Sorption of rubidium chloride by crown-containing polymer

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The kinetics and mechanism of the sorption of rubidium chloride from ethanol by granulated polymer containing immobilized dibenzo-18-crown-6 are studied. The sorption of RbCl is controlled by internal diffusion accompanied by complex formation in the polymer. The equilibrium constants of the sorption and diffusion coefficients of the electrolyte in the sorbent are calculated.

Key words: sorption, kinetics, mechanism, polymer, dibenzo-18-crown-6, RbCl, equilibrium constant, diffusion coefficients.

The sorption of electrolytes from polar solvents to a phase of gel crown-containing sorbents[1] synthesized by polycondensation of macrocyclic polyethers with formaldehyde as a block polymer[2] has previously been studied. It is shown[1] that when experimental data on the sorption of 1:1 electrolytes can be described by the linear dependence

$$\log \overline{m}_{\mathrm{MAn}} = a + b \log\left\{\left(E - \overline{m}_{\mathrm{MAn}}\right) m_{\mathrm{MAn}}^{2} \gamma_{\pm}^{2}\right\}, \qquad (1)$$

(where m_{MAn} and $\overline{m}_{\mathrm{MAn}}$ are the equilibrium molalities of electrolyte MAn in solution and crown-containing phase, respectively; $\gamma_{\pm}$ is the average ionic coefficient of activity; a and b are constants; and E is the concentration of crown ether in the adsorbent), the value of the angular coefficient b determines the type of equilibrium in the system. When the angular coefficient is equal to 0.5, the cations in the polymer phase react with immobilized crown ether to form complexes of 1:1 composition, and the anions exist in a free state. When the angular coefficient is equal to 1, only electroneutral complexes containing cations, anions, and ligands exist in the polymer.

In this work, the equilibrium constant of the sorption of rubidium chloride from ethanol by the granulated adsorbent based on dibenzo-18-crown-6 is determined, and diffusion coefficients of RbCl in the polymer phase are calculated.

Experimental

Anhydrous RbCl (reagent grade), ethanol containing 6.5 mol.% of water, and dibenzo-18-crown-6 prepared in the Novosibirsk Institute of Organic Chemistry, SB RAS, and characterized by the IR spectrum[3] were used.

The crown-containing sorbent was synthesized by the polycondensation of macrocyclic polyether with formaldehyde in the emulsion medium in the presence of a strong electrolyte. A polymer containing 69.2 % of carbon, 6.8 % of hydrogen, and crown ethers (2.4 $\mathrm{mol\,kg^{-1}}$) was obtained as spherical granules with controlled sizes. The integral curve of the size distribution of the spherical sorbent granules in the polymer sample is presented in Fig. 1. This sample was used for studying physico-

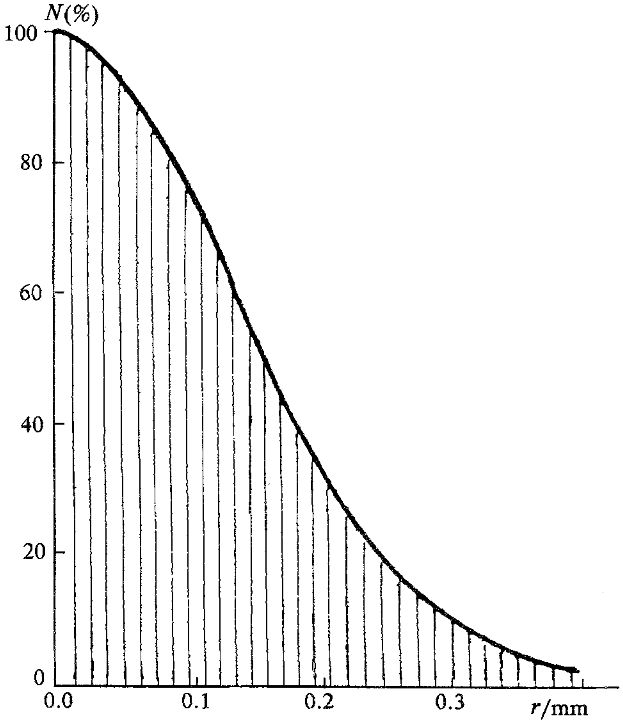

Fig. 1. Integral curve of the size distribution of spherical granules of the sorbent, *N* is the number of spherical particles of the sorbent with radii exceeding the *r* radius.

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chemical properties of the sorbent. The average diameter of the particles of the sorbent sample studied was calculated as the arithmetic mean of the sizes of 1000 spheres and was equal to 0.11 mm.

The equilibrium sorption of RbCl was studied under steady-state conditions at 298.15 K according to the procedure described previously.[4] The sorbent was washed with ten volumes of ethanol and thirty volumes of distilled water and dried over concentrated H_2SO_4 at 70°C to a static mass.

The sorption kinetics of RbCl were studied by the thin layer method[5] with sorption from an infinite volume of a solution of RbCl (10^{-3} mol dm^{-3}) at 298.15 K. The degree of conversion (f) was calculated by the formula

$$f = g_\tau/g, \qquad (2)$$

where g_τ/mol is the amount of RbCl sorbed to the time τ and g/mol is the equilibrium capacity of the sorbent layer for the sorption of RbCl from the solution. The error for the determination of the f value does not exceed 1 %. The experimental data obtained are presented in Fig.2.

Results and Discussion

It is known that the swollen RbCl-containing sorbent studied possesses ionic conductivity.[6] Therefore, the dissociated electrolyte exists in the polymer phase, and the calculated[5] electrochemical mobility of the chloride anion in the sorbent ($1.7 \cdot 10^{-6}$ cm^2 (V s)$^{-1}$) is higher than that of the rubidium cation ($3.4 \cdot 10^{-7}$ cm^2 (Vs)$^{-1}$).

Experimental data on the equilibrium distribution of rubidium chloride and ethanol in the coordinates of Eq. (1) are presented in Fig. 3. The treatment of these data by the least-squares method results in the dependence

$$\log \overline{m}_{\mathrm{RbCl}} = (2.6 \pm 0.2) + (0.53 \pm 0.03) \log\{(E - \overline{m}_{\mathrm{RbCl}}) m^2_{\mathrm{RbCl}} \gamma^2_{\pm}\} \qquad (3)$$

The correlation coefficient is 0.998, and the confidence interval is calculated with a probability of 0.95. The value of the angular coefficient in Eq.(3) shows[1] that the electrolyte in the polymer is completely dissociated and Rb^+ forms complexes with crown ether (CR) of 1:1 composition. Therefore, the transfer of RbCl to the granulated sorbent based on dibenzo-18-crown-6 from ethanol can be described by the following reaction:

$$\mathrm{Rb^+} + \mathrm{Cl^-} + \overline{\mathrm{CR}} \overset{K_4}{\rightleftharpoons} \overline{[\mathrm{RbCR}]^+} + \overline{\mathrm{Cl^-}}\,, \qquad (4)$$

where K_4 is the equilibrium constant, and the overscore indicates the polymer phase. The value of the logarithm of equilibrium constant (4) calculated with a confidence probability of 0.95 on the basis of the experimental data according to the formula

$$K_4 = \frac{\overline{m}^2_{\mathrm{RbCl}}}{\left(E - \overline{m}_{\mathrm{RbCl}}\right)\left(m_{\mathrm{RbCl}}\gamma_{\pm}\right)^2} \qquad (5)$$

is 4.86±0.05. The fact that $\log K_4$ is constant within the whole interval of equilibrium compositions confirms that Eq. (4) correctly describes the sorption of RbCl by the crown-containing polymer from alcoholic solutions.

When the reaction with the solvent is not taken into account, the sorption of rubidium chloride (4) can be presented by independent reactions of ion diffusion:

$$\mathrm{Rb^+} + \mathrm{Cl^-} \rightleftharpoons \overline{\mathrm{Rb^+}} + \overline{\mathrm{Cl^-}}\,, \qquad (6)$$

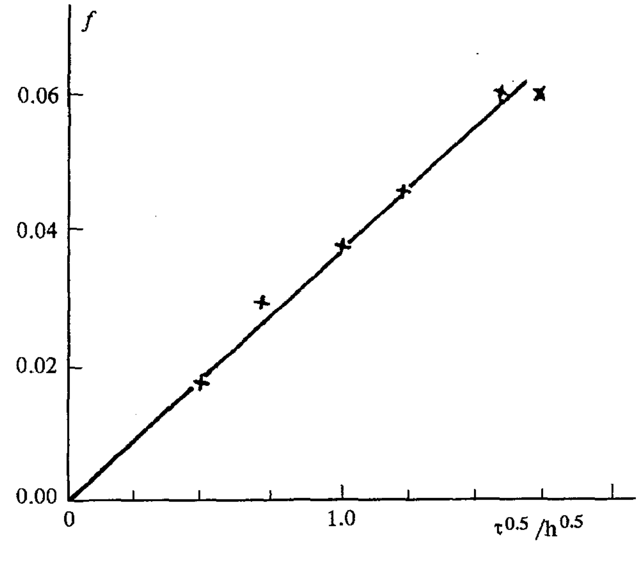

Fig. 2. Dependence of the degree of conversion (f) on time (τ) for the sorption of RbCl on the granulated crown-containing sorbent.

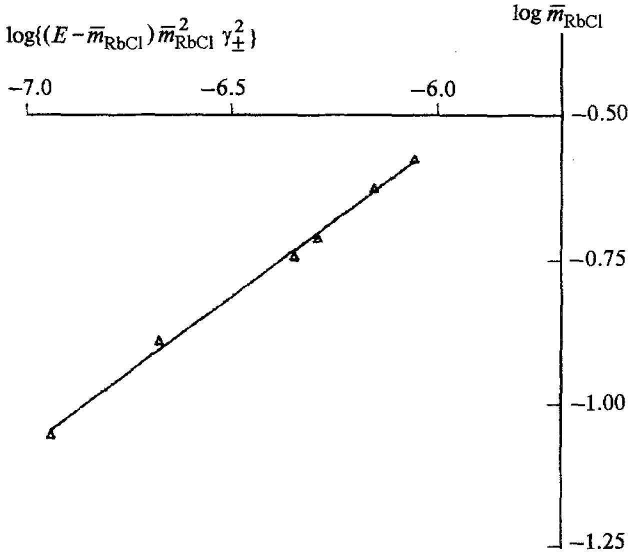

Fig. 3. Distribution of RbCl between the crown-containing polymer and ethanol in the coordinates of Eq. (1).

and complex formation in the sorbent phase:

$$\overline{\mathrm{Rb}}^{+} + \overline{\mathrm{CR}} \rightleftharpoons \overline{[\mathrm{RbCR}]}^{+} \ . \qquad (7)$$

Results of the kinetic measurements should be used for the interpretation of the mechanism of process (4). The analysis of the kinetic dependence presented in Fig. 2 (the function f *vs.* $\tau^{1/2}$ is linear, the coefficient of the linear correlation is equal to 0.99, and the function passes through the origin of the coordinates) in accordance with the corresponding criteria[7] testifies that the sorption of RbCl by the sorbent studied is controlled and can be formally described by the diffusion of the electrolyte in the polymer (in "gel").

The diffusion coefficient of RbCl is determined by the array of data presented in Fig. 2, using the known equation of internal diffusion treated by the iteration method:

$$f = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\exp\left(-\frac{Dn^2\pi^2\tau}{r^2}\right). \qquad (8)$$

Here D is the diffusion coefficient of the electrolyte, r is the radius of the sorbent grain, and τ is time.

The coefficients of the self-diffusion of ions are calculated by the Nernst—Einstein equation:

$$D_i = \frac{RT}{ZF}\,\frac{\varkappa t_i}{C_{\mathrm{R}}} \ , \qquad (9)$$

where D_i is the self-diffusion coefficient of an ion; R is the universal gas constant; T is the temperature; Z is the ion charge; F is Faraday's number; $\varkappa$ is the specific electric conductivity of the phase of the sorbent containing C_{R} moles of RbCl in a dm^3 of the polymer; and t_i is the transfer number of ion i (see Ref. 8).

The diffusion coefficient (D) of the RbCl electrolyte ($3 \cdot 10^{-12}$ cm^2 s^{-1}) obtained from the kinetic data is considerably lower than the values of the self-diffusion coefficients (D_i) of Rb$^+$ and Cl$^-$ ions ((5 to $8) \cdot 10^{-9}$ and (4 to $5) \cdot 10^{-8}$ cm^2 s^{-1}) calculated by the Nernst—Einstein equation. This inconsistency can be explained by Gupta's theory[9]: in systems with slow processes of internal diffusion accompanied by complex formation involving a diffusing component, a fast chemical reaction results in a decrease in the diffusion rate. In this case, Eq. (8) allows one to calculate only the effective diffusion coefficient (D_{eff}) related to the true diffusion coefficient of the electrolyte (D_{true}) by the correlation

$$D_{\mathrm{eff}} = \frac{D_{\mathrm{true}}}{P+1} \ , \qquad (10)$$

where P is the dimensionless value, which is equal to the ratio of the rate constants for direct and back reactions of complex formation,[9] and $P >> 0$.

In the system considered, D of the RuCl electrolyte calculated by Eq. (8) is much lower than D_i of Rb$^+$ and Cl$^-$ ions, because according to Gupta's theory, the slow diffusion of ions in "gel" is accompanied by fast complex formation between cations and a ligand in the sorbent phase (reaction (7)). Thus, the diffusion coefficient of an electrolyte calculated by Eq. (8) is in fact D_{eff}.

Gupta's theory makes it possible to estimate the K value for the formation of the complex between Rb$^+$ and crown ether in the polymer phase (reaction (7)). When the fact that the flows of cations and anions are the same ($D_{\mathrm{true}} = D_{\mathrm{Rb}}$) is taken into account, $P = (2$ to $3) \cdot 10^3$ according to Eq. (10). Since $\bar{m}_{\mathrm{RbCR}} << E$ and $\bar{m}_{\mathrm{CR}} \approx E$ within the interval of compositions studied, $P = E \cdot K_7$, where K_7 is the equilibrium constant of reaction (7). Therefore, $K_7 = 1 \cdot 10^3$ kg mol^{-1}. This value is comparable to the formation constant for the complex between Rb$^+$ and crown ether in organic solvents.

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