nature are widely investigated in CO oxidation. For development of new effective catalysts and detailed research of a nature of their active centres the study of the systems supported on zeolites in CO oxidation is perspective. It is interesting to investigate the mono- and bimetalcontaining systems on the base of Ag and Co as active components taking into account a stable activity of their oxides in oxidation processes [1].

In our work the influence of forming conditions of Ag- and Co-containing systems supported on Na-zeolites upon their activity in carbon monoxide oxidation was investigated. Ag-containing catalysts with a low (1-3 wt.%) and a high (up to 10wt.%) metal content and Co-Ag samples were obtained with impregnation of granulated zeolites (0.5 – 1 mm) of $Co(NO_3)_2$ and $AgNO_3$ solutions. The metal concentrations in solutions of precursors were determined with atom-absorption spectroscopy. The catalysts were previously calcinated at the aerobic conditions (T_{form}=20-350^{0}C, T_{form}=20-700^{0}C) or heated in the flow of gaseous mixture of hydrogen with argon (10%H_2+90%Ar) to 350°C with heating rate 2.5°C/min. The catalytic activity measure was the temperature of practically total CO conversion (T_{100}).

The investigation of activity in CO oxidation of catalysts 1 – 10 wt.% Ag-NaX, formed at the air in temperature range T_{form}=20-350°C, showed that temperature dependence of total CO conversion on silver content had polyextremal character. The highest activity was fixed for 3%Ag-NaX (T_{form}=20–350°C). In addition, the catalyst 3%Ag-NaX (T_{form}=20–350°C) with a low content of active component had higher activity in comparison with activity of 10%Ag-NaX sample formed under the same conditions, what could be caused with optimal quantity of active centres in surface layer of 3%Ag-NaX catalyst.

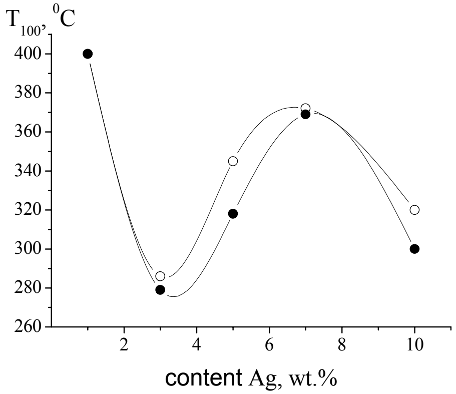

Fig.1. Catalytic activity of Ag-NaX systems in CO oxidation

It was established that the introducing of Co as second active component in common with silver leaded to demonstration of higher activity of samples Ag-Co-NaX ($T_{form.}$=20–350^{0}C) in CO oxidation as compared to 10%Ag-NaX. The difference of the temperatures of total CO conversion ((T100) for these systems is equal 39 - 63^{0}C in the first cycle of catalysis and 17 -74^{0}C in the second. High activity of Ag-Co-catalysts remains in the second cycle of catalysis.

It should be noted the high thermal stability of obtained Ag-Co-zeolite catalysts on the base of NaX – the twice increasing of the temperature of previous oxidative treatment of catalyst - from 350 to 700 ^{0}C did not lead to the decreasing of samples activity.

The influence of previous treatment (oxidative or reductive) on activity Ag-Co-NaX systems was found to be defined with a ratio of active components (Ag/Co) in catalyst. The catalysts with a higher cobalt content displayed a higher activity after their pretreatment at air. Reductive treatment was more favourable for catalyst with higher ratio Ag/Co in it.

Table 1. Catalytic activity of Ag- NaX systems (T_{form}=20-350^{0}C) in CO oxidation

Ag-catalyst	T_{100}, ^{0}C	
	I cycle	II cycle
1%Ag-NaX	400	400
3%Ag-NaX	286	279
5%Ag-NaX	345	318
7%Ag-NaX	372	369
10%Ag-NaX	320	300

Table 2. Catalytic activity of Ag-Co-containing zeolite systems in CO oxidation

Ag-Co-zeolite	T_{100}, ^{0}C					
	T_{form}=20-350^{0}C calcinated		T_{form}=20-700^{0}C calcinated		T_{form}=20-350^{0}C heated 10%H_2+90%Ar	
	I cycle	II cycle	I cycle	II cycle	I cycle	II cycle
7%Ag-3%Co-NaX	281	278	278	281	218	213
5%Ag-5%Co-NaX	249	237	243	236	261	265
3%Ag-7%Co-NaX	257	226	247	246	243	252

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STUDY OF INFLUENCE OF ADDITIONS OF Co, Ni OR Cu ON SENSITIVITY OF ADSORPTION SEMICONDUCTOR SENSOR TOWARDS H_2

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In recent years, research interest in hydrogen as a near-future fuel has increased because it is renewable, efficient, and unlike other alternatives, provides zero emissions.

However hydrogen is a dangerous gas that's why a control of its content in the environment air is required.

It's well known that adsorption semiconductor sensors are widely used to analyze different gas pollutants in air. The principle of action of such a sensor is based on change of its electrical resistance under the influence of the analyzed gas. The most processes running on the sensor surface are, in essence, the stages of the typical redox heterogeneous-catalytic reactions. That's why to increase the sensitivity of the sensor to H_2 addition of Pd is usually required.

In our work to reduce a cost of the adsorption semiconductor sensors, influence of additions of metals (Co, Ni or Cu) on the sensitivity of adsorption semiconductor sensor based on SnO_2 with Sb towards H_2 were investigated.

The adsorption-semiconductor materials for sensitive layer of the sensors were obtained through co-sedimentation of hydroxides from acidulous solutions of tin and antimony with consequent washing off, drying and calcination at high temperature. A view of the sensor is shown in Fig.1

To investigate the influence of Co, Ni or Cu on the sensor sensitivity, the semiconductor materials were impregnated with water solutions of different concentrations of corresponding chlorides of metals.

It was found that for each addition a dependence of the sensitivity of the sensors versus the concentration of impregnating solution had a maximum in all working temperatures of the sensor. And a dependence of the sensor sensitivity versus the temperature of the sensor had a maximum too (Fig 2). Besides, the electrical resistance of the sensor in air in all working temperatures was increasing when the concentration of addition was increasing. Using this fact it can suppose that for Co, Ni or Cu the bigger concentration of addition leads to increase a quantity of oxygen on the surface of the sensor. It contributes to increase a rate of chemical reaction of H_2 oxidation and thus the gas sensitivity of the sensor (Fig.2). But after some concentration of addition (for Co - 3,6; for Ni - 0,4; for Cu - 0,1) a quantity of the addition becomes so big that it blockades a surface of SnO_2. In this case a quantity of chemisorbed oxygen continues to grow but due to chemisorption on the surface of addition only. The rate of chemical reaction of H_2 oxidation, which focuses in this case on the surface of addition or on the borders of grains of the addition and the surface of SnO_2, probably, is growing. But this process doesn't affect processes of transfer of electrons in the conductivity zone of SnO_2 as it was in a case of small concentrations of additions when the reaction took place on the sensor surface directly. That's why, sensitivity of the sensor to H_2 is decreasing.

Heterogeneous catalytic mechanism explains an extremal view of the dependence of the sensor sensitivity versus its temperature also. Really, for each additions a rate of the reaction of H_2 oxidation increases at first, but starting with a certain temperature of the sensor (this temperature is a function of the addition nature) this rate is decreasing owing to readsorption of chemisorbed oxygen. For each addition, this phenomena was experimentally proved by decrease of

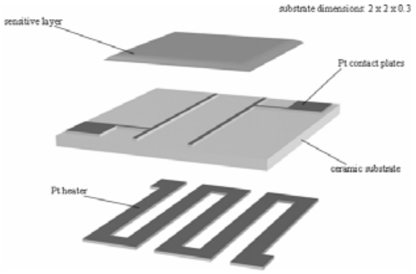

Fig.1 General view of the sensor

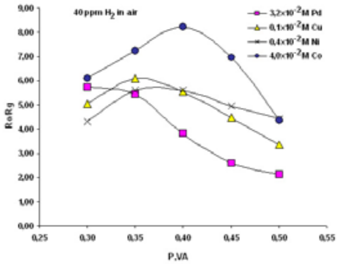

Fig.2 Dependence of the sensitivity of the sensors versus their temperature (power consumption) for the most active sensors with the metal additions

the electrical resistance of the sensor in air when temperature of the sensor was increasing.

So, addition of the metals allowed the sensors to obtain high sensitivity to H_2. And it can be seen, the sensor with Co allows to change usage of the sensor with Pd (Fig.2).

APPLICATION OF ORGANIZED SOLUTIONS OF SURFACTANT IN SAMPLE PREPARATION AND THIN-LAYER CHROMATOGRAPHIC ANALYSIS

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Organized solutions such as micellar solutions of surfactants are widely used in separation methods instead of flammable and toxic organic solvents. In present work the possibilities of application of micellar solutions of surfactants (cetylpyridinium chloride, sodium dodecylsulfate, Tween-80) as reagents for extraction and as eluents in thin-layer chromatography (TLC) for separation and determination of (i) purine bases in biological fluid; (ii) esters of 4-hydroxybenzoic acid (parabens) in cosmetics, (iii) mycotoxins (zearalenone, T-2 toxin, T-2 tetraol, HT-2) in grain have been studied.

The TLC plates Sorbfil-UV-254 (Sopolymer, Russia) have been used. The Rf, values, shape and intensity of spots have been used for choosing optimal separation condition. The mycotoxins have been detected under UV-light (365 nm) after spraying with sulphuric acid in methanol. The purine bases and parabens have been detected under short-wave UV-light (254 nm) as dark-violet spots on green fluorescent background of plates.

The micellar solution of Tween-80 at pH 7 has been chosen for extraction of purine bases from biological fluids and as eluent for TLC separation of purine bases. The technique has been successfully tested on the imitation samples (serum with known additive of caffeine) and on the real samples of rat's serum (previously, the rats had been receiving injection with appropriate dose of caffeine). The best separation of parabens is provided with micellar eluent that contains 0.01 M Tween-80 and 0.3 % (v/v) 1-pentanol. The micellar solution of $5.0\cdot10^{-3}$ M cetylpyridinium chloride with addition of formic acid has been used for extraction of parabens from cosmetics. The micellar solution that contains $5.0\cdot10^{-3}$ M cetylpyridinium chloride and $5.0\cdot10^{-3}$ M Tween-80 at pH 9 is most suitable for TLC-separation and identification of micotoxins. Chloroform has been replaced by 0.01 M cetylpyridinium chloride solution in sample preparation of grain for micotoxins determination.

Thus, micellar surfactant solutions can be used as solutions for extraction of analytes as well as effective eluents for TLC without necessity of chamber saturation.

CREATION OF ZnO QUANTUM DOTS ENSEMBLES ON THE SURFACE OF SILICA NANOPARTICLES

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In last decade, development of essentially new class of the functional optical materials on the basis of the ordered ensembles of semiconductor nanocrystals (quantum dots) has the considerable interest. Zinc oxide is well known wide band-gap semiconductor with large exiton binding energy (60 meV) and intensive UV-luminescence ($\lambda_{max} \sim 380$ nm) at room temperature. This semiconductor in the low-dimensional state (in the form of quantum dots, for example) is considered as one of the most promising materials for making high-selective and high-sensitive sensors, light-emitting devices for UV lasers and light diodes.

In the present work heteronanoparticles (SiO_2/ZnO) with a silica core (120 nm) and a shell of ZnO quantum dots ensembles have been obtained. ZnO quantum dots the given sizes (2-10 nm) at a narrow size distribution (< 15 %) have been grown up from solutions by a method of the colloid synthesis. The size of ZnO nanocrystals has been controlled during synthesis using surface-active agents. Synthesized ZnO nanocrystals in solution have been fastened on previously synthesized and modified nanotemplates (the colloid particles SiO_2). Uniform-sized silica nanoparticles (size distribution < 10 %) of the spherical form have been received by hydrolysis of tetraethylorthosilicate (described in the literature by Stober and Fink). To prepare heteronanoparticles SiO_2/ZnO, the surface of silica nanoparticles modified using bifunctional organic molecules. Organic molecules forms active centers on the silica surface for connection with organically capped ZnO nanocrystals. Thus, ordered ensembles of ZnO nanocrystals forms shell of SiO_2/ZnO heteronanoparticles.

The size and morphology of synthesized ZnO nanocrystals and SiO_2/ZnO heteronanoparticles have been examined by means of transmission electron microscopy. The phase composition of ZnO nanocrystals has been examined by X-ray diffraction. Optical properties of received SiO_2/ZnO heteronanoparticles have been investigated; quantum confinement effects in absorption spectra of ZnO quantum dots ensembles have been shown.

INFLUENCE OF THE REVERSE MICELLES CLUSTERIZATION ON SURFACE POTENTIAL OF PHASE BOUNDARY AND ON REACTION KINETICS

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The use of water-in-oil microemulsions as a reaction medium for enzymatic and non-enzymatic reactions is widely spreading. Particularly, the systems of reverse micelles based on anionic surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (AOT), are of frequent utilization. However, besides such properties as stability, narrow size distribution and possibility to change hydration level, the AOT-based reverse micelles manifest tendency to form clusters in the broad ranges of temperature and concentration of dispersed phase, which is accompanied by change in many of physico-chemical characteristics of the system.

In this work we present the data on clusterization phenomenon in the dispersions of AOT-based reverse micelles in the wide range of temperature, concentration of surfactant and water, obtained by means of NMR-diffusometry and conductometry, and the analysis of kinetic data for hydrolytic reactions on the background of this effect.

To a large extent our attention in the analysis of kinetic data is drawn to the changes in the surface potential of phase boundary and to related alteration in ionic processes in the water phase under clusterization of micelles.

The work is supported by the Russian Foundation for Basic Research (grant no. 05-03-33110a).

RESULTS OF *R_f* VALUES REPRODUCIBILITY INVESTIGATION BY INTERLABORATORY TLC STUDIES

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TLC is pharmacopoeial method applied for identification of active pharmaceutical ingredients (API) and excipients and for impurity control in limit tests. This method is also recommended by WHO and national drug authorities for identification and semiquantitative assay of API for detecting of possible counterfeiting of medicines in state drug control laboratories. R_f data are important information for API identification by TLC.

R_f values reproducibility is interesting in both theoretical and practical aspects. These data can give information about proficiency level of single laboratory and groups of laboratories in general.

In the framework of the Programme for combating against counterfeit drug, it was organized a collaborative study of sulfamethoxazole and trimethoprime tablet samples taken in pharmacies from all regions of Ukraine in 2004. 337 samples collected from 263 pharmacies were analysed during the study.

Accordingly to WHO recommendations on detecting of counterfeit drugs by TLC with two different mobile phases, 24 regional inspectorate laboratories carried out identification and semi-quantitative determination of the active ingredients by TLC in accordance with techniques of USP and Indian Pharmacopoeia monographs for the mentioned product. All laboratories worked in accordance with the same study protocol, used the same reference standards and TLC plates. It allowed to receive a very big set of comparative data on R_f values of sulfamethoxazole and trimethoprime spots.

Calculated confidence interval of R_f values reproducibility on single chromatographic plate was equal 0.018 and complied with Ukrainian State Pharmacopoeia requirement (no more than 0.02).

The statistically insignificant difference of R_f values between chromatographic plates in the one laboratory run up to 0.09. It testifies to unacceptable level of carrying out of TLC analysis by participated laboratories.

The statistically insignificant difference R_f values between different laboratories reached 0.30. It also testifies to unacceptable level of carrying out of TLC analysis by participated laboratories and incorrectness of R_f values using in medicine specifications for identification of analytes.

CORRODING AND ELECTROCHEMICAL CHARACTERISTICS OF CATHODIC COATINGS ON STEEL IN SOME AGGRESSIVE MEDIUMS

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The most prospective technology of obtaining the coatings of various functional purpose is vacuum metallization as one of the ecologically purest technological processes. Side by side with the coatings from fine metals the prospective direction is application of multicomponent vacuum coatings, in particular, the coatings from stainless steel. For determining of the fundamental opportunity of application of such coatings in the technological processes of food productions, the corroding and electrochemical investigation of condensed coatings from iron-nickel-chromium alloy in some model and natural mediums were carried out. The technology of obtaining the coverings corresponded to optimum modes of putting the coatings of this class [1] and provided obtaining of practically porousless coatings by 20-25 mcm order thickness. For comparison thinner coatings of 5 … 18 mcm have been used in the investigation.

3% sodium chloride solution, water, solution of 2% tartaric acid, 3% acetic acid and 3% oxalic acid have been used as pattern mediums. The natural food mediums were apple juice and tomato-paste (dilution 1:1). The solution, imitating product of man`s organism functioning represented diluted concentrated product of the following composition: NaCl – 178,5 g; $Na_2C_2H_3O$ – 140 g; $CaCl_2 \cdot 2H_2O$ – 6,35 g; $MgCl_2 \cdot 6H_2O$ – 6,64 g; $C_6H_{12}O_6$ – 6,18 g; HCl – 8,64 g; H_2O – 1000 g. The degree of dilution is 1:34 (in parts by mass).

It has been established that in all investigated mediums the coatings are cathodic with respect to the base. The reliable defence of the base from corrosion can be provided only in case of application of low porous and porousless coatings. The results of the investigation are the following: under prolonged. Keeping of the coatings patters and initial massive steel 12X18H9T, the potential of porousless coatings (20 … 25 mcm thickness) becomes more of steel, composing +75 mV and +100 … +110 mV in 24 hours and 720 hours of the investigation respectively. These difference can be connected with effect of fractionation and, as result, formation of more stable surface films on the surface of the condensed systems. This conclusion is confirmed by the results of potentiodynamic research. It has been show that on the porousless coatings the region of passivity under sufficient depth of anode polarization has been settled; massive steel is dissolved practically without difficulty already under the potential of order polarization +250 mV and the effect of sodium chloride solution on steel 12X15H9T is practically the same as on low-alloy steel of the sublayer.

Therefore, more resisting in comparison with massive steel 12X15H9T porousless vacuum coatings can be recommended for application for substitution of the items from massive steel, working in the sea water (in particular on floating fish-processing plants, where washing of the equipment is carried out by sea water and where the items from stainless steel of the type 12X18H9T are quickly put out of action).

In water-pipe water the behaviour of the coatings on low-alloy steel somewhat differ from the behaviour in chlorine-containing mediums and is characterized by high resistance. Unprotected steel 08 kp and its analogs (steel У8А, У10, steel 3) intensively corrode in water-pipe water; corroding losses make 29 mg/($mm^2 \cdot$ hour), while on the coatings of 16 … 18 mcm thickness and more, mass growth of the samples of 0,5 mg/(mm^2 · hour) type is fixed.

The analysis of electrode potentials of the coatings from the iron-nickel-chrome alloy in model and natural food mediums (see the table) has allowed to arrange the coatings by the degree of resistance in the following order: the most aggressive medium is the solution of acetic acid. The coatings of 5 … 12 mcm thickness, having substantial porousness, don`t possess resistance in none of the investigated model and natural food mediums and can`t be recommended for protection of low-alloy steels from corrosion.

The medium being investigated	The thickness of the coating mcm (material)	Electrode potentials, mV
2% tartaric acid	18...20	-0,075
3% acetic acid	18...25	+0,60
3% oxalic acid	20...25	-0,125
Apple juice	20...22	+0,40
	12X18H9T	+0,40
Tomato paste (1:1)	20...25	-0,22
	12X18H9T	0,20

Potentio-dynamic investigation of the porousless samples and massive steel 12X18H9T have shown that the greatest frictional action of electrode processes under external polarization is marked in acetic acid and apple juice. The data of polarizable investigations confirm the conclusion about high resistance of massive steel in comparison with coatings: under the same depth of polarization corroding current on the steel surface with coatings several times greater than on the surface of massive stainless steel.

Therefore, condensation coatings from iron-nickel-chrome alloys can be applied for protection of low-alloy steel from corrosion in some food mediums. We can consider the coatings of more than 25 mcm thickness practically porousless and these coatings safely protect low-alloy steel from corrosion. It is possible to apply thinner coatings, porousness of which can be reduced by using of the special technological modes, however during their corroding resistance estimation one should take into account the permissible content of iron in food products [2].

The results of the coatings investigations in water solutions of inorganic acids salts have shown that the reliable protection of low-alloy steel in the given aggressive medium is provided with coatings of about 15 … 20 mcm thickness, obtained under meanings of specific capacity of discharge of 20 w/cm^2 order on the stage of coating settling and having uniform structure and good decorative properties. It is significant that the rate of the corrosion under it ten times less than with unprotected steel.

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SOLVENT EFFECTS AND CONFORMATIONAL STABILITY OF BIOPOLYMERS: MOLECULAR DYNAMICS SIMULATIONS

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Studies of biomolecular hydration have more than a hundred year history. Nevertheless, there are still many unanswered questions in this area, one of them is: ’What is the influence of different ions and their concentrations on the conformation of a macromolecular solute?’. Indeed, the structural and thermodynamic properties of biopolymers are strongly influenced by cosolvents and cosolutes. There are also many processes relevant for modern biotechnology which are influenced by the concentration and type of salts present, including: biopolymer solubility, biopolymer denaturation temperatures, enzyme activity, biopolymer swelling, growth rates of bacteria, and the stability of protein macroaggregates.

In this work we are trying to gain insight on the molecular mechanisms of the salt effects on the conformational stability of biopolymers with use of modern fully atomistic Molecular Dynamics simulations techniques. Such ‘in silico’ approach allows us to obtain very realistic data on the time and scale resolutions that are unavailable for both ‘in vitro’ and ‘in vivo’ experimental techniques.

In general, there are three main effects of salts on the macromolecular conformation:

Debye-Huckel screening effect;

Electroselectivity: specific interaction with charges by the ion-pair formation.

Hofmeister effect - disruption of water structure which consequently results in an increase or decrease in the hydrophobic interaction of proteins and biomolecules.

If the Debye-Huckel screening has the major contribution, the effect of various ions will be determined *only* by the *ionic strength* of solution. If the specific interactions with charges are of the most importance, the effects of different ions should follow the *electroselectivity* series of the salts toward anion-exchange resins. The significance of the changes in hydrophobic interactions can be determined by comparing the effects of different ions with the *Hofmeister* series.

To validate these hypotheses we performed long timescale molecular dynamic simulations of several polypeptides and small proteins in alkali halide solutions with different concentrations of the salts. The results have been compared with available experimental data and simulations in bulk water solution.

From our results we conclude that all these three effects are present but their ‘weights’ vary with concentrations and type of salts. Therefore, the ‘right answer’ depends from the protein primary structure and the particular conditions of ionic solution (concentration, sort of ions, etc). In principal, all the above described effects (Debye-Huckel screening, electroselectivity and Hofmeister effects) are important and one cannot neglect none of them *a priori*. But for any given secondary structure of a macromolecule one can find its own “breakers’ and ‘stabilizers’, knowing basic principles of ion-water, ion – ion and ion –molecule interactions.

VOLUMETRIC AND ENTHALPIC H/D ISOTOPE EFFECTS OF HYDRATION OF UREA BICYCLIC DERIVATIVES AT 288–318 K

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Bicyclic derivatives of urea (the *bis*-ureas or glycolurils) have attracted ever-growing attention from investigators. Tetramethyl-*bis*-urea (TM*b*U) as the drug *Mebicarum* (Fig.1) plays an important role among similar compounds. Meanwhile, there are virtually no data on the structure-thermodynamic properties of aqueous solutions of TM*b*U. Also, interest in TM*b*U stems from the desire to study the structural transformations it causes in aqueous media. The effect is associated with the competition between the structure contributions arising from the hydrophobic and hydrophilic parts of the TM*b*U molecule in the course of hydration and to their joint action on the molecular packing of the solvent. Here, we report the results of studies of the volume and enthalpy effects of TM*b*U dissolution in ordinary and heavy water at 288.15–318.15 K. The isotope H/D substitution allows one to establish at the molecular level the role of hydrogen bonds in affecting structure that is manifested in the volumetric and enthalpic properties.

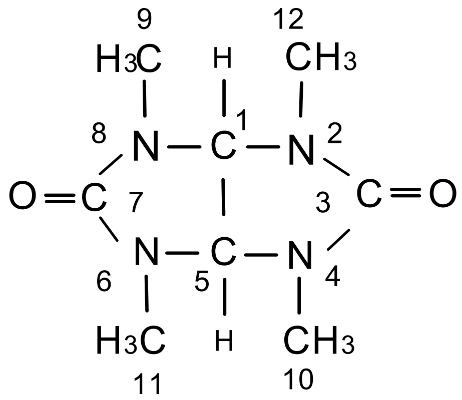

Fig.1. Structure of 2,4,6,8-tetra-methyl-2,4,6,8-tetraazabicyclo [3.3.0]octane-3,7-dione (TM*b*U)

It can be seen from Table that dissolution of TM*b*U in H_2O and D_2O is accompanied by heat absorption; with temperature rise, the dissolution becomes more endothermic. The molecular packing density of hydration complex of TMU increases as the temperature decreases. A change in the isotope composition of the solvent as a whole a slight influence on the values listed in Table.

However, the isotope effects $\delta\Delta_{\mathrm{sol}}H_2^{\infty}$ (H_2O→ D_2O) and $\delta V_{\phi,2}^{\infty}$ (H_2O→D_2O) reverse signs about 318 K (see also Fig.2).

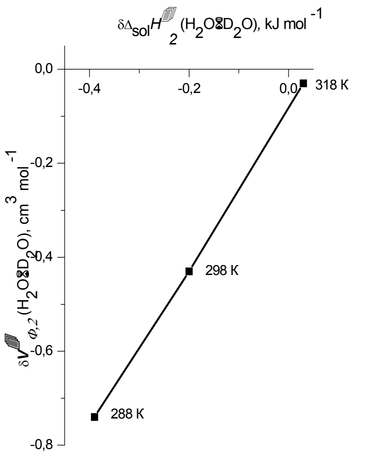

Table displays the data on the limiting apparent molar volumes, $V_{\phi,2}^{\infty}$, and expansibilities, $E_{p,\phi,2}^{\infty}$, and standard molar enthalpies of solution, $\Delta_{\mathrm{sol}}H_2^{\infty}$, of TM*b*U in H_2O and D_2O at various temperatures (in K) [1,2].

Fig.2. The correlation between the volume-isotope and enthalpy-isotope effects of solution of TMbU in water H/D isotopomers

Solvent	Property*	288.15	298.15	308.15	318.15
H_2O	$V_{\phi,2}^{\infty}$, cm^3·mol^{-1}	157.02	158.83	160.29	161.34
	$E_{p,\phi,2}^{\infty}$, cm^3·mol^{-1}·K^{-1}	0.201	0.163	0.125	0.087
	$\Delta_{\mathrm{sol}}H_2^{\infty}$, kJ·mol^{-1}	1.96	3.67	–	7.03
D_2O	$V_{\phi,2}^{\infty}$, cm^3·mol^{-1}	156.28	158.40	160.09	161.31
	$E_{p,\phi,2}^{\infty}$, cm^3·mol^{-1}·K^{-1}	0.235	0.190	0.145	0.100
	$\Delta_{\mathrm{sol}}H_2^{\infty}$, kJ·mol^{-1}	2.37	3.87	–	7.00

*The errors of measuring and computing above values are (no more than): $V_{\phi,2}^{\infty}$ (± 0.1 cm^3× mol^{-1}), $E_{p,\phi,2}^{\infty}$ (± 0.005 cm^3·mol^{-1}·K^{-1}), $\Delta_{\mathrm{sol}}H_2^{\infty}$ (± 0.1 kJ·mol^{-1}).

According to the recent NMR analysis of the evolution of carbon chemical shifts (^{13}C) in aqueous solutions of TM*b*U [3], the major contribution to the formation of TM*b*U···H_2O(D_2O) hydrogen bonds is made by the C=O groups of the solute. The protons at the C(1) and C(5) atoms (see Fig.1) are also capable of forming H-bonds with two water molecules.

For these reasons, both strengthening of the packing-compressed changes and weakening of TM*b*U hydration in D_2O at low temperatures may be attributed to the higher degree of structuring of heavy water medium caused by the formation of stronger D-bonds. With increasing temperature, the structural differences between H_2O and D_2O become less pronounced. Because of faster destruction of the hydrogen-bond network of heavy water (compared to H_2O), an increase in temperature is accompanied by enhancement of hydrophilic hydration of TM*b*U, and its hydrophobic hydration, on the contrary, is weakened. We believe that the sign inversion in the $\delta V_{\phi,2}^{\infty}$ *vs.* $\delta\Delta_{\mathrm{sol}}H_2^{\infty}$ function (Fig.2) is most likely due to superposition of several mutually canceling isotope effects, first of all caused by the thermal predestruction of the water structure.

The experimental data compiled in Table 1 and in Figs. 1 and 2 result in the conclusion that hydrophilic component of TM*b*U hydration dominates over the hydrophobic one, at least, in the temperature range under study. In other words, a hydrophobic hydration is probably not the predominant type of hydration in the H_2O (D_2O) – TM*b*U systems.

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PHOTOCATALYTIC ACTIVITY OF NANOPARTICLES BASED ON MIXED SULFIDES

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The analysis of literature devoted to nanoparticles was showed, that photophysical characteristics of these objects investigated very well in compare with photocatalytic possibilities. Nowadays the necessity in high activity photocatalysts is increasing. The nanotechnology application may be an alternative way for receive such photocatalysts.

In our work we obtained mixed sulfides and investigated their photocatalytic activity in destruction of anionic (eosin B) and cationic (safranine O, phenosafranine, methylene blue) dyes at pH 6, 45.

The synthesis of nanoparticles was conducted at pH 6,45 in aqueous solutions of corresponding salts by the methods based on reaction salts with sodium sulfide in the presence of stabilizer. As stabilizer we tried surface-active compounds (SAC): cationic (Methylbenzethonium chloride, Sigma), nonionic (Triton X100, Aldrich), anionic (Hexadecyltrimethyl ammonium bromide, Aldrich) as well as sodium polyphosphate (Aldrich). Among these substances methylbenzethonium chloride and sodium polyphosphate showed the best stabilization of sulfide nanoparticles.

Mixed sulfides (CdS/Ag_2S, CdS/In_2S_3, CdS/CoS, CdS/NiS, CdS/CuS) were obtained by substitution of metal cations in nanosized sulfide by cations of other metal. The quick formation of mix sulfide occurs if solubility product of second metal sulfides essentially exceed of solubility product of initial metal sulfides. Therefore, addition of cations to stabilized CdS nanoparticles leads to fast substitution of cadmium cations on corresponding cations with formation of mixed sulfides. As a results, we obtained mixed nanoparticles with different ratio of components.

Irradiation of water solutions of investigated dyes in the presence of nanoparticles leads to substrate destruction. All reactions obey the first order kinetics. The observed rate constants can vary by more than order of magnitude depending on nature of photocatalyst and substrate.

It was established, that the photocatalytic activity of investigated nanoparticles decreases in line $CdS/In_2S_3 > CdS/Ag_2S > CdS/CoS > CdS/NiS > CdS/CuS$. The most active were nanoparticles consist 60% CdS/40% In_2S_3 and 85% CdS/15% Ag_2S.

THE MECANISM OF CORROSION IN PORE OF CATHODE COATINGS

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Porosity is one of the main factors, that defined protective properties of cathode coatings [1]. For the first approaching, intensivity of corrosion process in pore determined by efficiency of coating action as a cathode. This method has been used for protection corrosion control of different coatings [1,2]. It lets to compare the protective properties of cathode coatings on steel for 72-hours tests, if electrochemical mechanism of corrosion is assumed. It's often observed the through failure of substrates with thick coatings during prolonged (up to 1000 h) tests, while in thin coatings damage local at film-substrate interface.

Developing principal position of Rosenfeld's galvanic element theory [3], we propose another mechanism of corrosion in pore of cathode coatings on steel have wich based on the presence of internal stresses in some type of cathode coatings [4]. The new corrosion using the classical ideas about corrosion nature of strain deformed metal surfaces as well as results of L.Petrov [5], we can explain not only final results of observed corrosion damage of steel in pores of cathode coatings, but also propose the new mechanism of corrosion failure seat development.

The initial cause of corrosion failure of steel in pore is the electrochemical processes, taking place in system «film - substrate». If the pore depth is nearly small (thin films), not only the walls of pore channel, but also adjacent parts of film surface may act as a cathode [6]. The corrosion current at the pore bottom for initial time-periods of immersion into solution may de written as

$$\mathbf{I}_{\mathbf{corr}} = \frac{\mathbf{\Delta E \cdot S_a}}{\mathbf{P_a}} \qquad (1)$$

Here ΔE - electromotive force of galvanic pair «pore bottom - coating»; P_a/S_a - specific polarizability of anode process.

Assumed, that anodic reaction polarizability P_a is time-indepedent or changes very slowly with time (by analogy with Petrov's theory of corrosion cracks [5]) and cathode process potential remains constant during observation period (E_k = const), the expression (1) may be rewritten as

$$\mathbf{I}_{\mathbf{corr}} = \frac{\mathbf{[\Delta E(t) \cdot S_a(t)}}{\mathbf{P_a}} \qquad (2)$$

The account of kinetics of electromotive force $\Delta E(t)$ and $S_a(t)$ [1] as well as E_{st} versus h [6] shows, that depth corrosion process development inhibits sharply with film thickness inreasing. It is in good agreement with natural testing results, but doesn't explain the appearance of deep and through corrosion failures in thick coatings as well as the cases of corrosion process under coatings.

Let us consider the role of mechanical factor in pore of thick cathode coatings. We imagine the corrosion process in such compressive strained coatings by following way. At the first step pitting formation process take place in consequence of galvanic pair action ΔE_2 (potential differences coating potential E_c and bottom potential E_b). The approximate rate of pitting motion is determined by follows:

$$\mathbf{V}_{\mathbf{pit}} = \frac{\mathbf{\Delta E_2 \cdot F}}{\rho \cdot \mathbf{P_a}} \qquad (3)$$

where F - electrochemical equivalent of iron, ρ - density of steel.

As pitting motion into strain deformed layers, its top become concentrator of stresses. In this moment of time become work the second galvanic pair $\Delta E_3 = \sigma \cdot \alpha$ (σ - stress level for given depth of pitting, α - deformation polarizability). The total rate of pitting motion is equal:

$$\mathbf{V}^{/}_{\mathbf{pit}} = \mathbf{F} \cdot \frac{\mathbf{\Delta E_2 + \Delta E_3}}{\rho \cdot \mathbf{P_a}} \qquad (4)$$

as far as both galvanic pair acting simultaneously. The conditions of such mechanism realization have been analyses in [1,4].

Considering the corrosion behavior of complicated electrode «porous coating - substrate), we assumed identity of physics-chemical processes in pore and in pitting. The estimation of veritable behavior of such complicated electrode and electrode process description may be produced only on the indirect indications. Recently the external evidence of corrosion process development in these system have been estimated by the following parameters [7]: corrosion elements current, anode current values, potential distribution along the sample surface, electrode potential dependence on film, measured from electrode potential kinetics [6], etc. The potential dates of electrodes being exposed to local corrosion, that one can find in literature, are uncertain and depend on reciprocal arrangement of comparative electrode and corroded sample surface.

We also proposed the estimation technique of the interplay between veritable potential distribution along the surface of complicated electrode «porous coating - substrate» and literature dates of stationary potential of such system [7]. Average potential shift for electrode, having N surface corrosion seats, may be determined as

$$\mathbf{\Delta E = \sum_{i=1}^{N} \Delta E_i = \frac{1}{S} \cdot \sum_{i=1}^{N} \int_{S_i} \delta E(S_i) \cdot dS}\,. \qquad (5)$$

Here ΔE - average potential shift for the sample, having total square S towards negative region consequence of electrical field distortion near i-seat; S_i - square of electrical fields distortion region near the i-seat; $\delta E(S_i)$ - the function, characterizing the field distortion near i-seat with respect to average electrode potential of coating material E_k; dS - electrode surface element.

Taking in account (5) the stationary potential of steel sample with porous cathode coating may be expressed:

$$\mathbf{E_{st} = E_k + \Delta E = E_k + \frac{1}{S} \cdot \sum_{i=1}^{N} \int_{S_i} \delta E(S_i) \cdot dS} \qquad (6)$$

Obviously, if the coating is unporous, the function $\delta E(S_i)$ is equal to zero for any seat (electric field distortion is absent) and measured stationary potential value $E_{st} = E_k$, so defined only by coating material properties.

The proposed simplified model [7] for estimation of interplay between veritable potential distribution along the surface of complicated electrode «porous coating - substrate» and stationary potential values, measured by distant probe, assume the presence of the information about potential values E for «coating - electrolyte» interface, that is in the pore outlet. This problem may be solved, using three-dimensional Laplace's equation for corrosion seat model as narrow capillary or narrow crack. For sufficiently narrow and long capillary, when axis system is realized, the total problem transfer to one-dimensional case. The example of such discussion have been annualized in [8].

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SOME THEORETICAL AND EMPIRICAL QUESTIONS OF RESEARCHING OF THE ELECTROCHEMICAL PROCESSES BEING ON THE POROUS COATING SURFACES

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The development of corrosion processes on the surface of substrate-cover is considered as special case of local corrosion, activated by the joint influencing of aggressive environments and mechanical stresses. It's well known that porosity is one of the main factors, which defined protective properties of cathode coatings. Intensivity of corrosion process in pore is determined by the cathode activity of coating materials. As the process of anodic dissolution concentrated at the bottom of pores, and the square of an anode (square of bottom) is many time less than square of the cathode (cover materials), the density of corrosion current can reach very large magnitudes. The measuring of local corrosion current density or corrosion current is difficult task. There are many experiments methods of corrosion intensivity or corrosion velocity defining in the original literature. These methods are based at the determination of integral characteristics of surface corrosion processes. We proposed a new method based at the mathematic and physic-chemical modeling of processes depending in cover pores.

We researched the mechanism of corrosion in pores of cathode cover. This mechanism is based at the classical ideas about corrosion nature of strain deformed metal surface. From these positions we try explain not only final results of corrosion damage of substrate in pore of cathode cover, but also the influence of internal stress, technological conditions of condensation process, porosity and thickness of coating on the corrosion process.

We proposed the following equation:

$$I_i^C = \frac{(\varphi_0 e^{-\beta\tau} - \varphi_C)\cdot\pi\cdot\varepsilon\cdot\varepsilon_0}{\tau\sum\limits_{k=1}^{f/8}\left(\frac{1}{\sqrt{H^2+k/n}}+\frac{1}{\sqrt{H^2+2k/n}}\right)} \qquad (1)$$

where φ_0 – initial electrode potential of substrate-cover specimen (V); φ_C – the electrode potential of strain state cover material (V); ε – relative dielectric environment characteristic; $\varepsilon_0 = 8{,}85\cdot10^{-12}$ F/m – vacuum dielectric environment characteristic; τ – time (s); H – distance between tip of reference electrode and surface of specimen (m); n – porosity (1/m^2); f – the pores` quantity being on the surface of the specimen (pores/m^2); $\beta\in$ [0,001…0,02] – empirical constant (1/s).

The equation (1) binds the local cathode current flowing from one pore with porosity and potential of specimen. The anodic current may be counted whereby following system of equations:

$$\begin{cases} C_1 + C_2 = I_A \\ \dfrac{C_1\cdot e^{\frac{h}{\gamma}}}{\gamma} - \dfrac{C_1\cdot e^{-\frac{h}{\gamma}}}{\gamma} = 0 \\ I_i^C = C_1\cdot e^{\frac{y}{\gamma}} + C_1\cdot e^{-\frac{y}{\gamma}} \end{cases} \qquad (2)$$

where h – thickness of cover (controlled technological parameter) (m); I_A – anodic current (A); $\gamma = \sqrt{\dfrac{R^K\cdot2\cdot\pi\cdot r}{\rho}}$ – characteristic parameter (m); R^C – polarization resistance of covering material (R^C – is depended by the internal stress and chemical nature of electrolyte) (Ωm^2); r – pores` radius (m); ρ – specific resistance of electrolyte (Ωm).

The influence of the mechanical internal residual stresses at the polarization resistance of chromium (cover materials) has been researched by us.

We proposed mathematic equations (1) (2) which allow to calculate the velocity of corrosion processes whereby evaluating of corrosion current density.

We also proposed the estimation technique of the interplay between variable potential distributions along the surface of complicated electrode "porous coating – substrate" and experimental dates stationary potentials of such system. The base position of this model has been already discussed.

INVESTIGATION ON SOLVATION THERMODYNAMICS OF GUAIACOL *p*-DERIVATIVES IN MIXED SOLVENTS WATER-ACETONE AND WATER-DIOXANE

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Acid ionization constants of eleven guaiacol p-derivatives (1), simulating fragments of coniferous lignin in mixed water-acetone and water-dioxane solvents were determined using spectrophotometric and potentiometric titration methods. It was ascertained that while proceeding from water to aprotic solvent acid strength decreases, appearing in 3-5 unit's growth of phenol hydroxyl groups pK_a.

Revealing the mechanism of solvent's effect on the phenol's acidity propose determining thermodynamic characteristic of transferring phenol molecules and corresponding phenolate ions from water to the mixed solvent.

In this connection, the purpose of the given work is to obtain the values of free Gibbs energy of transfer of vanillin and vanillin alcohol (that have the most typical for lignin *p*-substituents to phenol hydroxyl group) from water to mixed solvents.

Assessment of the contribution of nondissociated phenol molecule, phenolate ion and proton to solvation gross-effect was carried out for confirming mechanism of solvent's influence on the phenol's acidity.

While replacing the solvent, the changes of pK_a, expressed through transfer activity coefficients of the proton, neutral molecule and anion were used for partitioning Gibbs energy of the transfer according to Izmailov's method:

$$\Delta pK_a = pK_a(S) - pK_a(H_2O) = \lg\gamma_{0(\mathrm{H}^+)} + \lg\frac{\gamma_{0(An^-)}}{\gamma_{0(\mathrm{H}An)}}$$

The data on the solubility of vanillin and vanillin alcohol allowed obtaining ΔG_t for nondissociated phenol molecule from water to the mixed solvent. For reasons given, the energy of transferring phenolate anion was calculated.

As expected, vanillin anion shows lowest destabilization while changing the solvent, as it has minimal electron density at the reactive center due to inductive effect of carbonyl group.

Contrary to anions, proceeding from water to aprotic solvent leads to stabilization of weak acids' molecules due to higher solvation power of acetone and dioxane with respect to cations or functional groups, possessing electrophylic properties.

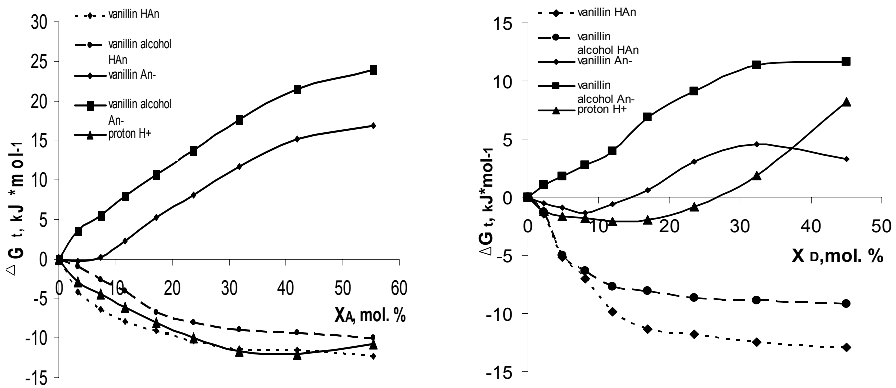

Figure 1. Gibbs free energy of transfer of vanillin and vanillin alcohol and relevant anions in the systems water-acetone (left) and water-dioxane (right) versus mole fraction of aprotic solvent at 298K.

According to obtained graphics, changing solvation of phenolate anion and nondissociated molecule comparably influence the acidity of guaiacylic phenols while replacing solvent in the media, containing up to 80 mass percents of organic component.

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