Тема 9 Полиэлектролиты. Описание равновесий с участием полимеров

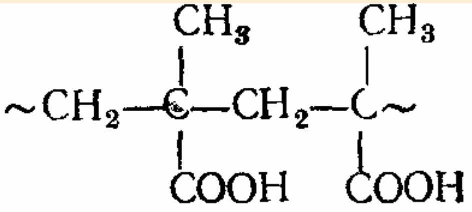
1. Определение и классификация ПЭ.
2. Равновесия в растворах ПЭ:

2а. Уравнение Качальского.

2б. Характеристическая константа.

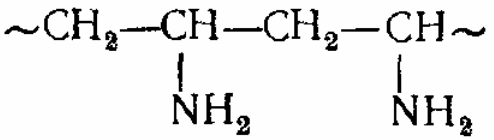
2в. Модель Тенфорда.

3. Полиэлектролитное набухание. Изоэлектрическая точка.
4. Ионный обмен. Ионообменная емкость
5. Равновесия ионного обмена. Уравнение Никольского
6. Равновесия лиганд-рецептор. Эффекты кооперативности.



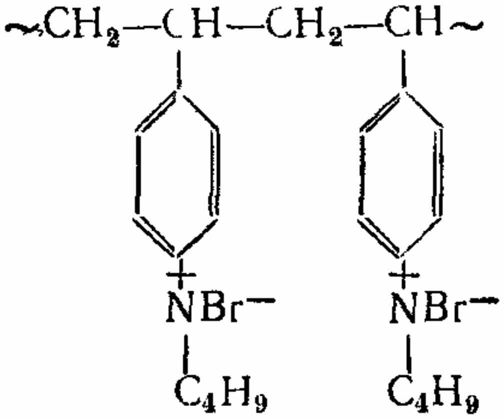
$$\sim CH_2-\underset{COOH}{\overset{CH_3}{C}}-CH_2-\underset{COOH}{\overset{CH_3}{C}}\sim$$

полиметакриловая кислота

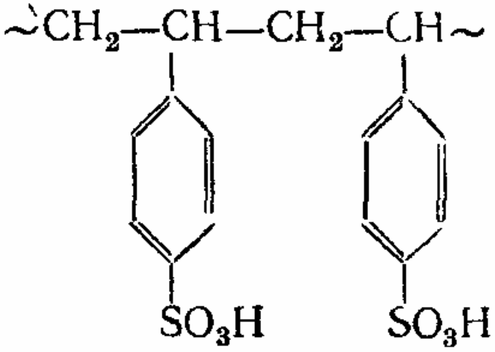


$$\sim CH_2-\underset{NH_2}{CH}-CH_2-\underset{NH_2}{CH}\sim$$

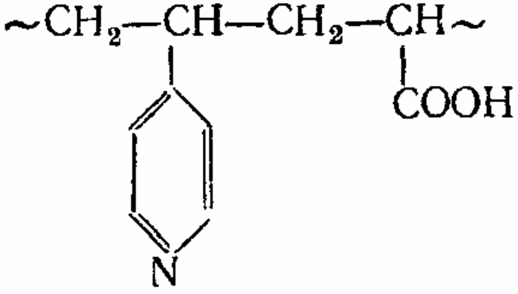
поливиниламин



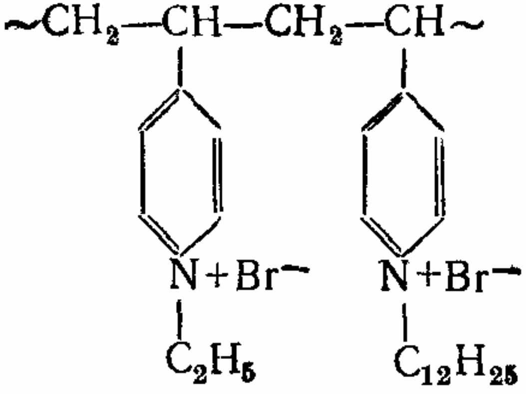
поливинил-*н*-бутилпиридиний-бромид



полистиролсульфокислота



сополимер акриловой кислоты и винилпиридина



сополимер 4 винил N этил и 4 винил N додецилпиридинийбромида (полимерное мыло)

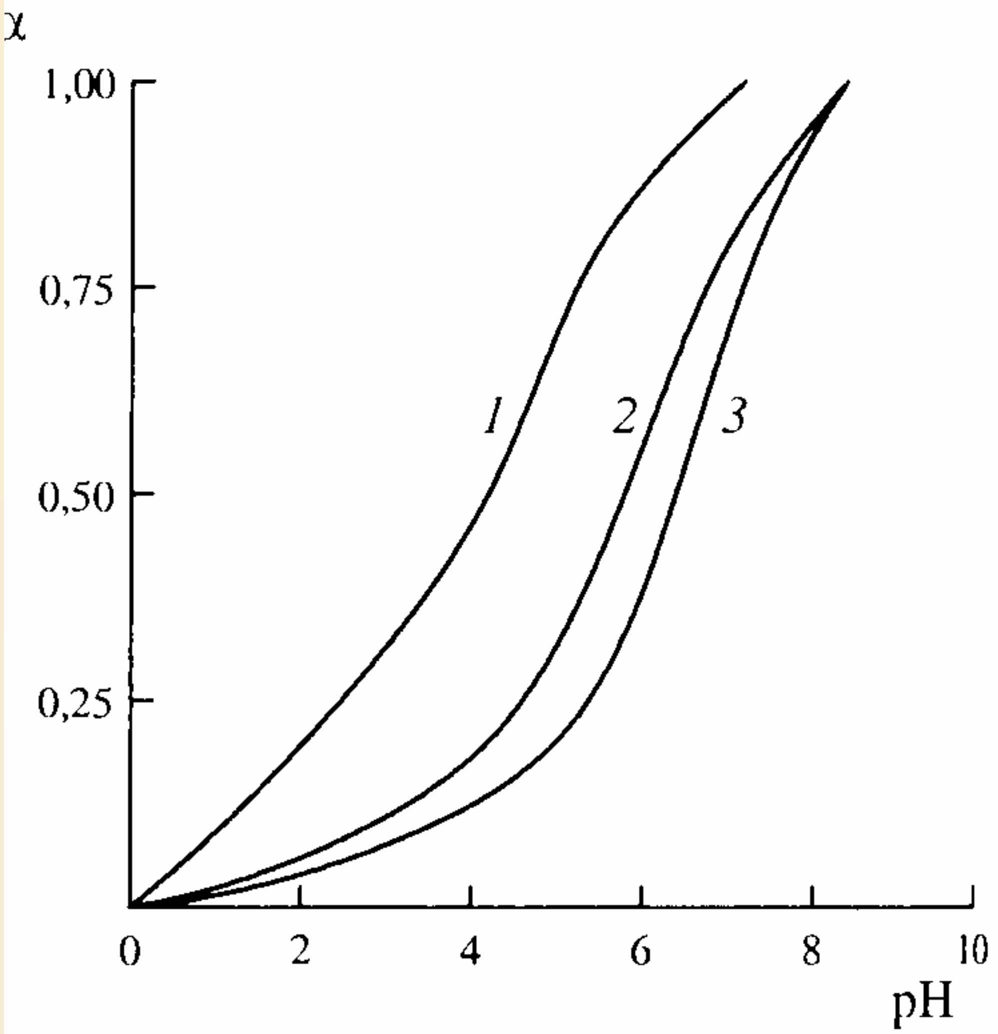
Уравнение Качальского для слабой поликислоты

$$\mathrm{pH} = \mathrm{p}K_0 + \Delta\mathrm{p}K\,(\alpha) + \lg\frac{\alpha}{1-\alpha}$$

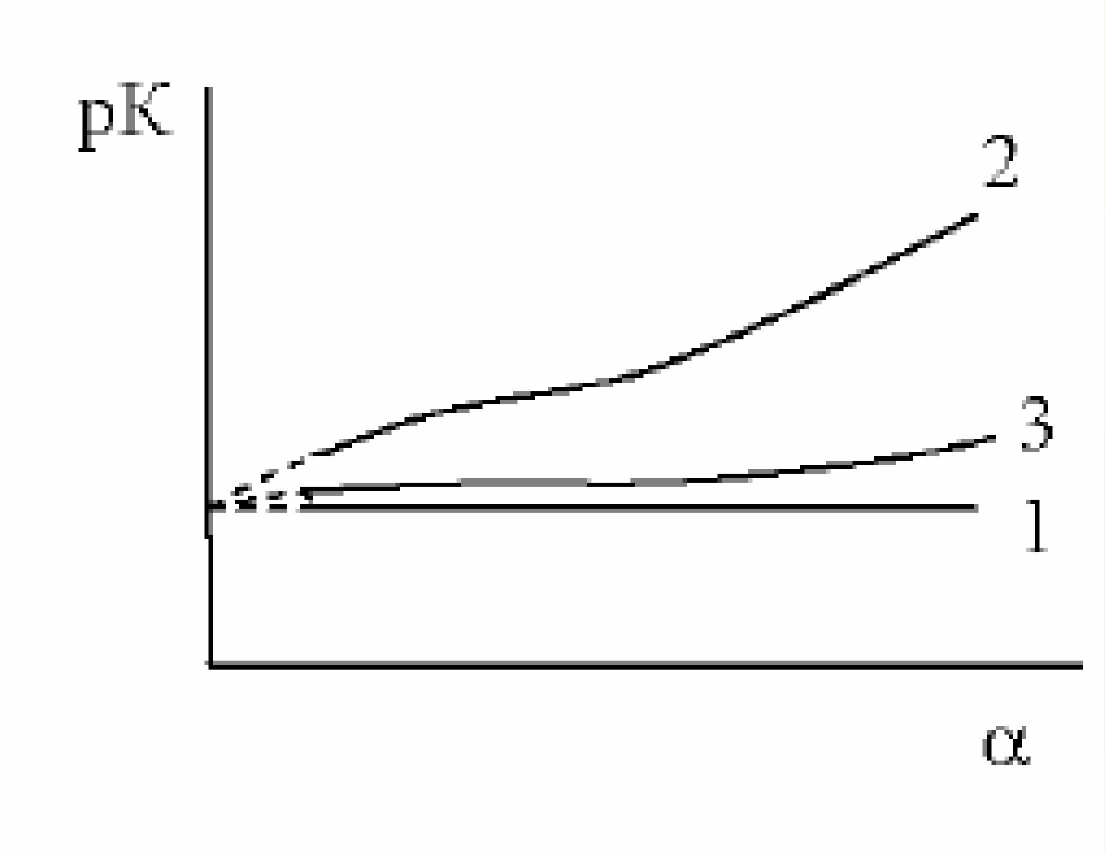
$$\Delta\mathrm{p}K\,(\alpha) = \frac{0{,}434}{kT}\,\frac{\partial F_{\text{эл}}}{\partial z} = \frac{0{,}434}{kT}\,e\psi$$

Эмпирическое уравнение

$$\mathrm{pH} = \mathrm{p}K^{0} + n \cdot \lg\left(\frac{\alpha}{1-\alpha}\right)$$



Кривые потенциометрического титрования растворов:
1 – пропионовой кислоты в воде;
2, *3* – синдио- и изотактической полиакриловой кислоты в воде

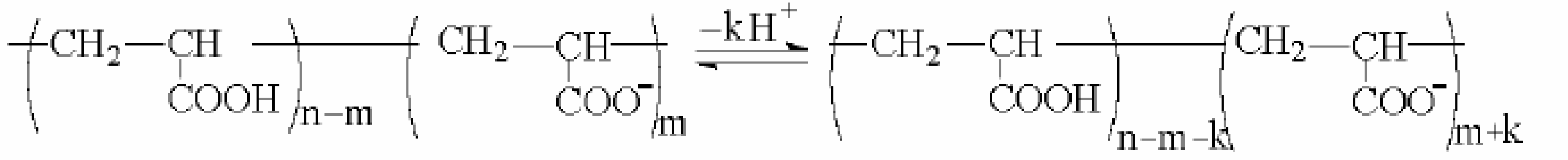


- Высокомолекулярная кислота в присутствии

сильного электролита

- Низкомолекулярная кислота
- Высокомолекулярная кислота в отсутствие сильного электролита

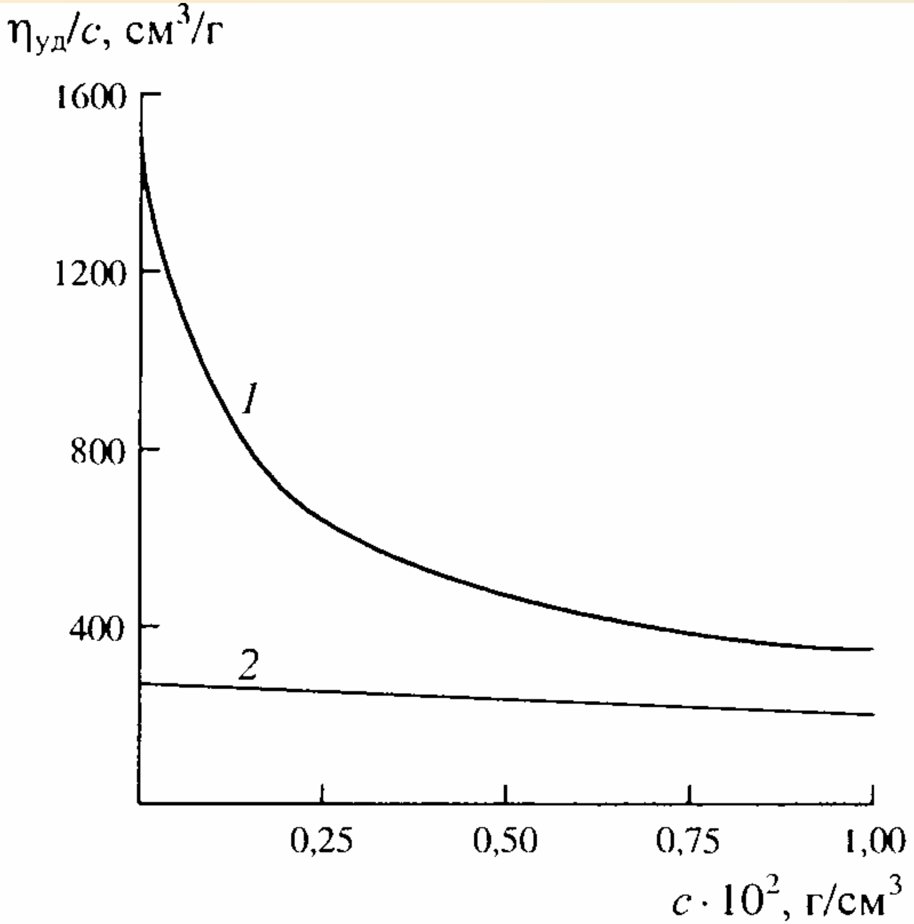
Полимер как единый центр свзяывания (по Ч. Тенфорду)



$$-\left(CH_2-\underset{\underset{COOH}{|}}{CH}\right)_{n-m}\left(CH_2-\underset{\underset{COO^-}{|}}{CH}\right)_m \xrightleftharpoons{-kH^+} -\left(CH_2-\underset{\underset{COOH}{|}}{CH}\right)_{n-m-k}\left(CH_2-\underset{\underset{COO^-}{|}}{CH}\right)_{m+k}$$

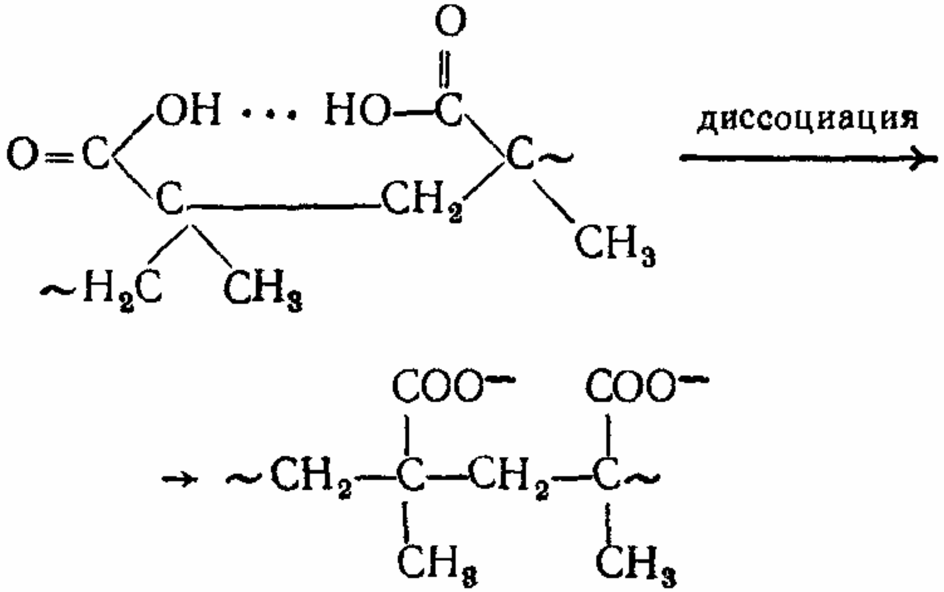
A

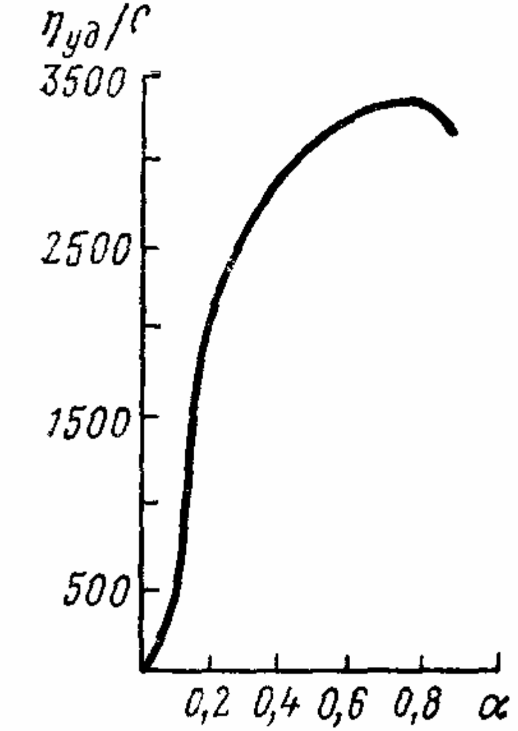
Вязкость растворов ПЭ. Полиэлектролитное набухание



Зависимость приведенной вязкости от концентрации раствора полиэлектролита: *1* – водный раствор поли-4-винил-N-бутилпиридиний-бромида, *2* – то же, с добавкой KBr

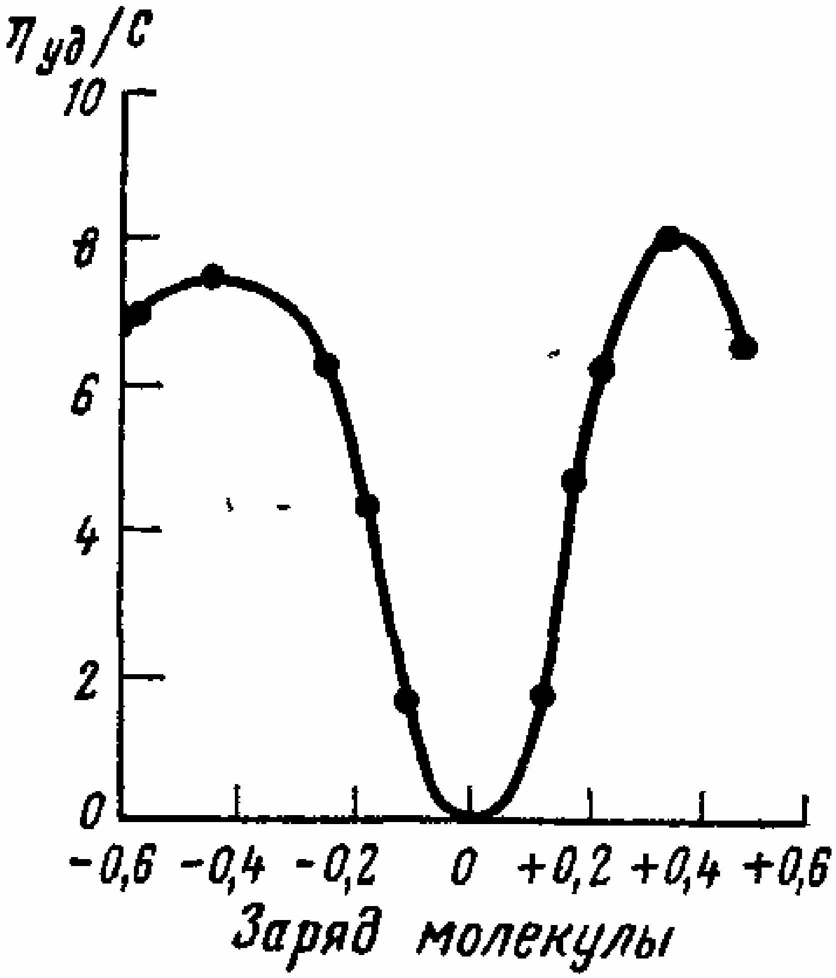
Вязкость растворов ПЭ. Полиэлектролитное набухание





Зависимость $\eta_{уд}/C$ от α для полиметакриловой кислоты

Изоэлектрическая точка



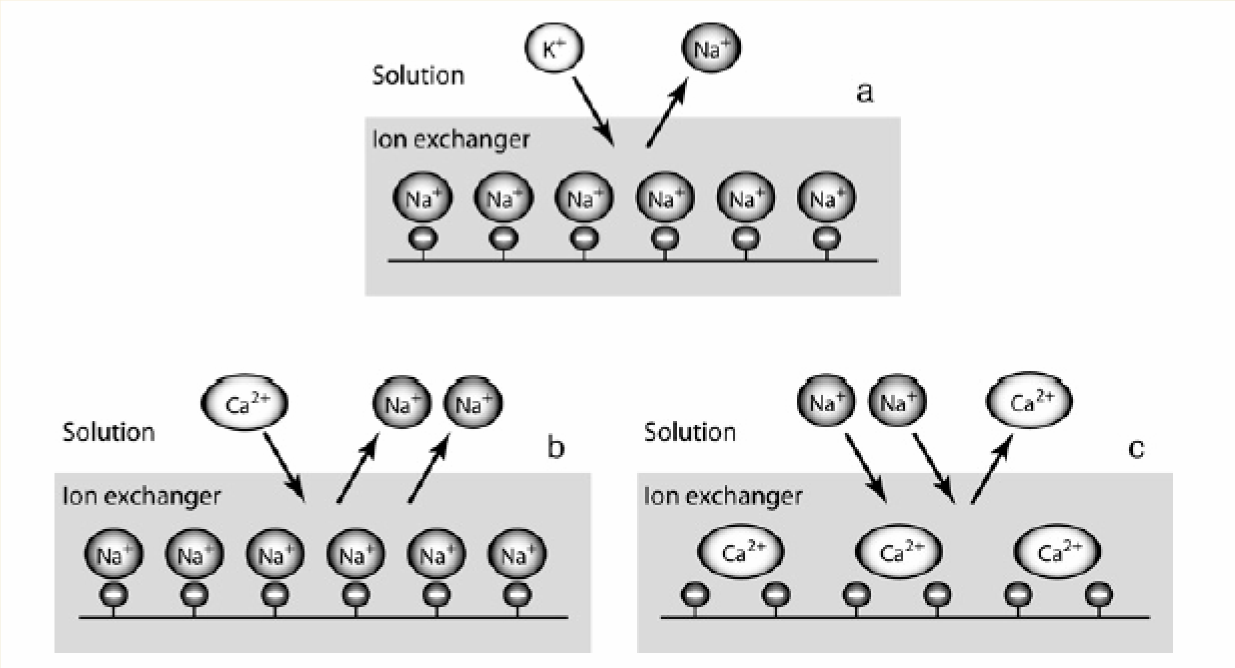
Зависимость $\eta_{уд}/C$ от заряда молекулы (pH среды) для полиамфолита

Ионный обмен, его эквивалентность

Виды ионообменной емкости

Методы определения

Применение


Solution
K^+
Na^+
a
Ion exchanger
Na^+ Na^+ Na^+ Na^+ Na^+ Na^+
Solution
Ca^{2+}
Na^+ Na^+
b
Ion exchanger
Na^+ Na^+ Na^+ Na^+ Na^+ Na^+
Solution
Na^+ Na^+
Ca^{2+}
c
Ion exchanger
Ca^{2+} Ca^{2+} Ca^{2+}

$$RSO_3^- H^+ + Na^+ + Cl^- \rightleftharpoons RSO_3^- Na^+ + H^+ + Cl^-$$

$$RNR_3^+ OH^- + Na^+ + Cl^- \rightleftharpoons RNR_3^+ Cl^- + Na^+ + OH^-$$

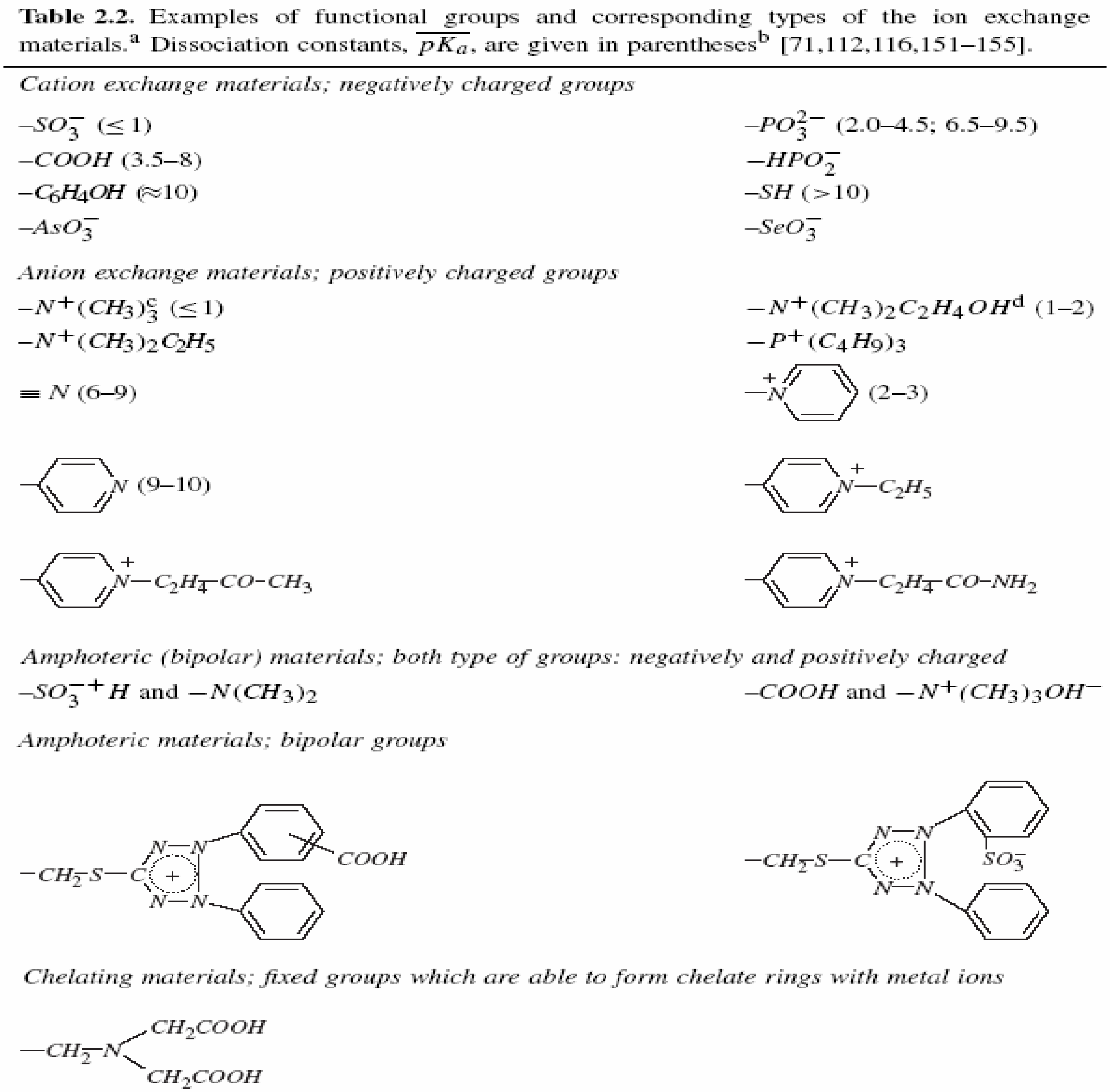


Table 2.2. Examples of functional groups and corresponding types of the ion exchange materials.[a] Dissociation constants, $\overline{pK_a}$, are given in parentheses[b] [71,112,116,151–155].

Cation exchange materials; negatively charged groups

$-SO_3^-$ (≤ 1)

$-COOH$ (3.5–8)

$-C_6H_4OH$ (≈ 10)

$-AsO_3^-$

$-PO_3^{2-}$ (2.0–4.5; 6.5–9.5)

$-HPO_2^-$

$-SH$ (>10)

$-SeO_3^-$

Anion exchange materials; positively charged groups

$-N^+(CH_3)_3^c$ (≤ 1)

$-N^+(CH_3)_2C_2H_5$

$\equiv N$ (6–9)

N (9–10)

$\overset{+}{N}-C_2H_4-CO-CH_3$

$-N^+(CH_3)_2C_2H_4OH^d$ (1–2)

$-P^+(C_4H_9)_3$

$-\overset{+}{N}$ (2–3)

$\overset{+}{N}-C_2H_5$

$\overset{+}{N}-C_2H_4-CO-NH_2$

Amphoteric (bipolar) materials; both type of groups: negatively and positively charged

$-SO_3^-{}^+H$ and $-N(CH_3)_2$

$-COOH$ and $-N^+(CH_3)_3OH^-$

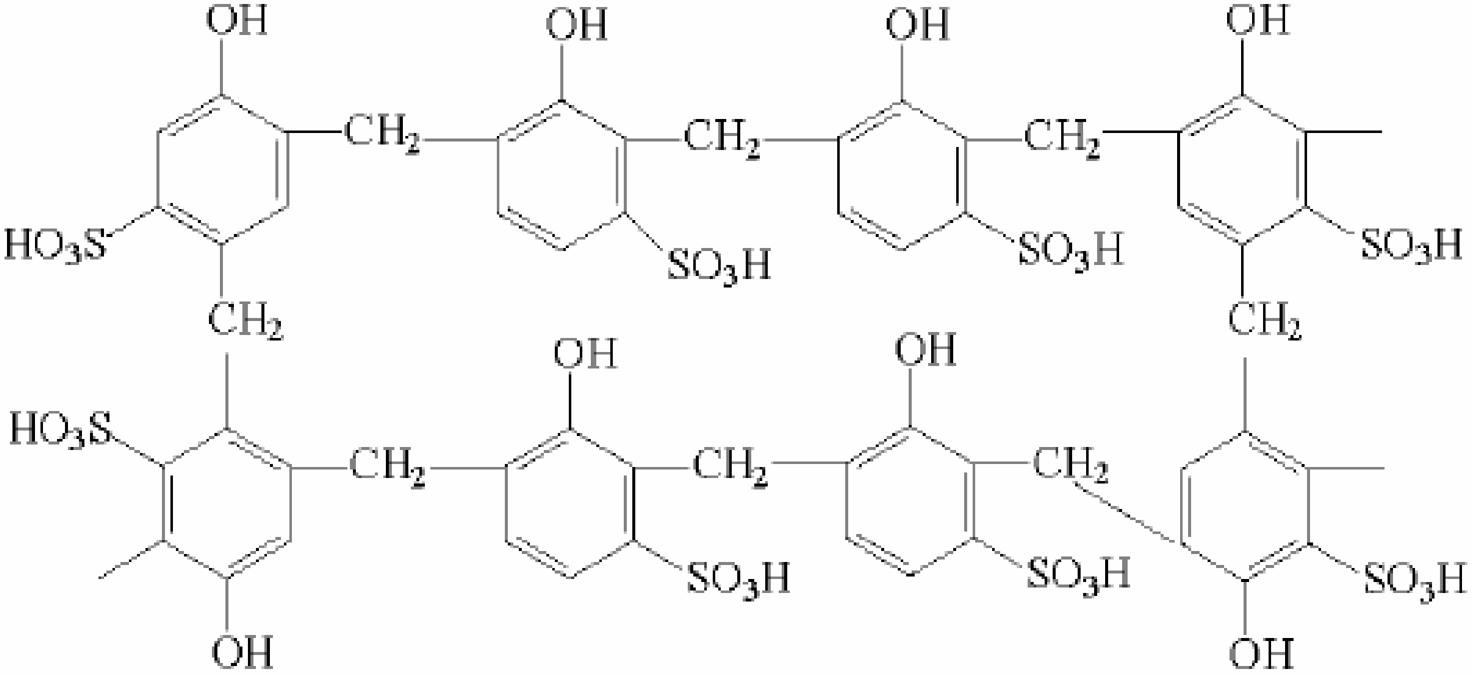
Amphoteric materials; bipolar groups

$-CH_2-S-C$, $N-N$, $N-N$, $+$, $COOH$

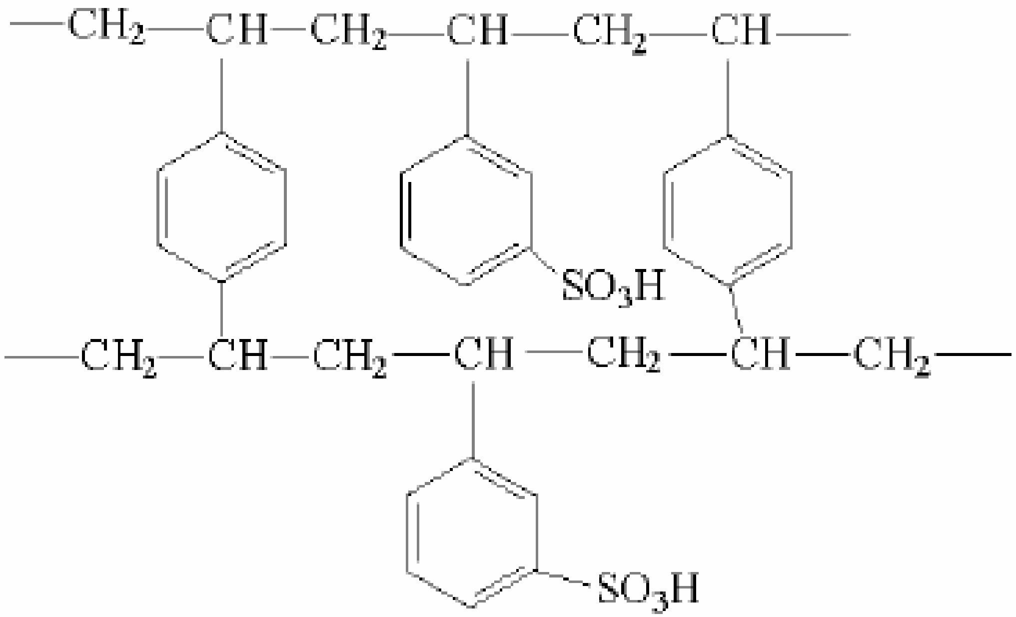
$-CH_2-S-C$, $N-N$, $N-N$, $+$, SO_3^-

Chelating materials; fixed groups which are able to form chelate rings with metal ions

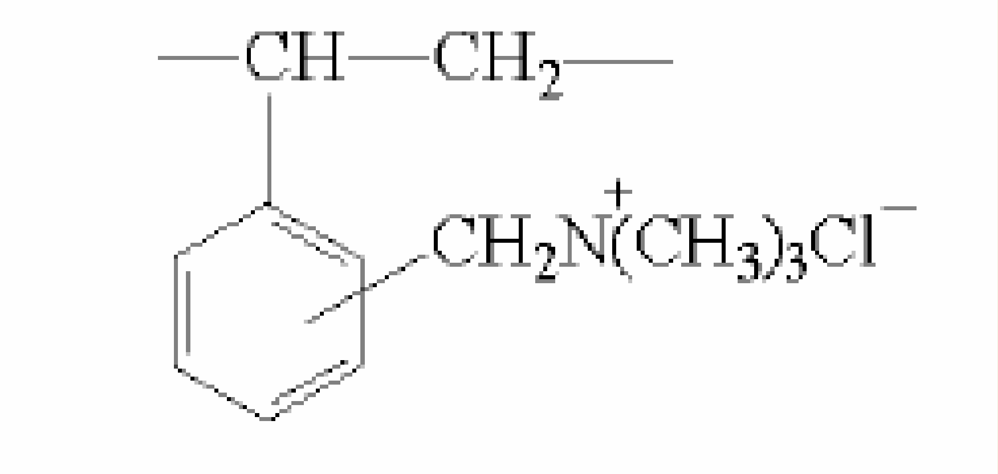
$-CH_2-N$, CH_2COOH, CH_2COOH



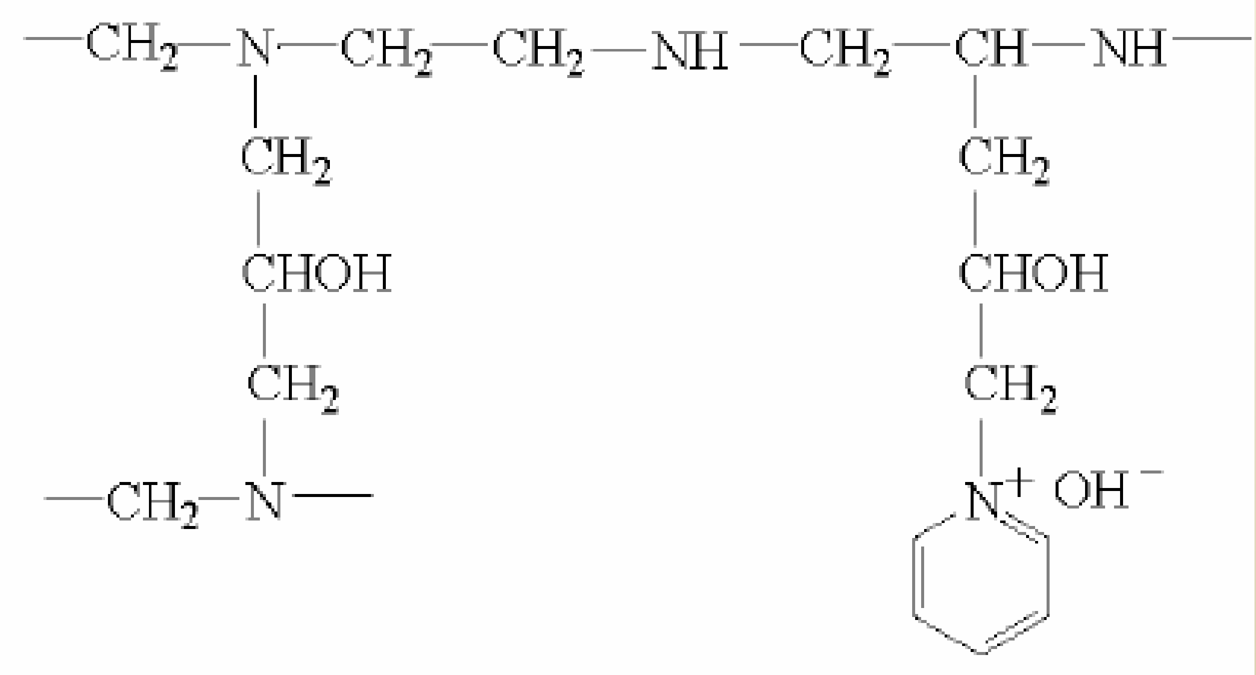
КУ−1



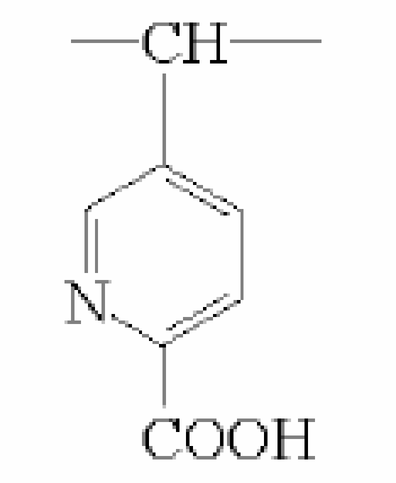
КУ −2



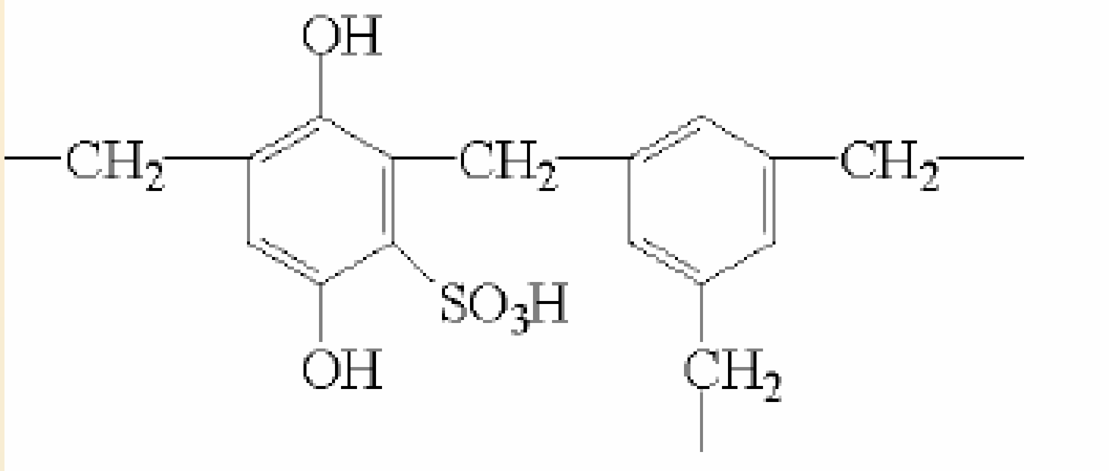
AB-17



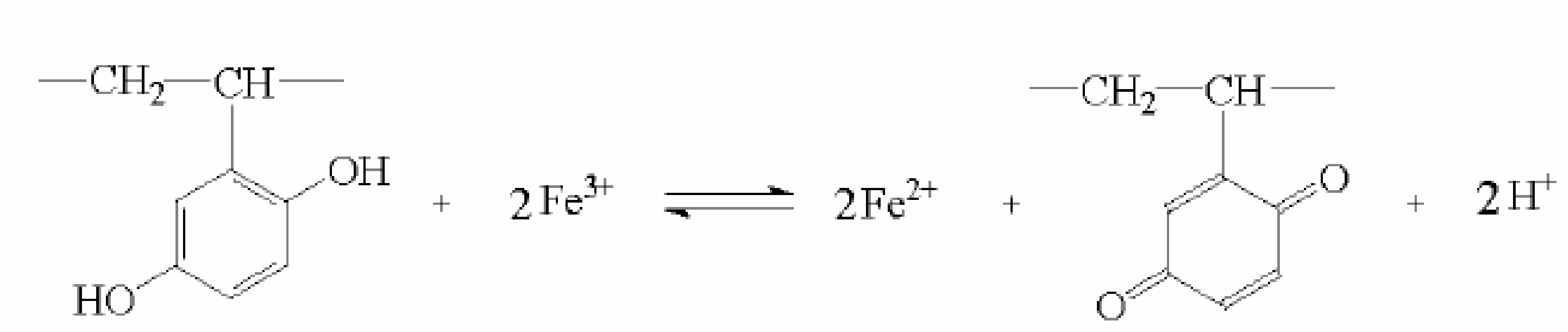
AB-16


CH
N
COOH

ВПК


OH
CH2
CH2
CH2
SO3H
OH
CH2

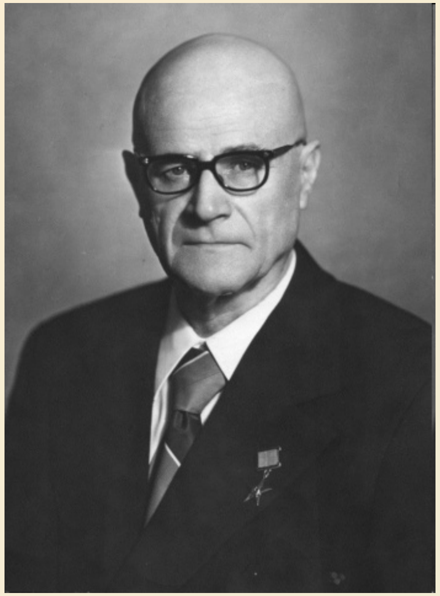
ЭО-7


CH2
CH
OH
HO
+
2 Fe3+
2Fe2+
+
CH2
CH
O
O
+
2 H+

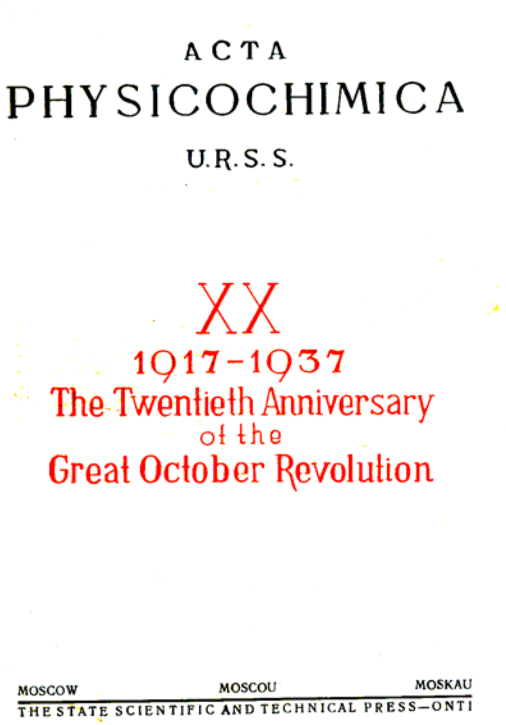
Уравнение Никольского

$$\mathrm{Na^+} + \overline{\mathrm{H^+}} \overset{K}{=} \overline{\mathrm{Na^+}} + \mathrm{H^+}$$

$$K = \frac{[\mathrm{Na^+}]\times[\overline{\mathrm{H^+}}]}{[\overline{\mathrm{Na^+}}]\times[\mathrm{H^+}]}$$



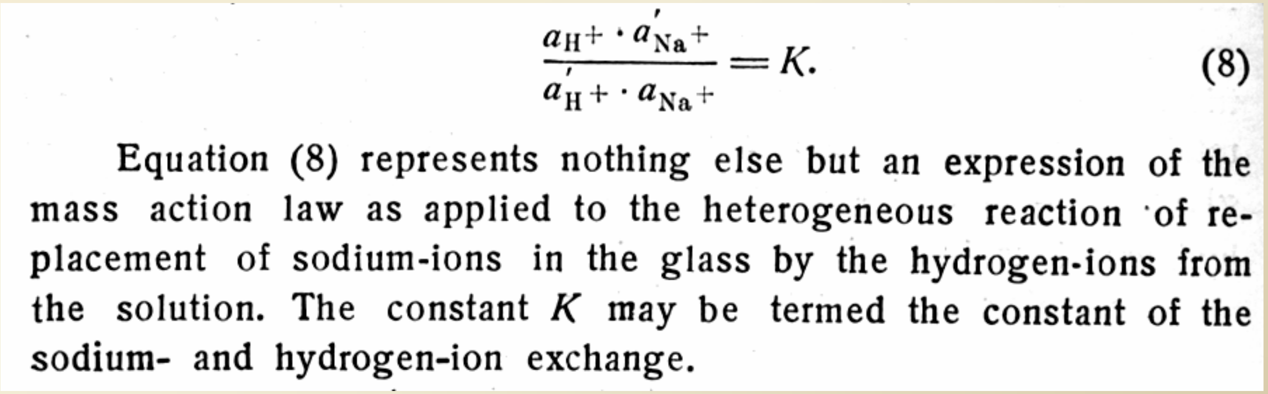
Б.П. Никольский, один из отцов советской плутониевой атомной боибы
Theory of Glass Electrode. I.
P. 597-610.



ACTA
PHYSICOCHIMICA
U.R.S.S.

XX
1917-1937
The Twentieth Anniversary
of the
Great October Revolution

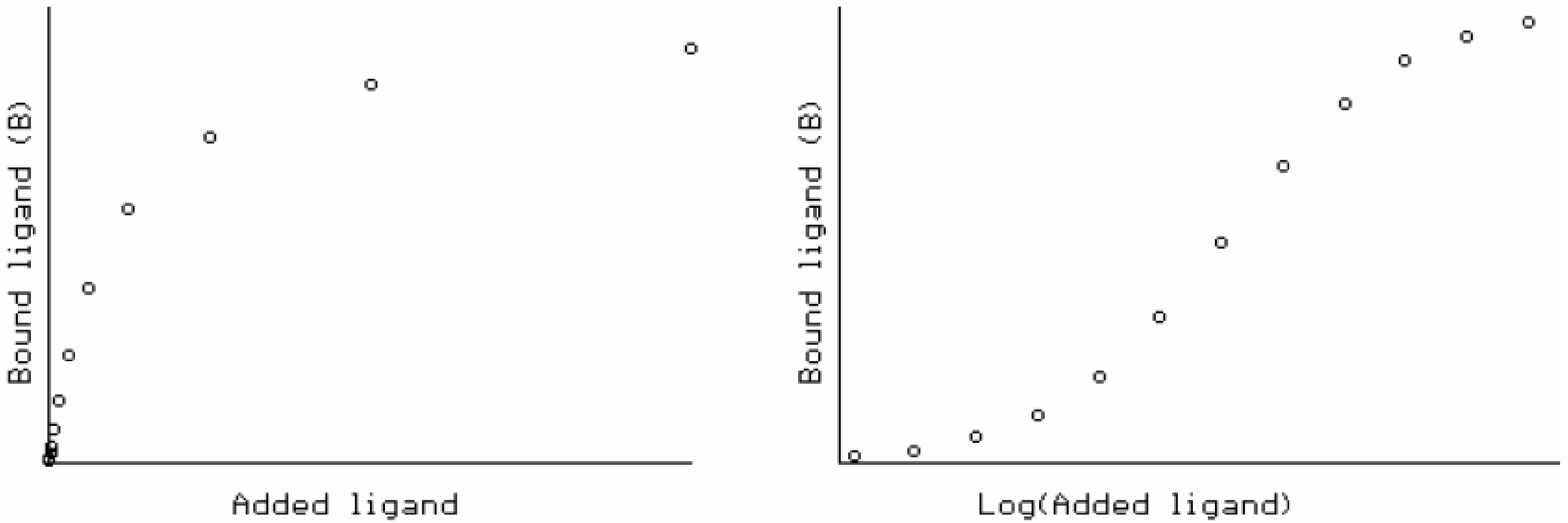
MOSCOW MOSCOU MOSKAU
THE STATE SCIENTIFIC AND TECHNICAL PRESS—ONTI



$$\frac{a_{\mathrm{H}^+}\cdot a'_{\mathrm{Na}^+}}{a'_{\mathrm{H}^+}\cdot a_{\mathrm{Na}^+}} = K. \qquad (8)$$

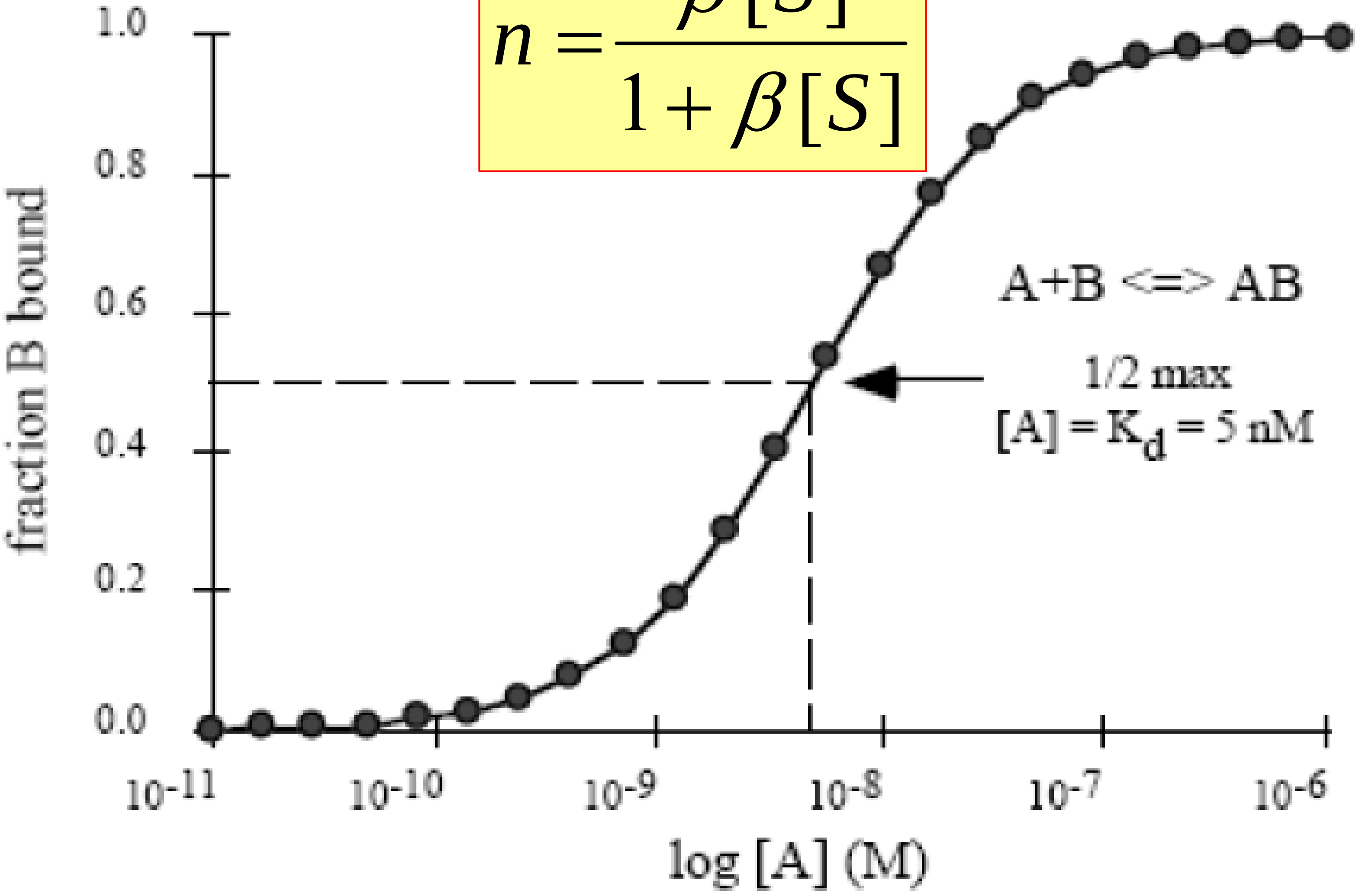
Equation (8) represents nothing else but an expression of the mass action law as applied to the heterogeneous reaction of replacement of sodium-ions in the glass by the hydrogen-ions from the solution. The constant K may be termed the constant of the sodium- and hydrogen-ion exchange.

Равновесия лиганд-рецептор. Эффекты кооперативности



$$S + \overline{Q} \overset{\beta}{=} \overline{SQ}$$

$$\bar{n} = \frac{\beta[S]}{1+\beta[S]}$$



$$S + \overline{Q} \overset{\beta}{=} \overline{SQ}$$

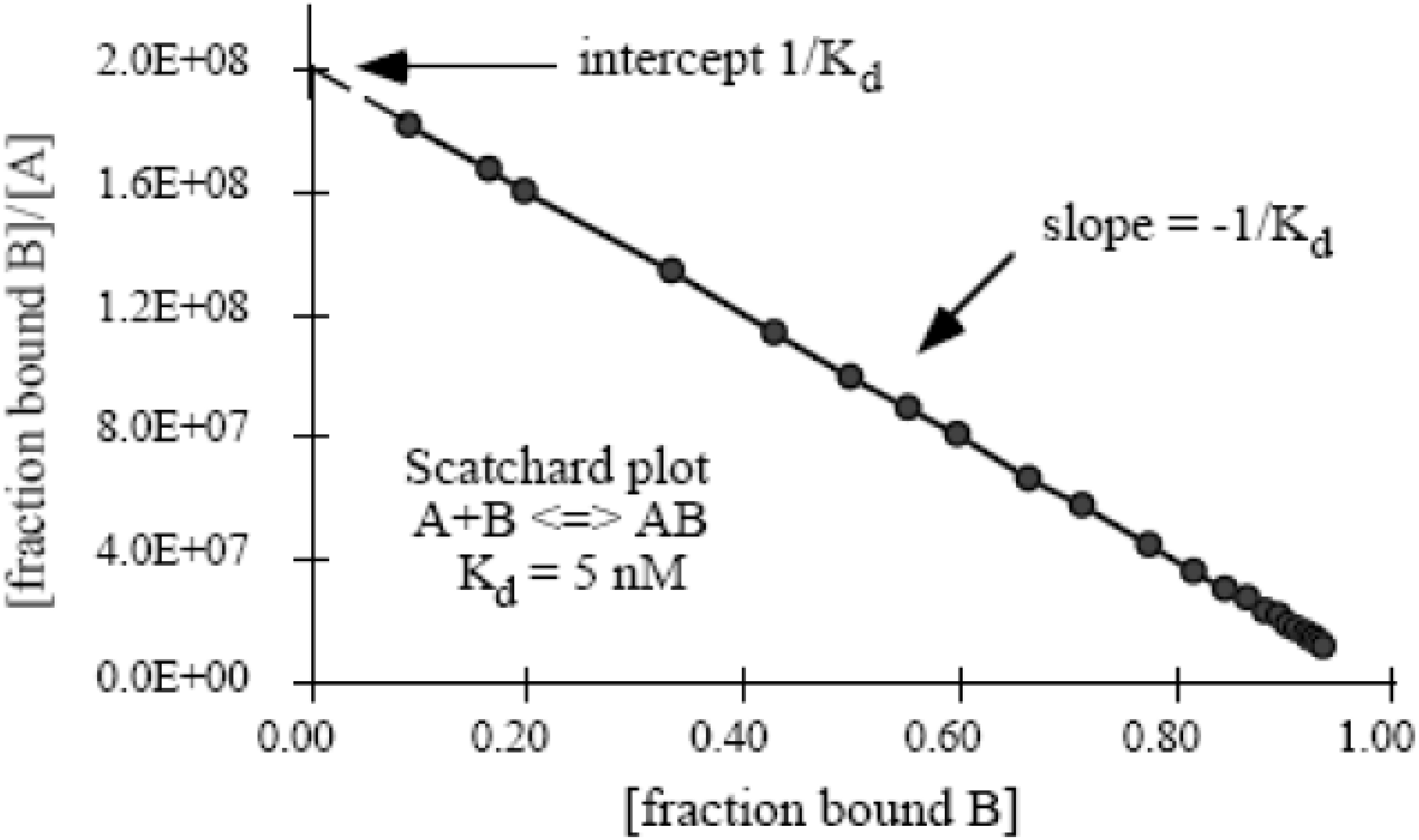
$$[\overline{SQ}] = t_Q \times \frac{\beta \cdot [S]}{1 + \beta \cdot [S]}$$

Уравнение Скэтчарда, 1949


George Scatchard

$$D = \frac{[\overline{SQ}]}{[S]} = t_Q \beta - \beta \times [\overline{SQ}]$$

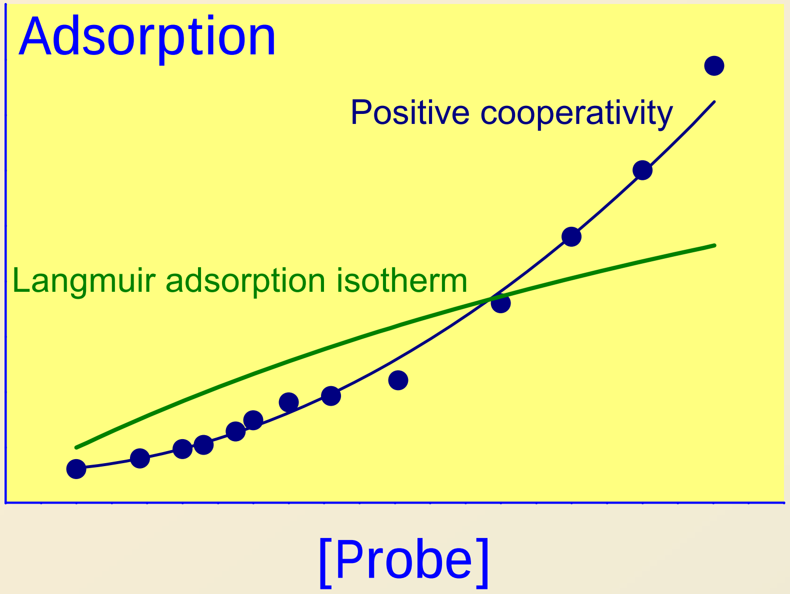
$$\frac{\theta}{[S]} = \beta - \beta \times [\overline{SQ}]$$

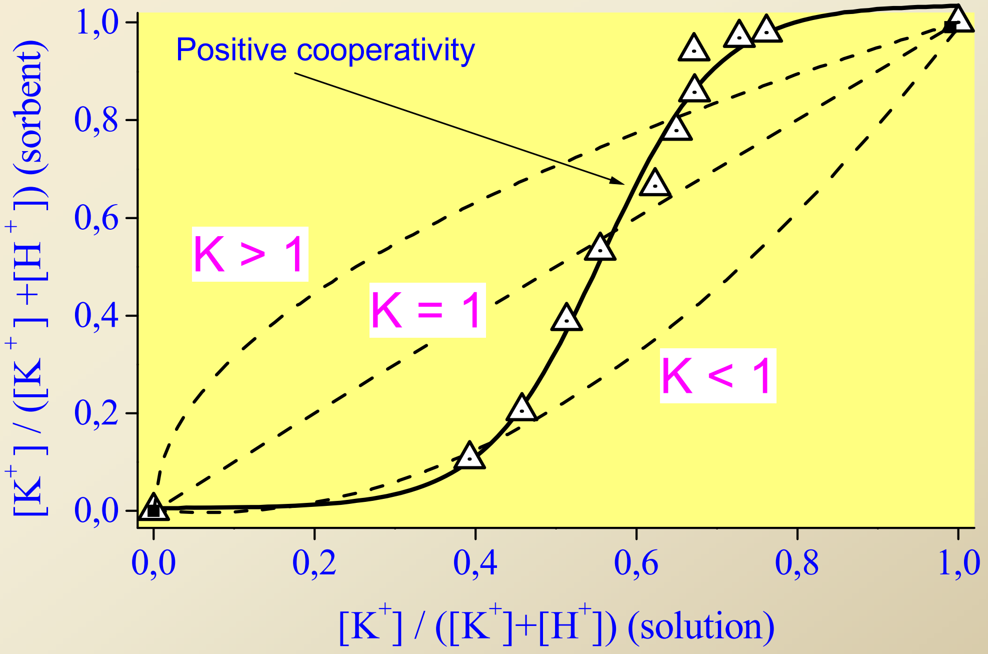

intercept $1/K_d$
slope = $-1/K_d$
Scatchard plot
A+B <=> AB
K_d = 5 nM
[fraction bound B]/[A]
2.0E+08
1.6E+08
1.2E+08
8.0E+07
4.0E+07
0.0E+00
0.00
0.20
0.40
0.60
0.80
1.00
[fraction bound B]

Эффекты кооперативности

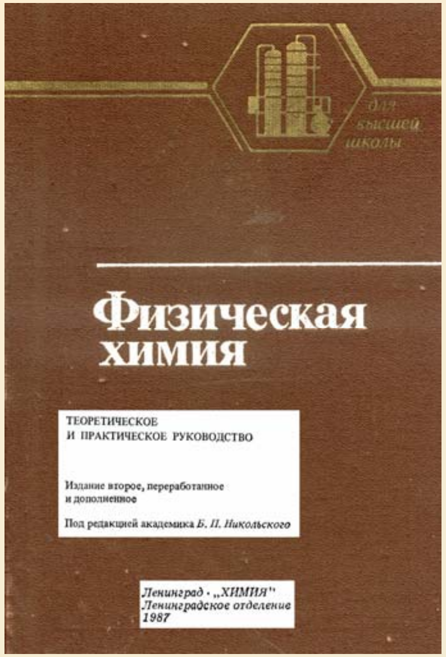
«Where **cooperativity** takes place the affinity of the ligand for the receptor site can be enhanced (**positive cooperativity**) or depressed (**negative cooperativity**) by previous occupation of sites»

Braibanti A., e.a. *React. Funct. Polymers*, 1998, **36**, P. 245.





Ion exchange



для высшей школы

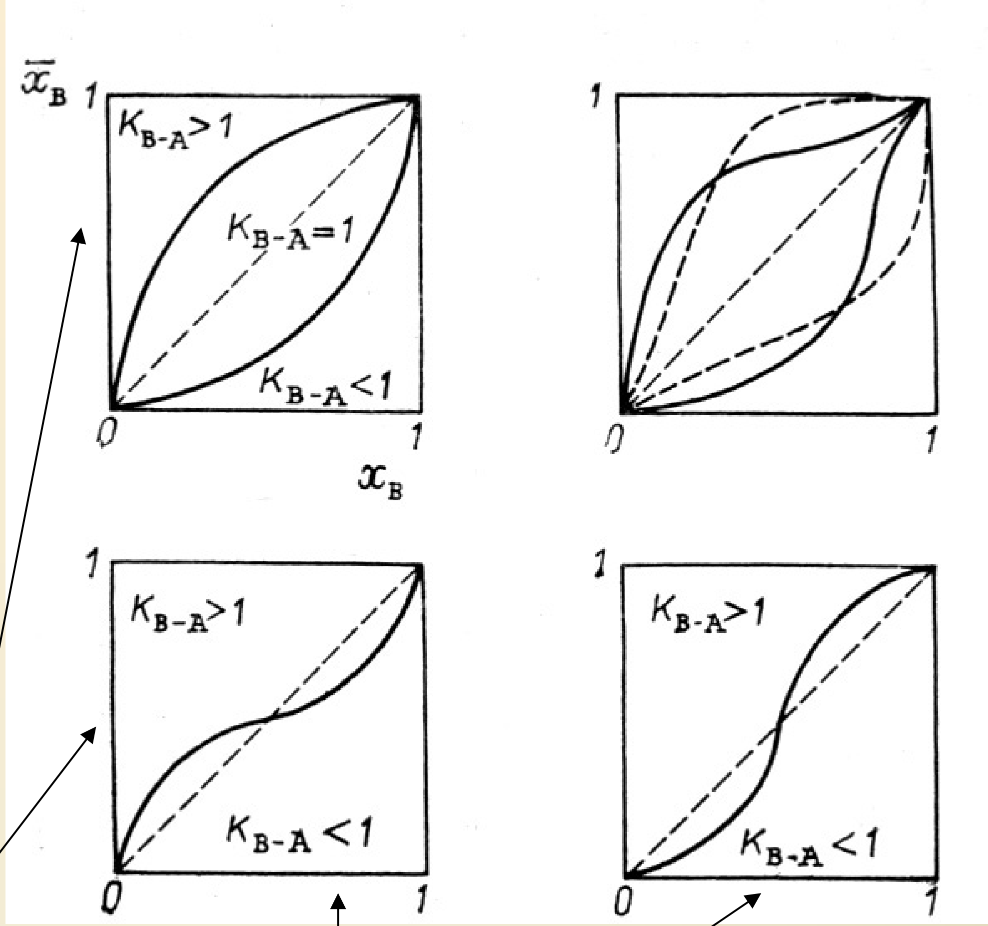
Физическая химия

ТЕОРЕТИЧЕСКОЕ
И ПРАКТИЧЕСКОЕ РУКОВОДСТВО

Издание второе, переработанное
и дополненное

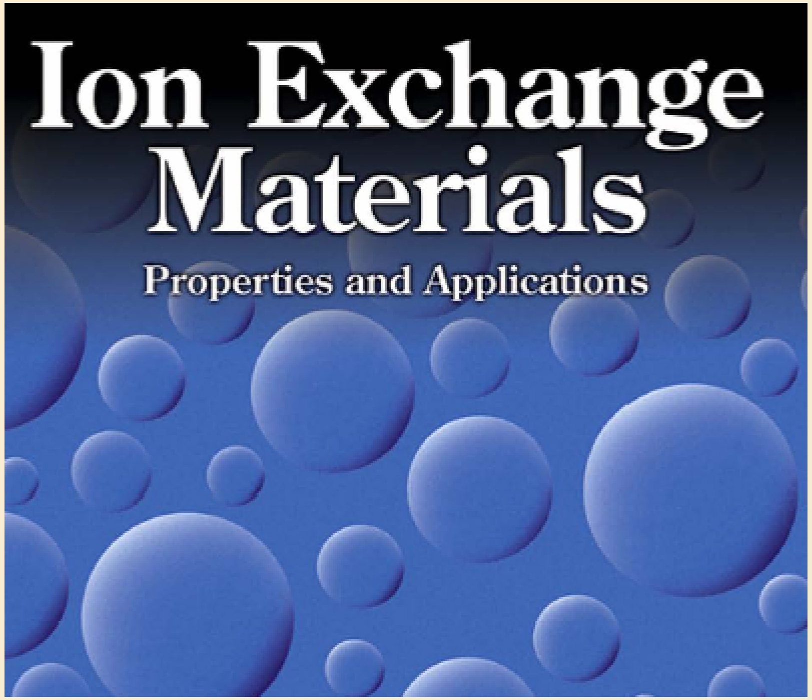
Под редакцией академика *Б. П. Никольского*

Ленинград · „ХИМИЯ"
Ленинградское отделение
1987



$$\alpha_{\overline{M}} = \frac{\overline{[M^+]}}{\overline{[M^+]}+\overline{[H^+]}} = \frac{\overline{[M^+]}}{\text{ion exchange capacity}}$$

$$\alpha_M = \frac{[M^+]}{[M^+]+[H^+]} = \frac{[M^+]}{\text{initial metal ion concentration}}$$



Ion Exchange Materials

Properties and Applications

Andrei A. Zagorodni
Royal Institute of Technology
Stockholm, Sweden

ELSEVIER

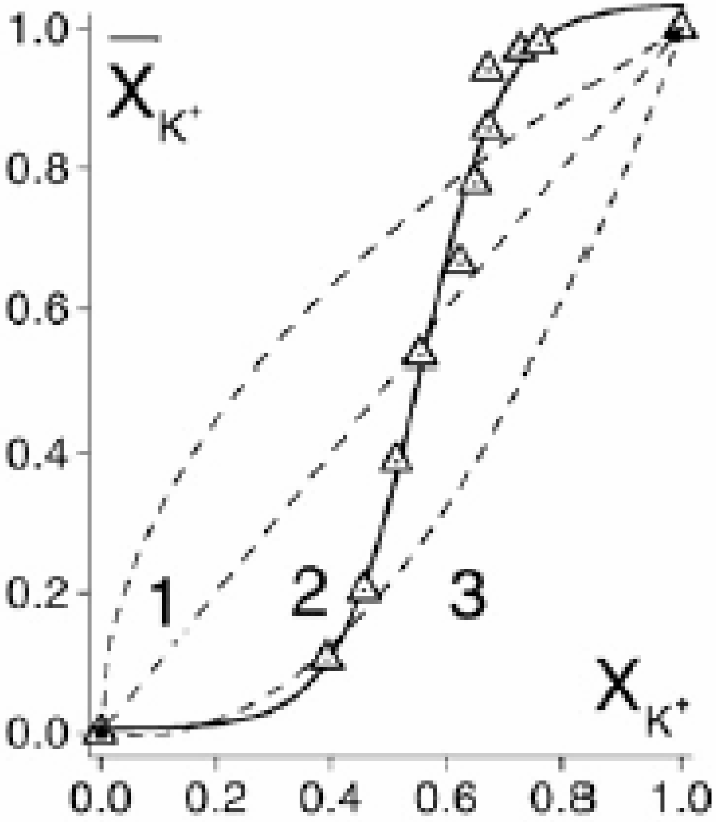


Fig. 8.2. Isotherm representing ion exchange of K^+ on the aluminium phosphate dispersed on a cellulose acetate fibre surface. Dashed lines correspond to the models of the ideal ion exchange with different preference of the material towards K^+: 1 – material preferentially takes up K^+; 2 – no preference is observed; 3 – material preferentially takes up the competing ion. Reprinted from *A. M. Lazarin, C. A. Borgo, Y. Gushikem, and Y. V. Kholin*, in: *Analytica Chimica Acta* [458] 2003, *Elsevier* ©.