Sorption of copper salts by a polymer based on dibenzo-18-crown-6

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The sorption of $Cu(NO_3)_2$ and $CuCl_2$ by a polymer containing immobilized dibenzo-18-crown-6 from binary and multicomponent ethanol solutions was studied. In the sorbent phase copper exists as the Cu^{2+} cations, which form a 1:1 complex with the macrocyclic ligand. The constant of the transfer of $Cu(NO_3)_2$ from the solution to the polymer was calculated.

Key words: polymer, dibenzo-18-crown-6; $Cu(NO_3)_2$, $CuCl_2$, $AgNO_3$, sorption; equilibrium constant.

It is known[1] that in the sorption of alkali metals, thallium, and silver salts by crown-containing polymers from aqueous and alcohol solutions the single-charged cations form 1:1 complexes with the crown ethers in the sorbent phase, while the anions diffuse freely. The energetic equivalence of the adsorption sites and the absence of sorbate—sorbate interaction allow one to describe the equilibrium distribution of the 1:1 mixture of electrolytes in the sorbent phase and in the solution as a linear combination of the equilibria in crown-containing polymer—binary electrolyte solution systems.[2] In the present paper the transfer of the copper salts $CuCl_2$ and $Cu(NO_3)_2$ from binary and multicomponent solutions to a polymer containing functional groups of dibenzo-18-crown-6 has been considered.

Experimental

The crystal hydrates, $CuCl_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 2H_2O$ ("analytical reagent" grade), and $AgNO_3$ ("special purity") were used. The sorbent (polydibenzo-18-crown-6, PDB-18-C-6) was synthesized by polycondensation of dibenzo-18-crown-6 with formaldehyde.[3] Polymer samples with 1—3 mm diameter granules taken from the same reaction series (C, 67.5 % and H, 6.75 %) were used in the experiments; 1 kg of dry PDB-18-C-6 contained 2.4 mol of the crown ether. Before the sorption the sorbent was washed with ethanol (EtOH : PDB-18-C-6 = 10 : 1, v/v) and distilled water (H_2O : PDB-18-C-6 = 30 : 1, v/v), then dried over concentrated H_2SO_4 at 70 °C till constant mass was achieved. To prepare the solutions of electrolytes a mixture of EtOH and H_2O (93.5 : 6.5, w/w) containing HCl or HNO_3 ($5 \cdot 10^{-4}$ mol kg^{-1}), which retard the hydrolysis of $CuCl_2$ and $Cu(NO_3)_2$, respectively, was used. The concentration of the salts in the starting solutions was varied from $1 \cdot 10^{-3}$ to $4 \cdot 10^{-2}$ mol kg^{-1} and the variation in the alcohol : water ratio in the solvent did not exceed 0.1 wt. %.

The sorption of $CuCl_2$ from the ethanol solutions was carried out in the glass columns at 298 K under dynamic conditions. The attainment of equilibrium was established by the coincidence of the concentrations of the salt in the starting solution and in the filtrate.

The investigation of the sorption of $Cu(NO_3)_2$ and $AgNO_3$ was carried out by a static method. A sample of the polymer (3 and 1.5 g for the $Cu(NO_3)_2$ solution and a mixture of electrolytes, respectively) was brought to equilibrium with 50 mL of a solution. The state of equilibrium was assumed to have been achieved when the concentration of electrolytes in the solution remained invariable for 20 days (pH of the starting and equilibrium solutions were the same). The concentration of $Cu(NO_3)_2$ in the sorbent in equilibrium with the solution was monitored by the desorption. For this the sorbent was separated from the equilibrium solution, placed into an ion-exchange column, then washed with distilled water and then with a solution of Trilon B untill the disappearance of Cu^{2+} cations in the filtrate.

After the sorption of copper salts from the solutions of $CuCl_2$ and HCl or $Cu(NO_3)_2$ and HNO_3 the concentrations of Cu^{2+} and Cl^- ions in the solutions were determined by trilonometric titration and mercurimetry, respectively. The concentrations of Cu^{2+} and Ag^+ ions in solutions containing both copper and silver nitrates were determined by atomic absorption using an S-115-M1 spectrometer (λ = 324.7 nm) and by titration with the potentiometric control, respectively.

ESR spectra were recorded* using a Radiopan SE/X-2542 spectrometer. To separate the polymer granules from the solution the sorbent was placed into a Schott filter fitted in a centrifuge tube and then centrifuged for 20 min (υ = 3000 rpm). Then the accurately weighed sorbent samples were placed into standard quartz tubes (3 mm in diameter) and the ESR spectra were recorded. The α,α-diphenyl-β-picrylhydrazyl (DPPH) radical was used as an external standard. The spectrum of the sorbent containing a copper salt showed a signal corresponding to the Cu^{2+} ions (Fig. 1) which is absent in the spectrum of the original sorbent. The concentration of the Cu^{2+} cations in the sorbent was calculated by comparing the areas of the peaks of the standard sample of DPPH and those of the samples studied.

The statistical processing of the experimental data was carried out using the least-squares method. The confidence

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* ESR spectra were obtained by V. P. Barveno.

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interval was calculated at a probability of 0.95. Average ionic activity coefficients ($\gamma_{\pm}$) were calculated from the Debye—Hückel theory.

Experimental data on the equilibrium distribution of the salts in the sorbent phase and in the solution are presented in Tables 1 and 2.

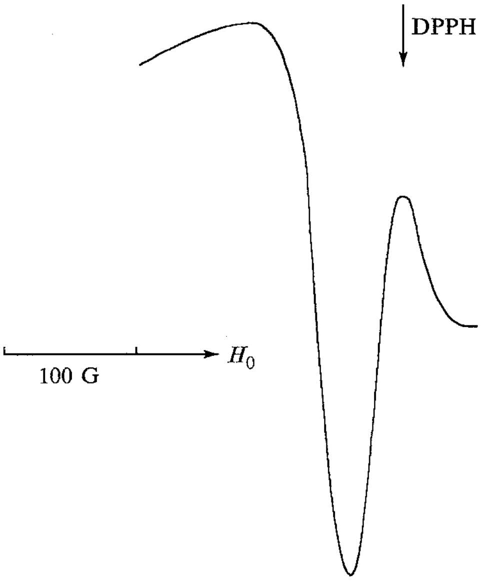

Fig. 1. The ESR spectrum of the polymer based on dibenzo-18-crown-6 containing $CuCl_2$ ($g = 2.0536 \pm 0.0005$).

Table 1. The equilibrium distribution of $CuCl_2$ in ethanol and in the crown-containing polymer at 298 K

Content of electrolytes in the solution		Composition of the polymer	
$m_{CuCl_2} \cdot 10^2$	$m_{HCl} \cdot 10^4$	$\overline{m}_{Cu} \cdot 10^2$	$\overline{m}_{Cl} \cdot 10^2$
1.89	5.0	5.2	12.0
2.51	5.0	6.6	13.1
3.04	5.0	7.8	15.8
3.67	5.0	7.9	16.0
4.27	5.0	8.6	17.2

Note: m_i and $\overline{m}_i$/mol kg^{-1} are the numbers of moles of the i-th component in 1 kg of a solution or in the dry polymer, respectively.

Table 2. The equilibrium distribution of $Cu(NO_3)_2$, $AgNO_3$, and HNO_3 between a solution and the crown-containing polymer after the sorption of the electrolyte mixture from ethanol at 298 K

Content of cations/mol kg^{-1}				$\log K_{Cu(NO_3)_2}$	$\log K_{AgNO_3}$
in the solution		in the polymer			
m_{Cu}	$m_{Ag} \cdot 10^4$	$\overline{m}_{Cu}$	$\overline{m}_{Ag}$		
0.0309	4.02	0.058	0.089	3.5	3.36
0.0306	4.94	0.048	0.121	3.5	3.44
0.0306	5.25	0.048	0.122	3.5	3.44
0.0308	8.34	0.041	0.180	3.6	3.47
0.0306	13.29	0.048	0.219	3.8	3.45
0.0316	18.54	0.021	0.281	3.5	3.42

Note: $m_{H^+} = 5.4 \cdot 10^{-4}$ mol kg^{-1}; $\overline{m}_{H^+} < 10^{-6}$ mol kg^{-1}.

Results and Discussion

As it is shown by the data in Table 1 the concentrations of both the copper and chloride ions in the sorbent in equilibrium with the $CuCl_2$ solution point to the existence of only Cu^{2+} ions in the polymer phase. According to the ESR spectroscopy data (see Fig. 1) the number of paramagnetic centers of Cu^{2+} in the polymer calculated by comparing the lines of DPPH and those of the sample is $3 \cdot 10^{22}$ per 1 kg of polymer, which corresponds to a concentration of $CuCl_2$ of 0.05 mol kg^{-1}. Moreover, it was shown that the concentration of $Cu(NO_3)_2$ in the PDB-18-C-6 calculated from the difference between the salt concentrations in the starting and equilibrium solutions coincides with the amount of $Cu(NO_3)_2$ desorbed (see Experimental). The data on the sorption—desorption equilibrium, the equivalent concentrations of Cu^{2+} cations and chloride anions in the polymer phase, and the coincidence of the data obtained from the numerous cycles of sorption and desorption carried out on one sample, together with the ESR spectroscopy data testify to the existence of copper in the polymer based on dibenzo-18-C-6 in the form of Cu^{2+} cations.

Assuming that the Cu^{2+} cations form 1:1 complexes with the macrocycles of the polymer phase one may describe the sorption of copper salts by Eqs. (1)—(3):

$$Cu^{2+} + 2\,An^- + \overline{CR} \xrightleftharpoons{K_1} \overline{[CuCR]}^{2+} + 2\,\overline{An}^- \,, \tag{1}$$

$$Cu^{2+} + 2\,An^- + \overline{CR} \xrightleftharpoons{K_2} \overline{[CuCRAn]}^{+} + \overline{An}^- , \tag{2}$$

$$Cu^{2+} + 2\,An^- + \overline{CR} \xrightleftharpoons{K_3} \overline{[CuCRAn_2]} \,, \tag{3}$$

where an overscore denotes the polymer phase; An^- is an anion; CR is the crown ether fragment of the polymer.

The equilibrium constants of Eqs. (1)—(3) may be obtained from Eqs. (4)—(6), respectively.

$$K_1 = \frac{4\,\overline{m}_{Cu}^3}{(E - \overline{m}_{Cu})m_{Cu}(m_{An})^2\gamma_{\pm}^3} \tag{4}$$

$$K_2 = \frac{\overline{m}_{Cu}^2}{(E - \overline{m}_{Cu})m_{Cu}(m_{An})^2\gamma_{\pm}^3} \tag{5}$$

$$K_3 = \frac{\overline{m}_{Cu}}{(E - \overline{m}_{Cu})m_{Cu}(m_{An})^2\gamma_\pm^3} \qquad (6)$$

Here m_i and $\overline{m}$ are the molalities of the i-th component in the solution and in the crown-containing phase, respectively; $\gamma_\pm$ is the average ionic activity coefficient; and E is the overall molality of the crown ether in the polymer.

Taking the logarithm of Eqs. (4)—(6) we obtain the linear equation

$$\log\overline{m}_{Cu} = a + b\log\left[(E - \overline{m}_{Cu})m_{Cu}(m_{An})^2\gamma_\pm^3\right]. \qquad (7)$$

The angular coefficients (b) in Eq. (7) are 1/3, 1/2, and 1 for Eqs. (1), (2), and (3), respectively.

The equilibrium distribution of $Cu(NO_3)_2$ and $CuCl_2$ in the solution and in the crown-containing phase is shown in Fig. 2 in the coordinates of Eq. (7). The coincidence between the experimental data and linear Eq. (7) (Table 3) points both to the formation of 1:1 coordination compounds in the polymer and to the energetic equivalence of the adsorption sites. The sorption of $Cu(NO_3)_2$ is described by a linear equation with the angular coefficient $b = 0.33$. Within the limits of experimental error this value corresponds to Eq. (1), when both complex cations $[CuCR]^{2+}$ and free anions are present in the polymer.

The experimental data on the transfer of $Cu(NO_3)_2$, $AgNO_3$, and HNO_3 to the sorbent from a multicomponent solution (see Table 2) showed that the affinity of the crown-containing polymer for the cations decreases in the order $Ag^+ > Cu^{2+} \gg H^+$. Knowing the regularities of $AgNO_3$ (see Ref. 1) and $Cu(NO_3)_2$ sorption from a binary solution one may describe the equilibrium distribution of the mixture of electrolytes in the solution and in the polymer phase by the system of equations (8),

$$\begin{cases} K_{Cu(NO_3)_2} = \dfrac{\overline{m}_{Cu}\overline{m}_{NO_3}^2}{(E - \overline{m}_{Cu} - \overline{m}_{Ag})m_{Cu}(m_{NO_3})^2\gamma_\pm^3} \\ K_{AgNO_3} = \dfrac{\overline{m}_{Ag}\overline{m}_{NO_3}}{(E - \overline{m}_{Cu} - \overline{m}_{Ag})m_{Ag}m_{NO_3}\gamma_\pm^2} \\ m_{NO_3} = m_{Ag} + 2\ m_{Cu} \\ \overline{m}_{NO_3} = \overline{m}_{Ag} + 2\ \overline{m}_{Cu} \end{cases} \qquad (8)$$

where K_{AgNO_3} and $K_{Cu(NO_3)_2}$ are the equilibrium constants of sorption from multicomponent solutions.

Table 2 presents the values of the constants calculated from Eqs. (8) based on the experimental data on the equilibrium composition of the phases after the sorption of $Cu(NO_3)_2$ and $AgNO_3$ by the crown-containing polymer from the ethanol solution. In the range of concentrations studied these values are constants identical to the equilibrium constants of the sorption of the corresponding electrolytes from binary solutions. After the sorption of $Cu(NO_3)_2$ and $AgNO_3$ from binary solutions these values are 3.5±0.1 (see Table 1) and 3.47±0.03 (see Ref. 1), respectively. Hence, it was confirmed that in the studied range of concentrations the sorption of $Cu(NO_3)_2$ and $AgNO_3$ is described by a mechanism according to which, in a sorbent based on dibenzo-18-crown-6, the cations form 1:1 coordination compounds while the anions diffuse freely.

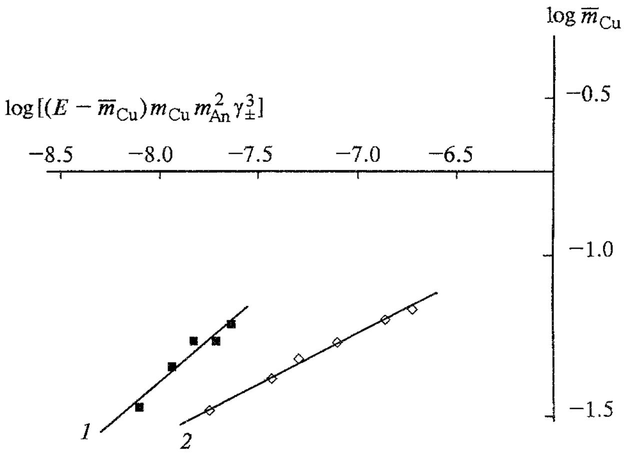

Fig. 2. Transfer of $Cu(NO_3)_2$ (*1*) and $CuCl_2$ (*2*) from ethanol to the crown-containing polymer in the coordinates of Eq. (7).

Table 3. Transfer of $Cu(NO_3)_2$ and $CuCl_2$ to the crown-containing sorbent from the ethanol solution

Electrolyte	r *	b**	$\log K_1$
$Cu(NO_3)_2$	0.99	0.32±0.03	3.5±0.1
$CuCl_2$	0.97	0.53±0.15	

* Correlation coefficient obtained from Eq. (7). ** Coefficient in Eq. (7).

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