

# Electrical Conductances of Some Ammonium and Tetraalkylammonium Halides in Aqueous Binary Mixtures of 1,4-Dioxane at 298.15 K

Mahendra Nath Roy\*, Biswajit Sinha, Vikas Kumar Dakua and Anuradha Sinha

Department of Chemistry, University of North Bengal, Darjeeling-734013, India

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**Abstract.** Electrical conductances of some ammonium and tetraalkylammonium halides have been measured in different mass (20-80%) of 1,4-dioxane + water mixtures at 298.15 K. The limiting molar conductivity ( $\Lambda_0$ ), the association constant ( $K_A$ ), and association distance (R) in the solvent mixtures have been evaluated using Fuoss conductance equation (Fuoss, 1978). Based on the composition dependence of Walden product ( $\Lambda_0\eta_0$ ), the influence of the mixed solvent composition on the solvation of ions has been also discussed. The results have been considered in terms of ion-solvent and ion-ion interactions and the structural changes in the mixed solvent systems.

**Keywords:** 1,4-dioxane, ammonium and tetraalkylammonium halides, limiting molar conductivity, association constant, solvation, Walden product, ion-solvent and ion-ion interactions, Fuoss conductance equation

## Introduction

Studies on ionic solvation of ammonium and tetraalkylammonium salts in solvents of low permittivity are very few. Such studies have significant importance because of their applications in modern technology (Jasinski, 1967). 1,4-dioxane and its aqueous binary mixtures are very important solvents, widely used in various industries. These solvents figure prominently in the high-energy battery technology, having also found application in organic syntheses as manifested from the numerous physicochemical studies in these media (Roy *et al.*, 2001; Roy, 2000; Roy and Hazra, 1994; Janz, 1973). With a system of varying dielectric constant in the mixed solvents, there exists scope of variation of solvent-solvent interactions since composition of the solvents in a binary mixture is varied. Thus, studies in mixed solvents may provide information regarding both the specific and non-specific solvent effects on the ion-association phenomena.

In the present work, an attempt has been made to ascertain the complete nature of ion-solvent and solvent-solvent interactions of ammonium and tetraalkylammonium salts in aqueous binary mixtures of 1,4-dioxane at 298.15 K.

## Materials and Methods

1,4-dioxane (Merck, India) was kept several days over KOH, refluxed for 24 h and distilled over  $\text{LiAlH}_4$ , as described earlier (Roy *et al.*, 2001). The purified solvent had a density of  $1.03052 \text{ g.cm}^{-3}$  and viscosity co-efficient of 1.20011 cp at 298.15 K, which compared well with the values reported in literature (Covington and Dickinson, 1973).

Five salts, namely,  $\text{Me}_4\text{NCl}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$  and  $\text{Bu}_4\text{NI}$  (A.R. grade), were purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium. After filtration, the salts were dried in an oven for few hours. The ammonium halide salts,  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$ , were dried at about  $80\text{-}100^\circ\text{C}$  in a vacuum oven for 48 h before use (Perrin and Armarego, 1988). Stock solutions of each salt were prepared by mass, and the working solutions were obtained by mass dilution. The values of dielectric constant ( $\epsilon$ ) were taken from those reported in the literature (Covington and Dickinson, 1973), whereas the densities ( $\rho_0$ ) and viscosities ( $\eta_0$ ) of the solvent mixtures were measured by an Ostwald-Sprengel type pycnometer and suspended-level Ubbelohde type viscometer, respectively, as described in detail earlier (Roy *et al.*, 2001). The conductance measurements were carried out in a systronic 306 conductivity bridge (accuracy  $\pm 0.1\%$ ), using a dip-type immersion conductivity cell, CD-10 having cell constant  $1.0 \pm 10\%$ . Measurements were made in a waterbath maintained within  $298.15 \pm 0.01 \text{ K}$ .

## Results and Discussion

The solvent properties of the different aqueous binary mixtures of 1,4-dioxane are given in Table 1, where  $\epsilon$  is the dielectric constant,  $\rho_0$  the density ( $\text{g.cm}^{-3}$ ),  $\eta_0$  the viscosity (cp), and  $x_1$  the mole fraction of 1,4-dioxane. Molar conductances ( $\Lambda$ ) of the electrolyte solutions, as a function of molar concentration (c), are given in Table 2 for the different solvent mixtures at 298.15 K.

The analysis of conductance data in terms of limiting molar conductance ( $\Lambda_0$ ) and ion-association constant ( $K_A$ ) of the electrolytes have been carried out iteratively according to

\*Author for correspondence; E-mail: mnrchem@hotmail.com

Shedlovsky equation using least square treatment for the reasons described earlier (Gill and Chauhan, 1984). Shedlovsky method involves the linear extrapolation using the following equation (Bag *et al.*, 2000):

$$1/\Lambda S(z) = 1/\Lambda_0 + [K_A/\Lambda_0^2]c\Lambda f_{\pm}^2 S(z) \quad (1)$$

where:

$\Lambda$  = the equivalent conductance at the concentration  $c$

$c$  = molar concentration (mol.lit<sup>-1</sup>)

$\Lambda_0$  = the limiting equivalent conductance

$K_A$  = the observed association constant

The other symbols are given by:

$$\begin{aligned} S(z) &= [(z/2) + \sqrt{(1 + (z/2)^2)}]^2 \\ z &= [(\alpha\Lambda_0 + \beta)/\Lambda_0^{3/2}](c\Lambda)^{1/2} \\ \alpha &= 0.8204 \times 10^6/(\epsilon T)^{3/2}; \beta = 82.501/\eta(\epsilon T)^{1/2} \end{aligned} \quad (2)$$

where:

$\epsilon$  = the dielectric constant

$\eta$  = the viscosity of the medium

$T$  = absolute temperature

The degree of dissociation ( $\tau$ ) is related to  $S(z)$  by:

$$\tau = \Lambda S(z)/\Lambda_0$$

$f_{\pm}$  = the mean activity co-efficient of the free ions, which was calculated by the following equation:

$$-\log f_{\pm} = \Lambda(\tau c)^{1/2}/[1 + BR(\tau c)^{1/2}] \quad (3)$$

where:

$$\Lambda = 1.8246 \times 10^6/(\epsilon T)^{3/2}$$

$$B = 0.5029 \times 10^{10}/(\epsilon T)^{1/2}$$

$R$  = association distance

The initial  $\Lambda_0$  values for the iteration procedure were, thus, obtained from Shedlovsky extrapolation of the data (Roy *et al.*, 1993a).

The conductance data were analyzed using Fuoss conductance equation (Fuoss, 1978), which was programmed in a computer. So, with a given set of conductivity values ( $c_j, \Lambda_j; j = 1, \dots, n$ ), three adjustable parameters, i.e.,  $\Lambda_j, K_A$  and  $R$  were derived from the Fuoss equation. Here,  $R$  is the association distance, i.e., the maximum centre-to-centre distance between the ions in the solvent separated ion-pairs. There is no precise method for determining the  $R$ -value (Doe *et al.*, 1990), but in order to treat the data in our system,  $R$ -value was assumed to be:

$$R = a + d$$

where:

$a$  = the sum of the crystallographic radii of ions, which varies from 2 to 7Å

$d$  = the average distance corresponding to the side of a cell occupied by a solvent molecule

The distance  $d$ (Å) is given by (Fuoss, 1978):

$$d = 1.183(M/\rho_0)^{1/3} \quad (4)$$

where:

$M$  = the molecular weight

$\rho_0$  = the density of the solvent

For mixed solvents,  $M$  is replaced by the mole fraction average molecular weight ( $M_{AV}$ ), which is given by:

$$M_{AV} = M_1 M_2 / [W_1 M_2 + W_2 M_1] \quad (5)$$

where:

$W_1$  = the weight fraction of the first component of molecular weight,  $M_1$

$W_2$  = the weight fraction of the second component of molecular weight,  $M_2$

Though, this is an over-simplification, which ignores the possible selective solvation, it at least provides a self-consistent approach to obtain an acceptable value for the parameters when a broad range of  $R$ -values fit the data.

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = \rho[\Lambda_0(1+R_X) + E_L] \quad (6)$$

$$\rho = 1 - \alpha(1 - \gamma) \quad (7)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (8)$$

$$-\ln f = \beta \kappa / 2(1 + K_R) \quad (9)$$

$$\beta = e^2 / \epsilon k_B T \quad (10)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_S) \quad (11)$$

where:

$R_X$  = the relaxation field effect

$E_L$  = the electrophoretic counter current constant

$\kappa^{-1}$  = the radius of the ionic atmosphere

$\epsilon$  = the relative permittivity of the solvent

$e$  = the electric charge

$k_B$  = the Boltzmann constant

$\gamma$  = the fraction of solute present as unpaired ion

$c$  = the molarity of the solution

$f$  = the activity coefficient

$T$  = the temperature in absolute scale

$\beta$  = twice the Bjerrum distance

$K_R$  = formation and separation of the solvent-separated pairs by diffusion in and out of the sphere of dia R around cations

$K_S$  = a constant describing the short-range process by which contact pairs form and dissociate

We input into the programme the number of data,  $n$ ; followed by dielectric constant of the solvent mixture,  $\epsilon$ ; initial  $\Lambda_0$  values,  $T$ ,  $\rho$ ; molecular weight of the solvents along with  $c_j$ ,  $\Lambda_j$  values (where  $j = 1, 2, \dots, n$ ); and an instruction to cover pre-selected range of R-values.

In practice, calculations were performed by finding the values of  $\Lambda_0$  and  $\sigma$ , which minimized the standard deviation ( $\sigma$ ), for a sequence of R-values and then plotting  $\sigma$  against R:

$$\sigma^2 = \sum_{j=1}^n \frac{[\Lambda_j(\text{calc}) - \Lambda_j(\text{obs})]^2}{(n-2)} \quad (12)$$

The best-fit R corresponds to the minimum of the  $\sigma$  versus 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. Thus, the corresponding  $\Lambda_0$  and  $K_A$  values were noted. The  $\Lambda_0$ ,  $K_A$ , R, and Walden products ( $\Lambda_0\eta_0$ ) for the ammonium and tetraalkylammonium halides in different aqueous binary mixtures of 1,4-dioxane were thus reported in Table 3.

The association constants,  $K_A$  recorded in Table 3 indicate that all the electrolytes were highly associated in these solvent mixtures. This was quite expected due to the low dielectric constant of 1,4-dioxane (2.209). The most outstanding feature was that the electrolytes containing smaller cations showed considerable amount of association. Here, values of  $K_A$  decreased as

the size of the cation increased with the exception of  $\text{Bu}_4\text{N}^+$  ion, whereas  $\Lambda_0$  increased. The possible explanation is that it may be due to the larger size of the cations, which are less solvated than the smaller ones. Similar results have been reported earlier by some workers (Mukhopadhyay and Pal, 2002) during the conductance study of 1-ethyl-4-cyanopyridinium iodide in aqueous binary mixtures of 1,4-dioxane.

The  $K_A$  values of various tetraalkylammonium halides in these solvent mixtures follow the order:



However, in the case of ammonium halides, the value of  $\Lambda_0$  enhanced in the order:



This trend of variation indicates the relative actual sizes of these anions, having common ammonium ion as they existed in the solution. Thus, the sizes of these anions as they existed in these solutions followed the order:



This shows that  $\text{F}^-$  was the most solvated and  $\text{Br}^-$  was the least solvated in any mole fraction of 1,4-dioxane. Roy *et al.* (1993b) found similar trends for many of the alkali metal halides in tetrahydrofuran (THF) +  $\text{H}_2\text{O}$  mixtures. In the case of  $\text{Bu}_4\text{NI}$ , the value of  $K_A$  was greater than that of  $\text{Bu}_4\text{NBr}$ . This was expected owing to the larger size of  $\text{I}^-$  anion as compared to  $\text{Br}^-$  anion.

From Table 3 it may be observed that  $K_A$  values were noted to increase, whereas  $\Lambda_0$  values decreased in aqueous binary mixtures of 1,4-dioxane with the increase of the mole fraction of 1,4-dioxane. This indicates that association of ions increased with the addition of 1,4-dioxane to the mixture rendering decreased mobility of ions in the mixture. The significantly large values of  $K_A$  and exothermic ion-pair formation in the solvent

**Table 1.** Physical properties of 1,4-dioxane + water mixtures at 298.15 K;  $\rho_0$  = density;  $\eta_0$  = viscosity;  $\epsilon$  = dielectric constant;  $x_1$  = mole fraction of 1,4-dioxane

$x_1$	$\epsilon$	$\rho_0/(\text{g}\cdot\text{cm}^{-3})$		$\eta_0/(\text{cp})$	
		present work	literature <sup>a</sup>	present work	literature <sup>b</sup>
0	78.3	0.99707	0.9971	0.89041	0.8903
0.04863	63.5	1.01612	1.0143	1.29671	1.30
0.11996	44.4	1.03127	1.0284	1.69701	1.74
0.23472	27.5	1.04011	1.0360	1.98712	1.98
0.44991	12.1	1.04053	1.0350	1.78589	1.73
1	2.209	1.03052	1.0269	1.20011	1.196

a =  $\rho_0$ ; b =  $\eta_0$  (Covington and Dickinson, 1973)

**Table 2.** Molar conductances ( $\Lambda$ ) and corresponding molarities ( $c$ ) of some tetraalkylammonium halides and ammonium halides in different aqueous binary mixtures of 1,4-dioxane at 298.15 K ( $x_1$  = mole fraction of 1,4-dioxane)

$c \times 10^4$ (mol.lit <sup>-1</sup> )	$\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> )	$c \times 10^4$ (mol.lit <sup>-1</sup> )	$\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> )	$c \times 10^4$ (mol.lit <sup>-1</sup> )	$\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> )	$c \times 10^4$ (mol.lit <sup>-1</sup> )	$\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> )
<b><math>x_1 = 0.04863</math></b>							
<b>NH<sub>4</sub>F</b>		<b>NH<sub>4</sub>Cl</b>		<b>NH<sub>4</sub>Br</b>		<b>Me<sub>4</sub>NCl</b>	
42.7	49.26	48.1	71.93	48.5	81.44	46.2	55.63
55.9	48.65	61.9	71.24	62.4	80.77	56.5	54.69
68.6	48.00	74.8	70.59	75.4	80.24	65.2	54.45
80.8	47.82	86.9	70.20	87.6	79.79	72.6	53.86
92.6	47.55	98.2	69.55	99.0	79.19	79.0	53.67
104.0	47.31	108.8	69.39	109.7	78.85	84.6	53.31
125.7	46.61	118.8	69.02	119.8	78.71	89.6	53.01
136.0	46.40	128.2	68.49	129.3	78.50	94.0	52.66
<b>Et<sub>4</sub>NBr</b>		<b>Pr<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NI</b>	
44.8	66.96	45.6	78.24	51.7	87.62	47.1	60.65
57.6	65.97	54.2	77.47	67.8	86.92	61.6	59.64
69.6	65.09	69.1	76.52	75.2	86.51	66.1	59.33
80.8	64.36	75.6	74.04	82.1	86.25	74.7	58.78
91.3	63.86	81.6	75.76	88.6	86.07	78.8	58.53
101.2	63.34	92.2	75.28	94.8	85.91	82.8	58.48
110.5	62.81	96.9	74.99	97.8	85.82	97.6	57.62
119.3	62.45	101.3	74.91	100.7	85.67	104.4	57.24
<b><math>x_1 = 0.11996</math></b>							
<b>NH<sub>4</sub>F</b>		<b>NH<sub>4</sub>Cl</b>		<b>NH<sub>4</sub>Br</b>		<b>Me<sub>4</sub>NCl</b>	
25.6	45.31	22.5	59.11	20.2	72.65	17.8	47.49
34.8	43.97	25.8	58.02	26.0	71.08	21.2	46.45
38.4	43.75	33.8	57.24	29.8	70.89	26.6	45.63
43.7	43.25	38.5	57.15	39.1	69.84	37.0	44.35
55.5	42.34	48.9	55.51	48.1	68.67	43.9	43.34
71.4	41.18	56.1	55.18	73.6	65.31	48.7	42.69
79.0	40.76	69.7	53.68	89.3	63.92	57.8	41.79
93.4	39.83	82.4	52.80	104.2	62.66	66.4	41.04
<b>Et<sub>4</sub>NBr</b>		<b>Pr<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NI</b>	
17.9	59.74	24.5	72.68	19.4	82.62	16.8	53.88
21.1	59.58	29.6	71.86	23.2	82.26	31.8	52.06
24.2	58.97	34.4	71.24	26.7	81.66	36.5	51.22
30.1	57.76	36.7	70.76	28.4	81.37	45.3	50.24
32.9	57.34	43.1	70.10	35.8	80.75	49.5	49.87
35.6	56.91	50.8	69.63	37.1	80.73	53.5	49.36
43.1	55.77	54.3	69.40	38.4	80.49	61.2	48.75
47.8	55.29	57.6	69.06	40.8	80.38	68.4	48.18
<b><math>x_1 = 0.23472</math></b>							
<b>NH<sub>4</sub>F</b>		<b>NH<sub>4</sub>Cl</b>		<b>NH<sub>4</sub>Br</b>		<b>Me<sub>4</sub>NCl</b>	
9.7	23.09	3.7	35.07	5.4	40.37	3.7	37.45
11.4	22.81	10.9	33.39	7.2	39.58	6.1	36.52
13.1	22.44	14.5	32.76	9.0	39.33	7.8	35.82
16.3	21.90	18.1	31.99	12.6	37.62	9.4	35.55
19.3	21.45	23.3	31.33	16.2	36.98	13.5	34.74
24.7	20.69	28.4	30.99	23.2	35.78	16.4	34.34
27.1	20.48	31.8	30.50	28.3	35.69	17.8	34.18
34.6	19.94	35.2	29.83	33.4	34.73	19.2	33.94
<b>Et<sub>4</sub>NBr</b>		<b>Pr<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NI</b>	
3.7	48.56	5.2	51.69	4.1	56.76	4.3	43.88
6.1	47.62	6.7	51.49	5.9	56.32	6.2	43.19
7.1	46.97	10.3	51.08	6.4	56.22	7.1	42.94
8.8	46.14	11.2	51.00	7.4	56.02	10.5	41.76
10.3	45.87	13.9	50.81	8.4	55.93	11.3	41.48
11.8	45.59	15.2	50.68	10.3	55.45	14.1	41.13
16.1	44.50	18.8	50.56	11.1	55.38	15.4	40.88
21.3	43.74	22.1	50.39	11.9	55.24	16.6	40.75
<b><math>x_1 = 0.44991</math></b>							
<b>NH<sub>4</sub>F</b>		<b>NH<sub>4</sub>Cl</b>		<b>NH<sub>4</sub>Br</b>		<b>Me<sub>4</sub>NCl</b>	
1.9	2.12	0.3	5.88	0.5	5.98	0.6	23.12
3.2	1.85	0.7	5.51	0.7	5.80	0.9	22.30
3.7	1.79	1.4	5.08	1.2	5.51	1.0	21.40
4.9	1.65	1.7	4.78	1.7	5.32	1.2	20.90
6.8	1.50	2.1	4.55	2.2	5.07	1.9	18.80
7.9	1.46	2.9	4.51	2.5	4.94	2.4	17.33
9.5	1.41	3.3	4.27	3.2	4.69	2.7	17.11
9.9	1.39	3.9	4.36	3.5	4.54	2.8	16.82
<b>Et<sub>4</sub>NBr</b>		<b>Pr<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NI</b>	
0.4	33.40	0.7	39.71	1.2	41.50	0.7	31.60
0.6	31.50	1.5	34.93	1.7	40.32	0.9	31.22
1.2	27.83	1.7	34.53	2.0	39.90	1.2	29.50
1.5	26.80	2.0	33.85	2.5	39.12	1.4	28.50
1.8	25.44	2.2	33.68	2.8	38.86	1.6	27.63
2.3	24.78	2.5	32.88	3.3	38.24	1.9	26.32
2.7	23.80	3.2	32.13	3.6	37.89	2.0	26.25
3.1	21.60	3.5	31.57	4.1	37.37	2.2	25.68

**Table 3.** Values of  $\Lambda_0$ ,  $K_A$ ,  $\Lambda_0\eta_0$ ,  $R$  and  $\sigma$  for some ammonium and tetraalkylammonium halides in different aqueous binary mixtures of 1, 4-dioxane at 298.15 K

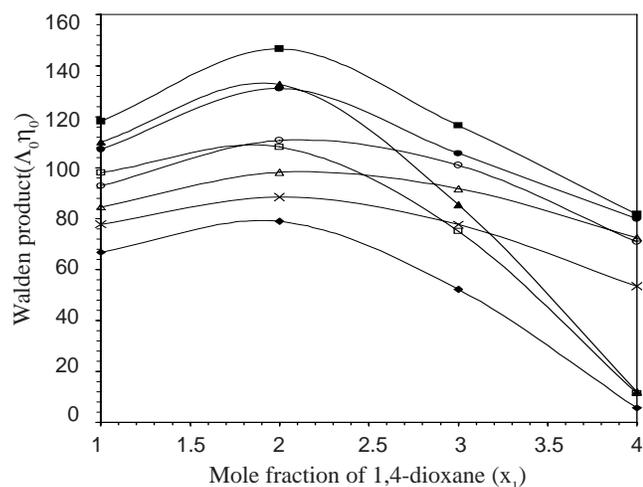
$x_1$	$\Lambda_0$ ( $S.cm^2.mol^{-1}$ )	$K_A$ ( $dm^3.mol^{-1}$ )	$R$ ( $\text{\AA}$ )	$\Lambda_0\eta_0$	$\sigma$
<b>NH<sub>4</sub>F</b>					
0.04863	51.53 ± 0.12	8.42	6.18	66.82	0.12
0.11996	49.36 ± 0.11	36.45	6.41	78.89	0.11
0.23472	26.27 ± 0.08	149.62	6.71	52.20	0.08
0.44991	3.14 ± 0.02	4535.07	7.21	5.61	0.02
<b>NH<sub>4</sub>Cl</b>					
0.04863	75.58 ± 0.10	8.03	6.66	98.01	0.10
0.11996	63.67 ± 0.26	32.92	6.88	108.05	0.26
0.23472	37.76 ± 0.30	107.84	7.19	75.03	0.30
0.44991	6.36 ± 0.11	2500.04	7.68	11.36	0.11
<b>NH<sub>4</sub>Br</b>					
0.04863	84.87 ± 0.11	5.85	6.69	110.05	0.11
0.11996	78.14 ± 0.28	33.76	7.02	132.60	0.28
0.23472	42.96 ± 0.36	100.72	7.33	85.37	0.36
0.44991	6.72 ± 0.06	2247.41	7.82	12.00	0.06
<b>Me<sub>4</sub>NCl</b>					
0.04863	59.98 ± 0.12	16.78	8.65	77.78	0.12
0.11996	52.12 ± 0.15	59.64	8.67	88.45	0.15
0.23472	39.07 ± 0.16	90.51	9.17	77.64	0.16
0.44991	29.94 ± 0.28	6215.89	9.67	53.47	0.28
<b>Et<sub>4</sub>NBr</b>					
0.04863	71.59 ± 0.07	14.79	9.32	92.83	0.07
0.11996	65.19 ± 0.16	47.24	9.53	110.63	0.16
0.23472	50.77 ± 0.24	94.19	9.85	100.89	0.24
0.44991	39.69 ± 0.49	5682.46	10.34	70.88	0.49
<b>Pr<sub>4</sub>NBr</b>					
0.04863	82.65 ± 0.11	11.19	9.84	107.17	0.11
0.11996	77.21 ± 0.19	22.65	10.06	131.03	0.19
0.23472	53.10 ± 0.01	73.70	10.37	105.52	0.01
0.44991	44.74 ± 0.59	2253.78	10.86	79.90	0.59
<b>Bu<sub>4</sub>NBr</b>					
0.04863	91.13 ± 0.06	5.56	10.26	118.17	0.06
0.11996	86.37 ± 0.11	16.39	10.48	146.57	0.11
0.23472	58.63 ± 0.01	30.94	10.79	116.50	0.01
0.44991	45.68 ± 0.08	659.09	11.28	81.58	0.08
<b>Bu<sub>4</sub>NBI</b>					
0.04863	65.18 ± 0.01	15.63	10.47	84.52	0.01
0.11996	57.80 ± 0.11	39.08	10.69	98.09	0.11
0.23472	46.17 ± 0.16	91.24	11.01	91.75	0.16
0.44991	40.57 ± 0.31	5107.55	11.49	72.45	0.31

$x_1$  = mole fraction of 1,4-dioxane;  $\Lambda_0$  = limiting molar conductance;  $K_A$  = observed association constant;  $\Lambda_0\eta_0$  = Walden product;  $R$  = association distance between ions;  $\sigma$  = standard deviation

mixtures indicated the presence of specific short-range interaction within the ion-pair.

The variation of Walden product,  $\Lambda_0\eta_0$  with  $x_1$ , the mole fraction of 1,4-dioxane for the electrolytes studied at 298.15 K, are shown in Fig. 1. The values of Walden product pass through a maximum at about  $x_1 = 0.11996$  mole fraction of 1,4-dioxane, whereas the maximum viscosity of the aqueous binary mixtures at 298.15 K was observed at about  $x_1 = 0.23472$  mole fraction of 1,4-dioxane. It is known that the variation of Walden product indicates the change of solvation (Doe *et al.*, 1990). The increase of Walden products indicates weak solvation of ions, which attains a maximum value at a particular solvent composition ( $x_1 = 0.11996$ ). Such results have been interpreted in terms of microheterogeneity in the mixtures (Marcus and Migron, 1991).

On the water-rich side, there exists a region where the water structure remains more or less intact as the 1,4-dioxane molecules are added into the cavities in this structure. The cluster of water molecule has lower ability to donate a hydrogen atom to the solvation of ions. This may cause hydrophobic dehydration of cations (Mukhopadhyay and Pal, 2002), or may reduce the ability of hydrophobic ions to promote the structure in the water-rich region resulting in excess mobility, which in turn results an increase in Walden products to attain a maximum. As the percentage of 1,4-dioxane in the mixture increases, the self-associated structure gradually breaks at an increased mole fraction of 1,4-dioxane and thus preferential solvation occurs due to specific solute-solvent interaction leading to a decrease of Walden product (Taniewska-Osinska *et al.*, 1989). However, this decrease in the Walden product in



**Fig. 1.** Plots of mole fractions of 1,4-dioxane ( $x_1$ ) versus Walden products ( $\Lambda_0\eta_0$ ) for  $\text{NH}_4\text{F}$  (◆),  $\text{NH}_4\text{Cl}$  (□),  $\text{NH}_4\text{Br}$  (▲),  $\text{Me}_4\text{NCl}$  (x),  $\text{Et}_4\text{NBr}$  (○),  $\text{Pr}_4\text{NBr}$  (●),  $\text{Bu}_4\text{NBr}$  (■), and  $\text{Bu}_4\text{NI}$  (△) at 298.15 K.

large part may be due to the Zwanzig solvent relaxation effect also (Das and Hazra, 1995).

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