Thermodynamics of sorption of KNO_3 by a crown-containing polymer

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The equilibrium of sorption of KNO_3 from aqueous solutions by a granular polymer containing immobilized dibenzo-18-crown-6 was studied. The thermodynamic characteristics for sorption of an electrolyte by a crown-containing polymer were determined. It was shown that the adsorption sites are energetically equivalent in the range of compositions studied.

Key words: polymer, dibenzo-18-crown-6; KNO_3, sorption; equilibrium constant; enthalpy; calorimetry.

To describe sorption of electrolytes by gelatinous crown-containing polymers, we proposed[1,2] equations taking into account the possibility of formation of 1 : 1 complexes of crown ethers with electrolytes in the polymer phase.

$$M^+ + An^- + \overline{CR} \overset{K_1}{\rightleftharpoons} \overline{[MCR]^+} + \overline{An^-}, \qquad (1)$$

$$M^+ + An^- + \overline{CR} \overset{K_2}{\rightleftharpoons} \overline{MCRAn}\ . \qquad (2)$$

Here M^+ is a cation; An^- is an anion; CR is the crown-ether fragment of the polymer; K_i are equilibrium constants; and the overbar denotes the polymer phase. Let us assume that the adsorption sites are energetically equivalent; then the equilibrium constants for reactions (1) and (2) can be found using the following expressions:

$$K_1 = \bar{m}_M{}^2/B,\ K_2 = \bar{m}_M/B, \qquad (3)$$

where $B = (E - \bar{m}_M)m_M m_{An}\gamma_\pm{}^2$; m_i and $\bar{m}_i$ are the equilibrium molalities of the components in the solution and in the crown-containing phase; $\gamma_\pm$ is the average ion activity coefficient; and E is the total molality of the crown ether in the polymer. Analysis of experimental data on the phase compositions of the polymer and the solution in the coordinates of the linear dependence, obtained by taking the logarithm of Eq. (3)

$$\ln\bar{m}_M = a + b\ln[(E - \bar{m}_M)m_M m_{An}\gamma_\pm{}^2], \qquad (4)$$

makes it possible to estimate the contributions of independent reactions (1) and (2) to the sorption of an electrolyte. If the equilibrium in the system is described by reaction (1), the coefficient b in Eq. (4) is equal to 0.5, and reaction (2) is characterized by a slope equal to 1.

In this work, we studied the equilibrium and determined the partial enthalpies for sorption of KNO_3 from aqueous solutions by a granular polymer containing 18-crown-6-ether fragments as functional groups.

The heat of sorption of an electrolyte by a polymer can be represented by the following equation:

$$Q = n_{in}h_{in} + (n_{in} - n_{tot})(\Delta\bar{H})_{\bar{m}_M} - n_{tot}h_{tot}, \qquad (5)$$

where Q is the heat of the process (determined by calorimetry); h_{in} and h_{tot} are enthalpies of dilution of solutions of KNO_3 with the initial and final concentrations, respectively; n_{in} and n_{tot} are the numbers of moles of the electrolyte in the solutions; $(\Delta\bar{H})_{\bar{m}_M}$ is the partial enthalpy of sorption of KNO_3 from an infinitely dilute solution by a polymer of the composition $\bar{m}_M$. The partial enthalpy of sorption is normally a function of the concentrations of components in the polymer; therefore, the $(\Delta\bar{H})_{\bar{m}_M}$ value corresponds, as a rule,[3] to the average electrolyte concentration over the range from $\bar{m}_{M,in}$ to $\bar{m}_{M,tot}$. It follows from Eq. (5) that

$$(\Delta\bar{H})_{\bar{m}_M} = \frac{Q + n_{tot}h_{tot} - n_{in}h_{in}}{n_{in} - n_{tot}}. \qquad (6)$$

The partial enthalpies of sorption, obtained from the data of calorimetric measurements, were compared with the values calculated from the temperature dependence of the equilibrium constants at fixed concentrations of the components in the polymer phase, as has been proposed[3,4] for sorption processes:

$$(\Delta\bar{H})_{\bar{m}_M} = -R\left(\frac{\ln K_{T_1} - \ln K_{T_2}}{1/T_1 - 1/T_2}\right)_{\bar{m}_M}. \qquad (7)$$

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Experimental

"Chemically pure" grade KNO_3 and a granular sorbent, synthesized by emulsion polycondensation of dibenzo-18-crown-6 ether with formaldehyde in the presence of a strong electrolyte,[5] were used in the experiments. The experiments were carried out using polymer samples with a grain diameter of 1—2 mm; 1 kg of the dry polymer contained 2.4 moles of the crown ether. The pre-adsorption preparation of the polymer included washing of the sorbent with a 10-fold volume of ethanol and a 30-fold volume of distilled water and drying to a constant weight.

The equilibrium of sorption of KNO_3 was studied under dynamic conditions. An aqueous solution of KNO_3 with a known concentration was filtered through a layer of the polymer. The equilibrium was considered to be attained if the electrolyte concentration in the initial solution and in several samples taken successively at the outlet of the column became equal. The content of the sorbed electrolyte in the polymer, calculated from the difference of the salt concentrations in the initial solution and in the filtrate, corresponded to the amount of desorbed electrolyte. To determine the concentration of KNO_3 in the solution, it was filtered through a layer of the AB-17-8 anion exchanger in the Cl-form, and then the ion-exchange column was washed with distilled water until the filtrate no longer contained the electrolyte. When the potassium nitrate solution passed through the ion exchanger, all the NO_3^- anions in the solution were replaced by Cl^- anions. The content of the chloride in the filtrate was determined by mercurimetry. The average ion activity coefficient was calculated from the Debye—Hückel equations. The experimental data on the equilibrium distribution of KNO_3 between the crown-containing polymer and aqueous-solution phases are presented in Fig. 1 in the coordinates of Eq. (4).

The heats of sorption were measured using a DAK 1-1A differential microcalorimeter under conditions of automatic compensation of the thermal emf at 298 K. A KSPR-4 potentiometer was used as the recording instrument. The microcalorimeter was calibrated using dissolution of chemically pure rubidium chloride in water. The value $\Delta H^\circ_{sol}(RbCl)$ = 17.01±0.03 kJ mol^{-1} at 298.15 K needed for calculations was taken from a reference book.[6] The measurements were carried out using standard (reference and test) 6 mL stainless-steel ampules, in which 5.3 mL of an aqueous solution of KNO_3 or 5.3 mL of water had been preliminarily placed. The swollen polymer ($(5—6) \cdot 10^{-5}$ kg) was introduced into the test ampule, while the solution or water ($(3—4) \cdot 10^{-5}$ kg) was introduced in the reference ampule pneumatically using polyethylene tubes. The relative error in the determination of Q did not exceed 2%. The error of determination of the partial heats depended on the error of determination of the overall heat of the process and the amount of the electrolyte desorbed or sorbed; therefore, the accuracy of determination of the partial heats increased in the case of desorption into the pure solvent. The enthalpies of dilution of the solution of KNO_3 were calculated using the reference data.[7] The enthalpies of sorption were calculated from Eq. (7) in the 298—363 K temperature range using the difference method for the investigation of the temperature dependences of equilibrium constants.[8] A solution of KNO_3 of a known concentration was passed through a column filled with the polymer (~0.5 g). After the equilibrium in the system was attained at 298±0.05 K, the temperature was raised, and the same solution was filtered through the polymer until a new equilibrium at 363±0.05 K was established. Thus, a single polymer sample was brought into equilibrium with a solution of constant composition at different temperatures. The change in the amount of the sorbed compound was determined from the difference between the content of KNO_3 in the filtrate after a new equilibrium state was attained and checked based on the subsequent desorption. The partial heats of sorption of KNO_3 by the polymer, containing 18-crown-6-ether fragments, found by calorimetry, and those calculated from the temperature dependence of the constants of sorption are listed in Table 1.

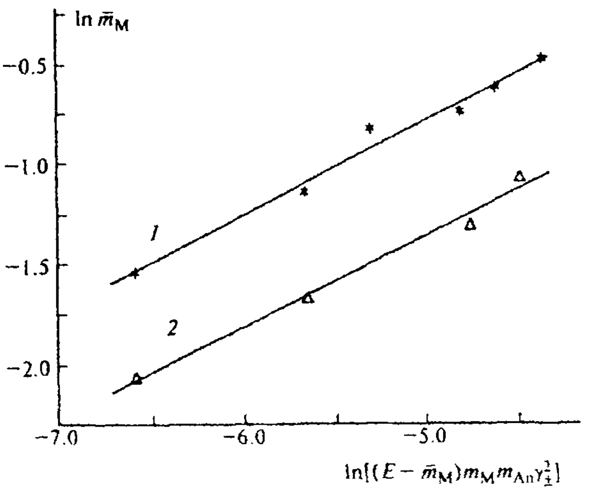

Fig. 1. Sorption of KNO_3 from aqueous solutions by the polymer based on dibenzo-18-crown-6 ether at 298 K (*1*) and 363 K (*2*) in the coordinates of Eq. (4).

Table 1. Enthalpy of sorption of KNO_3 from aqueous solutions by a granular polymer based on dibenzo-18-crown-6 ether

$\bar{m}_M$ $\frac{mol}{kg}$	$-(\Delta\bar{H})_{\bar{m}_M M}$ $\frac{kJ}{mol}$	Method*	Q /J	Change in the molality of KNO_3 in the polymer	
				$\bar{m}_{M,in}$	$\bar{m}_{M,tot}$
0.09	12.1±1.5	C	−0.0587	0	0.180
0.14	13.7±0.8	C	0.0317	0.224	0.064
0.18	14.3±1.5	T		0.224	0.134
0.31	14.5±1.5	T		0.394	0.233
0.32	13.7±0.2	C	0.298	0.562	0.086
0.36	13.4±0.3	C	0.160	0.562	0.157
0.46	13.5±1.5	T		0.562	0.358

* Method used to determine the enthalpy: C is calorimetry; T is calculation from Eq. (7).

The experimental data were processed using a confidence interval with a probability of 0.95.

Results and Discussion

Figure 1 shows the experimental data for the equilibrium compositions of the polymer and solution phases at 298 K and 363 K in the coordinates of Eq. (4). The least-squares processing of these results shows that they are described by linear equations. The correlation coefficients are 0.99. The linearity of the functions indicates that coordination compounds of the composition 1 : 1

are formed in the polymer and that the equilibrium constants are invariable over the whole range of concentrations of the electrolyte in the polymer studied. The slopes of the straight lines (0.46±0.06 at 298 K and 0.45±0.07 at 363 K) show that sorption of the electrolyte can be described by Eq. (1), according to which the cations form complexes of the composition $[KCR]^+$ in the polymer phase, while the anions remain uncoordinated. This model for the sorption of KNO_3 is consistent with the relatively high electrochemical mobility of anions in a crown-containing polymer.[9] The equilibrium constant for the sorption of potassium nitrate calculated from Eq. (3) based on the equilibrium compositions of the phases at 298 K was $\log K_{\rm I} = 1.53\pm0.04$.

It can be seen from Table 1 that sorption of KNO_3 from aqueous solutions by the polymer derived from the dibenzo-18-crown-6 ether ($\bar{m}_{\rm M,in} < \bar{m}_{\rm M,tot}$) is accompanied by heat evolution ($Q < 0$), whereas desorption of the electrolyte ($\bar{m}_{\rm M,in} > \bar{m}_{\rm M,tot}$) is accompanied by heat consumption ($Q > 0$). The differential enthalpies of sorption calculated from Eq. (7) and those determined by direct calorimetric measurements coincide and remain constant within the experimental errors over the whole range of polymer compositions. The facts that the equilibrium constant remains invariable and that the $(\Delta\bar{H})_{\bar{m}_{\rm M}}$ values do not depend on the determination method or on the degree of filling of the polymer with the electrolyte prove that in the range of compositions studied, the adsorption sites in the solid phase are energetically equivalent and the $K_{\rm I}$ value is the thermodynamic equilibrium constant characterizing the sorption process.[4]

Let us consider a hypothetical solution of KNO_3 of unit concentration possessing the properties of an infinitely dilute solution, the pure polymer ($\bar{m}_{\rm M} = 0$, $\bar{m}_{\rm CR} = E$), and a hypothetical polymer containing a stoichiometric amount of the sorbed electrolyte ($\bar{m}_{\rm M} = E$) as the standard states of the components. Then, provided that the sorption sites are energetically equivalent, the partial enthalpy of transfer of the electrolyte to the sorbent coincides with the standard enthalpy of sorption of the electrolyte. The change in the standard Gibbs energy (ΔG) and the entropy of sorption (ΔS) can be found from the equations

$$\Delta G°_{298} = -RT\ln K_{298} \text{ and}$$

$$\Delta S°_{298} = \frac{(\Delta H°_{298} - \Delta G°_{298})}{298}.$$

The calculation leads to the following values of the thermodynamic functions for the sorption of KNO_3 from aqueous solutions by a granular polymer containing 18-crown-6-ether units as functional groups: $\Delta G°_{298} = -(8.7\pm0.2)$ kJ mol^{-1}, $\Delta H°_{298} = -(13.7\pm0.8)$ kJ mol^{-1}, $\Delta S°_{298} = -16.8$ J mol^{-1} K^{-1}.

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