

Conductance Studies in Acetonitrile-Water Mixtures

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The conductance of NaI in acetonitrile-water mixtures was measured at 25.000 ± 0.001 °C for the whole composition range of the mixed solvent, the salt molarity ranging from $5 \cdot 10^{-5}$ to $1 \cdot 10^{-2}$. Using the Fuoss-Hsia equation with the Fernandez-Prini parameters, the association constants were computed for several values of the ion-ion distances. The influence of the mixed solvent composition on the ionic association is discussed. An arranging effect of the sodium ions, postulated previously, is confirmed.

The acetonitrile-water mixtures exhibit several structural discontinuities [1–8], which may affect significantly the solvation of ions and ion-pair formation. The solvation of sodium, chloride and iodide ions has been discussed in the previous paper [9] basing on the measured ionic self-diffusion coefficients. It has been postulated that the preferential solvation of sodium ions by acetonitrile induces the formation of an acetonitrile microphase. Thus ionic association should depend significantly on the composition of the acetonitrile-water mixtures. The present conductance studies of the acetonitrile-water-NaI system have been undertaken to calculate the association constant as a function of the solvent composition.

Experimental

Acetonitrile (spectroscopy grade, Merck), dried as described by Vogel [10], double distilled, degassed water and NaI, dried in vacuum, were used to prepare the solutions. The specific conductance of solvents was $< 5 \cdot 10^{-6}$ S cm⁻¹. All solutions were prepared by weight just before use. The salt molarity was varied between $5 \cdot 10^{-5}$ and $1 \cdot 10^{-2}$. The conductances were measured with conductolyzer LKB 5300 B. The measuring cells were calibrated using 0.01 M KCl solutions. All experiments were performed at 25.000 ± 0.001 °C.

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Results and Discussion

The conductance data were analyzed by means of the Fuoss-Hsia [11] equation in the form proposed by Barthel [12] for the partially dissociated electrolytes:

$$\lambda = \alpha [\lambda^0 - S(\alpha c)^{1/2} + E \alpha c \ln(\alpha c) + J_1(R) \alpha c + J_2(R) (\alpha c)^{3/2}]. \quad (1)$$

To evaluate the limiting equivalent conductance λ^0 and the degree of dissociation α , the Fernandez-Prini parameters [13] were applied. Starting with the approximate value of λ^0 obtained by the Shedlovsky method [14], the coefficients S and E were calculated. Two distance dependent parameters, $J_1(R)$ and $J_2(R)$, were computed for a fixed distance equal to the Bjerrum distance q and for several values within the range 3.2–20.0 Å. During the fitting procedure the value of α was given as the current iterated one. The calculation of α was stopped when $|\alpha_{i+1} - \alpha_i|$ was $< 1.0 \cdot 10^{-5}$. The fitting procedure was repeated several times with the new value of λ^0 , and it was ended when $|\lambda_{j+1}^0 - \lambda_j^0|$ was $< 1.0 \cdot 10^{-4}$. The standard deviation σ was calculated as

$$\sigma = \sqrt{\sum [\lambda(\text{exp}) - \lambda(\text{cal})]^2 / (n - 3)}. \quad (2)$$

Assuming the activity coefficient of the ionic pair to be unity, the association constant K_A was calculated from

$$K_A = \frac{1 - \alpha}{\alpha^2 c f_{\pm}^2}, \quad (3)$$

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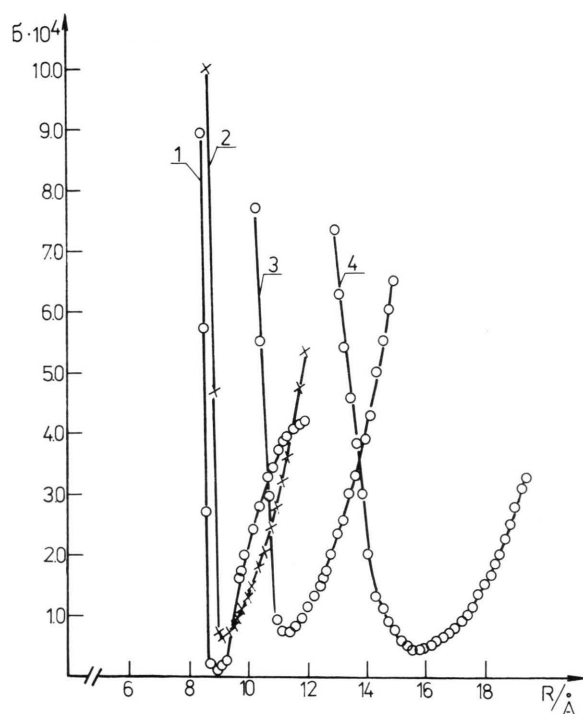
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Table 1. Limiting equivalent conductances λ^0 , association constants K_A and standard deviations σ obtained for the ion-ion distance R corresponding to the best fit of (1) and to the Bjerrum distance q .

x_{AN}	R (Å)	$\sigma \cdot 10^4$	λ^0 (S cm ² mol ⁻¹)	K_A	q (Å)	$\sigma \cdot 10^4$	λ^0 (S cm ² mol ⁻¹)
0.000	9.2	0.12	127.000 ₂	2.6 ± 0.4	3.6	956	127.09 ₂
0.103	9.2	0.15	106.500 ₀	3.6 ± 0.2	4.0	230	106.64 ₀
0.147	9.0	0.19	104.741 ₀	4.2 ± 0.3	4.7	74	104.76 ₉
0.256	9.0	0.27	106.699 ₇	4.5 ± 0.5	4.8	38	107.92 ₇
0.341	8.6	0.40	106.750 ₀	3.3 ± 0.3	5.3	9.3	107.58 ₂
0.508	15.6	0.43	118.659 ₄	24.3 ± 2.2	6.0	5.2	118.87 ₀
0.733	13.0	0.40	147.559 ₈	44.7 ± 1.8	6.3	2.0	147.58 ₉
0.805	11.0	0.57	157.100 ₀	45.5 ± 1.6	6.9	1.2	157.10 ₀
0.876	10.0	0.67	168.499 ₆	46.5 ± 1.3	7.2	3.4	168.49 ₈
0.912	9.8	0.90	172.499 ₆	41.4 ± 1.7	7.5	3.8	172.50 ₀
1.000	9.9	0.14	178.995 ₄	36.8 ± 1.3	7.8	3.1	178.98 ₉

Fig. 1. The dependence of the standard deviation σ , (2), on the fixed distance R between the ions. 1: aqueous solution ($x_{AN} = 0.0$); 2: acetonitrile solution ($x_{AN} = 1.0$); 3: mixed solvent $x_{AN} = 0.805$; 4: mixed solvent $x_{AN} = 0.508$.

where f_{\pm} denotes the activity coefficient of free ions obtained from

$$f_{\pm} = \exp \left[- \frac{A(x \cdot c)^{1/2}}{1 + B \cdot R(x \cdot c)^{3/2}} \right] \quad (4)$$

with $A = 2.791 \cdot 10^6 / (\epsilon T)^{3/2}$, $B = 50.29 / (\epsilon T)^{1/2}$ and the distance parameter R given in Å. The data of

the static dielectric constant were taken from [15] and of the solvent viscosity from [4].

The dependence of the standard deviation σ on the distance R between the ions should pass through a minimum, as it has been reported previously [16–18]. Some examples of these functions are presented in Figure 1. The best values corresponding to the minimum of σ are summarized in Table 1 along with the respective σ , and they are compared with the values of λ^0 , σ and K_A computed for the Bjerrum distance q .

As can be seen from Table 1, the variation of the distance parameter does not affect significantly the λ^0 values, as it was reported previously [16, 19], and the greatest difference between the λ^0 values obtained for the Bjerrum distance and for the best value of R is $< 0.1\%$.

The influence of the solvent composition on the limiting equivalent conductance λ^0 is presented in Fig. 2 and compared with the solvent viscosity. The minimum of λ^0 is at about 20 mol% CH₃CN and does not correspond to the maximum of the solvent viscosity, which is at about 7 mol% CH₃CN.

The Walden product $\lambda^0 \eta$ (see Fig. 3) decreases with increasing percentage of acetonitrile up to about 75 mol% CH₃CN and then becomes constant.

The variation of the Walden product reflects the change of the total solvation [20]. The decrease of that product indicates an increase of the total solvation from the one in pure water with increasing concentration of acetonitrile. The constant value of $\lambda^0 \eta$ above 75 mol% CH₃CN reflects the same solvation in the acetonitrile rich solvents, as in pure acetonitrile. Such a result is in accordance with the conclusion drawn previously [9] from the studies of

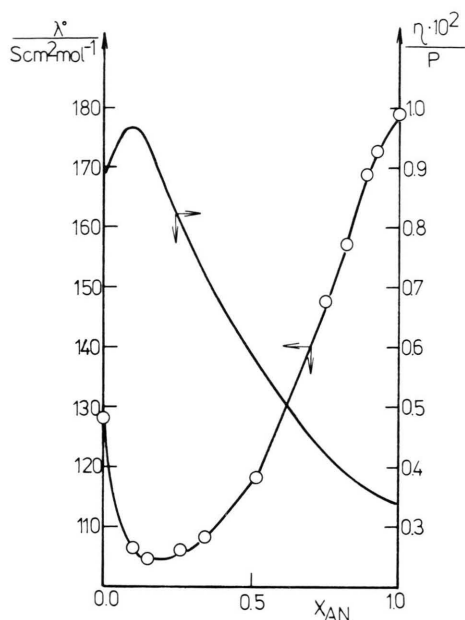


Fig. 2. Variation of the limiting equivalent conductance λ° and of the solvent viscosity (η) with the solvent composition.

the ionic self-diffusion. In the acetonitrile-water mixtures the same solvation as in pure acetonitrile was observed from 35 mol% CH_3CN for the sodium ions and from 75 mol% CH_3CN for the iodide ions.

As can be seen from Table 1, the standard deviation σ calculated for the Bjerrum distance q is several times greater than the smallest one. This means that the Bjerrum distance does not fit the experimental data, which seems to be reasonable because the q value depends on the dielectric constant only, and in our system which exhibits a phase separation [1–3] it is probably an unrealistic parameter.

In Fig. 4 the R values corresponding to the best fit of the experimental data are plotted vs. the mixed solvent composition. For comparison the q values are also shown. The Bjerrum distance is smaller and increase monotonously with increasing concentration of acetonitrile. The R values in pure water and in the water rich solvents (below 35 mol% CH_3CN) are the same; in the region of the phase separation they increase rapidly and then decrease to that in pure acetonitrile, which is practically the same as in pure water and equal to about 9 Å.

According to Fuoss [16] the R value corresponds to the distance between ions forming a contact or

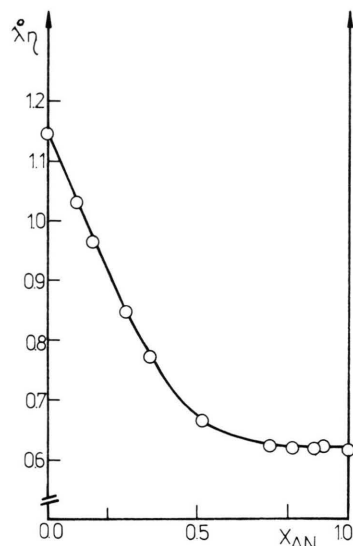


Fig. 3. Variation of the Walden product $\lambda^\circ \eta$ with the solvent composition.

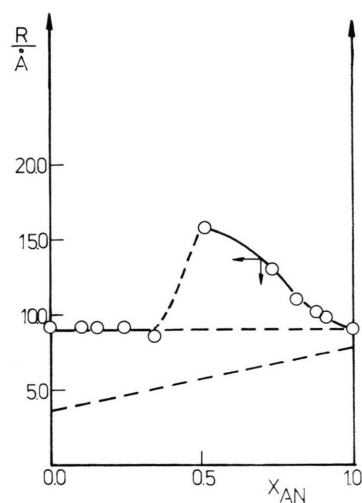


Fig. 4. Variation of the distance between ions R with the solvent composition. The dashed line represents the Bjerrum distance q .

solvent separated ion pair. For a solvent separated ion pair the distance between the ions is given by

$$R = (a + mS), \quad m = 1, 2, 3, \dots, \quad (5)$$

where a and S denote the sum of the crystallographic radii of the ions and the diameter of a sphere corresponding to the average volume per solvent molecule, respectively. The radii of the sodium and iodide ions are 0.98 Å and 2.20 Å [21], respectively. The S values are 2.8 Å and 5.6 Å for

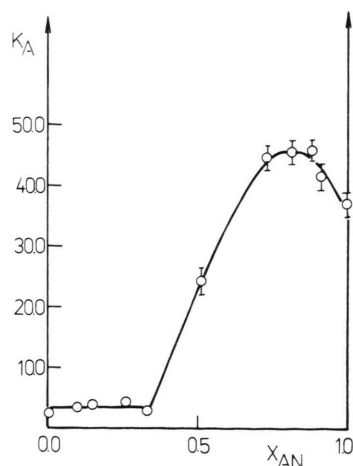


Fig. 5. Variation of the association constant K_A with the solvent composition.

water and acetonitrile, respectively. The average values of m calculated from (5) are 1.6 and 1.0 for aqueous and acetonitrile solutions, respectively. One can suppose that in acetonitrile solution ions forming an ion pair are separated by one solvent molecule, whereas in aqueous solution solvent separated pairs of higher order are also present.

The fairly great values of R found in the region of the phase separation (between 40 and 80 mol% CH_3CN) reflect probably an inhomogeneous distribution of ions between two microphases. Sodium ions have been found to be able to induce the formation of acetonitrile globules; thus they are dissolved mostly in the acetonitrile microphase, whereas the iodide ions are distributed between both.

In Fig. 5 the association constant K_A as a function of the solvent composition is shown. Below 35 mol%

CH_3CN the dielectric constant is high ($\epsilon > 50$) and, as it was expected, the K_A values are practically negligible ($K_A < 10$, [18]). With increase of the acetonitrile concentration the K_A values increase rapidly and pass through a flat maximum between 70 and 85 mol% CH_3CN . The observed maximum is unexpected. It can be explained by assuming that in the presence of electrolyte the region of the phase separation is extended to higher concentrations of acetonitrile. Both ions are solvated by acetonitrile; thus they occupy the acetonitrile microphase only and their concentration in that phase is greater than that calculated for a homogeneous distribution. The higher values of K_A as compared to that one in pure acetonitrile do not reflect the real increase of the ionic association but result from the calculation of the concentration.

The results presented here lead to the following conclusions:

In water rich solvents (below 35 mol% CH_3CN), similar as in pure water, only free ions exist ($K_A < 10$), but if the first or the second hydration shell of an ion and its counterion is common, the nonconducting species are formed.

In pure acetonitrile a weak association of ions occurs ($K_A \sim 35$) and a nonconducting pair is created if the first solvation shell of opposite by charged ions is common.

The region of the phase separation for an electrolyte solution is extended to higher concentration of CH_3CN , as compared with salt free mixed solvent. Both ions are distributed in the acetonitrile microphase and the ionic association is similar to that in pure acetonitrile.

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