Interaction of immobilized 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene with Na^+, Cs^+, and NH_4^+ ions and organic cations

G. N. Al'tshuler, L. A. Sapozhnikova, and L. P. Abramova*

Institute of Carbon Materials Chemistry, Siberian Branch of the Russian Academy of Sciences,
18 Sovetskii prosp., 650099 Kemerovo, Russian Federation.
Fax: +7 (384 2) 36 4966. E-mail: sorbent@sorben.kemerovo.su

The equilibrium in the system water—electrolyte—cross-linked polymer containing immobilized 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene was studied. Immobilized calixarene **1** was shown to form 1 : 1, 1 : 2, 1 : 3, and 1 : 4 compounds with inorganic cations (Na^+, Cs^+, and NH_4^+), and with organic cations (hexamethylentetramine and β-diethylaminoethyl *p*-aminobenzoate) 1 : 1 compounds are formed. The affinity of immobilized calixarene **1** increases in the series of cations: hexamethylenetetramine < Na^+, Cs^+, NH_4^+ < β-diethylaminoethyl *p*-aminobenzoate.

Key words: polymer, 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene, cations, hexamethylenetetramine, β-diethylaminoethyl *p*-aminobenzoate, equilibrium, selectivity.

Design and synthesis of biomimetic models make it possible to simulate some physicochemical processes occurring in nature. In this work, we studied the equilibrium in the system water—electrolyte—polymer phase-immobilized 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (immobilized calixarene).

Immobilized calixarene (**2**) was obtained by polycondensation of 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (**1**) with formaldehyde (Scheme 1).

Immobilized calixarene **2** can enter the cation exchange reaction

$$\overline{RH} + Cat^+ \rightleftharpoons \overline{RCat} + H^+ \tag{1}$$

(the dash above the symbol implies that the latter belongs to the polymer phase; Cat^+ is the sorbed cation), whose equilibrium constant (K) is described by the equation

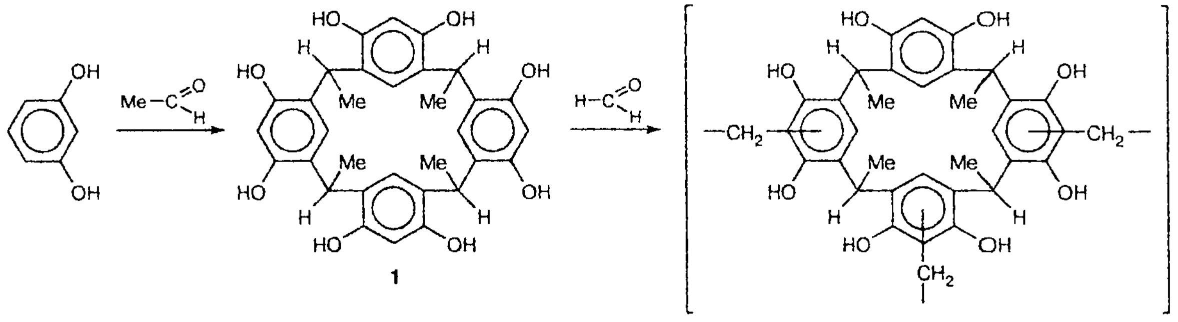
$$K = \frac{\bar{a}_{Cat} a_{H^+}}{\bar{a}_{H^+} a_{Cat}}, \tag{2}$$

$\bar{a}_i$ and a_i are the activities of components in the polymer and solution, respectively.

Experimental

Compound **1** was obtained by condensation of resorcinol with acetaldehyde.[1] For monohydrate **1**, found (%): C, 68.82; H, 6.35; calculated (%): C, 68.33; H, 6.05. M.p. 330 °C (decomp.). For identification of **1**, its acetate was synthesized. For the product obtained, found (%): C, 65.35; H, 5.78; calculated (%): C, 65.45; 5.45. M.p. 280 °C (decomp.), which corresponds to the published data.[3] Melting points were deter-

Scheme 1



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mined in sealed capillaries in an argon atmosphere. The geometric parameters of the computer model of compound **1** calculated by the Alchemy II (Tripos Associates Inc.) program[4] on PC K6 PR-200 correspond to the structure of cavitands according to the X-ray diffraction data.[1]

Immobilized calixarene **2** was obtained in 90% yield by catalytic resol polycondensation of compound **1** with formaldehyde. The content of fragments **1** in the polymer is 1.34 mol kg^{-1} (according to the data of elemental analysis and potentiometric titration). Particles with diameter <0.25 mm were sifted from the polymer batch, and the polymer was conditioned by alternating treatments with solutions of NaCl and HCl according to the common procedure of ion-exchanger conditioning[2] and washed with distilled water to pH 5.5 in the filtrate.

The following reagents were used: NaCl, $CsOH \cdot H_2O$, NH_4Cl, HCl, and H_2SO_4 (reagent grade); NaOH, NH_4OH, and CsCl (analytically pure grade); and β-diethylaminoethyl ether of *p*-aminobenzoic acid (Novocaine) corresponded to requirements for medicinal remedies.[5] Concentrations of solutions of NaOH and CsOH were determined by titration with HCl; the concentration of ammonium ions was determined by the formaldehyde method;[6] the concentration of hexamethylenetetramine (urotropin) was determined by titration with a solution of HCl in the presence of the mixed indicator (Methyl Orange and Methylene Blue); and the concentration of Novocaine was measured on an SF-26 spectrophotometer at the isobestic point (λ 274 nm).

The exchange capacity of the polymer was determined on columns by passing the solutions through the polymer bed until the concentrations of cations at the inlet and outlet of the column coincided. The H-form of the polymer was used for sorption of Na^+, Cs^+, and NH_4^+ ions and urotropin, and the NH_4-form was used for sorption of Novocaine. The value of exchange capacity was referred to 1 g of the polymer dried at 105 °C.

To obtain potentiometric titration curves, weighed samples of the polymer ($0.250 \pm 5 \cdot 10^{-4}$ g) were kept for 15—30 days with aqueous solutions (25 mL) of metal hydroxides with different concentrations or with 0.2 *M* solutions of chlorides of the corresponding metals (NaCl, CsCl, and NH_4Cl). Then the polymer was separated from the solution, and the pH of the solution was measured on an I-130 ionometer with an accuracy of 0.005 pH units. The number of cations absorbed by the polymer was determined by the difference of their concentrations in the starting and equilibrium solutions. In addition, the polymer was examined by elution of cations. The data on sorption and desorption coincided.

Selectivity coefficients of ion exchange[7] were determined upon sorption of organic compounds under dynamic conditions by passing solutions of Novocaine and urotropin through columns filled with the polymer until the equilibrium was achieved. The ionization degrees of organic compounds (for p*K* values, see Refs. 8 and 9) were taken into account in the calculation. Activity coefficients of ions in solutions of inorganic bases containing no salt additives were calculated by the limiting Debye—Hückel law. Average activity coefficients of ions in solutions containing salt additives were determined using reference data[10] on binary solutions of electrolytes.

The potentiometric titration curves of the polymer (Fig. 1) correspond to the titration curves of polyfunctional cation exchangers[11] of the polyphenolsulfonic acid type in an alkaline medium (pH > 7) when protons of phenolic hydroxy groups participate in the ion exchange reaction. The presence of salt additives[11] shifts the titration curves to lower pH values, and the ion exchange starts without addition of hydroxy ions as well. The type of cation exchanger (except for H^+) has almost no effect on the character of titration curves. As can be seen in Fig. 1, immobilized calixarene reacts with Na^+, Cs^+, and NH_4^+ hydroxides, and the composition of the compounds formed depends on the pH value of the equilibrium solution. The maximum number of metal ions sorbed by one molecule of immobilized calixarene approaches the overall dynamic exchange capacity, which is (with respect to 0.1 *M* NaOH) 4 moles per one molecule of immobilized calixarene.

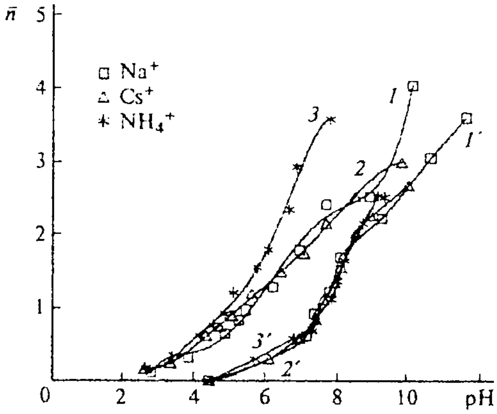

Fig. 1. Titration curves of polymer **2** containing immobilized calixarene **1** in the presence (*a*) and absence of salt additives (*b*): titration with solutions of NaOH (*1, 1′*), CsOH (*2, 2′*), and NH_4OH (*3, 3′*) with addition of 0.2 *M* solutions of NaCl (*1*), CsCl (*2*), and NH_4Cl (*3*), respectively ($\bar{n}$ is the number of absorbed ions per one mole of immobilized calixarene (**2**), mol mol^{-1}).

Results and Discussion

Equation (2) can be presented in the form

$$\log K = \log\frac{\overline{m}_{\mathrm{Cat}}}{\overline{m}_{\mathrm{H^+}}} + \log\frac{\bar{\gamma}_{\mathrm{Cat^+}}}{\gamma_{\mathrm{H^+}}} - \log(m\gamma_\pm)_{\mathrm{Cat}} - \mathrm{pH}\,. \quad (3)$$

Here $\bar{m}_i$ and m_i are the molalities of the component in the polymer phase and solution, respectively; $\bar{\gamma}_i$ is the activity coefficient of the cation in the polymer; and $\gamma_\pm$ is the average ion molal activity coefficient of the electrolyte in the solution.

Equation (3) is valid for the description of equilibria in systems containing immobilized calixarene and aqueous solutions of electrolytes with and without a salt additive. For equilibrium in systems with one type of cations, an unchanged counterion composition of the polymer phase, and a constant activity of water, the equilibrium constants remain unchanged, as well as the first and second terms on the right side of Eq. (3). The changes in the third and fourth terms in Eq. (3) on going from systems containing salt additives (″) to those containing no salt additives (′) are described by the equation

$$\left[\log\frac{(m\gamma_\pm)''_{\mathrm{Cat}}}{(m\gamma_\pm)'_{\mathrm{Cat}}}\right]_{\overline{m}_{\mathrm{Cat}},a_{\mathrm{w}}} = \left[\mathrm{pH}' - \mathrm{pH}''\right]_{a_{\mathrm{w}}}. \quad (4)$$

Table 1. Ratio of logarithms of equilibrium activities of exchanging cations in solution at unchanged counterion composition of polymer **2** containing immobilized calixarene **1**

$\bar{n}$*	Activity of cations in solution		$\left[\log\frac{(m\gamma_\pm)''_{\mathrm{Cat}}}{(m\gamma_\pm)'_{\mathrm{Cat}}}\right]_{a_w}$	pH′ − pH″
	$(m\gamma_\pm)'_{\mathrm{Cat}}$[a]	$(m\gamma_\pm)''_{\mathrm{Cat}}$[b]		
	Sorption of NH_4^+ cations			
1/2	$2.44 \cdot 10^{-4}$	0.1457	2.775±0.25	2.7
3/2	$8.25 \cdot 10^{-4}$	0.1461	2.25±0.20	2.4
5/2	$1.21 \cdot 10^{-3}$	0.1462	2.08±0.15	2.2
	Sorption of Cs^+ cations			
1/2	$1.62 \cdot 10^{-4}$	0.1406	2.94±0.25	2.7
3/2	$2.91 \cdot 10^{-3}$	0.1388	1.68±0.20	1.7
5/2	$0.97 \cdot 10^{-2}$	0.1411	1.16±0.15	1.1

* $\bar{n}$/mol mol^{-1} is the number of absorbed ions per one mole of immobilized ligand **1**.

[a] Without salt. [b] With salt addition.

For unchanged counterion composition of the polymer phase, the change in the abscissa in Fig. 1 at a constant ordinate corresponds in modulus to a change in the logarithm of the cation activity in the solution.

The equilibrium compositions of solutions of electrolytes at fixed values of cation concentrations in the polymer for the **2**—NH_4^+—water and **2**—Cs^+—water systems are presented in Table 1. They were calculated from the experimental values presented in Fig. 1. The data in Table 1 and experimentally observed coincidence of the numbers of sorbed cations and desorbed protons (equivalent character of the exchange) indicate that this is the cation exchange.

The selectivity coefficients $k_{\mathrm{Cat/H}}$ of the H^+—Cat^+ ion exchange on the polymer containing immobilized calixarene are presented in Table 2. They were calculated from the equation

$$k_{\mathrm{Cat/H}} = \frac{\bar{m}_{\mathrm{Cat}}}{\bar{m}_{\mathrm{H}}} \cdot \frac{m_{\mathrm{H}}}{m_{\mathrm{Cat}}} \qquad (5)$$

at the same content of sorbed cations ($\bar{n}$) in the polymer phase.

	Na^+	Cs^+	NH_4^+	Urotropin	Novocaine
$k_{\mathrm{Cat/H}} \cdot 10^4$	1.0	1.0	1.0	0.2	4.4

$\bar{n}$ = 0.5 mol mol^{-1}

The data presented show that the polymer containing immobilized calixarene exhibits selectivity increasing in the following series: urotropin < Na^+, Cs^+, NH_4^+ < Novocaine. The high selectivity of ion exchanger **2** with respect to Novocaine is most likely related to complex formation. In fact, the computer simulation shows that Novocaine cations are complementary to immobilized calixarene.

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