

## Superheated solutions in dual-temperature ion exchange separations

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### ABSTRACT

The problem of experimental determination of the differential enthalpy of ion exchange is considered. The determination of the enthalpy from experimental equilibrium coefficients is characterized by a high degree of error. A considerably more accurate method of determination of the differential enthalpy of ion exchange on selective ion exchangers is proposed. The method is based on the analysis only of the composition of the solution in the equilibrium system at two temperatures. The influence of temperature on the exchange of mono- and divalent ions on polyacrylic and polymethacrylic cation exchangers within the range from 273 K to 400 K is studied. It is shown that for all exchangers under study the differential enthalpy linearly increases with temperature. The role of the increase of  $\Delta H_{\bar{n}}$  with temperature in the process of a single-step dual-temperature separation is estimated. It is found that the increase of the upper temperature boundary leads to a very sharp increase of the degree of dual-temperature separation. This effect is most pronounced in superheated solutions. It is shown that when predicting changes in selectivity with temperature and the extent of purification of solutions of alkali metal salts from admixtures of divalent ions, it is necessary to take the temperature dependence of the ion exchange enthalpy into account.

### 1. Introduction

In recent years, in separation science and in particular in ion-exchange chromatography an interest has arisen in the use of “superheated water” (at temperatures above 373 K) [1–3]. It is explained by the fact that the dielectric constant of water considerably decreases with temperature, so at temperatures above 373 K some properties of water approach the properties of some organic solvents or water-organic solutions. Therefore, with the increase of temperature the same effects can be achieved as with the use of organic liquids as eluting solutions.

However, for a long time the role of temperature in ion-exchange separation processes was underestimated, as we already pointed out in our works [4,5], as did other scientists working in various areas where ion exchangers are used, for example, in ion chromatography [6]. In the basic monographs on ion exchange [7–9] it was generally stated that the changes of enthalpy in the reactions of ion exchange are usually small and do not exceed 1–2 kcal/equiv., so the role of temperature in ion exchange is relatively small. Such a conclusion was partly due to the fact that the main attention was focused on polystyrene resins with strongly acidic and strongly basic exchange groups.

The study of this problem for ion exchangers with complexing groups and other types of highly selective ion exchangers made it possible to detect ion exchange systems in which the temperature had a

sufficiently strong effect on the ion-exchange equilibrium. Using this effect, it was possible to create a number of separation processes in which auxiliary reagents are not used. In addition to the well-known dual-temperature process for partial desalting of natural waters [10,11] a number of new dual-temperature separation processes were developed, such as reagentless processes of purification of concentrated solutions of alkali metal salts from admixtures of alkaline earth ions [12,13], separation of alkali metal salts [14,15], concentrating of potassium from sea water on a natural zeolite to produce potassium fertilizers [16–19], concentrating of bromide from sea water [17] and iodide from natural brines [20,21], extraction of thiocyanates from solutions [22] and others. The review of these works as well as theoretical considerations of dual-temperature separation are presented in [23–26]. These processes are based on the fact that the sorption of the components of interest from the solutions is carried out at a temperature providing increased selectivity, and the displacement from the ion exchanger is achieved by the same initial solution, but at a different temperature that provides a lower selectivity. It is important to emphasize that in all these processes, as well as in studying the effect of temperature on the ion-exchange properties of materials, the upper temperature limit did not exceed 373 K.

When discussing the effect of temperature on ion-exchange selectivity, in most cases the average value of the enthalpy of the ion exchange reaction for a certain temperature interval is used. In many

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cases it is justified by the fact that the dependence of the logarithm of the equilibrium constant (or equilibrium coefficient) on reciprocal temperature is linear [27–31]. However in many cases the authors do not even consider the character of this dependence and simply calculate the mean value.

At the same time already in the classical works of Bonner [32–34] it was shown that in the cases of the exchange of ions of sodium, ammonium, copper and thallium for the hydrogen ion, and also in some cases of reciprocal exchange of divalent ions on sulfonic resins with 8% and 16% of divinylbenzene (DVB) in the range from 273 K to 373 K the dependencies of the logarithm of the equilibrium constant on reciprocal temperature are not linear and the standard enthalpy changes are not constant. Variations of the enthalpy of ion exchange with temperature were also found in works [35,36] for the exchange of various cations in trace quantities on H<sup>+</sup>- and Na<sup>+</sup>-forms of sulfonic cation exchanger with 12% DVB and for the exchange of trace quantities of Br<sup>-</sup> on Cl<sup>-</sup>-form of a strongly basic anion exchanger with 10% DVB.

The character of the influence of temperature on the ion exchange selectivity was also studied in [2,3] in connection with the use of “superheated water” in ion exchange chromatography, and the variability of the enthalpy upon exchange of alkali and alkali earth cations on sulfonic ion exchangers was also noted.

Previously, we found a very significant increase of the enthalpy of ion exchange with temperature for Ca<sup>2+</sup> and Na<sup>+</sup> on some industrial polymethacrylic and polyacrylic cation exchangers [5,37]. Some of this data pertain to the region of “superheated” solutions with the temperature above 373 K. In the present work we present new data on the influence of temperature on the enthalpy of ion exchange reactions Ni<sup>2+</sup> – Na<sup>+</sup> and Mg<sup>2+</sup> – Na<sup>+</sup>, analyze the role of this influence in the dual-temperature separation processes, and also discuss the possibility of the use of superheated solutions in dual-temperature separations of electrolytes. First we will give the necessary information on thermodynamics of ion exchange.

### 1.1. Thermodynamics of ion exchange

We will use the nomenclature recommended in [38].

For the exchange of ions A and B with the charges  $z_A$  and  $z_B$  on an ion exchanger

$$\frac{1}{z_A} \bar{A}^{z_A} + \frac{1}{z_B} \bar{B}^{z_B} = \frac{1}{z_A} A^{z_A} + \frac{1}{z_B} B^{z_B} \quad (1)$$

the thermodynamic equilibrium constant

$$K = \frac{\bar{a}_B^{1/z_B} \cdot a_A^{1/z_A}}{\bar{a}_A^{1/z_A} \cdot a_B^{1/z_B}} \quad (2)$$

is related to the standard changes in Gibbs energy  $\Delta G^\circ$  and the enthalpy  $\Delta H^\circ$  of the ion exchange Reaction (1) by the equations [39]:

$$RT \ln K = -\frac{1}{z_B} \bar{\mu}_B^\circ - \frac{1}{z_A} \bar{\mu}_A^\circ + \frac{1}{z_A} \mu_A^\circ - \frac{1}{z_B} \mu_B^\circ = -\Delta G^\circ \quad (3)$$

$$\left( \frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta H^\circ}{RT^2} \quad (4)$$

Here  $\bar{a}_i$ ,  $a_i$  and  $\bar{\mu}_i^\circ$ ,  $\mu_i^\circ$  are the activities and the standard chemical potentials of the components in the ion exchanger and in the solution respectively, the overbar indicates that the parameter corresponds to the ion exchanger phase. The standard quantities  $\Delta G^\circ$  and  $\Delta H^\circ$  characterize the exchange of one equivalent of ions A in the ion exchanger for one equivalent of ions B from the solution, when ions A and B both in the ion exchanger and in the solution are in the standard states. If mono-ionic forms are chosen as the standard states of the ions in the ion exchanger, then these quantities integrally characterize the complete transfer of the ion exchanger from the form of the ion A to the form of ion B. In such a thermodynamic analysis of ion-exchange equilibria, the molarities, molalities or total mole fractions of the exchanged ions

should be used as concentrations with regard to all substances, including the solvent and sorbed substances [38].

As shown in [40], the corrected coefficient of ion-exchange equilibrium

$$\tilde{K} = \frac{\bar{c}_B^{1/z_B} \cdot a_A^{1/z_A}}{\bar{c}_A^{1/z_A} \cdot a_B^{1/z_B}} \quad (5)$$

by

$$RT \ln \tilde{K} = -\Delta G_{\bar{r}} + RT \ln(\bar{c}_B^{1/z_B} / \bar{c}_A^{1/z_A}) \quad (6)$$

is related to the differential Gibbs energy

$$\Delta G_{\bar{r}} = \frac{1}{z_B} \bar{\mu}_B - \frac{1}{z_A} \bar{\mu}_A + \frac{1}{z_A} \mu_A^\circ - \frac{1}{z_B} \mu_B^\circ = RT \ln(a_B^{1/z_B} / a_A^{1/z_A}) \quad (7)$$

where  $\bar{c}_A$  and  $\bar{c}_B$  are the concentrations of the exchanging ions in the ion exchanger.

The experimental determination of molalities, molarities, and total mole fractions of the exchanging ions in the ion exchanger is more complicated (and therefore leads to greater errors) than determination of their equivalent fractions. However, when studying differential thermodynamic quantities, it is possible to use the scale of equivalent fractions of the exchanged ions in the ion exchanger. To show this, we write the equilibrium coefficient, analogous to (5), in the form

$$\tilde{k} = \frac{y_B^{1/z_B} \cdot a_A^{1/z_A}}{y_A^{1/z_A} \cdot a_B^{1/z_B}} \quad (8)$$

where  $y_i = z_i \bar{c}_i / (z_A \bar{c}_A + z_B \bar{c}_B)$  is the equivalent fraction of ion  $i$  in the ion exchanger. Then we write the relation of this coefficient with the equilibrium constant

$$\ln \tilde{k} = \ln K + \ln \frac{y_B^{1/z_B}}{y_A^{1/z_A}} + \ln \frac{\bar{a}_A^{1/z_A}}{\bar{a}_B^{1/z_B}} \quad (9)$$

and perform simple transformations

$$\begin{aligned} RT \ln \tilde{k} &= -\left( \frac{1}{z_B} \bar{\mu}_{B_0} - \frac{1}{z_A} \bar{\mu}_{A_0} - \frac{1}{z_B} \mu_{B_0} + \frac{1}{z_A} \mu_{A_0} \right) + RT \ln \frac{y_B^{1/z_B}}{y_A^{1/z_A}} + RT \ln \frac{\bar{a}_A^{1/z_A}}{\bar{a}_B^{1/z_B}} \\ &= -\left( \frac{1}{z_B} \bar{\mu}_B - \frac{1}{z_A} \bar{\mu}_A - \frac{1}{z_B} \mu_{B_0} + \frac{1}{z_A} \mu_{A_0} \right) + RT \ln \frac{y_B^{1/z_B}}{y_A^{1/z_A}} \end{aligned} \quad (10)$$

Finally we obtain the equation

$$RT \ln \tilde{k} = -\Delta G_{\bar{r}} + RT \ln(y_B^{1/z_B} / y_A^{1/z_A}) \quad (11)$$

with the same differential Gibbs energy (7).

First, we note that Eqs. (6) and (11) differ from relation (3) by their general form. Second, it is more convenient to calculate the differential Gibbs energy  $\Delta G_{\bar{r}}$  of the ion exchange reaction by relation (7) on the basis of the activities of the exchanged ions in the solution equilibrated with an ion exchanger of a certain composition (characterized by the concentrations  $\bar{c}_A$  and  $\bar{c}_B$  or equivalent fractions  $y_A$  and  $y_B$ ). The concentrations of the exchanged ions in the ion exchanger do not participate in the calculation of  $\Delta G_{\bar{r}}$ , they are necessary only to represent the composition of the ion exchanger to which the calculated value corresponds

By differentiating (6) and (11) with respect to temperature at constant pressure and ion exchanger composition, the equations analogous to the van't Hoff Eq. (4) are obtained [40,41]:

$$\left( \frac{\partial \ln \tilde{K}}{\partial T} \right)_{p, \bar{n}} = \left( \frac{\partial \ln \tilde{k}}{\partial T} \right) = \frac{\Delta H_{\bar{r}}}{RT^2} \quad (12)$$

where  $\Delta H_{\bar{r}} = \frac{1}{z_B} \bar{h}_B - \frac{1}{z_A} \bar{h}_A - \frac{1}{z_B} h_B^\circ + \frac{1}{z_A} h_A^\circ$  is the differential enthalpy change ( $\bar{h}_i$  is the partial molar enthalpy of the  $i$ -th component, and the subscripts  $p$  and  $\bar{n}$  indicate that the pressure and the amounts of all

components of the phase are constant). The condition of the constancy of the ion exchanger composition with respect to all components upon temperature variations, which is necessary for the fulfillment of (12), cannot be strictly satisfied because even at fixed ratio of exchanging ions the degree of swelling and the electrolyte sorption depend on temperature. However, it was shown in [40,42] that the influence of this factor is comparatively small even for such “thermosensitive” ion exchangers as polyacrylic and polymethacrylic.

The differential thermodynamic functions  $\Delta G_{\bar{n}}$  and  $\Delta H_{\bar{n}}$  relate to the ion exchanger at constant composition with respect to all components (at constant numbers of moles of exchanging ions A and B, water, cations X and fixed groups R of the ion exchanger  $\bar{n}_A, \bar{n}_B, \bar{n}_{H_2O}, \bar{n}_X, \bar{n}_R$ ). They reflect the changes in the Gibbs energy and the enthalpy upon exchange of one equivalent of ions B from the solution for one equivalent of ions A from an infinitely large amount of ion exchanger of a certain composition, when ions A and B in the solution are in the standard states. That means that the differential thermodynamic functions  $\Delta G_{\bar{n}}$  and  $\Delta H_{\bar{n}}$  characterize the exchange of ions on the ion exchanger with the definite extent of exchange and therefore are more informative than the standard values, which was repeatedly pointed out by a noted expert in the field of thermodynamics of ion exchange V.S. Soldatov [39,43].

If we use the corrected equilibrium coefficient (6), expressed in terms of the molar concentrations of the ions in the ion exchanger, it should be remembered that even at constant quantities of all components in the ion exchanger, the molar concentrations in the ion exchanger can vary with temperature due to the thermal change in volume. But in practice the change is almost always very small and can be neglected [44].

Under the condition of constancy of  $\Delta H_{\bar{n}}$ , from (12) we obtain the integral equation

$$\Delta H_{\bar{n}} = \frac{RT_1 T_2}{T_2 - T_1} \ln \left( \frac{\tilde{K}_{T_2}}{\tilde{K}_{T_1}} \right) = \frac{RT_1 T_2}{T_2 - T_1} \ln \left( \frac{\tilde{k}_{T_2}}{\tilde{k}_{T_1}} \right)_{\bar{n}} \quad (13)$$

The subscripts  $T_1$  and  $T_2$  denote equilibrium coefficients related to two different temperatures. The determination of  $\Delta H_{\bar{n}}$  by Eq. (13), that is analogous to the integral form of the van't Hoff Eq. (4), is complicated by a high relative error [45]. It turns out that with the error in  $\tilde{k}$  of the order of 10–15% and  $T_2 - T_1 \approx 20$  K, the error in  $\Delta H_{\bar{n}}$  in the systems under consideration can reach tens or even hundreds of percent [45,46]. Such a high error significantly reduces the value of the enthalpy of ion exchange thus obtained. However, with the exchange on selective ion exchangers, the situation becomes simpler.

When the suspension of a selective ion exchanger is heated with a limited volume of the solution containing a mixture of electrolytes, in which the more strongly sorbed ion is a microcomponent, the ratio of the exchanging ions changes mainly in the solution, and the ionic composition of the ion exchanger changes very little [37,45]. This change in the composition of the ion exchanger is usually much smaller than the error of the direct analytical determination of the composition of the ion exchanger, so this change can be neglected. This means that the differential enthalpy can be determined much more accurately on the basis of the analysis of only the composition of the solution in the equilibrium system at two temperatures using the equation

$$\Delta H_{\bar{n}} = \frac{RT_1 T_2}{T_2 - T_1} \ln \left( \frac{a_A^{1/z_A} / a_B^{1/z_B}}{a_A^{1/z_A} / a_B^{1/z_B}} \right)_{T_2, \bar{n}} \quad (14)$$

The described approach to the determination of the differential enthalpy of ion exchange can be realized in the form of the static and dynamic methods described in [45]. Only the first of them is used in the present work.

## 2. Experimental part

### 2.1. Materials. Preparation of the ion exchangers

We used gel-type carboxylic polymethacrylic cation exchanger KB-4P2 with 2.5% DVB (about 1 mol of cross-links to 60 mol of methacrylic monomers), gel-type polyacrylic cation exchanger KB-2e4 cross-linked with 4% triethylene glycol dimethacrylate (about 1 mol of cross-links to 100 mol of acrylic monomers), and macroporous polyacrylic resin Purolite C104.

Prior to the experiments, all ion exchangers were regenerated. For this purpose twofold excess (with respect to the capacity) of 0.5 N HCl solution was passed through the ion exchanger in a column. Then the ion exchanger was washed with water, and after that twofold excess (with respect to the capacity) of 0.5 N NaOH solution was passed through it. Then to remove the excess of the alkali from the intergrain space, the column was washed with a small amount of distilled water or 2.5 N NaCl solution with pH ~ 8–9 (approximately twofold excess with respect to the volume of the ion exchanger in the column). As a result, the Na form of the ion exchanger was obtained.

The ion exchangers in mixed Mg, Na- and Ni, Na-forms with a defined fraction of the divalent ion  $M^{2+}$  ( $Mg^{2+}$  or  $Ni^{2+}$ ) were prepared as follows. The suspension of the ion-exchange resin in Na-form was divided into two portions with certain volumes. One portion was placed in a column and transferred to M-form with an excess of 0.5 N of  $MCl_2$  solution. The column was then washed with a small amount of water. The portions of the ion exchanger in Na- and M-forms were transferred into the flask using a small amount of 2.5 N NaCl solution and stirred for 24 h to ensure the same ion composition of the individual grains.

### 2.2. Determination of the enthalpy of ion exchange

A suspension of the ion exchanger in a mixed M, Na-form of a given composition (the volume of the suspension ~ 200 mL) was put into a flask, then were added 150–300 mL of mixed 2.3–2.8 N NaCl and  $MCl_2$  solution, corresponding to the equilibrium with the required ion exchanger composition at  $T_1$ . The flask was placed in a thermostat with temperature  $T_1$ , the suspension was stirred periodically and the concentration of  $M^{2+}$  in the solution was analyzed by complexometric titration to verify the equilibrium state of the system.

Then the temperature was raised by 10–25 K (to the value of  $T_2$ ), the system was again brought to equilibrium and the composition of the equilibrium solution was analyzed. The equilibration time depends on temperature and varies from 3 h at 298 K to several minutes at higher temperatures. After the equilibrium was established,  $Na^+$  concentration was determined by means of emission flame photometry (it was ascertained that NaCl concentration in the solution varied insignificantly). Then the temperature was raised and the solution was analyzed successively several more times, reaching a certain maximum temperature under the experimental conditions.

In some of the experiments carried out according to this technique, the temperature was higher than 373 K. In these cases, the thick-walled glass flask was used. The flask was tightly closed with a Teflon cap with a rubber gasket and a valved Teflon capillary, one end of which was immersed in the solution inside the flask (Fig. 1). The pressure in the flask with the valve closed increased due to the equilibrium water vapor pressure. With the valve opened, the increased pressure provided the flow of the solution through the capillary and the sampling for the analysis.

After that, the reverse experiment was performed with a gradual decrease in temperature from the value reached at the end of the direct experiment to the initial value through the same stages.

At the end of the series of experiments, the ion exchanger from the flask was quickly transferred to the column, the solution was removed from the intergranular space with a vacuum pump, and an excess of 0.5 N HCl solution was passed through the column. The amounts of

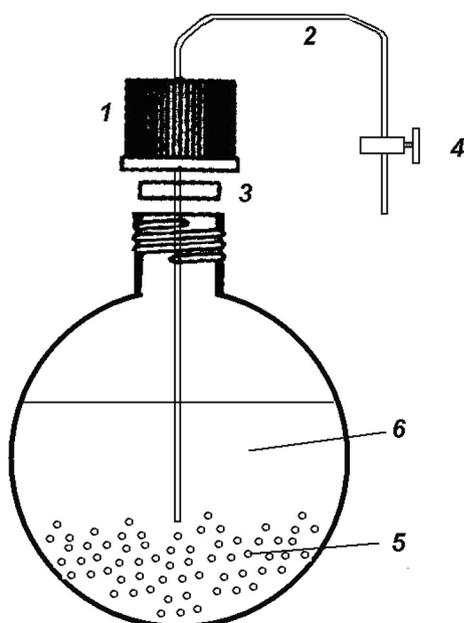


Fig. 1. The flask for the investigation of the ion-exchange equilibrium at temperatures above 373 K. (1, Teflon cap; 2, Teflon capillary; 3, rubber gasket; 4, valve; 5, ion exchanger; 6, solution).

displaced  $M^{2+}$  and  $Na^+$  ions were determined in the filtrate.

The degree of swelling of polymethacrylic and polyacrylic cation exchangers decreases somewhat with temperature (the change in the volume of ion exchanger reaches 18–20% with a change in temperature from 293 K to 363 K [39]) and the solution is diluted with water from the ion exchanger phase. However, for a small difference in temperatures  $T_1$  and  $T_2$  of the order of 20 K, the change in the solution concentration is very small.

The change of the composition of the ion exchanger with temperature in the experiments was calculated by the following formula

$$y_M(T_2) = y_M(T_1) + \frac{V \cdot (c_M(T_2) - c_M(T_1))}{W \cdot \bar{c}_0} \quad (15)$$

where  $W$  and  $V$  are the volume of the suspension of the ion exchanger and the volume of the solution in the flask (mL),  $\bar{c}_0$  is the concentration of the exchanging ions in the ion exchanger (mg-equiv./mL of the suspension),  $c_M(T)$  is the equilibrium concentration of ions  $M$  in the solution (mg-equiv./mL) at temperature  $T$ . It turned out that in all experiments with increasing temperature (both in a relatively narrow range – by 10–20 K, and in a broader range – by ~70 K), the composition of the ion exchanger changed only by 0.5–2%. Such a small change in the composition of the ion exchanger cannot be reliably established by analytical methods. We can assume that the conditions of the constancy of the ion exchanger composition in the experiments were well satisfied, and therefore it is permissible to use the proposed methods for determination of the differential enthalpy of ion exchange.

### 2.3. Processing of the experimental data

The equilibrium coefficient, the differential enthalpy of exchange of  $M^{2+}$  and  $Na^+$  ions, and the heat capacity change of the ion exchange reaction were calculated from the following relations [5,37]:

$$\tilde{k} = \frac{y_M^{1/2} \cdot c_{Na}}{y_{Na} \cdot c_M^{1/2}} \quad (16)$$

$$\Delta H_{\bar{r}} = \frac{RT_1 T_2}{T_2 - T_1} \left[ \ln \frac{(c_{Na}/c_M^{1/2})_{T_2}}{(c_{Na}/c_M^{1/2})_{T_1}} + \ln \frac{(f_{\pm NaCl}^2 / f_{\pm MCl_2}^{3/2})_{T_2}}{(f_{\pm NaCl}^2 / f_{\pm MCl_2}^{3/2})_{T_1}} \right] \quad (17)$$

$$\Delta C_{p,\bar{r}} = \left( \frac{\partial \Delta H_{\bar{r}}}{\partial T} \right)_p \quad (18)$$

In these relations  $y_M$  and  $y_{Na}$  are the equivalent fractions of  $M^{2+}$  and  $Na^+$  ions in the ion exchanger,  $c_M$  and  $c_{Na}$  are molar concentrations of the ions in the solution,  $f_{\pm MCl_2}$  and  $f_{\pm NaCl}$  are the molar activity coefficients of the salts in the solution.

The use of molar concentrations and activity coefficients is due to the fact that in deriving these relations using the expression for the chemical potential of the ion, a solution with a concentration of 1 mol/L was chosen as the standard state [45]. However, the calculated value of  $\Delta H_{\bar{r}}$  has units of kJ/equiv. in accordance with the equation of the ion exchange reaction, to which these relations correspond.

The data on the activity coefficients of electrolytes in reference publications are presented in the molal scale of concentrations. Therefore, instead of the ratio  $f_{\pm NaCl}^2 / f_{\pm MCl_2}^{3/2}$  in the molar scale, an analogous ratio of the activity coefficients  $\gamma_{\pm NaCl}^2 / \gamma_{\pm MCl_2}^{3/2}$  in the molal scale was used. However, for the solutions under study, the difference in these ratios does not exceed 3%.

The temperature dependences of the activity coefficients of the electrolytes in the mixed solutions under study are not available in the reference literature. Therefore, they were evaluated using the general form of the temperature dependence of the activity coefficient

$$\ln \gamma_{\pm} = A/T + B + C \cdot \ln T \quad (19)$$

where  $A_i$ ,  $B_i$ ,  $C_i$  are temperature-independent coefficients. This dependence is derived as a result of integration of the relations known from thermodynamics

$$dh_i = c_{p,i} dT \quad (20)$$

$$ds_i = \frac{c_{p,i} dT}{T} \quad (21)$$

(where  $h_i$ ,  $s_i$ ,  $c_{p,i}$  are the partial enthalpy, entropy, and heat capacity of the solution components) under the assumption that the heat capacity is independent of temperature, and the subsequent substitution into the equations which relate the chemical potential

$$\mu_i(T) = h_i(T) - T \cdot s_i(T) \quad (22)$$

and the activity of the electrolyte

$$\ln a_i = \frac{\mu_i - \mu_i^0}{RT} \quad (23)$$

Earlier in [41], all data found in the reference literature for individual solutions of NaCl and binary solutions containing  $CaCl_2$  were processed using Eq. (19). As a result, for 2.5 M mixed solution of NaCl and  $CaCl_2$  (the concentration of the latter was varied in the range  $2.5 \times 10^{-4}$ –0.125 M) the following dependencies were obtained:

$$\ln \gamma_{\pm NaCl} = -\frac{2100}{T} + 44.0 - 6.55 \cdot \ln T \quad (24)$$

$$\ln \gamma_{\pm CaCl_2} = -\frac{2500}{T} + 54.5 - 8.21 \cdot \ln T \quad (25)$$

Reference data on the activity coefficients of  $NiCl_2$  and  $MgCl_2$  in mixed solutions with NaCl are even more limited. However it is known that in concentrated solutions of NaCl with low admixtures of divalent cation salts, the values of the mean ionic activity coefficients of the macrocomponent depend very weakly on the concentration of the admixture [47]. Therefore, the dependence (24) obtained for NaCl was used in the present work to determine the activity coefficients of NaCl

in mixed solutions containing low admixtures of  $\text{MgCl}_2$ . The dependence of the mean ionic activity coefficients of  $\text{MgCl}_2$  on temperature in mixed solutions with  $\text{NaCl}$  were derived with the use of the third approximation of the Debye–Hückel theory in the formulation of Güntelberg:

$$\ln \gamma_{\pm} = -\frac{A \cdot |z_+ z_-| \sqrt{I}}{1 + \sqrt{I}} + CI$$

First, from the experimental data on temperature dependences of the activity coefficients for mixed solutions of 2.5 M  $\text{NaCl}$  with  $\text{CaCl}_2$  as a micro component, the empirical coefficient  $C$  was calculated for different temperatures. It was ascertained that for each component the coefficient  $C$  linearly depends on temperature with the proportionality factor  $|z_+ z_-|$ . Now, using the data of [48] on the values of  $\gamma_{\pm \text{MgCl}_2}$  at 298 K in a mixed 2.5 M  $\text{NaCl}$  solution with  $\text{MgCl}_2$  as a microcomponent, the temperature dependence of the empirical coefficient  $C$  is obtained. Then the mean ionic activity coefficients of magnesium chloride are calculated from the Debye–Hückel equation at different temperatures and are represented for convenience as the following function

$$\ln \gamma_{\pm \text{MgCl}_2} = -\frac{1811}{T} + 41.45 - 6.30 \cdot \ln T \quad (26)$$

When studying the enthalpy of the exchange of  $\text{Ca}^{+2}\text{-Na}^+$  ions, it was shown in [45] that the contribution of

$$\Delta H_{\bar{r}}(f_{\pm}) = \frac{RT_2}{T_2 - T_1} \ln \left[ \frac{\left( \frac{f_{\pm \text{NaCl}}^2 / f_{\pm \text{CaCl}_2}^{3/2}}{f_{\pm \text{NaCl}}^2 / f_{\pm \text{CaCl}_2}^{3/2}} \right)_{T_2}}{\left( \frac{f_{\pm \text{NaCl}}^2 / f_{\pm \text{CaCl}_2}^{3/2}}{f_{\pm \text{NaCl}}^2 / f_{\pm \text{CaCl}_2}^{3/2}} \right)_{T_1}} \right]_{\bar{r}}$$

to the value of  $\Delta H_{\bar{r}}$  is very small and practically independent of temperature. Therefore, possible inaccuracies in the estimation of the temperature dependences of activity coefficients of salt in solution can not affect the obtained dependencies of the differential enthalpy on temperature. It will be shown below that a similar conclusion can be drawn for the system  $\text{MgCl}_2\text{-NaCl}$ . Therefore, the role of the temperature dependences of the activity coefficients for the system  $\text{NiCl}_2\text{-NaCl}$  was not evaluated.

### 3. Results and discussions

Fig. 2 shows the dependencies of the equilibrium coefficient for the exchange of (a)  $\text{Ni}^{2+}\text{-Na}^+$  and (b)  $\text{Mg}^{2+}\text{-Na}^+$  on temperature at 0.45 equivalent fraction of divalent ion in the ion exchanger. These data reflect the same significant increase in the selectivity of cation exchangers of polyacrylic and polymethacrylic types with the temperature that was reported earlier in our work [37] for the exchange of  $\text{Ca}^{2+}\text{-Na}^+$ . A particularly significant increase in the selectivity of the

ion exchanger occurs at temperatures above 373 K. The maximum increase in the equilibrium coefficient with temperature is observed for the exchange of  $\text{Ni}^{2+}\text{-Na}^+$ , it is less significant for the system  $\text{Ca}^{2+}\text{-Na}^+$  [37], and the least effect for the systems considered is observed for the exchange of  $\text{Mg}^{2+}\text{-Na}^+$ .

Fig. 3a and b show the experimental dependences of the differential enthalpy on temperature for the exchange of ions  $\text{Ni}^{2+}\text{-Na}^+$  and  $\text{Mg}^{2+}\text{-Na}^+$ . The dash line in Fig. 3b shows the dependence of the enthalpy of  $\text{Mg}^{2+}\text{-Na}^+$  exchange with allowance made for the effect of temperature on the activity coefficients of the salts. As can be seen from the graph, this contribution is small and does not significantly affect the form of the dependence obtained.

It follows from this data that on the polymethacrylic resin the differential enthalpy of the exchange of ions  $\text{Ni}^{2+}\text{-Na}^+$  increases with temperature more strongly than of ions  $\text{Ca}^{2+}\text{-Na}^+$  [37,40]. Thus, in the exchange of  $\text{Ca}^{2+}\text{-Na}^+$  in the temperature range from 273 K to 400 K, the differential enthalpy increases from 4 to 6 kJ/equiv. to 22–28 kJ/equiv. [37], and in the exchange of  $\text{Ni}^{2+}\text{-Na}^+$  in the same temperature range, from 4 to 6 kJ/equiv. to 28–34 kJ/equiv. (without taking into account the effect of temperature on the coefficients of activity of salts). The effect of the ionic composition of the ion exchanger on the differential enthalpy is much less than the effect of temperature.

In the case of the exchange of  $\text{Mg}^{2+}\text{-Na}^+$  ions, the values of the differential enthalpy turned out to be lower, but  $\Delta H_{\bar{r}}$  also increased quite sharply with temperature.

The reasons for the sharp increase in the selectivity of carboxylic ion exchangers with temperature in the exchange of monovalent ions for divalent ions were considered in detail earlier [12] and were explained by the predominant role of the change in the hydration of the exchanging ions upon their transition from one phase to another.

Here we call attention to the fact that the temperature dependence of  $\Delta H_{\bar{r}}$  is linear, which indicates the constancy of  $\Delta_r C_p$  (the heat capacity change for the reaction of exchange of differently charged ions). The obtained values are presented in Table 1. These quantities are used below to estimate the role of temperature in the ion-exchange separation processes.

#### 3.1. The role of the influence of temperature on the enthalpy of ion exchange in the processes of reagent-free separation

The effect of a significant increase of the enthalpy of ion exchange with temperature observed in our studies can play an important role in the processes of reagent-free dual-temperature purification of concentrated solutions of alkali metal salts from admixtures of divalent ions. The use of such processes is very important, since in all natural

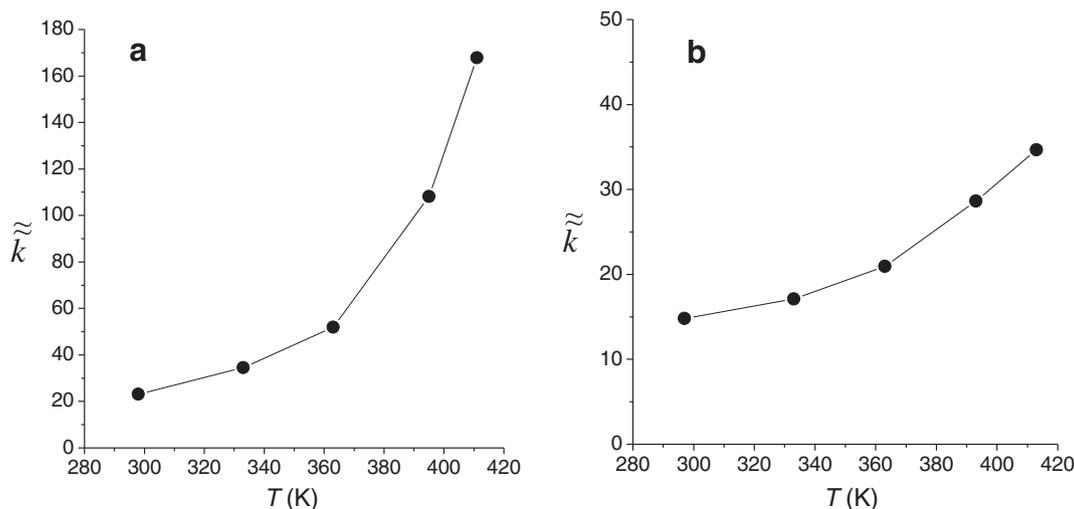
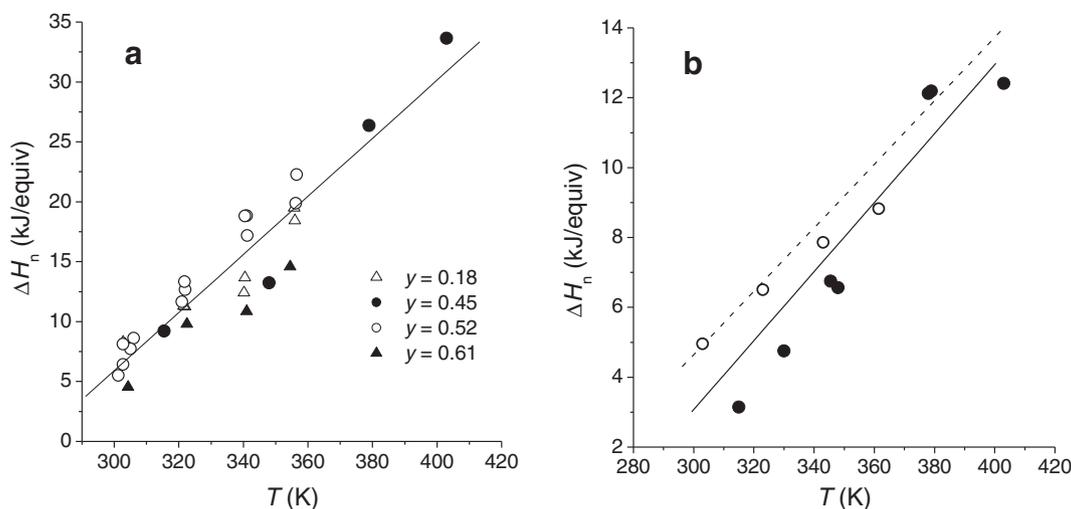


Fig. 2. The dependence of the equilibrium coefficient for the exchange of (a)  $\text{Ni}^{2+}\text{-Na}^+$  and (b)  $\text{Mg}^{2+}\text{-Na}^+$  on temperature at 0.45 fraction  $\text{M}^{+2}$  in the ion exchanger.



**Fig. 3.** The dependencies of  $\Delta H_{\bar{n}}$  on temperature for the exchange of (a)  $\text{Ni}^{2+}$  and  $\text{Na}^+$  and (b)  $\text{Mg}^{2+}$  and  $\text{Na}^+$  on KB-4P2 cation exchanger. The equivalent fraction  $y$  of the divalent ion in the ion exchanger is shown in the graphs. The straight lines are linear approximations of the data points. The dash line indicates the dependence of the enthalpy of exchange calculated by formula (17).

**Table 1**  
The heat capacity change for the reaction of exchange of differently charged ions<sup>a</sup>.

No.	Ion exchanger	Fraction of $\text{M}^{+2}$ in the resin, $y_M$	$\Delta_r C_p$ , J/equiv./K
Exchange of ions $\text{Ca}^{+2}-\text{Na}^+$			
1	KB4-P2	0.20–0.38	190
2		0.40–0.54	210
3		0.75–0.82	94
4	KB4	0.23–0.26	77
5		0.30–0.37	93
6		0.50–0.56	130
7	KB-2e4	0.54–0.58	150
8	CNP-80	0.68–0.70	110
9	C104-FL	0.62–0.70	130
Exchange of ions $\text{Ni}^{+2}-\text{Na}^+$			
10	KB4-P2	0.18	200
11		0.44	290
12		0.51–0.52	260
13		0.58–0.61	180
Exchange of ions $\text{Mg}^{+2}-\text{Na}^+$			
14	KB4-P2	0.45	115
15		0.35	67

<sup>a</sup> The values of  $\Delta_r C_p$  for the exchange  $\text{Ca}^{+2}-\text{Na}^+$  are calculated from temperature dependencies of  $\Delta H_{\bar{n}}$  presented in [37].

waters, sodium salts are accompanied by calcium and magnesium compounds. Therefore, in the processes of complex processing of natural hydromineral raw materials, the importance of which will continuously increase with the exhaustion of mineral resources and the tightening of environmental constraints, there will inevitably be a need for simple processes for separating compounds of differently charged ions.

An example of such a process (for which the role of the increase of the differential enthalpy with temperature is estimated below) is dual-temperature purification of concentrated sodium chloride solution from divalent ions on polymethacrylic cation exchanger [12,13]. In this process the solution is continuously passed through the column with the ion exchanger, and the temperature is periodically changed at certain moments. As the temperature rises, the concentration of calcium ions in the solution decreases due to an increase of the selectivity of the ion exchanger, and upon subsequent cooling of the column the selectivity of the ion exchanger decreases, calcium ions excessively sorbed by the ion exchanger return to the solution and, as a result, the ion exchanger is regenerated. Just as an illustration the elution curve of one of such experiments is shown in Fig. 4. From the presented data it can be seen

that in a “hot” stage in a sufficiently large volume of the filtrate a significant decrease of the concentration of impurity  $\text{Ca}^{2+}$  ions is observed, and in the regeneration stage at 293 K their concentration is significantly increased in comparison with the initial one.

We now estimate the role of the increase of the differential enthalpy of ion exchange with temperature in the process of the single-stage dual-temperature purification of a concentrated solution of sodium chloride from divalent calcium ions on a polymethacrylic resin. We represent the dependence of the enthalpy of ion exchange on temperature by the Kirchhoff equation with a constant value of the heat capacity change of the reaction

$$\Delta H_{\bar{n},T} = \Delta H_{\bar{n},T_1} + \Delta C_{p,\bar{n}} \cdot (T - T_1) \quad (27)$$

and substitute it in (12)

$$\left( \frac{\partial \ln \tilde{k}}{\partial T} \right)_{p,\bar{n}} = \frac{\Delta H_{\bar{n},T_1}}{RT^2} + \frac{\Delta C_{p,\bar{n}}}{RT^2} \cdot (T - T_1) \quad (28)$$

Integrating from  $T_1$  to  $T_2$ , we get:

$$\ln \frac{\tilde{k}_{T_2,\bar{n}}}{\tilde{k}_{T_1,\bar{n}}} = \frac{T_2 - T_1}{RT_1 T_2} \cdot \Delta H_{\bar{n},T_1} + \frac{\Delta C_{p,\bar{n}}}{R} \left( \ln \frac{T_2}{T_1} + \frac{(T_1 - T_2)}{T_2} \right) \quad (29)$$

Since the equilibrium coefficients at two temperatures refer to the same composition of ion exchanger, then

$$\ln \frac{\left( \frac{c_{\text{Na}}}{c_{\text{M}}} \right)_{T_2,\bar{n}}^{1/2}}{\left( \frac{c_{\text{Na}}}{c_{\text{M}}} \right)_{T_1,\bar{n}}^{1/2}} = \frac{T_2 - T_1}{RT_1 T_2} \cdot \Delta H_{\bar{n},T_1} + \frac{\Delta C_{p,\bar{n}}}{R} \left( \ln \frac{T_2}{T_1} + \frac{(T_1 - T_2)}{T_2} \right) \quad (30)$$

If we assume that the sodium ion is a macrocomponent in the solution and its concentration remains practically constant upon the exchange of ions, then the ratio is simplified:

$$\ln \frac{(c_{\text{M}})_{T_2,\bar{n}}}{(c_{\text{M}})_{T_1,\bar{n}}} = \left[ \frac{2(T_2 - T_1)}{RT_1 T_2} \cdot \Delta H_{\bar{n},T_1} + \frac{2\Delta C_{p,\bar{n}}}{R} \left( \ln \frac{T_2}{T_1} + \frac{(T_1 - T_2)}{T_2} \right) \right] \quad (31)$$

Relations (29) and (31) make it possible to estimate the effect of temperature on the ratio of the equilibrium coefficients and the concentrations of the divalent ion in the solution in the ion exchange system at the upper and lower values of the temperature interval, taking into account the dependence of the differential enthalpy of ion exchange on temperature.

Figs. 5–7 show the results of calculations using Eqs. (29) and (31)

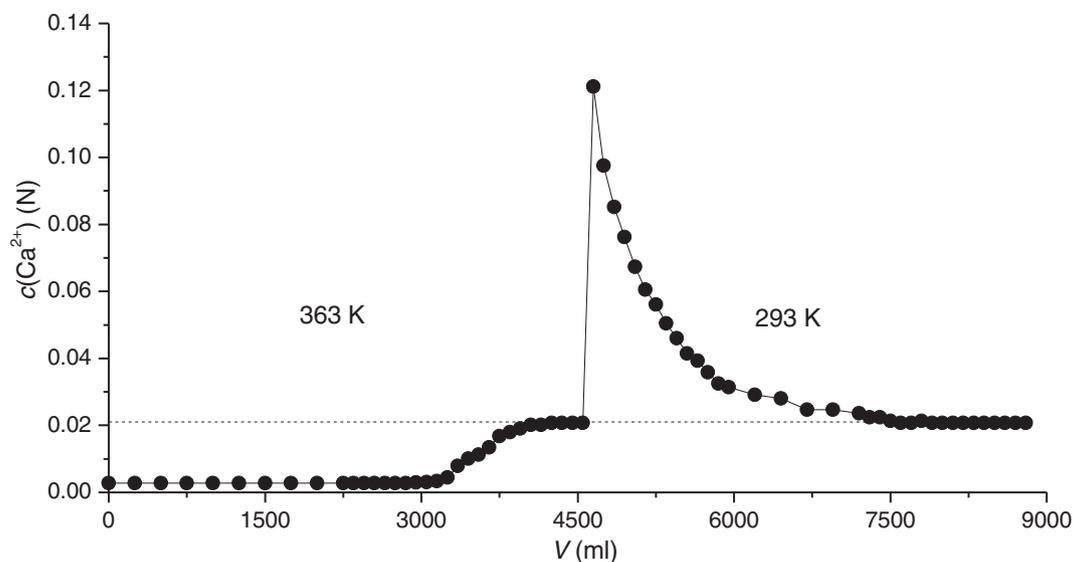


Fig. 4. Elution curves for the purification of 2.5 N NaCl solution from 0.021 N  $\text{CaCl}_2$  (363 K) and the regeneration of KB-4P2 cation exchanger (293 K).

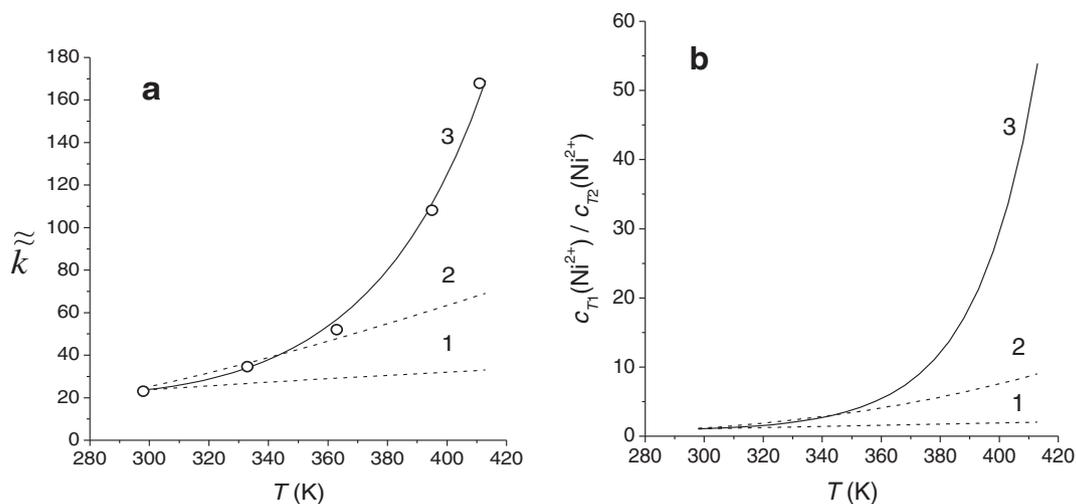


Fig. 5. Dependencies (a) of the equilibrium coefficient and (b) of  $c_{T_1}(\text{Ni}^{2+})/c_{T_2}(\text{Ni}^{2+})$  on  $T_2$  for the exchange of  $\text{Ni}^{2+}\text{-Na}^+$  on KB-4P2 cation exchanger at  $\gamma \sim 0.5$ , calculated (1) with  $\Delta H_{\bar{n}} = 3.0$  kJ/g-equiv., (2) with  $\Delta H_{\bar{n}} = 9.2$  kJ/g-equiv., (3) with regard to the temperature dependence of  $\Delta H_{\bar{n}}$  with  $\Delta_r C_p = 258$  J/g-equiv.K. Circles are experimental data.

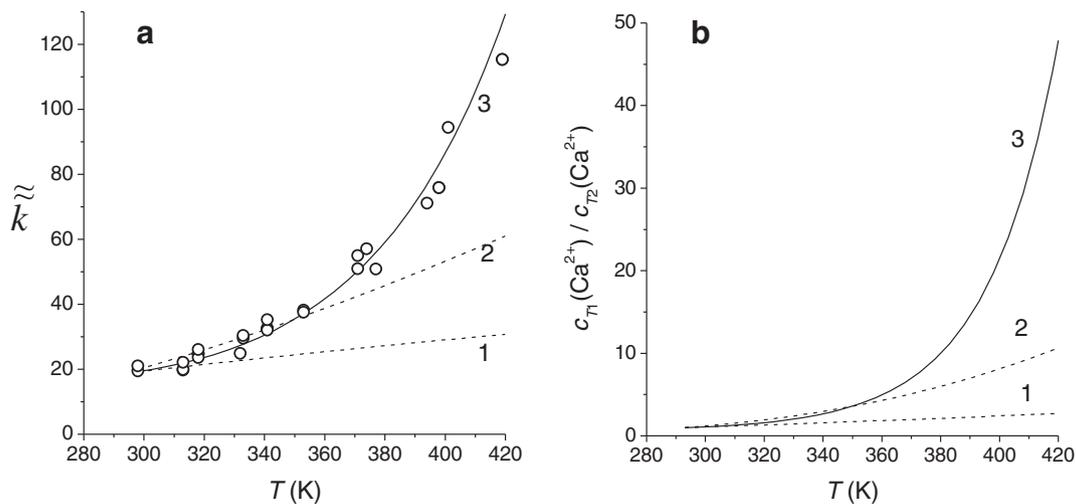


Fig. 6. Dependencies (a) of the equilibrium coefficient and (b)  $c_{T_1}(\text{Ca}^{2+})/c_{T_2}(\text{Ca}^{2+})$  on  $T_2$  for the exchange of  $\text{Ca}^{2+}\text{-Na}^+$  on KB-4P2 cation exchanger at  $\gamma \sim 0.5$ , calculated (1) with  $\Delta H_{\bar{n}} = 4.0$  kJ/g-equiv., (2) with  $\Delta H_{\bar{n}} = 9.5$  kJ/g-equiv., (3) with regard to the temperature dependence of  $\Delta H_{\bar{n}}$  with  $\Delta_r C_p = 207$  J/g-equiv.K. Circles are experimental data.

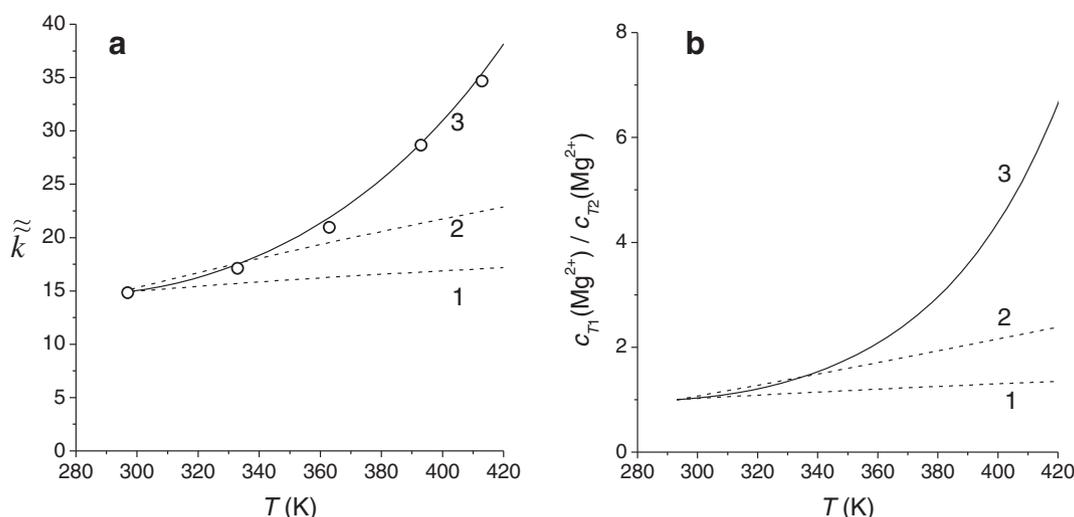


Fig. 7. Dependencies (a) of the equilibrium coefficient and (b)  $c_{T_1}(\text{Mg}^{2+})/c_{T_2}(\text{Mg}^{2+})$  on  $T_2$  for the exchange of  $\text{Mg}^{+2}\text{-Na}^+$  on KB-4P2 cation exchanger at  $\gamma \sim 0.5$ , calculated (1) with  $\Delta H_{\bar{n}} = 1.2$  kJ/g-equiv., (2) with  $\Delta H_{\bar{n}} = 3.5$  kJ/g-equiv., (3) with regard to the temperature dependence of  $\Delta H_{\bar{n}}$  with  $\Delta_r C_p = 115$  J/g-equiv.K. Circles are experimental data.

for the exchange of ions  $\text{Ni}^{+2}\text{-Na}^+$ ,  $\text{Ca}^{+2}\text{-Na}^+$  and  $\text{Mg}^{+2}\text{-Na}^+$  on KB-4P2 cation exchanger. Dependencies 3 are calculated with regard to the temperature dependence of the enthalpy. Dependencies 1 and 2 are calculated neglecting  $\Delta C_{p,\bar{n}}$  in Relations (29) and (31) with the constant values of  $\Delta H_{\bar{n}}$  corresponding to 293 K (dependencies 1) and to the average value of  $\Delta H_{\bar{n}}$  for the temperature range 293–333 K (dependencies 2). Calculating the last two dependencies, we had in mind that, when evaluating the effect of temperature on the behavior of an ion-exchange system, often used are either calorimetric values of the enthalpy of ion exchange measured at a temperature of the order of 293 K, or the average enthalpy of ion exchange calculated using the van't Hoff equation from the experimental equilibrium data for two values of temperature in a sufficiently wide range.

It can be seen that an increase in the endothermicity of the exchange reaction of differently charged ions with temperature makes a very significant contribution to the increase of the selectivity of the ion exchanger to the divalent ion and strongly affects the depth of purification in the ion-exchange separation processes. This effect is most significant in superheated solutions.

In Figs. 5a–7a, the experimental and calculated temperature dependences of the equilibrium coefficients for the exchange  $\text{M}^{+2}\text{-Na}^+$  ions on the KB-4P2 cation exchanger ( $\gamma_M \sim 0.5$ ) are compared. The dependences obtained from (30) are in good agreement with the experimental data (presented on the same graphs), while the other two widely used estimation methods give many times underestimated results.

An increase of the upper temperature boundary in dual-temperature separations leads to a very sharp increase of the degree of separation. According to the estimation by Relation (32), the concentration of  $\text{Ni}^{+2}$  ions in the purification process decreases by 76 times with the increase of temperature from 293 K to 420 K (Fig. 5b), and the concentration of  $\text{Ca}^{+2}$  ions in the same temperature range decreases by 50 times (Fig. 6b), and  $\text{Mg}^{+2}$  ions by 7 times (Fig. 7b). The results of the estimation are in good agreement with the obtained experimental data on the depth of purification upon exchange of the corresponding ions on KB-4P2 under nonisothermal conditions. At the same time, if we neglect the dependence of the enthalpy on temperature and use the enthalpy value at 293 K or the mean value for the 293–333 K interval (as in the other two mentioned calculation methods), then the calculation would predict that the concentration of  $\text{Ni}^{+2}$  in the purification process under the same conditions would decrease only by 2 and 10 times,  $\text{Ca}^{+2}$  by 3 and 10 times, and  $\text{Mg}^{+2}$  by 1.3 and 2.3 times, respectively (Figs. 5b–7b).

It is known that to multiply the single effect achieved in the process of dual-temperature separation, one can use the parametric pumping method [10]. However, on carboxylic cation exchangers, the sharp increase of the endothermicity of the ion exchange reaction makes it possible to achieve sufficiently high degrees of separation simply by raising the upper temperature boundary. It should be borne in mind that polyacrylic and polymethacrylic cation exchangers have sufficient thermal stability and allow this to be done.

#### 4. Conclusions

Thus, for the exchange of differently charged ions on polyacrylic and polymethacrylic cation exchangers, the differential enthalpy very strongly increases linearly with temperature. Then, when predicting changes in selectivity with temperature and the extent of purification of solutions of alkali metal salts from admixtures of divalent ions, it is extremely necessary to take the temperature dependence of the ion exchange enthalpy into account. From the results of the study of the enthalpy of ion exchange and from the evaluations made it follows that as the upper temperature boundary is raised in the dual-temperature separation of electrolytes, the depth of solution purification in the “hot” stage will significantly increase. This effect is most pronounced in superheated solutions.

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