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Ion Exchanger as Gibbs Canonical Assembly

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1. Introduction

Ion exchange is one of the fundamental reversible processes occurring in nature. Predicting of the equilibrium compositions for ion exchange presents of considerable practical and scientific interest.

If two types of ions i and j with the same charge are exchanged in equivalent ratios, the ion exchange process can be presented by the following equation

$$i + \overline{j} \rightleftarrows \overline{i} + j, \tag{1}$$

where the overbar indicates that a species belongs to the polymer phase.

The reversible process (1) is determined by the change of Gibbs energy, enthalpy, entropy and constant of thermodynamic equilibrium. The thermodynamic constant of ion exchange equilibrium (1) is described by the formula

$$K_{i/j} = \frac{\overline{a}_i \cdot a_j}{\overline{a}_j \cdot a_i}, \tag{2}$$

where a_i is the activity of component i.

The value of $K_{i/j}$ is calculated by the formula (Reichenberg, 1966)

$$\ln K_{i/j} = \int_0^1 \ln k^a_{i/j} d\overline{x}_i, \tag{3}$$

based on the choice of the ion exchanger in the monoionic forms as the standard states for components i and j in the polymer phase. In formula (3), $k^a_{i/j}$ is the corrected selectivity coefficient of ion exchange, which can be presented as

$$k^a_{i/j} = \frac{\overline{x}_i \cdot a_j}{\overline{x}_j \cdot a_i}, \tag{4}$$

where $\overline{x}_i$ is the mole fraction of i- component in the ion exchanger phase; for ion exchange from dilute solution of 1-1 electrolytes with constant ionic strength, if the solution corresponds to Debye-Huckel theory, the corrected selectivity coefficient, $k^a_{i/j}$, equal to

selectivity coefficient of ion exchange equilibrium, $k_{i/j}$; where $k_{i/j} = \frac{\bar{x}_i \cdot x_j}{\bar{x}_j \cdot x_i}$ and x_i is the mole fraction of i - component in the external solution.

Features of interaction of exchangeable ions with ionogenic groups can be reflect by the dependences of partial (differential) thermodynamic functions of process (1) from the content of exchangeable ions in polymer.

Partial Gibbs energy, $\Delta\bar{G}$, was calculated by the equation $\Delta\bar{G} = RT[(z_j - z_i) - \ln k^a_{i/j}]$ corresponding to (Gaines & Thomas, 1953).

Partial enthalpy of ion exchange was calculated as partial derivative of heat of ion exchange with respect to the quantity of sorbed ions, $\Delta\bar{H} = (\partial\Delta H / \partial\bar{x}_i)_T$.

For ion exchange in a multicomponent system containing *n* ions with the same charge, the phase composition is determined by solving a set of (n – 1) homogeneous equations for the selectivity coefficients of binary ion exchanges in conjunction with an equation of material balance (Tondeur & Klein, 1967). In addition, was postulated that the selectivity coefficients are constant in the entire range of compositions of the ion exchanger phase (Tondeur & Klein, 1967). A similar solution was obtained for an ion exchange complicated by the complexation (Al'tshuler et al., 1984).

In most cases, the selectivity coefficients of ion exchange are the functions of the ionic composition of the phases. The dependence of the selectivity coefficient from polymer composition was explained by an energetic inhomogeneity of the ion exchanger phase (Reichenberg, 1966). Thus, calculation results systematically deviate from experimental data (Soldatov & Bychkova, 1988). The known methods for calculating of ion exchanger phase compositions for multicomponent exchanges with consideration for the dependence of the selectivity coefficients on the compositions of the phases are applicable only within a limited region of the diagram of compositions (Tondeur & Klein, 1967). To extend region of the diagram of compositions correction coefficients were introduced (Soldatov & Bychkova, 1988). This provided satisfactory results only after several successive adjustments (Soldatov & Bychkova, 1988). How to determine the ion exchanger composition as a fraction of the structural conformers was discussed (Soldatov et al., 1994). Ion exchanger compositions for weakly acidic (Horst et al., 1990) and chelating ion exchangers (Horst et al., 1991) were calculated from the electrostatic potential by the Gouy-Chapman model, which is based on the Maxwell-Boltzmann distribution for an ideal gas. In this chapter we have shown, that it is possible in reality to calculate the phase compositions when the ion exchange with variable selectivity coefficients take a place from the multicomponent solutions if the ion exchanger represents Gibbs canonical assembly.

2. The theory. Ion exchanger as Gibbs canonical assembly

Consider an ion exchanger as the Gibbs canonical assembly. The Gibbs canonical distribution is

$$\rho = \exp\left(\frac{\Psi - \varepsilon}{\theta}\right), \tag{5}$$

where $\rho(\varepsilon)$ is the density of probability to find the phase having an energy ε; Ψ is a constant; θ is the modulus of distribution. If $\theta >> \psi - \varepsilon$, then ρ and ε are proportional:

$$\rho = 1 + (\psi - \varepsilon)/\theta\,. \tag{6}$$

For an ion exchanger containing two exchangeable ions $\Delta\bar{H}, \Delta\bar{G}, \ln k^{a}_{i/j}$ are continuous functions of energy, which vary along the ion exchange isotherm from $\Delta\bar{H}, \Delta\bar{G}, \ln k^{a}_{i/j}$ at $\bar{x}_i = 0$ to its values at $\bar{x}_i = 1$. In this case, the ion exchanger composition measured in mole fractions of the i-component corresponds to the probability density for the individual phases at statistical equilibrium. In other words, for a binary ion exchange, the canonical energy distribution results in a linear dependences both of the differential enthalpy and of differential Gibbs energy (or the logarithm of the corrected selectivity coefficient) of ion exchange from the mole fraction of counterions in the ion exchanger phase. For binary ion exchange systems, the relation between ρ and ε coincides with formulas (7), (8)

$$\Delta\bar{H} = a + b\bar{x}_i, \tag{7}$$

$$\Delta\bar{G} = c + g\bar{x}_i, \quad \text{or} \quad \ln k^{a}_{i/j} = A_{i/j} + B_{i/j}\bar{x}_i, \tag{8}$$

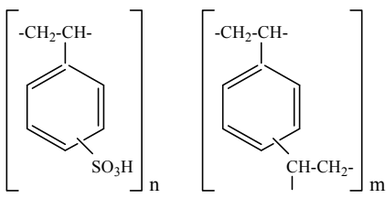
where a, b, c, g, $A_{i/j}; B_{i/j}$ are constants. Really, experimental results show, that at compositions $0 \le \bar{x}_i \le 1$, the $\Delta\bar{H}(\bar{x}_i)$, $\Delta\bar{G}(\bar{x}_i)$, $k^{a}_{i/j}(\bar{x}_i)$ dependences can be approximated by the linear equations (Al'tshuler et al., 1984), (Al'tshuler & Shkurenko, 1990). Apparently, both the partial enthalpy and partial Gibbs free energy of the individual components additively contribute to the total energy of ion exchange process (1). For this reason, we examined the ion exchanger phase as a system consisting of non-interacting elements (for example, electrically neutral resinates) within the region of validity of (5)-(8) formulas. This is also true for a multicomponent system consisting of non-interacting parts, i.e., a system described by a comprehensive canonical assembly.

3. Results and discussion

3.1 Ion exchange from the solutions containing two electrolytes

According to experimental data $\Delta\bar{H}(\bar{x}_i)$, $\ln k^{a}_{i/j}(\bar{x}_i)$ linear dependences are observed in next exchangers: strong - acid cross – linked polystyrene sulfonate cation exchangers (Boyd & Larson, 1967), (Soldatov et al., 1976), (Soldatov & Bychkova, 1988); cross-linked polystyrene phosphonic acid cation exchangers (Becker et al., 1966); zeolities (Al'tshuler & Shkurenko, 1990), calixarene-containing ion exchangers and strong - base anion exchangers. Short characteristics of ion exchangers and some of the specified dependences are summarized below.

Strong - acid cross – linked polystyrene sulfonate cation exchangers. Polystyrene sulfonate cation exchanger cross-linked with divinylbenzene (DVB). An ion exchanger contains only one type of ionogenic groups – sulfonic acid groups (SO_3H). The structure of repeating unit of cross-linked polystyrene sulfonate cation exchanger (1) is represented below.



1

The ion exchanger contains nonequivalence ion exchange sites (Reichenberg, 1966) in spite of presence of only one type of ionogenic groups. The attempt to explain energy nonequivalence of ion exchange sites by the structure differences in cross-linking agent was made (Soldatov et al., 1994). The dependences (Soldatov et al. 1976) of corrected selectivity coefficients of ion exchange from mole fraction of sorbed potassium cations in variously cross-linked strong-acid sulfonate exchanger (KRS) were shown in fig.1.

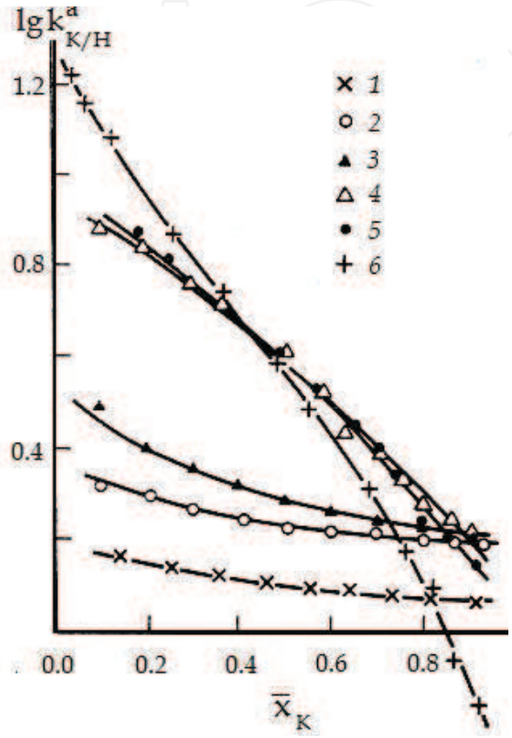


Fig. 1. Dependence of $\lg k^{a}_{K/H}$ from $\bar{x}_K$ of $H^+ \rightarrow K^+$ ion exchange in variously cross-linked strong-acid sulfonate exchanger (KRS). Nominal DVB, % : (*1*)-1, (*2*)-4, (*3*)-8, (*4*)-12, (*5*)-16, (*6*)-25. (Soldatov et al. 1976)

As we seen from fig.1, the energy nonequivalence of ion exchange sites of polymer rises with increasing of quantity of cross-linking agent. In that case any can to say that presented dependences (fig. 1) are described by the linear equations taking into account experimental errors (Soldatov & Suchover, 1968).

$\Delta\bar{H}(\bar{x}_i)$, $\ln k^{a}_{i/j}(\bar{x}_i)$ dependences of $Li^+ \rightarrow Cs^+$ ion exchange in middle-acid exchangers containing phosphonic acid groups (Becker et al., 1966) are shown in fig.2. Two types of phosphonic acid exchangers were used: a polystyrene-divinylbenzene cross-linked (5.5% DVB) preparation, $-C_6H_4-PO(OH)_2$, in which the phosphonate groups were attached to a benzene nucleus, and a polystyrene-divinylbenzene cross-linked (5.5% DVB) methylene phosphonic acid exchanger, $-C_6H_4-CH_2-PO(OH)_2$, in which the phosphonate was separated from the benzene ring by a methylene group.

The logarithms of selectivity coefficients are linear functions from Li^+ mole fraction in both phosphonic acid exchangers as can be seen from the fig. 2*a* and was noted (Becker et al., 1966). The measured heats of partial exchange are shown in fig. 2*b* by a chord for each experiment. The curves for the differential heat of exchange $\Delta\bar{H} = (\partial\Delta H / \partial\bar{x}_{Li})_T$ are the

best least-squares fit through the midpoints of the chords. $\Delta\overline{H}$ are linear with respect to $\overline{x}_{Li}$ for both the nuclear phosphonic acid exchanger and ethylene phosphonic acid exchanger.

The energy nonequivalence of ion exchange sites was intensified on cation exchanger with methylene phosphonic acid groups. It was reflected in an evolution of $\Delta\overline{H}$ and $\lg k_{Li/Cs}$ of exchangers at $\overline{x}_{Li} = 0.0$ and $\overline{x}_{Li} = 1.0$. The magnitudes of partial enthalpy are in the range from 0 to 2000 cal per mole on the polymer in which the phosphonate groups were attached to a benzene nucleus. Partial enthalpy is increased from -500 to 3500 cal per mole on polystyrene-divinylbenzene cross-linked (5.5% DVB) methylene phosphonic acid exchanger.

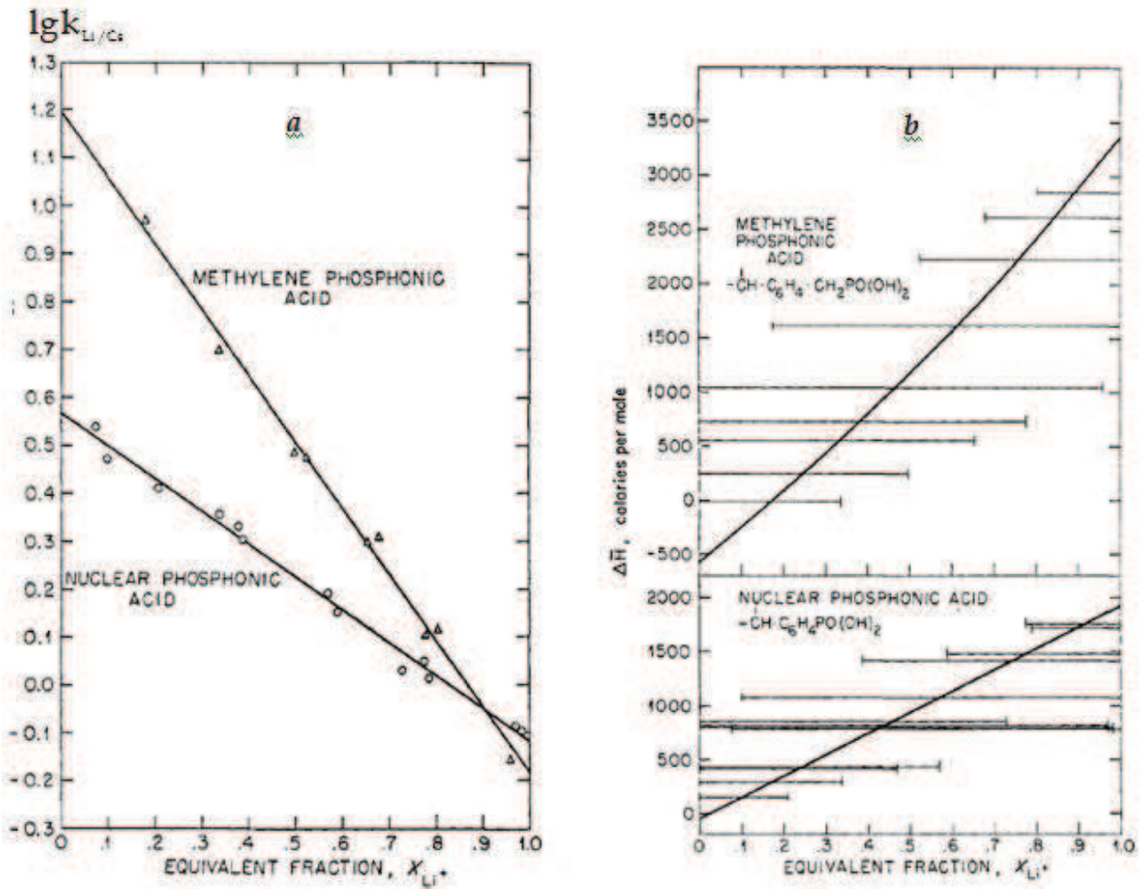
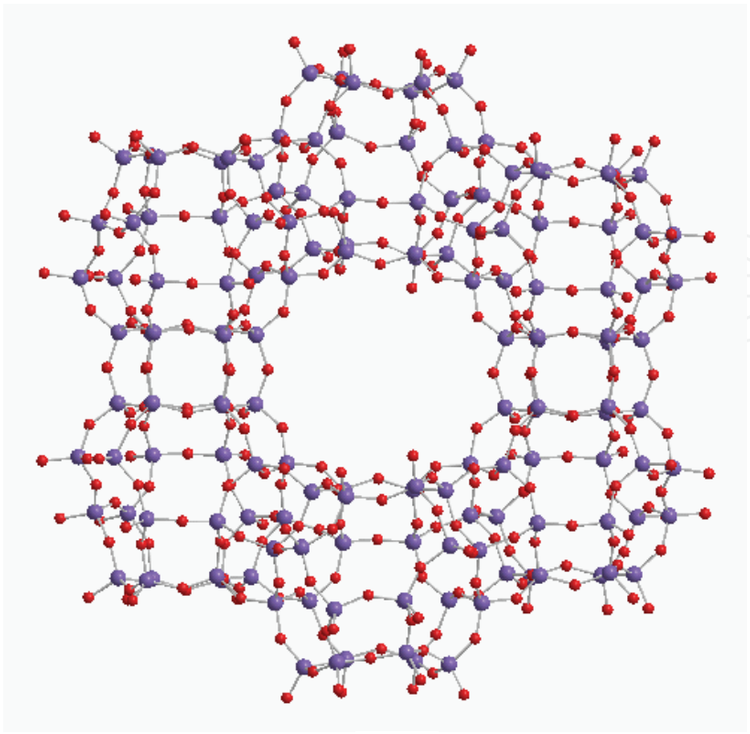


Fig. 2. Ion exchange of $Cs^+ \rightarrow Li^+$ in nominal 5.5% DVB cross-linked phosphonic acid ion exchangers: *a* –logarithmic function of selectivity coefficients, $\lg k_{Li/Cs}$ vs $\overline{x}_{Li}$; *b*-partial heat of exchange, $\Delta\overline{H}$ vs $\overline{x}_{Li}$ (Becker et al., 1966)

Zeolites (crystalline aluminium silicates) are weakly-acid cation exchangers. Particularity of ion exchange properties of zeolites is defined by crystal lattice structure and exchange cations distribution on the different position of the channels and cavities. In fig. 3 is shown a typical structure of zeolite repeating unit (2), presented in the templates of program Chem3D Ultra 8.0.



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Fig. 3. Repeating unit of zeolite

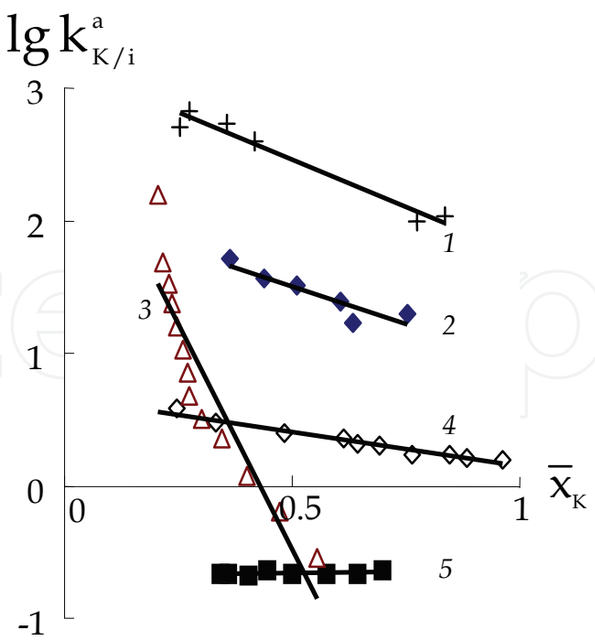


Fig. 4. Cation exchange in the natural heulandite (Al'tshuler & Shkurenko, 1990). $\lg k^{a}_{K/Cat}$ vs $\bar{x}_K$. Cat: (*1*)-Li^+; (*2*)-Na^+; (*3*)-Rb^+; (*4*)-NH_4^+; (*5*)-Cs^+

The ion exchange thermodynamic functions in the heulandite – binary electrolyte solutions system were defined (Al'tshuler & Shkurenko, 1990). Natural heulandite (zeolite Sr-R), deposit of Kemerovo region, Russia. Idealized composition of elementary cell is $Ca_4[(AlO_2)_8(SiO_2)_{28}]\cdot 24H_2O$. Two – dimensional channel system was formed by rings, consisting from 8- and 10- members. Sizes of windows are: 4.0×5.5 Å , 4.1×4.7 Å , 4.4×7.2 Å (Breck, 1974). Cations of alkali metals and alkaline earth metals are the mobile exchangeable ions. The total ion exchange capacity of natural heulandite from Kemerovo region is 2.2 milliequivalents per gram of ion exchanger (Al'tshuler & Shkurenko, 1990). The isotherms of binary $Cat^+ \rightarrow K^+$ ion exchanges on natural heulandite are shown at the fig.4.

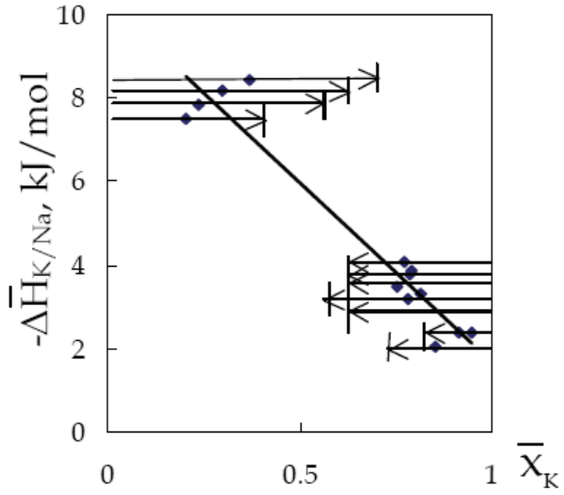
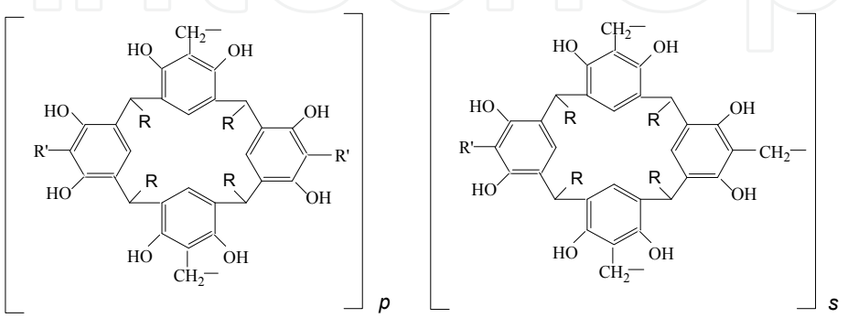


Fig. 5. Cation exchange of $Na^+ \rightarrow K^+$ in the natural heulandite (Al'tshuler & Shkurenko, 1990). $\Delta\bar{H}$ vs $\bar{x}_K$. Arrows reflect the change of heulandite composition

The dependence of differential enthalpy ($\Delta\bar{H}$) of $Na^+ \rightarrow K^+$ ion exchange from counterion composition in heulandite is shown in fig. 5. It is seen (fig. 4, fig. 5) partial thermodynamic functions of cation exchange linearly depend from counterion composition. The linear correlation coefficients are high, for example, its value equals to 0,97 for $\Delta\bar{H}(\bar{x}_i)$ function. The slope angle of the line depends on the energy nonequivalence of ion exchange sites.

Calixarenecontaining cationexchangers (3) have a common structure of polymer repeating unit



3a: R=CH_3, R'=H;
3b: R=CH_3, R'=CH(OH)Fur;
3c: R=C_6H_4–$PO(OH)_2$, R'=H;
3d: R=C_6H_4–SO_3H, R'=H

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The experimental differential thermodynamic functions of ion exchange from aqueous solutions on weakly–acid cation exchangers 3a, 3b and strong–acid sulfonate cation exchanger 3d are shown in fig. 6-fig. 9.

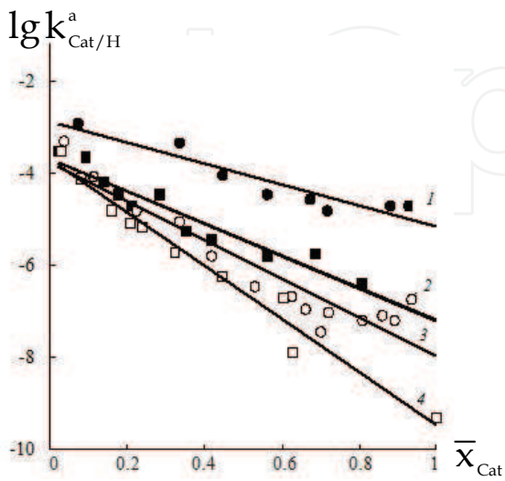


Fig. 6. Corrected selectivity coefficients of $H^+ \rightarrow NH_4^+$ ion exchange at 293 K in weakly – acid calixarenecontaining cation exchangers: (*1*) - in 3b, (*2*) - in 3a; $H^+ \rightarrow Na^+$ ion exchange: (*3*) - in 3b, (*4*) – in 3a (Al'tshuler et al., 2004)

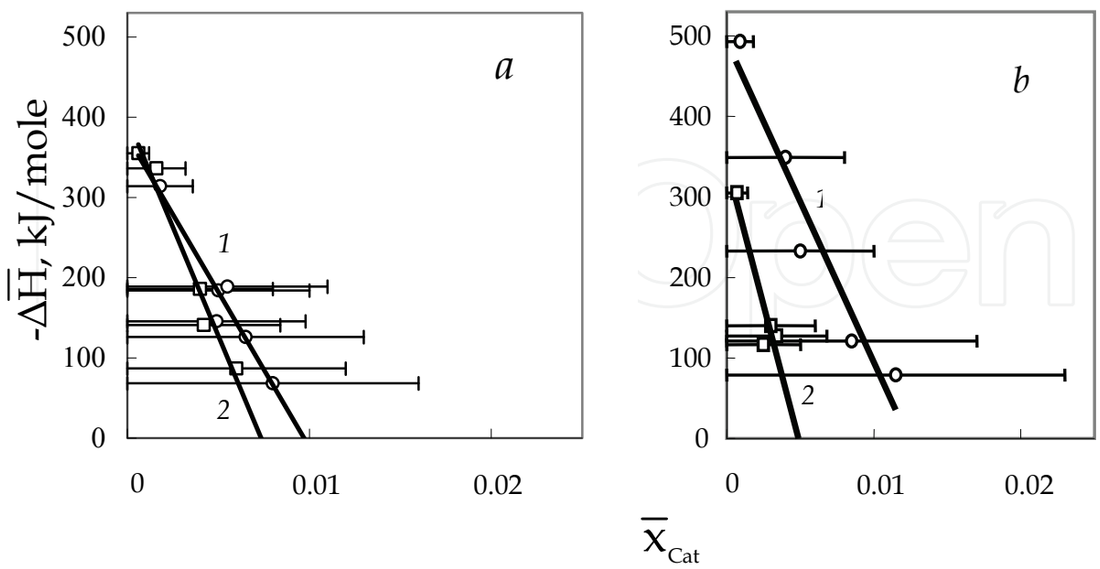


Fig. 7. Partial heat of $H^+ \rightarrow NH_4^+$ (*1*), $H^+ \rightarrow Na^+$ (*2*) cation exchange at 298 K in weakly – acid calixarenecontaining cation exchangers: (*a*) – in 3a, (*b*) – in 3b (Al'tshuler et al., 2004)

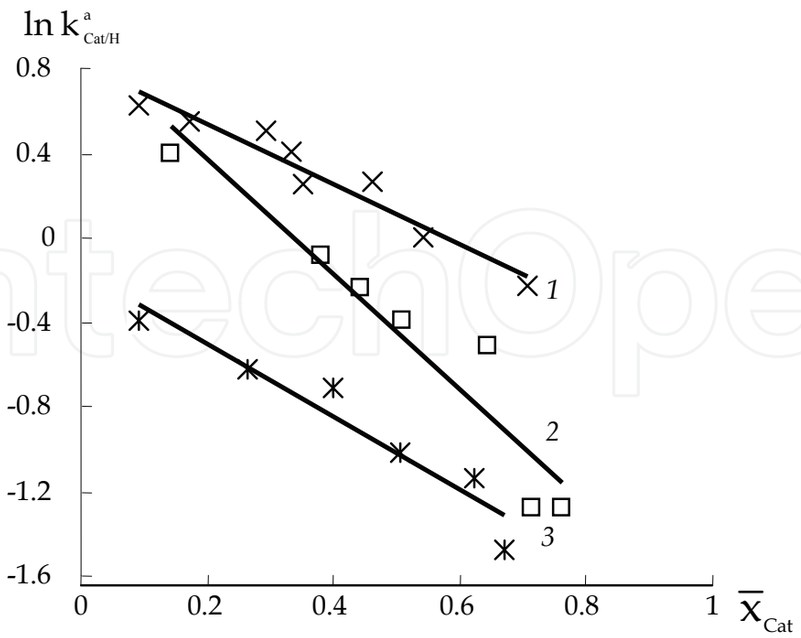


Fig. 8. Dependence of $\ln k^{a}_{Cat/H}$ from $\bar{x}_{Cat}$ of ion exchanges: (*1*) $H^+ \rightarrow Ag^+$, (*2*) $H^+ \rightarrow Na^+$, (*3*) $H^+ \rightarrow Li^+$ in strong – acid sulfonate cation exchanger 3d based on cis-tetraphenylcalix[4]-resorcinarene at 293 K (Al'tshuler et al., 2008

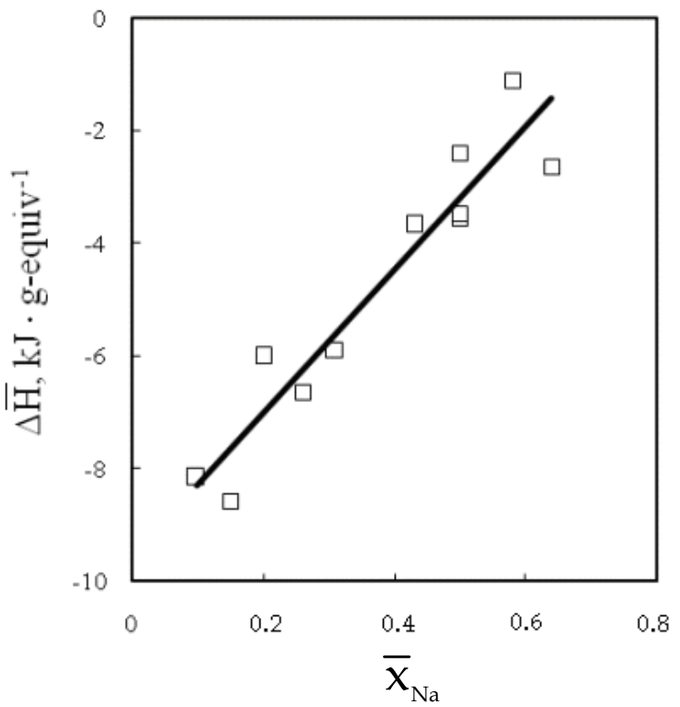


Fig. 9. Partial heat of $H^+ \rightarrow Na^+$ ion exchange in strong – acid sulfonate cation exchanger 3d based on cis-tetra-phenylcalix[4]resorcinarene, $\Delta\bar{H}$ vs $\bar{x}_{Na}$ (Al'tshuler et al., 2008)

The dependences of $\ln k^{a}_{Cat/H}$ vs $\bar{x}_{Cat}$ in the cation exchangers 3a-3d are shown in table 1.

Polymer	Cat	$\ln k^{a}_{Cat/H}$ ($\bar{x}_{Cat}$)	linear correlation coefficients
3a	Na^+	$\ln k^{a}_{Na/H} = -8.36 - 12.4\bar{x}_{Na}$	-0.96
3a	NH_4^+	$\ln k^{a}_{NH_4/H} = -8.12 - 7.99\bar{x}_{NH_4}$	-0.96
3b	Na^+	$\ln k^{a}_{Na/H} = -8.70 - 9.60\bar{x}_{Na}$	-0.94
3b	NH_4^+	$\ln k^{a}_{NH_4/H} = -5.96 - 5.98\bar{x}_{NH_4}$	-0.94
3c	K^+	$\ln k^{a}_{K/H} = -2.33 - 5.96\bar{x}_{K}$	–0.98
3d	Li^+	$\ln k^{a}_{Li/H} = -0.16 - 1.72\bar{x}_{Li}$	–0.99
3d	Na^+	$\ln k^{a}_{Na/H} = 0.91 - 2.73\bar{x}_{Na}$	–0.95
3d	Ag^+	$\ln k^{a}_{Ag/H} = 0.82 - 1.43\bar{x}_{Ag}$	–0.96

Table 1. Dependency of $\ln k^{a}_{Cat/H}$ vs $\bar{x}_{Cat}$ in calixarenecontaining cation exchangers

From the data about $\ln k^{a}_{i/j}(\bar{x}_i)$ and $\Delta\bar{H}(\bar{x}_i)$ linear dependences we can make a intermediate conclusion that investigated polymers 3a-3d in the form of single charge metal cations are Gibbs canonical assemblies in all intervals of counterion compositions.

From the experimental data (Soldatov& Bychkova, 1988) for Dowex-50W×12 strong - acid cation exchanger the following functions for independent binary exchanges were obtained:

$$\ln k^{a}_{NH_4^+/H^+} = 1.213 - 0.937\bar{x}_{NH_4^+}, \quad (9)$$

$$\ln k^{a}_{NH_4^+/Na^+} = 0.428 - 0.359\bar{x}_{NH_4^+}. \quad (10)$$

Strong-base anion exchangers. The ion exchange equilibria on strong-base anion exchanger of the Dowex-1 type were experimentally studied in aqueous solutions containing two types of anions: salicylate (Sal^-) – hydroxide (OH^-); nitrate (NO_3^-) – hydroxide; chloride (Cl^-) - hydroxide. The Dowex-1 is polystyrene cross-linked with divinylbenzene molecular network which carries the benzyltrimethylammonium ionogenic groups ($-CH_2C_6H_4-N^+(CH_3)_3$). The experimental data about the equilibrium phase composition for the binary ion exchanges on anion exchanger (Dowex-1) are presented here (fig. 10).

The equilibria for the binary exchanges on Dowex-1 can be described by the linear equations

$$\ln k^{a}_{Sal^-/OH^-} = 6.88 - 2.18\bar{x}_{Sal^-}, \quad (11)$$

$$\ln k^{a}_{NO_3^-/OH^-} = 4.815 - 1.17\bar{x}_{NO_3^-}, \quad (12)$$

$$\ln k^{a}_{Cl^-/OH^-} = 3.00 - 0.872\bar{x}_{Cl^-}. \quad (13)$$

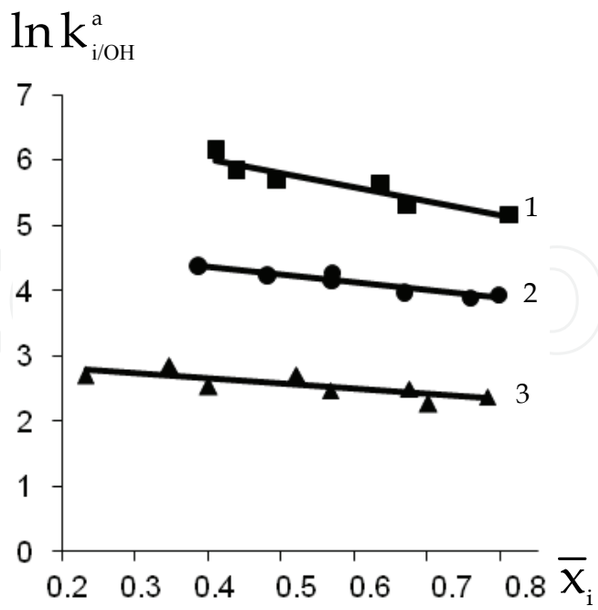


Fig. 10. Dependence of corrected selectivity coefficients of binary exchanges in Dowex-1 anion exchanger from mole fraction, $\bar{x}_i$, of sorbed anion: (*1*) - Sal^-, (*2*) - NO_3^-, (*3*) - Cl^-

3.2 Ion exchange from multicomponent solutions

For a multicomponent ion exchange the function $\ln k^a_{i/j}(\bar{x}_i)$ depends on the position of i and j ions in the series of selectivity. For any arbitrary point of interval of composition the following condition must be fulfilled

$$k^a_{i/k} = k^a_{i/j} / k^a_{k/j}. \tag{14}$$

Using the concept of reversible step reactions (Bjerrum, 1961) for a multicomponent ion exchange system containing n distinct ions with the same charge, the corrected selectivity coefficient is described by the equation (15)

$$\ln k^a_{1/n} = A_{1/n} + \sum_{i=1}^{n} B_{i/n} \bar{x}_i, \tag{15}$$

where n is the number (position) of the ion in the series of decreasing ion exchanger selectivity: $K_{1/n} > K_{2/n} > \ldots K_{i/n} \ldots > 1$; $A_{1/n}, B_{i/n}$ - are constants for binary exchanges of ions 1 and n; i and n. To calculate equilibria with participation of *n* exchangeable ions, we used a set of equations composed of (n - 1) equations of type (15), (n - 1) equations of type (4) for $k^a_{1/n}$, and the equation (16)

$$\sum_{i=1}^{n} \bar{x}_i = 1. \tag{16}$$

Thus, to calculate the phase composition of the ion exchanger for the system with n exchangeable ions, one should solve the following set of equations (17)

$$\begin{cases} \ln k^{a}_{1/2} = A_{1/2} + B_{1/2}\bar{x}_1 \\ \ln k^{a}_{1/3} = A_{1/3} + B_{1/3}\bar{x}_1 + B_{2/3}\bar{x}_2 \\ \ldots \\ \ln k^{a}_{1/n} = A_{1/n} + B_{1/n}\bar{x}_1 + B_{2/n}\bar{x}_2 + \ldots + B_{n-1/n}\bar{x}_{n-1} \\ k^{a}_{1/2} = \dfrac{\bar{x}_1 \cdot a_2}{\bar{x}_2 \cdot a_1} \\ k^{a}_{1/3} = \dfrac{\bar{x}_1 \cdot a_3}{\bar{x}_3 \cdot a_1} \\ \ldots \\ k^{a}_{1/n} = \dfrac{\bar{x}_1 \cdot a_n}{\bar{x}_n \cdot a_1} \\ \bar{x}_1 + \bar{x}_2 + \ldots + \bar{x}_n = 1. \end{cases} \quad (17)$$

The coefficients A and B were calculated from the experimental isotherms for independent binary exchanges by formulas (8) and (14).

We tested the proposed method for a vast array of experimental data on ion exchange equilibria in multicomponent systems in accordance with recommendations for testing new model (Soldatov & Bychkova, 1988). We imposed the following restrictions: ion exchange equilibria were considered at constant temperature, at constant ionic strengths of the solutions and only for monofunctional ion exchangers of specific chemical structure, for example, styrene-divinylbenzene sulfonate cation exchangers or anion exchangers containing only benzyltrimethylammonium groups. The equilibrium phase compositions were calculated for ion exchangers in which all exchange sites are accessible to exchangeable ions (the total exchange capacity of ion exchanger did not depend on the type of the sorbed ion). We considered ion exchange is not accompanied by complexation in the solution. Sorbate-sorbate interactions (Dmitryenko & Hale, 1965) don't present in ion exchanger phase. Exchange with participation of multicharged ions leads to nonlinear dependences of partial energies from counterion composition of calixarenecontaining polymers (Al'tshuler et al, 2008). High content of cross-linking agent creates additional difficulties (Vaslow & Boyd, 1966). Given these restrictions, a close agreement of calculated and experimental data was observed. All calculations were conducted on a computer with Intel (R) Core(TM)2 Duo T7300 2.00 GHz processor.

3.2.1 Three electrolytes in a solution

Consider thermodynamic system: sulfonate cation exchanger (Dowex-50W×12) – aqueous solution containing NH_4^+, Na^+ and H^+ cations. That system is recommended as a test (Soldatov & Bychkova, 1988) for calculating of the phase composition of an ion exchanger from data of binary exchanges.

$\bar{x}_{NH_4^+}$		$\bar{x}_{Na^+}$		$\bar{x}_{H^+}$	
exp.	calc.	exp.	calc.	exp.	calc.
0.123	0.117	0.142	0.159	0.735	0.724
0.132	0.125	0.066	0.085	0.802	0.79
0.115	0.105	0.268	0.285	0.617	0.61
0.104	0.097	0.384	0.391	0.512	0.512
0.096	0.090	0.483	0.486	0.421	0.424
0.085	0.085	0.573	0.572	0.342	0.343
0.082	0.081	0.654	0.654	0.264	0.265
0.079	0.078	0.727	0.732	0.194	0.190
0.072	0.074	0.804	0.810	0.124	0.116
0.224	0.218	0.062	0.076	0.714	0.706
0.215	0.207	0.132	0.145	0.653	0.648
0.201	0.189	0.250	0.264	0.549	0.547
0.186	0.176	0.358	0.367	0.456	0.457
0.165	0.166	0.461	0.459	0.374	0.375
0.438	0.427	0.201	0.216	0.361	0.357
0.404	0.408	0.308	0.308	0.288	0.284
0.388	0.394	0.392	0.394	0.220	0.212
0.374	0.381	0.474	0.476	0.152	0.143
0.360	0.372	0.555	0.555	0.085	0.073
0.558	0.553	0.048	0.055	0.394	0.392
0.540	0.540	0.104	0.106	0.356	0.354
0.521	0.517	0.193	0.203	0.286	0.280
0.498	0.498	0.282	0.291	0.220	0.211
0.486	0.484	0.362	0.375	0.152	0.141
0.625	0.632	0.055	0.052	0.320	0.316
0.611	0.620	0.104	0.101	0.285	0.279
0.154	0.158	0.549	0.544	0.297	0.298
0.146	0.151	0.629	0.626	0.225	0.223
0.139	0.146	0.704	0.704	0.157	0.150
0.131	0.142	0.781	0.782	0.088	0.076
0.361	0.357	0.059	0.065	0.580	0.578
0.347	0.343	0.119	0.126	0.534	0.531
0.328	0.321	0.224	0.235	0.448	0.444
0.304	0.304	0.331	0.332	0.365	0.364
0.285	0.290	0.422	0.421	0.293	0.289
0.468	0.472	0.448	0.456	0.084	0.072
0.269	0.279	0.509	0.504	0.222	0.217
0.261	0.271	0.585	0.584	0.154	0.145
0.250	0.264	0.657	0.662	0.093	0.074
0.456	0.463	0.063	0.060	0.481	0.477
0.447	0.450	0.115	0.115	0.438	0.435
0.592	0.598	0.191	0.193	0.217	0.209

Table 2. Experimental (exp.) and calculated (calc.) phase compositions of Dowex-50W×12

The series of selectivity of sulfonate cation exchanger (Dowex-50W×12) is: $NH_4^+ > Na^+ > H^+$. By using (9) and (10) the set of equations (17) is reduced to

$$\begin{cases} \ln k^a_{NH_4^+/Na^+} = 0.428 - 0.359\,\bar{x}_{NH_4^+} \\ \ln k^a_{NH_4^+/H^+} = 1.213 - 0.937\,\bar{x}_{NH_4^+} + 0.578\,\bar{x}_{Na^+} \\ k^a_{NH_4^+/Na^+} = \dfrac{\bar{x}_{NH_4^+} \cdot a_{Na^+}}{\bar{x}_{Na^+} \cdot a_{NH_4^+}} \\ k^a_{NH_4^+/H^+} = \dfrac{\bar{x}_{NH_4^+} \cdot a_{H^+}}{\bar{x}_{H^+} \cdot a_{NH_4^+}} \\ \bar{x}_{NH_4^+} + \bar{x}_{Na^+} + \bar{x}_{H^+} = 1. \end{cases}$$

In the table 2 are compared the experimental (Soldatov & Bychkova, 1988) and calculated in present work equilibrium phase compositions of Dowex-50W×12 cation exchanger for the $NH_4^+ - Na^+ - H^+$ three –ion exchange from aqueous solutions.

3.2.2 Four electrolytes in a solution

According to the obtained data (Fig. 10), the selectivity of the strong-base anion exchanger (Dowex-1) with respect to the studied anions decreases in the series: $Sal^- > NO_3^- > Cl^- > OH^-$. Equations (11)-(13) were used to calculate many – ion exchange equilibria by the set of equations (17). The experimental and calculated (by eqs. (17)) compositions of anion exchanger (Dowex-1) phase at equilibrium with aqueous solutions containing four competing anions (Sal^-, NO_3^-, Cl^- and OH^-) are presented in Table 3.

$\bar{x}_{Sal^-}$		$\bar{x}_{NO_3^-}$		$\bar{x}_{Cl^-}$		$\bar{x}_{OH^-}$	
exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
0.208	0.205	0.592	0.603	0.149	0.147	0.050	0.050
0.341	0.337	-	-	0.289	0.298	-	-
0.432	0.410	-	-	0.339	0.341	-	-
0.519	0.526	0.239	0.229	0.100	0.102	0.142	0.143
0.598	0.604	0.102	0.101	0.202	0.198	0.098	0.098

Table 3. Experimental (exp.) and calculated (calc.) data of the $Sal^- – NO_3^- – Cl^- – OH^-$ tetra - ion exchange in strong-base anion exchanger (Dowex-1)

4. Conclusion

The predictive power of the calculation method was characterized by the mean absolute deviation for the entire array (Soldatov & Bychkova, 1988):

$$\Delta \overline{x} = \left(\sum_{i=1}^{n} \sum_{r=1}^{s} \left| \overline{x}_{ir\ exp} - \overline{x}_{ir\ calc} \right| \right) \Big/ ns, \tag{18}$$

where n is the number of exchangeable ions and s is the number of experimental points in many-ion equilibria. Processing the data of Table 2 by formula (18) gives $\Delta\overline{x}$ =0.006, a value that corresponds to the most accurate among the calculation methods that were considered early (Soldatov & Bychkova, 1988). Processing the data from Table 3 by formula (18) yields $\Delta\overline{x}$ =0.005. This results show that the proposed method has a high predictive power. The consideration of ion exchanger as a canonical assembly explains why the corrected ion exchange selectivity coefficient linearly depends on the ion exchanger composition. This circumstance makes it possible to predict many-ion exchange equilibria.

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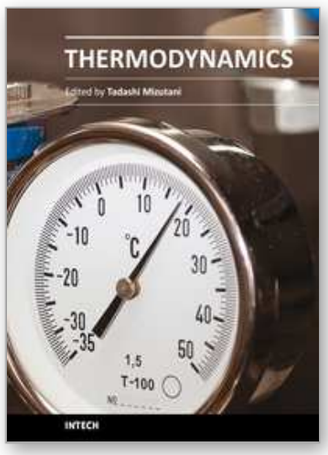
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