Hydration of complexes of 18-crown-6 with potassium nitrate or potassium picrate in the polymer phase

*G. N. Al'tshuler** *and O. N. Fedyaeva*

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

Adsorption of water vapor by granular polymer based on dibenzo-18-crown-6 and containing potassium nitrate or potassium picrate in the polymer phase was studied by the isopiestic method at 298 K. The adsorption of water vapor is described by isotherms corresponding (according to BDDT classification) to polymolecular adsorption with a high adsorptive potential. In terms of the Aranovich model of polymolecular adsorption, the monolayer capacity and differential heat of adsorption were calculated, and the stoichiometry of hydration of the potassium nitrate and potassium picrate complexes with immobilized crown ether was estimated.

Key words: hydration, stoichiometry, dibenzo-18-crown-6, polymer phase, KNO_3, potassium picrate.

We have previously studied[1] the thermodynamics and mechanism of interaction of crown-containing sorbents with electrolytes in polar solvents. The interaction of the crown-containing polymer phase with an electrolyte[1] with account for the solvent effect is described by the following scheme:

$$\overline{Cr \cdot mH_2O} + M_{aq}^+ + An_{aq}^- = \{\overline{CrM^+} + \overline{An^-}\} \cdot \overline{nH_2O} + aq. \qquad (1)$$

Here Cr is the macrocyclic ligand, An_{aq}^- and M_{aq}^+ are the anion and cation in the solution, and the dash designates the polymer phase. Process (1) can be expressed by a combination of independent reactions: the formation of a complex *in vacuo* (a), hydration of the macrocyclic ligand (b), cation (c), anion (d), and the complex formed (e).

$$\overline{Cr} + M^+ + An^- = \overline{CrM^+} + \overline{An^-}, \qquad (a)$$

$$\overline{Cr} + mH_2O = \overline{Cr_m \cdot mH_2O}, \qquad (b)$$

$$M^+ + aq = M_{aq}^+, \qquad (c)$$

$$An^- + aq = An_{aq}^-, \qquad (d)$$

$$\{\overline{CrM^+} + \overline{An^-}\} + nH_2O = \{\overline{CrM^+} + \overline{An^-}\} \cdot \overline{nH_2O}. \qquad (e)$$

The purpose of the present work is to study the contribution of hydration of the polymer to the Gibbs free energy of formation of potassium nitrate and picrate complexes with macrocyclic ligands in the polymer phase.

Experimental

Polymer obtained by the granular polycondensation of dibenzo-18-crown-6 with formaldehyde by the known procedure[2] was used. The polymer contained 2.4 moles of the crown ether per kg polymer.

Potassium nitrate (reagent grade) was used. Potassium picrate was obtained by neutralization of potassium hydroxide with picric acid. The content of picrate ions was determined by spectrophotometry at λ = 335 nm. The concentration of nitrate ions was determined by exchange for chloride ions on AB-17-8, and chloride ions were controlled by mercurimetry. Sorption of electrolytes was carried out under static conditions at 298 K.

Adsorption isotherms of water vapor were obtained by the isopiestic method at 298.15 K using the known procedure.[3] Solutions of sulfuric acid with different concentrations were used as the liquids creating a specified pressure of water vapor.

The experimental data on adsorption of water vapor by the polymer are presented in Fig. 1. The equation of polymolecular adsorption was used for processing of the experimental data:[4]

$$a_w/(1 - a_w)^{0.5}q = 1/q_m C + a_w/q_m, \qquad (2)$$

where a_w is the activity of water; q is the adsorption value; q_m is the capacity of the monomolecular layer; $C = [\exp(-Q/RT) - 1]\rho_v/\rho_l$, where Q is the pure heat of adsorption; ρ_v is the density of water vapor; ρ_l is the density of the liquid; T is temperature; and R is the universal gas constant. The experimental results were processed by the least-square method with confidence probability 0.95.

The integral free energy of polymer swelling was calculated by the equation:[5]

$$\Delta G_{sw} = -RT \int_0^{p_w/p_0} s\,d\ln(p_w/p_0) + sRT\ln(p_w/p_0), \qquad (3)$$

where the first term is the change in the free energy when 1 mole of the dry polymer is added to an infinitely large

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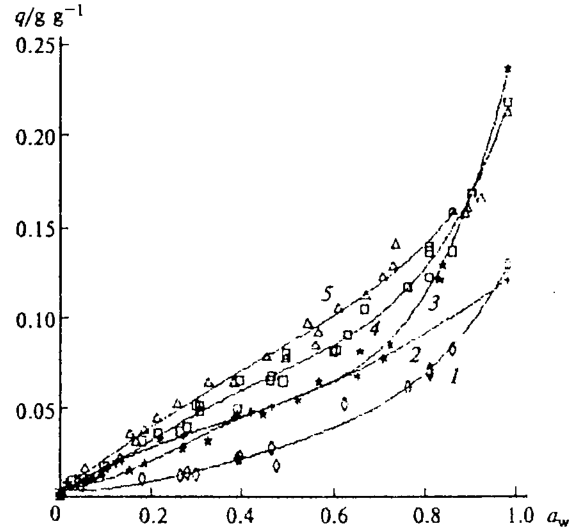

Fig. 1. Adsorption of water vapor by granular polymer based on dibenzo-18-crown-6 containing potassium picrate (0.18 mol kg^{-1}) (*1*); potassium nitrate (0.20 mol kg^{-1}) (*2*); potassium nitrate (0.48 mol kg^{-1}) (*3*); containing no electrolyte (*4*); isotherm of desorption of water vapor from polymer containing no electrolyte (*5*).

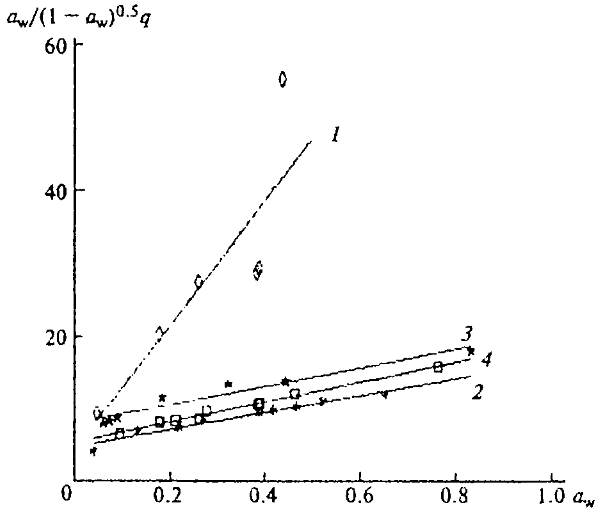

Fig. 2. Adsorption isotherms of water vapor by granular polymer containing potassium picrate (0.18 mol kg^{-1}) (*1*), potassium nitrate (0.20 mol kg^{-1}) (*2*), potassium nitrate (0.48 mol kg^{-1}) (*3*), and containing no electrolyte (*4*) in coordinates of Eq. (2).

amount of water vapor with the partial pressure p_w; the second term is the change in the free energy when s moles of water are transferred from the pure liquid under the p_0 pressure to an infinitely large amount of the polymer, which is in equilibrium with water vapor at the pressure p_w.

Results and Discussion

The shape of the experimental adsorption isotherms of water vapor (see Fig. 1) by the polymer containing potassium nitrate or picrate as complexes with the immobilized crown ether corresponds, according to the BDDT classification,[6] to polymolecular adsorption with a high adsorption potential.

The experimental data processed in the linear coordinates of Eq. (2) are presented in Fig. 2. As can be seen in Fig. 2, Eq. (2) describes the results obtained at an activity of water equal to 0.05—0.80. The value of the linear correlation coefficient is 0.94—0.99.

The results of processing of the experimental data on adsorption of water vapor by the crown-containing polymer in terms of the model of polymolecular adsorption (Eq. (2)) are presented in Table 1: q_m is the capacity of the monolayer in grams of adsorbed water per g dry polymer; nm is the capacity of the monolayer expressed as the number of adsorbed water molecules per crown ether group in the polymer; C is the parameter in the equation of the isotherm; Q is the heat of adsorption referred to one mole of adsorbed water.

The data in Table 1 show that in the first coordination sphere, approximately two water molecules (except complexes of potassium picrate) fall on one crown ether group. This corresponds to the data[7] of quantum-chemical calculations by the CNDO/2 method from a decrease in the intrinsic energy of coordination compounds of 18-crown-6 with K^+ cations hydrated by two water molecules compared to the nonhydrated complexes *in vacuo*. Perhaps, adsorbed water molecules are localized near polar functional groups of the crown ether or its complexes with electrolytes, and the introduction of potassium nitrate in the polymer phase does not change the capacity of the monomolecular layer.

Thus, in terms of the model of polymolecular adsorption used, we can estimate the stoichiometry of

Table 1. Parameters of adsorption of water vapor by polymer containing potassium nitrate or picrate in complexes with immobilized crown ether

Composition of complex		$q_m \cdot 10^{-2}$	n_m	C	$-Q$
Ligand	Electrolyte (mol kg^{-1})	/g_{H_2O} g^{-1}	/mol_{H_2O} mol_{Cr}^{-1}		/kJ mol^{-1}
Cr		7.01±0.22	1.62±0.05	2.73±0.08	28.87±0.07
Cr	KNO_3 (0.20)	7.2±0.7	1.69±0.15	3.83±0.25	29.71±0.16
Cr	KNO_3 (0.48)	8.7±0.9	2.00±0.20	1.39±0.26	27.2±0.5
Cr	KPic (0.18)	1.39±0.06	0.32±0.01	11.78±0.18	32.49±0.04

process (1). When potassium nitrate is chosen as the electrolyte, process (1) can be written in the form of the following reaction

$$\overline{\mathrm{Cr\cdot 2H_2O}} + \mathrm{K_{aq}}^+ + \mathrm{NO_{3aq}}^- =$$
$$= \{\ \overline{\mathrm{CrK}}^+ + \overline{\mathrm{NO_3}^-}\ \}\cdot \overline{\mathrm{2H_2O}} + \mathrm{aq}. \qquad (4)$$

The introduction of potassium picrate into the polymer (see Table 1, row 4) decreases the value of adsorption capacity q_m. This is probably due to the large size of the organic anion and its hydrophobicity. In the given case, the number of adsorbed water molecules per adsorption center (n_m) calculated in terms of the model[4] is a formal value. The heat of adsorption changes insignificantly.

The free energy ΔG of reaction (4) includes the energies of ligand—electrolyte interaction ΔG_a, solvation of ligand ΔG_b, solvation of cation ΔG_c and anion ΔG_d, and the free energy of solvation of the complex formed ΔG_e.

$$\Delta G = \Delta G_a - \Delta G_b - \Delta G_c - \Delta G_d + \Delta G_e \qquad (5)$$

We present the values of the Gibbs free energy (ΔG/kJ mol^{-1}) for process (4) and reactions (a), (b), (c), (d), and (e) using the transfer of potassium nitrate from water into the crown-containing polymer as the example (the molality of the complex in the polymer is equal to 0.48 mol kg^{-1}):

ΔG	ΔG_a	ΔG_b	ΔG_c	ΔG_d	ΔG_e
−3.8±0.1	−460.3	−50.3±1.0	−330.54	−288.70	−213±8

The value of the free energy of solvation of the ligand ΔG_b was obtained by Eq. (3) using the experimental data on adsorption of water molecules by the polymer containing no electrolyte (see Fig. 1, curve *4*). The values of energies of complex formation ΔG and hydration of cation ΔG_c and anion ΔG_d in the polymer phase are taken from Refs. 8 and 9. The free energy of solvation of the complex formed ΔG_e was calculated from the additive formula (6) for partial molar values:[10]

$$\Delta G_{sw} = x_1\Delta G_b + x_2\Delta G_e. \qquad (6)$$

Here ΔG_{sw} is the free energy of swelling calculated by Eq. (3) from the experimental data on adsorption of water vapor by the polymer containing the free ligand and complex in the polymer phase (see Fig. 1, curve *3*); x_1 and x_2 are the molar fractions of the free ligand and complex in the polymer phase, respectively; and ΔG_b and ΔG_e are the molar free energies of hydration of the components in the polymer phase. The ΔG_a value of the energy of interaction of potassium nitrate with the macrocyclic ether calculated by Eq. (5) agrees with the calculated data[7] on the formation of complexes with 18-crown-6 with similar compositions without account for conformational changes in the ligand.

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