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Effect of Temperature on the Equilibrium of the Exchange of Calcium and Sodium Ions on Purolite S950 Aminophosphonic Polyampholyte

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Abstract—The equilibrium of the sorption of calcium and sodium ions from 2.5–2.6 M mixed solutions of their chlorides ($[CaCl_2] = 2.5 \times 10^{-3}$–$4 \times 10^{-2}$ M) at 294 and 354 K was experimentally studied. The thermodynamic functions for the exchange of these ions on Purolite S950 aminophosphonic polyampholyte were estimated.

Studying the effect of temperature on the characteristics of ion-exchange equilibrium on an aminophosphonic polystyrene polyelectrolyte is a continuation of a series of works on the role of temperature in ion exchange [1–8]. Interest in this problem was stimulated by the following circumstances. For a long time, only sulfonic ionites have been extensively studied, with the conclusion drawn that the temperature only slightly affects ion-exchange equilibrium. However, the authors of the present work have observed a strong influence of temperature on ion-exchange equilibrium for a number of other types of cationites (for example, for the exchange of ions of the first and second groups on polymethacrylic cationites), results that modified the views regarding this problem. Studying ionites of various types has revealed that the magnitude of the effect of temperature on ion-exchange equilibrium depends on the structure of the ionite. Ionites based on styrene–divinylbenzene copolymers containing aminophosphonic groups have not yet been studied, although ionites of this type are produced in large amounts and used for removing calcium, magnesium, and other metals from concentrated solutions of alkali metal salts (for example, during the preparation of brines for electrolysis) and for extracting heavy metals (zinc, lead, etc.) [9, 10].

In the present work, we experimentally studied the equilibrium of the ion exchange of calcium and sodium ions from mixed solutions of their chlorides at a total concentration of 2.48–2.61 M (the concentration of $CaCl_2$ was varied within 2.5×10^{-3}–4×10^{-2} M) and various temperatures and evaluated the thermodynamic functions for the exchange of ions on aminophosphonic polyampholytes.

EXPERIMENTAL

Objects. Methods for Studying Equilibria

The experiments were performed with Purolite S950, a macroporous polyampholyte prepared on the basis of a styrene–divinylbenzene copolymer with aminophosphonic ($-CH_2NHCH_2PO_3M_2$) active groups (M is the counterion (H^+, Na^+, Ca^{2+} and other ions).

The characteristics of ion-exchange equilibrium were measured as follows. Two ~5-g air-dry portions of the ionite, in the Na^+ and Ca^{2+} forms, respectively, were brought in equilibrium with an excess amount of a mixed $NaCl$–$CaCl_2$ solution in which $CaCl_2$ was a microcomponent. The equilibrium solution was then separated from the ionite and their compositions were analyzed. When the final compositions of the ionites (initially in the different (Na^+ or Ca^{2+}) forms) coincided, ion-exchange equilibrium was considered attained. This method (described in detail in [1–3, 6]) made it also possible to determine the volume of the equilibrium ionite phase and the concentrations of the exchangeable ions per unit volume of ionite. The pH values (pH ~ 8–9) and concentrations of the solutions under study ensured that the exchange capacity of the ionite for the cations was used in full.

Using the obtained experimental results on the ion-exchange reaction

$$\overline{Na}^+ + (1/2)Ca^{2+} = Na^+ + (1/2)\overline{Ca}^{2+}, \qquad (1)$$
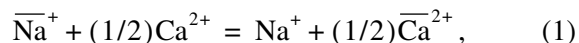
we calculated the equilibrium and selectivity coefficients:

$$\tilde{K} = \frac{\bar{c}_{Ca}^{1/2} c_{Na}}{\bar{c}_{Na} c_{Ca}^{1/2}} \quad \text{and} \qquad (2)$$

$$K_{x,y} = \frac{y_{Ca}^{1/2} x_{Na}}{y_{Na} x_{Ca}^{1/2}}, \qquad (3)$$

where $\bar{c}$ and c are the molar concentrations of the ions in the ionite phase and in the external solution, respectively; y and x are the equivalent fractions of the components in the ionite and external solution, respectively; the overbar denotes that the ion or the parameter refers to the ionite phase. The maximum relative errors in $\tilde{K}$ and $K_{x,\,y}$ (10–15%) were determined by adding the errors contributed by each analytical operation.

To estimate the contribution from superequivalent sorption, an excess amount of a 2.5 M NaCl solution with pH 9.0 was passed through a ~30-ml portion of a Na^+-form Purolite S950 suspension in a column, after which the equilibrium solution was separated from the ionite with a water-jet pump (in the same manner as when studying ion-exchange equilibrium) and water was then passed through the column. The NaCl superequivalent sorption value was calculated from the content of Cl^- ions in the filtrate (determined by mercurimetric titration) and their total amount (which is known).

Differential Thermodynamic Functions

The experimental results obtained were used to calculate the corrected ion-exchange equilibrium coefficient

$$\tilde{K} = \frac{\bar{c}_{Ca}^{1/2}\, c_{Na}\gamma_{\pm NaCl}^2}{\bar{c}_{Na}\, c_{Ca}^{1/2}\gamma_{\pm CaCl_2}^{3/2}}, \tag{4}$$

from which the differential Gibbs energy change was calculated (according to the theoretical treatment presented in [5]):

$$\Delta G_{\bar{n}} = \frac{1}{2}\bar{\mu}_{Ca} - \bar{\mu}_{Na} + \mu_{Na}^{\circ} - \frac{1}{2}\mu_{Ca}^{\circ}$$
$$= RT\ln\frac{a_{Ca}^{1/2}}{a_{Na}} = RT\ln\frac{c_{Ca}^{1/2}\gamma_{\pm CaCl_2}^{3/2}}{c_{Na}\gamma_{\pm NaCl}^2}, \tag{5}$$

where a_i is the activity of ion i in the solution at equilibrium with an ionite of specified composition, R is the universal gas constant, T is the temperature, $\gamma_{\pm}$ is the mean ionic activity coefficient for the salt, $\bar{\mu}_i$ is the chemical potential of ion i in the ionite, and μ_i° is the standard chemical potential of ion i in the solution.

The differential Gibbs energy change $\Delta G_{\bar{n}}$ characterizes an ionite at the fixed numbers of moles of each component (calcium $\bar{n}_{Ca}$, sodium $\bar{n}_{Na}$, water $\bar{n}_{H_2O}$, coions $\bar{n}_{Cl}$, $\bar{n}_R$ and fixed ionite groups). This quantity can be interpreted as the Gibbs energy change for the substitution of 1g-equiv of Ca^{2+} ions from a solution for 1 g-equiv of Na^+ ions in an infinitely large amount of an ionite under conditions when Ca^{2+} and Na^+ exist in the solution in the standard state.

When performing calculations, we used, as in [7], the molal activity coefficients, since the activity coefficients reported in the literature are given in the molal scale. The activity coefficient for $CaCl_2$ in a 2.5 m mixed solution, in which $CaCl_2$ is a microcomponent, was calculated by the correlation equation [7]

$$\ln\gamma_{\pm CaCl_2} = -2502/T + 54.54 - 8.206\ln T. \tag{6}$$

The values of $\gamma_{\pm NaCl}$ were identical to that found for an individual 2.5 m NaCl solution [11]. The calculations performed demonstrated that, for the solutions under study, the ratio of the activity coefficients in Eq. (5) changes within 2.5% in passing from the molar to the molal concentration scale.

Differentiating Eq. (5) at constant pressure and ionite composition yield a relationship analogous to the van't Hoff isobar [5]:

$$\left(\frac{\partial\ln\tilde{K}}{\partial T}\right)_{p,\,\bar{n}_j} = \frac{\Delta H_{\bar{n}}}{RT^2}. \tag{7}$$

Like $\Delta G_{\bar{n}}$, the differential enthalpy change, $\Delta H_{\bar{n}} = \frac{1}{2}\bar{h}_{Ca} - \bar{h}_{Na} - \frac{1}{2}h_{Ca}^{\circ} + h_{Na}^{\circ}$, refers to an ionite of fixed composition and can be interpreted in the same manner $\Delta G_{\bar{n}}$ (h_i is the partial molar enthalpy of the ion, while the subscripts p and $\bar{n}_j$ denote conditions under which the pressure and the numbers of moles of the components in the ionite phase are constant).

It is known [6, 12] that at fixed numbers of moles of ions exchanged, the degree of swelling (water sorption) of ionites prepared from crosslinked polyelectrolytes is temperature-dependent. Under these conditions, it is impossible to maintain the ionite's composition at a constant level as the temperature changes. Therefore, the temperature dependence of $\tilde{K}$ measured under conditions when only the ratios between the concentrations of the ions (equivalent fractions y) in the ionite phase are constant yields ΔH_y, which is formally defined (by analogy with (7)) as

$$\left(\frac{\partial\ln\tilde{K}}{\partial T}\right)_{p,\,y} = \frac{\Delta H_y}{RT^2}. \tag{8}$$

In contrast to the differential enthalpy ΔH_y, $\Delta H_{\bar{n}}$ has no obvious physical meaning. The difference between ΔH_y and $\Delta H_{\bar{n}}$ is determined by the change in the ratio of the activity coefficients of the counterions in the ionite associated with the temperature dependence of the water content (the degree of swelling of the ionite) at constant composition for the rest of the components; therefore, this difference is normally difficult to estimate [7].
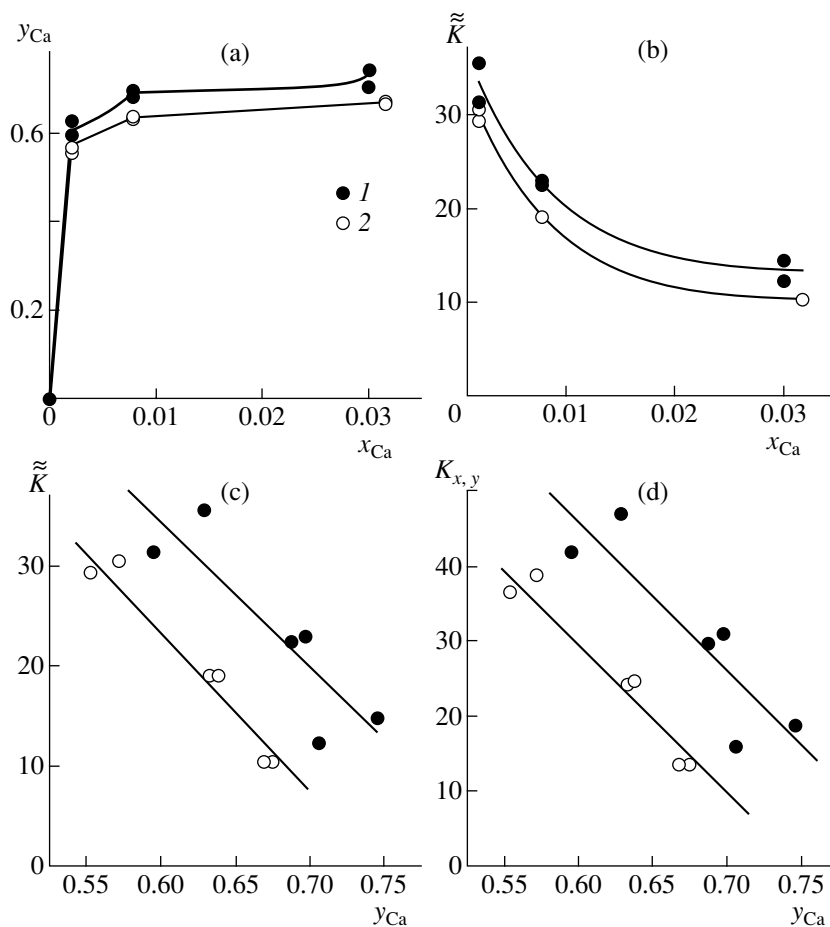
Fig. 1. Equilibrium characteristics for the exchange of calcium and sodium ions from 2.5–2.6 M mixed solutions of the chlorides on Purolite S950 ionite at (*1*) 354 and (*2*) 294 K; for (a–d), see the text.

The quantity ΔH_y was calculated from the measured dependences of $\tilde{K}$ on the ionic composition of the ionite at various temperatures by the formula

$$\Delta H_y = [\ln \tilde{K}(T_2) - \ln \tilde{K}(T_1)]_y RT_1 T_2/(T_2 - T_1), \quad (9)$$

which is equivalent to (8) if ΔH_y is temperature-independent. In this manner, we determined the values averaged over the temperature range covered (294–354 K).

RESULTS AND DISCUSSION

Since Purolite S950 is a macroporous ionite, it is characterized by a large contribution from nonexchange sorption in highly concentrated solutions. The contribution from nonexchange sorption for a 2.5 M NaCl solution at 293 K was found to be 50% of its exchange capacity. At higher temperatures, the contribution from nonexchange sorption was lower by ~10%. Thus, the selectivity and thermodynamic characteristics of Purolite S950 in 2.5 g-equiv/l solutions are determined by the contribution from the sorption of the exchangeable ions on fixed groups and nonexchange

sorption of the electrolytes. However, the first factor is a predominant one.

The experimental data displayed in Figs. 1a and 1b suggest that the temperature only slightly influences the equilibrium of the exchange of sodium and calcium ions between Purolite S950 and a given external solution, in agreement with the results reported in [3, 4, 6]. According to these results, for iminodiacetate and vinylpyridine polyampholytes, the temperature produces a very small effect on the equilibrium state, in contrast to all types of cationites without donor nitrogen-containing groups (sulfonic, carboxylic, and phosphonic), for which the selectivity with respect to doubly charged ions increases markedly with temperature.

At the same time, for the aminophosphonic polyampholyte, the values of $\tilde{K}$ and $K_{x,y}$ (Figs. 1c and 1d) and the calculated values of $\tilde{K}$ and $-\Delta G_{\bar{n}}$ (Fig. 2) at a constant fraction of calcium ionites in the ionite phase increase markedly with the temperature. This increase proved to be somewhat higher than that for VPK and ANKB-50 polyampholytes but weaker than that for cat-
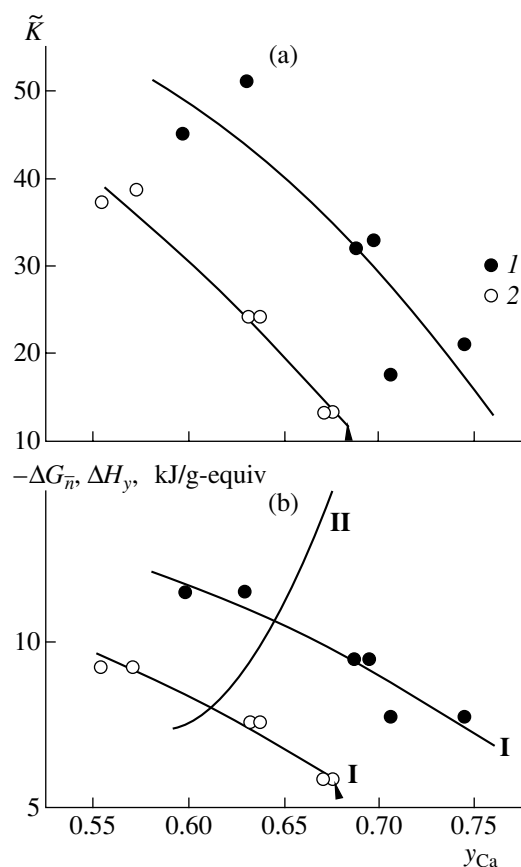
Fig. 2. Dependences of (a) $\tilde{K}$ and (b) (**I**) $-\Delta G_{\bar{n}}$ and (**II**) ΔH_y on the equivalent fraction of calcium ions in the Purolite S950 ionite at (*1*) 354 and (*2*) 294 K.

Fig. 3. Total concentration of the exchangeable ions in the Purolite S950 ionite phase as a function of the calcium ion fraction at (*1*) 354 and (*2*) 294 K.

electrolyte are formed; such complexes have the highest stability. As the content of the metal ion in the ionite phase increases, the limited mobility of the polymer chains (and the conformational and steric restrictions involved) gives rise to a situation where less stable complexes with coordination sites partially occupied by coions or solvent molecules are formed.

ionites. Accordingly, for Purolite S950, the obtained values of ΔH_y were found to be rather high, 7–14 kJ/g-equiv. Since the ionite's ability to swell is weakly temperature-dependent at a given y_{Ca}, ΔH_y can be considered virtually identical to the differential enthalpy $\Delta H_{\bar{n}}$. The dependences of the total concentration of exchangeable ions in the ionite phase on the fraction of calcium ions at two temperatures (Fig. 3) suggest that the swelling ability of the ionite is weakly temperature-dependent. The difference between the concentration of calcium ions in an ionite with a constant ionic composition at 294 and 354 K is below 5–7%.

For the system under study, the characteristics of exchange equilibrium of ions ($\tilde{\tilde{K}}$ and $K_{x,y}$ (Fig. 1) and $\tilde{K}$ and $-\Delta G_{\bar{n}}$ (Fig. 2)) increase with decreasing relative content of the doubly charged ion in the ionite phase. This can be explained by assuming that the structure of the complexes formed depends on the polyelectrolyte's composition. At low concentrations of the doubly charged ion in the ionite phase, complexes with the maximum degree of occupation of the coordination sites of the metal atom by ligand groups of the poly-
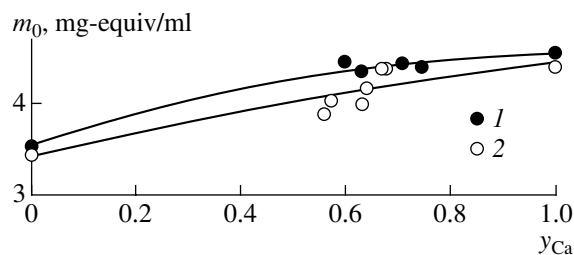
REFERENCES

1. V. D. Timofeevskaya, V. A. Ivanov, and V. I. Gorshkov, Zh. Fiz. Khim. **62**, 2531 (1988).
2. V. A. Ivanov, V. D. Timofeevskaya, V. I. Gorshkov, and S. N. Grishenina, Zh. Fiz. Khim. **63**, 1867 (1989).
3. V. A. Ivanov, V. D. Timofeevskaya, V. I. Gorshkov, and T. V. Eliseeva, Zh. Fiz. Khim. **65**, 2455 (1991).
4. V. A. Ivanov, V. I. Gorshkov, V. D. Timofeevskaya, and N. V. Drozdova, React. Funct. Polym. **38** (2–3), 205 (1998).
5. V. A. Ivanov, V. D. Timofeevskaya, and V. I. Gorshkov, Zh. Fiz. Khim. **74**, 730 (2000) [Russ. J. Phys. Chem. **74**, 637 (2000)].
6. V. A. Ivanov, V. D. Timofeevskaya, N. V. Drozdova, and V. I. Gorshkov, Zh. Fiz. Khim. **74**, 734 (2000) [Russ. J. Phys. Chem. **74**, 641 (2000)].
7. V. A. Ivanov, V. D. Timofeevskaya, V. I. Gorshkov, and N. V. Drozdova, Zh. Fiz. Khim. **74**, 917 (2000) [Russ. J. Phys. Chem. **74**, 812 (2000)].
8. V. A. Ivanov, V. D. Timofeevskaya, V. I. Gorshkov, and N. V. Drozdova, Zh. Fiz. Khim. **77**, 2235 (2003) [Russ. J. Phys. Chem. **77**, 2018 (2003)].
9. J. J. Wolff and R. E. Anderson, AIChE Symp. Ser. **78** (219), 46 (1982).
10. H. Eccles and H. Greenwood, Solvent Extr. Ion Exch. **10** (4), 713 (1992).
11. *Chemist's Handbook*, Ed. by B. P. Nikol'skii (Khimiya, Leningrad, 1965), Vol. 3 [in Russian].
12. V. S. Soldatov, *Simple Ion-Exchange Equilibria* (Nauka i Tekhnika, Minsk, 1972) [in Russian].