ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2007, Vol. 81, No. 7, pp. 1011–1015. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © G.N. Al'tshuler, L.A. Sapozhnikova, E.V. Ostapova, O.G. Al'tshuler, 2007, published in Zhurnal Fizicheskoi Khimii, 2007, Vol. 81, No. 7, pp. 1159–1164.

CHEMICAL THERMODYNAMICS
AND THERMOCHEMISTRY

The Thermodynamic Characteristics of Ion Exchange in a Sulfonated Polymer Based on *cis*-Tetraphenylcalix[4]resorcinarene

G. N. Al'tshuler, L. A. Sapozhnikova, E. V. Ostapova, and O. G. Al'tshuler

Institute of Solid-State Chemistry and Mechanochemistry (Kemerovo Branch), Siberian Division,
Russian Academy of Sciences, Kemerovo, Russia
e-mail: sorbent@kemnet.ru

Received April 21, 2006

Abstract—The selectivity and thermodynamic characteristics of exchange of protons in SO_3H groups of a sulfonated network polymer based on *cis*-tetraphenylcalix[4]resorcinarene for Na^+, Cu^{2+}, and In^{3+} cations from aqueous solutions are considered. Semiempirical quantum-chemical calculations of molecular ensembles modeling the structure of the elementary polymer unit in the H and Na forms were performed. The experimental data on the equilibrium phase compositions and the heat of exchange were used to calculate the thermodynamic equilibrium constants, Gibbs energy, enthalpy, and entropy of ion exchange.

DOI: 10.1134/S0036024407070011

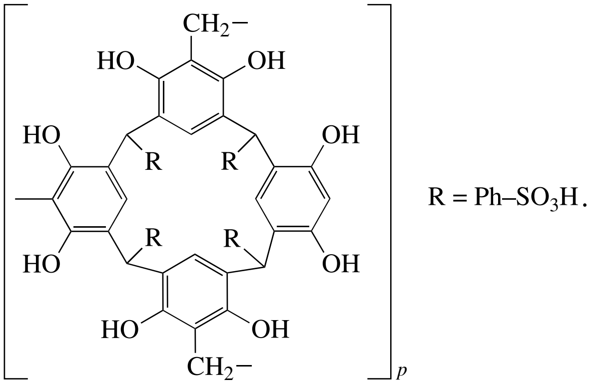
INTRODUCTION

Network polymers based on *cis*-calix[4]resorcinarenes are new ion exchangers that can participate in cationic exchange reactions [1]. The purpose of this work was to study the selectivity and thermodynamic characteristics of the exchange of protons of high-acidity SO_3H groups of a sulfonated network polymer based on *cis*-tetraphenylcalix[4]resorcinarene,

$$z\overline{\mathrm{H}}^+ + \mathrm{Cat}^{z+} \rightleftharpoons \overline{\mathrm{Cat}}^{z+} + z\mathrm{H}^+, \qquad (1)$$

where bars label polymeric phase constituents.

The elementary unit of the sulfonated network polymer based on *cis*-tetraphenylcalix[4]resorcinarene is (tetrasulfonatophenyl)calix[4]resorcinarene cross-linked with neighboring macrorings by methylene groups,



To solve the problem formulated above, we determined the equilibrium compositions of the polymer and solution phases involved in Cat^{z+}–H^+ ion exchange (Cat^{z+} = Na^+, Cu^{2+}, and In^{3+}), measured the heat effects of the Na^+–H^+ and Cu^{2+}–H^+ exchange processes, and performed semiempirical quantum-chemical calculations of ensembles of the *cis*-(tetrasulfonatophenyl)calyx[4]resorcinarene anion $L(SO_3^-)_4$ with the H_3O^+ and Na^+ cations; these ensembles modeled the structure of the elementary polymer unit in the H and Na forms.

EXPERIMENTAL

The polymer was prepared by twice sulfonating the network polymer synthesized by the resol polycondensation of *cis*-tetraphenylcalix[4]resorcinarene with formaldehyde following the procedure described in [1]. The total ion-exchange capacity of the sulfonated polymer with respect to 0.1 M NaOH was 5.65 equivalents per kg dry polymer. Of these, 2.45 equivalents correspond to the exchangeable SO_3H protons.

Solutions were prepared using HCl and NaCl of kh. ch. (chemically pure) grade and $CuCl_2 \cdot 2H_2O$ of ch. (pure) grade. $InCl_3$ was obtained from indium metal of os. ch. (special purity) grade by dissolving it in hydrochloric acid [2]. The amount of cations sorbed and desorbed in ion exchange was calculated from changes in ion concentrations in solution. The concentration of H^+ was determined by acid-base titration with methyl red as an indicator. Cu^{2+} and In^{3+} were determined by complexonometric titration, the indicator was 1-(2-pyridylazo)-2-naphthol [3, 4]. Low concentrations of In^{3+} were determined photometrically [4].

Table 1. Equilibrium phase compositions and ion exchange selectivity coefficients for sulfonated polymer based on *cis*-tetraphenylcalix[4]resorcinarene at 293 K

m_{Cat}	m_{H}	x_{Cat}	$k_{\mathrm{Cat/H}}$ (2)	$\gamma_{\pm\mathrm{CatCl}_z}$	$\gamma_{\pm\mathrm{HCl}}$	$k^a_{\mathrm{Cat/H}}$ (3)
Na^+						
0.0100	0.0900	0.142	1.49	0.778	0.778	1.49
0.0401	0.0599	0.381	0.92	0.778	0.778	0.92
0.0504	0.0496	0.443	0.78	0.778	0.778	0.78
0.0605	0.0395	0.508	0.67	0.778	0.778	0.67
0.0752	0.0248	0.644	0.60	0.778	0.778	0.60
0.0900	0.0100	0.713	0.28	0.778	0.778	0.28
0.0920	0.0080	0.760	0.275	0.778	0.778	0.275
Cu^{2+}						
0.00250	0.0965	0.249	1.64	0.600	0.780	2.80
0.00500	0.0910	0.382	1.66	0.592	0.779	2.94
0.0102	0.0820	0.554	1.84	0.592	0.776	3.20
0.0156	0.0715	0.656	1.82	0.587	0.767	3.18
0.0256	0.0511	0.789	1.81	0.579	0.767	3.20
0.0406	0.0208	0.920	1.53	0.567	0.758	2.77
In^{3+}						
0.00030	0.0990	0.0559	0.22	0.504	0.780	0.75
0.00162	0.0936	0.160	0.14	0.502	0.780	0.49
0.00325	0.0887	0.292	0.18	0.496	0.779	0.65
0.00330	0.0900	0.263	0.14	0.495	0.777	0.53
0.00588	0.0820	0.505	0.40	0.489	0.773	1.45
0.00832	0.0750	0.584	0.41	0.482	0.769	1.57
0.0116	0.0650	0.727	0.84	0.474	0.764	3.31
0.0127	0.0592	0.777	1.14	0.474	0.763	4.47

The selectivity of ion exchange was studied by the dynamic method [5]. The polymer in the salt or H form was placed into a column, through which aqueous solutions containing two electrolytes, HCl and NaCl, HCl and $CuCl_2$, or HCl and $InCl_3$, were passed until the column was equilibrated at 293 K. Equilibrium was considered established when the concentrations of electrolytes in the initial solution and several sequentially taken filtrate samples coincided. The equilibrium ion composition of the polymer phase was independent of the initial polymer form. The equilibrium phase compositions and ion exchange selectivity coefficients are listed in Table 1. The selectivity coefficients were calculated by the equation

$$k_{\mathrm{Cat/H}} = (x_{\mathrm{Cat}}/x_{\mathrm{H}}^{z})(m_{\mathrm{H}}^{z}/m_{\mathrm{Cat}}), \qquad (2)$$

where x_i is the experimental cation fraction in the polymer and m_i is the cation molality in solution.

The heat effects of ion exchange were measured at 293 K on a DAK-1-1A microcalorimeter under isothermal conditions with automatically balancing thermal EMF at the expense of the Peltier effect. The microcalorimeter was calibrated by dissolving chemically pure cesium chloride in water; the reference value used in calculations was $\Delta_{\mathrm{aq}}H^{\circ}_{\mathrm{CsCl}} = 17205 \pm 5$ J/mol [6]. Measurements were performed in standard (control and measuring) stainless steel flasks of volume 6 ml. An accurately weighed amount of swollen ionite was immersed into an aqueous solution of an electrolyte (5.3 ml, measuring flask) and water (5.3 ml, control flask) to determine the difference of the corresponding heat effects. The weight of the swollen polymer was 0.0100–0.0300 g. The polymer in the H form was immersed into 0.001–0.005 M solutions of $CuCl_2$ or 0.01–0.1 M solutions of NaCl, and the polymer in the salt form, into 0.001–0.006 M solutions of HCl. The heat flux was 10^{-5}–10^{-4} W. The sensitivity of the calorimeter was 0.04 V/W.

The mean ionic molal activity coefficients of electrolytes in solutions were calculated by the Debye–Hückel equation on the assumption that the closest approach distances were 4.5 Å for $CuCl_2$ and 6 Å for $InCl_3$ ions [7].

Quantum-chemical calculations were performed by the MNDO semiempirical method with the PM3 Hamiltonian parametrization using the MOPAC 2000 program (the Chem 3D Ultra 9.0 CambridgeSoft Corporation package).

RESULTS AND DISCUSSION

Model Consideration

The calculated structure of $\mathrm{L(SO_3^-)_4(H_3O)_4^+}$ minimized with respect to the enthalpy of formation is shown in Fig. 1. The sulfur atoms in this structure are in the vertices of a distorted parallelogram. The calculated interatomic distances are listed in Table 2.

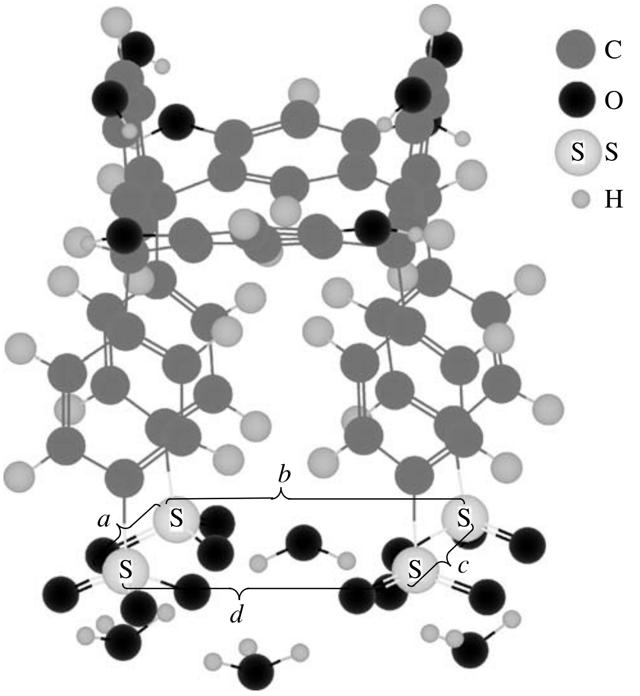


Fig. 1. Structure of $\mathrm{L(SO_3^-)_4(H_3O)_4^+}$ minimized with respect to the enthalpy of formation in MNDO/PM3 calculations.

This table shows that all parallelogram edges formed by sulfur atoms in $\mathrm{L(SO_3^-)_4(H_3O)_4^+}$ are equal, of 5–5.5 Å. The distance between sulfur atoms in $\mathrm{L(SO_3^-)_4(Na^+)_4}$ and $\mathrm{L(SO_3^-)_4(Na^+)_4 \cdot 4(H_2O)}$ is as large as 8.7 Å; in addition, the distances between cations and between cations and sulfur atoms increase. It follows that the replacement of hydroxonium cations with $\mathrm{Na^+}$ or $\mathrm{Na^+ \cdot H_2O}$ cations causes structure loosening.

Corrected Ion Exchange Selectivity Coefficients

Corrected cation exchange selectivity coefficients $k^a_{\mathrm{Cat/H}}$ [8] were calculated from the experimental data on equilibrium solution and polymer compositions (Table 1) taking into account solution nonideality by the equation

$$k^a_{\mathrm{Cat/H}} = \frac{x_{\mathrm{Cat}}}{x_{\mathrm{H}}^z}\frac{m_{\mathrm{H}}^z}{m_{\mathrm{Cat}}}\frac{\gamma^{2z}_{\pm\mathrm{HCl}}}{\gamma^{(z+1)}_{\pm\mathrm{CatCl}_z}}, \qquad (3)$$

where $\gamma_\pm$ is the mean ionic molal activity coefficient of the electrolyte in aqueous solution.

The dependences of $\log k^a_{\mathrm{Cat/H}}$ on the equivalent fraction of cations in the ionite x_{Cat} are shown in Fig. 2. The dependence of $\log k^a_{\mathrm{Cat/H}}$ on x_{Cat} for singly charged $\mathrm{Na^+}$ cations is described by the equation $\log k^a_{\mathrm{Na/H}} = -1.18x_{\mathrm{Na}} + 0.04$ (the linear correlation coefficient is 0.95). For doubly charged $\mathrm{Cu^{2+}}$ cations, the corrected selectivity coefficient remains virtually constant at all x_{Cu} values, and, for triply charged $\mathrm{In^{3+}}$, the $\log k^a_{\mathrm{In/H}}(x_{\mathrm{In}})$ function is approximated by the polynomial

$$\log k^a_{\mathrm{In/H}} = -4.75x^3_{\mathrm{In}} + 8.31x^2_{\mathrm{In}} - 2.77x_{\mathrm{In}} - 0.015$$

at a 0.99 confidence level.

The corrected ion exchange selectivity coefficients for the systems studied depend substantially on the counterion composition of the polymer phase when cations with odd charges ($\mathrm{Na^+}$ and $\mathrm{In^{3+}}$) are sorbed. For singly charged $\mathrm{Na^+}$ cations, a decrease in $\log k^a_{\mathrm{Na/H}}$ as x_{Na} increases is determined by the well-known energy nonequivalence of exchange sites [9]. The suggestion was made [10] that, for sorption of multiple-charge cat-

Table 2. Interatomic distances (Å) in *cis*-(tetrasulfonatophenyl)calix[4]resorcinarene anion compounds with the $\mathrm{H_3O^+}$ and $\mathrm{Na^+}$ cations according to the MNDO/PM3 data

Compound	Sulfur–sulfur				Sulfur–cation	Cation–cation
	a	*b*	*c*	*d*		
$\mathrm{L(SO_3^-)_4(H_3O)_4^+}$	5.06	5.27	5.52	5.47	3.2; 3.5	4.0; 5.0
$\mathrm{L(SO_3^-)_4(Na^+)_4}$	5.45	5.44	7.55	7.46	3.8; 4.0	5.35; 7.62
$\mathrm{L(SO_3^-)_4(Na^+)_4 \cdot 4(H_2O)}$	5.38	5.55	8.68	7.57	3.9; 4.0	5.2–9.1

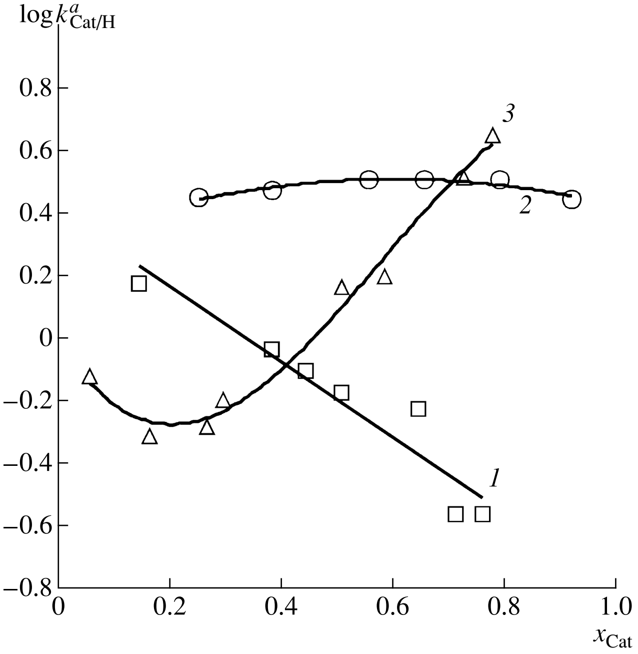


Fig. 2. Dependences of corrected ion exchange selectivity coefficients for the (*1*) Na^+–H^+, (*2*) Cu^{2+}–H^+, and (*3*) In^{3+}–H^+ reactions on the equivalent fraction of cations in the sulfonated polymer based on *cis*-tetraphenylcalix[4]resorcinarene at 293 K.

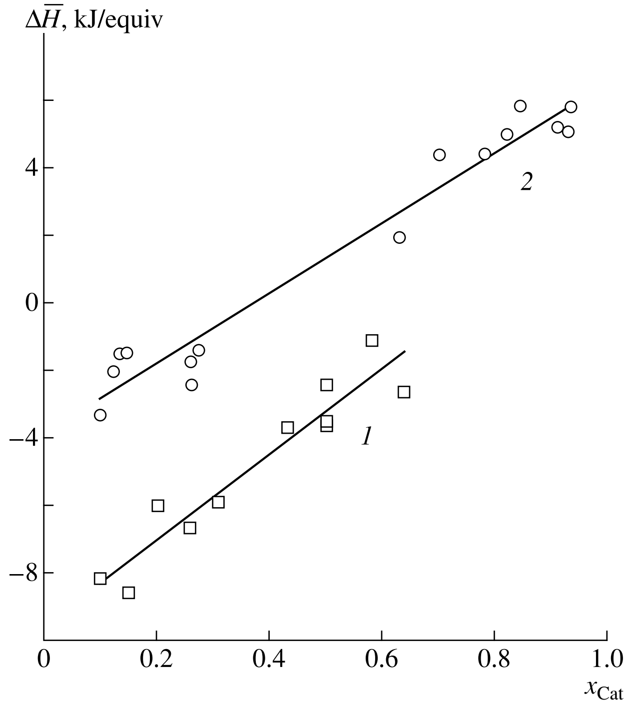


Fig. 3. Differential enthalpy of exchange for the (*1*) Na^+–H^+ and (*2*) Cu^{2+}–H^+ reactions in the sulfonated polymer based on *cis*-tetraphenylcalix[4]resorcinarene at 293 K.

ions, $\log k^a_{\mathrm{Cat/H}}(x_{\mathrm{Cat}})$ increases as x_{Cat} grows because electrostatic interactions between multiple-charge cations and sulfo group anions from different polymer chains draw neighboring polymer chains closer to each other. Triply charged In^{3+} cations can likely interact with anions of neighboring polymer chains, which results in an increase in the selectivity coefficient as x_{In} grows.

The elementary polymer unit contains four SO_3^- groups. According to model concepts, the smallest distance between two SO_3^- groups is 5 Å (Table 2, Fig. 1). It is natural to suggest that the SO_3^- groups of one elementary unit and sorbed doubly charged Cu^{2+} cations make up supramolecular ensembles with fairly strict geometry and stoichiometry. The form of the $\log k^a_{\mathrm{Cu/H}}(x_{\mathrm{Cu}})$ function is likely determined by the constant Gibbs energy of formation of ensembles of doubly charged cations with an even number of SO_3^- group.

The Thermodynamic Functions of Ion Exchange

The data presented in Fig. 2 allowed us to calculate the thermodynamic constants of ion exchange (1), $K_{\mathrm{Cat/H}}$, using the Gaines–Thomas equation [11]

$$\ln K_{\mathrm{Cat/H}} = (z_{\mathrm{H}} - z_{\mathrm{Cat}}) + \int_0^1 \ln k^a_{\mathrm{Cat/H}} dx_{\mathrm{Cat}},$$

where z_i is the charge of the cation. The $K_{\mathrm{Na/H}}$, $K_{\mathrm{Cu/H}}$, and $K_{\mathrm{In/H}}$ values are 0.637, 1.042, and 0.206, respectively. The thermodynamic constant for ion exchange with differently charged cations is likely influenced by the statistical effect [12], which decreases $K_{\mathrm{Cat/H}}$.

The differential enthalpies of exchange of protons for sodium and copper cations, $\Delta\overline{H} = (\partial \Delta H/\partial x_{\mathrm{Cat}})_T$, are shown in Fig. 3. The $\Delta\overline{H}$ values correspond to $\bar{x}_{\mathrm{Cat}}$ at the middle of the interval of changes in the counterion polymer composition during measurements of the heat effect of ion exchange. The $\Delta\overline{H}(x_{\mathrm{Cat}})$ dependences are rectilinear (the linear correlation coefficients of the $\Delta\overline{H}(x_{\mathrm{Na}})$ and $\Delta\overline{H}(x_{\mathrm{Cu}})$ functions are 0.95 and 0.98, respectively). The integral enthalpies of ion exchange calculated by the equation

$$\Delta H = \int_0^1 (\partial \Delta H/\partial x_{\mathrm{Cat}}) dx_{\mathrm{Cat}},$$

were −3.2 ± 0.7 and 1.4 ± 0.7 kJ/equiv for the Na^+–H^+ and Cu^{2+}–H^+ exchange processes, respectively. The ΔH values obtained are the standard enthalpies of ion

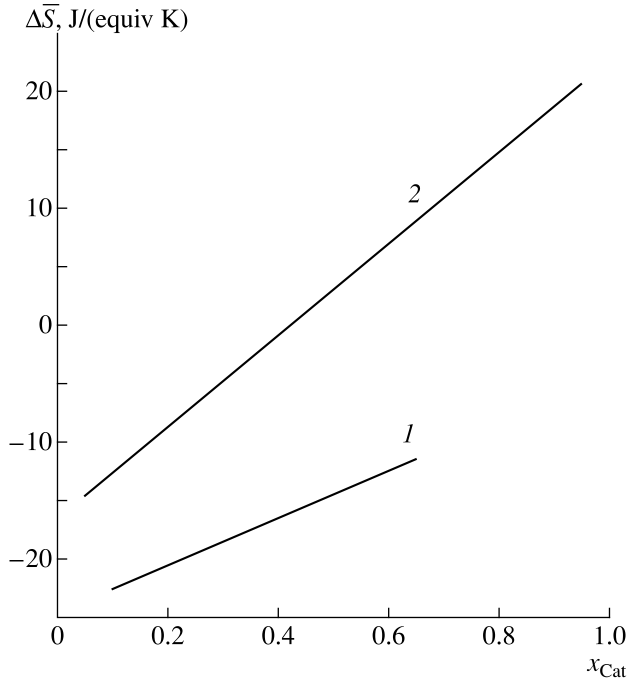


Fig. 4. Differential entropy of exchange for the (*1*) Na^+–H^+ and (*2*) Cu^{2+}–H^+ reactions in the sulfonated polymer based on *cis*-tetraphenylcalix[4]resorcinarene at 293 K calculated according to (4).

exchange because the heats of mixing and the difference in heat content between 0.1 M solutions of NaCl and HCl or 0.005 M solutions of $CuCl_2$ and HCl are smaller than measurement errors.

The standard thermodynamic functions of ion exchange are strongly influenced by the difference in the resolvation energies of the ions involved in exchange [9]. The dependences of the differential thermodynamic functions of ion exchange on the counterion polymer composition are determined by changes in the interaction between the ions involved and ionogen groups. Taking [11] into account, the differential Gibbs energy was calculated as $\Delta\bar{G} = RT[(z_{\mathrm{H}} - z_{\mathrm{Cat}}) - \ln k^{a}_{\mathrm{Cat/H}}]$. The behavior of the $\Delta\bar{G}\,(x_{\mathrm{Cat/H}})$ functions was characterized by considering the $\log k^{a}_{\mathrm{Cat/H}}\,(x_{\mathrm{Cat}})$ functions plotted in Fig. 2. An increase in the differential enthalpy of ion exchange as the content of metal cations in the polymer grows (Fig. 3) is determined by the energy nonequivalence of exchange sites in the polymer. The differential entropies of ion exchange $\Delta\bar{S}$ calculated by the equation

$$(\Delta\bar{S})_{T,\,x_{\mathrm{Cat}}} = ((\Delta\bar{H} - \Delta\bar{G})/T)_{T,\,x_{\mathrm{Cat}}} \tag{4}$$

are shown in Fig. 4. We see that the entropy of the system increases as the fraction of metal cations in the polymer grows for both Na^+–H^+ and Cu^{2+}–H^+ exchange processes. This is in agreement with the model concept of a decrease in polymer phase ordering as hydroxonium ions are replaced by metal cations.

To summarize, model considerations and the experimental data obtained show that the type of the cation sorbed and the structure and counterion polymer composition substantially influence the character and values of the thermodynamic functions of ion exchange for the sulfonated polymer based on *cis*-tetraphenylcalix[4]resorcinarene.

REFERENCES

1. H. Altshuler, E. Ostapova, O. Fedyaeva, et al., Macromol. Symp. **181**, 1 (2002).
2. S. V. Bleshinskii and V. F. Abramova, *Chemistry of Indium* (Akad. Nauk Kirg. SSR, Frunze, 1958) [in Russian].
3. G. Schwarzenbach and H. Flaschka, *Die komplexometrische Titration* (F. Enke, Stuttgart, 1965; Khimiya, Moscow, 1970).
4. A. I. Busev, V. G. Tiptsova, and V. M. Ivanov, *Practical Manual on Analytical Chemistry of Rare Elements* (Khimiya, Moscow, 1996) [in Russian].
5. M. Marhol, *Ion Exchangers in Analytical Chemistry: Their Properties and Use in Inorganic Chemistry*, vol. 14 of *Comprehensive Analytical Chemistry* (Elsevier, Amsterdam, 1982; Mir, Moscow, 1985).
6. *Thermodynamic Properties of Pure Substances: A Handbook*, Ed. by L. V. Gurvich (Nauka, Moscow, 1982), Vol. 4, p. 486 [in Russian].
7. R. A. Robinson and R. M. Stokes, *Electrolyte Solutions: The Measurement and Interpretation of Conductance, Chemical Potential, and Diffusion in Solutions of Simple Electrolytes*, 2nd ed. (Academic, New York, 1959; Inostrannaya Literatura, Moscow, 1963).
8. *International Union of Pure and Applied Chemistry: Commission on the Nomenclature of Organic Chemistry: Nomenclature of Organic Chemistry*, 4th ed., Ed. by J. Rigaudy and S. P. Klesney (Pergamon, Oxford, 1979; VINITI, Moscow, 1979).
9. *Ion Exchange: Series of Advances*, Ed. by J. Marinsky (New York, 1966; Mir, Moscow, 1968), Vol. 1.
10. V. S. Soldatov and V. A. Bychkova, *Ion-Exchange Equilibria in Multicomponent Systems* (Nauka i Tekhnika, Minsk, 1988) [in Russian].
11. G. L. Gaines, Jr. and H. C. Thomas, J. Chem. Phys. **11** (4), 714 (1953).
12. N. Bjerrum, Z. Phys. Chem. **106**, 219 (1923).