



Quantitative Physico-Chemical Analysis of Processes at Interfaces of Hybrid Silica-Organic Materials

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Topics to be discussed

- What is the quantitative physico-chemical analysis (QPCA)? What information can be extracted from the QPCA results?
- Main steps of the QPCA. The ill-posed nature of the computational step.
- The energetic heterogeneity of immobilized reagents: toward the exact estimation.
- Cooperativity effects: revealing and quantitative characterization.
- Overcoming the ill-posed nature of the parametric identification of the models: significance of the chemometrics tools.
- Surface modified silicas: the generalization of the QPCA results.

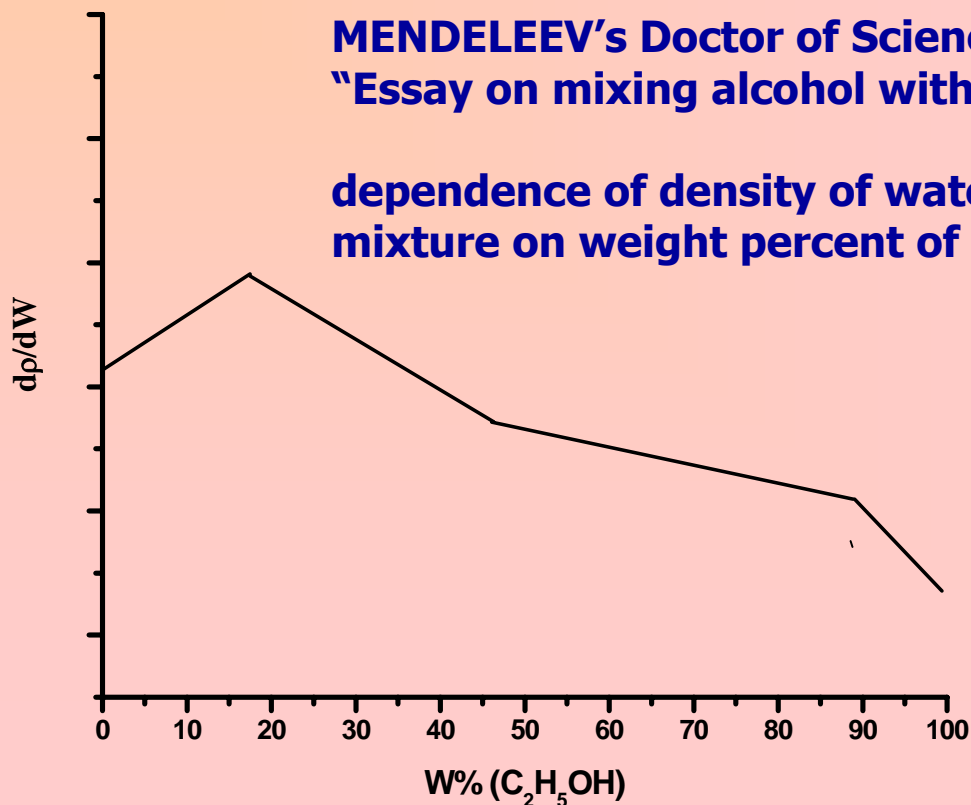


DMITRY MENDELEEV

Quantitative Physico-Chemical Analysis:
the set of experimental and calculation tools for the determination of stoichiometric composition and physico-chemical (in particular, thermodynamic) characteristics of species in equilibrium systems by analyzing the composition–property dependencies.

**MENDELEEV's Doctor of Science Thesis
"Essay on mixing alcohol with water" (1865)**

**dependence of density of water-ethanol
mixture on weight percent of ethanol**



Silica-organics hybrid materials

Hybrid is not the sum of silica and organic modifier!



Properties

- high surface area, regulated capacity, possibility to set up the affinity for target species
- rather favorable kinetic characteristics
- powder, monolith, film, fibre

Preparation routes

- silanization of silica surface
- post-silanization chemical modification
- sol-gel synthesis
- non-covalent immobilization

Some target applications

- sorption
- analysis
- catalysis
- sensors



How immobilization of organic reagents affects their affinity to “ligands”?

Factors: morphology, surface topography, micro-environment of fixed species, energetic heterogeneity and others

Possible effects: energetic heterogeneity of reagents, cooperativity effects, uncommon composition or/and stability of immobilized complexes, ...



Primary experimental data: composition-property dependencies

$$A_k = \zeta(\lambda, n_{*k})$$

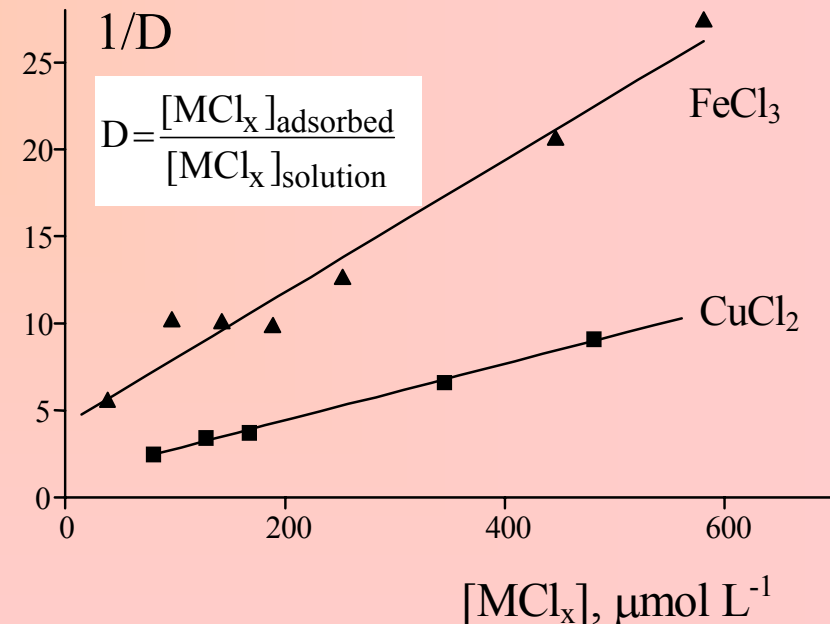
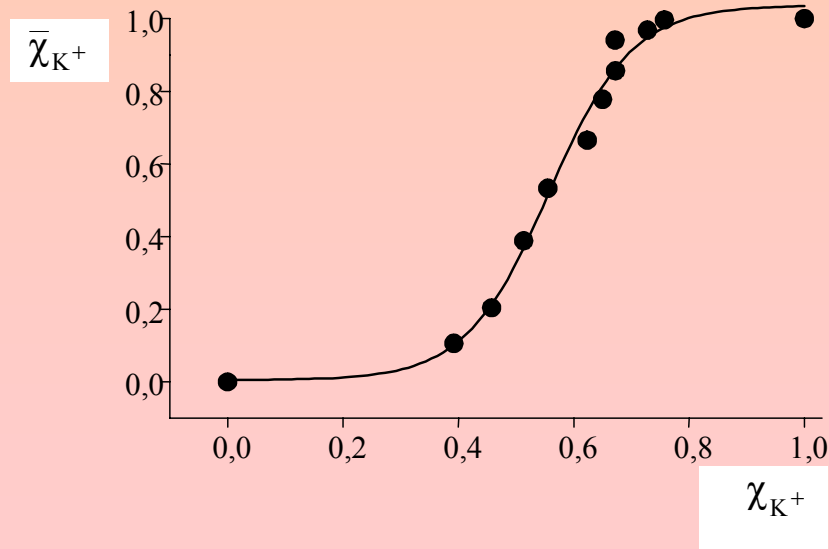
A is the measured property (pH, absorbance, distribution coefficient, etc);
k is the number of the studied mixture (experimental points), $1 \leq k \leq N$

N is the number of points;

λ is the analytical position;

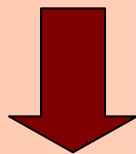
n_{*k} are the initial quantities of reagents;

ζ is a function.

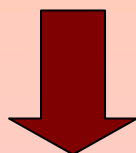




The single composition–property dependency



- ✓ Number of species present in the system at equilibrium;
- ✓ stoichiometric compositions of complexes;
- ✓ estimations of equilibrium constants;
- ✓ yields of species;
- ✓ distribution of active centers in respect to their affinity to ligands;



Optimal conditions of separation, isolation, masking, detection and determination of “ligands”.



Array of the QPCA results

Meaningful and/or formal
mathematical analysis

Information from structure
sensitive methods

Forecast of stability constants and yields of species dependently of
properties of reaction medium, nature of reagents, surface
topography, polarity, chemical and energetic heterogeneity



Main steps of the QPCA

1. Measurement of the composition-property dependence.

$$A_{lk} = \sum_{i=1}^S \alpha_{li} [L_i]_k$$

2. Structural identification of the model (assignment of the form of ζ).

3. Parametric identification of the model: computation of fitting parameters θ that provide the “best” approximation of the experimental data, $|\theta\rangle = \arg \min U(\theta)$.

4. Examination of the model adequacy and verification of the model.



The ill-posed nature of the computational step

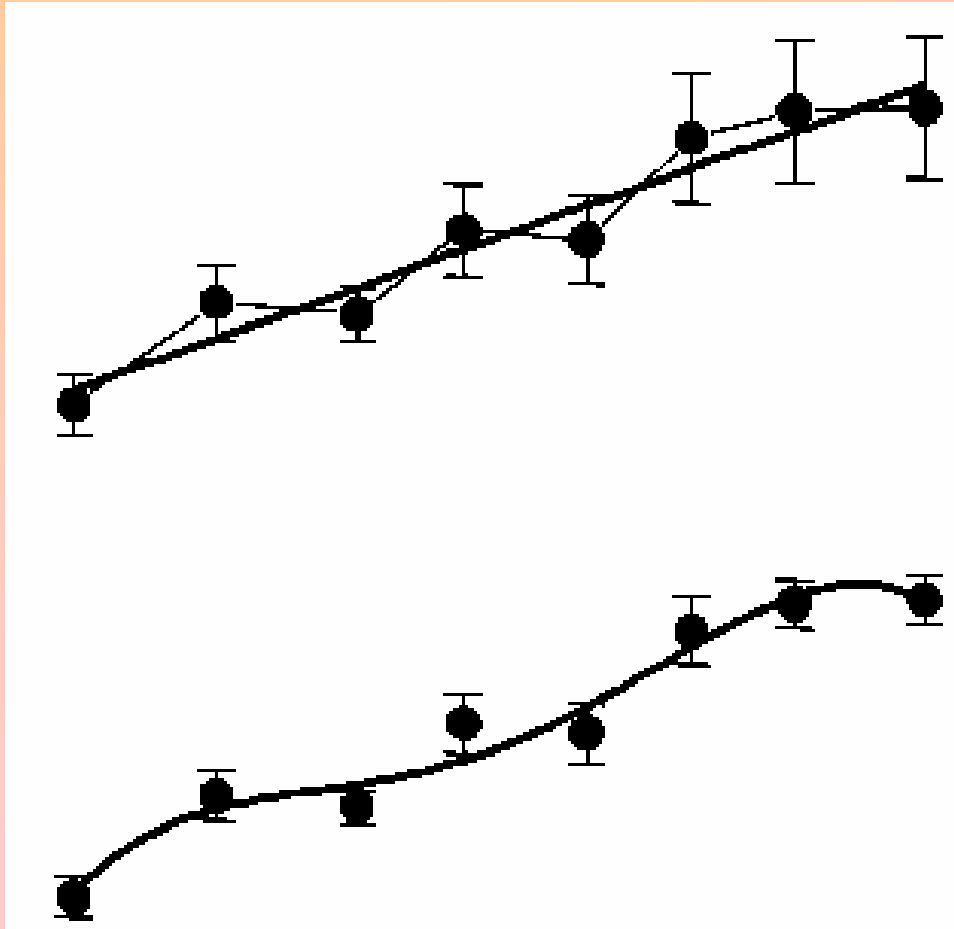
The composition – property dependency is set by **a table of values** rather than an analytical expression,

and the **density of the experimental errors** is unknown.

There several (many? infinitely many?) models describing the results of measurements inside their errors.



The ill-posed nature of the computational step



What model is better?

Does the model include
redundant (false)
parameters?

Is it possible to trust to
the least-squares
estimations?

$$|\theta\rangle = \arg \min U(\theta)$$

$$U(\theta) = \sum_{k=1}^N w_k \Delta_k^2 \quad \Delta_k = \hat{A}_k - A_k$$



Energetic heterogeneity of surfaces

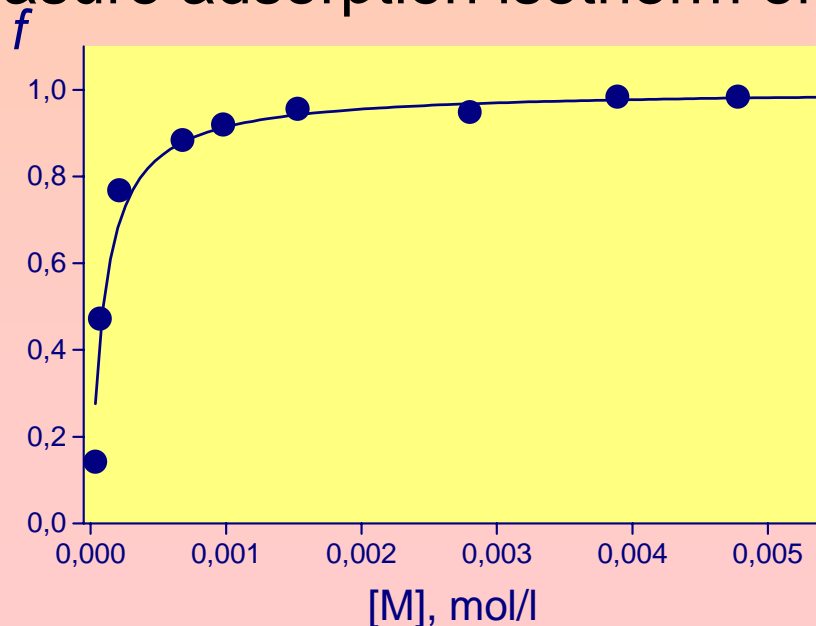
Material: active centers Q

Sorbate entity: M

Meaningful model: $M + \overline{Q} \xrightleftharpoons{K} MQ$

Experiment:

- to find occupation degrees $f([M]) = \frac{\{c^0(M) - [M]\} \times V}{m} = \frac{[\overline{MQ}]}{[\overline{Q}] + [\overline{MQ}]}$
- to measure adsorption isotherm of M;





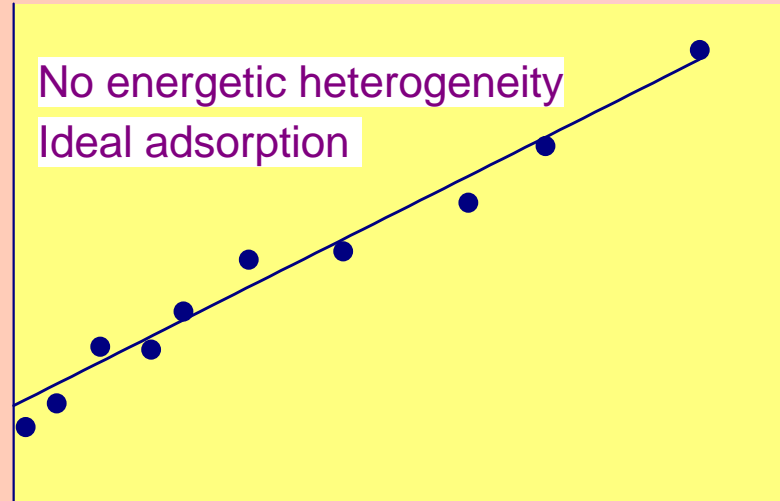
$$\overline{[MQ]} = t_Q \times \frac{K \cdot [M]}{1 + K \cdot [M]}$$

$$\frac{1}{D} = \frac{1}{K \cdot t_Q} + \frac{1}{t_Q} \times [M]$$



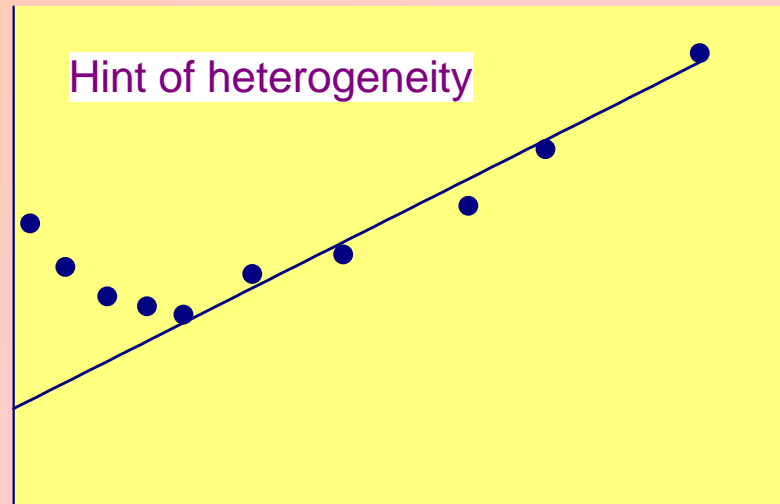
$$f([M]_k) = \sum_j^J p(K)_j \times \frac{K_j \cdot [M]_k}{1 + K_j \cdot [M]_k}$$

1/D

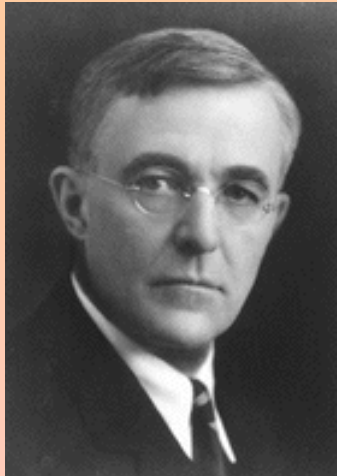


[M], mol/l

1/D

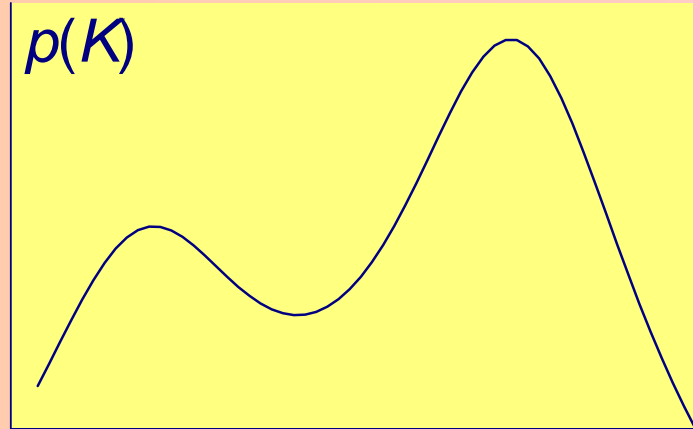


[M], mol/l



Irving Langmuir
1918

Continuous affinity distribution

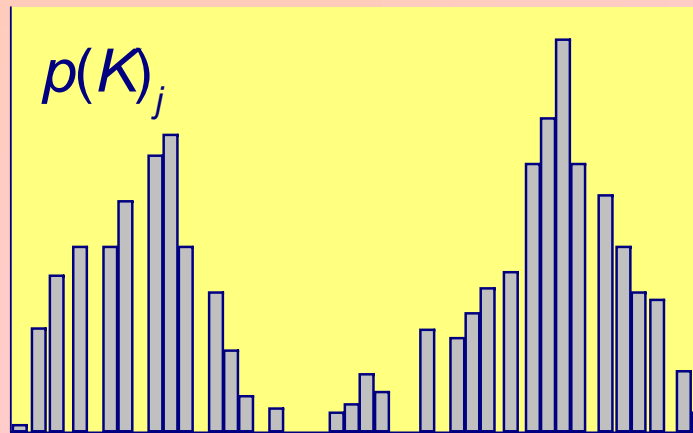


$$p(K) \geq 0$$

$$\int_0^{\infty} p(K) dK = 1$$

K

Discrete affinity distribution



$$p(K)_j \geq 0$$

$$\sum_j p(K)_j = 1$$

K_j



To calculate $p(K)$ it is necessary to solve the first kind Fredholm integral equation

The ill-posed problem!

$$f([M]) = \int_0^{\infty} \theta^{\text{local}}([M], K) \cdot p(K) dK$$

$$\theta^{\text{local}}([M], K) = \frac{K \cdot [M]}{1 + K \cdot [M]}$$

Tikhonov's regularization constitutes the dominating approach

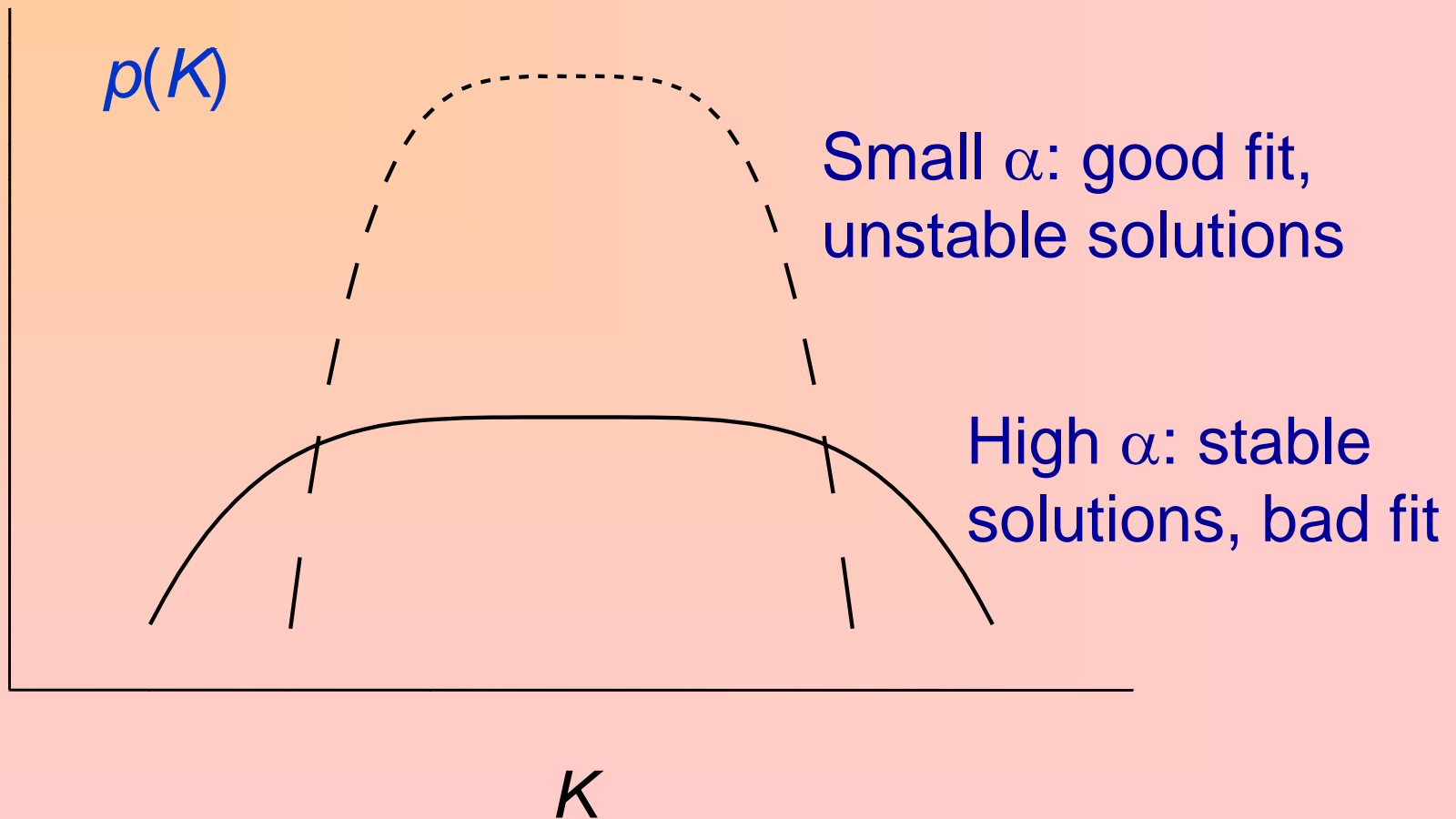
The search for $p(K)$ that minimizes

$$U_{\alpha} = \sum_{k=1}^N \left(f_k^{\text{calculated}} - f_k^{\text{measured}} \right)^2 + \alpha \cdot \Omega(p)$$

$$\Omega = \| p(K) \| = \int_0^{\infty} p^2(K) dK$$



Regularization of ill posed problems: where does its power end?





Maxent approach

Experimental data are considered as restrictions imposed on the searched density function $p(K)$

$$\tilde{f}_k = \sum_{j=1}^J p(K_j) \frac{K_j \cdot [M]_k}{1 + K_j \cdot [M]_k} \quad k = 1, 2, \dots, N$$

Yu. Kholin and S. Myerniy, Energetic Heterogeneity of Sorbents: Numerical Calculation of Affinity Distributions. *V.N.Karazin Kharkiv University Bulletin. 2004. No 626. Chemical Series. Iss. 11 (34).* P. 351-364.



Restrictions in the form of inequalities

$$\sum_{j=1}^J p(K_j) \times \frac{K_j \cdot [M]_k}{1 + K_j \cdot [M]_k} \geq \tilde{f}_k - \Delta, \quad k = 1, 2, \dots, N,$$

$$\sum_{j=1}^J p(K_j) \times \frac{K_j \cdot [M]_k}{1 + K_j \cdot [M]_k} \leq \tilde{f}_k + \Delta, \quad k = 1, 2, \dots, N,$$

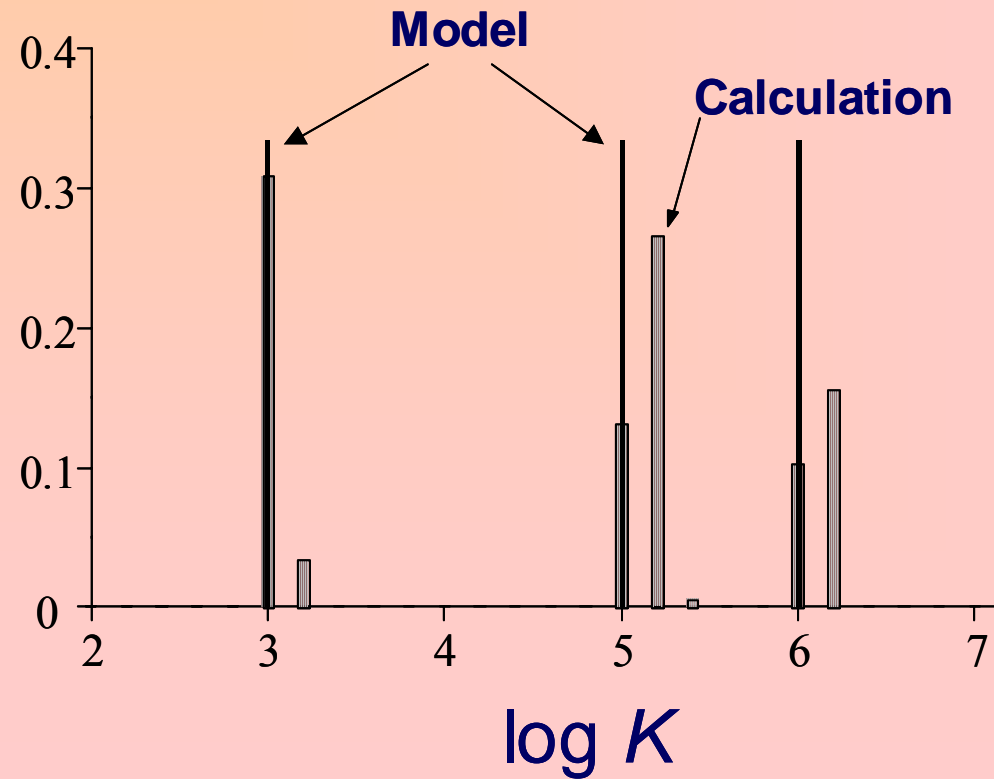
$$\sum_{j=1}^J p(K_j) = 1, \quad p(K_j) \geq 0,$$



Numerical example

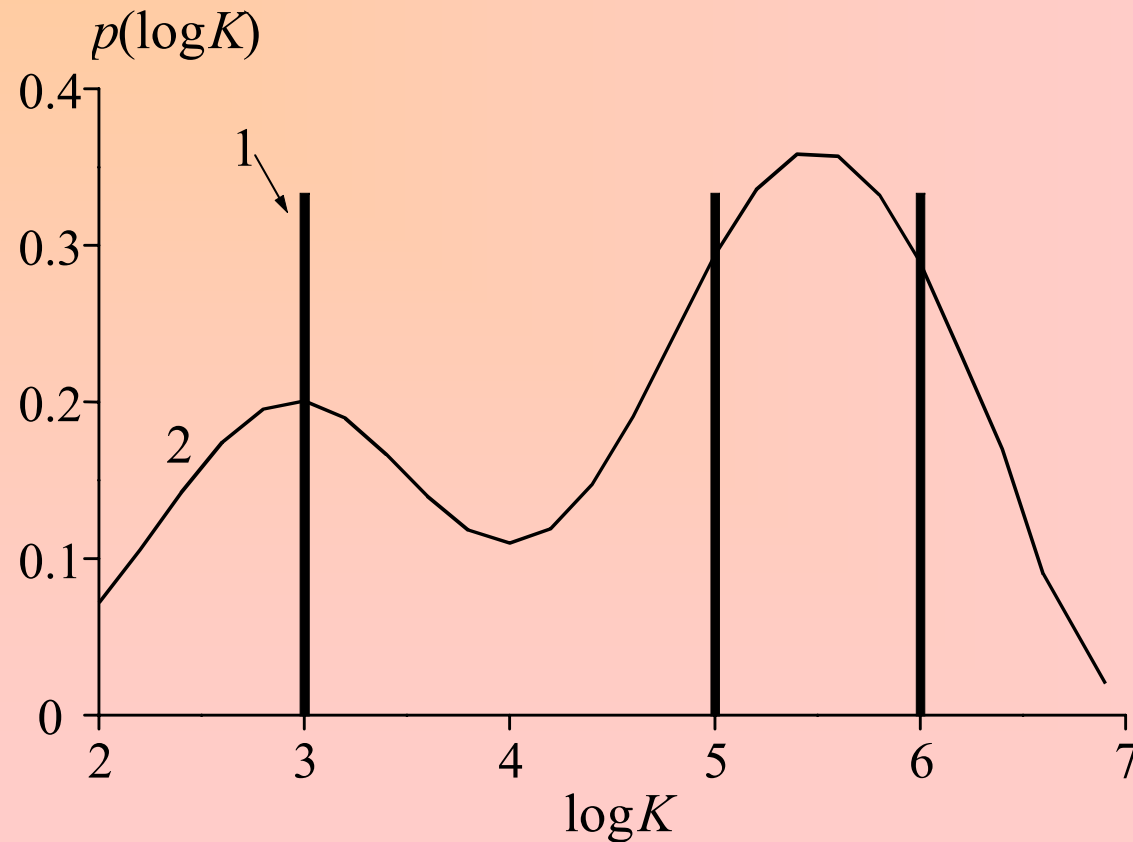
$$p(\log K = 2) = p(\log K = 5) = p(\log K = 6) = 1/3$$

The density function $p(\log K)$
 $p(\log K)$





The density function $p(\log K)$ calculated by the conventional α -regularization algorithm from exact data

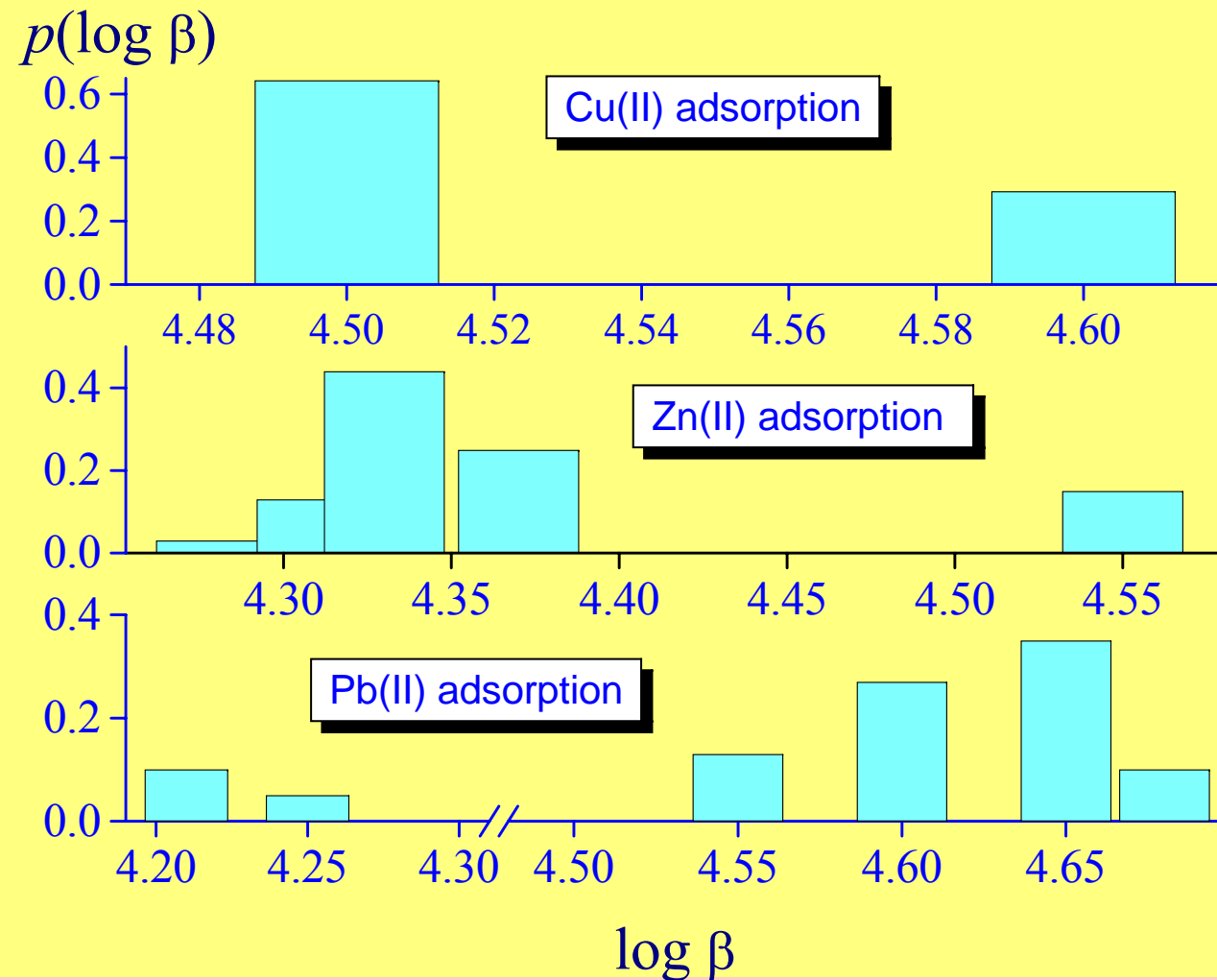




Affinity distribution of active sorption centers (density functions)

**Xerogel with
immobilized
Xylenol
Orange**

pH 5.6-5.8





Cooperativity effects investigated with the aid of the model of polydentate binding

“...Where cooperativity takes place the affinity of the ligand for the receptor site may be enhanced (positive cooperativity) or depressed (negative cooperativity) by previous occupation of sites”

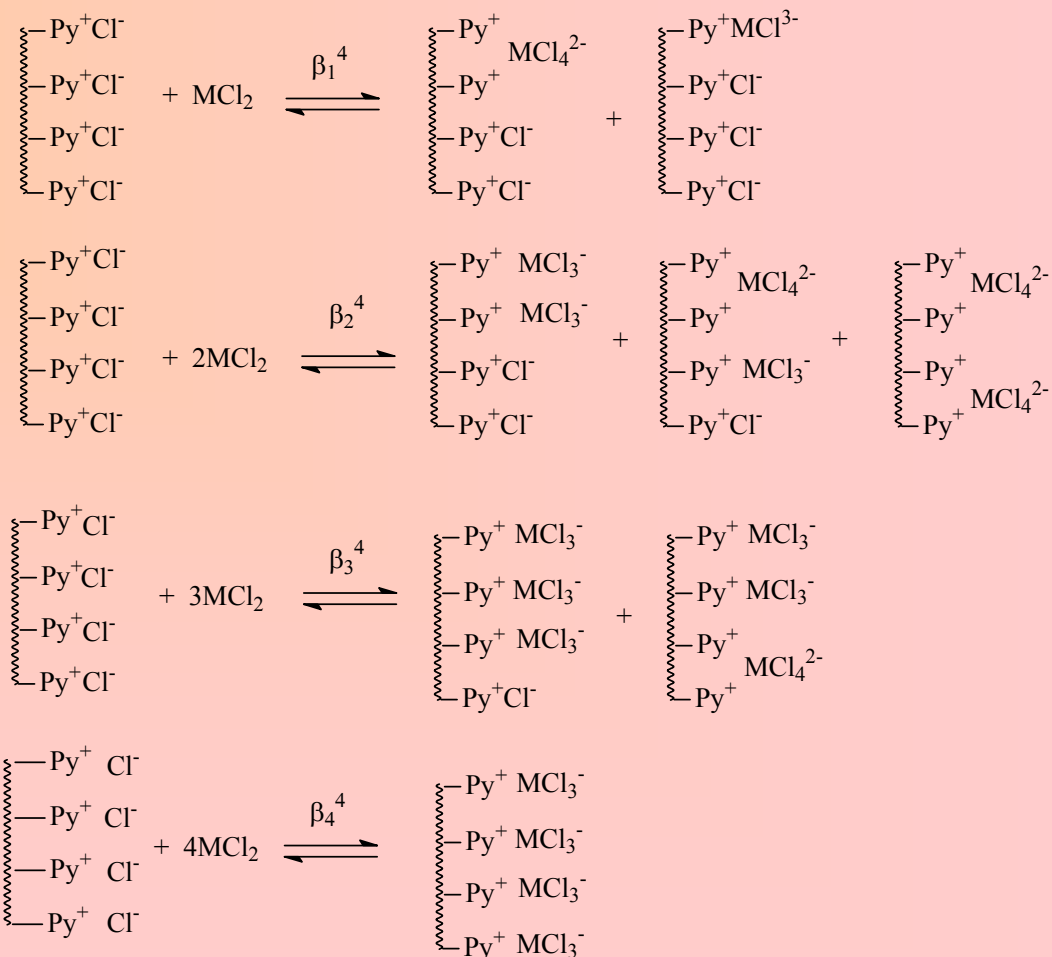
A. Braibanti, e.a., *Reactive&Functional*

Polymers 36 (1998) 245.

Strauss U.P., e.a. 1979.

Belinskaya F.A., 1987

G.V. Kudryavtsev, e.a., 1990.





Interpretation of results of simulation

No cooperativity

$$K_{i+1}^{(Z)} / K_i^{(Z)} = \frac{(Z - i + 1)(i + 1)}{i(Z - 1)}$$

Negative cooperativity

$$K_{i+1}^{(Z)} / K_i^{(Z)} < \frac{(Z - i + 1)(i + 1)}{i(Z - 1)}$$

Positive cooperativity

One or more of inequalities are not kept

$$K_i^{(Z)} < K_{i-1}^{(Z)} < \dots < K_1^{(Z)}$$

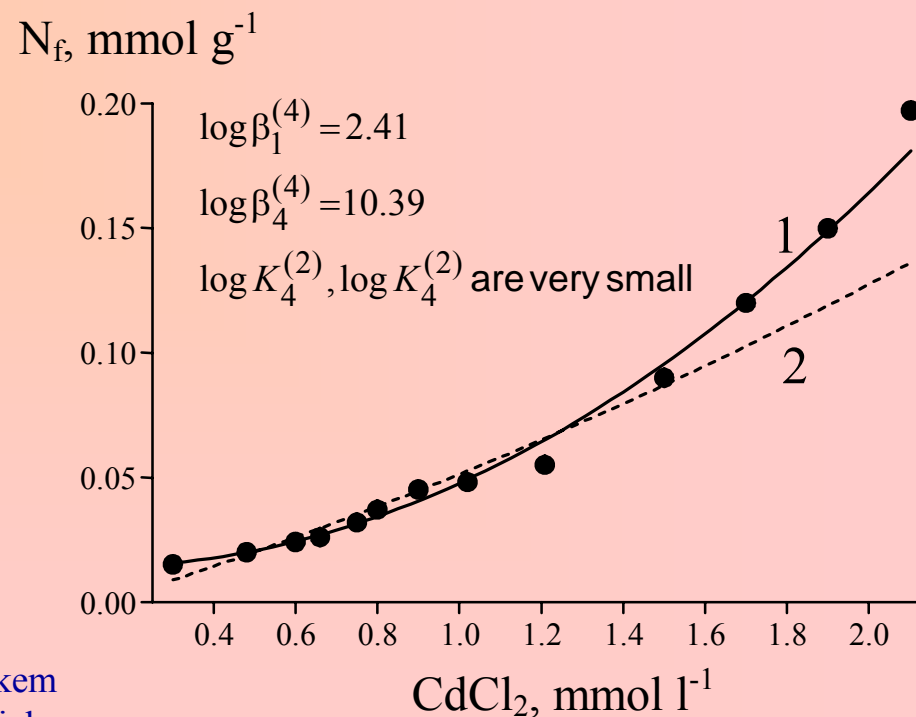
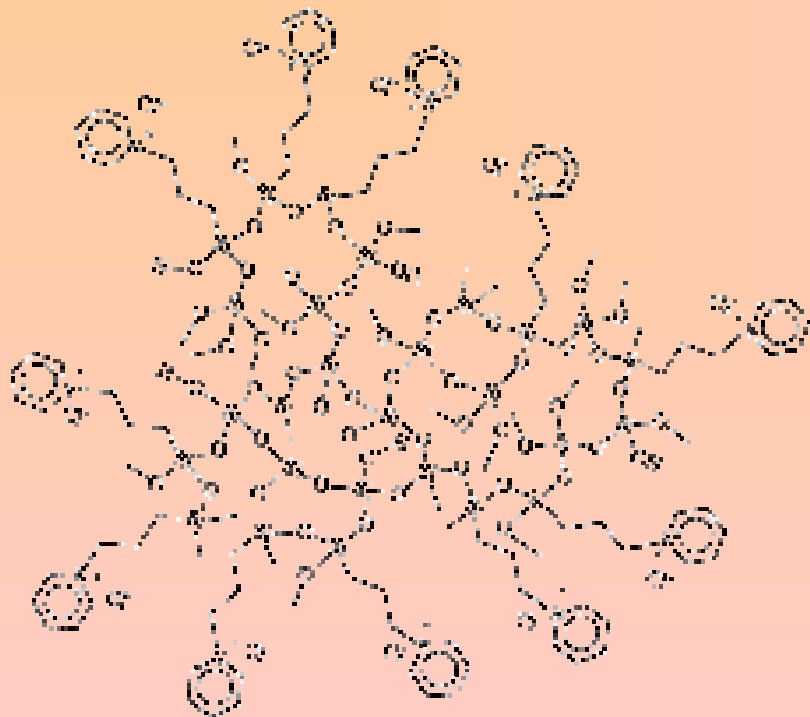


Example of simulation

CdCl_2 adsorption isotherm

1 – model of fixed tetradentate centers,

2 – model of bidentate centers.



Lucho A.M.S., Panteleimonov A.V., Kholin Y.V., Gushikem Y. Simulation of Adsorption Equilibria on Hybrid Materials. *J. Colloid Interf. Sci.* 2007, V. 310. P.47-56.



Some chemometrics tools applied to overcome the ill-posed nature of the parametric identification

Only two remarks

- Criterion to be minimized (infirmity of the least-squares method, robust estimators).
- Insufficiency of the statistical adequacy (effects of leverage points, cross-validation).

Robust regression (Huber's M-estimates) vs. least squares

$$A_k = \tilde{f}(\mathbf{X}_k, \boldsymbol{\theta}) + \varepsilon_k = \hat{A}_k + \varepsilon_k, \quad k = 1, 2, \dots, N$$

$$\text{LS: } \boldsymbol{\theta} = \arg \min \sum_{k=1}^N [\hat{A}_k - A_k]^2$$



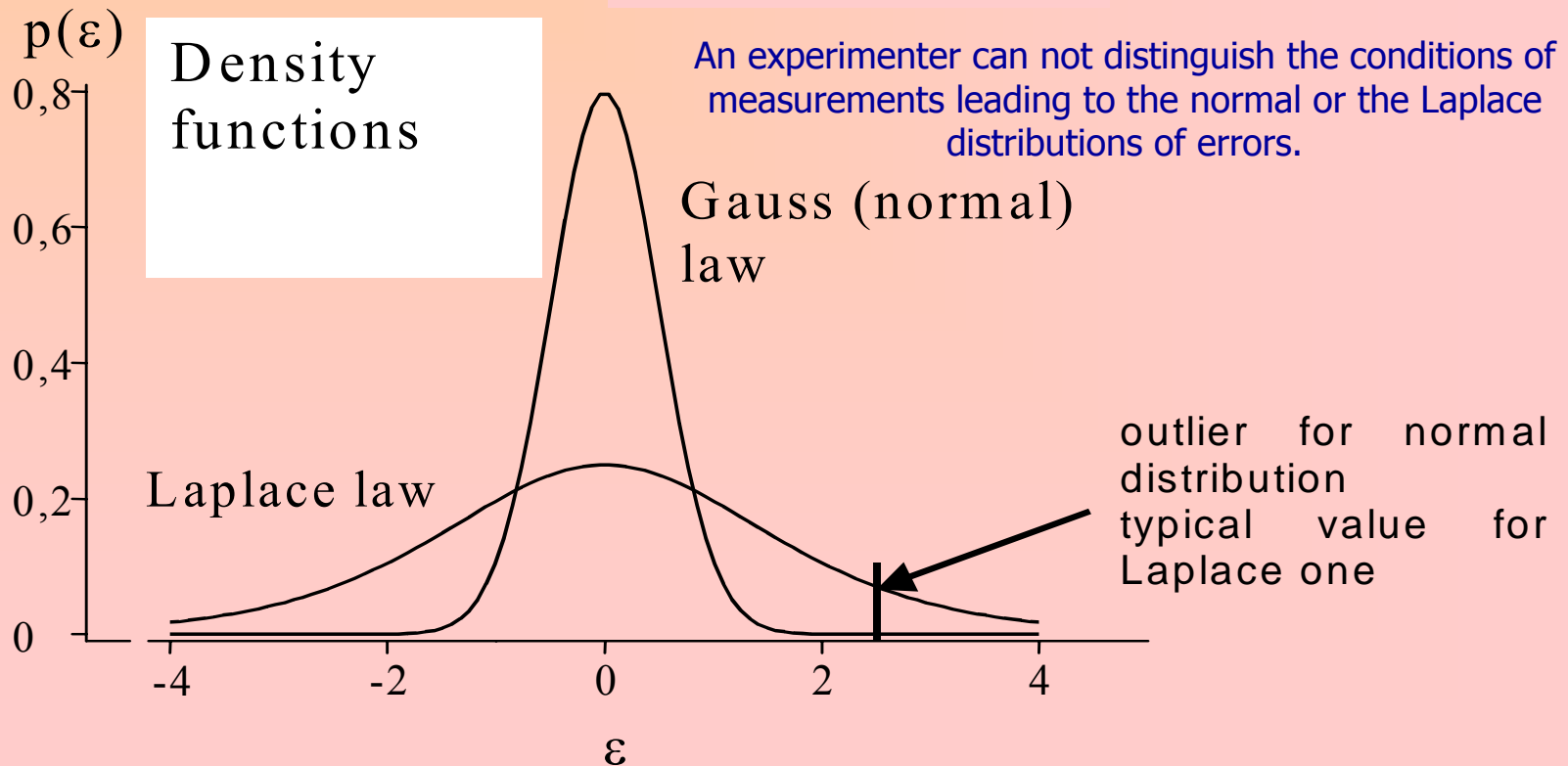
The model of gross errors

$$p(\varepsilon) = [(100 - \delta) \cdot \varphi(\varepsilon) + \delta \cdot h(\varepsilon)] / 100,$$

$\varphi(\varepsilon)$ – density function of the normal distribution,

$h(\varepsilon)$ – long-tails density function (“gross errors” density function),

δ – intensity of “gross errors”





Robust Huber's M-estimations

$$M = \sum_{k=1}^N \rho(\xi_k; \theta) = \min \quad \xi_k = \hat{A}_k - A_k$$
$$\rho(\xi) = \begin{cases} (1/2)\xi^2, & \text{at } |\xi| \leq c \\ c|\xi| - (1/2)c^2, & \text{at } |\xi| > c \end{cases}$$

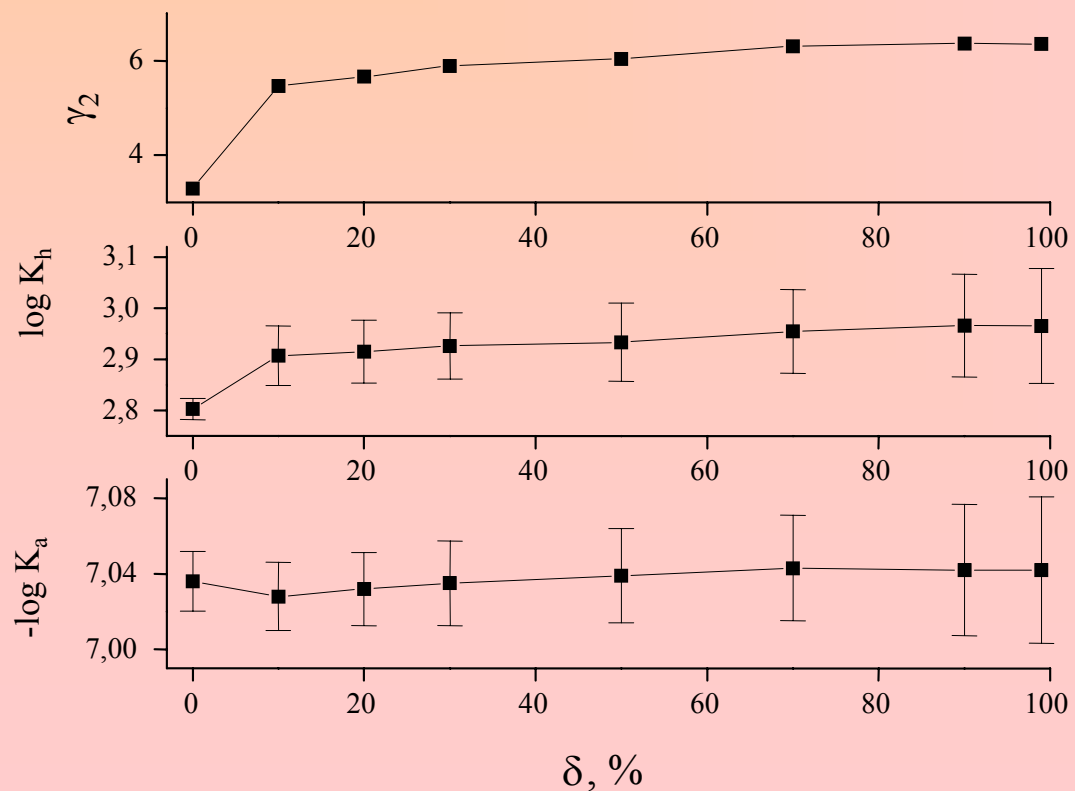
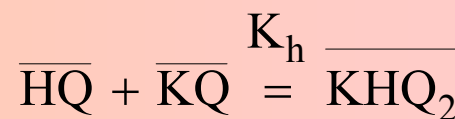
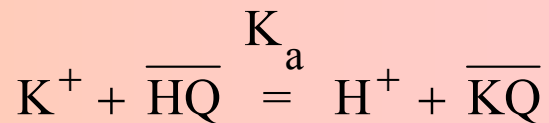
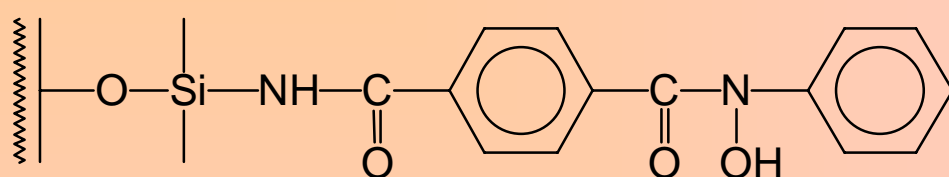
c_{out} depends on the intensity of the "gross errors" (δ)

Merits

- both normal and Laplace distributions are limiting laws,
 - conditions of their formation are close (experiment),
- robust Huber's M-estimates are theoretically substantiated,
- data analysis is performed easily by varying hypothesis about δ .

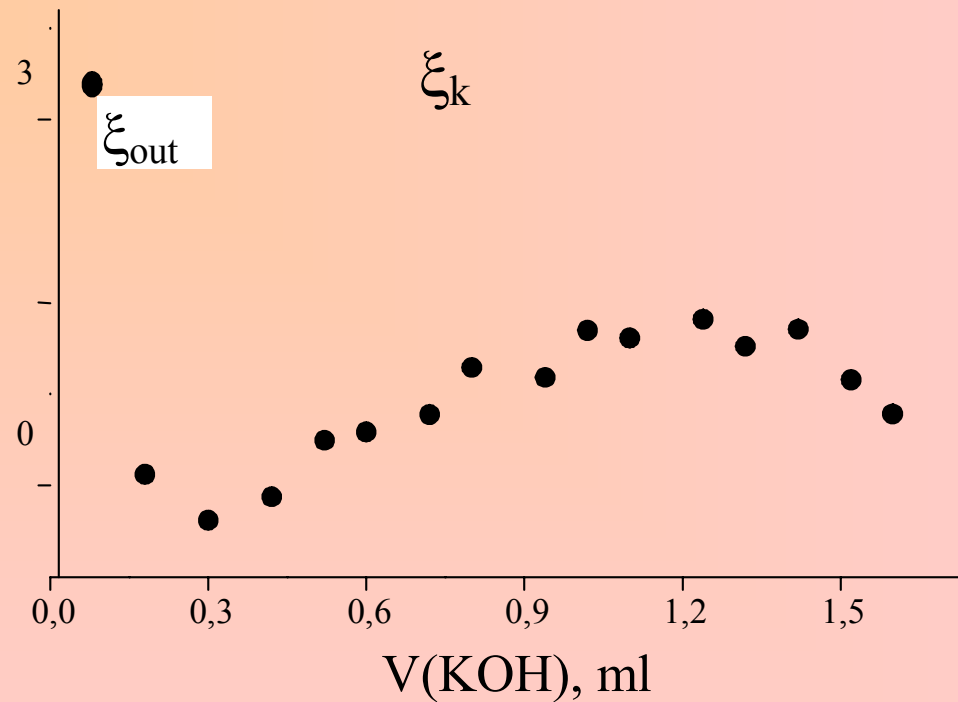


Example: Protolytic properties of BPHA on silica surface from the pH-metric titration data





Identification of outliers and leverage points



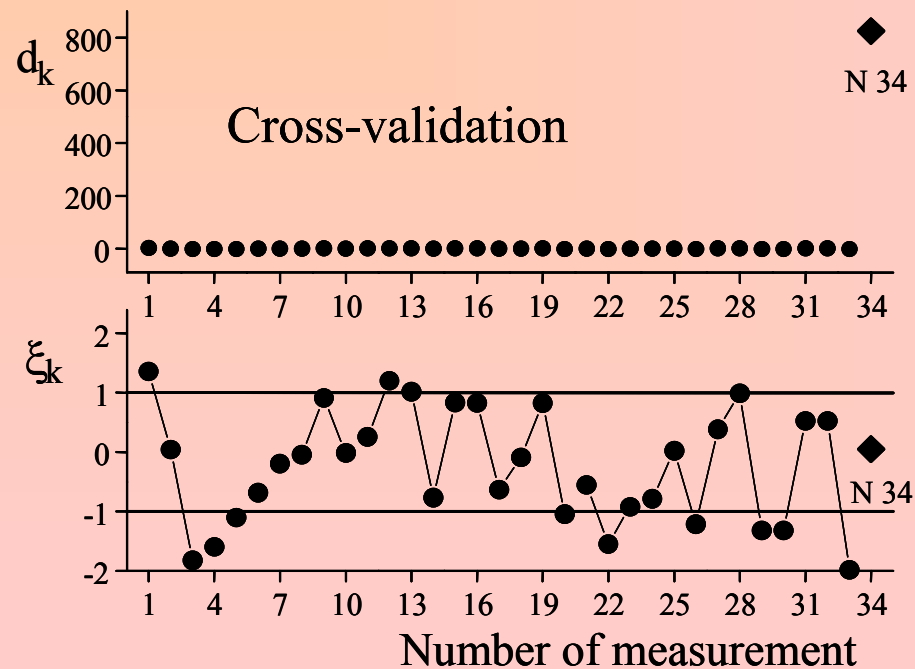
Good situation: outlier is detected easily



Cross-validation

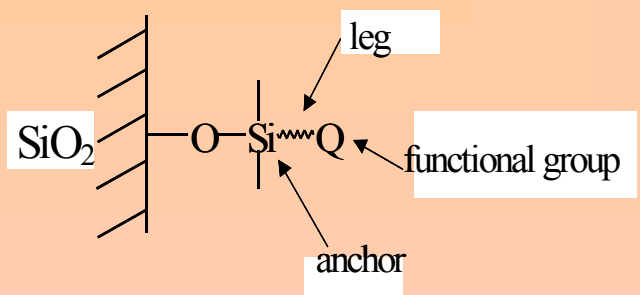
From the array of the experimental data (N points) the g-th point (only one) is excluded, the unknown parameters are calculated and the weighed residues of cross-validation are found:

$$d_g = w_g^{1/2} \cdot (\hat{A}_g - A_g)$$



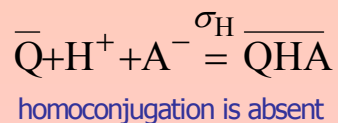
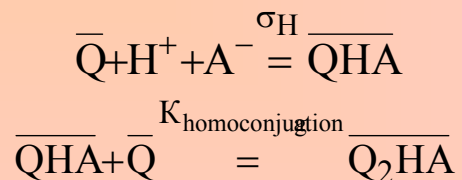


Protolytic and complexing properties of aliphatic amines grafted on silica surface



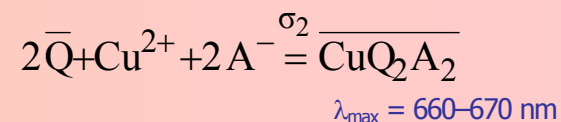
More than
40 samples

Model of protolytic equilibria

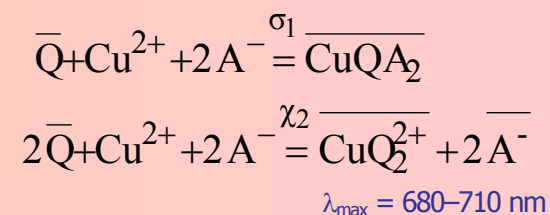


(20 – 40) °C

Model of complexation equilibria

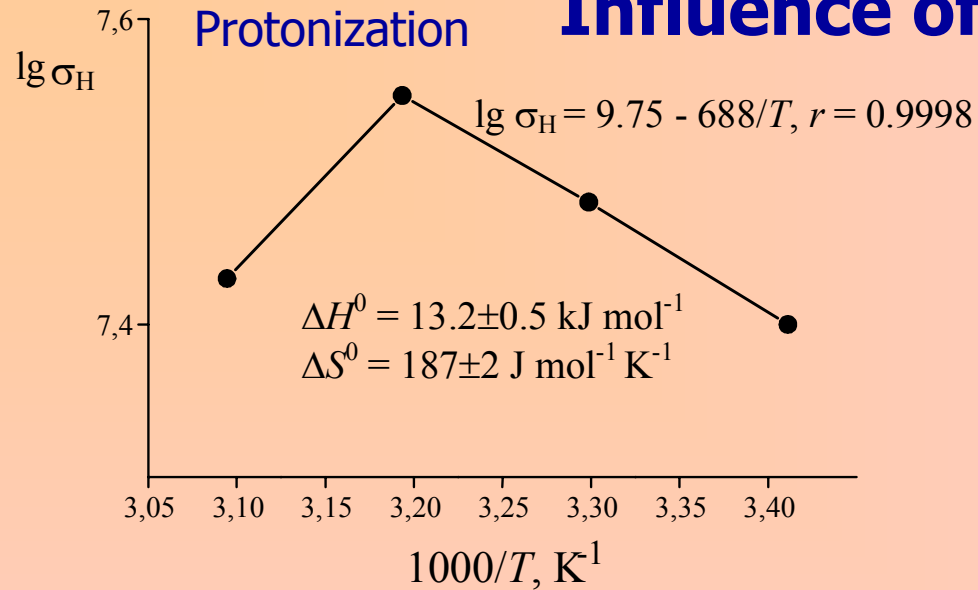


50 °C



Q is organic amine, grafted on silica surface

Influence of temperature



n-propylamine:

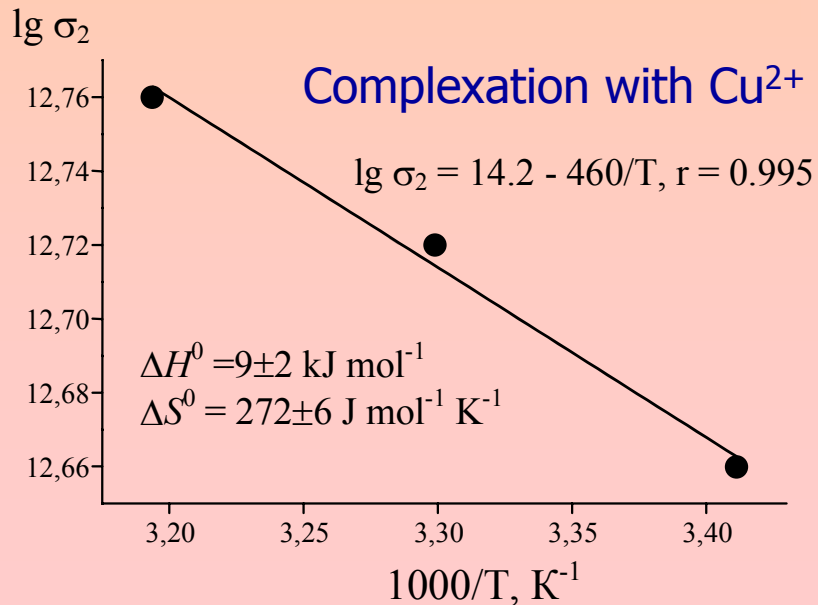
$$\Delta H_{298}^0 = -57 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^0 = 17 \text{ J mol}^{-1} \text{ K}^{-1}$$

ammonia:

$$\Delta H_{298}^0 = -54 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^0 = \sim 0$$



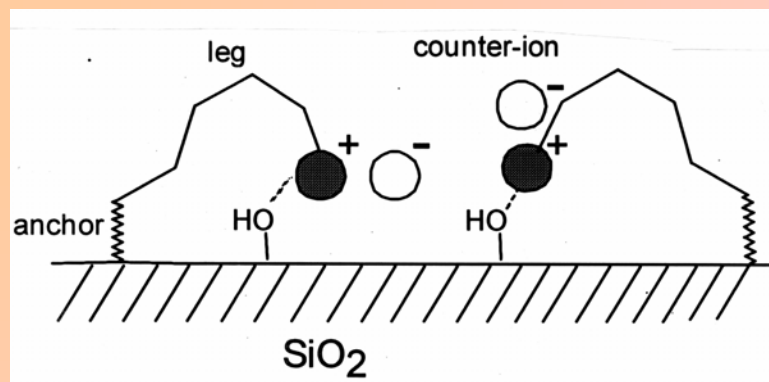
$\text{Cu}(\text{NH}_3)_2^+$:

$$\Delta H_{298}^0 = -44 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^0 = \sim 0$$

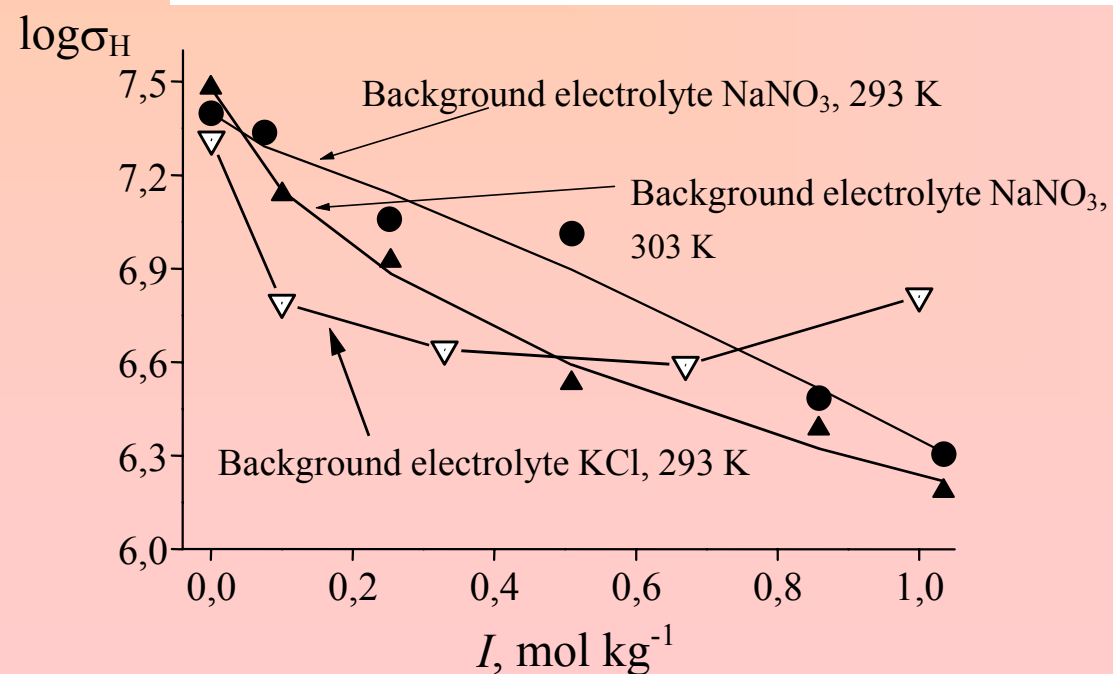


Strong fixation of counter-ions



Determination of thermodynamic equilibrium constants

Approximation on the base of the Pitzer method

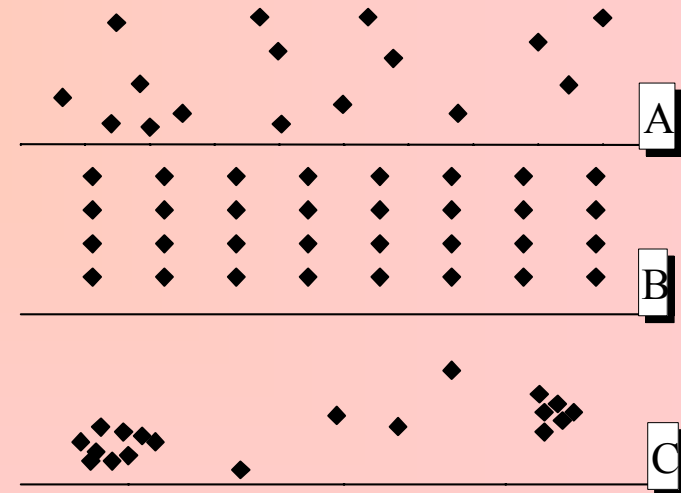
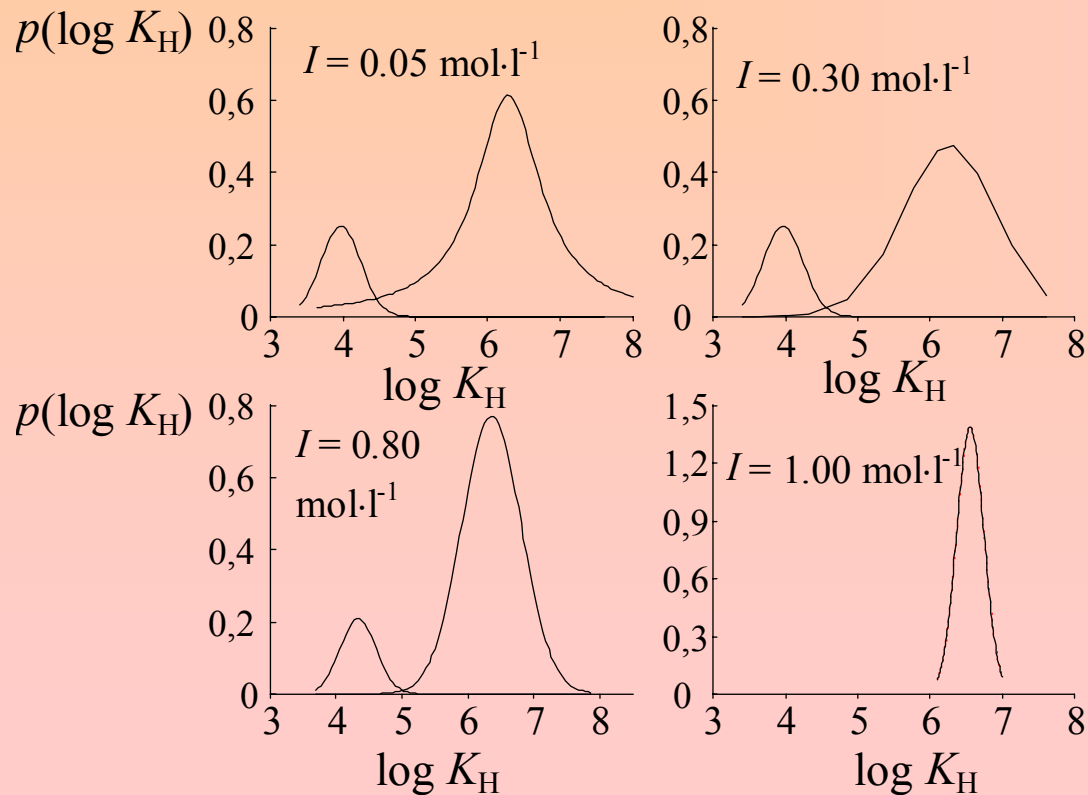




Conclusions about surface topography

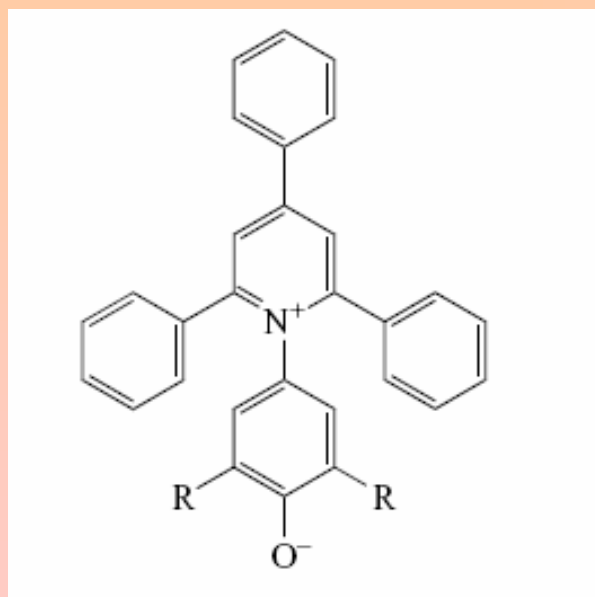
Distribution of n-propylamine groups grafted on silica surface on logarithms of protonization constants

Possible types of surface topography





Probing surfaces of aminosilicas with Reichardt's solvatochromic indicators



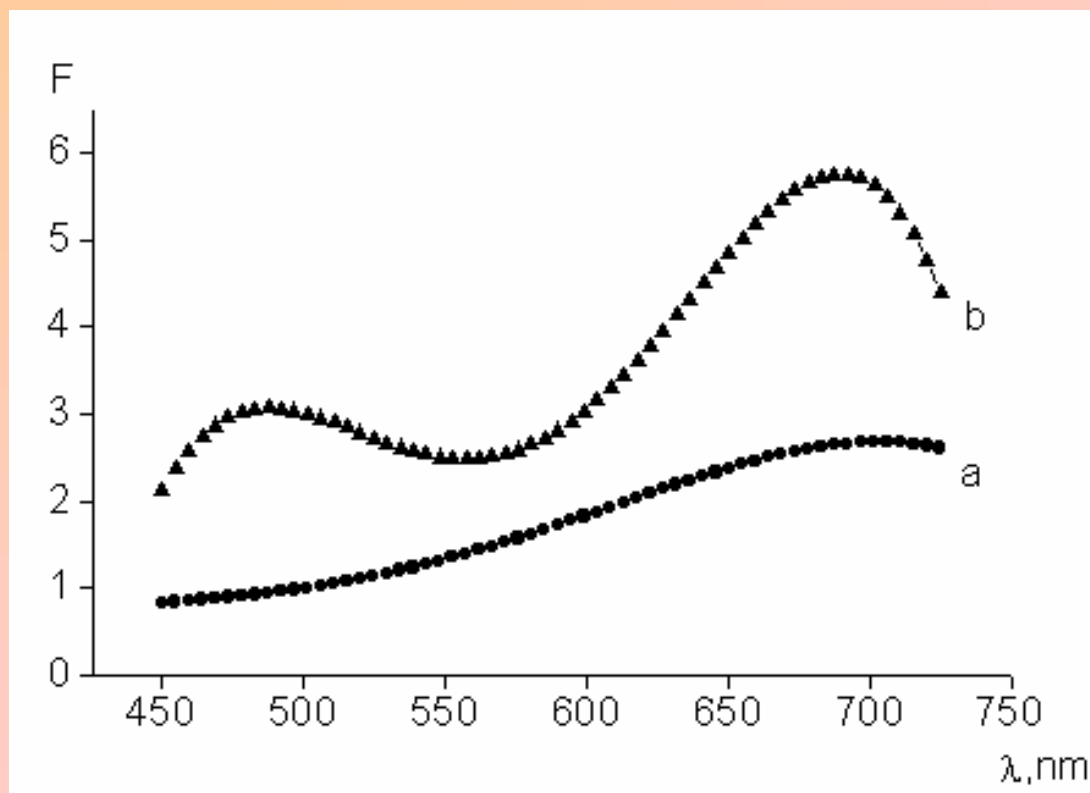
For standard Reichardt's indicator **R = Ph**



Colors of solutions of the standard Reichardt's indicator in n-butanol, n-propanol, ethanol, methanol, acetophenone, acetonitrile, and acetone.



Absorption spectra of standard Reichardt's indicator on the surface of silochrome with grafted amine



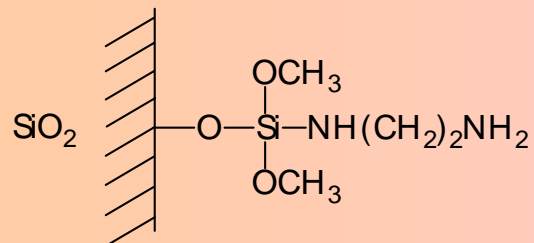
a: $c = 0.028 \mu\text{mol/g}$
b: $c = 0.29 \mu\text{mol/g}$

I. Khristenko, Y. Kholin, N. Mchedlov-Petrosyan, C. Reichardt, V. Zaitsev,
Probing surfaces of chemically modified silicas with solvatochromic
N-pyridino-N-phenolate betaine indicators. 2006. *Colloid. Journ.* V. 68. No 4.

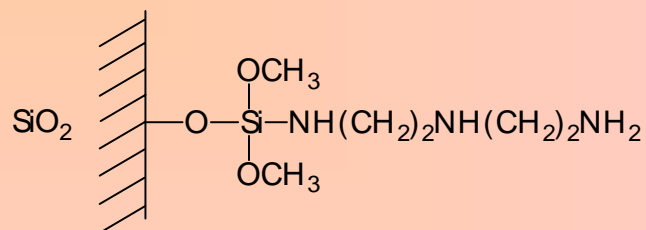


Influence of the type of the leg

Flexible aliphatic legs

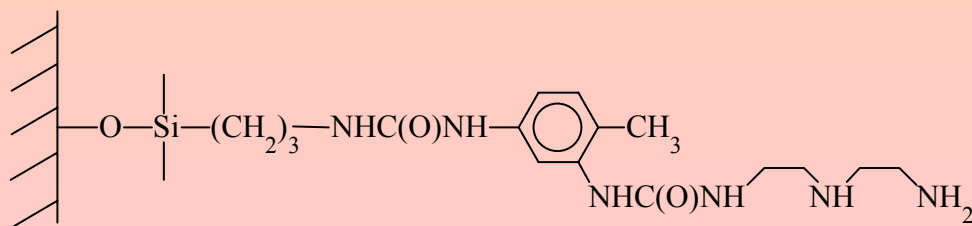


$$\log \beta_{11}(\text{Cu}^{2+} + \text{En} = \text{CuEn}^{2+}) = 6.7$$



$$\log \beta_{11}(\text{Cu}^{2+} + \text{Dien} = \text{CuDien}^{2+}) = 9.6$$

Flexible aliphatic legs

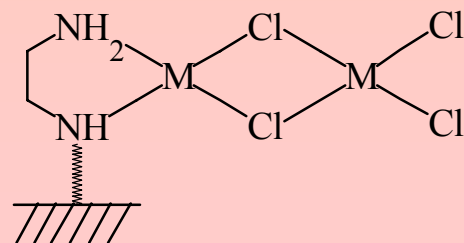
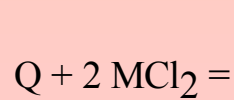
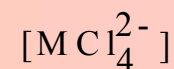
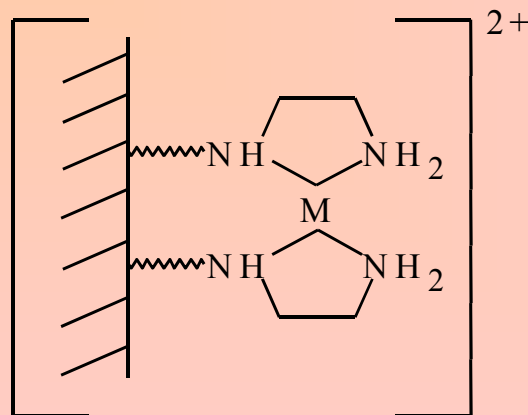
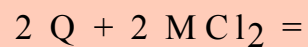
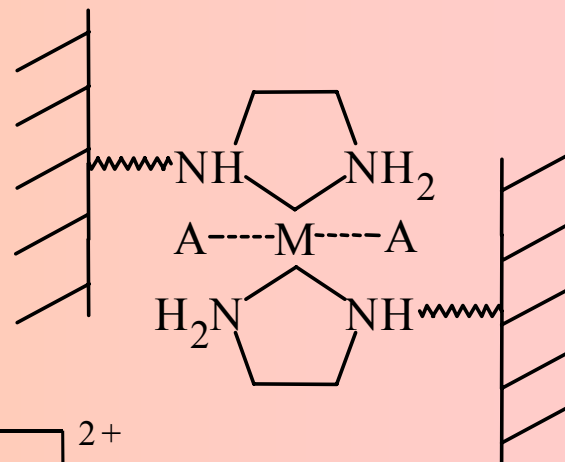
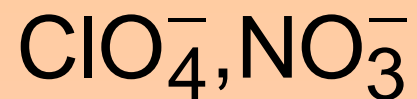


$$\log \beta_{11}(\text{Cu}^{2+} + \text{En} = \text{CuEn}^{2+}) = 4.16$$

$$\log \beta_{11}(\text{Cu}^{2+} + \text{Dien} = \text{CuDien}^{2+}) = 5.9$$

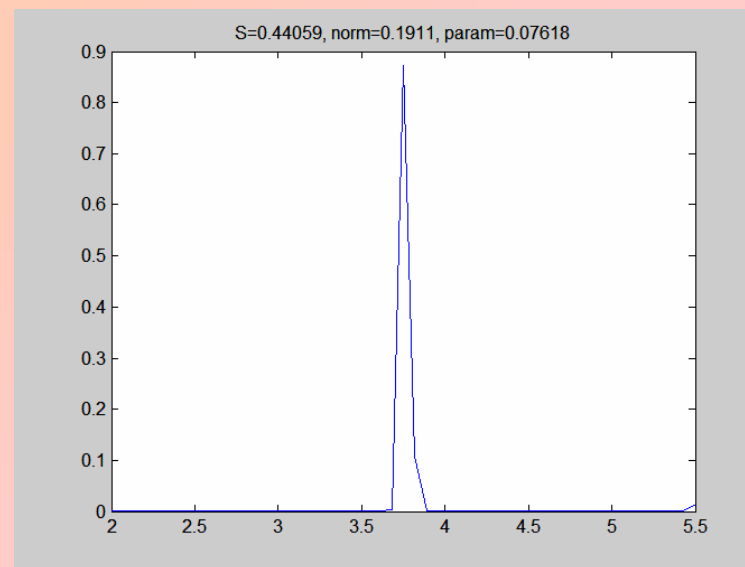
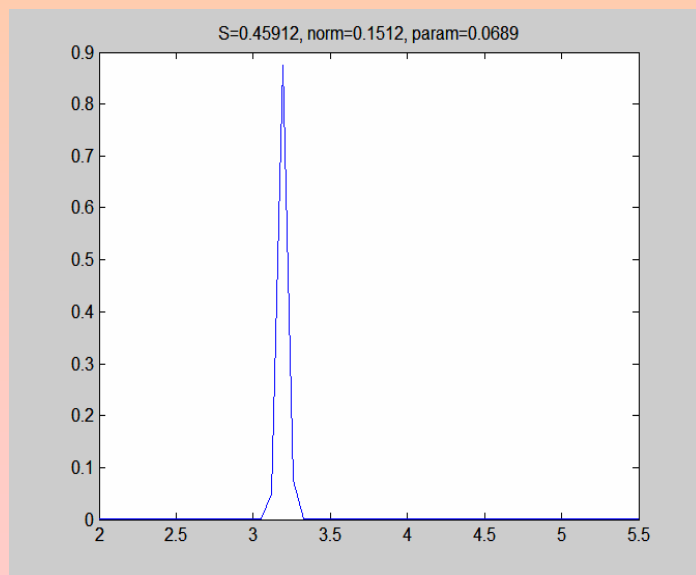
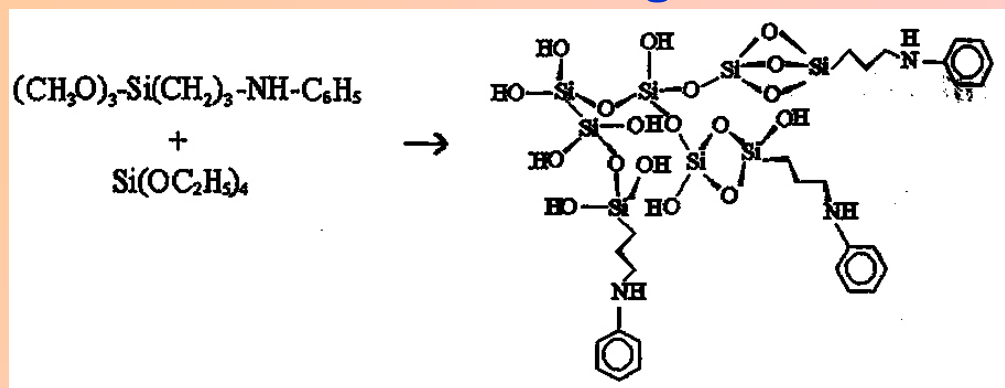


Influence of the type of anion





Low energetic heterogeneity of materials prepared with the aid of sol-gel method



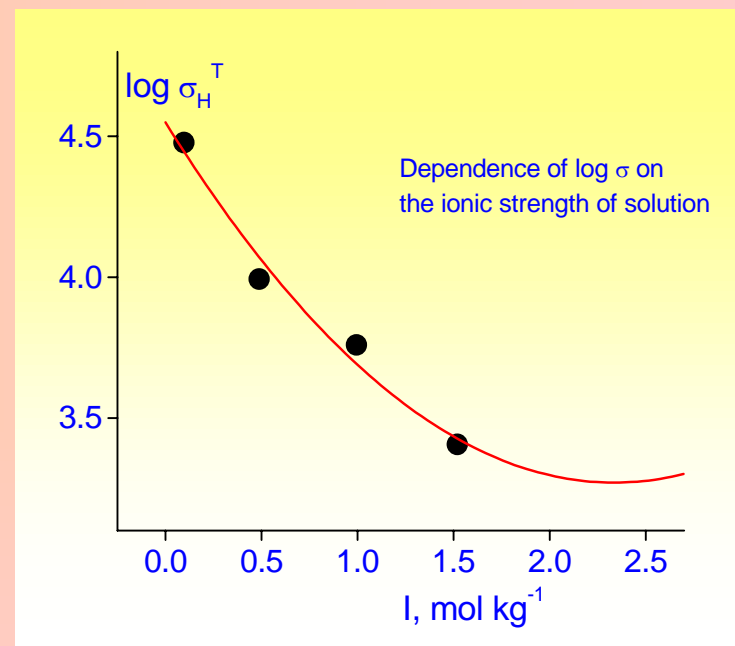
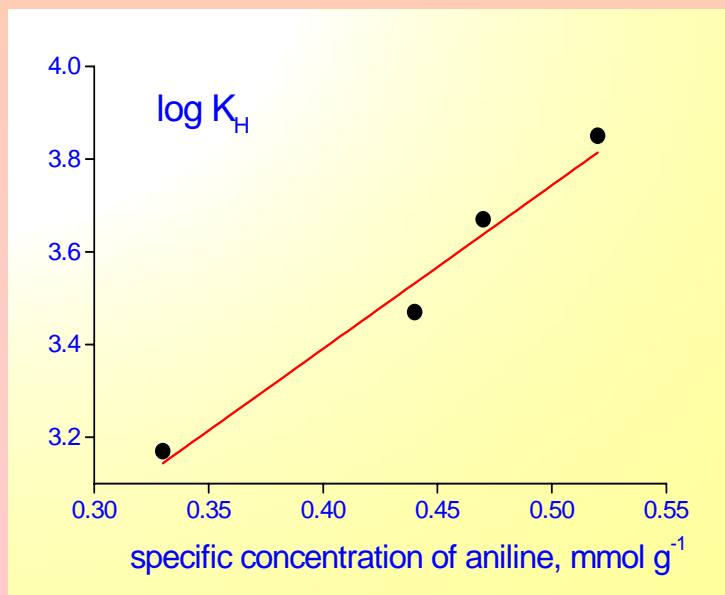
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Features of material prepared with the aid of sol-gel method

Results of simulation of the H^+ chemisorption

Sample	Strong fixation of counter-ions		Mobile counter-ions	
	$\log \sigma_H$	χ_{exp}^2	$\log \beta_H$	χ_{exp}^2
1	4.20	6.1	0.26	34.4
2	4.87	17.5	1.14	25.4





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