

Ionic Association and Conductances of Some Symmetrical Tetraalkylammonium Perchlorates in 2-Methoxyethanol + Water at 298.15 K

Bijan Das and Dilip K. Hazra*

Department of Chemistry, North Bengal University, Darjeeling 734 430, India

Precise conductance measurements are reported for tetraethylammonium perchlorate (Et_4NClO_4), tetrapropylammonium perchlorate (Pr_4NClO_4), and tetrabutylammonium perchlorate (Bu_4NClO_4) in 2-methoxyethanol (1) + water (2) at 298.15 K. The limiting molar conductivity (Λ°), the association constant (K_A), and the association distance (R) in the solvent mixtures have been evaluated from the conductance–concentration data using the 1978 Fuoss conductance equation. The results have been explained in terms of ion–ion interactions and the structural changes in the solvent mixtures.

Introduction

Extensive studies on the electrolytic conductivities in the binary mixtures of water with various organic solvents have been made in recent years (Niazi et al., 1993; Roy et al., 1993; Papadopoulos and Ritzoulis, 1989; Das and Hazra, 1988; Bahadur and Ramanamurti, 1984; Raju et al., 1982) to examine the magnitude and the nature of ion–ion and ion–solvent interactions. The solvent properties such as the viscosity and the dielectric constant have also been taken into account in determining the extent of ion association and the solute–solvent interactions.

The present paper reports the molar conductivities of three symmetrical tetraalkylammonium perchlorate, viz., Et_4NClO_4 , Pr_4NClO_4 , and Bu_4NClO_4 in 2-methoxyethanol (1) + water (2) ranging in composition from 20 to 80 mass % of 2-methoxyethanol at 298.15 K. The values of the limiting molar conductivity (Λ°) and the association constant (K_A) have been derived and interpreted in terms of ion–ion and ion–solvent interactions.

Experimental Section

2-Methoxyethanol (G.R.E. Merck, >99% pure) was distilled twice in an all-glass distillation set and the middle fraction distilling between 397.15 K and 398.15 K was collected. The fractionally distilled solvent had a specific conductance less than $(1 \text{ to } 3) \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$. Triply distilled water with a specific conductance less than $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ was used for the preparation of the mixtures.

Tetraalkylammonium perchlorate were Fluka purum or puriss grade (purity $\geq 99\%$). These were recrystallized twice from conductivity water and dried in vacuo at 343.15 K for 24 h.

A stock solution for each salt was prepared by mass, and the working solutions were obtained by weight dilution. The conversion of the molality into molarity was done by using density values measured with an Ostwald-Sprengel type pycnometer. The bulb volume of the pycnometer was about 25 cm^3 , and the internal diameter of the capillary was about 0.1 cm. Details have been described earlier (Das and Hazra, 1993, 1995a; Saha et al., 1995).

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell (cell constant = 0.751 cm^{-1}) with an accuracy of 0.01%. The cell was calibrated by the method of Lind and co-workers (Lind et al., 1959) using

aqueous potassium chloride solutions. Measurements were made in an oil bath maintained at $(298.15 \pm 0.005) \text{ K}$, as described earlier (Das and Hazra, 1992, 1995b). Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductance of the solvent. The experimental values of the densities (ρ), viscosities (η), and the dielectric constants (D) of 2-methoxyethanol (1) + water (2) at 298.15 K are not available at the relevant compositions in which conductance measurements have been carried out. The available values of ρ and η (from Das and Hazra, 1993) and those of D (from Sadek et al., 1971) are, therefore, plotted against the mass fraction of 2-methoxyethanol, and the values of ρ , η , and D at all the desired compositions have been generated from the smooth master curves and are given in Table 1.

Results

Molar conductance (Λ) of electrolyte solutions as a function of molar concentration (c) are given in Table 2 in different solvent mixtures at 298.15 K.

The conductance data have been analyzed by the 1978 Fuoss conductance–concentration equation (Fuoss, 1978a,b). For a given set of conductivity values (c_j , Λ_j , $j = 1, \dots, n$), three adjustable parameters, the limiting molar conductivity (Λ°), association constant (K_A), and the cosphere diameter (R), are derived from the following set of equations:

$$\Lambda = p[\Lambda^\circ(1 + R_X) + E_L] \quad (1)$$

$$p = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta k/2(1 + kR) \quad (4)$$

$$\beta = e^2/Dk_B T \quad (5)$$

$$K_A = K_R/(1 - \alpha) = K_R(1 + K_S) \quad (6)$$

where R_X is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radius of the ion atmosphere, D is the dielectric constant of the solvent, e is

Table 1. Densities (ρ), Viscosities (η), and Dielectric Constants (D) for 2-Methoxyethanol (1) + Water (2) at 298.15 K^a

x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$ ^b	$\eta/\text{mPa}\cdot\text{s}$ ^b	D^c
0.00	0.997 07	0.8903	78.30
0.20	1.002 40	1.5165	69.73
0.40	1.006 90	2.3654	57.41
0.60	1.002 33	2.8849	42.11
0.80	0.986 72	2.5751	26.53
1.00	0.960 02	1.5414	16.93

^a x_1 is the mass fraction of 2-methoxyethanol. ^b From Das and Hazra, 1993. ^c From Sadek et al., 1971.

the electron charge, k_B is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial Λ° values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set ($c_j, \Lambda_j, j = 1, \dots, n$), n, D, η, T , initial value of Λ° , and instruction to cover a preselected range of R values.

In practice, calculations are made by finding the values of Λ° and α which minimize the standard deviation, σ ,

$$\sigma^2 = \sum [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2 / (n - 2) \quad (7)$$

for a sequence of R values and then plotting σ against R ; the best-fit R corresponds to the minimum in the σ vs R curve. First, approximate runs over a fairly wide range of R values are made to locate the minimum and then a fine scan around the minimum is made. Finally, with this minimizing value of R , the corresponding Λ° and K_A are calculated.

In the present analysis, however, since a rough scan using unit increments of R values from 4 to 20 gave no significant minima in the σ - R curves, the R value was assumed to be $R = a + d$, where a is the sum of the crystallographic radii and d is given by (Fuoss, 1978b)

$$d/\text{\AA} = 1.183(M/\rho_0)^{1/3} \quad (8)$$

where M is the molecular weight of the solvent and ρ_0 its density.

The values of Λ° , K_A , and R obtained by this procedure are reported in Table 3.

Discussion

The Λ° values of tetraalkylammonium perchlorates decrease as the alkyl chain length increases (Table 3). This is in agreement with earlier findings in several pure and mixed solvents (Fernandez-Prini, 1973; Muhuri and Hazra, 1991; Das and Hazra, 1992; Islam et al., 1989). The size and structure-forming effect decrease as the alkyl chain length increases, and consequently, the mobility is in the reverse order.

It is also found that the limiting molar conductance of each salt decreases with the corresponding increase in viscosity of the solvent mixture, but these variations do not compensate each other to give the Walden product a constant value, which passes through a maximum at about $x_1 = 0.60$ of 2-methoxyethanol. The variation of the Walden product with composition is indicative of selective solvation of the ions in these solvent mixtures. 2-Methoxyethanol first dehydrates the ions and then solvates them as its concentration increases in the solvent mixtures. This type of behavior has also been observed in other binary

Table 2. Molar Conductances (Λ) and Corresponding Molarities (c) of Tetraalkylammonium Perchlorates in 2-Methoxyethanol (1) + Water (2) at 298.15 K

$10^4 c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$10^4 c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
Et ₄ NClO ₄			
$x_1 = 0.20$		$x_1 = 0.40$	
640.169	63.06	376.045	52.85
525.060	64.47	324.998	53.50
474.998	65.13	256.106	54.58
410.077	66.04	228.018	55.08
355.862	66.86	200.100	55.51
300.010	67.77	150.011	56.23
251.125	68.64	101.025	57.70
201.152	69.62	69.112	58.55
110.146	71.80	38.006	59.69
$x_1 = 0.60$		$x_1 = 0.80$	
148.801	50.53	36.942	28.40
125.116	51.10	33.120	28.57
100.005	51.84	30.511	28.74
84.915	52.33	25.011	29.10
75.030	52.63	19.982	29.40
54.453	53.43	14.868	29.82
45.966	53.81	12.017	30.10
34.218	54.33	6.050	30.71
20.001	55.18		
Pr ₄ NClO ₄			
$x_1 = 0.20$		$x_1 = 0.40$	
675.001	53.23	377.129	43.57
550.122	54.61	301.146	44.52
474.986	55.56	254.498	45.16
409.868	56.42	200.164	45.99
351.008	57.29	151.266	46.84
299.989	58.04	100.105	47.90
250.004	58.91	74.342	48.53
200.012	59.86	37.978	49.67
101.215	62.11		
$x_1 = 0.60$		$x_1 = 0.80$	
148.002	44.64	36.994	24.79
131.639	45.04	33.015	25.01
101.652	45.83	30.115	25.17
85.181	46.32	25.002	25.49
74.966	46.65	19.989	25.83
56.022	47.32	15.020	26.22
45.008	47.76	12.011	26.49
35.612	48.18	8.129	26.89
15.001	49.38	4.004	27.44
Bu ₄ NClO ₄			
$x_1 = 0.20$		$x_1 = 0.40$	
634.475	50.85	375.102	39.93
503.417	52.61	326.998	40.75
451.624	53.37	270.065	41.81
402.601	54.13	201.142	43.25
311.112	55.68	155.733	44.35
250.068	56.85	104.493	45.80
202.779	57.86	59.101	47.42
148.662	59.17	40.065	48.30
100.510	60.55		
$x_1 = 0.60$		$x_1 = 0.80$	
148.420	39.86	36.403	22.40
132.268	40.46	32.234	22.75
105.506	41.67	28.985	23.05
88.187	42.51	25.037	23.43
76.062	43.10	20.102	23.95
60.024	44.05	14.992	24.56
48.653	44.80	12.131	24.95
35.349	45.74	8.415	25.53
20.066	47.15	5.020	26.19

solvent systems (Bahadur and Ramanamurti, 1984; Das and Hazra, 1988).

The K_A values of the electrolytes in the solvent mixtures indicate that tetrabutylammonium perchlorate starts ion association after $x_1 = 0.40$ of the cosolvent whereas for tetraethyl- and tetrapropylammonium perchlorates ion association is appreciable only in the solvent mixtures with $x_1 \geq 0.60$.

Table 3. Derived Conductivity Parameters for Tetraalkylammonium Perchlorates in 2-Methoxyethanol (1) + Water (2) at 298.15 K

x_1	$\Lambda^\circ/S\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$K_A/\text{dm}^{-3}\cdot\text{mol}^{-1}$	$R/\text{\AA}$	$\Lambda^\circ\eta_0/S\cdot\text{cm}^2\cdot\text{mol}^{-1}\cdot\text{P}$	$100\sigma/\Lambda^\circ$
	Et ₄ NClO ₄				
0.20	78.12 ± 0.01	3.49	9.30	1.185	0.01
0.40	62.92 ± 0.02	4.80	9.80	1.488	0.03
0.60	57.95 ± 0.02	9.00	12.60	1.672	0.02
0.80	32.46 ± 0.02	31.92	21.90	0.836	0.02
1.00 ^a	47.81 ± 0.16	326	11.50	0.737	0.15
	Pr ₄ NClO ₄				
0.20	67.87 ± 0.02	3.93	9.80	1.029	0.02
0.40	52.58 ± 0.01	5.11	10.40	1.244	0.01
0.60	51.63 ± 0.01	9.74	13.00	1.490	0.01
0.80	28.84 ± 0.01	38.10	21.50	0.743	0.01
1.00 ^a	42.85 ± 0.16	304	12.00	0.660	0.09
	Bu ₄ NClO ₄				
0.20	66.67 ± 0.01	5.22	10.90	1.011	0.01
0.40	51.82 ± 0.01	9.58	12.10	1.226	0.01
0.60	50.61 ± 0.01	23.66	14.90	1.460	0.03
0.80	28.14 ± 0.01	83.71	23.50	0.724	0.01
1.00 ^a	40.80 ± 0.11	389	12.40	0.629	0.06

^a From Das and Hazra, 1992.

In each solvent system, the K_A values are observed to be in the order



indicating that R_4N^+ -solvent electrostriction should follow the reverse order (the anion being the common entity).

Literature Cited

- Bahadur, L.; Ramanamurti, M. V. Conductance Studies in Amide-Water Mixtures. VI. Nitrates of Sodium, Potassium, and Ammonium in N,N-Dimethylformamide-water Mixtures at 25 °C. *Can. J. Chem.* **1984**, *62*, 1051–1056.
- Das, S.; Hazra, D. K. Conductance Studies of Tetraalkylammonium Iodides in Dimethylsulphoxide-Water Mixtures. *Indian J. Chem.* **1988**, *27A*, 1073–1079.
- Das, B.; Hazra, D. K. Studies on the Viscosities, Conductances, and Adiabatic Compressibilities of Some Tetraalkylammonium Perchlorates in 2-Methoxyethanol. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3470–3476.

- Das, B.; Hazra, D. K. Viscosities and Excess Molar Volumes for 2-Methoxy-1-ethanol + Water at Different Temperatures. *J. Chem. Eng. Data* **1993**, *38*, 361–363.
- Das, B.; Hazra, D. K. Apparent and Partial Molar Volumes of Some Symmetrical Tetraalkylammonium Perchlorates in 2-Methoxyethanol at 25, 35, and 45 °C. *Bull. Chem. Soc. Jpn.* **1995a**, *68*, 734–737.
- Das, B.; Hazra, D. K. Conductometric, Viscometric, and Spectroscopic Investigations on the Solvation Phenomena of Alkali-Metal Ions and Ion Pairs in 2-Methoxyethanol. *J. Phys. Chem.* **1995b**, *99*, 269–273.
- Fernandez-Prini, R. In *Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickinson, T., Eds.; Plenum Press: London, 1973; Chapter 5.
- Fuoss, R. M. Paired Ions: Dipolar Pairs as Subset of Diffusion Pairs. *Proc. Natl. Acad. Sci. U.S.A.* **1978a**, *75*, 16–20.
- Fuoss, R. M. Conductance-Concentration Function for the Paired Ion Model. *J. Phys. Chem.* **1978b**, *82*, 2427–2440.
- Islam, N.; Zaidi, S. B. A.; Ansari, A. A. Conductometric Studies of Ionic Association of Tetraalkylammonium Halides and Tetraphenylborate in N,N-Dimethylformamide-Methyl Ethyl Ketone Mixtures at 25 °C. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 309–316.
- Lind, J. E., Jr.; Zwolenik, J. J.; Fuoss, R. M. Calibration of Conductance Cells at 25 ° with Aqueous Solutions of Potassium Chloride. *J. Am. Chem. Soc.* **1959**, *81*, 1557–1559.
- Muhuri, P. K.; Hazra, D. K. Electrical Conductances for Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate and Tetrabutylammonium Tetrabutylborate in Propylene Carbonate at 25 °C. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3511–3513.
- Niazi, M. S. K.; Jabeen, I.; Shah, S. S. Ionic Association and Conductances of Sodium Perchlorate in N,N-Dimethylformamide + Water and Tetrahydrofuran + Water at 298 K. *J. Chem. Eng. Data* **1993**, *38*, 285–287.
- Papadopoulos, N.; Ritzoulis, G. Conductance of CsCl in Acetonitrile-Water Mixtures at 10, 20, and 30 °C. *Ann. Chim.* **1989**, *79*, 389–395.
- Raju, U. G. K.; Sethuram, B.; Rao, N. Conductometric Study of Ion-Ion and Ion-Solvent Interactions. III. Conductances of Silver Acetate in Acetonitrile-water Mixtures at 25 °C. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 293–296.
- Roy, M. N.; Nandi, D.; Hazra, D. K. Conductance Studies of Alkali Metal Chlorides and Bromides in Aqueous Binary Mixtures of Tetrahydrofuran 25 °C. *J. Indian Chem. Soc.* **1993**, *70*, 121–129.
- Sadek, H.; Tadros, Th. F.; El-Harakany, A. A. Thermodynamics of Hydrochloric Acid in Water-Methyl Cellosolve Mixtures. I. Standard Potentials of the Silver/Silver Chloride Electrode. *Electrochim. Acta* **1971**, *16*, 339–352.
- Saha, N.; Das, B.; Hazra, D. K. Viscosities and Excess Molar Volumes for Acetonitrile + Methanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1264–1266.

Received for review June 6, 1996. Accepted August 13, 1996.[⊙]

JE9601974

[⊙] Abstract published in *Advance ACS Abstracts*, September 15, 1996.