Brief Communications

The reaction of *C*-phenylcalix[4]resorcinarene-based polymer with quaternary ammonium and potassium cations

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The resol polycondensation of *C*-phenylcalix[4]resorcinarene with formaldehyde affords a cross-linked polymer possessing ion-exchange ability. The ion-exchange capacity of the polymer with respect to NH_4^+, Me_4N^+, Et_4N^+, Bu_4N^+, and K^+ cations was determined. The equilibrium in the systems *C*-phenylcalix[4]resorcinarene-based polymer—binary or ternary aqueous solutions of electrolytes was studied by potentiometric titration and quantum-chemical MNDO/PM3 calculation.

Key words: *C*-phenylcalix[4]resorcinarene, polymer, quaternary ammonium bases, potassium hydroxide, ion exchange, potentiometric titration, quantum-chemical calculation, MNDO/PM3 method.

Calixarenes possess unique biomimetic properties.[1] We have shown[2] that the tetramethylcalix[4]resorcinarene-based polymer can enter an ion-exchange reaction. In this work, we studied the equilibria in the systems *C*-phenylcalix[4]resorcinarene-based polymer—binary or ternary aqueous solutions of NH_4^+, Me_4N^+, Et_4N^+, Bu_4N^+, and K^+ hydroxides and chlorides.

The resol polycondensation of *C*-phenylcalix[4]resorcinarene (**1**) with formaldehyde affords the cross-linked polymer (**2**) (Scheme 1).

Polymer **2** can enter into the exchange reaction between the protons of the OH groups and cations of a solution. Due to substantial differences in the ionization constants of the OH groups of resorcinol ($pK_{a1} = 9.15$, $pK_{a2} = 11.33$),[3] four protons of the elementary unit of polymeric molecule **2** (one proton per resorcinol fragment) can be expected to participate in the cation exchange. The ion-exchange reaction is described by the equation

$$\overline{RH_4} + n\,Cat^+ + n\,OH^- = \overline{RH_{4-n}Cat_n} + n\,H_2O. \quad (1)$$

Here the line above the symbol designates belonging to the polymeric phase; Cat^+ is the sorbed cation; and n is an integer, $n \le 4$.

Experimental

C-Phenylcalix[4]resorcinarene was prepared by the condensation of resorcinol with benzaldehyde.[4] To identify **1**, its acetate was synthesized.[5] The melting points and IR spectra of **1** and its acetate were in correspondence with the published data.[4,5]

The polymer was obtained as spherical granules with an average diameter of 0.25 mm by the catalytic resol polyconden-

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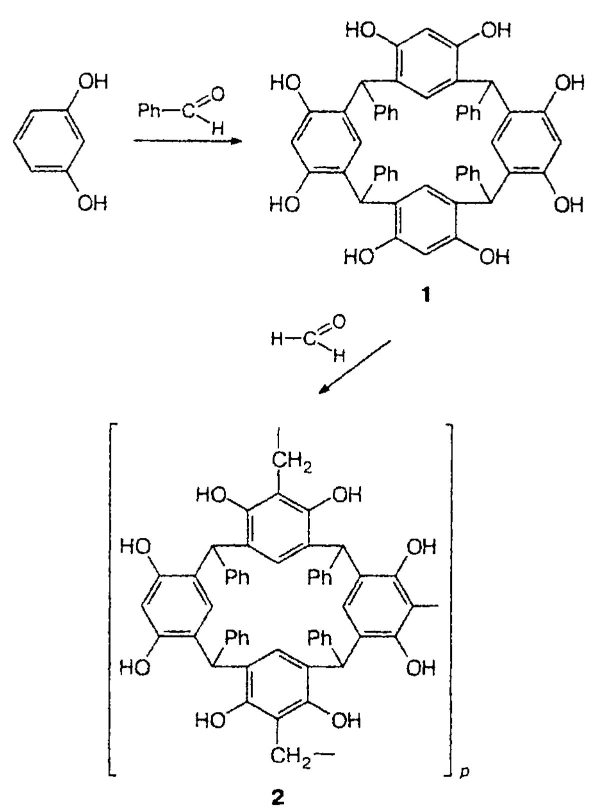
Scheme 1



sation of compound **1** and formaldehyde in a molar ratio of 1 : 3 (90% yield recalculated per **1**). IR spectrum of **2** (KBr), ν/cm^{-1}: 3404, 2920, 2860, 1600, 1472, 1212, 1072, 830. According to the data of the determination of the dynamic ion-exchange capacity, 1 kg of the dry polymer contained 0.9 moles of fragments of phenylcalix[4]resorcinarene. Compound **2** was conditioned by the procedure of ionite preparation[6] and washed with bidistilled water to pH 5.5 in the filtrate.

The dynamic ion-exchange capacity was determined and **2** was potentiometrically titrated according to the previously described procedure.[2] The experimental data are presented in Table 1 and Fig. 1.

Quantum-chemical calculations were performed by the MNDO/PM3 method with full optimization of the geometric parameters using the MOPAC 3.5 programs.

Results and Discussion

The total dynamic ion-exchange capacity of **2** with respect to 0.1 *M* KOH is equal to 3.6 mol kg^{-1}, which is comparable with the parameters[6] of high-acidity cationites and exceeds that of resorcinol-formaldehyde resins. It is seen in Table 1 that the ion-exchange capacity of **2** with respect to Me_4N^+ and Et_4N^+ cations is equal to the total dynamic ion-exchange capacity. For the sorption of tetrabutylammonium cations (diameter 9.98 Å), we observed a decrease in the ion-exchange capacity due, most likely, to a restricted accessibility of the sorption center of polymer **2**.

Table 1. Dynamic ion-exchange capacity of polymer **2**

Cation	Diameter* /Å	Dynamic ion-exchange capacity/mol kg^{-1}
K^+	2.66	3.6±0.2
Me_4N^+	6.94	3.6±0.2
Et_4N^+	8.00	3.6±0.2
Bu_4N^+	9.98	2.7±0.2

* Published data.[7]

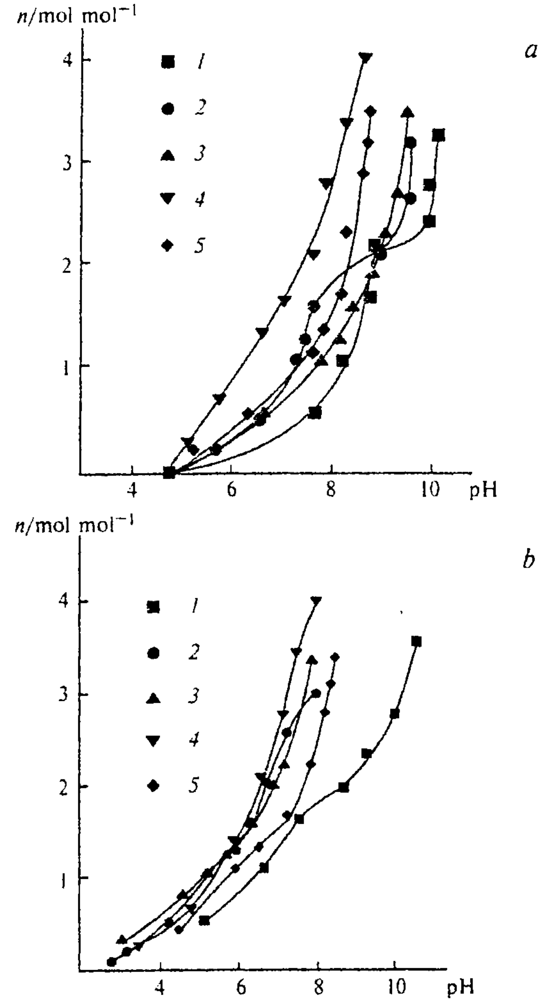


Fig. 1. Potentiometric titration curves of the calixarene-containing polymer with K^+ (*1*), Me_4N^+ (*2*), NH_4^+ (*3*), Et_4N^+ (*4*), and Bu_4N^+ (*5*) hydroxides in the absence (*a*) and presence (*b*) of the salt additive; *n* is the number of cations absorbed by the polymer calculated per elementary unit.

The potentiometric titration curves of **2** (Fig. 1, *a*) are similar to those[8] of the resorcinol-formaldehyde resins containing the active OH groups, but are shifted toward lower pH values. As can be seen in Fig. 1, *a*, the polymer exhibits a higher affinity to R_4N^+ cations than to K^+ cations. In particular, equal amounts of the Et_4N^+ and K^+ cations are sorbed (*n* = const) at the pH of the equilibrium solution of KOH, which exceeds the pH of the Et_4NOH solution by two units.

Table 2. Enthalpies of formation (ΔH_f°) calculated by the MNDO/PM3 method; the change in the enthalpy (ΔH_n^{ex}) for process (2)*; the enthalpies of particular stages ($\Delta H_n = \Delta H_n^{ex} - \Delta H_{n-1}^{ex}$) of reaction (2) at 298 K

Compound	n	$-\Delta H_f^\circ$	$-\Delta H_n^{ex}$	$-\Delta H_n$
		kcal mol^{-1}		
LH_4	0	138.6	—	—
LH_3K_1	1	225.3	144.0	144.0
LH_2K_2	2	317.0	293.0	149.0
LH_1K_3	3	395.4	428.7	135.7
LK_4	4	471.5	562.1	133.4

* For the calculation of ΔH_n^{ex}, we used ΔH_f° equal to 21.4, −17.5, and −53.4 kcal mol^{-1} for K^+, OH^-, and H_2O, respectively, obtained by the MNDO/PM3 method.

The experimental titration curves of the polymer (see Fig. 1, *a*) with K^+ and Me_4N^+ hydroxides are stepped. The inflection point corresponds to $n = 2$, where half of the ionogenic groups of the polymer have entered the ion-exchange reaction. The inflection of the n(pH) function is probably due to the differences in the equilibrium constants of the second ($n = 2$) and third ($n = 3$) stages of reaction (1).

We considered the change in the enthalpy ΔH^{ex} of the ion exchange *in vacuo* (reaction (2)), modeling reaction (1) and ignoring the solvation of the components.

$$LH_4 + n\,K^+ + n\,OH^- = LH_{4-n}K_n + n\,H_2O. \qquad (2)$$

Here $LH_{4-n}K_n$ is the compound formed due to the exchange of protons of the hydroxyl groups of **1** (LH_4) by potassium cations.

To determine ΔH^{ex}, we performed the quantum-chemical calculation of the enthalpies of formation ΔH_f° of possible structures* of **1** and $LH_{4-n}K_n$. The ΔH_f° values corresponding to the structures with the lowest enthalpies of formation are presented in Table 2.

It is seen from the data in Table 2 that the enthalpy of the first and second stages of overall reaction (2), *i.e.*, ΔH_1 and ΔH_2, is 10—15 kcal lower than ΔH_3 and ΔH_4. This is most likely reflected in the decrease in the ion-exchange constants of the third and fourth stages and, hence, in the appearance of the inflection point at $n = 2$ on the titration curves of the polymer with potassium and tetramethylammonium hydroxides.

The presence of a salt additive during the potentiometric titration of the polymer (see Fig. 1, *b*) shifts the titration curve toward higher equilibrium concentrations of protons. This indicates the presence of ion exchange at high concentrations of cations and in the absence of an alkaline agent. In addition, an increase in the ionic strength of the equilibrium solution aligns the stepwise character of the titration curves.

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* Geometric and energy parameters of the structures $LH_{4-n}K_n$ are presented on the Internet at http://www.kemsc.ru/chemistry.