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Abstract

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DIFFUSION OF WATER MOLECULES IN THE PRESENCE OF HYDRATED IONS

(Presented by Academician B. P. Konstantinov, 15 III 1962)

At present there is no quantitative theory of diffusion in liquids. More or less rigorous theoretical treatments lead to expressions containing unknown parameters, i.e., they cannot predict the value of the diffusion coefficient ($^{1-4}$). As for diffusion in concentrated electrolyte solutions, in this case there is not even a qualitative description of the phenomenon.

In this article a particular question is considered: the diffusion of water molecules in the presence of hydrated ions. An attempt is made, on the basis of a simplified model, to obtain an expression describing the dependence of the self-diffusion coefficient of water on the composition of the solution. Since the forces of interaction of an ion with water molecules decrease rapidly with distance, only interaction with the nearest molecules may be taken into account. Investigation of aqueous solutions of alkali-halide compounds by the nuclear magnetic resonance method showed that singly charged ions exert a significant influence only on water molecules entering the first coordination sphere of the ion (^{5}).

Proceeding from this, we assume that water molecules which are not the nearest neighbors of the ion (free molecules) perform the same motions as in pure water. We also suppose that water molecules situated in the hydration shell of the ion (n_1 molecules per ion) move together with it as a single whole and, consequently, the diffusion of such a complex is described by a single diffusion coefficient D_i.

Then the diffusion coefficient $D_{\mathrm{H_2O}}$ of water molecules in solution is written in the form

$$D_{\mathrm{H_2O}} = D_i N_i + D^0_{\mathrm{H_2O}}(1 - N_i) \tag{1}$$

or

$$D_{\mathrm{H_2O}} = D^0_{\mathrm{H_2O}} - (D^0_{\mathrm{H_2O}} - D_i)N_i. \tag{2}$$

Here D_i is the self-diffusion coefficient of the ions in solution, $D^0_{\mathrm{H_2O}}$ is the self-diffusion coefficient of pure water, and N_i is the mole fraction of water diffusing with the velocity of the ion.

Let us introduce some refinements. A comparatively immobile hydrated ion blocks the path for motion in one of the six possible directions for neighboring water molecules, i.e., for molecules located in the second coordination sphere of the ion. We denote their number by n_2. The velocity of molecular motion in this direction is determined by the velocity of the ion. This effect is equivalent to the fact that, in addition to the molecules bound to the ion and moving with the latter' s velocity, a further $n_2/6$ free molecules per ion diffuse. In the tetrahedral structure $n_2 = 12$, and thus $n_2/6 = 2$. The number of "slow" (moving with the velocity of the ion) water molecules is equal to $n_1 + 2$. The ratio of the number of ions to the total number of water molecules is equal to $m/55.5$, where m is the concentration of the solution in gram-moles per 1000 g of water.

Taking the above into account, we rewrite (2) as

$$D_{\mathrm{H_2O}} = D^0_{\mathrm{H_2O}} - (D^0_{\mathrm{H_2O}} - D_i)\frac{(n_1 + 2)m}{55.5}. \tag{3}$$

In the present work diffusion was studied in aqueous solutions of LiCl and $\mathrm{LiNO_3}$, containing hydrating $\mathrm{Li^+}$ ions and weakly hydrating $\mathrm{Cl^-}$ and $\mathrm{NO_3^-}$ ions. The effect of $\mathrm{Cl^-}$ and $\mathrm{NO_3^-}$ ions on the diffusion of water molecules is insignificant. The latter was checked experimentally: the diffusion coefficient of water molecules changed little upon dissolution of salts containing these anions and the nonhydrating cation $\mathrm{K^+}$ (the increase did not exceed 5% in a 2 m solution at 25°).

Since the lithium ion is of low mobility and is hydrated by 4-6 water molecules (^{6}), according to formula (3) a considerable slowing of the diffusion of water molecules in its presence is to be expected. Measurements of the coefficients of mutual diffusion of isotopic ions $\mathrm{Li^6}$–$\mathrm{Li^7}$ (7.5-30% $\mathrm{Li^6}$) and isotopic molecules $\mathrm{H_2O}$–HDO (0-1% D) were carried out by the method of a cell with a porous partition ($^{7-9}$). The improvement of the method made in the present work consisted in the fact that, owing to a change in the configuration of the magnetic field by means of a double pair of pole pieces placed on the magnet, wear of the porous partition of the stirrer was eliminated. The cell was calibrated with aqueous solutions (0.2-0.7 m) of NaCl, for which the data (^{10}) were used.

The isotopic composition of water separated from the solution by vacuum distillation was determined by the quartz-float method (^{11}) with an accuracy of 0.001 at. %. The isotopic composition of lithium was determined by comparing the densities of LiF crystals prepared from the samples analyzed. (Accuracy 0.01 at. %.)

The results obtained are presented in Table 1.

Table 1

Coefficients of mutual diffusion of isotopic lithium ions and isotopic water molecules

T-ra, °C	$D^0_{H_2O} \cdot 10^5$, cm²/sec in pure water	$D_{Li^+} \cdot 10^5$, cm²/sec	$D_{H_2O} \cdot 10^5$, cm²/sec, exp.	$D_{H_2O} \cdot 10^5$, cm²/sec, by (3)	T-ra, °C	$D^0_{H_2O} \cdot 10^5$, cm²/sec in pure water	$D_{Li^+} \cdot 10^5$, cm²/sec	$D_{H_2O} \cdot 10^5$, cm²/sec, exp.	$D_{H_2O} \cdot 10^5$, cm²/sec, by (3)
2 *M* **solution LiCl**	**2** *M* **solution LiCl**	**2** *M* **solution LiCl**	**2** *M* **solution LiCl**	**2** *M* **solution LiCl**	**5** *M* **solution $LiNO_3$**	**5** *M* **solution $LiNO_3$**	**5** *M* **solution $LiNO_3$**	**5** *M* **solution $LiNO_3$**	**5** *M* **solution $LiNO_3$**
15	1.78	0.69	1.50	1.54	15	–	0.568	1.11	1.12
25	2.29	0.89	1.92	1.99	25	–	0.728	1.39	1.44
35	2.89	1.15	2.42	2.51	35	–	0.917	1.73	1.83
45	3.51	1.41	2.99	3.05	45	–	1.11	2.12	2.21

The experiments showed that both D_{Li^+} and D_{H_2O} are independent, within the limits of experimental accuracy (1%), of replacement of the Cl^- ion by NO_3^- ($2m$ solution). The diffusion coefficients given in Table 1 are mean values from several experiments. The calculated values of D_{H_2O} were obtained from formula (3) with the adopted value $n_1 = 4$. As is seen from these data, the experimental values of D_{H_2O} are very close to the calculated ones.

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