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Hydration Numbers of Sodium Chloride in Dioxane–Water Mixtures and the Volume Change Accompanying Hydration

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The density and the ultrasonic velocity were measured for dioxane–water solutions of sodium chloride at 25 °C. The hydration numbers of sodium chloride were estimated and were compared with those determined by electrical-conductivity measurements. The difference between them was discussed. The volume change caused by the dissociation of sodium chloride in a 60 wt % aqueous dioxane solution was determined from the data of the apparent molal volume. This value is in good agreement with that calculated from the excess ultrasonic absorption.

In a dioxane–water mixture with a lower dielectric constant than water, NaCl would dissociate incompletely and a dissociation equilibrium may be attained between the Na^+ ions, the Cl^- ions, and the undissociated NaCl molecules. If the water molecules bound to ions are considered to be incompressible, then a volume change attributable to ionization would be found. The volume change was estimated from density measurements of aqueous dioxane solutions of sodium chloride and was compared with that calculated from excess ultrasonic absorption, as reported in the previous paper.[1] The sound velocity increases with an increase in the concentration of NaCl in dioxane–water mixtures. This increase reflects a decrease in the compressibility of the solvent caused by hydration. The hydration numbers due to the ionization of NaCl were calculated using some assumptions.

Experimental

The densities were measured by a float method similar to that used by Desnoyers and Arel.[2] A float was suspended in the pan of a balance by means of a nylon thread 0.1 mm in diameter and was then placed in the solution in a thermostated cell. The volume of the float used was about 230 cm^3.

The difference between the density of a solution, d, and that of water, d_0, is related to the weights, W and W_0, of the float in the solution and in water respectively by

$$d - d_0 = (W_0 - W)/V, \qquad (1)$$

where V is the volume of the float. Measurements were made at 25 °C.

The ultrasonic velocities were measured by the interference method of the pulse wave and the continuous wave at 5 MHz. The molalities of sodium chloride in mixed solvents containing 0 to 60 wt % dioxane were in the range of 0.1—1.0 m.

Results

The ultrasonic velocities in solutions of NaCl in dioxane–water mixtures are shown in Fig. 1.

The apparent molal volume, ϕ_v, and the apparent molal compressibility, ϕ_k, are given by

$$\phi_v = \frac{V-V_s}{n_2} = \frac{1000}{mdd_s}(d_s-d) + \frac{M}{d}, \qquad (2)$$

and

$$\phi_k = -\left(\frac{\partial \phi_v}{\partial p}\right)_T = \frac{\beta V-\beta_s V_s}{n_2} = \frac{1000(\beta-\beta_s)}{md_s} + \beta\phi_v, \qquad (3)$$

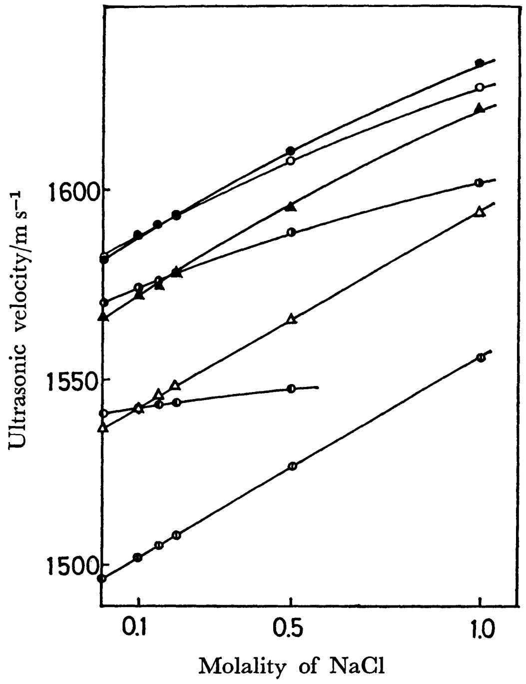

Fig. 1. Ultrasonic velocity in solutions of NaCl in dioxane–water mixtures at 25 °C.
Dioxane wt %: ⦶ 0, △ 10, ▲ 20, ● 30, ○ 40, ◑ 50, ◐ 60.

where n_2, m, and M are the number of moles, the molality (mole per 1000 g of solvent), and the molecular weight of NaCl respectively. V, d, and β are the volume, density, and compressibility of the solution respectively. The subscript s denotes the solvent. A typical example of the plot of ϕ_v *vs.* $(\text{molality})^{1/2}$ is shown in Fig. 2.

Discussion

Hydration Number of Sodium Chloride. In the solution of NaCl in a dioxane–water mixture, both water and dioxane molecules may participate in the formation of solvation shells around ions. As the dipole moment of a dioxane molecule is much smaller than that of water, the electrostrictive effect of the ions on dioxane molecules in the solvation shells might be negligible[3] in comparison with the electrostriction on water molecules. Therefore, the volume of dioxane molecules would be unchangeable in the solution. Assuming that the compressibilities of the ions and water molecules bound to the ions are equal to zero,

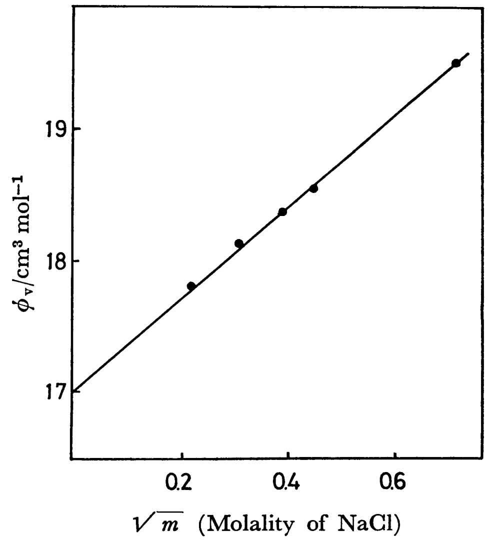

Fig. 2. Apparent molal volume of NaCl in 60 wt % aqueous dioxane solution at 25 °C.

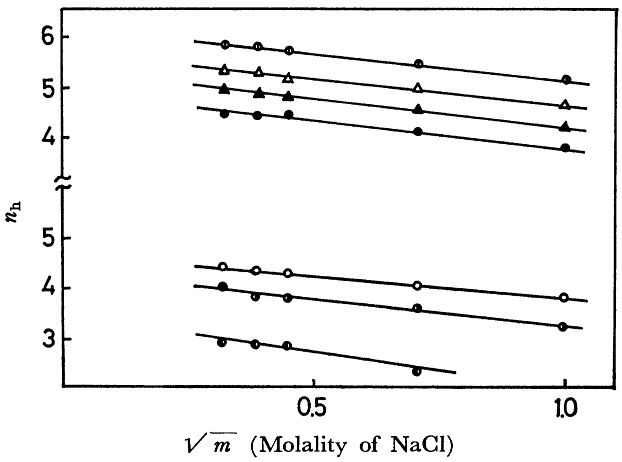

Fig. 3. Hydration numbers of NaCl in dioxane-water mixtures at 25 °C.
Dioxane wt %: ⦶ 0, △ 10, ▲ 20, ● 30, ○ 40, ◑ 50, ◐ 60.

the compressibility of the solution, β, is given by

$$\beta = -\frac{1}{V}\frac{\partial}{\partial p}\{V_0(n_1-n_i)+V_3n_3\}$$
$$= -\frac{1}{V}\{n_i\beta_0V_0-\beta_sV_s\}, \quad (4)$$

where n_1 is the total number of moles of water in the solution, n_i is the number of water molecules bound to the ions, V_0 is the molal volume of free water not bound to the ions, β_0 is the compressibility coefficient of pure water, and V_3 and n_3 are the molal volume and the number of moles of dioxane.

According to Eqs. 3 and 4, the hydration number, n_h, of sodium chloride in a dioxane–water mixture is expressed as

$$n_h = \frac{n_i}{\alpha n_2} = -\frac{\phi_K}{\alpha\beta_0V_0}, \quad (5)$$

where α is the degree of dissociation of NaCl. The values of n_h are shown in Fig. 3. In 0, 10, 20, and 30 wt % dioxane aqueous solutions, α is assumed to be approximately 1.

The dissociation equilibrium constants of NaCl in dioxane–water mixtures were obtained by electrical conductance measurements.[4–6] NaCl is considered to be in an equilibrium[6] such as

$$\text{NaCl(aq)} + k\text{H}_2\text{O} \overset{K^\circ}{\rightleftharpoons} \text{Na(aq)}^+ + \text{Cl(aq)}^-,$$

$$K^\circ = \frac{K}{C^k_{H_2O}}, \text{ and } K = \frac{C_{Na^+}\cdot C_{Cl^-}}{C_{NaCl}}, \quad (6)$$

where C_{H_2O} is the molar concentration of water and where k is the net change in the waters of solvation upon the dissociation of NaCl and corresponds to the hydration number. K° and k are found to be independent of C_{H_2O} and to vary only with the temperature:

$$\log K^\circ = -10.00, \quad k = 6.4 \ (25\,°\text{C})^{6)}$$
$$\log K^\circ = -11.13, \quad k = 7.0 \ (50\,°\text{C})^{6)} \quad (7)$$

As may be seen in Fig. 3, the hydration number, n_h, of NaCl in an aqueous solution is close to k (=6.4) at an infinite dilution, but n_h in dioxane–water mixtures decreases with an increase in the concentration of dioxane. The difference between n_h and k in a dioxane–water mixture might be caused by differences in the models used for the hydrated ion and the assumptions associated with these models. If the hydration number is constant and independent of the concentration of dioxane in dioxane–water mixtures, the compressibilities of hydrated ions must have definite values. The existence of dioxane molecules might influence the electrostriction of the ions in relation to the surrounding water molecules.

Volume Change Accompanying the Dissociation of Sodium Chloride. It is useful to estimate further the volume change which accompanies the ionization of NaCl in dioxane–water mixtures. The apparent molal volume of NaCl, ϕ_v, derived from Eq. 2, is related to the degree of dissociation, α, by

$$\phi_v = (1-\alpha)\phi_u + \alpha\phi_i, \quad (8)$$

where ϕ_i and ϕ_u are the apparent molal volumes of NaCl in the ionized and un-ionized states respectively.

The volume change caused by hydration, ΔV, is given by

$$\Delta V = \phi_i - \phi_u. \quad (9)$$

NaCl in dioxane–water mixture might be ionized completely at an infinite dilution; therefore, ϕ_i, can be approximately determined by the extrapolation of ϕ_v to zero concentration:

$$\phi_i \simeq \phi_v^\circ, \quad (10)$$

where ϕ_v° is the apparent molal volume at an infinite dilution.

As may be seen in Fig. 2., the value of ϕ_v° in a 60 wt% dioxane aqueous solution is 17.0 cm^3/mol. This value is a little larger than the ϕ_v° value of 16.628 cm^3/mol[7] in water. From Eqs. 8, 9, and 10, we obtain $\Delta V \approx -7$ cm^3/mol.

On the other hand, ΔV was estimated on the basis of ultrasonic absorption measurements.[1] In this paper, ΔV was calculated by considering the enthalpy change,

ΔH, for the reaction. The maximum excess ultrasonic absorption per wavelength at the relaxation frequency, $\mu_{\max}$, is given by[8,9]

$$\mu_{\max} = \frac{\pi}{2\beta RTV}\left(\Delta V - \frac{l}{dC_p}\Delta H\right)^2 \frac{1}{\chi}$$

$$\chi = \left(\frac{1}{n_{\mathrm{Na}^+}} + \frac{1}{n_{\mathrm{Cl}^-}} + \frac{1}{n_{\mathrm{NaCl}}}\right), \qquad (11)$$

where l is the coefficient of thermal expansion, C_p is the heat capacity at a constant pressure, and n_{Na^+}, n_{Cl^-}, and n_{NaCl}, are the numbers of the moles of the sodium ion, the chloride ion, and undissociacted sodium chloride. The value of l/dC_p in a 60 wt % dioxane aqueous solution at 25 °C was estimated by interpolation of the literature values.[9]

The variation in the dissocication constant with the temperature is given by

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

Taking the values derived from Eqs. 6 and 7, we find:

$$\Delta H \approx -6.6\,\mathrm{kcal/mol}$$

Using these values in Eq. 11, we calculate $\Delta V \approx -8$ cm^3/mol. This value is in better agreement with the ΔV estimated from the density measurements than with $\Delta V \approx -5$ cm^3/mol, which was determined by neglecting ΔH in Ref. 1.

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