

Physico-chemical Studies in Mixed Solvents: Part V—Conductance Behaviour of Tetraethylammonium Bromide & Perchlorate in Dimethyl Sulphoxide-Water Mixtures at 25°C

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Received 12 March 1987;
revised 8 October 1987; accepted 21 December 1987

The conductances of Et_4NBr and Et_4NClO_4 have been measured at 25°C in dimethyl sulphoxide (DMSO)-water mixtures containing 5.5, 13.3, 25.7, 35.0, 48.0, 67.5, 81.4 and 100 mol% DMSO. The data have been analysed by Fuoss-Hsia equation as expanded by Fernandez-Prini equations, to calculate limiting equivalent conductance (Λ_0) and association constant (K_A). The limiting ionic conductances (λ_0) and relative ionic Walden products (R) of the ions in different DMSO-water mixtures have also been calculated.

In continuation of our earlier studies on the conductances and transport numbers of silver perchlorate¹ and viscosities of a few electrolytes² in dimethyl sulphoxide(DMSO)-water mixtures in the entire composition range, conductances of tetraethylammonium perchlorate and bromide have now been measured in DMSO-water mixtures and the results are interpreted in terms of changes in the structure of the solvent system.

The DMSO-water mixtures have been suggested to be highly structured though there is no general agreement on the structural characteristics of these mixtures. Some workers³⁻⁵ have concluded that DMSO behaves as a strong structure maker, while others⁶⁻⁹ have suggested that DMSO breaks down the water structure.

DMSO (Riedel) was purified as reported¹ (b.p. 68-68.5/7 mm Hg; sp. conductance $2.5 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$; density, 1.0956 g ml^{-1} ; viscosity, 0.0196 p, all at 25°C). Conductivity water (sp. conductance $4.6 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$; density, 0.9970 g ml^{-1} ; viscosity, 0.008937 p at 25°C) was obtained as described earlier¹.

Tetraethylammonium perchlorate was prepared in the laboratory, recrystallised from water, dried by heating at about 100°C in a water bath *in vacuo* and cooled in a vacuum desiccator before use. Tetraethylammonium bromide (Fluka AG) was used after drying *in vacuo*.

The preparation of solutions and conductance measurements were carried out by the methods reported before¹. Conductances were accurate within $\pm 0.02 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Conductances of tetraethylammonium bromide and perchlorate were measured at 25°C in different DMSO-water mixtures containing 5.5, 13.3, 25.7, 35.0, 48.0, 67.5, 81.4 and 100 mol% DMSO. The conductance data were analysed by the general expressions (Eqs. 1-3) for conductance of symmetrical electrolytes in dilute solutions¹⁰.

$$\Lambda = \gamma[\Lambda_0 - S(C\gamma)^{\dagger} + EC\gamma \log C\gamma + JC\gamma + J_{3/2}(C\gamma)^{3/2}] \quad \dots (1)$$

$$K_A = \frac{1 - \gamma}{\gamma^2 C f_{\pm}^2} \quad \dots (2)$$

$$\ln f_{\pm} = - \frac{A(C\gamma)^{\dagger}}{1 + BR(C\gamma)^{\dagger}} \quad \dots (3)$$

Equations (1-3) were obtained by expanding¹¹⁻¹³ the Fuoss-Hsia expressions¹⁴; in these equations the symbols have their usual significance. The distance parameters in Eq. (1), i.e. J and $J_{3/2}$ have been taken to be equal to Bjerrum critical distance, $q = Z^2 e^2 / 2DKT$. The expressions for J and $J_{3/2}$ used here are those given by Fernandez-Prini¹¹. The parameters, Λ_0 and K_A were adjusted by least squares method to fit the experimental data and the values, thus obtained are reported in Table 1.

The results of analysis of conductance data by Fuoss-Onsager-Skinner equations¹⁵ used by us in our previous publications are also recorded in Table 1 for comparison. It is clear from Table 1 that the values obtained by the two methods do not differ significantly, though some differences are noticed in K_A values. The K_A values obtained by Fuoss-Hsia and Fernandez-Prini methods are larger than those obtained by Fuoss-Onsager-Skinner method of analysis. These differences may be attributed to the influence of the term $(C\gamma)^{3/2}$, the Bjerrum distance used in J and $J_{3/2}$ and the use of complete Debye-Hückel expression for the activity coefficient in the former method. The similar differences in K_A values have also been noticed in other solvents^{12,13,16}.

Inspection of Table 1 shows that the limiting equivalent conductances (Λ_0) for both the electrolytes decrease sharply with the increase in DMSO concentration upto 35.0-48.0 mol % and thereaf-

Table 1 – Limiting Equivalent Conductances (Λ_0) and Association Constants (K_A) of Et_4NBr and Et_4NClO_4 in Different DMSO-Water Mixtures at 25°C

Mol % DMSO	Fuoss-Hsia Fernandez-Prini			Fuoss-Onsager-Skinner		
	Λ_0	K_A	$\sigma\Lambda$	Λ_0	K_A	$\sigma\Lambda$
Et_4NBr						
0.00	110.90*					
5.50	77.71 $\pm$ 0.01	22.29 $\pm$ 0.03	0.01	77.70 $\pm$ 0.01	20.48 $\pm$ 0.08	0.01
13.30	44.57 $\pm$ 0.02	3.31 $\pm$ 0.16	0.02	44.67 $\pm$ 0.08	7.40 $\pm$ 4.44	0.02
25.70	28.33 $\pm$ 0.04	6.28 $\pm$ 0.43	0.04	28.35 $\pm$ 0.04	—	0.04
35.00	25.12 $\pm$ 0.03	9.19 $\pm$ 0.48	0.02	25.02 $\pm$ 0.02	—	0.02
48.00	27.90 $\pm$ 0.02	4.09 $\pm$ 0.20	0.02	27.99 $\pm$ 0.08	8.64 $\pm$ 5.57	0.02
67.50	31.53 $\pm$ 0.05	5.97 $\pm$ 0.54	0.05	31.86 $\pm$ 0.20	25.23 $\pm$ 11.70	0.05
100.00	40.29 $\pm$ 0.01	3.57 $\pm$ 0.12	0.01	40.33 $\pm$ 0.03	—	0.03
Et_4NClO_4						
0.00	100.06*	—				
5.50	62.20 $\pm$ 0.02	—	0.02	62.19 $\pm$ 0.01		0.02
13.30	37.06 $\pm$ 0.01	—	0.01	37.07 $\pm$ 0.01		0.01
25.70	23.94 $\pm$ 0.01	—	0.01	23.94 $\pm$ 0.01		0.01
35.00	22.14 $\pm$ 0.01	—	0.01	22.14 $\pm$ 0.01		0.01
48.00	24.03 $\pm$ 0.01	—	0.02	24.06 $\pm$ 0.02		0.03
67.50	30.05 $\pm$ 0.02	—	0.03	30.11 $\pm$ 0.03		0.04
81.40	34.84 $\pm$ 0.01	—	0.02	34.91 $\pm$ 0.02		0.04
100.00	40.74 $\pm$ 0.01	—	0.01	40.88 $\pm$ 0.03		0.04

*Data have been taken from literature (Harned H S & Owen B B, The physical chemistry of electrolytic solutions, Reinhold, New York, 1950).

Table 2 – Limiting Ionic Conductances ($\lambda_0^\pm$) and R-Values for Et_4N^+ , Br^- and ClO_4^- in DMSO-water Mixtures at 25°C.

Mol % DMSO	λ_0			R		
	Et_4N^+	Br^-	ClO_4^-	Et_4N^+	Br^-	ClO_4^-
0.00	32.60	78.30	68.00			
5.50	21.24	56.46	40.95	1.01	1.11	0.93
13.30	13.28	31.24	23.78	1.02	1.00	0.87
25.70	9.59	18.61	14.35	1.14	0.92	0.82
35.00	9.62	15.40	12.52	1.24	0.83	0.78
48.00	10.92	16.94	13.14	1.29	0.83	0.75
67.50	13.31	18.55	16.79	1.23	0.72	0.75
81.40	15.29	—	19.61	1.21	—	0.74
100.00	17.50	23.60	24.15	1.18	0.66	0.78

ter it gradually increases. The λ_0 of Et_4N^+ ions in different DMSO-water mixtures were calculated from the corresponding Λ_0 values of Et_4NClO_4 and limiting ionic conductances of ClO_4^- ion reported earlier¹, using Kohlrausch law of independent migration of ions: The λ_0 of Et_4N^+ ions are used to calculate λ_0 of Br^- ion in different DMSO-water mixtures. All the results are recorded in Table 2.

The ratio (R) of limiting ionic Walden product of an electrolyte for a solvent mixture and that in pure water, $R = [(\lambda_0^\pm \eta_0) / (\lambda_0^\pm \eta_0)]_{\text{H}_2\text{O}}$ may provide better understanding^{17,18} of the nature of solu-

tions. The R-values of ions in DMSO-water mixtures have been obtained from $\lambda_0^\pm$ values of ions calculated in the present study and η_0 values taken from literature¹⁹. These are recorded in Table 2.

The relative ionic Walden product (R) for Et_4N^+ increases with increase in DMSO concentration and is maximum at 50 mol % DMSO and thereafter it decreases gradually. Et_4N^+ possesses low charge density and, therefore, cannot be considered to interact strongly with solvent molecules. The increase in R for this ion may arise by the hydrophobic dehydration of the ion. The hydrophobic interaction is a specific property of tetraalkyl or tetraaryl ammonium ions in water due to its structure. With increase in concentration of cosolvent, the magnitude of hydrophobic interaction decreases and hence R increases in this region. Similar behaviour has also been shown by this ion in other solvent systems²⁰. Beyond the maximum value of R, the ion seems to interact weakly with DMSO molecules and this may be due to more basic nature of DMSO.

The behaviour of Et_4N^+ may be compared with the solvation effects of large Bu_4N^+ inferred from thermochemical data²¹. The Bu_4N^+ undergoes desolvation in the entire solvent composition range, with maximum desolvation occurring at

about 20.2-27.6 mol % DMSO. This solvent composition is very close to $\text{DMSO} \cdot 2\text{H}_2\text{O}$, at which aqueous DMSO shows maximum structure. The behaviour of Et_4N^+ exactly goes parallel to this solvation behaviour.

The R-value for Br^- is maximum at about 5.5 mol % DMSO, while for ClO_4^- ion, the R-value decreases with increase in DMSO concentration over the entire range of composition (Table 2). The behaviour of ClO_4^- ion is in agreement with the results of Petrella and coworkers^{22,23} in water-rich region of aqueous DMSO mixtures, though no maximum was observed for Br^- ion. The small maximum in case of Br^- ion has also been observed in the case of ethanol-water and *t*-butyl alcohol-water systems²⁴. The initial increase in R cannot be attributed mainly to the preferential solvation of ions because DMSO being dipolar aprotic solvent cannot preferentially solvate the anion.

Perchlorate ion, on the other hand, shows fairly good solvation. There is a gradual decrease in R with increase in concentration of DMSO, indicating increasing solvation of anion with increase in DMSO concentration. This is expected since oxianions generally show specific interaction in aqueous mixtures^{20,25}.

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