

**CHAPTER - V**

A Conductance Study of the Tetraalkylammonium  
Bromides in 2-Methoxy Ethanol at 25°C

2-Methoxy ethanol (ME) or methyl cellosolve is a widely used and potential organic solvent for various industrial processes<sup>1-3</sup>. It has unique solvational properties associated with its quasi-aprotic character<sup>4</sup>. As it is a mono-methyl ether of ethylene glycol, it is very likely to show its physico-chemical characteristics lying intermediate between protic and dipolar aprotic solvents. Hence, it becomes of very much interest to study the behaviour of electrolytes in such a solvent media.

In this chapter we report the results of our conductance measurements carried out on dilute solutions of symmetrical tetraalkylammonium bromides,  $R_4NBr$  ( $R = C_2H_5$  to  $C_7H_{15}$ ) and two reference electrolytes, viz.  $Bu_4NBBu_4$  and  $Bu_4NBPh_4$  in 2-methoxy ethanol at 25°C. Since transference number data for solutions of these salts in ME are not available in the literature, single ion conductivities have been evaluated using two reference electrolytes in an effort to provide the reliable values of ionic mobilities.

#### Experimental

2-methoxy ethanol (G.R.S. Merck) was distilled twice in an all glass distillation set before use. The physical

properties at 25°C obtained for the purified sample were 0.96002 g cm<sup>-3</sup> for the density, 1.5414 cP for the viscosity ( $\eta_0$ ) and  $1.01 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$  for the specific conductance and these values are in good agreement with the literature values<sup>5</sup>.

Tetraalkylammonium bromides were of Fluka's purum or puriss grade and purified in the manner as given at the literature<sup>6</sup> and also described by us earlier<sup>7</sup>. The salts were purified by recrystallisation and the higher homologues were recrystallised second time to ensure highest purity. The recrystallised salts were dried in vacuum at elevated temperatures for 12 hours.

Tetrabutylammonium tetraphenyl borate ( $\text{Bu}_4\text{NBPb}_4$ ) was prepared by mixing equimolar quantities of  $\text{NaBPb}_4$  and  $\text{Bu}_4\text{NBr}$  as described in the literature<sup>8</sup>. Tetrabutylammonium tetrabutylborate ( $\text{Bu}_4\text{NBu}_4$ ) (Alfa product) was purified as suggested by Lawrence et al.<sup>9</sup>.

Conductance measurements were made by a Pye Unicam PW 9509 conductivity meter at a frequency of 2 MHz using a dip-type cell of cell constant 0.731 cm<sup>-1</sup>. Conductivity cell was sealed to the side of a 500 cm<sup>3</sup> conical flask closed by a ground glass cap fitted with a side arm through which dry and pure nitrogen (GC-grade IOL AR - 2) passed to prevent the admission of air into the cell when solvent or solution were added. The measurements were made in an oil bath maintained at  $25 \pm 0.005^\circ\text{C}$  by means of a mercury in glass thermoregulator

and the absolute temperature was determined by a calibrated platinum resistance thermometer and miller bridge.

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

The dielectric constant of ME was taken from the literature<sup>10</sup>.

### Results

The equivalent conductances,  $\Lambda$ , of electrolytes measured at the corresponding concentrations,  $C$ , are given in table I. The data were analysed by the 1978 Fuoss conductance equation<sup>11,12</sup> which can be expressed as:

$$\Lambda = P \left[ \Lambda^0 (1 + R\alpha) + EL \right] \quad \dots(1)$$

$$P = \left[ 1 - \alpha (1 - \gamma) \right] \quad \dots(2)$$

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

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

$$\beta = e^2 / \epsilon RT \quad \dots (5)$$

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

where  $R_X$  and  $SL$  are relaxation and hydrodynamic terms respectively as derived by Fuoss and other terms have their usual significance. The parameters  $\Lambda^\circ$ ,  $K_A$  and  $R$  were obtained by solving the above equations. The calculations were performed on a Nipre 2-650 computer using the programme furnished by Prof. S.M. Fuoss. Initial  $\Lambda^\circ$  values for the iteration procedure were obtained from Shedlovsky extrapolations of the data (Table 2).

In practice, calculations were made by finding the values of  $\Lambda^\circ$  and  $\alpha$  which minimize

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

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

As the dielectric constant of ME ( $\epsilon = 16.93$ )<sup>10</sup> is very low, a wide range of R values reproduced the data equally well in most of the cases except for  $\text{Bu}_4\text{NBBu}_4$  and  $\text{Bu}_4\text{NBF}_4$  where a fairly well defined minima in  $\sigma/\omega$ -R curve were obtained. This insensitivity of goodness of fit to the parameter R was also observed by Fuoss<sup>12</sup>.

In order to treat the data for which  $\sigma/\omega$ -R curves did not show a sharp minimum, R was arbitrarily preset<sup>12</sup> at the centre-to-centre distance of solvent separated pair.

$$R = a + d \quad \text{as} \quad a + d \gg \frac{R}{2} \quad \dots (8)$$

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

$$d = \left(\frac{M}{N\rho}\right)^{1/3} = \left[1.183 \left(\frac{M}{\rho}\right)^{1/3} \text{ \AA} \right] \quad \dots (9)$$

where M is the molecular weight of ME and  $\rho$  is its density.

The values of  $\Lambda^\circ$ ,  $R_a$  and R obtained by this procedure are reported in table 3. The limiting ion conductances of  $\text{R}_4\text{N}^+$  ions based on the  $\Lambda^\circ$  values of  $\text{Bu}_4\text{NBF}_4$  and  $\text{Bu}_4\text{NBBu}_4$  are given in table 4. The Walden product and the Stokes' radii of the ions have also been reported in table 4.

### Discussion

Table 3 shows that the limiting equivalent conductances of the tetraalkyl ammonium bromides decrease as the alkyl chain length increases. This is in agreement with the earlier findings in several pure and mixed solvents<sup>13</sup> and is attributed with the size and structure forming effect of the cations<sup>14</sup> (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 due to the low dielectric constant of the solvent. Further,  $K_A$  decreases as the size of the cation increases with the exception of  $Pr_4NBr$  and  $Hex_4NBr$ . In general, tetraalkylammonium halides are more associated in alcohols<sup>15</sup> than other aprotic solvents of similar dielectric constants. In alcohols,  $K_A$  goes through a minima for  $R = Pr$  in case of iodides<sup>15</sup>. Kay et al<sup>16</sup> analysed their data for tetraalkylammonium 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 alcohols<sup>15</sup> and also with the tetraalkylammonium salts in acetone. However, we observe that the  $K_A$  value of  $Hept_4NBr$  is greater than  $Hex_4NBr$  and this may be probably due to the formation of clathrate-like structure 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<sup>16</sup>. In the absence of accurate transference number data of tetraalkylammonium ions in ME, we have also used the 'reference-electrolyte' method for the division of  $\Lambda^{\circ}$  into single ion value. To test the reliability of the method we have taken two reference electrolytes viz.  $\text{Bu}_4\text{NBBu}_4$  and  $\text{Bu}_4\text{NBF}_4$ .

Lawrence and Sacco<sup>17-19</sup> and Gill et al<sup>20</sup> have successfully used  $\text{Bu}_4\text{NBBu}_4$  as reference electrolytes in separating viscosity B-coefficients and in calculating the limiting ionic conductances in organic solvents assuming

$$\lambda_{\text{Bu}_4\text{N}^+}^{\circ} = \lambda_{\text{Bu}_4\text{B}^-}^{\circ} \quad \dots (10)$$

We have also used the above relationship in calculating the limiting ionic conductances for  $\text{R}_4\text{N}^+$  ions in ME. The reason behind the choice of  $\text{Bu}_4\text{NBBu}_4$  as reference electrolyte is due to the fact that the cation and anion in this case is symmetrically shaped and have almost equal vander Waals' volumes.  $\text{Bu}_4\text{NBF}_4$  has also been utilised by various authors<sup>21,22</sup> to calculate the limiting ion conductances assuming

$$\lambda^{\circ}, \text{Bu}_4\text{N}^+ = \lambda^{\circ}, \text{Ph}_4\text{B}^- \quad \dots(11)$$

though its validity is questionable in several solvents due to the unequal size of the cation and anion and also due to the unequal electronic environment of the + ve charge on N atom and - ve charge on B atom. In case of this reference electrolyte, instead of equal division, we have calculated ionic conductances using the following relationship<sup>23</sup> :

$$\frac{\lambda^{\circ}, \text{Bu}_4\text{N}^+}{\lambda^{\circ}, \text{Ph}_4\text{B}^-} = \frac{r_{\text{Ph}_4\text{B}^-}}{r_{\text{Bu}_4\text{N}^+}} = \frac{5.35}{5.00} = 1.07 \quad \dots(12)$$

The ionic radii of  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{B}^-$  have been taken from the work of Gill and Sekhri<sup>20, 24</sup>. The virtual organic solvent independence of the solvation radii of large  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{B}^-$  ions made Krungvalz<sup>23</sup> to suggest that these ions are unsolvated in organic solvents and their radii were calculated from the equation

$$r_{\pm} = \frac{|z|F^2}{6\pi N\eta_0 \lambda_{\pm}^{\circ}} \quad \dots(13)$$

Corresponding to their true dimensions in the solvent. Though nothing can be said definitely regarding the accuracy of the method (eqn. 12) but some indirect evidences regarding the reliability of the values may be provided. Thus the value of the ratio  $\lambda^{\circ}, \text{BPh}_4^- / \lambda^{\circ}, \text{Bu}_4\text{N}^+$  becomes 1.06 if we choose

$\tau_{\text{Bu}_4\text{N}^+} = 3.05 \text{ } \Lambda^\circ$  and  $\tau_{\text{Ph}_4\text{B}^-} = 4.08 \text{ } \Lambda^\circ$  as suggested by Krumholz<sup>23,25,26</sup> (eqn 13).

Fuoss et al<sup>27-30</sup> from an extensive measurements of  $\Lambda^\circ$ -values of  $\text{R}_4\text{NBPh}_4$  salts in various mixed solvents assumed that the limiting transference number of  $\text{Bu}_4\text{N}^+$  in  $\text{Bu}_4\text{NBPh}_4$  is 0.519 and is independent of solvent. This means a value of 1.079 for  $\lambda^\circ_{\text{Bu}_4\text{N}^+} / \lambda^\circ_{\text{BPh}_4^-}$ , which is close to our value.

D'Aprano and Fuoss<sup>30</sup> used  $\text{Bu}_4\text{NBPh}_4$  to calculate single ion conductances in mixed organic solvents applying the relationship,  $\lambda^\circ_{\text{Bu}_4\text{N}^+} = 0.213/\eta_0$  and  $\lambda^\circ_{\text{BPh}_4^-} = 0.201/\eta_0$  which means the ratio of  $\lambda^\circ_{\text{Bu}_4\text{N}^+} / \lambda^\circ_{\text{BPh}_4^-}$  is 1.06. Recently Gill et al<sup>31</sup> have proposed the following equation

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

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

The  $\lambda^\circ_{\pm}$  values of  $\text{R}_4\text{N}^+$  ions obtained by using the above two methods have been presented in table 4. 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 suggest 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 corresponds well with the experimental values calculated from the transference number measurements in many other organic solvents.<sup>16</sup>

The Walden product  $\lambda_{\pm}^{\circ} \eta_0$  and Stokes' radii ( $r_s$ ) of  $R_4N^+$  ions have been reported in table 4. Krungalz<sup>23</sup> suggested that the large tetraalkylammonium ions remains unsolvated (in the kinetic sense) in solution of organic solvents. Then it follows that for large  $R_4N^+$  ions,  $\lambda_{\pm}^{\circ} \eta_0$  will be constant and the values will be independent on the nature of all organic solvents. By taking  $\lambda_{\pm}^{\circ}$  values from transference number measurements, Krungalz<sup>16</sup> calculated the average  $\lambda_{\pm}^{\circ} \eta_0$  values of  $R_4N^+$  ions. Comparison of our results with those of Krungalz reveals that in case of  $Et_4N^+$ ,  $Pr_4N^+$  and  $Bu_4N^+$  ions the values are 3-7% higher and for  $Pent_4N^+$ ,  $Hex_4N^+$  and  $Hept_4N^+$  ions the values are 1-12% lower than the proposed values of Krungalz. Hence very weak solvation cannot be ruled out though nothing can be said definitely in the absence of precise transference number data.

Table 1 : Equivalent conductances of the Tetraalkylammonium Bromides,  $Bu_4NBr$ , and  $Bu_4NBH_4$  in 2-methoxy ethanol at 25°C

$10^3 c$ (mol dm <sup>-3</sup> )	$\wedge$ ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ )	$10^4 c$ (mol dm <sup>-3</sup> )	$\wedge$ ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ )
$Bt_4NBr$		$Bt_4NBr$	
15.012	23.500	15.995	29.625
13.990	25.001	9.490	31.750
8.498	28.200	8.002	32.350
7.002	30.850	6.998	32.625
5.992	30.902	6.001	33.000
4.001	33.100	4.999	33.560
2.995	34.230	4.010	34.100
2.000	35.500	2.998	34.750
		2.002	35.375

Contd..

Table 1 (Contd..)

	Su <sub>4</sub> NBr		Pent <sub>4</sub> NBr	
16.001	25.875	15.997	24.900	
13.995	26.710	13.959	25.210	
12.001	27.375	12.002	25.700	
9.995	27.800	9.995	26.500	
9.490	28.500	9.501	26.900	
8.001	29.000	7.999	27.410	
5.997	30.001	5.997	28.280	
5.002	30.625	5.001	28.860	
1.998	32.750	2.003	30.803	
	Hex <sub>4</sub> NBr		Hept <sub>4</sub> NBr	
16.001	24.190	16.002	22.980	
13.996	24.810	13.998	23.600	
12.000	25.250	11.989	24.090	
9.855	25.901	10.012	24.704	
9.501	26.150	9.495	25.050	
8.004	26.525	8.010	25.450	
5.996	27.220	5.897	26.110	
5.001	27.650	4.998	26.580	
1.999	29.170	2.001	28.200	

Table 1 (Contd..)

	$\text{Bu}_4\text{NEBu}_4$		$\text{Bu}_4\text{NEPh}_4$		
15.997		22.500		15.996	19.350
10.001		23.200		9.897	20.101
9.497		23.501		9.500	20.850
7.001		24.200		6.989	21.871
5.988		24.500		6.020	22.259
5.002		24.900		5.090	22.352
3.998		25.300		4.119	22.801
3.001		25.800		2.998	23.400
1.957		26.401		1.989	24.861

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Table 2 : Conductance parameters of tetraalkylammonium salts in 2-Methoxy Ethanol at 25 °C using Shedlovsky's Method.

Salt	$\Lambda^{\circ}$	$K_A$
Tetraethyl ammonium bromide	44.27	1124.14
Tetrapropyl ammonium bromide	38.38	148.67
Tetrabutyl ammonium bromide	36.31	281.49
Tetrapentyl ammonium bromide	34.17	253.21
Tetrahexyl ammonium bromide	31.28	148.77
Tetraheptyl ammonium bromide	30.99	184.50
Tetrabutyl ammonium tetrabutyl borate	28.41	90.27
Tetrabutyl ammonium tetraphenyl borate	27.02	253.52

Table 3 : Conductance parameters of Tetraalkyl ammonium bromide in ME at 25°C

salts	$\Lambda^{\circ}/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	$K_A/\Omega\text{m}^3\text{mol}^{-1}$	Walden product	$R/\Lambda^{\circ}$	$\delta\%$
$\text{Et}_4\text{NBr}$	43.74 ( $\pm 0.29$ )	1114.67 ( $\pm 98.50$ )	0.674	11.033	0.618
$\text{Pr}_4\text{NBr}$	38.80 ( $\pm 0.14$ )	216.94 ( $\pm 12.08$ )	0.598	11.553	0.341
$\text{Bu}_4\text{NBr}$	36.74 ( $\pm 0.27$ )	372.64 ( $\pm 24.02$ )	0.566	11.970	0.544
$\text{Pent}_4\text{NBr}$	34.54 ( $\pm 0.23$ )	353.79 ( $\pm 21.20$ )	0.532	12.320	0.496
$\text{Hex}_4\text{NBr}$	32.22 ( $\pm 0.17$ )	233.25 ( $\pm 15.28$ )	0.496	12.630	0.442
$\text{Hept}_4\text{NBr}$	31.34 ( $\pm 0.19$ )	276.12 ( $\pm 18.06$ )	0.483	12.910	0.483
$\text{Bu}_4\text{NBu}_4$	28.83 ( $\pm 0.13$ )	142.31 ( $\pm 11.04$ )	0.444	8.000	0.413
$\text{Bu}_4\text{NBPh}_4$	27.64 ( $\pm 0.28$ )	369.17 ( $\pm 21.20$ )	0.426	8.600	0.519

Table 4 : Limiting ionic conductances, Walden products and Stokes' radii values for  $R_4N^+$  ions in 2-Methoxy ethanol at 25°C

Ion	$\lambda_+^{\circ}(a)$	$\lambda_+^{\circ}(b)$	$\lambda_+^{\circ}\eta_0(a)$	$\lambda_+^{\circ}\eta_0(b)$	$r_g(a)$	$r_g(b)$
$Et_4N^+$	21.42	21.29	0.331	0.328	2.453	2.498
$Pr_4N^+$	16.48	15.35	0.251	0.252	3.228	3.253
$Bu_4N^+$	14.42	14.29	0.222	0.220	3.690	3.722
$Pent_4N^+$	12.32	12.09	0.188	0.186	4.352	4.399
$Hex_4N^+$	9.90	9.77	0.152	0.150	5.373	5.444
$Hept_4N^+$	9.02	8.89	0.139	0.137	5.899	5.985

<sup>a</sup>Calculations based on  $Bu_4NBu_4$

<sup>b</sup>Calculations based on  $Bu_4NBPh_4$

## R E F E R E N C E S

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