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Thermodynamics of ion exchange of H^+ by Na^+ or NH_4^+ on ion-exchange resins based on *C*-tetramethylcalix[4]resorcinarene

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The corrected selectivity coefficients of the ion exchange H^+—Na^+ and H^+—NH_4^+ on ion-exchange resins based on *C*-tetramethylcalix[4]resorcinarene were calculated from the experimental data obtained from studying ion-exchange equilibria. The preference of the ion-exchange resins for cations increases in the sequence: $Na^+ < NH_4^+ << H^+$, and the ion-exchange resin based on (2-furyl)hydroxymethyltetramethylcalix[4]resorcinarene has a higher preference for ammonium cations. According to the results of microcalorimetric measurements, the exchange H^+—Na^+ on this ion-exchange resin is accompanied by the highest change in the differential enthalpy. It follows from the quantum-chemical calculations that the introduction of a (2-furyl)hydroxymethyl group into the structure of the polymer induces additional electrostatic interactions between an ammonium cation and an elementary unit of the ion-exchange resin.

Key words: cation-exchange resin, *C*-tetramethylcalix[4]resorcinarene, ammonium cation, sodium cation, corrected selectivity coefficient of ion exchange, differential enthalpy, quantum-chemical calculation.

We have previously shown[1,2] that network polymers containing calix[4]resorcinarenes in an elementary unit can be involved in ion exchange due to the presence of resorcinol OH groups capable of dissociating to form free protons. The total ion-exchange capacity of the calix-containing ion-exchange resins with 0.1 *M* NaOH corresponds to the substitution of four protons in one calixresorcinarene fragment of the polymer.[2]

The purpose of this work is to consider from the thermodynamic viewpoint the sorption of Na^+ and NH_4^+ cations by cation-exchange resins based on *C*-tetramethylcalix[4]resorcinarene and, specifically, in the reaction

$$\overline{\mathrm{LH}} + \mathrm{Cat}^+ \rightleftarrows \overline{\mathrm{LCat}} + \mathrm{H}^+, \qquad (1)$$

where the line refers to the component in the polymeric phase; Cat^+ is the Na^+ or NH_4^+ cation, and $\overline{\mathrm{LH}}$ is cation-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2560—2563, December, 2004.

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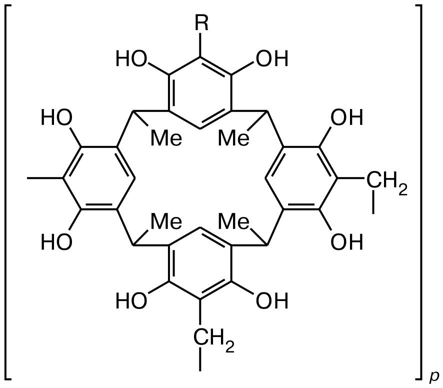
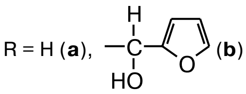


1a,b



exchange resin **1a** or **1b** in the H form. To solve the problem, we obtained the data on the equilibrium compositions of the phases and derived the selectivity of ion-exchange reactions. The differential enthalpy of process (1) was calculated from the results of microcalorimetric measurements. To analyze the influence of the elementary unit structure on the preference of cation-exchange resins for ions Na^+ and NH_4^+, we performed the semiempirical quantum-chemical calculation of salt forms of *C*-tetramethylcalix[4]resorcinarene.

Experimental

Cation-exchange resin **1a** [1] was prepared by the catalytic resol polycondensation of *C*-tetramethylcalix[4]resorcinarene with formaldehyde. Cation-exchange resin **1b** [3] was obtained by the condensation of formaldehyde with the product of the reaction of *C*-tetramethylcalix[4]resorcinarene with furfurol. The total dynamic ion-exchange capacity of cation-exchange resins **1a** and **1b** was 5.0 and 3.8 moles, respectively, of monocharged cations per kg of the dry polymer in the H form. The cation-exchange resins were conditioned by the successive treatment with solutions of NaCl, NaOH, HCl, and H_2O according to a known procedure[4] for the preparation of ion-exchange resins.

To equilibrate ion-exchange systems, exactly weighed portions of the H form of the ion-exchange resins (0.2500±0.0005 g) were stored for 60 days at 298 K in 25 mL of 0.2 *M* solutions of sodium or ammonium chloride containing 0—1.25 mmoles of sodium or ammonium hydroxide, respectively. Then the ion-exchange resin was separated from a solution, and equilibrium concentrations of cations were determined. The number of cations sorbed by the ion-exchange resin was calculated from the difference in H^+ concentrations in the initial and equilibrated solutions. The concentration of protons in solutions was found by acid-base titration. The checking analysis of the counterion composition of the ion-exchange phase was carried out by the elution of cations with 0.01 *M* HCl. The content of Na^+ cations in the ion-exchange resin was calculated from a change in the H^+ concentration in the eluate, and the content of NH_4^+ cations in the ion-exchange resin was found from the direct measurements of the NH_4^+ concentration in the eluate by the formaldehyde method.[5] The molar fractions of cations Na^+ or NH_4^+ in the phase of the cation-exchange resin ($\bar{x}_{Cat}$) was calculated relatively to the total amount of counterions determined by the total dynamic ion-exchange capacity of the cation-exchange resins. The mean ion activity coefficients in a solution were obtained by a macroelectrolyte with the common anion.[6]

Heat effects of ion exchange were measured at 298 K on a DAK 1-1A differential microcalorimeter in the isothermal regime with an automated compensation of the thermoelectromotive force by the Peltier effect. The microcalorimeter was calibrated by dissolving chemically pure cesium chloride in water. The reference[7] value of the enthalpy of solvation $\Delta H^\circ_{solv}(CsCl) = 17205\pm5\ J\ mol^{-1}$ at 298.15 K was used in calculations. Measurements were carried out using standard (checking and measuring) stainless steel 6-mL flasks. The difference in thermal effects was detected when a swollen ion-exchange resin in the H form (0.05 g) was placed in a measuring flask containing an 0.2 *M* NaCl or 0.2—0.5 *M* NH_4Cl solution (5.3 mL) and in a checking flask containing water (5.3 mL). The thermal flow was 10^{-5}—10^{-4} W, and the calorimeter sensitivity was 0.04 V W^{-1}. The amount of sorbed cations Na^+ and NH_4^+ was determined from the pH values of the solution before and after calorimetric measurements of ion exchange. The pH values of the solution were measured on an I-130 ionometer with an accuracy of 0.005 pH units. Since the cation-exchange resins possess a high proton affinity, thermal effects of reaction (1) were determined at a small filling of the ion-exchange resins with cations NH_4^+ or Na^+. A higher content of cations in the polymer can be obtained by their sorption from alkaline solutions, which is accompanied, however, by a heat release that exceeds the thermal effect of process (1) and is related to neutralization.

The MOPAC program package was used for quantum-chemical calculations.

Results and Discussion

Selectivity coefficients of ion exchange. The corrected selectivity coefficients of ion exchange were calculated from the data on the equilibrium compositions of the solution and polymeric phase

$$k^{a}_{Cat/H} = 10^{-pH}\bar{m}_{Cat} / (\bar{m}_{H^+}m_{Cat}\gamma_{\pm}). \qquad (2)$$

Here $k^{a}_{Cat/H}$ is the corrected selectivity coefficient of ion exchange[8]; m_{Cat} and $\bar{m}_{Cat}$ are the equilibrium concentrations of cations in aqueous solutions and in the phase of ion-exchange resins, respectively; $\bar{m}_{H^+}$ is the concentration of H^+ ions in the phase of ion-exchange resins; $\gamma_{\pm}$ is the mean ion molar activity coefficient.

The plots of $\log k^{a}_{Cat/H}$ *vs.* molar fraction of Na^+ or NH_4^+ ions in the phase of ion-exchange resins **1a** and **1b** are presented in Fig. 1. They are well approximated by straight lines (linear correlation coefficients calculated by the least-squares method are 0.93—0.98). The mutual positions of straight lines in Fig. 1 reflects the relative selectivity of ion-exchange resins **1a** and **1b** toward cations

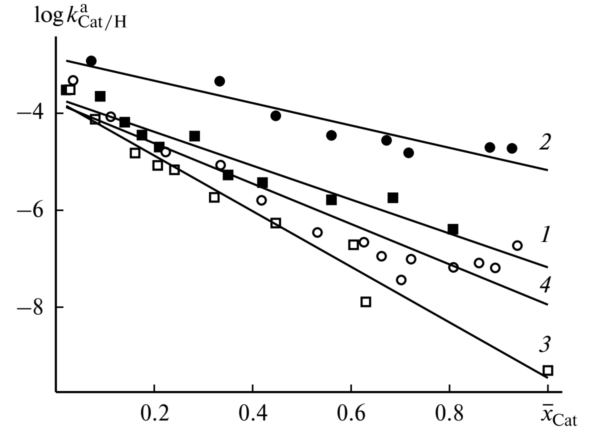


Fig. 1. Logarithms of the corrected selectivity coefficient of ion exchange of H^+ by NH_4^+ in cation-exchange resins **1a** (*1*) and **1b** (*2*) and of H^+ by Na^+ in cation-exchange resins **1a** (*3*) and **1b** (*4*) *vs.* molar fraction of ions NH_4^+or Na^+ in the cation-exchange resins at 298 K.

Na^+ and NH_4^+. The corrected selectivity coefficients and affinity of the resins to cations increases in the sequence $Na^+ < NH_4^+ \ll H^+$. At the same time, the $\log k^{a}_{NH_4/H}$ values with a change in $\bar{x}_{NH_4^+}$ (see Fig. 1, line *2*) for resin **1b** are higher in the whole interval of compositions than similar values for ion-exchange resin **1a** (see Fig. 1, line *1*). Therefore, compared to resin **1a**, the ion-exchange resin based on (2-furyl)hydroxymethyltetramethylcalix[4]resorcinarene exhibits a higher preference for ammonium cations.

Enthalpy of ion exchange. The differential enthalpies of ion exchange $\Delta\bar{H} = (\partial H / \partial\bar{x}_{Cat})_T$ are marked in Fig. 2 by points in the middles of the sections reflecting the change in $\bar{x}_{Cat}$ during measuring the thermal effect of ion exchange. In the studied interval of compositions, they depend almost linearly on the filling of the resins with the Na^+ or NH_4^+ cations. The linear correlation coefficients are 0.93—0.98. The shape of the function $\Delta\bar{H}(\bar{x}_{Cat})$ reflects the energetic heterogeneity of exchange sites of the cation-exchange resins. Line *2* (see Fig. 2) that displays a decrease in the enthalpy of ion exchange H^+—NH_4^+ in the resin based on (2-furyl)hydroxymethyltetramethylcalix[4]resorcinarene, as the function $\log k^{a}_{NH_4/H}\left(\overline{x_{NH_4}}\right)$ (see Fig. 1), lies statistically reliably above lines *1*, *3*, and *4*. The sorption of small amounts of cations ($\bar{x}_{Cat} < 0.02$) is accompanied by a heat evolution of 100—500 kJ per mole of the cation. The differential enthalpy of ion exchange is lowest in the studied interval of compositions for the sorption of the NH_4^+ cations with resin **1b**.

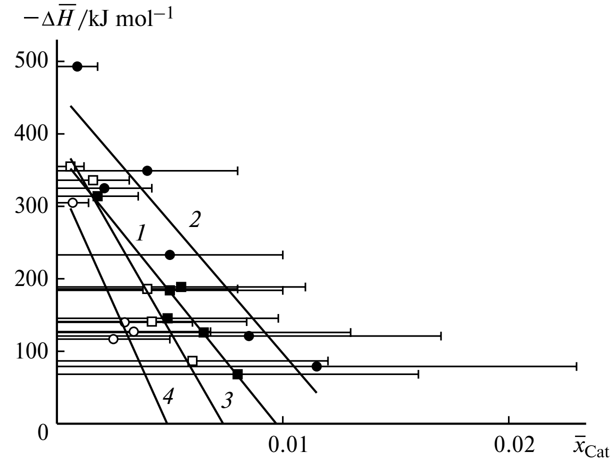
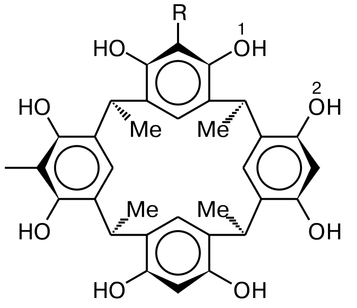
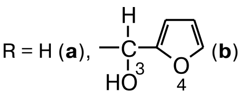


Fig. 2. Differential enthalpies of the ion exchange of H^+ by NH_4^+ in **1a** (*1*) and **1b** (*2*) and of H^+ by Na^+ in **1a** (*3*) and **1b** (*4*) *vs.* molar fraction of ions NH_4^+ or Na^+ in the cation-exchange resins at 298 K.

Model. The different preference of ion-exchange resins **1a** and **1b** for the same cation can be caused by the specific features of its interaction with immobilized calixarene. To estimate these features, we performed the quantum-chemical calculation of *C*-tetramethylcalix[4]resorcinarenes **2a** and **2b** and their salt forms obtained by the substitution of mobile protons at the resorcinol OH groups by cations NH_4^+ or Na^+ in molecules **2a** and **2b**.



2a,b



According to the data of quantum-chemical calculations, for the compounds containing one NH_4^+ or Na^+ cation, the structures obtained by the substitution of the proton at the O(1) atom (in both molecules **2a** and **2b**) have the minimum heat of formation. The distances between the Na^+ or NH_4^+ cation and oxygen atoms O(1), ..., O(4) calculated by the MNDO/PM3 method in salts formed by **2a** and **2b** are presented in Table 1. It is seen that the distances between the Na^+ cations and O(1) atoms increase from 0.24 (**2a**) to 0.27 nm (**2b**), and due to this increase can the electrostatic interactions in sodium salts **2b** are weaker. In ammonium salts **2a** and **2b**, the distances from the cations to the O(1) atom are equal to each other, being 0.27 nm, whereas the distances to the O(2) atom are 0.32 and 0.31 nm, respectively. At the

Table 1. Interatomic distances* (calculated by the MNDO/PM3 method) in salts of compounds **2a** and **2b** in which the proton at the O(1) atom is substituted by the Na^+ or NH_4^+ cation

Compound	Cat^+	Distance to O atoms/nm			
		O(1)	O(2)	O(3)	O(4)
2a	Na^+	0.241	0.366	—	—
	NH_4^+	0.266	0.317	—	—
2b	Na^+	0.271	0.335	0.371	0.430
	NH_4^+	0.270	0.313	0.385	0.395

* The distances from the Na or N atoms to the corresponding O atoms are presented.

same time, the distances between the NH_4^+ cation and O(3) and O(4) atoms in salts **2b** are 0.39 nm. This indicates additional electrostatic interactions between the NH_4^+ cation and anion of (2-furyl)hydroxymethyltetramethylcalix[4]resorcinarene.

An analysis of the experimental data on the selectivity coefficients and differential enthalpies of ion exchange and the results of quantum-chemical calculations suggest that the introduction of the (2-furyl)hydroxymethyl substituent into the elementary unit structure of the polymer enhances the interaction of cations with the calixarene anions and increases the preference of cation-exchange resin **1b** for ammonium cations.

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Received April 9, 2004;
in revised form June 30, 2004