

CHEMICAL THERMODYNAMICS
AND THERMOCHEMISTRY

Changes in Thermodynamic Functions in the Two-Temperature
Process of Concentration and Purification of Electrolyte Solutions
on KB-4P2 Polymethacrylic Ionite

E. A. Karpyuk, O. I. Korotkikh, and V. A. Ivanov

Department of Chemistry, Moscow State University, Moscow, 119991 Russia

e-mail: ivanov@phys.chem.msu.ru

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Abstract—Temperature dependences of the differential Gibbs energies and sorption enthalpies of water on KB-4P2 polymethacrylic ionite in Ca^{2+} , Mg^{2+} , Ni^{2+} , and Na^+ forms are determined. It is shown that during the two-temperature concentration and purification of electrolyte solutions, the content of the so-called “free” water in the ionite, the absorption of which by the latter is characterized by very low differential values of the Gibbs energy and enthalpy, changes with a change in the temperature of the polymethacrylic cationite suspension and electrolyte solution. It is established that the rather energy-consuming step of heating the phase of ionite and solution contributes mainly to the enthalpy of this process. Equations for the temperature dependences of the activity of water for solutions of sodium, magnesium, calcium, and nickel chlorides of various concentrations are given.

Keywords: solutions of electrolytes, KB-4P2 ionite, thermodynamic functions.

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INTRODUCTION

Polymer materials, which have the properties of effective absorbents of water and other hydrophilic liquids, are widely used in many fields. The possibility of using these materials for the concentration and purification of electrolyte solutions was mentioned in [1, 2]. It was noted that water absorption predominates when hydrophilic polymers are immersed in an electrolyte solution, and liquid can come from the polymer phase, as the solution is purified from the electrolyte considerably during the contraction of polymers as a result of a change in temperature or any other physicochemical parameters. So far, however, these processes have not been tested, and this area remains essentially unstudied.

We showed in [3, 4] that there is a substantial change in the concentration of solutions of doubly charged ion salts in the intergranular space of a grain copolymer suspension of methacrylic acid and divinylbenzene (KB-4P2 cationite) due to the change in temperature that produces a change in the polymer's degree of swelling. The two-temperature concentration and purification of electrolyte solutions was suggested, which involves continuously passing this solution through a column with polymethacrylic cationite upon a periodic change in temperature. As a result of the increase in temperature, ionite contracts in column, and water transfers from it to the intergranular solution and dilutes it. This solution is displaced into

the filtrate. Upon a further decrease in temperature, the ionite in the column swells again, absorbing water from the intergranular solution and concentrating it. As a result, a more concentrated solution is displaced into the filtrate. The obvious advantage of this method relative to conventionally used ion-exchange methods is that no auxiliary reagents are needed.

In this work, we assess the changes in thermodynamic functions during the interface rearrangement of water between ionite and solution in this two-temperature process.

THERMODYNAMIC FUNCTIONS
OF WATER SORPTION BY IONITE

A condition of chemical equilibrium for water sorption by ionite from an electrolyte solution ($\text{H}_2\text{O}=\overline{\text{H}_2\text{O}}$) is the correspondence of its chemical potentials in two phases:

$$\overline{\mu}_w = \overline{\mu}_w^\circ + RT \ln \overline{a}_w = \mu_w^\circ + RT \ln a_w = \mu_w. \quad (1)$$

Here and below, the overline denotes the parameters related to the phase of ionite; deg, as usual, denotes the standard chemical potentials; a_w , the activity of water; R , the universal gas constant; and T , the temperature.

In the thermodynamics of ion-exchange systems, the state of water in ionite in equilibrium with pure water under normal pressure is quite often the chosen

standard. The standard change in Gibbs energy upon water being distributed between the ionite and external

solution $\Delta G_w^\circ = \bar{\mu}_w^\circ - \mu_w^\circ = 0$ and the activities of water in the equilibrium phases is

$$\bar{a}_w = a_w. \quad (2)$$

The latter result obtained in this version of the standard states of water in phases is quite suited to the thermodynamics of systems with ionites and is used below. The differential thermodynamic functions of process of distribution of water related to the sorption of water by ionite of definite composition convey more information.

Let us consider that the composition of ionite, the definite exchange groups of which are in the form of ions A with charge z (we denote them as R_zA), corresponds to the equilibrium with a definite solution of electrolyte AX_z , so that their activities are limited by condition (2). Let us write the change in Gibbs energy upon the transition of dn_w mole of pure water under a pressure of 1 bar into this ionite with a water activity of \bar{a}_w , assuming that $dn_w = d\bar{n}_w$:

$$dG = (\bar{\mu}_w - \mu_w^\circ)dn_w = (\bar{\mu}_w^\circ + RT \ln \bar{a}_w - \mu_w^\circ)dn_w = RT \ln \bar{a}_w dn_w. \quad (3)$$

Value

$$\Delta G_{w,\bar{n}} = \bar{\mu}_w - \mu_w^\circ = \left(\frac{\partial G}{\partial \bar{n}_w} \right)_{p,T,\bar{n}_i \neq w} = RT \ln \bar{a}_w \quad (4)$$

is the differential change in Gibbs energy related to the definite composition of ionite, which is characterized by the number of moles of counterion with \bar{n}_{RA} ions fixed on the matrix of ionite, low-molecular electrolyte \bar{n}_{AX} sorbed superequivalently, and water \bar{n}_w . We can interpret $\Delta G_{w,\bar{n}}$ as the change in Gibbs energy upon the transition of 1 mol of water from the liquid phase in the standard state to an infinitely large amount of ionite of given composition. The differential Gibbs energy $\Delta G_{w,\bar{n}}$ is considerably more informative than the standard value ΔG° , since it reflects the reaction of water with an ionite of definite composition. According to relationship (4), $\Delta G_{w,\bar{n}}$ is calculated simply from the activity of water in a solution in equilibrium with an ionite of a given composition.

Let us divide (4) by RT and differentiate by temperature under constant pressure and composition of ionite using the familiar equation [5] written for the phase of ionite and the similar relationship for the aqueous phase:

$$\left[\frac{\partial(\bar{\mu}_w/T)}{\partial T} \right]_{p,\bar{n}} = -\bar{h}_w \frac{1}{T^2}, \quad (5)$$

where \bar{h}_w is the partial molar enthalpy of water in ionite, subscript indices p and \bar{n} denote the constancy of

the ionite phase for all components, and

$$\frac{\Delta H_{w,\bar{n}}}{RT^2} = \frac{1}{RT^2}(\bar{h}_w - h_w^\circ) = -\left(\frac{\partial \ln \bar{a}_w}{\partial T} \right)_{p,\bar{n}}. \quad (6)$$

Value $\Delta H_{w,\bar{n}} = \bar{h}_w - h_w^\circ$ is the differential change in enthalpy, and is associated (as the value $\Delta G_{w,\bar{n}}$) to an ionite of definite composition and is interpreted in the same way.

The constancy of the composition of ionite upon a change in temperature is possible if the water sorption at certain contents of counterions and the superequivalent sorption of electrolytes do not depend on temperature. We consider a case in which the swelling of polymethacrylic ionite of definite ionic composition depends on the temperature. The change in the pressure of the ionite phase (which can be observed upon a change in its swelling) can be ignored. This change in pressure (as high as 50–300 atm [6]) affects the values of the chemical potentials of the components in the liquid and solid phases very weakly [7]. Since the superequivalent sorption of electrolytes is low on polyacrylic and polymethacrylic gel ionites, the effect of temperature on it can be ignored. Accordingly, let us consider the chemical potential of the water in the ionite for the surface of phase equilibrium as the function $\bar{\mu}_w(T, p, \bar{n}_{RA}, \bar{n}_{AX}, \bar{n}_w(T, p, \bar{n}_{RA}, \bar{n}_{AX}))$ and differentiate $\bar{\mu}_w/T$ by temperature under constant pressure and the number of moles of all the components except water:

$$\begin{aligned} \left[\frac{\partial(\bar{\mu}_w/T)}{\partial T} \right]_{p,\bar{n}_i,\bar{n}_i \neq w} &= -\frac{\bar{\mu}_w}{T^2} + \frac{1}{T} \left(\frac{\partial \bar{\mu}_w}{\partial T} \right)_{p,\bar{n}_i,\bar{n}_i \neq w} \\ &= -\frac{\bar{\mu}_w}{T^2} + \frac{1}{T} \left(\frac{\partial \bar{\mu}_w}{\partial T} \right)_{p,T,\bar{n}_i,\bar{n}_i \neq w} \left(\frac{\partial \bar{n}_w}{\partial T} \right)_{p,\bar{n}_i,\bar{n}_i \neq w}. \end{aligned}$$

Let us use a relationship equivalent to (5):

$$\begin{aligned} \left[\frac{\partial(\bar{\mu}_w/T)}{\partial T} \right]_{p,\bar{n}_i,\bar{n}_i \neq w} &= -\frac{\bar{h}_w}{T^2} \\ &+ \frac{1}{T} \left(\frac{\partial \bar{\mu}_w}{\partial \bar{n}_w} \right)_{p,T,\bar{n}_i,\bar{n}_i \neq w} \left(\frac{\partial \bar{n}_w}{\partial T} \right)_{p,\bar{n}_i,\bar{n}_i \neq w}. \end{aligned} \quad (7)$$

The second addend on the right part of (7) reflects the change in the chemical potential of water in the ionite due to the change in the content of water with temperature at a constant composition of all other components.

Let us differentiate (4) by temperature using relationship (7) for the phase of ionite and a relationship analogous to (4) for the phase of the solution:

$$\begin{aligned} \frac{H_{w,\bar{n}}}{RT^2} - \frac{1}{RT} \left(\frac{\partial \bar{\mu}_w}{\partial \bar{n}_w} \right)_{p,T,\bar{n}_i,\bar{n}_i \neq w} \left(\frac{\partial \bar{n}_w}{\partial T} \right)_{p,\bar{n}_i,\bar{n}_i \neq w} &= \frac{\bar{h}_w - h_w^\circ}{RT^2} \\ - \frac{1}{RT} \left(\frac{\partial \bar{\mu}_w}{\partial \bar{n}_w} \right)_{p,T,\bar{n}_i,\bar{n}_i \neq w} \left(\frac{\partial \bar{n}_w}{\partial T} \right)_{p,\bar{n}_i,\bar{n}_i \neq w} &= - \left(\frac{\partial \ln \bar{a}_w}{\partial T} \right)_{p,\bar{n}_i,\bar{n}_i \neq w}, \end{aligned} \quad (8)$$

Coefficients of temperature dependences (10) for CaCl₂, MgCl₂, NiCl₂, and NaCl solutions

<i>m</i>	<i>-A</i>	<i>B</i>	<i>C</i>
CaCl ₂			
1.5	-0.01281	6.06905	1.07927 × 10 ⁻⁶
2.0	0.04499	7.973	1.5 × 10 ⁻⁹
2.5	0.09121	0.00103	2.07273 × 10 ⁻⁶
3.0	0.20959	9.49154	2.29714 × 10 ⁻⁶
3.5	0.39235	5.4844	2.04 × 10 ⁻⁶
MgCl ₂			
0.5	0.0234	0.344261	9.1044 × 10 ⁻⁸
1.0	0.05849	0.749157	2.36229 × 10 ⁻⁷
2.0	0.022954	-1.82406	1.21004 × 10 ⁻⁷
NiCl ₂			
1.0	0.04787	1.46274	3.73293 × 10 ⁻⁷
2.0	0.20852	-0.0716431	5.70974 × 10 ⁻⁷
2.5	0.2918	0.392649	9.4157 × 10 ⁻⁷
3.0	0.64123	-13.6	6.37186 × 10 ⁻⁷
3.5	0.69263	-9.82174	3.28068 × 10 ⁻⁷
NaCl			
1.0	-0.03124	3.87162	5.69827 × 10 ⁻⁷
1.5	0.01014	2.49493	3.69046 × 10 ⁻⁷
2.0	0.00907	4.81024	7.14056 × 10 ⁻⁷
2.5	0.02063	6.73397	9.99758 × 10 ⁻⁷
3.0	0.00651	7.1798	1.0643 × 10 ⁻⁶
3.5	0.0067	7.84598	1.17643 × 10 ⁻⁶
4.0	0.042232	0.00125	1.89142 × 10 ⁻⁶

where $\Delta H_{w,\bar{n}} = \bar{h}_w - h_w^\circ$ is the differential enthalpy of water sorption by ionite.

Since

$$\frac{1}{RT} \left(\frac{\partial \bar{\mu}_w}{\partial \bar{n}_w} \right)_{p, T, \bar{n}_i, \bar{n}_i \neq w} \left(\frac{\partial \bar{n}_w}{\partial T} \right)_{p, \bar{n}_i, \bar{n}_i \neq w} = \left(\frac{\partial \ln \bar{a}_w}{\partial \bar{n}_w} \right)_{p, T, \bar{n}_i, \bar{n}_i \neq w} \left(\frac{\partial \bar{n}_w}{\partial T} \right)_{p, \bar{n}_i, \bar{n}_i \neq w}$$

and

$$\left(\frac{\partial \ln \bar{a}_w}{\partial T} \right)_{p, \bar{n}_i, \bar{n}_i \neq w} = \left(\frac{\partial \ln \bar{a}_w}{\partial T} \right)_{p, \bar{n}_i, \bar{n}_w} + \left(\frac{\partial \ln \bar{a}_w}{\partial \bar{n}_w} \right)_{p, T, \bar{n}_i, \bar{n}_i \neq w} \left(\frac{\partial \bar{n}_w}{\partial T} \right)_{p, \bar{n}_i, \bar{n}_i \neq w},$$

we obtain relationship (6) in this case as well as a result of our transformations of (8). Because the activities of water in ionite and in a solution in equilibrium with it are equivalent, the value $\Delta H_{w,\bar{n}}$ is determined by the

effect of temperature on the activity of water in an equilibrium solution of definite composition.

ASSESSING THE DIFFERENTIAL THERMODYNAMIC FUNCTIONS OF THE SORPTION OF WATER BY KB-4P2 IONITE IN THE TWO-TEMPERATURE PROCESS OF THE CONCENTRATION AND PURIFICATION OF ELECTROLYTE SOLUTIONS

For sufficiently concentrated solutions (from 1.0 to 3.5*m*), the required values for the activities of water or the osmotic coefficients for various concentrations of electrolytes at various temperatures are taken from [8–11] for CaCl₂; [8, 9, 11, 12] for MgCl₂; [8, 9, 13] for NiCl₂; and [8] for NaCl. Because most of these data in the literature are given as values of the osmotic coefficient, the activity coefficients of water were determined using a familiar relation that reflects two methods of considering a nonideal state of a solution:

$$\mu_w = \mu_w^\circ + RT \ln a_w = \mu_w^\circ + \phi RT \ln N_w,$$

where ϕ is a rational osmotic coefficient and N_w is the molar fraction of water in solution, from which it follows that

$$\ln a_w = \phi \ln N_w = \phi \ln(1 - N_{AX}),$$

where N_{AX} is the molar fraction of dissolved substance AX_z. In the above range of concentrations, N_{AX} is taken as $\ll 1$; therefore

$$\ln(1 - N_{AX}) \approx -N_{AX} \approx -\frac{vmM_w}{1000},$$

where v is the number of ions in a molecule of electrolyte AX_z, m is the molality of the solution, and M_w is the molecular mass of the water. The obtained relation

$$\ln a_w \approx -\phi vmM_w/1000 \quad (9)$$

is used in practical calculations in order to determine the connection between activity and the osmotic coefficient, and the osmotic coefficient in it is referred to as the molal osmotic coefficient [8]. From the numerical values a_w determined using relation (10) at various temperatures, approximating equations for the dependence of $\ln a_w$ on temperature were obtained for solutions of sodium, magnesium, calcium, and nickel chlorides of different concentrations,

$$\ln a_w = A - 10^{-4}BT + CT^2, \quad (10)$$

the coefficients of which are given in the table. Using these equations, we then determined the temperature dependences $\Delta G_{w,\bar{n}}$ and $\Delta H_{w,\bar{n}}$ for water sorption by ionite whose composition corresponds to equilibrium with CaCl₂, NiCl₂, MgCl₂, and NaCl solutions with different concentrations according to relationships (1), (4), and (8).

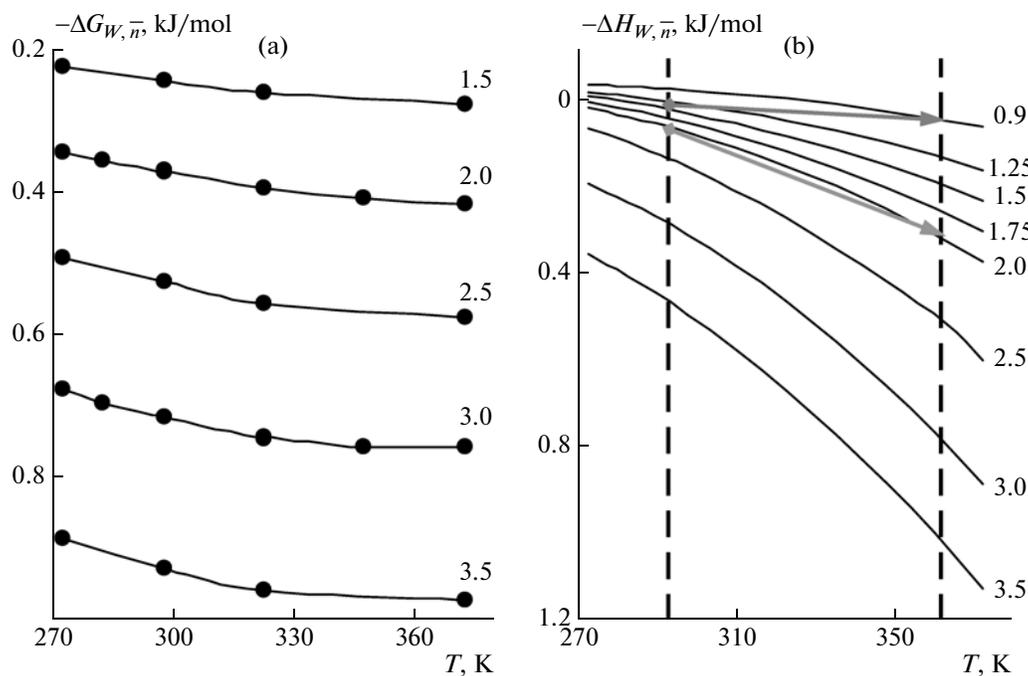


Fig. 1. Temperature dependences (a) $\Delta G_{w, \bar{n}}$ and (b) $\Delta H_{w, \bar{n}}$ of water sorption by ionite in equilibrium with CaCl_2 solution at various concentrations m .

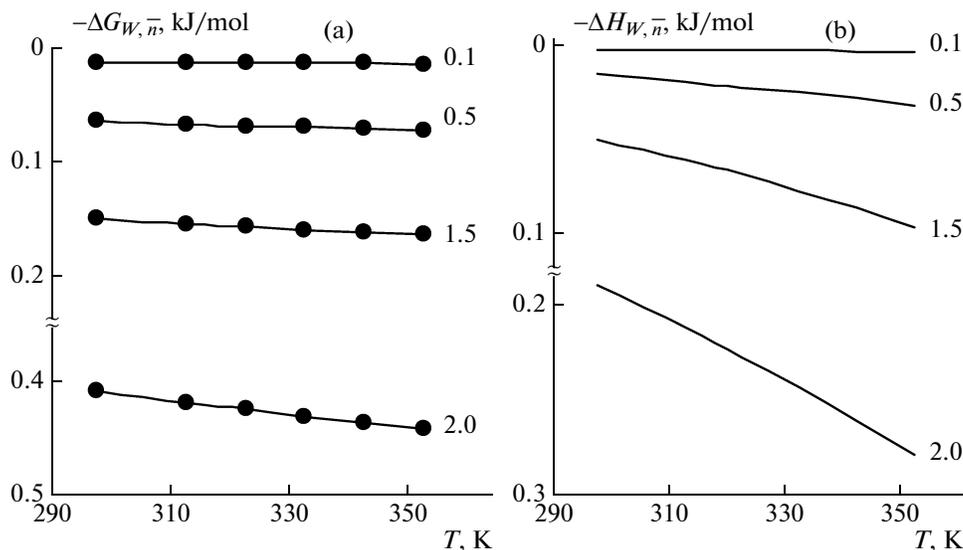


Fig. 2. Temperature dependences (a) $\Delta G_{w, \bar{n}}$ and (b) $\Delta H_{w, \bar{n}}$ of water sorption by ionite in equilibrium with MgCl_2 solution at various concentrations m .

As follows from data in Figs. 1–3, water sorption by ionite whose composition corresponds to equilibrium with CaCl_2 , MgCl_2 , and NiCl_2 solutions with concentrations of 1.0 to 3.5 m is characterized by rather low values of $\Delta G_{w, \bar{n}}$ and $\Delta H_{w, \bar{n}}$. For ionite in the Na form, value $\Delta H_{w, \bar{n}}$ generally differs insubstantially from 0 (Fig. 4). This means that in the two-temperature con-

centration and purification of electrolyte solutions [3, 4], a change in temperature leads to rearrangement of the water bonded very weakly to ionite between phases (usually referred to as “free” water). Our temperature dependences $\Delta H_{w, \bar{n}}$ allow us to assess the changes in enthalpy at each of the steps of the two-temperature concentration and purification of solutions.

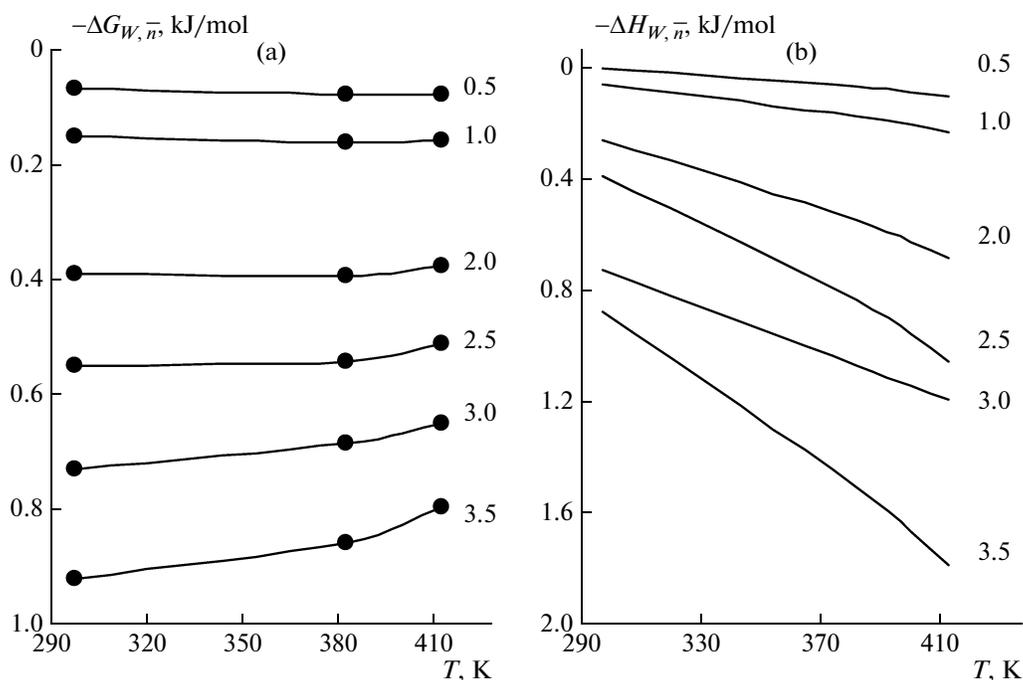


Fig. 3. Temperature dependences (a) $\Delta G_{w, \bar{n}}$ and (b) $\Delta H_{w, \bar{n}}$ of water sorption by ionite in equilibrium with NiCl_2 solution at various concentrations m .

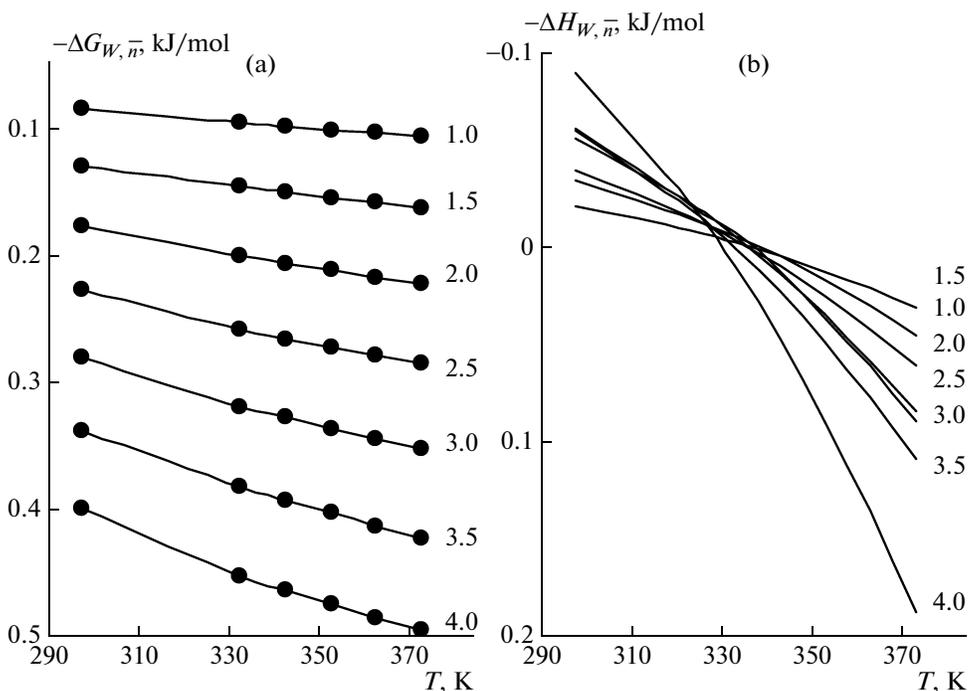
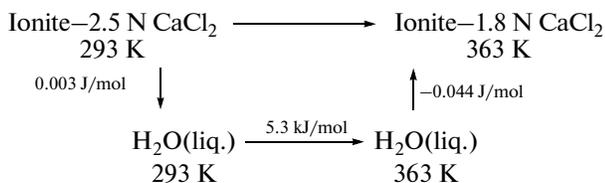


Fig. 4. Temperature dependences (a) $\Delta G_{w, \bar{n}}$ and (b) $\Delta H_{w, \bar{n}}$ of water sorption by ionite in equilibrium with NaCl solution at various concentrations m .

Let us assume that a dense layer of KB-4P2 ionite in the Ca-form is initially in equilibrium with a 2.5 N ($\sim 1.25m$) solution of CaCl_2 at a temperature of 293 K. After increasing the temperature of the system to 363 K,

the fraction of weakly bonded water from ionite transitions to an external solution, and (as was demonstrated experimentally in [3]) the solution in intergranular space is then diluted to 1.8 N ($\sim 0.9m$). Let us

write this step of the two-temperature process as three consecutive steps: the elimination of 1 mole of water from ionite equilibrium with a 2.5 N solution of CaCl_2 as pure liquid water at 293 K, its heating to 363 K, and the subsequent transition of 1 mol H_2O from the liquid phase at 363 K to ionite equilibrium with 1.8 N CaCl_2 solution at 363 K:



According to the data from Fig. 1, the change in enthalpies in the first and third steps are 0.003 and -0.044 kJ/mol, respectively. These values are far less than the heating enthalpy of liquid water in this temperature range, which is 5.3 kJ/mol with allowance for the averaged value of the heat capacity (75.4 J/(mol K) [14]). In the same experiment with a 4.0 N ($\sim 2.0m$) CaCl_2 solution, in which the concentration of solution fell to 3.5 N ($\sim 1.75m$) [3] with an increase in temperature, the changes in enthalpy in the first and third steps was 0.058 and -0.322 kJ/mol. In Fig. 1b, the arrows indicate the trajectories of the change in enthalpies in these processes.

CONCLUSIONS

Our data show that temperature changes the content of so-called “free” water in ionite in the proposed two-temperature process for the concentration and purification of solutions, the absorption of which by the ionite is characterized by very low values of enthalpy. The rather energy-consuming step of heating the phase of ionite and solution contributes largely to the enthalpy of this process. This analysis was performed for the concentration and purification of a solution of CaCl_2 , but a similar picture is observed for

solutions of sodium, magnesium, and nickel chlorides as well. If we compare these data with the vaporization enthalpy of water (~ 40 kJ/mol), we may conclude that the two-temperature concentration of electrolytes on ionites can be more advantageous energetically than the widely used method based on the vaporization of solvent. It should also be noted that low-potential waste heat can be used for the process we described in [3].

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