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(PAPER 7/718)

Conductance Studies of Tetra-alkylammonium Bromides in 2-Methoxyethanol at 25 °C

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Conductance measurements are reported for six symmetrical tetra-alkylammonium halides, R_4NBr ($R = \text{ethyl to heptyl}$) and two 'reference electrolytes', viz. tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) and tetrabutylammonium tetraphenylborate (Bu_4NBPPh_4) in 2-methoxyethanol (ME) at 25 °C. The data have been analysed by the 1978 Fuoss conductance equation in terms of the limiting molar conductivity, Λ^0 , the association constant, K_a , and the association distance, R . The limiting ion conductances have been determined from the appropriate division of the Λ^0 -values of Bu_4NBBu_4 and Bu_4NBPPh_4 . The results indicate that all these salts are highly associated in this solvent media. The K_a values are generally found to decrease with increasing cationic size from Et_4N^+ to $Heptyl_4N^+$ but decreases sharply for Pr_4NBr . The individual limiting ion conductance (λ_i^0) obtained separately from the two reference electrolytes are in good agreement with each other, suggesting that any one of them can be used as a reference electrolyte in ME. The Walden products and the Stokes radii of the ions have been evaluated. The values indicate that R_4N^+ ions are poorly solvated in this solvent media.

2-Methoxyethanol (ME; methyl Cellosolve) is a widely used and potential organic solvent for various industrial processes.¹⁻³ It has unique solvating properties associated with its quasi-aprotic character.⁴ As it is a monomethyl ether of ethylene glycol, it is very likely to show physico-chemical characteristics midway between protic and dipolar aprotic solvents. Hence, it is of much interest to study the behaviour of electrolytes in such solvent media.

In this paper we report the results of our conductance measurements carried out on dilute solutions of symmetrical tetra-alkylammonium bromides, R_4NBr ($R = C_2H_5$ to C_7H_{15}) and two reference electrolytes, viz. Bu_4NBBu_4 and Bu_4NBPPh_4 in 2-methoxyethanol at 25 °C. Since transference number data for solutions of these salts in ME are not available in the literature, single ion conductivities were evaluated using two reference electrolytes in an effort to provide the reliable values of ionic mobilities.

Experimental

2-Methoxyethanol (G. R. E. Merck) was distilled twice in an all-glass distillation apparatus before use. The physical properties at 25 °C obtained for the purified sample were d 0.96002 g cm⁻³, viscosity (η_0) 1.5414 cP and specific conductance $1.01 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. These values are in good agreement with the literature values.⁵

Tetra-alkylammonium bromides (Fluka) were of purum or puriss grade and were purified as described in the literature⁶ and also described earlier by us.⁷ The salts were purified by recrystallization and the higher homologues were recrystallised twice to ensure maximum purity. The recrystallised salts were dried under vacuum at elevated temperatures for 12 h.

Tetrabutylammonium tetraphenylborate (Bu_4NBPPh_4) was prepared by mixing

equimolar quantities of NaBPh₄ and Bu₄NBr as described in the literature.⁸ Tetrabutylammonium tetrabutylborate (Bu₄NBBu₄; Alfa) was purified as suggested by Lawrence *et al.*⁹

Conductance measurements were made by a Pye-Unicam PW 9509 conductivity meter at a frequency of 2 kHz using a dip-type cell of cell constant 0.7311 cm⁻¹. The conductivity cell was sealed to the side of a 500 cm³-conical flask closed by a ground glass cap fitted with a side arm through which dry and pure nitrogen (GC-grade IOL AR-2) was passed to prevent the admission of air into the cell during the addition of the solvent or solution. Measurements were made in an oil bath maintained at 25 ± 0.005 °C by means of a mercury in glass thermoregulator and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

The density at 25 °C was determined using a pycnometer of ca. 25 ml capacity. The viscosity was measured with an Ubbelohde suspended-level type viscometer as described previously.⁷

The dielectric constant of ME was taken from the literature.¹⁰

Results

The equivalent conductances, Λ , of electrolytes measured at the corresponding concentrations, c , are given in table 1. The data were analysed by the Fuoss conductance equation^{11,12} which can be expressed as

$$\Lambda = \rho[\Lambda_0(1 + RX) + EL] \quad (1)$$

$$\rho = [1 - \alpha(1 - \gamma)] \quad (2)$$

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

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

$$\beta = \frac{e^2}{\epsilon k T} \quad (5)$$

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

where RX and EL are relaxation and hydrodynamic terms, respectively as derived by Fuoss, and other terms have their usual significance. The parameters Λ^0 , K_A and R were obtained by solving the above equations. The calculations were performed on a Wipro Z-650 computer using the program devised by Fuoss. Initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolations of the data.

In practice, calculations were made by finding the values of Λ^0 and α which minimize

$$\sigma^2 = \sum_j [\Lambda_j(\text{calc}) - \Lambda_j(\text{obs})]^2 / (n - 2) \quad (7)$$

for a sequence of R -values and then plotting $\sigma\% = 100\sigma/\Lambda^0$ against R , the best fit R corresponds to the maximum in the $\sigma\%$ vs. R curve. First approximate runs over a fairly wide range of R values were made to locate the minimum and then a fine scan around the minimum was made. Finally the minimizing value of R was read into the computer and the corresponding values of Λ^0 and α were calculated.

As the dielectric constant of ME ($\epsilon = 16.93$)¹⁰ is very low, a wide range of R values reproduced the data equally well in most of the cases except for Bu₄NBBu₄ and BuNBPh₄ where a fairly well defined minima in the $\sigma\%$ vs. R curve were obtained. This insensitivity of goodness of fit to the parameter R was also observed by Fuoss.¹²

In order to treat the data for which $\sigma\%$ vs. R curves did not show a sharp minimum,

Table 1. Equivalent conductances of the tetra-alkylammonium bromides Bu_4NBBu_4 and Bu_4NBPh_4 in 2-methoxyethanol at 25 °C

| Et_4NBr | | Pr_4NBr | |
|-----------------------------|---|-----------------------------|---|
| $10^4 c/\text{mol dm}^{-3}$ | $\Lambda/\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ | $10^4 c/\text{mol dm}^{-3}$ | $\Lambda/\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ |
| 16.012 | 23.50 | 15.995 | 29.62 |
| 13.990 | 25.00 | 9.490 | 31.75 |
| 8.498 | 28.20 | 8.002 | 32.35 |
| 7.002 | 30.85 | 6.998 | 32.62 |
| 5.992 | 30.90 | 6.001 | 33.00 |
| 4.001 | 33.10 | 4.999 | 33.56 |
| 2.995 | 34.23 | 4.010 | 34.10 |
| — | — | 2.998 | 34.75 |
| 2.000 | 35.50 | 2.002 | 35.37 |
| Bu_4NBr | | $\text{Pentyl}_4\text{NBr}$ | |
| 16.001 | 25.87 | 15.997 | 24.50 |
| 13.995 | 26.71 | 13.999 | 25.21 |
| 12.001 | 27.37 | 12.002 | 25.70 |
| 9.995 | 27.80 | 9.995 | 26.50 |
| 9.490 | 28.50 | 9.501 | 26.90 |
| 8.001 | 29.00 | 7.999 | 27.41 |
| 5.997 | 30.00 | 5.987 | 28.28 |
| 5.002 | 30.62 | 5.001 | 28.86 |
| 1.998 | 32.75 | 2.003 | 30.80 |
| hexyl_4NBr | | $\text{heptyl}_4\text{NBr}$ | |
| 16.001 | 24.19 | 16.002 | 22.98 |
| 13.996 | 24.81 | 13.998 | 23.60 |
| 12.000 | 25.25 | 11.989 | 24.09 |
| 9.855 | 25.90 | 10.012 | 24.70 |
| 9.501 | 26.15 | 9.495 | 25.05 |
| 8.004 | 26.52 | 8.010 | 25.45 |
| 5.996 | 27.22 | 5.897 | 26.11 |
| 5.001 | 27.65 | 4.998 | 26.58 |
| 1.999 | 29.17 | 2.001 | 28.20 |
| Bu_4NBBu_4 | | Bu_4NBPh_4 | |
| 15.997 | 22.50 | 15.996 | 19.35 |
| 10.001 | 23.20 | 9.897 | 20.10 |
| 9.497 | 23.50 | 9.500 | 20.85 |
| 7.001 | 24.20 | 6.989 | 21.87 |
| 5.988 | 24.50 | 6.020 | 22.25 |
| 5.002 | 24.90 | 5.090 | 22.35 |
| 3.998 | 25.30 | 4.119 | 22.80 |
| 3.001 | 25.80 | 2.998 | 23.40 |
| 1.957 | 26.40 | 1.989 | 24.86 |

Table 2. Conductance parameters of tetra-alkylammonium bromide in ME at 25 °C

| salt | $\Lambda^0/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ | $K_A/\text{dm}^3 \text{ mol}^{-1}$ | Walden product | R/A^0 | σ |
|-----------------------------------|---|------------------------------------|----------------|---------|----------|
| Et ₄ NBr | 43.74 (±0.29) | 1114.67 (±98.50) | 0.674 | 11.03 | 0.27 |
| Pr ₄ NBr | 38.80 (±0.14) | 216.93 (±12.08) | 0.598 | 11.55 | 0.13 |
| Bu ₄ NBr | 36.74 (±0.27) | 372.64 (±24.02) | 0.566 | 11.97 | 0.20 |
| Pent ₄ NBr | 34.53 (±0.23) | 353.79 (±21.21) | 0.532 | 12.32 | 0.17 |
| Hex ₄ NBr | 32.22 (±0.17) | 233.25 (±15.28) | 0.496 | 12.63 | 0.14 |
| Hept ₄ NBr | 31.34 (±0.19) | 276.11 (±18.06) | 0.483 | 12.91 | 0.15 |
| Bu ₄ NBBu ₄ | 28.83 (±0.13) | 142.21 (±11.04) | 0.444 | 8.00 | 0.12 |
| Bu ₄ NBPh ₄ | 27.64 (±0.28) | 369.17 (±21.20) | 0.426 | 8.60 | 0.14 |

Table 3. Limiting ionic conductances, Walden products and Stokes radii values for R₄N⁺ ions in 2-methoxyethanol at 25 °C

| ion | λ_+^{0a} | λ_+^{0b} | $\lambda_+^0 \eta_0^a$ | $\lambda_+^0 \eta_0^b$ | r_s^a | r_s^b |
|------------------------------------|------------------|------------------|------------------------|------------------------|---------|---------|
| Et ₄ N ⁺ | 21.42 | 21.29 | 0.331 | 0.328 | 2.48 | 2.49 |
| Pr ₄ N ⁺ | 16.48 | 16.35 | 0.251 | 0.252 | 3.22 | 3.25 |
| Bu ₄ N ⁺ | 14.42 | 14.29 | 0.222 | 0.220 | 3.69 | 3.72 |
| Pentyl ₄ N ⁺ | 12.22 | 12.09 | 0.188 | 0.186 | 4.35 | 4.39 |
| Hexyl ₄ N ⁺ | 9.90 | 9.77 | 0.152 | 0.150 | 5.37 | 5.44 |
| Heptyl ₄ N ⁺ | 9.02 | 8.89 | 0.139 | 0.137 | 5.89 | 5.98 |

^a Calculations based on Bu₄NBBu₄. ^b Calculations based on Bu₄NBPh₄.

make table measure

R was arbitrarily preset¹² at the centre-to-centre distance of the solvent-separated pair

$$R = f + \frac{1}{2} \text{ as } a + d > \beta/2 \quad (8)$$

where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d = (M/N\rho)^{1/3} = [1.183(M/\rho)^{1/3}A^0] \quad (9)$$

where M is the molecular weight of ME and ρ is its density.

The values of Λ^0 , K_A and R obtained by this procedure are reported in table 2. The limiting ion conductances of R₄N⁺ ions based on the Λ^0 values of Bu₄NBPh₄ and Bu₄NBBu₄ are given in table 3. The Walden product and the Stokes radii of the ions are also given in table 3.

Discussion

Table 2 shows that the limiting equivalent conductances of the tetra-alkyl ammonium bromides decrease as the alkyl chain length increases. This is in agreement with earlier findings in several pure and mixed solvents¹³ and is attributed with the size- and structure-forming effect of the cations¹⁴ (anions being the same). Size and structure forming effect decrease as the alkyl chain length increases and so the mobility is in the reverse order.

We find that all these salts are highly associated in this solvent media. This is quite expected owing to the low dielectric constant of the solvent. Further, K_A decreases as the size of the cation increases with the exception of Pr₄NBr and Hexyl₄NBr. In general, tetra-alkylammonium halides are more associated in alcohols¹⁵ than other aprotic

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solvents of similar dielectric constants. In alcohols, K_A goes through a minimum for $R = Pr$ in case of iodides.¹⁵ Kay *et al.*⁶ analysed their data for tetra-alkylammonium salts in acetone and found that K_A also decreased with the cationic size. Our results are thus in conformity with the earlier works on alcohols¹⁶ and also with the tetra-alkylammonium salts in acetone. However, we observe that the K_A value of Heptyl₄NBr is greater than Hexyl₄NBr and this may be probably due to the formation of clathrate-like structures around the hydrocarbon side chains, which is a characteristic property of these salts.

The calculation of the limiting ionic equivalent conductance in organic solvent is a very difficult task and, until now, reliable experimental data for ionic transference numbers in most of the non-aqueous solvents are not available. However, attempts have been made to separate the limiting equivalent conductances into its ionic components using the various indirect methods.¹⁶ In the absence of accurate transference-number data of tetra-alkylammonium ions in ME, we used the 'reference-electrolyte' method for the division of Λ^0 into a single ion value. To test the reliability of the method we used two reference electrolytes *viz.* Bu₄NBBu₄ and Bu₄NBPh₄.

Lawrence and Sacco¹⁷⁻¹⁹ and Gill *et al.*²⁰ have successfully used Bu₄NBBu₄ as reference electrolytes in separating viscosity B -coefficients and in calculating the limiting ionic conductances in organic solvents assuming

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Bu}_4\text{B}^-). \quad (10)$$

We also used the above relationship in calculating the limiting ionic conductances for R₄N⁺ ions in ME. The reason behind the choice of Bu₄NBBu₄ as the reference electrolyte is the fact that the cation and anion in this case are symmetrical in shape and have almost equal van der Waals volumes. Bu₄NBPh₄ has also been utilised by various authors^{21, 22} to calculate the limiting ion conductances assuming

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Ph}_4\text{B}^-) \quad (11)$$

although its validity is questionable in several solvents owing to the unequal size of the cation and anion and also to the unequal electronic environment of the positive charge on the nitrogen atom and the negative charge on the boron atom. In case of this reference electrolyte, instead of equal division, we calculated ionic conductances using the following relationship:²³

$$\frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{Ph}_4\text{B}^-)} = \frac{r_{\text{Ph}_4\text{B}^-}}{r_{\text{Bu}_4\text{N}^+}} = \frac{5.35}{5.00} = 1.07. \quad (12)$$

The ionic radii of Bu₄N⁺ and Ph₄B⁻ were taken from the work of Gill and Sekhri.^{20, 24} The virtual organic solvent independence of the solvation radii of large Bu₄N⁺ and Ph₄B⁻ ions led Krumgalz²³ to suggest that these ions are not solvated in organic solvents and their radii were calculated from the equation

$$r_{\pm} = \frac{|Z|F^2}{G\pi N\eta_0 \lambda_0^{\pm}} \quad (13)$$

corresponding to their true dimensions in the solvent. Though nothing can be said definitely regarding the accuracy of the method [eqn (12)] some indirect evidence regarding the reliability of the values may be provided. Thus the value of the ratio $\lambda_0(\text{BPh}_4^-)/\lambda_0(\text{Bu}_4\text{N}^+)$ becomes 1.06 if we choose $r_{\text{Bu}_4\text{N}^+} = 3.85 \text{ \AA}$ and $r_{\text{Ph}_4\text{B}^-} = 4.08 \text{ \AA}$ as suggested by Krumgalz^{23, 25, 26} [eqn (13)].

Fuoss *et al.*,²⁷⁻³⁰ from extensive measurements of Λ^0 values of R₄NBPh₄ salts in various mixed solvents, assumed that the limiting transference number of Bu₄N⁺ in Bu₄NBPh₄ is 0.519 and is independent of the solvent. This leads to a value of 1.079 for $\lambda_0(\text{Bu}_4\text{N}^+)/\lambda_0(\text{BPh}_4^-)$, which is close to our value.

D'Aprano and Fuoss³⁰ used Bu_4NBPh_4 to calculate single ion conductances in mixed organic solvents applying the relationship, $\lambda_0(\text{Bu}_4\text{N}^+) = 0.213/\eta_0$ and $\lambda_0(\text{BPh}_4^-) = 0.201/\eta_0$ which means the ratio of $\lambda_0(\text{Bu}_4\text{N}^+)/\lambda_0(\text{Ph}_4\text{B}^-)$ is 1.06. Recently Gill *et al.*³¹ proposed the following equation

$$\frac{\lambda_0, \text{Bu}_4\text{N}^+}{\lambda_0, \text{Ph}_4\text{B}^-} = \frac{5.35 - (0.0103\epsilon_0 + r_y)}{5.00 - (0.0103\epsilon_0 + r_y)} \quad (14)$$

which is almost the same as that used by us. The ratio in this case is also close to 1.07.

The λ_0^\pm values of R_4N^+ ions obtained by using the above two methods are presented in table 3. It can be readily seen that the limiting ionic conductances obtained from the above two methods are in very close agreement with each other. This suggests that either of the two methods can be used to calculate the limiting ionic conductances in organic solvents. Further, the limiting ionic conductances thus obtained correspond well with the experimental values calculated from the transference number measurements in many other organic solvents.¹⁶

The Walden product $\lambda_0^+ \eta_0$ and Stokes' radii (r_s) of R_4N^+ ions are reported in table 3. Krumgalz²³ suggested that the large tetra-alkylammonium ions remain unsolvated (in the kinetic sense) in solution in organic solvents. It then follows that for large R_4N^+ ions, $\lambda_0^\pm \eta_0$ will be constant and the values will be independent of the nature of the organic solvents. By taking λ_0^\pm values from transference number measurements, Krumgalz¹⁶ calculated the average $\lambda_0^\pm \eta_0$ values for R_4N^+ ions. Comparison of our results with those of Krumgalz reveals that in the case of Et_4N^+ , Pr_4N^+ and Bu_4N^+ ions, the values are 3–7% higher and for $\text{Pentyl}_4\text{N}^+$, Hexyl_4N^+ and $\text{Heptyl}_4\text{N}^+$ ions, the values are 1–12% lower than the values proposed by Krumgalz. Hence very weak solvation cannot be ruled out, although nothing can be said definitely in the absence of precise transference number data.

We thank Prof. R. M. Fuoss for furnishing the computer programing of this equation. D.D. thanks the C.S.I.R., New Delhi for the award of a research fellowship. We thank Dr G. Ali Qureshi of Karolinska Institute, Sweden for gift sample of tetrabutylammonium tetrabutylborate.

References

- 1 J. F. Garst, *Solute-Solvent Interactions*, ed. J. F. Coetzee and C. D. Ritchie (Marcel Dekker, New York, 1969), chap. 8.
- 2 A. P. Kreshkov, *Osnovy Analyticheskoi Khimii* (Fundamentals of Analytical Chemistry), (Izd. Khimiya, Moscow, 1970), vol. 5.
- 3 A. G. Schwartz and J. B. Barkar, *Talanta*, 1975, **22**, 773.
- 4 F. Franks and D. J. G. Ives, *Q. Rev.*, 1966, **20**, 1.
- 5 J. A. Riddick and W. B. Bunger, in *Techniques of Chemistry, vol. II, Organic Solvents*, ed. A. Weissburger (Wiley, New York, 3rd edn, 1970).
- 6 D. F. Evans, C. Zawoyski and R. L. Kay, *J. Phys. Chem.*, 1965, **69**, 387.
- 7 S. Das, D. K. Hazra and S. C. Lahiri, *Z. Phys. Chem. N.F.*, 1983, **138**, 185.
- 8 M. Castagnolo, A. Sacco and A. D. Giglio, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2669.
- 9 K. G. Lawrence and A. Sacco, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 615.
- 10 H. Sadek, Th. F. Tadros and A. A. El-Harakany, *Electrochim. Acta*, 1971, **16**, 339.
- 11 R. M. Fuoss, *Proc. Natl Acad. Sci. U.S.A.*, 1978, **75**, 16.
- 12 R. M. Fuoss, *J. Phys. Chem.*, 1978, **82**, 2427.
- 13 R. Fernandez-Prini, *Physical Chemistry of Organic Solvent Systems*, ed. A. K. Covington and T. Dickinson (Plenum Press, London, 1973), chap. 5.
- 14 Lal Bahadur and M. V. R. Murti, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1409.
- 15 R. Fernandez-Prini, *ref. (13)*, p. 566.
- 16 B. S. Krumgalz, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 571 and references therein.
- 17 K. G. Lawrence and A. Sacco, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 615.