

The Conductance of NaI and Tetraethylammonium Iodide in Mixtures of Methanol with Acetonitrile and Water

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Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

The conductance of NaI and Et₄NI in methanol-acetonitrile and methanol-water mixtures was measured at $25 \pm 0.005^\circ\text{C}$ for the whole range of the solvent compositions, the salt molarity ranging from $5 \cdot 10^{-5}$ up to $1 \cdot 10^{-2}$. Several equations describing the influence of the salt concentration on the equivalent conductance are examined and the Fuoss-Hsia equation with the Fernandez-Prini parameters is found to be the most appropriate one for systems with weak ionic association. Variations with the solvent composition of the limiting equivalent conductance, the distance between ions forming ion pairs and the association constant are discussed. Nonmonotonous changes of the association constant are concluded to be a feature of microheterogeneous systems.

Although the association of the ions in acetonitrile-water solutions of NaI and Et₄NI is weak, the composition of the solvent affects their association constant K_A and, what seems to be interesting, not in the same way. One expects a monotonous increase of K_A with increasing mole fraction of acetonitrile due to the monotonous decrease of the static dielectric constant [1]. This is indeed the case for Et₄NI [2], whereas for NaI K_A exhibits a maximum at about 80 mol% CH₃CN [3] indicating a preferential solvation.

Self-diffusion studies have led to the conclusion that tetraethylammonium ions are unsolvated and do not affect the structure of the acetonitrile-water mixture [2]. Sodium ions, preferentially solvated by acetonitrile [4], induce the formation of acetonitrile globules, which enhances the microheterogeneity of the system [5, 6]. In acetonitrile rich mixtures ($x_{\text{AN}} > 0.75$), iodide ions are also preferentially solvated by acetonitrile [4], which results in an increase of the salt concentration in the acetonitrile microphase, leading to the observed maximum of K_A , which does not reflect a real increase of the ionic association but is the result of the higher concentration in that microphase as compared to the average chemical concentration. Thus one might expect nonmonotonous variations of K_A with the solvent composition for other microheterogeneous systems with a preferential solvation of ions.

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In order to confirm this supposition, the ionic association in methanol-acetonitrile and methanol-water solutions of NaI and Et₄NI has been studied. Both these binary solvents have been found to be microheterogeneous systems [7, 8]. In the latter one the sodium ions are preferential by hydrated [7–9].

Experimental

Tetraethylammonium iodide (p. a. USRR) was purified by double crystallization from methanol solutions and dried in vacuum. NaI (Merck, suprapur) was used without further purification. All solutions were prepared by weight from acetonitrile (Merck, spectroscopy grade) dried with P₂O₅, methanol (Merck, spectroscopy grade) dried with magnesium methoxide, and double distilled, degassed water.

The conductances were measured with the conductolyzer LKB 5300 B. The measuring cells were calibrated using 0.01 m KCl. The specific conductances of all solvents did not exceed $5 \cdot 10^{-6} \text{ S cm}^{-1}$. The salt molarity was varied between $5 \cdot 10^{-5}$ and $2 \cdot 10^{-2}$. All experiments were performed at $25 \pm 0.005^\circ\text{C}$.

Results and Discussion

All models proposed to express the influence of the salt concentration c on the equivalent conductance λ of partially dissociated 1:1 electrolytes have led to the

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x_M	NaI			Et ₄ NI		
	$\frac{R}{\text{\AA}}$	λ^0 S cm ² mol ⁻¹	K_A	$\frac{R}{\text{\AA}}$	λ^0 S cm ² mol ⁻¹	K_A
0.000	9.0	178.995	36.8 ± 1.3	13.0	188.180	44.1 ± 0.3
0.115	11.5	174.543	36.7 ± 1.5	13.0	184.147	43.5 ± 0.5
0.206	11.6	171.517	36.6 ± 2.0	13.5	180.267	44.0 ± 0.5
0.302	11.6	165.928	36.8 ± 1.7	13.5	175.539	44.1 ± 0.8
0.394	11.5	161.640	36.8 ± 2.7	13.5	172.435	45.3 ± 0.9
0.464	11.6	158.703	36.9 ± 2.5	—	—	—
0.565	11.6	154.009	38.3 ± 1.9	13.5	161.652	47.0 ± 1.9
0.060	11.6	144.339	40.1 ± 2.1	—	—	—
0.722	10.6	139.812	41.0 ± 1.7	13.5	148.747	50.2 ± 1.8
0.796	10.5	132.509	42.5 ± 2.5	13.3	142.239	53.1 ± 2.7
0.867	10.0	126.615	44.1 ± 2.4	13.0	135.275	54.5 ± 2.8
1.000	9.5	108.703	46.3 ± 2.7	13.0	124.005	56.1 ± 2.5

Table 1. Limiting equivalent conductances λ^0 , association constants K_A and distance parameters R for NaI and Et₄NI solutions in methanol-acetonitrile mixtures at 25.0 °C.

Data of the solvent viscosity were taken from [8] and of the solvent static dielectric constant from [18].

x_M	NaI			Et ₄ NI		
	$\frac{R}{\text{\AA}}$	λ^0 S cm ² mol ⁻¹	K_A	$\frac{R}{\text{\AA}}$	λ^0 S cm ² mol ⁻¹	K_A
0.000	6.5	128.425	2.6 ± 0.1	11.0	109.450	9.9 ± 0.2
0.100	5.0	109.711	12.5 ± 0.9	10.0	85.932	8.1 ± 0.2
0.229	5.5	87.298	18.0 ± 1.9	10.0	66.112	10.5 ± 0.4
0.310	5.5	76.663	18.5 ± 1.5	10.0	60.062	12.3 ± 0.3
0.400	6.0	68.510	18.5 ± 1.6	10.5	59.695	16.0 ± 0.5
0.471	6.8	73.244	18.5 ± 1.4	11.0	64.403	18.7 ± 1.1
0.551	7.0	76.892	18.7 ± 1.8	11.5	67.973	24.9 ± 1.8
0.641	7.3	84.210	18.4 ± 1.9	11.8	74.903	30.1 ± 1.6
0.690	7.5	88.305	19.4 ± 1.8	12.2	78.669	32.9 ± 2.1
0.817	8.0	97.661	21.5 ± 2.5	12.5	89.809	40.5 ± 2.0
0.900	8.5	102.691	30.5 ± 2.3	13.0	99.391	48.0 ± 2.7
1.000	9.5	108.934	46.3 ± 2.5	13.0	112.167	56.1 ± 2.5

Table 2. Limiting equivalent conductances λ^0 , association constants K_A and distance parameters R for NaI and Et₄NI solutions in methanol-water mixtures at 25.0 °C.

Data of the solvent viscosity were taken from [19] and of the solvent static dielectric constant from [1].

general equation

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

where λ^0 and α are the limiting equivalent conductance and the degree of dissociation, respectively. The coefficients S and E depend on λ^0 , temperature and solvent properties such as the static dielectric constant ϵ_0 and the viscosity η_0 , but they are independent of the assumed model. The coefficients $J_1(R)$ and $J_2(R)$ depend on the parameters mentioned before and also on the model through the distance R between ions forming ion pairs. Therefore according to (1) the equivalent conductance becomes a function of three unknown parameters, i.e. λ^0 , R and the concentration of free ions (αc).

The standard approach to determine these parameters is to find the values of λ^0 and α which minimize

the standard deviation σ defined as

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

for a sequence of R values. The best fit corresponds to the minimum of σ vs. R .

As has been stressed by Fouss [10], λ^0 is almost independent of R , which means that it is independent of the assumed model. The association constant K_A , however, depends on R in two ways: R affects strongly the degree of dissociation α and influences also the activity coefficient of free ions defined by

$$f_i = \exp \left[- \frac{A(\alpha c)^{1/2}}{1 + BR(\alpha c)^{1/2}} \right] \quad (3)$$

with $A = 4.203 \cdot 10^{-6} / (\epsilon_0 T)^{3/2}$ and $B = 50.29 / (\epsilon_0 T)^{1/2}$ for R given in Å, applied to calculate K_A via.

$$K_A = \frac{1 - \alpha}{\alpha^2 c f_i^2}. \quad (4)$$

A comparison of K_A values obtained with various models for one component solvents is found in [11]. To our knowledge such a comparison does not exist for binary solvents. Therefore we have used several models to analyze experimental data [10, 12–16]. The fitting procedure was as follows: For a fixed distance R the calculations started with an approximate value of λ^0 obtained by Shedlovsky's method [17] and α as iterated value. The iteration was stopped when $\left| \frac{\Delta \alpha_i}{\alpha_i} \right| < 0.01\%$, and the calculations were repeated with a new value of λ^0 . They were finished when $\left| \frac{\Delta \lambda_j^0}{\lambda_j^0} \right| < 0.01\%$. The R values started from the sum of the ionic crystal radii and were expanded up to 20 Å.

A well pronounced minimum of σ vs. R we only have found for the model proposed by Fouss and Hsia [15] in the form elaborated by Fernandez-Prini [16] (FHFP model), and the values of σ were by about two orders of magnitude smaller than for the other models. Examining several published data sets we have found similar features for solutions with weak ionic association, ($K_A < 100$), whereas for strongly associated electrolytes the differences between the models became negligible. Therefore, if weak association may be expected, the FHFP model seems to be the appropriate one.

Values of R from the best fit of the FHFP model and corresponding values of λ^0 and K_A for methanol-acetonitrile and methanol-water mixtures are summarized in Tables 1 and 2, respectively.

In methanol-acetonitrile solutions the λ^0 values of NaI and of Et₄NI decrease monotonously with increasing x_M (Figure 1a). The lack of an effect of the solvent composition on the Walden product (Fig. 1b) lead to the conclusion that the variations of λ^0 are due to changes of the solvent viscosity. For both salts the $\lambda^0 \eta^0$ values in the mixed solvents are reduced as compared to those in the net ones. If variations of the Walden product reflect changes of the total solvation of an electrolyte [20] such an effect might be expected because a slight increase of the solvation of iodide ions has been deduced from self-diffusion studies [8].

The influence of the composition of the methanol-water mixtures on λ^0 is shown in Figure 2a. For both salts a minimum is observed, which might be expected because the viscosity of the solvent exhibits a maximum [19]. The position of the viscosity maximum does not, however, coincide with that of the λ^0 minimum, neither for NaI nor for Et₄NI, and for both

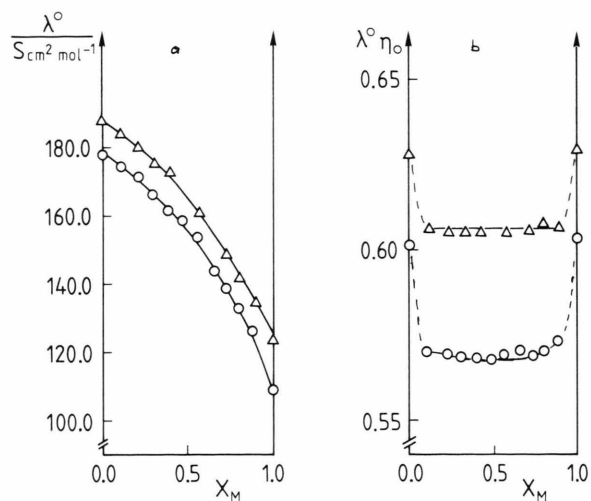


Fig. 1. Isotherms at 25 °C of the limiting equivalent conductance λ^0 (a) and the Walden product $\lambda^0 \eta^0$ (b) of NaI (○) and Et₄NI (Δ) in methanol-acetonitrile solutions. x_M = mole fraction of methanol.

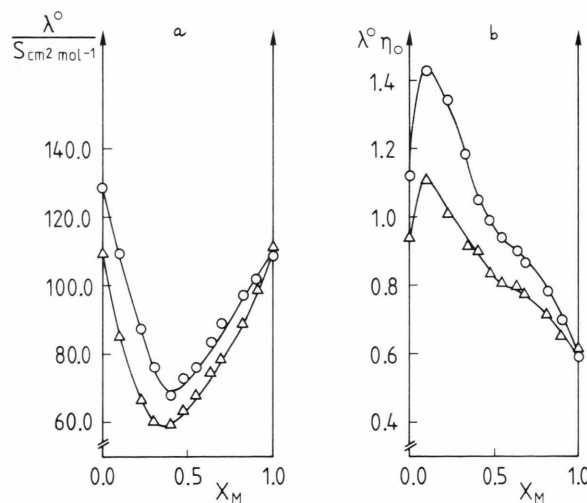


Fig. 2. Isotherms at 25 °C of λ^0 (a) and $\lambda^0 \eta^0$ (b) of NaI (○) and Et₄NI (Δ) in methanol-water solutions. x_M = mole fraction of methanol.

salts the Walden product exhibits a maximum at $x_M = 0.1$ (Figure 2b). This indicates a significant decrease of the total solvation both of NaI and Et₄NI. In water rich mixtures a noticeable reduction of the solvation of sodium and iodide ions has been found previously [9].

The effect of the solvent composition on R and K_A is shown in Figure 3.

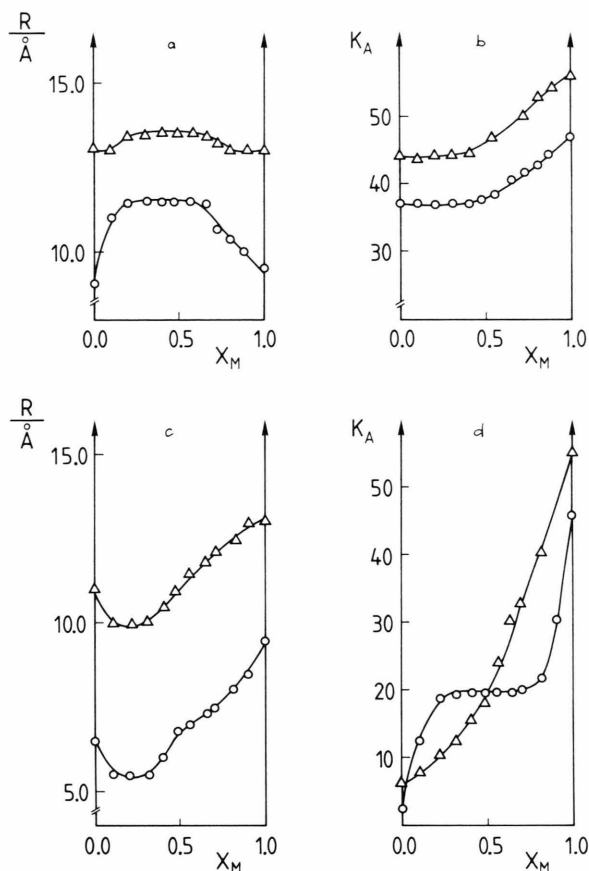


Fig. 3. Isotherms at 25°C of the distance parameter R and the association constant K_A of NaI (○) and Et₄NI (Δ) in methanol-acetonitrile (a and b) and methanol-water (c and d) solutions. x_M = mole fraction of methanol.

According to Fuoss [10], R corresponds to the distance between ions forming a pair, either a contact or a solvent separated one, and is given by

$$R = (a + mS) \quad \text{with} \quad m = 0, 1, 2, \dots, \quad (5)$$

where a and S denote the sum of the crystallographic ionic radii and the diameter of a sphere corresponding to the average volume per solvent molecule, respectively.

As long as the composition of the solvation shell of an ion in mixed solvents is not known, the above equation allows to calculate the value of m for net

components only, but using it one can distinguish solvent separated and contact ion pairs.

The sum of the ionic radii of NaI and Et₄NI is 3.2 Å and 6.4 Å, respectively, whereas the S values for acetonitrile, methanol and water are 5.6; 5.0 and 3.8 Å, respectively. Thus from (5) comes the conclusion that in the net components both salts form solvent separated pairs. For NaI the average values of m in acetonitrile, methanol and aqueous solutions are 1.0; 1.3 and 1.0, respectively, whereas for Et₄NI they are 1.0; 1.3 and 1.3, respectively. Therefore one can suppose that both salts in acetonitrile solutions and NaI in aqueous ones form an ionic pair separated by one solvent molecule, whereas both in methanol solutions of Et₄NI and of NaI as well as in aqueous solutions of Et₄NI solvent separated pairs of higher order are also present.

In methanol-acetonitrile solutions the K_A values of both salts increase monotonously with increasing x_M , which probably results from the decrease of the static dielectric constant [18]. The same effect of x_M has been found for Et₄NI in methanol-water mixtures, whereas for NaI that effect is quite different. K_A increases rapidly with x_M for $x_M < 0.3$, is constant for $0.3 < x_M < 0.75$ and increases rapidly for $x_M > 0.75$. Such an effect can be explained if we assume this binary solvent to be a microheterogeneous system in which the preferential solvation of sodium ions, postulated previously [9], enhances its microheterogeneity, as it has been deduced from the self-diffusion of the solvent components [7]. One can suppose that the lack of the effect of x_M on K_A for $0.3 < x_M < 0.75$ is due to an increasing contribution of that microphase, which contains probably both components, in which NaI is dissolved. The rapid increase of K_A for $x_M > 0.75$ indicates probably that water is unable to create that microphase, resulting in an increase of the association constant.

The result presented here confirm the hypothesis that in a microheterogeneous solvent variations of the association constant do not result only from changes of a static dielectric constant. Therefore the non-monotonous dependence of K_A on the composition of binary solvents may indicate that in such systems a preferential solvation of ions occurs.

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