

Acetonitrile-Water Solutions of Sodium Halides: Viscosity and Self-Diffusion of CH₃CN and H₂O

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Measurements of the viscosity of solutions of NaCl and NaI in acetonitrile-water mixtures at 25 °C, and of the self-diffusion coefficients of CH₃CN and H₂O in these liquids, using ¹⁴C and ³H as tracers, are reported. The results confirm the previously postulated preferential solvation of the ions by acetonitrile.

The acetonitrile-water system shows a large positive deviation from Raoult's law [1] and exhibits a phase separation with an upper critical point at about 272 K and 38 mol % CH₃CN [2]. Based on Naberukhin and Rogov's [3] structural model of aqueous solutions of non-electrolytes, three structural regions have been distinguished: in water rich ($x_{AN} < 0.2$) and acetonitrile rich ($x_{AN} > 0.7$) regions the structure of the respective pure component is retained, whereas for $0.2 < x_{AN} < 0.7$ two microphases of fixed composition coexist. Results on viscosity [4], water proton chemical shift [5], luminescence [6] and self-diffusion [7] have confirmed the structural discontinuities and indicated at least five structurally distinct regions.

Addition of electrolytes might significantly affect the structural discontinuities, especially if preferential solvation of the ions occurs. From measurements of the ionic self diffusion coefficients a preferential solvation of Na⁺, Cl[−] and I[−] by acetonitrile was concluded [8]. Similar conclusions were drawn from measurements of the B-viscosity coefficients [9].

On the other hand, the ionic solvation was also studied by measurements of the free energy change on transfer of an ion from water to acetonitrile-water mixtures. The silver ion, which is known to be preferentially solvated by acetonitrile [10–13], is usually chosen as the reference ion. From the measurements a preferential hydration of alkali and halide ions was concluded [14–16].

This discrepancy may result from ion induced structural effects which contribute to the free energy of

transfer [13]. If microphases coexist, different salts may differently affect the structure. It is known that AgNO₃ lowers, whereas NaNO₃ heightens the upper critical temperature of mixing [17]. Therefore the structural effects of these electrolytes might be quite different and probably silver ion should not to be taken as the reference ion to deduce the solvation properties of alkali ions from the free energy of transfer.

As has been shown previously [18–20], the influence of electrolytes on the self-diffusion of the solvent preferentially forming the solvation shell is more significant than on that of the cosolvent.

In the present work, the viscosities and the self-diffusion coefficients of acetonitrile and water in their mixtures and in their solutions of NaI and NaCl were measured in order to find which coefficients change upon the addition of the electrolytes more noticeably.

Experimental

The solutions were prepared from NaCl suprapur (Merck), NaI suprapur (Merck), acetonitrile for spectroscopy (Merck) dried in the usual way [21], doubly distilled and degassed water, [14c]acetonitrile and [3H]water.

The self-diffusion coefficients were determined by the open-end capillary method described previously [22]. The viscosities of the solutions were determined using an Ubbelohde type viscosimeter with about 250 s outflow time of water. Water at 25 °C with density $d_w = 0.99708 \text{ g/cm}^3$ and viscosity $\eta_w = 0.8903 \text{ mNs/m}^2$ [23] was chosen as the reference liquid. The accuracy

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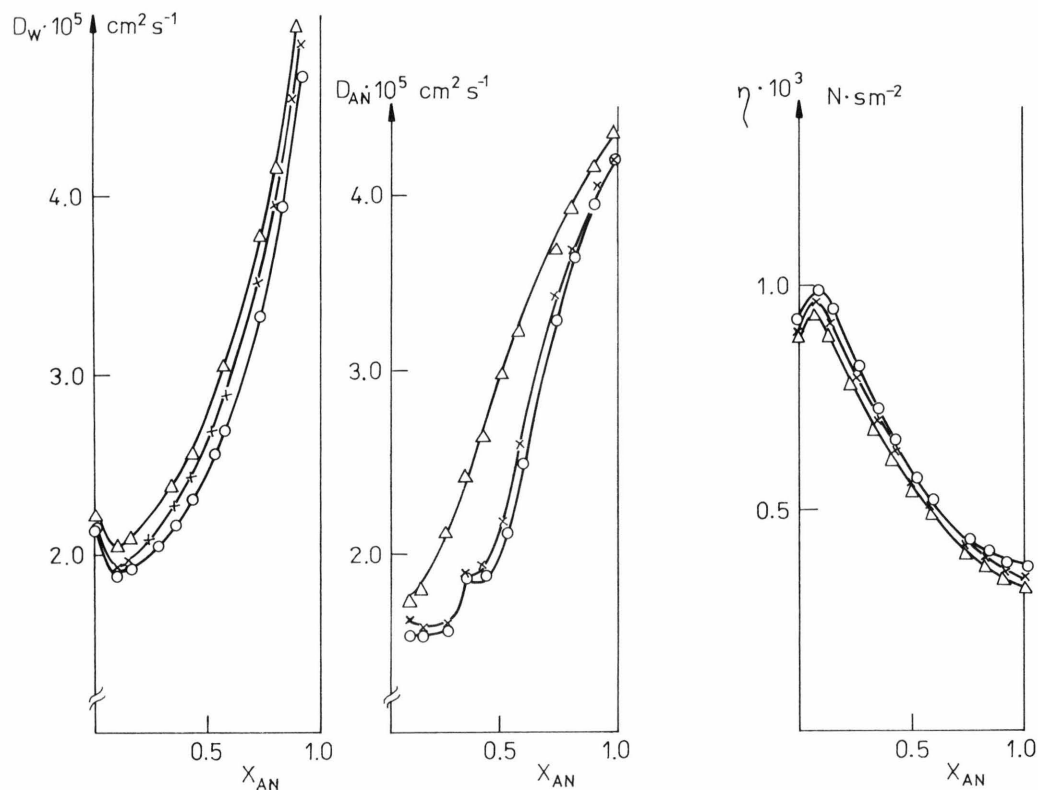


Fig. 1. Variation of the water and acetonitrile self-diffusion coefficients and the viscosity with the acetonitrile mole fraction x_{AN} . Concentration of salt (mol salt per 100 mol of solvent): (Δ) : 0.0; (\times) : 0.1; (\circ) : 0.2.

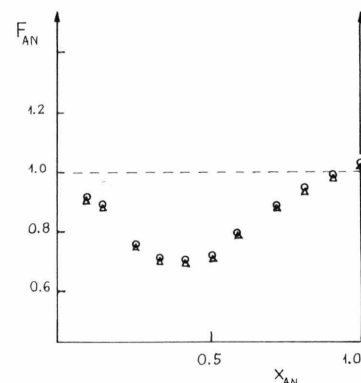


Fig. 4. Dependence of F_{AN} on the acetonitrile mole fraction. $c_{\text{salt}} = 0.1 \text{ mol}/100 \text{ mol}$. (\circ) : NaI; (Δ) : NaCl.

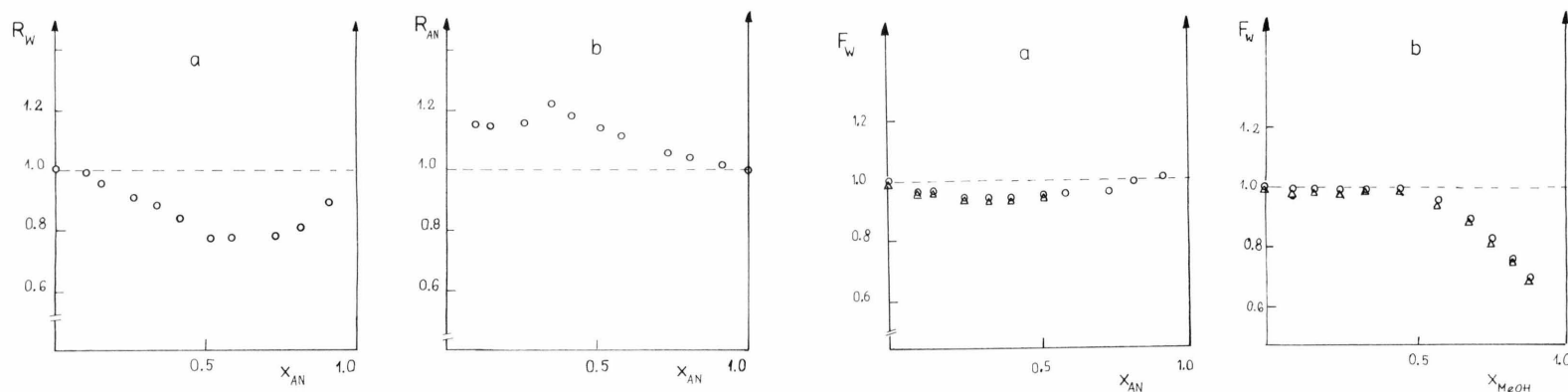


Fig. 2. Dependences of R_W and R_{AN} on x_{AN} .

Fig. 3. Dependences of F_W on composition of acetonitrile-water (a) and F_{MEOH} on composition of acetonitrile-water (b). $c_{\text{salt}} = 0.1 \text{ mol}/100 \text{ mol}$. (\circ) : NaI; (Δ) : NaCl.

Table 1. Self-diffusion coefficients of acetonitrile, $D_{AN} \cdot 10^5$ ($\text{cm}^2 \text{s}^{-1}$) in acetonitrile-water solutions of NaI and NaCl at 25.0°C (concentration of electrolyte in mole of salt per 100 mole of solvent).

x_{AN}	c_{salt}	0.1		0.2	
		NaI	NaCl	NaI	NaCl
0.103	1.75	1.65	1.65	1.58	1.59
0.147	1.82	1.60	1.60	1.58	1.59
0.256	2.15	1.62	1.61	1.58	1.57
0.341	2.44	1.90	1.90	1.88	1.87
0.408	2.66	1.95	1.95	1.88	1.88
0.508	3.00	2.20	2.19	2.12	2.10
0.579	3.25	2.65	2.65	2.50	—
0.733	3.69	3.50	3.50	3.30	—
0.805	3.91	3.70	3.71	3.65	—
0.912	4.15	4.00	4.01	3.91	—
1.000	4.34	4.25	4.24	4.29	—

Table 2. Self-diffusion coefficients of water, $D_w \cdot 10^5$ ($\text{cm}^2 \text{s}^{-1}$) in acetonitrile-water solutions of NaI and NaCl at 25.0°C (concentration of electrolyte in mole of salt per 100 mole of solvent).

x_{AN}	c_{salt}	0.1		0.2	
		NaI	NaCl	NaI	NaCl
0.000	2.23	2.20	2.20	2.16	2.16
0.103	2.04	1.92	1.92	1.88	1.86
0.147	2.09	2.00	1.99	1.95	1.94
0.256	2.25	2.12	2.11	2.08	2.08
0.341	2.39	2.30	2.29	2.19	2.19
0.408	2.52	2.48	2.48	2.32	2.31
0.508	2.75	2.70	2.71	2.56	2.54
0.579	3.04	2.90	2.90	2.79	—
0.733	3.75	3.50	3.51	3.32	—
0.805	4.10	3.90	3.90	3.89	—
0.912	4.90	4.80	4.82	4.64	—

of these measurements was better than 0.5%. All self-diffusion and viscosity measurements were carried out at (298.15 ± 0.01) K.

Results

The measured self-diffusion coefficients of acetonitrile, D_{AN} , are summarized in Table 1. The results on salt free mixture agree excellently with those of Eastal [7], whereas the spin-echo technique [24] yielded higher values of D_{AN} . This can be due to the recalculation of the values measured for CD_3CN to those for CH_3CN .

As seen from Table 1, the D_{AN} values for NaI and NaCl solutions are the same within the experimental

error. These values are smaller than those for the salt free mixtures. The D_{AN} vs. x_{AN} functions for the electrolyte solutions and the salt free mixtures are different (see Figure 1.): In the electrolyte solutions D_{AN} is independent of x_{AN} for $x_{AN} < 0.35$ and then rapidly increases. The latter cannot be due to a rapid decrease in the viscosity of the solutions (see Figure 1). For the salt free mixtures and the NaCl and NaI solutions the variations of the viscosity with x_{AN} are similar. A maximum occurs at x_{AN} about 0.1.

The water self-diffusion coefficients D_w are listed in Table 2. For the salt free mixtures the agreement between the D_w values obtained here and those of Eastal [7] is excellent but, similar as for D_{AN} , they are smaller than those obtained with spin-echo technique [24]. The D_w values for solutions of NaI and NaCl are the same within the experimental error. As seen from Fig. 1, the D_w vs. x_{AN} functions for the salt free mixture and the electrolyte solutions are similar. They pass through minimum at x_{AN} about 0.1, which corresponds to the maximum of the viscosity.

Discussion

The component self-diffusion coefficients, D_i , and the viscosity of the respective liquid, η , are often supposed to be interrelated by the Stokes-Einstein equation

$$D_i = \frac{kT}{\alpha_i \pi \eta r_i}, \quad (1)$$

where r_i is the hydrodynamic radius of the diffusing species and α_i is a parameter resulting from the solute-solvent boundary condition; α_i varies from 4 for perfect slipping to 6 for perfect sticking.

The applicability of (1) is still controversial in self-diffusion studies [25], although for several binary organic mixtures, which are believed to be ideal, the product $D_i \eta$ for both components was found to be independent of the mixture composition [26, 27]. On the other hand one finds that the diameters of the component molecules evaluated from the molar volume data do not fit the Stokes-Einstein equation. Such an agreement is, however, not to be expected if self-diffusion results from motion of molecular aggregates.

Based on (1), it is supposed in the following that the ratios $(D_i \eta)_{\text{mix}} / (D_i \eta)_0$ correspond to ratios $(r_i)_0 / (r_i)_{\text{mix}}$ of the hydrodynamic radii of diffusing aggregates containing a component i , in the neat component and a

mixture, respectively:

$$R_i = \frac{(r_i)_0}{(r_i)_{\text{mix}}} = \frac{(D_i \eta)_{\text{mix}}}{(D_i^0 \eta^0)} \quad (2)$$

The influence of the composition of the acetonitrile-water system on the radii of the diffusing water and acetonitrile aggregates is shown in Figure 2. As seen, over the whole range of the mixture $R_W < 1$, which indicates that the diffusing water aggregates are greater in the mixtures than in pure water. The size might be enlarged if either water self-association or formation of water-acetonitrile complexes occurs. Although these components are not very likely to form complexes with each other, because the mixtures exhibit a large positive deviation from Raoult's law [1], the formation of water-acetonitrile complexes has been postulated as a result of spectroscopic studies [26–30]. The results of water-acetonitrile velocity correlation factors [24] indicate, however, that such complexes should not play any role in diffusion and self-diffusion processes. On the other hand formation of water aggregates, causing slow water motion, was excluded also for the water-acetonitrile mixtures [24].

As has been shown before [31], the hydrodynamic radius may be discussed as a feature of the environment of the diffusing species. For the water-acetonitrile mixtures the coexistence of two microphases, water and acetonitrile ones, has been postulated [3]. As seen from Fig. 2, R_W decreases, with increasing acetonitrile concentration and reaches a minimum between 50 and 75 mol% CH_3CN . This indicates that the water microphase is more ordered than pure water. The increase of R_W above 75% CH_3CN can indicate the disappearance of that microphase. This conclusion is in good agreement with the variation of R_{AN} with x_{AN} . As seen from Fig. 2b, R_{AN} is increased if the concentration of acetonitrile is less than 75 mol%. This can

indicate that the acetonitrile microphase is less ordered than pure acetonitrile. In water rich mixtures, $x_{\text{AN}} < 0.3$, R_{AN} is independent of x_{AN} . This probably results from the disappearance of the acetonitrile microphase.

The effect of electrolytes on the structure of both microphases may be investigated in a similar way, by comparison of the products for the electrolyte solutions $(D_i \eta)_{\text{salt}}$ and the salt free mixture $(D_i \eta)_{\text{mix}}$:

$$F_i = \frac{(r_i)_{\text{mix}}}{(r_i)_{\text{salt}}} = \frac{(D_i \eta)_{\text{salt}}}{(D_i \eta)_{\text{mix}}} \quad (3)$$

An influence of the salts on the structure of the water microphase is shown in Figure 3a. As seen, F_W is close to unity over the whole range of mixture composition, which indicate that ions do not affect the structure of the water microphase. This confirms the previous conclusion [8] that a preferential hydration of ions does not occur.

For comparison, F_W obtained previously for water-methanol solutions of NaI [18] and NaCl [19] is shown in Figure 3b. In water-methanol solutions these ions are believed to be preferentially hydrated [20, 32–34] and in the methanol rich region ($x_{\text{MeOH}} > 0.6$) F_W decreases rapidly.

The effect of salts on the acetonitrile microphase is shown in Figure 4. In the whole range of x_{AN} , F_{AN} is much smaller than 1, which means that electrolytes affect significantly the structure of the acetonitrile microphase, making it more ordered than the salt free mixture. That “structure making” effect results from the preferential solvation of sodium ions, which has been postulated previously [8]. The key role of sodium ions one can conclude from the fact that the smallest values of R_{AN} are observed in the range (40 and 75 mol% CH_3CN) when only the solvation sphere of sodium ions is completely formed.

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