Solvation of Ions in Aqueous Solutions of Hydrophobic Solutes

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The self-diffusion of Na^+, Et_4N^+ and I^- in mixtures of water with *n*-propanol at 25 °C and with *tert*-butanol at 30 °C was measured as function of salt concentration and solvent composition. The limiting self-diffusion coefficients of the ions were used to compute the ionic radii. The influence of the composition of the solvent on the solvation of the ions is discussed. In aqueous solutions of both alcohols the effective ionic radii are reduced. The strongest influence is found for the same solvent composition for which the highest concentration of the alcohol clusters has been reported. Hydration of the clusters of *n*-propanol causes a vanishing of the second hydration shell of Na^+ and the first one of Et_4N^+ and I^-. In the case of *tert*-butanol even the first hydration shell of Na^+ is partially reduced.

Much attention has recently been paid to the hydration of hydrophobes and hydrophobic association. These effects are believed to be responsible for the stability of proteins and nucleic acids as well as for the formation of micelles [1]. Both hydrophobic phenomena cause an inhomogeneity of the solution on the molecular level, therefore they should affect the other molecular interactions occurring in the system.

We are interested in the solvation of ions in solutions containing hydrophobic compounds. *n*-Propanol and *tert*-butanol have been chosen as examples of the hydrophobic solutes. Both alcohols are completely miscible with water, but their aqueous solutions are microheterogeneous [2, 3]. That inhomogeneity is the consequence of the hydrophobic effects, as might be seen from X-ray diffraction [1, 4–6], neutron [7] and light [8–11] scattering experiments.

In order to gain an insight into the solvation of ions, their self-diffusion has been investigated. Sodium and tetraethylammonium iodides have been chosen as the model salts because of their relatively high solubility in both mixed solvents. The other reason for this choice was that we wanted to compare the effect of the hydrophobic solutes on the hydration of sodium and tetra-ethylammonium cations [12].

Experimental

n-Propanol (spectroscopy grade, Merck), *tert*-butanol (spectroscopy grade, Merck), NaI (suprapure, Merck) and tetraethylammonium iodide (suprapure, Merck) were used as received. Water was deionized, double distilled and degassed. Its specific conductivity was smaller than 1 μS/cm. All solutions were prepared by weight.

The self-diffusion coefficients have been measured by the open-end capillary method using ^{22}Na and ^{125}I as the radioactive tracers. The radioactivities of the labelled compounds were measured in toluene-ethanol solutions of 2,5-diphenyloxazole (PPO) with a liquid scintillation counter RackBeta (LKB).

The experimental values of the ionic self-diffusion coefficients were calculated as the mean value from at least 9 independent experiments. Their statistical error, calculated at 0.95 confidence level does not exceed 0.5%.

Results

In mixtures of water with *n*-propanol (NPA) the self-diffusion coefficients of sodium D_{Na^+} and iodide D_{I^-} have been determined over the whole range of the solvent composition for salt molarities ranging between 5×10^{-4} and 5×10^{-2}. The self-diffusion experiments were carried out at 25.0 ± 0.01 °C.

The experimental values of the ionic self-diffusion coefficients D_i were used to compute the limiting self-diffusion coefficient D_i^∞. As has been shown previously [13], the influence of the salt molarity m on D_i is given by

$$D_i = D_i^\infty \times \left\{1 - \frac{2.806 \times 10^6}{(\varepsilon_0 \times T)^{1.5}} \times \left[1 - \sqrt{\frac{B_i + 3}{4(B_i + 1)}}\right] \times \sqrt{m}\right\}, \quad (1)$$

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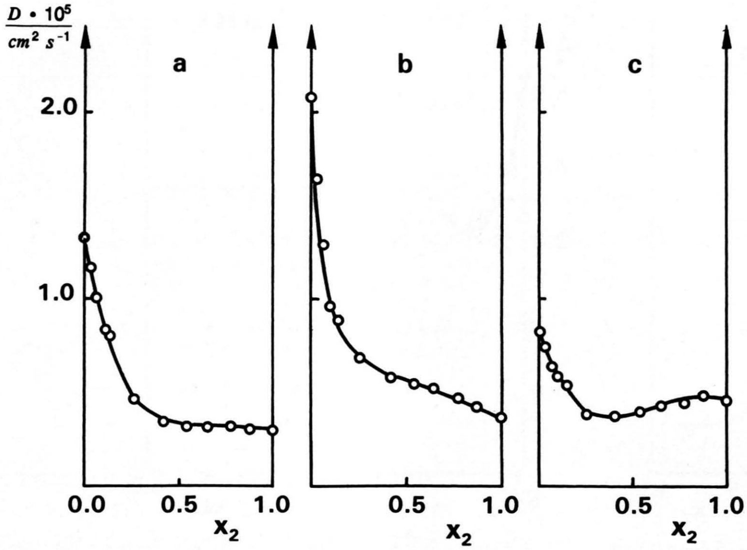

Fig. 1. Variation of the limiting self-diffusion coefficient D^{∞} of Na^+ (a), I^- (b) and Et_4N^+ (c) with the mole fraction x_2 of NPA at 25.0 °C.

where T and ε_0 denote temperature and the static dielectric constant of the solvent, respectively, and B_i is the parameter resulting from ion-ion interactions and equals the ratio of the limiting self-diffusion coefficients of the ion under study D_i^{∞} and its counter ion D_j^{∞} $(B_i = D_i^{\infty}/D_j^{\infty})$.

The D^{∞}-values for the sodium and iodide ions were calculated by the current iteration of the experimental D-values for both ions simultaneously. Details of the computation procedure were given in [13]. Data of the static dielectric constant ε_0 were taken from [14].

The limiting self-diffusion coefficients of Et_4N^+ ions (D_{TEA}) were obtained via the Nernst relation

$$D_{\mathrm{TEA}}^{\infty} = \frac{RT}{F^2} \times \lambda^0 - D_{\mathrm{I}^-}^{\infty}\,, \tag{2}$$

where R and F denote the gas and Faraday constants, respectively. Values of the limiting conductivity of Et_4NI, λ^0, have been reported previously [15].

The measured dependence of D^{∞} on the mole fraction of NPA (x_2) for all studied ions is summarized in Table 1 and plotted in Figure 1.

If x_2 is smaller than 30 mol%, D^{∞} decreases considerably for all studied ions with increasing x_2. This behaviour is expected, because the solvent viscosity increases rapidly. In spite of the viscosity maximum at about 27 mol% NPA [16], the self-diffusion coefficients of the sodium and iodide ions do not show any minimum but decrease monotonously over the whole range of the solvent composition. D^{∞} of the tetraethylammonium ions, however, shows a minimum (see Fig-

Table 1. Limiting self-diffusion coefficients of sodium D_{Na^+}, iodide D_{I^-} and tetraethylammonium D_{TEA} ions in mixtures of water with *n*-propanol (NPA) at 25 °C (x_{NPA} = mole fraction of NPA).

x_{NPA}	$D_{\mathrm{Na}^+} \cdot 10^5$ $\mathrm{cm^2\,s^{-1}}$	$D_{\mathrm{I}^-} \cdot 10^5$ $\mathrm{cm^2\,s^{-1}}$	$D_{\mathrm{TEA}} \cdot 10^5$ $\mathrm{cm^2\,s^{-1}}$
0.000	1.325	2.094	0.82
0.023	1.170	1.627	0.74
0.046	0.991	1.270	0.63
0.107	0.828	0.953	0.58
0.138	0.805	0.881	0.53
0.265	0.461	0.690	0.37
0.419	0.360	0.575	0.37
0.546	0.320	0.554	0.39
0.658	0.323	0.510	0.43
0.783	0.321	0.462	0.44
0.878	0.305	0.412	0.49
1.000	0.306	0.370	0.45

Table 2. Limiting self-diffusion coefficients of sodium D_{Na^+} and iodide D_{I^-} ions in mixtures of water with *tert*-butanol (TBA) at 30.0 °C (x_{TBA} = mole fraction of TBA).

x_{TBA}	$D_{\mathrm{Na}^-} \cdot 10^5$ $\mathrm{cm^2\,s^{-1}}$	$D_{\mathrm{I}^-} \cdot 10^5$ $\mathrm{cm^2\,s^{-1}}$
0.000	1.375	2.120
0.025	1.135	1.587
0.050	0.97	1.164
0.100	0.75	0.77
0.15	0.56	0.64
0.20	0.47	0.55
0.25	0.41	0.48
0.30	0.38	0.44
0.40	0.31	0.35
0.60	0.24	0.29
0.80	0.20	0.24

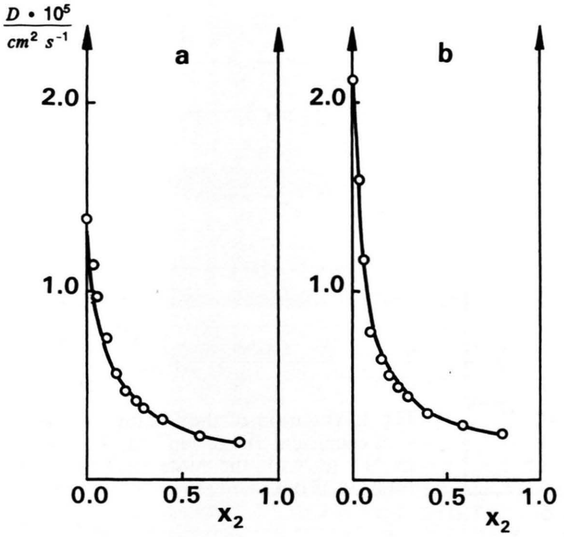

Fig. 2. Variation of the limiting self-diffusion coefficient D^∞ of Na^+ (a) and I^- (b) with the mole fraction x_2 of TBA at 30.0 °C.

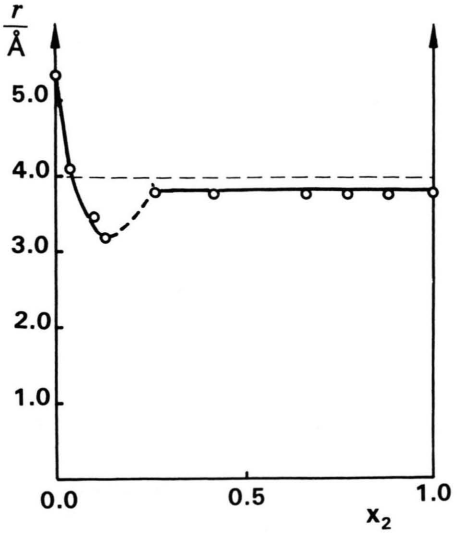

Fig. 3. Dependence of the radius of Et_4N^+ on the mole fraction x_2 of NPA (the dashed line denotes the radius in crystal).

ure 1 c) at the solvent composition where the viscosity is maximum, but the minimum is rather flat as compared with the viscosity maximum.

In mixtures of water with *tert*-butanol (TBA) the self-diffusion coefficients of Na^+ and I^- have been determined at 30.0 ± 0.01 °C for alcohol concentrations smaller than 80 mol% and molarities of NaI between 5×10^{-4} and 2×10^{-2}. The results of D^∞ with ε_0 values taken from [17] are summarized in Table 2 and plotted in Figure 2.

The D^∞-values for both ions decrease with increasing TBA concentration, and despite of the viscosity maximum at about 27 mol% TBA [18], a minimum of D^∞ does not appear.

Discussion

In order to discuss the influence of the concentration of NPA and TBA on the solvation of the ions, the effective ionic radius r_i was calculated from the equation

$$r_i = \frac{k_B T}{4\pi \eta D_i^\infty} + 0.0103\, \varepsilon_0 \,, \qquad (3)$$

where η denotes the viscosity of the solvent.

The above equation is a modified [13] Gill's approximation, in which both viscous and dielectric friction forces are taken into account. Contrary to Gill's approach [19], the first term in (3), resulting from the viscous friction, is written for perfect slipping, which is believed to be more adequate to describe the transport of ions [20–22].

The variation of the radius of Et_4N^+ with the mole fraction of NPA is shown in Figure 3. In pure water the radius is greater than in crystal because the cations bind several water molecules. The addition of NPA causes a significant reduction of the ionic radius, r_i becoming smaller than in crystal. Such a feature can be understood if one considers the ionic radius as that of a spherical force field [23]. The smallest value of r_i is observed at about 17 mol% NPA. At that composition several properties of the solvent are anomalous [6, 7, 24]. As far as hydrophobic phenomena are concerned, for that composition the concentration of the alcohol aggregates is highest [6, 9]. These clusters are of the micelle type and need several water molecules to be stabilized [9]. The observed coincidence of the highest cluster concentration and the strongest reduction of the ionic radius leads to the conclusion that water molecules "prefer" to hydrate alcohol clusters rather than tetraethylammonium cations. Further increase of NPA concentration causes only a slight increase of the ionic radius. At about 30 mol% NPA the radius of Et_4N^+ reaches a constant value, about the same as that in crystal. This indicates that NPA molecules cannot solvate the cation, therefore the cations remain unsolvated.

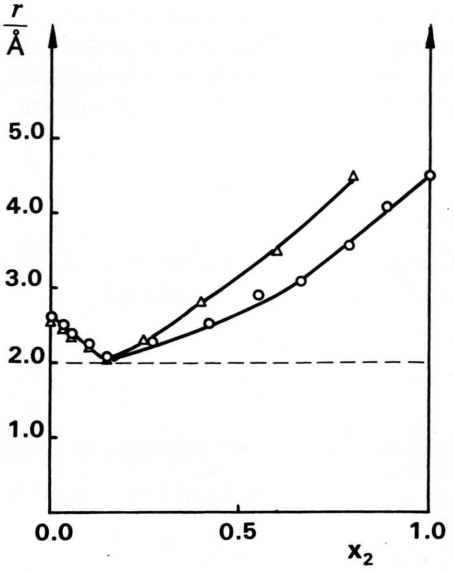

Fig. 4. Dependences of the radius of I^- on the mole fraction x_2 of the alcohol in mixtures of water with NPA (○) and with TBA (△) (the dashed line denotes the radius in crystal).

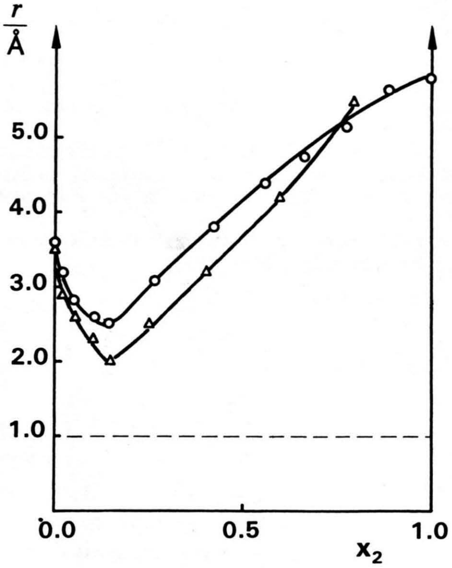

Fig. 5. Dependences of the radius of Na^+ on the mole fraction x_2 of the alcohol in mixtures of water with NPA (○) and with TBA (△) (the dashed line denotes the radius in crystal).

The influence of both NPA and TBA on the radius of iodide ions is shown in Figure 4. In pure water the radius is slightly greater than in crystal, indicating that the hydration shell of anions consists of only a few water molecules, as is generally the case [25]. With increasing concentration of the alcohol the radius of I^- decreases and it reaches its smallest value at about 17 mol% of alcohol. That value equals the radius in crystal, which means that the hydration shell has disappeared. Instead, the alcohol clusters are hydrated. In aqueous solutions of both TBA [4, 7] and NPA [6, 9] at 17 mol% alcohol the concentration of micelle type aggregates is highest. A further increase of the alcohol concentration causes an increase of the ionic radius. The dependence of r_i on x_2 is almost linear, which may suggest that the solvation shell, which is newly forming, has the same composition as the bulk solvent.

In Fig. 5 variation of the Na^+ radius with the mole fraction of alcohol is shown. In pure water r_i is much greater than in crystal, which suggests that the diffusing entity contains not only the first but also the second hydration shell. The effect of alcohol addition on the ionic radius is dramatic. The smallest radius is again observed at about 17 mol% of alcohol and it is smaller for the TBA than for the NPA solutions. This might be understood, because the stabilization of micelle type aggregates at TBA involves much more water molecules [6]. Thus the observed difference confirms the supposition that water molecules "prefer" to hydrate alcohol clusters to ions. A comparison of the radii of Na^+ in solutions with that in crystal allows to estimate its hydration numbers. In aqueous solution of NPA the smallest hydration number of sodium ions is 6, which means that the first solvation shell remains undisturbed [25], whereas that value obtained for the TBA solution is equal to 4. This leads to the conclusion that the hydration of TBA clusters can compete successfully even with interactions between cation and water molecules in the first solvation shell. The reduction of the hydration number from 6 to 4 seems to be reasonable, because in aqueous solution the hydration of Na^+ is of $4+2$ type [26]. Further increase of the alcohol concentration causes an increase of the ionic radius. In solutions of NPA that increase is almost linear, but if we compare the plot of r_i vs. x_2 with the ionic radii in one component solvents, e.g. in pure water and in pure NPA, the negative deviation from the additivity might be estimated which suggests a weak preferential hydration of ions. One may suppose that even in alcohol rich solvents the first solvation shell consists of water molecules, whereas there is a random solvation in the second shell. Similar behaviour is observed in solutions of TBA. Starting from its smallest value, the ionic radius increases linearly with increasing TBA concentration. Therefore the solvation of a sphere, which consists of the cation and its first hydration shell, formed by 4 water molecules, is a random one. Thus even in alcohol rich mixtures the sodium ions are preferentially hydrated.

Our results indicate that the solvation of ions is very sensitive on the presence of hydrophobic solutes. The hydration of alcohol clusters competes successfully not only with the hydration of Et_4N^+ and iodide anions, but also with the strong hydration of sodium cations. We would like also to emphasize that we have not observed any effect of the formation of clathrates, which are believed to be the result of the hydrophobic hydration of alcohol molecules [4–6], on the solvation of ions.

Acknowledgement

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