

Conductance Studies of Alkali Metal Chlorides and Bromides in Aqueous Binary Mixtures of Tetrahydrofuran at 25°

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Precise conductance measurements are reported for alkali metal chlorides and bromides, MX ($M^+ = Li, Na, K, Rb$ and Cs ; $X^- = Cl$ and Br) in tetrahydrofuran (THF) + water mixtures at 25°. The limiting molar conductivity (Λ°), the association constant (K_A) and association distance (R) in the solvent mixtures have been evaluated using the Fuoss conductance equation (1978). The analysis of data indicates that the electrolytes are almost unassociated at 0.059 mole fraction of THF, whereas at 0.143, 0.273 and 0.500 mole fraction of THF, the association was very strong. The values for alkali metal cations (anion being the same) are found to be in the order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The results have been explained in terms of ion-solvent interactions and structural changes in the mixed solvents.

Studies on ionic solvation of alkali metal ions in solvents of low permittivity are very few. Such studies have been assumed importance because of their applications in modern technology¹. Tetrahydrofuran (THF), a solvent of low permittivity ($\epsilon = 7.58$), has also been found its probability of applications in high energy batteries and organic syntheses as manifested from the physicochemical studies in this medium^{2,3}. Renard and Justice⁴ studied the conductances of CsCl in THF+water mixtures to reveal the nature of ionic association and mobility of ions in this mixed solvent system. In the present communication, an attempt has been made to ascertain the complete nature of solute-solvent interactions of alkali metal salts (chlorides as well as bromides) in THF+H₂O mixtures through the measurements of their conductances.

Results and Discussion

The solvent properties of THF+H₂O mixtures are given in Table I, where ϵ is the dielectric constant, d , the density ($g\ cm^{-3}$), η , the viscosity (CP), L_0 , the specific conductance ($\Omega^{-1}\ cm^{-1}$), W the weight percent of THF in the aqueous mixtures and X_1 , the corresponding mole fraction. Dielectric constants of solvent mixtures were obtained by extrapolation of ϵ versus $W\%$ plots, the original values were taken from the work of Renard and Justice⁴. The equivalent conductance at infinite dilution (Λ°) and the association constant (K_A) were calculated using the Fuoss conductance equation⁵,

$$\Lambda = P[\Lambda^\circ(1 + RX) + EL] \quad (1)$$

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

$$\gamma = 1 - \frac{K_A C^2}{f^2} \quad (3)$$

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

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

where the terms have their usual significance. The parameters K_A and R were obtained from the above equations by finding the values of Λ° and α which minimize

$$\sigma^2 = \sum_i [\Lambda_i(\text{cal}) - \Lambda_i(\text{obs})]^2 / (n-2) \quad (6)$$

for a sequence of R values. Initial Λ° value for the iteration procedure was taken from Shedlovsky extrapolations of the data.

A scan using unit increment of R values from 4 to 20, however, gave no significant minima in the σ^2 - R curve for CsCl, NaBr, RbBr and CsBr at 0.273 mole fraction of THF, and also for the electrolytes (except LiCl) at 0.500 mole fraction of THF. The computations in these cases were carried out from arbitrarily presetting⁶ of R values at $R = a + d$. Here a is the sum of the crystallographic radii of the ions and d the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d(\text{\AA}) = (M/N\rho)^{1/3} = 1.183 (M/\rho)^{1/3} \quad (7)$$

TABLE I—PHYSICAL PROPERTIES OF THF-WATER MIXTURES AT 25°

$W\%$	X_1	d $g\ cm^{-3}$	$10^3 \eta$ cp	$10^5 L_0$ $\Omega^{-1}\ cm^{-1}$
0	0	78.54	0.99707	0.8903
20	0.059	57.25	0.98668	1.4900
40	0.143	44.50	0.96840	1.7521
60	0.273	32.00	0.94600	1.4904
80	0.500	19.50	0.91592	0.9237
100	1.000	7.58	0.88072	0.4630

where M is the molecular weight of solvent and ρ is its density. For mixed solvents, M is replaced by the mole fraction average molecular weight (M_{av}) which is given by

$$M_{av} = M_1 M_2 / (W_1 M_2 + W_2 M_1) \quad (8)$$

where W_1 is the weight fraction of the first component of molecular weight M_1 . Though, this is an over simplification which ignores possible selective solvation, it at least provides a self-consistent way to obtain an acceptable value for the parameter when a broad range of R -values fit the data. The values of A° , K_A and R obtained by this procedure are recorded in Table 2.

From Table 1, we see that viscosity (η°) of the solvent mixture (THF + H₂O) increases rapidly to a maximum at about 0.143 mole fraction or 40 wt% of THF and thereafter decreases. Such characteristic in the viscosity vs composition curve is a manifestation of strong specific interaction⁶ between unlike molecules predominated by hydrogen bonding interaction.

Table 2 shows that A° values for alkali metal halides increase as the size of the cation increases in any mole fraction of mixed solvent. However, for any particular electrolyte, A° continuously decreases with the addition of THF and Walden products are found to be different; viscosity of solvent-mixture does not coincide with the observed trend in A° value.

From Table 2, we also see that A° values of alkali metal salts of common anion follow the sequence: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Further, the A° for the alkali metal bromides are greater than those for the corresponding alkali metal chlorides. For CsCl, the A° value at 0.500 mole fraction of THF is in close proximity with the value reported by Renard and Justice⁴. The trend of variation of A° values also indicates the relative actual sizes of these ions as they exist in solution. Thus, the sizes of these cations as they exist in solution, follow the order: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, and for anions, $Cl^- > Br^-$. This shows that Li^+ is the most solvated and Cs^+ is the least one in any mole fraction of THF.

It may be observed from Table 2 that the association constant (K_A) is very low for all the electrolytes at 0.059 mole fraction of THF. This indicates that these salts almost remain unassociated in this composition of the solvent mixture having high dielectric constant. However, at higher mole fraction of THF ($\epsilon > 57.25$)-association occurs in the solvent mixtures (for NaCl, KCl and CsCl ion association takes place above 0.143 mole fraction of THF) and that the K_A values increase with the increase of cationic as well as anionic sizes in all cases (except NaBr at 0.500 mole fraction of THF). Thus we see that CsBr in spite of its greater size, is associated maximum than the other bromides at higher percentages of mixed solvents. D'Aprano and Fuoss⁵ found similar trends for many of the alkali metal halides in dioxane-water mixtures.

The values of Walden products ($A^\circ\eta^\circ$) for the studied electrolytes pass through a maximum at about 0.059 mole fraction of THF and then decrease continuously. A representative plot for the alkali

TABLE 2 - DERIVED CONDUCTANCE PARAMETERS

X_1	A°	K_A	R	$A^\circ\eta^\circ$	η°
Lithium chloride					
0 ^a	115.12 ± 0.01	0.79	5.49	1.023	0.03
0.059	60.88 ± 0.05	1.90 ± 0.60	11.41	0.907	0.06
0.143	48.57 ± 0.08	13.92 ± 0.03	12.83	0.841	0.06
0.273	41.28 ± 0.04	20.60 ± 0.40	16.00	0.617	0.07
0.500	30.40 ± 0.17	102.74 ± 0.50	13.26	0.281	0.19
Sodium chloride					
0 ^a	126.53 ± 0.01	0.81	5.56	1.126	0.02
0.059	80.44 ± 0.023	2.96 ± 0.03	10.66	1.198	0.03
0.143	59.76 ± 0.04	6.32 ± 0.09	11.26	1.035	0.05
0.273	46.01 ± 0.05	25.40 ± 0.61	15.27	0.686	0.05
0.500	39.04 ± 0.49	206.53 ± 0.01	7.14	0.361	0.36
Potassium chloride					
0 ^a	149.90 ± 0.01	0.56	4.65	1.334	0.02
0.059	96.10 ± 0.04	2.92 ± 0.05	5.99	1.432	0.83
0.143	72.18 ± 0.03	9.51 ± 0.06	13.00	1.250	0.03
0.273	53.01 ± 0.05	24.11 ± 0.30	16.50	0.790	0.05
0.500	44.92 ± 0.30	228.55 ± 74.80	7.43	0.415	0.90
Rubidium chloride					
0 ^a	153.64 ± 0.01	0.26	3.35	1.367	0.02
0.059	98.19 ± 0.05	4.67 ± 0.04	11.00	1.463	0.07
0.143	74.61 ± 0.07	12.35 ± 0.16	13.00	1.212	0.07
0.273	55.86 ± 0.04	35.64 ± 0.34	15.44	0.833	0.04
0.500	46.84 ± 0.18	458.73 ± 75.29	7.82	0.432	0.94
Cesium chloride					
0 ^a	153.04 ± 0.02	0.62	3.62	1.362	0.02
0.059	100.42 ± 0.04	4.52 ± 0.03	10.97	1.496	0.05
0.143	75.33 ± 0.05	6.41 ± 0.07	11.00	1.305	0.06
0.273	55.51 ± 0.21	31.19 ± 1.70	7.32	0.843	0.25
0.500	50.89 ± 0.46	649.80 ± 36.29	7.84	0.470	0.29
Lithium bromide					
0 ^a	116.88	—	—	1.040	—
0.059	70.23 ± 0.22	2.89 ± 0.25	6.02	1.051	0.25
0.143	55.35 ± 0.06	14.86 ± 0.19	16.60	0.958	0.06
0.273	48.70 ± 0.04	20.35 ± 0.30	17.70	0.726	0.05
0.500	45.93 ± 1.20	265.79 ± 32.73	7.06	0.424	0.75
Sodium bromide					
0 ^a	128.42	—	—	1.143	—
0.059	88.82 ± 0.10	11.70 ± 0.11	13.50	1.323	0.10
0.143	64.57 ± 0.11	28.32 ± 0.41	19.00	1.118	0.12
0.273	53.33 ± 0.81	120.08 ± 12.00	6.82	0.795	0.65
0.500	50.94 ± 0.69	224.28 ± 27.60	7.30	0.470	0.73
Potassium bromide					
0 ^a	157.77	—	—	1.405	—
0.059	103.33 ± 0.06	2.72 ± 0.04	10.80	1.340	0.07
0.143	75.92 ± 0.08	17.10 ± 0.20	14.20	1.315	0.09
0.273	61.39 ± 0.11	45.87 ± 0.84	19.00	0.915	0.13
0.500	52.26 ± 0.66	440.92 ± 42.10	7.62	0.483	0.62
Rubidium bromide					
0 ^a	156.37	—	—	1.392	—
0.059	105.98 ± 0.06	8.79 ± 0.05	11.60	1.579	0.06
0.143	78.03 ± 0.11	22.59 ± 0.32	13.00	1.352	0.11
0.273	66.56 ± 0.65	90.09 ± 6.36	7.29	0.992	0.64
0.500	54.95 ± 1.03	593.02 ± 71.48	7.77	0.507	0.90
Cesium bromide					
0 ^a	155.51	—	—	1.384	—
0.059	109.41 ± 0.04	6.67 ± 0.03	9.90	1.630	0.04
0.143	79.83 ± 0.08	23.13 ± 0.23	17.30	1.383	0.09
0.273	67.75 ± 0.05	8.58 ± 4.80	7.48	1.010	0.50
0.500	58.54 ± 1.71	1001.53 ± 140.56	7.96	0.541	0.98

^aRef. 9. Dr. L. KAY and D. F. EVANS, *J. Phys. Chem.*, 1966, 70, 2325.

metal bromides has been given in Fig. 1. Though the variation of the Walden product with solvent composition is difficult to interpret quantitatively, still its variation with solvent composition can be explained by preferential solvation⁹ of alkali metal ions by water and THF molecules respectively. At low mole-fraction of THF, these ions are preferentially solvated by water than THF and the viscosity of the solvent in the vicinity of these ions is lower than that of the bulk solvent (Table 1). Since the bulk viscosity value is used in the calcula-

tion of Walden product, the calculated values of $\Lambda^0 \eta_0$ are high upto the point corresponding to viscosity maximum of the solvent mixtures and then the values decrease gradually causing a maximum in the Walden product. The decrease in the Walden products after 0.143 mole-fraction of THF indicates the preferential solvation of alkali metal ions (having the same anion) by THF in THF+water mixtures. However, this decrease in large part may be due to the Zwanzig¹⁰ solvent relaxation effect also.

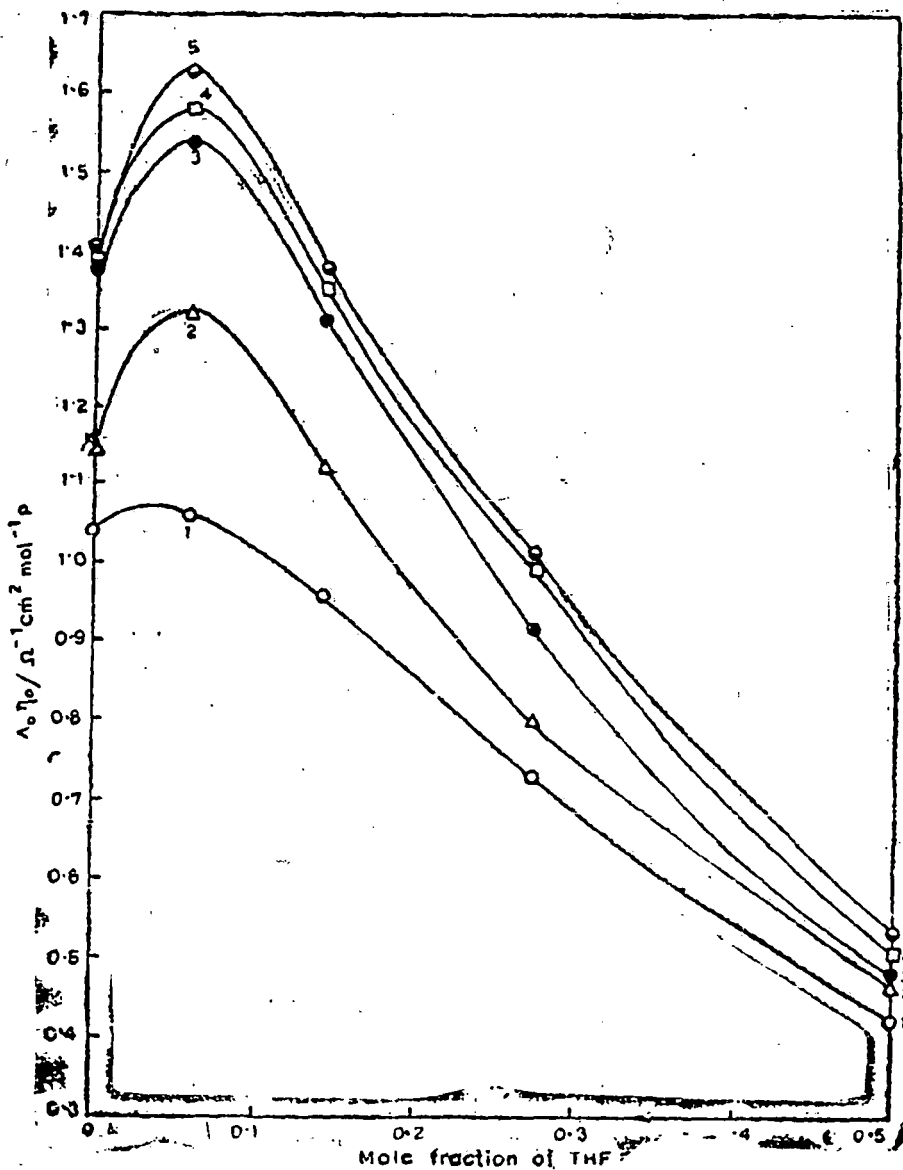


Fig. 1. Variation of Walden products ($\Lambda^0 \eta_0$) with compositions of solvent mixtures: (1) LiBr, (2) NaBr, (3) KBr, (4) RbBr and (5) CsBr.

Experimental

Tetrahydrofuran (Merck) was kept several days over KOH, then refluxed for 24 h and distilled over LiAlH_4 . Its boiling point, density and viscosity were compared well with the literature values¹¹. The specific conductance of THF was $\text{ca. } 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 25° .

Alkali metal salts (Fluka, purum or puriss grade) were purified as described earlier¹². A stock solution for each salt ($\sim 0.1 M$) in the appropriate solvent mixture was prepared (by weight) and the working solutions were obtained by weight dilution. The molar concentration of the solution was calculated from molality and density values. The mixed solvents of THF were prepared by mixing the requisite amounts of THF and water (by weights).

Density and viscosity of solvent mixtures were measured in an Ostwald-Sprengel type pycnometer and suspended-level Ubbelohde viscometer at $25 \pm 0.01^\circ$ with a precision of $\pm 3 \times 10^5 \text{ g cm}^{-3}$ and 0.05% respectively. A Pye-Unicam PW 9509 conductivity meter was used for measuring the conductance at the frequency of 2000 Hz with a dip-type cell constant 0.861 cm^{-1} and having an accuracy of $\pm 0.1\%$. The cell was calibrated with aqueous KCl solutions in the usual way. The measurements were carried out in an oil-bath maintained at $25 \pm 0.005^\circ$. The details of experimental procedure have

been described earlier¹³. Several independent solutions were prepared and runs were performed to ensure the reproducibilities of the results. All data were corrected at 25° with the specific conductance of the solvent. The corrected values were analysed by means of the Fuoss conductance equation¹⁴.

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Electrical Conductances for Tetraalkylammonium Bromides, LiBF₄ and LiAsF₆ in Tetrahydrofuran at 25°

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Electrical conductance data have been reported for tetraalkylammonium bromides, R₄NBr (R = butyl to heptyl), lithium tetrafluoroborate (LiBF₄) and lithium hexafluoroarsenate (LiAsF₆) in tetrahydrofuran (THF) at 25°. Analysis of data by the Fuoss-Kraus theory of conductance reveals the presence of both ion-pairs and triple ions. The ion-pair (K_p) and triple-ion (K_T) formation constants of these salts in tetrahydrofuran (THF) have been compared with the values obtained in 1,2-dimethoxyethane (1,2-DME). The comparison shows that the lower homologues of the studied R₄NBr salts are more associated in THF than in 1,2-DME whereas the K_T values in majority cases are much higher in 1,2-DME than in THF with the exception of LiAsF₆. The results have been explained with the help of configurational entropy and molecular model theory.

Progress in battery technology using the lithium electrolytes in etheral solutions¹ has occurred largely in the last decade. Recently, there has been a renewed interest², after the classical work of Fuoss and Kraus³ in the thirties, in the study of association and dimerisation of electrolytes in media of low permittivity. This has been particularly so important because knowledge of the state of association of the electrolytes and the type and the structure of the complex species in solution is essential for the optical choice of solvents and electrolytes. Previously, Sellers *et al*⁴ interpreted the conductance behaviour of weak acids and bases in non-aqueous solvents in terms of complex equilibria. Hejo *et al*⁵ investigated the formation of triple ions for substituted ammonium halides in acetonitrile from conductivity and voltammetric data. The molecular relaxation dynamics and structure of lithium salts have been studied by Petrucci *et al*.^{2,6-10} from ultrasonic absorption and electrical conductivity measurements in media of low permittivity. The conductivity of tetraalkylammonium salts in polyaromatic solvents has also been studied recently by Abbot and Schiffman¹¹ who showed the formation of triple ions by fitting the Fuoss-Kraus equation to the conductance data.

Recently, we have reported the formation of triple ions of tetraalkylammonium bromides in 1,2-dimethoxyethane (ε = 7.01) from conductivity measurements¹². The study has been extended to tetrahydrofuran, a solvent having similar physical characteristics like 1,2-dimethoxyethane and the result is discussed herein.

Results and Discussion

The equivalent conductance (Λ) vs the concentration (c) data of the electrolytes in THF at 25° are recorded in Table 1. Fig. 1 presents the plots of (Λ) vs c for tetra-butyl-, tetra-pentyl-, tetra-hexyl-, tetra-heptyl-bromides (lower homologues are insoluble in THF), LiBF₄ and LiAsF₆ at 25°. A minimum is clearly visible in every case.

The conductance data have been analysed by the Fuoss-Kraus triple-ion theory¹³ in the form as given below,

$$\Lambda g(c)^{1/2} = \frac{\Lambda_0}{K_p^{1/2}} + \frac{\Lambda_0^T K_T}{K_p^{1/2}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (1)$$

$$g(c) = \frac{\exp\left(-\frac{\beta}{\Lambda_0^{1/2}}(c\Lambda)^{1/2}\right)}{\left(1 - \frac{S}{\Lambda_0^{1/2}}(c\Lambda)^{1/2}\right) \left(1 - \frac{\Lambda}{\Lambda_0} g\right)^{1/2}} \quad (2)$$

(c)
2
Λ₀
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TABLE 1 - ELECTRICAL CONDUCTIVITY OF ELECTROLYTES IN TETRAHYDROFURAN AT 25°

10 ⁻⁴ c mol dm ⁻³	Λ S cm ² mol ⁻¹	10 ⁻⁴ c mol dm ⁻³	Λ S cm ² mol ⁻¹	10 ⁻⁴ c mol dm ⁻³	Λ S cm ² mol ⁻¹
	But ₄ NBr		Pent ₄ NBr		Hex ₄ NBr
2.969	4.23	4.879	3.01	6.032	2.53
4.690	3.12	6.524	2.62	8.565	2.07
5.850	2.70	8.059	2.32	9.983	1.89
7.239	2.35	9.006	2.21	10.690	1.82
9.050	2.12	10.958	1.95	12.698	1.66
10.550	1.94	22.500	1.44	15.983	1.49
14.896	1.71	35.765	1.26	21.852	1.31
21.550	1.53	43.892	1.23	30.918	1.18
35.242	1.44	55.898	1.21	39.894	1.12
58.126	1.40	65.498	1.20	46.596	1.08
74.126	1.40	84.958	1.20	56.894	1.06
91.215	1.40	93.958	1.20	63.698	1.05
103.514	1.40	100.151	1.21	71.455	1.05
149.173	1.42	109.895	1.22	84.134	1.05
209.185	1.46	129.454	1.23	109.842	1.08
298.473	1.50	145.699	1.25	126.492	1.09
365.298	1.55	167.894	1.26	155.131	1.12
420.589	1.56	175.623	1.27	169.482	1.14
623.970	1.65	189.857	1.28	183.586	1.15
		221.539	1.32	208.934	1.19
		282.492	1.39	230.416	1.21
		314.596	1.40	241.253	1.22
		612.558	1.64	292.956	1.27
				351.611	1.33
	Hept ₄ NBr		LiBF ₄		LiAsF ₆
8.494	2.26	9.480	1.42	7.698	16.51
9.010	2.19	15.987	1.06	9.279	15.55
9.895	2.04	29.829	0.79	15.895	12.92
10.957	1.95	37.985	0.71	43.897	9.48
23.985	1.73	48.580	0.64	74.875	8.27
15.315	1.65	53.500	0.62	90.766	8.00
17.987	1.55	74.598	0.55	109.764	7.68
20.285	1.46	90.386	0.51	132.983	7.45
25.316	1.27	115.765	0.47	148.925	7.35
29.849	1.23	223.943	0.41	169.021	7.39
36.983	1.17	272.149	0.40	180.943	7.27
43.895	1.13	307.826	0.40	213.792	7.27
56.986	1.08	382.967	0.40	224.976	7.26
80.689	1.07	439.467	0.40	309.267	7.53
94.986	1.07	576.928	0.42	378.769	7.79
120.289	1.08	615.938	0.43	484.693	8.02
139.468	1.09	871.613	0.47		
156.489	1.10	938.538	0.48		
189.542	1.14	1098.562	0.52		
268.498	1.22	1098.562	0.53		
319.286	1.26	1165.823	0.54		
356.894	1.30	1214.960	0.57		
		1289.710			

$$\beta = \frac{1.8247 \times 10^6}{(\epsilon T)^{3/2}} \quad (3)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8206 \times 10^6}{(\epsilon T)^{3/2}} \Lambda_0 + \frac{82.501}{\eta_0 (\epsilon T)^{1/2}} \quad (4)$$

In the above equation β is the Debye-Huckel activity coefficient, S the limiting Onsager coefficient and the other terms have their usual significance. Also, Λ_0 is the sum of the equivalent conductances of the simple ions at infinite dilution and Λ^T the sum of the values for the two kinds of triple-ions: $R_4N(Br_2)^-$ and $(R_4N)^+ Br$ for R_4NBr salts, $Li(BF_4)_2^-$ and $Li_2(BF_4)^+$ for $LiBF_4$ and $Li(AsF_6)_2^-$ and $Li_2(AsF_6)^+$ for $LiAsF_6$. K_P and K_T are the ion-pair and triple-ion formation constants respectively. The symmetrical approximation of the two possible formation constant of triple-ions equal to each other has been considered⁷.

Neglecting Λ/Λ_0 , $(S/\Lambda_0^2)(cA)^{1/2}$ and assuming $f_{\pm} = 1$, lead to $g(c) = 1$ in equation (1) and we get,

$$\Lambda(c)^{1/2} = \frac{\Lambda_0}{K_P} + \frac{\Lambda_0^2 K_T}{K_P^2} c \quad (5)$$

For the present data, it was found that equation (5) was inadequate, the data showing a downward curvature when plotted as $\Lambda(c)^{1/2}$ vs c . On the contrary, equation (1) gives reasonably straight line (a representative plot for Hept₄NBr is shown in Fig. 2). For evaluation of K_P and K_T values from equation (1), the average $\Lambda_0 \eta_0$ values of R_4NBr salts at 25° were taken from the work of Krumgalz¹⁴. $\Lambda_0 \eta_0$ -value for $LiBF_4$ and $LiAsF_6$ in 1,2-DME at 25° was taken from literature^{2,7}. Therefore, from Walden's rule the Λ_0 -values of all the salts in THF at 25° have been calculated and presented in Table 2. Linear regression analysis of equation (1) gives correlation coefficient (r^2), intercept and slope and the values have been reported in Table 2. In solving equation (1), Λ_0^T , the triple-ion conductance, was set equal to $2/3\Lambda_0^{1.5}$. This has been specially done so for relative comparison of K_T values for the same electrolytes in different solvents¹⁶. The K_P and K_T values thus evaluated

TABLE 2 — VALUES OF COEFFICIENTS FROM REGRESSION ANALYSIS

Salt	S cm ² mol ⁻¹	r ²	Intercept	Slope
Bu ₄ NBr	123.33	0.9835	6.85 × 10 ⁻² (±0.0003)	5.281 (±0.008)
Pen ₄ NBr	118.33	0.9952	6.21 × 10 ⁻² (±0.0002)	5.200 (±0.005)
Hex ₄ NBr	114.63	0.9972	5.12 × 10 ⁻² (±0.0001)	5.166 (±0.002)
Hep ₄ NBr	112.24	0.9968	5.54 × 10 ⁻² (±0.0001)	4.813 (±0.002)
LiBF ₄	122.61	0.9944	3.65 × 10 ⁻² (±0.0019)	1.079 (±0.002)
LiAsF ₆	132.50	0.9960	45.65 × 10 ⁻² (±0.0001)	25.961 (±0.105)

TABLE 3 — ION-PAIR AND TRIPLE-ION FORMATION CONSTANTS IN THF AT 25°C

Salt	K _p × 10 ⁶ (mol dm ⁻³) ⁻¹	K _t (mol ² dm ⁻⁶) ⁻¹
Bu ₄ NBr	3.24	135.68
Pen ₄ NBr	6.63	125.61
Hex ₄ NBr	5.02	151.47
Hep ₄ NBr	4.11	130.42
LiBF ₄	11.30	44.36
LiAsF ₆	0.08	85.30

where $Q(b) = \int_2^b y^{-4} \exp y \, dy$

and $b = \frac{|Z_1 Z_2| e^2}{q_B \epsilon k T}$

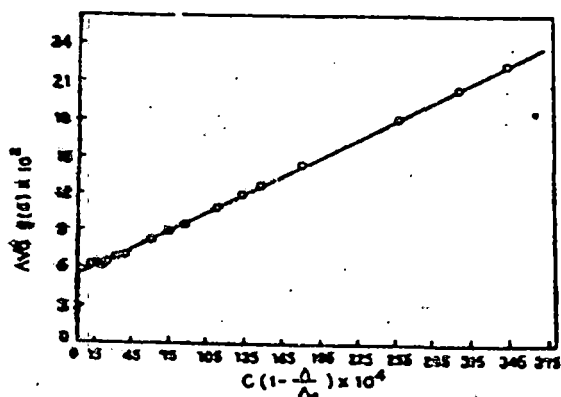


Fig. 2. Representative plot of $\Lambda g(c)c^{1/2}$ vs $C \left(1 - \frac{\Lambda}{\Lambda_0}\right)$ for Hept₄NBr in THF at 25^o.

are recored in Table 3. It is clear from Table 3 that major portion of the electrolytes exist as ion-pairs with only a major proportion as triple-ions. Using the values of K_p from Table 3, the interionic distance paramet (q_B) has been calculated with the help of the Bjerrum's theory of ionic association¹⁷ which can be written as

$$K_p = \frac{4 \pi N_A}{1000} \left(\frac{|Z_1 Z_2| e^2}{\epsilon k T} \right)^3 Q(b) \quad (6)$$

The q_B values obtained by the above procedure are recorded in Table 4. The Q(b) values have been taken from literature¹⁸. Table 4 reveals that q_B is almost similar for all the tetraalkylammonium salts whereas the actual ionic size changes by 0.94 Å This may be accounted by assuming that the Br⁻ ion can easily penetrate to some extent into the void spaces between the alkyl chains, as suggested by Abbott and Schiffrin¹¹ in other systems. Thus increase in chain-length in case of tetraalkylammonium ions does not greatly affect the distance of closest approach between the two ions. However, we see that an increase in the chain-length increases the ion-pair association constant to some extent. The q_B values calculated from equation (6) are much less in comparison with the r_c values (sum of the crystallographic radii) as reported in the literature¹⁹, suggesting that contact ion-pairs for tetraalkylammonium bromides probably exist in solution. This may cause a decrease in the degree of freedom of the cation in the ion-pair, which results in the loss of configurational entropy for the contact pair. Generally, K_p values do not change significantly for quaternary ammonium ions with chain-lengths greater than C₃. The small changes in the K_p values as observed in Table 3 may thus be related to entropic contributions as discussed above. Table 3 also shows that K_p values of LiBF₄ is much higher than that of LiAsF₆. Also from the q_B values reported in Table 4 we see that the minimum distance between ions in ion-pairs for these two

From the corresponding ρ_{15} values but the values are much less than

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electrolytes is much higher than the size of the average ionic diameter as reported in the literature^{11,16}. This indicates that in case of LiBF₄ and LiAsF₆ perhaps some solvent molecules have been included in the first coordination shell of the central ion. Further, a decrease in dielectric constant generally causes an increase in the association constant of the free ions. In case of LiBF₄, BF₄⁻ ion probably experiences a lower dielectric constant resulting in a lower interionic distance value than that of LiAsF₆ (the ratio q_{15}^2/ϵ is 1.29 and 1.44 for LiBF₄ and LiAsF₆ respectively) and this is most likely the effect which is being observed here.

σ_T , so σ_T values were calculated by an iterative procedure with the help of equation (7) and given in Table 4. The table shows that σ_T values of the electrolytes are greater than the expected theoretical result, $\sigma_T = 1.5 q_{15}$. This may be due to repulsive forces between the two anions or two cations in the case of the triple-ions MA₂⁺ or M₂A⁻ respectively.

It is interesting to compare the values of K_p and K_T (Table 5) with the corresponding data for these electrolytes in 1,2-DME ($\epsilon = 7.01$, $\eta_0 = 0.041$ P). A comparison shows that the electrolytes Bu₄NBr and Pent₄NBr are more associated in THF than in 1,2-DME. In case of LiAsF₆, the value of K_p is very close to each other in these two solvent media. The triple-ion formation constants (K_T) of these electrolytes in 1,2-DME are much higher than that in THF with the exception of LiAsF₆, where reverse trend has been observed. The observed difference in K_p and K_T values can be explained by molecular scale model². It is likely that chelation of R₄N⁺ and Li⁺ by 1,2-DME shifts equilibrium (8) toward the left, thus decreasing K_p .

TABLE 4 - THE q_{15} , σ_T AND π_2 VALUES FOR THE SALTS IN THF AT 25°

Salt	$q_{15} \cdot 10^8$ cm	$\sigma_T \cdot 10^8$ cm	$\pi_2 \cdot 10^8$ cm
Bu ₄ NBr	4.06	4.50	6.75 ^a
Pent ₄ NBr	4.03	4.37	7.00 ^a
Hex ₄ NBr	3.96	3.70	7.45 ^a
Hep ₄ NBr	4.01	4.29	7.68 ^a
LiBF ₄	3.80	-	2.05 ^a
LiAsF ₆	5.61	4.80	3.90 ^b

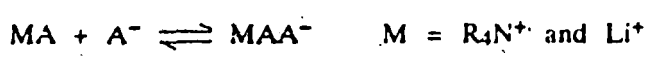
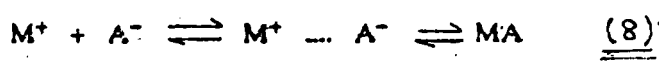
^a Ref. 14. ^b Ref. 16.

The interionic distance (σ_T) for a triple ion has also been calculated for these electrolytes according to the original theory of Fuoss and Kraus³ as given by the expressions,

$$K_T = \frac{2\pi N_A a_T^2 V}{1000} \quad (7)$$

where $I(b_3) = \frac{e^2}{a_T \epsilon k T}$

$I(b_3)$ is a double integral which has been tabulated in the literature¹⁸ for a wide range of values of b_3 . Since the term $I(b_3)$ is also a function of



On the other hand, the steric hindrance caused by the -CH₂- group adjacent to the etheral group of the THF may cause solvation hindrance which favours the anion as a competitor for the first

TABLE 5 - COMPARISON OF K_p AND K_T VALUES IN THF AND 1,2-DME AT 25°

Salt	C°		10 ⁴ C _p		10 ⁴ C _T		10 ⁻⁶ K _p		K _T	
	THF	DME	THF	DME	THF	DME	THF	DME	THF	DME
Bu ₄ NBr	0.062	0.03 ^a	588.85	271.90	9.92	8.99	3.24	2.39	115.68	267.58
Pent ₄ NBr	0.061	0.03 ^a	578.91	270.11	9.93	9.43	6.63	1.12	125.61	192.01
Hex ₄ NBr	0.035	0.03 ^a	335.88	281.39	4.43	5.95	5.02	5.18	151.47	260.64
Hep ₄ NBr	0.035	0.03 ^a	336.44	282.69	4.21	5.51	4.11	4.74	130.42	230.74
LiBF ₄	0.129	0.10 ^b	1270.50	4.55	6.11	4.56	11.30	12.00	44.36	50
LiAsF ₆	0.048	0.20 ^c	379.96	0.30	3.08	0.03	0.08	0.10	85.30	28

^a Maximum concentrations at which calculations have been made

^b Ref. 12. ^c Ref. 7. ^d Ref. 16.

MA₂⁺
M₂A⁻

del. A, put.

put
del. A, put.

3.63

coordination shell around M^+ . This may shift equilibrium (8) toward the right, increasing K_p .

The ion-pair and triple-ion concentrations (C_p and C_T respectively) of the electrolytes are reported in Table 5 at the highest concentrations for individual ions as tabulated in Table 1 using the relations,

$$C_p = C(1 - \alpha - 3\alpha_T) \quad (9)$$

$$\alpha = (K_p^2 C)^{-1/2} \quad (10)$$

$$\alpha_T = (K_T/K_p^2) C^{1/2} \quad (11)$$

$$C_T = (K_T/K_p^2) C^{3/2} \quad (12)$$

The results indicate that the ions are mainly present as ion-pairs even at such high concentrations with a small fraction as triple-ions.

Experimental

Tetrahydrofuran (THF) was kept for several days over KOH, then refluxed for 24 h and distilled over $LiAlH_4$. The b.p. (66°), density (0.8807 g cm^{-3}) and viscosity ($\eta_0 = 0.0046 \text{ P}$) compared well with the literature values⁸. The specific conductance of THF was ca. $0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 25° . Tetraalkylammonium bromides (Fluka) were purified as described earlier¹². $LiBF_4$ and $LiAsF_6$ (Fluka, Puriss) were redried under reduced pressure at 60° for 36 h.

Conductance measurements were made by a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 0.747 cm^{-1} and having an accuracy of $\pm 0.1\%$. The measurements were made in an oil-bath maintained at $25 \pm 0.005^\circ$. The details of experimental procedure have been described earlier²⁰. Solutions for conductance work were prepared by weight. The stock solution was kept in desiccator and used within 6–8 h. The conversion of molality into molarity was done using the density values.

Density and viscosity of solvent solutions were measured in an Ostwald-Sprengel type Pyknometer and suspended level Ubbelohde-type viscometer at

$25 \pm 0.01^\circ$ with an accuracy of $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$ and $\pm 0.05\%$ respectively. The dielectric constant of THF ($\epsilon = 7.58$) was taken from the literature¹⁹.

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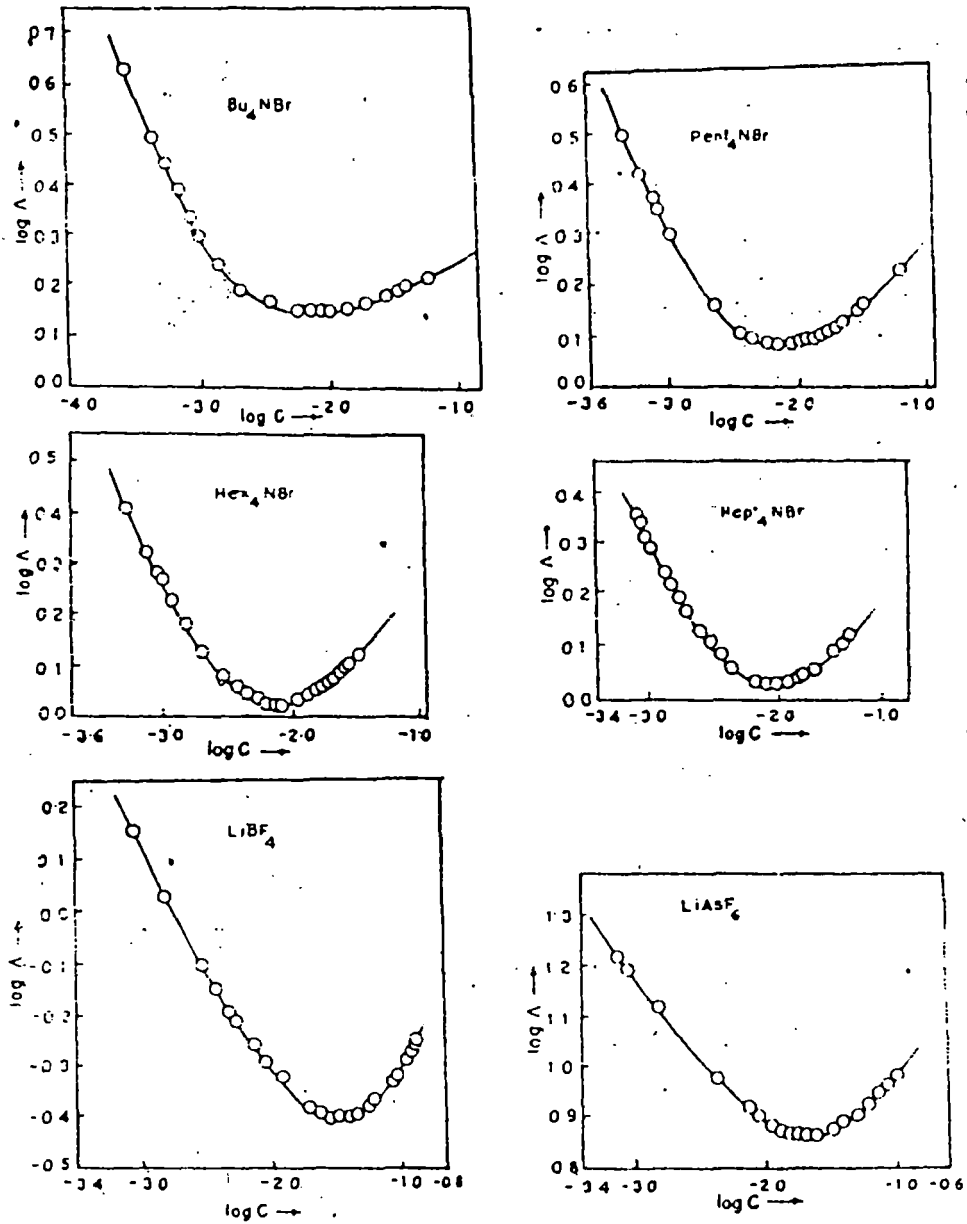


Fig. 1. Plots of $\log \Delta$ vs $\log c$ for Bu_4NBr , Pent_4NBr , Hex_4NBr , Hep_4NBr , LiBF_4 and LiAsF_6 in THF at 25°C