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# Ion-exchange selectivity of a network calixarene-containing polymer obtained by the template synthesis on $Na^+$, $K^+$, and $Ba^{2+}$ matrices

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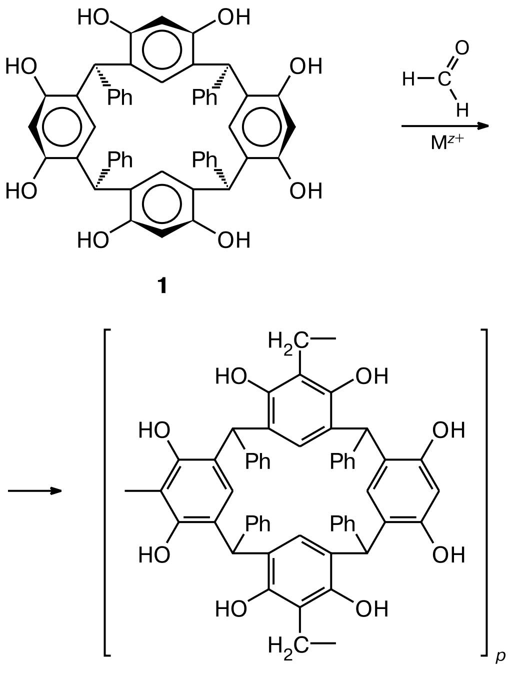
The ion-exchange equilibrium in network polymers obtained from *cis*-2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene by template synthesis on cations $Na^+$, $K^+$, and $Ba^{2+}$ as matrices was studied. The selectivity coefficients of ion exchanges $Ba^{2+}$—$H^+$, $Na^+$—$H^+$, $K^+$—$H^+$, $Na^+$—$K^+$, and $Na^+$—$NH_4^+$ were determined. The template synthesis enhanced the affinity of the polymers to matrix-forming cations by 6—8 kJ $mol^{-1}$.

**Key words:** network polymer, *cis*-2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene, ion exchange, selectivity, sodium, potassium, barium, ammonium.

Design and experimental studies of supramolecular polymeric systems provide information on the properties of multicomponent self-consistent natural assemblies and enable one to mimic their behavior at the molecular level. Immobilized calix[4]arenes are shown[1—7] to form supramolecular assemblies in the polymeric phase with alkali[1,2,4—6] and transition[3,5] metal cations, as well as ammonium.[7] Functionalization of immobilized calixarenes through introduction of carboxyl,[3] phosphate,[5] and furyl(hydroxy)methyl[6] groups enhances the selectivity of interaction of the polymers with cations. An approach that provides prerequisites for the recognition of components of the assembly is the use of template synthesis of network polymers, whose three-dimensional structure is formed according to the sol—gel technology on a matrix of organic and inorganic substrates. For instance, the template synthesis of polymeric pseudo-crown ether, which is network on the matrix of $Ni^{2+}$ cations, induces a considerable increase in the affinity of the polymer to the matrix-forming cation.[8]

We have previously synthesized network polymers on the matrix of $Na^+$ cations by the resol polycondensation of *cis*-tetramethylcalix[4]resorcinarene,[1] *cis*-tetraphenylcalix[4]resorcinarene,[2] and their derivatives[6] with formaldehyde. These polymers were shown[1,2,7] to interact with electrolyte solutions according to a cation-exchange mode. It is of interest to study the effect of the matrix cations on the sorbability of the network calixarene-containing polymers obtained by the template synthesis. In the present work, we studied the ion-exchange selectivity of network polymers synthesized by the polycondensation of *cis*-2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (**1**) with formaldehyde using the sol—gel technology in the presence of cations $Na^+$, $K^+$, and $Ba^{2+}$ (Scheme 1).

**Scheme 1**



**1**

**2a—c**

M = Na (**a**), K (**b**), Ba (**c**)

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## Experimental

Compound **1** was obtained by the condensation of resorcinol with benzaldehyde.[9] The physicochemical parameters (m.p., IR spectra) of compound **1** and its acetate, which was synthesized by treatment of **1** with $Ac_2O$ in the presence of Py,[10] agree with published data.[9,10]

**Polymer 2a.** Compound **1** (10 mmol) was dissolved in an aqueous solution containing NaOH (40 mmol). Then an aqueous solution of formaldehyde (40 mmol) was added. The mixture was kept for 20 h at 90 °C. Excess alkali was washed off the gel that formed with cold water, and the washed gel was kept for 100 h at 100 °C in water, converted into the $H^+$ form by treatment with 0.1 *M* HCl, and dehydrated with ethanol in the Soxhlet extractor. The yield of the product was 85%. According to the data of potentiometric titration, the content of fragments **1** in polymer **2a** was 1.0 mol $kg^{-1}$.

**Polymer 2b.** Compound **1** (10 mmol) was dissolved in an aqueous solution containing KOH (85 mmol). Polymer **2b** was isolated as described above for compound **2a**. The yield of the product was 70%. The content of fragments **1** in polymer **2b** was 0.96 mol $kg^{-1}$.

**Polymer 2c.** Compound **1** (10 mmol) was dissolved in an aqueous solution containing NaOH (40 mmol), and aqueous solutions of formaldehyde (40 mmol) and $BaCl_2$ (10 mmol) were added. Polymer **2c** was isolated as described above for compound **2a**. The yield of the product was 80%. The content of fragments **1** in polymer **2c** was 1.02 mol $kg^{-1}$.

The polymers were conditioned using a conventional procedure for the preparation of ion-exchange resins.[11]

The total dynamic ion-exchange capacities of the polymers were determined in columns by passing a 0.1 *M* solution of NaOH through a layer of the polymer in the $H^+$ form until the cation concentrations in the eluate and the eluent coincided. The total dynamic ion-exchange capacity of the polymers was 4.0 (**2a**), 3.8 (**2b**), and 4.3 (**2c**) moles of $Na^+$ cations per kg of the polymer in the $H^+$ form dried to a constant weight at 105 °C.

The selectivity of ion exchange in the sorption of cations $Na^+$, $K^+$, and $Ba^{2+}$ was studied by the static method. Weighed samples (0.2500±0.0005 g) of the polymer in the $H^+$ form for the exchanges $Na^+$—$H^+$, $K^+$—$H^+$, and $Ba^{2+}$—$H^+$ were kept for 3 months at 298 K in solutions (25 mL) of metal hydroxides with different concentrations. The concentrations of solutions of NaOH and KOH were determined by potentiometric titration with 0.1 *M* HCl, and that of the cation $Ba^{2+}$ was determined by complexonometric titration.[12] For the $Na^+$—$NH_4^+$ exchange, the polymers in the $Na^+$ form were equilibrated at 298 K with solutions of $NH_4Cl$ with different concentrations and the ionic strength not exceeding 0.1 mol $L^{-1}$. The content of $NH_4^+$ in the solution was determined by the formaldehyde method.[13]

The mean ionic molal activity coefficients in binary solutions were calculated by the limiting Debye—Hückel law. The mean ionic molal activity coefficients in solutions of $NH_4Cl$ were calculated using tabulated data.[14]

The semiempirical quantum chemical calculations of the enthalpy of formation of four-charge anions of *cis*-2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene was performed by the MNDO method with the PM3 parametrization of the Hamiltonian. Then two similar ionized molecules of **1** with the lowest enthalpies of formation were linked through the —$CH_2$— group to form a dimer. The structure and potential energy of an assembly containing the ionized dimer and eight singly-charged or four doubly-charged metal cations were calculated by the MM2 molecular mechanics method. All calculations were carried out in the framework of the CambridgeSoft Corporation Chem3D Pro program package (version 5.0).

## Results and Discussion

The calculation of the geometry and relative energies of sodium, potassium, and barium salts of the dimer, which simulates the simplest structural unit of network polymers **2a—c**, showed that the compounds with the fragments of **1** in the boat conformation with their hydrophilic parts directed toward each other have the lowest energy. In the case of the barium salt, the boats of **1** form an angle of 90° relative to each other. The $Ba^{2+}$ cations are localized inside the hydrophilic rim of the macrocycle and "pull together" the units of the dimer. On going from the barium salt to the sodium and then potassium salts, the angle changes (by 8—10°) and the distances between the macrocycles increase (by 2—2.5 Å). A part of singly-charged cations are arranged inside the hydrophilic rim of the macrocycle, and the rest are outside the macrocycle and "loosen" the dimer. Thus, the structures of the salt forms of the *cis*-2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene dimer minimized by energy in the MM2 framework differ somewhat in their organization. Therefore, it should be expected that polymers **2a—c** obtained by the resol polycondensation of **1** with formaldehyde in solutions with different cations would be structurally different. These differences can appear as an increased selectivity of the polymer for the sorption of a matrix-forming cation from solutions.

Polymers **2a—c** in the $H^+$ form absorb cations from solutions according to the ion-exchange reaction

$$\overline{H^+} + (1/z)Cat^{z+} \rightleftharpoons (1/z)\overline{Cat^{z+}} + H^+. \qquad (1)$$

Here tilde designates the polymeric phase, and $z$ is the cation charge. Equilibrium (1) is conventionally[15] characterized by the corrected selectivity coefficient of ion exchange

$$k^a{}_{Cat/H} = \frac{\overline{m_{Cat}^{1/z}}}{\overline{m_H}} \cdot \frac{a_H}{m_{Cat}^{1/z}(\gamma_\pm)^{1/z}},$$

where $k^a{}_{Cat/H}$ is the corrected selectivity coefficient of the ion exchange $Cat^{z+}$—$H^+$; $\bar{m}_i$ and $m_i$ are the molalities of the component in the polymer and in solution, respectively; $a_H$ is the proton activity in the solution; $\gamma_\pm$ is the mean ionic molal activity coefficient of the electrolyte.

**Exchange $Ba^{2+}$—$H^+$.** The plot of the logarithm of the corrected selectivity coefficient of the $Ba^{2+}$—$H^+$ ion exchange *vs.* molar fraction of the $Ba^{2+}$ cations ($\bar{x}_{Ba}$) in

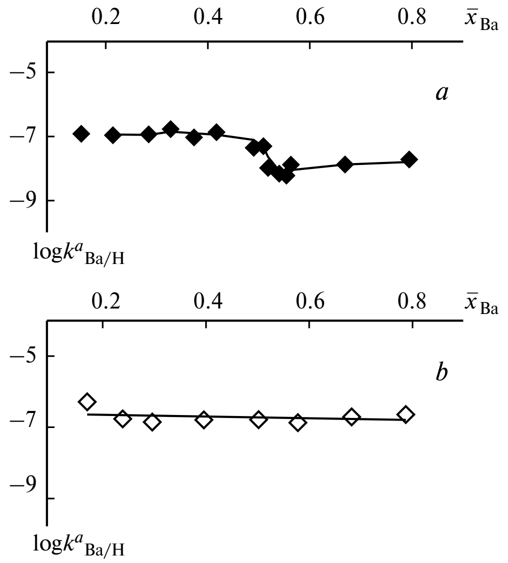

**Fig. 1.** Logarithms of the corrected selectivity coefficients for the $Ba^{2+}$—$H^+$ exchange on polymer **2a** synthesized on the $Na^+$ matrix (*a*) and polymer **2c** obtained on the $Ba^{2+}$ matrix (*b*).

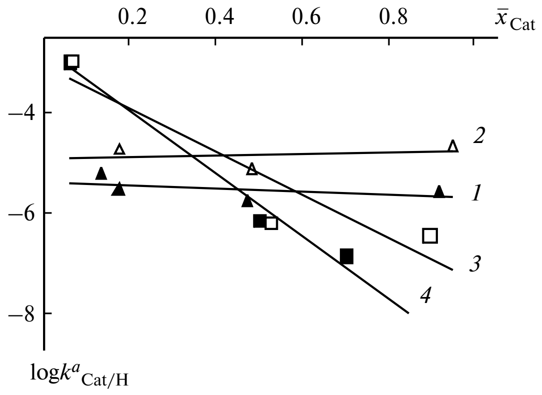

**Fig. 2.** Logarithms of the corrected selectivity coefficients for the $Cat^+$—$H^+$ exchange: $K^+$—$H^+$ exchange on polymers **2a** (*1*) and **2b** (*2*) and $Na^+$—$H^+$ exchange on polymers **2a** (*3*) and **2b** (*4*).

polymer **2a** formed on the $Na^+$ matrix is shown in Fig. 1, *a*. A similar plot for polymer **2c** formed on the $Ba^{2+}$ matrix is presented in Fig. 1, *b*.

The threshold change in the $\log k^a{}_{Ba/H}(\bar{x}_{Ba})$ function at $\bar{x}_{Ba} = 0.5$, where the polymeric phase contains one $Ba^{2+}$ cation per elementary unit of the polymer, is seen in Fig. 1, *a*. The $\log k^a{}_{Ba/H}$ magnitude has two statistically different values in the intervals $0 < \bar{x}_{Ba} < 0.5$ and $0.5 < \bar{x}_{Ba} < 1$. We believe that the decrease in the selectivity coefficient of ion exchange is caused by the weakening of the interaction between polymer **2a** and the second $Ba^{2+}$ cation.

The sorption of barium by polymer **2c** synthesized on the $Ba^{2+}$ matrix (see Fig. 1, *b*) is characterized by a constant value of the ion-exchange selectivity coefficient in the whole concentration interval of metal cations incorporated into the polymer. All ion-exchange sites of the polymer are energetically equivalent. The selectivity coefficient value (see Fig. 1, *b*) coincides with its maximum value for the sorption of barium by polymer **2a** obtained on the $Na^+$ matrix. The decrease in the differential Gibbs energy of the ion exchange $Ba^{2+}$—$H^+$ in polymer **2c** as compared with that in polymer **2a** was calculated using the equation

$$\Delta\Delta G_{Ba/H} = -RT[\ln(k^a{}_{Ba/H})_{\mathbf{2c}} - \ln(k^a{}_{Ba/H})_{\mathbf{2a}}].$$

In the interval $0.5 < \bar{x}_{Ba} < 1$, this decrease is 6.5 kJ $mol^{-1}$. Thus, the affinity of polymer **2c** to the $Ba^{2+}$ cation at $\bar{x}_{Ba} > 0.5$ increases by 6.5 kJ $mol^{-1}$.

**Exchanges $Na^+$—$H^+$ and $K^+$—$H^+$.** The plots $\log k^a{}_{Na/H}(\bar{x}_{Na})$ and $\log k^a{}_{K/H}(\bar{x}_K)$ for polymers **2a** and **2b** synthesized on the $Na^+$ and $K^+$ matrices are presented in Fig. 2. It is seen that the corrected selectivity coefficients of ion exchange are higher for the polymers obtained on the matrices of the corresponding cations. The selectivity coefficient $k^a{}_{Na/H}(\bar{x}_{Na})$ is higher for polymer **2a** synthesized on the $Na^+$ matrix. The selectivity coefficient $k^a{}_{K/H}(\bar{x}_K)$ is higher for polymer **2b** obtained on the $K^+$ matrix. The differences are statistically reliable.

For the quantitative estimation of the enhancement of the affinity of polymers **2a** and **2b** to the matrix-forming cation, we considered the cation exchanges $Na^+$—$K^+$ and $Na^+$—$NH_4{}^+$.

**Exchange $Na^+$—$K^+$.** The differences in free energies of the ion exchange $Na^+$—$K^+$ on polymer **2a** synthesized on the $Na^+$ matrix and on polymer **2b** obtained on the $K^+$ matrix are illustrated in Fig. 3. Figure 3 contains the plots of $\log k^a{}_{Na/K}$ *vs.* molar fraction of the $Na^+$ cations in polymers **2a** and **2b**. The $k^a{}_{Na/K}$ values were calculated from the experimental data for the pairwise exchanges $Na^+$—$H^+$ and $K^+$—$H^+$ using the formula[16]

$$k^a{}_{Na/K}(\bar{x}_{Na}) = [k^a{}_{Na/H}(\bar{x}_{Na})]/[k^a{}_{K/H}(\bar{x}_K = 1 - \bar{x}_{Na})].$$

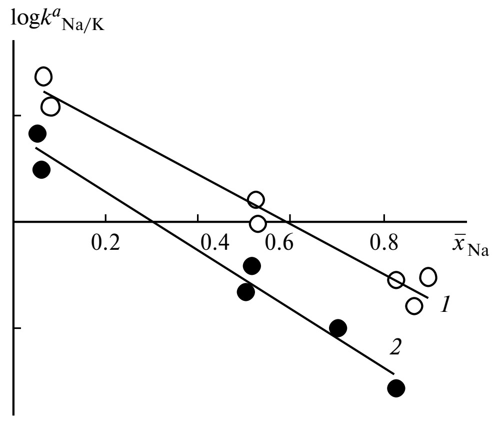

**Fig. 3.** Plots of $\log k^a{}_{Na/K}$ *vs.* molar fraction of $Na^+$ cations in polymers **2a** (*1*) and **2b** (*2*).

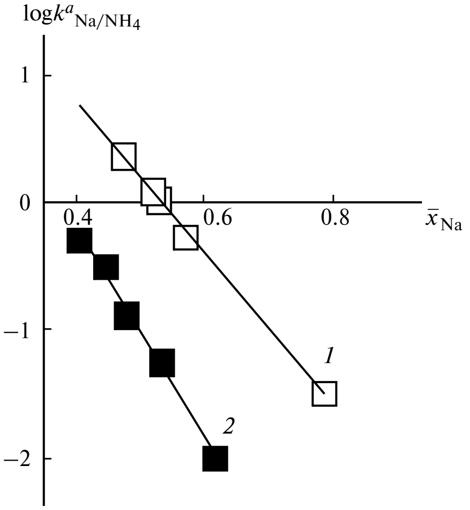

**Fig. 4.** Plots of $\log k^a{}_{Na/NH_4}$ *vs.* molar fraction of $Na^+$ cations in polymers **2a** (*1*) and **2b** (*2*).

The decrease in the differential Gibbs energy of the $Na^+$—$K^+$ cation exchange calculated by the equation

$$\Delta\Delta G_{Na/K} = -RT[\ln(k^a{}_{Na/K})_{\mathbf{2a}} - \ln(k^a{}_{Na/K})_{\mathbf{2b}}],$$

is approximately 8 kJ mol$^{-1}$. Most likely, the increase in the selectivity of ion exchange is caused by differences in the energies of configurations that appear upon the template synthesis of polymers **2a** and **2b** on the matrices of cations $Na^+$ and $K^+$.

**Exchange $Na^+$—$NH_4^+$.** The corrected selectivity coefficients of the $Na^+$—$NH_4^+$ cation exchange were determined by the formula

$$k^a{}_{Na/NH_4} = (\bar{m}_{Na}/\bar{m}_{NH_4})[m_{NH_4}\gamma_{\pm(NH_4Cl)}/m_{Na}\gamma_{\pm(NaCl)}].$$

The plots $\log k^a{}_{Na/NH_4}(\bar{x}_{Na})$ (Fig. 4) for polymers **2a** and **2b** synthesized on the $Na^+$ and $K^+$ matrices show that the $\log k^a{}_{Na/NH_4}(\bar{x}_{Na})$ functions are linear (correlation coefficients 0.99). The $(\log k^a{}_{Na/NH_4})_{\bar{x}_{Na}}$ values are higher for polymer **2a** synthesized on the $Na^+$ matrix; the differences are reliable. The difference in the $\Delta G_{Na/NH_4}$ values for polymers **2a** and **2b** is −7.5 kJ mol$^{-1}$.

Thus, the template synthesis of the network polymers based on *cis*-2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene enhances substantially (by 6—8 kJ mol$^{-1}$) their affinity to the matrix-forming cation.

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