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ON THE QUESTION OF THE MECHANISM OF ION EXCHANGE

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The existing views on the mechanism of ion exchange do not provide a sufficient understanding of the influence of changes in the conditions under which the reaction is carried out—for example, temperature and solvent—on ion-exchange equilibrium.

On the basis of the results obtained by us in studying ion-exchange equilibrium, as well as a number of phenomena known from the literature (the presence of ion association in electrolyte solutions, the dependence of the capacity of weak-acid resins on the pH of the medium, a certain decrease in the capacity of sulfo resins in alcohol, the possibility of ion exchange between two resins, etc.), the following scheme of the cation-exchange process may be proposed.

A resin is a high-molecular-weight polyacid. When immersed in a polar solvent, for example in water, it ionizes as a result of interaction with the solvent molecules. But since the anions of the resin are bound to one another, they cannot be distributed throughout the entire volume of the solution. Because of the action of electrostatic forces, the cations also cannot spread throughout the entire volume of the solution. As a result, an "ionic cloud" with a rather high concentration of cations is formed near the surface of the resin. But in solutions of strong electrolytes at concentrations above 0.05 N, as was shown by Semenchenko (^{1}) and subsequently by Bjerrum (^{2}), association of ions may occur—the approach of ions of opposite sign under the action of electrostatic forces. Such association must take place for the cations and anions of the resin. At the external surface of the resin a diffuse ionic layer may form with sufficiently deep penetration of the cations into the solvent; however, inside the resin network, because of repulsion by opposing cations, the thickness of the diffuse layer is considerably less than the thickness of the external diffusion layer, and the closer the dissociating groups are situated, the smaller it is. Therefore, in a first approximation, the equilibrium in the general case may be written as a two-stage process:

$$\mathrm{ABR} \rightleftarrows \mathrm{A^+B^-R} \rightleftarrows \mathrm{A^+} + \mathrm{B^-R}, \tag{1}$$

Fig. 1. Dependence of $-\lg K$ on $1/T$ for exchange on the H-form of espatite: 1 —NaCl; 2—KCl

Figure 1: Fig. 1. Dependence of $-\lg K$ on $1/T$ for exchange on the H-form of espatite: 1—NaCl; 2—KCl

where A^+ is the resin cation; B^-R is the anionic group; ABR is the resin; A^+B^-R is the association of the cation and the anionic group.

If the resin is in a very finely divided state or is a low-polymerized product (the so-called soluble resins), then the concentration of ions at its surface will not be very high, and the equilibrium is shifted to a considerable extent to the right. In this case an "ionic cloud" is formed at the surface of the particles. This is evidenced by the exchange of cations between soluble and insoluble resins, which proceeds at a considerable rate (^{3}).

For ordinary resins that do not form sols, the principal role is played by the equilibrium

$$\mathrm{ABR} \rightleftarrows \mathrm{A^+B^-R}. \tag{2}$$

It determines the total exchange capacity of the resin, i.e., the number of ions capable of exchanging under the given conditions. Depending on the nature of the exchange groups and on the conditions in which the resin is found, the equilibrium is shifted to one side or the other. Thus, in water, for weakly acidic groups—OH, —COOH—it is shifted to the left and depends strongly on the pH of the solution. For sulfo groups it is shifted to the right.

In alcoholic solutions, owing to the lower polarity of alcohol molecules, even for sulfo resins the equilibrium is shifted somewhat to the left, and the capacity of the resin in anhydrous alcohol should be somewhat lower than in water.

Lowered capacity values were in fact obtained by us in some experiments on the equilibrium of NaCl exchange on sulfo resins in 100% CH_3OH. It was found that the more moisture there is in the resin, the closer the capacity is to its value for water. Apparently, even small traces of moisture in the resin phase shift equilibrium (2) to the right. As soon as there is enough water for all the H^+ ions to be hydrated, the capacity of the resin in alcohol will be equal to the capacity in water.

Fig. 1. Dependence of $-\lg K$ on $1/T$ for exchange on the H-form of espatite: 1—NaCl; 2—KCl

Upon addition of other cations to the solution, some of them replace the cations of the resin, and after some time equilibrium is established. For simplicity let us consider the exchange of monovalent ions.

For the reaction $Me^+ + H^+SO_3^-R \rightleftarrows H^+ + Me^+SO_3^-R$, it may be assumed that the change in free energy under standard conditions, $-\Delta F = RT \ln K$, consists of two terms: the electrostatic component ΔF_{el}, equal to the change in free energy upon replacement of the hydrogen ion in the ion pair $H^+SO_3^-R$ by a metal ion, and ΔF_{nonel}, which takes into account effects associated with the interaction of solvent molecules with the ions participating in the reaction. The first term is equal to the work performed in replacing the H^+ ion by the Me^+ ion; this work is equal to the difference in the energies of electrostatic interaction of the H^+ and Me^+ cations with the anion of the resin.

Since the interaction energy of the H^+ ion with the monovalent ion SO_3^-R is $E_{H^+} = \varepsilon^2/2Da_{H^+}$, where D is the dielectric constant; ε is the charge of the H^+ ion; a_{H^+} is the distance between the H^+ and SO_3^-R ions, and analogously $E_{Me^+} = \varepsilon^2/2Da_{Me^+}$, then

$$\Delta F_{\text{el}} = \frac{N\varepsilon^2}{2D}\left(\frac{1}{a_{H^+}} - \frac{1}{a_{Me^+}}\right),$$

where N is Avogadro’ s number. Consequently,

$$-\lg K = \frac{\Delta F_{\text{nonel}}}{2.3RT} + \frac{N\varepsilon^2}{4.6DRT}\left(\frac{1}{a_{H^+}} - \frac{1}{a_{Me^+}}\right).$$

This formula makes it possible to explain a number of regularities found in the study of ion-exchange equilibrium. Thus, for one and the same solvent, for example water, for the exchange of alkali-metal ions for hydrogen there should be a linear dependence of $\lg K$ on $1/a_{Me^+}$. We took for a_{Me^+} the values of the parameter a^0, calculated from activity coefficients by the Debye–Hückel formula

$$\lg \gamma_\pm = -\frac{A\sqrt{M}}{1 + Ba^0\sqrt{M}}, \tag{4}$$

and, indeed, for a number of sulfo resins studied by us we obtained a linear dependence. This also agrees with literature data (^{4,5}).

The different magnitude of the exchange constants of the same metal on different resins is connected with the difference in ΔE_{nonel}, which is due to the different structure of the hydrocarbon skeleton of the resins.

For one and the same pair of exchanging ions in a given solvent

a linear dependence should be obtained—$\lg K$ on $1/T$. Such a dependence was in fact obtained by us for the exchange of Na^+ and K^+ ions on the H-form of several sulfonic resins (Fig. 1).

Further, for constant $\Delta F_{\text{nonsolv}}$ and $(1/a_{H^+} - 1/a_{Me^+})$, a linear dependence of $-\lg K$ on $1/D$ should be obtained.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Such assumptions may be made for aqueous-alcohol solutions with a low alcohol concentration, since in such media the ions are predominantly hydrated (as may be judged, for example, from measurements of ion mobilities in aqueous-alcohol solutions ([6])). The addition of alcohol is reflected here, in the first approximation, only in a change in the dielectric constant.

In studying the equilibrium of exchange of alkali-element ions on sulfonic resins in aqueous-alcohol solutions with alcohol concentrations up to 60%, we obtained a linear dependence of $-\lg K$ on $1/D$ (Fig. 2).

Fig. 2. Dependence of $-\lg K$ on $1/D$ for exchange on the H-form of eosphatite in mixtures H_2O—CH_3OH:
1–LiCl; 2–NaCl, 3–KCl

It is of interest that the difference in the structure of the hydrocarbon framework of the resin does not affect the character of the change in the equilibrium constant with the composition of the solvent. This is indicated by the identical values of the ratios of the exchange constants Na^+—H^+ in aqueous-alcohol solutions to the exchange constants Na^+—H^+ in water for three different sulfonic resins (Fig. 3).

Incidentally, in a number of studies on the effect of alcohol additions on the dissociation constant of acids ([7,8]), the instability constant of complexes ([9]), and normal electrode potentials ([10,11]), a simple linear dependence of $\lg K$ or of the normal potentials on $1/D$ of the solvent at not very high alcohol concentrations was also found. This also indicates the possibility of applying a simple electrostatic model to reactions in such solutions.

Fig. 3. Dependence of

$$\lg \frac{K_{\text{mixed solution}}}{K_{H_2O}}$$

on $1/D$ for exchange of NaCl on the H-form of eosphatite, SBS and SDV-3 in mixtures H_2O—CH_3OH

When the alcohol concentration is increased above 60%, the linear dependence of $-\lg K$ on $1/D$ is disrupted and the curve passes through a minimum (see Fig. 2). No linear dependence is obtained either in the exchange of alkali-metal ions for hydrogen in aqueous-acetone solutions (Fig. 4). However, such a dependence in aqueous-acetone solutions is obtained when alkali-metal ions are exchanged for one another.

Fig. 4. Dependence of $-\lg K$ on $1/D$ for exchange on SBS in aqueous acetone solutions: 1—Li^+—H^+; 2—Na^+—H^+; 3—K^+—H^+; 4—Na^+—Li^+.

Figure 4: Fig. 4. Dependence of $-\lg K$ on $1/D$ for exchange on SBS in aqueous acetone solutions: 1—Li^+—H^+; 2—Na^+—H^+; 3—K^+—H^+; 4—Na^+—Li^+.

For an explanation it is necessary to take into account the behavior of acids in these solvents. The fact is that, along with solvation and interaction of solvated ions, which is characteristic of solutions of all electrolytes, there is also a specific chemical interaction of the hydrogen ion—the proton—with the first molecule of the solvent, with formation of a lyonium ion (in the case of water, the hydroxonium ion H_3O^+), which is subsequently solvated like ordinary monovalent ions through orientation of the dipolar molecules of the solvent ([12]). Such a specific interaction with the first molecule of solvent is either absent or very weak for all other ions.

In aqueous-alcohol solutions of acids, the hydrogen ions are predominantly hydrated ([13]). The interaction of the proton with alcohol molecules begins be apparent only at high alcohol concentrations. In the formula derived earlier this will appear in a change of $\Delta F_{\text{nonel.}}$.

Acetone is a solvent different from alcohols and water because the dipole moment of its molecules (2.95 debye) is large in comparison with the dipole moments of water (1.84 debye) and alcohols (1.69 debye for methyl alcohol, 1.70 debye for ethyl alcohol [14]). Because of this, the interaction of the proton with acetone molecules begins to be apparent at lower concentrations than with methyl alcohol.

N. A. Izmailov, in studying the behavior of a series of acids in aqueous acetone solutions, showed [7,15] that $\lg K_{\text{diss}}$ of individual acids does not vary linearly with $1/D$ (as for aqueous-alcoholic solutions), but the logarithm of the ratio of the constants of two acids varies linearly. This indicates the specific character of the interaction of the proton with solvent molecules.

Fig. 4. Dependence of $-\lg K$ on $1/D$ for exchange on SBS in aqueous acetone solutions: 1—Li^+—H^+; 2—Na^+—H^+; 3—K^+—H^+; 4—Na^+—Li^+.

A similar picture is obtained for ion exchange in aqueous acetone solutions: $\lg K$ for the exchange of an alkali metal for hydrogen does not depend linearly on $1/D$, but the logarithm of the exchange constant of two alkali metals for one another, obtained by dividing the constants for the exchange of the ions of these metals for hydrogen, depends linearly on $1/D$ (see Fig. 4).

Thus, in ion-exchange reactions in acetone-water solutions without the participation of the hydrogen ion, the influence of acetone is manifested only in a change of the dielectric constant of the solvent, and a linear dependence of $\lg K$ on $1/D$ is obtained; in reactions with the participation of the hydrogen ion, the interaction of the proton with molecules of the mixed solvent is also manifested, and no linear dependence of $\lg K$ on $1/D$ is obtained.

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Note: Figure translations are in progress. See original paper for figures.