CHAPTER - II

Electrical Conductances for Tetraalkylammonium Bromides, $LiBF_4$ and $LiAsF_6$ in Tetrahydrofuran at 25°C.

Electrical conductance data have been reported for tetraalkylammonium bromides, R_4NBr (R = butyl to heptyl), Lithium tetrafluoroborate ($LiBF_4$) and lithium hexafluoroarsenate ($LiAsF_6$) in tetrahydrofuran (THF) at 25°C. Analysis of the 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 constant for 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 R_4NBr 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 possible exception of $LiAsF_6$. 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 solutions[1] has occurred largely in the last decade.

Recently, there has been a renewed interest[2], after the classical work of Fuoss and Kraus[3] of the thirties, in the study of association and dimerization 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. Hojo[5] has investigated the formation of triple ions for substituted ammonium halides in acetonitrile from conductivity and voltametric data. The molecular relaxation dynamics and structure of lithium salts have been studied by petrucci[2,6-10] from ultrasonic absorption and electrical conductivity measurements in media of low permittivity . The conductivity of tetra-alkylammonium salts in polyaromatic solvents has also been recently studied by Schiffrin et al[11] and showed the formation of triple ions by fitting the Fuoss-Kraus equation to the conductance data.

Recently, we have also reported the formation of triple ions of tetraalkylammonium bromides in 1,2-dimethoxyethane (ϵ = 7.012) from conductivity measurements[12]. Now we extend our study to tetrahydrofuran a solvent having similar physical characteristics like 1,2-dimethoxyethane and the result is discussed below.

Experimental

Tetrahydrofuran (THF) was kept several days over KOH, refluxed for 24h and distilled over $LiAlH_4$. The boiling point (66°C), density (0.8807 g cm^{-3}) and viscosity (η_o = 0.0046 p) compared well with the literature values[8] . The specific conductance of THF was ca. 0.81 X 10^{-6} ohm^{-1} cm^{-1} at 25°C.

Tetraalkylammonium bromides were of Fluka products and purified as described earlier[12].

Tetrabutylammonium bromide (Bu_4NBr) (Fluka, Puriss) was taken in minimum volume of acetone. Ether was added till the commencement of precipitation. The solution was then cooled and the resulting crystals were filtered in a glass funnel. After a preliminary drying, the salt was finally grounded in a morter and dried at 333°K for 48 hours.

Tetrapentylanmonium bromide ($Pent_4NBr$) (Fluka, puriss) was recrystallised from (acetone + ether) mixtures and dried in vacuo at 333°K for 48 hours.

Tetrahexylammonium bromide (Hex_4NBr) (Fluka, Purum) was washed with ether and dried in vacuo at room temperature for three days.

Tetraheptylammonium bromide ($Hept_4NBr$) (Fluka, Purum) was recrystallised and washed with ether and dried in vacuo at room temperature for 48 hours.

Lithium tetrafluoro borate ($LiBF_4$) (Fluka, puriss) was recrystallised and dried in vacuo at room temperature for three days.

Lithium hexafluoro arsenate ($LiAsF_6$) (Fluka, Puriss) was recrystallised and dried in vacuo at room temperature for 48 hours.

$LiBF_4$ and $LiAsF_6$ (Fluka, Puriss) were redried under vacuum at 60°C for 36h.

Conductance measurements were made by Pye-Unicam PW 9509 conductivity meter at a frequency of 2 kHz using a dip-type cell of cell constant 0.747 cm^{-1}. The conductivity cell was sealed to the side of a 500 cm^3-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 details of experimental procedure have been described previously[13].

Solutions for conductance work wer prepared by weight. The stock solution was kept in desiccator, and used within 6 - 8h from its preparation. The conversion of molality into molarity was done using the density values.

Densities and viscosities of solvent and solutions were measured in an Ostwald-Sprengel type pycknometer and suspended level Ubbelohde-type viscometer at 25 ± 0.01°C with a precision of ± 3 X 10^{-5} g cm^{-3} and 0.05% respectively. The dielectric constant of THF (ϵ = 7.58) was taken from the literature[14].

Results and Discussion

The equivalent conductance (Λ) vs. the concentration (C) of the electrolytes in THF at 25°C have been recorded in – Table 1. Fig. 1 reports the plot of Λ vs. c in a log-log plot for tetrabutyl-, tetrapentyl-, tetrahexyl-, tetraheptyl bromides (lower homologues are insoluble in THF), LiBF$_4$ and LiAsF$_6$ at 25°C. A minimum is clearly visible in very case.

The conductance data have been analysed by the Fuoss-Kraus triple ion[15] theory in the form as given below :

$$\Lambda g(c)^{1/2} = \frac{\Lambda_o}{K_P^{1/2}} + \frac{\Lambda_o^T K_T}{K_P^{1/2}} \left(1 - \frac{\Lambda}{\Lambda_o}\right) c \qquad (1)$$

$$g(c) = \frac{exp\left(-\frac{\beta'}{\Lambda_o^{1/2}}(c\Lambda)^{1/2}\right)}{\left(1 - \frac{S}{\Lambda_o^{3/2}}(c\Lambda)^{1/2}\right)\left(1 - \frac{\Lambda}{\Lambda_o}\right)^{1/2}} \qquad (2)$$

$$\beta' = \frac{1.8247 \times 10^6}{(\epsilon T)^{3/2}} \qquad (3)$$

$$S = \alpha\Lambda_o + \beta = \frac{0.8206 \times 10^6}{(\epsilon T)^{3/2}}\Lambda_o +$$

$$\frac{82.501}{\eta_o(\epsilon T)^{1/2}} \qquad (4)$$

In the above β is the Debye-Hückel activity co-efficient, and S is the limiting Onsager co-efficient and the other terms have their usual significance. Also, Λ_o is the sum of the eqivalent conductances of the simple ions at infinite dilution and Λ_o^T is the sum of the values for the two kinds of triple-ions : $R_4N(Br_2)^-$ and $(R_4N)_2^+Br$ 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 considered [7].

Neglecting Λ/Λ_o, $(S/\Lambda_o^{3/2})(C\Lambda)^{1/2}$ and assuming $f \pm = 1$ lead to $g(C) = 1$ in equation (1) and we get

$$\Lambda(c)^{1/2} = \frac{\Lambda_o}{K_P^{1/2}} + \frac{\Lambda_o^T K_T}{K_P^{1/2}} c \qquad (5)$$

For the present data, it was found that eqn. (5) was inadequate, the data showing a downward curvature when plotted as $\Lambda(C)^{1/2}$ vs c. On the contrary eqn. (1) gives reasonably straight line (a representative plot for $Hept_4NBr$ is shown in Fig. 2). For evaluation of K_P and K_T values from eqn. (1), the average $\Lambda_o\%$ values of R_4NBr salts at 25°C were taken from the work of Krumgalz[16]. $\Lambda_o\%$-value for $LiBF_4$ and $LiAsF_6$ in 1,2-DME at 25°C was taken from literature[2,7]. Therefore, from Walden's rule the Λ_o-values of all the salts in THF at 25°C have been calculated and are presented in Table 2. Linear regression analysis of eqn. (1)

gives correlation co-efficient (r^2), intercept and slope and the values have been reported in Table 2. In solving the eqn. (1), Λ_o^T, the triple-ion conductance, was set equal to $2/3 \Lambda_o$[17]. This has been specially done so for relative comparison of K_T values for the same electrolytes in different solvents[18]. The K_P and K_T values thus evaluated have been recorded in Table 3.

It is clear from Table 2 that major portion of the electrolytes exist as ion-pairs with only a minor proportion as triple-ions. Using the values of K_P from Table 2, the interionic distance parameter, 'q_B' has been calculated with the help of the Bjerrum's theory of ionic association[19] which can be written as

$$K_P = \frac{4 \pi N_A}{1000} \left(\frac{|z_1 z_2| e^2}{\epsilon R T} \right)^3 Q(b) \qquad (6)$$

where

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

and

$$b = \frac{|z_1 z_2| e^2}{q_B \epsilon R T}$$

The 'q_B' values obtained by the above procedure have been recorded in Table 4. The $Q(b)$ values have been taken from literature[20]. From Table 4 we see that the interionic distance parameter 'q_B' is almost similar for all the tetraalkylammonium salts whereas the actual ionic size changes by 0.94 A°. 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 suggerted by Schiffrin et al[11] 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 eqn. (6) are much less in comparison to r_c values (sum of the crystallographic radii) as reported in the literature[14], 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 configrational entropy for the contact pair. Generally, K_P values do not change significantly for quarternary ammonium ions with chain lengths greater than C_3. The small changes in the K_P values as observed in Table 2 may thus be related to entropic contributions as discussed above. Table 2 also shows that K_P values of $LiBF_4$ in much higher than that of $LiAsF_6$. Also from the 'q_B' values reported in Table 4 we see that the minimum distance between ions in ion-pairs for these two electrolytes is much higher than the size of the average ionic diameter as reported in the literature[11,18]. This indicates that in case of $LiBF_4$ and $LiAsF_6$ perhaps some solvent molecules have been included in the first co-ordination shell of the central ion. Further, a decrease in dielectric constant generally causes in the association constant of the free ions. In case of $LiBF_4$, BF_4^- ions probably experiences a lower dielectric constant resulting in a lower interionic distance value than that of $LiAsF_6$ (the ratio q_B / r_c is 1.29 and 1.44 for $LiBF_4$

and $LiAsF_6$ respectively) and this is most likely the effect which is being observed here.

The interionic distance, a_T , for a triple ion has also been calculated for these electrolytes according to the original theory of Fuoss and Kraus[3] as given by the expressions

$$K_T = \frac{2 \pi N_A a_T^3}{1000} I(b_3) \qquad (7)$$

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 literature[20] for a wide range of values of b_3 . Since the term $I(b_3)$ is also function of a_T, so a_T values were calculated by a iterative procedure with the help of eqn, (7) and given in Table 4. The table shows that the a_T values of the electrolytes are greater than the corresponding q_B values but the values are much less than the expected theoretical result $a_T = 1.5 q_B$. This may be due to repulsive forces between the two anions or two cations in the case of the triple ions MA_2^- or M_2^+A 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 (ϵ = 7.01, η_o = 0.0041 P). The comparison shows that the electrolytes Bu_4NBr and $Pent_4NBr$ are more associated in

THF than in 1.2-DME. In case of LiAsF$_6$, the value of K$_P$ is very close to each other in these two solvents media. The triple ions formation constants (K$_T$) of these electrolytes in 1,2-DME are much higher than in THF with the exception of LiAsF$_6$, where reverse trend has been observed. The observed differences in K$_P$ and K$_T$ values can be explained by molecular scale model[2]. It is likely that chelation of R$_4$N$^+$ and Li$^+$ by 1,2-DME shifts equilibrium (8)

$$M^+ \ + \ A^- \rightleftharpoons M^+ \ldots \ldots \ A^- \rightleftharpoons MA \qquad (\ 8 \ )$$

$$MA \ + \ A^- \rightleftharpoons MAA^- \qquad M \ = \ R_4N^+ \text{ and } \ Li^+$$

$$MA \ + \ M^+ \rightleftharpoons MAM^+ \qquad A \ = \ Br^-, BF_4^- \text{ and } AsF_6^-$$
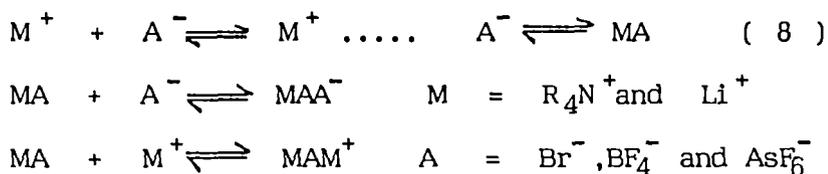
toward the left, thus decreasing K$_P$. On the other hand, the steric hindrance caused by the -CH$_2$- group adjacent to the etheral group of the THF may cause solvation hindrance which favours the anion as a competitor for the first co-ordination shell around M$^+$. This may shift equilibrium (8) toward the right, increasing. K$_P$.

The ion-pair and triple ion concentrations, C$_P$ and C$_T$ respectively, of the electrolytes have been reported in Table 5 at the highest concentrations for individual ions as tabulated in Table 1 using the following relations   :

$$C_P \ = \ C(\ 1 - \alpha - 3\alpha T) \qquad (9)$$

$$\alpha \ = \ (\ K_P^{\frac{1}{2}} \ C^{\frac{1}{2}} \ )^{-1} \qquad (10)$$

$$\alpha_T = (K_T / K_P^{1/2}) C^{1/2} \tag{11}$$

$$C_T = (K_T / K_P^{1/2}) C^{3/2} \tag{12}$$

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

R E F E R E N C E S

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TABLE - 1

Electrical conductivity of eletrolytes in Tetrahydrofuran at 25°C

$C/10^{-4}$ mol dm^{-3}	Λ/S cm^2 mol^{-1}	$C/10^4$ mol dm^{-3}	Λ/S cm^2 mol^{-1}	$c/10^4$ mol dm^{-3}	Λ/S cm^2 mol^{-1}
Bu$_4$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	68.498	1.20	46.598	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

87

C/10^{-4} mol dm^{-3}	Λ/S cm^{2}mol^{-1}	C/10^{-4} mol dm^{-3}	Λ/S cm^{2}mol^{-1}	C/10^{-4} mol dm^{-3}	Λ/S cm^{2}mol^{-1}
Bu$_4$NBr		Pent$_4$NBr		Hex$_4$NBr	
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
		221.589	1.32	208.934	1.19
		289.492	1.39	230.418	1.21
		314.596	1.40	241.253	1.22
		612.558	1.64	292.956	1.27
				351.611	1.33

C/10^{-4} mol dm^{-3}	Λ/S cm² mol^{-1}	C/10^{-4} mol dm^{-3}	Λ/S cm² mol^{-1}	C/10^{-4} mol dm^{-3}	Λ/S cm² mol^{-1}
	Hept$_4$NBr		LiBF$_4$		LiAsF$_6$
8.494	2.26	9.489	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	90.768	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	118.765	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

$C/10^{-4}\,mol\,dm^{-3}$	$\Lambda\,/S\ cm^2\,mol^{-1}$	$C/10^{-4}\,mol\,dm^{-3}$	$\Lambda\,/S\ cm^2\,mol^{-1}$	$C/10^{-4}\,mol\,dm^{-3}$	$\Lambda\,/S\ cm^2\,mol^{-1}$
Hept$_4$NBr		LiBF$_4$		LiAsF$_6$	
43.895	1.13	307.826	0.40	213.792	7.27
66.986	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	1165.823	0.53		
319.286	1.26	1214.960	0.54		
356.894	1.30	1289.710	0.57		

TABLE - 2

Values of Co-efficients from Regression Analysis

Salts	Λ° (Scm^{2}mole^{-1})	r^2	Intercept	Slope
Bu$_4$NBr	123.33	0.9835	6.85 X 10^{-2} (±0.0003)	5.281 (±0.008)
Pent$_4$NBr	118.33	0.9952	6.21 X 10^{-2} (±0.0002)	5.200 (±0.005)
Hex$_4$NBr	114.63	0.9972	5.12 X 10^{-2} (±0.0001)	5.166 (±0.002)
Hept$_4$NBr	112.24	0.9968	5.54 X 10^{-2} (±0.0001)	4.813 (±0.002)
LiBF$_4$	112.61	0.9944	3.65 X 10^{-2} (±0.0019)	1.079 (±0.002)
LiAsF$_6$	132.80	0.9960	45.65 X 10^{-2} (±0.0001)	25.961 (±0.105)

TABLE - 3

Ion-pair and Triple-ion Formation Constants in THF at 25°C

Salts	K_P X 10^{-6} (mol dm^{-3})$^{-1}$	K_T (mol dm^{-3})$^{-1}$
Bu$_4$NBr	3.24	115.68
Pent$_4$NBr	3.63	125.61
Hex$_4$NBr	5.02	151.47
Hept$_4$NBr	4.11	130.42
LiBF$_4$	11.30	44.36
LiAsF$_6$	0.08	85.30

TABLE – 4

The q_B, a_T and r_c values for the salts in THF at 25°C

Salts	q_B X 10^8 (cm)	a_T X 10^8 (cm)	r_c X 10^8 (cm)
Bu$_4$NBr	4.06	4.50	6.74[a]
Pent$_4$NBr	4.03	4.37	7.09[a]
Hex$_4$NBr	3.96	3.70	7.40[a]
Hept$_4$NBr	4.01	4.29	7.68[a]
LiBF$_4$	3.80	–	2.95[a]
LiAsF$_6$	5.61	4.80	3.90[b]

[a] Ref.14,   [b] Ref. 18

Comparison of K_P and K_T values in THF and 1,2-DME at 25°C

	C^*		$C_P \times 10^4$		$C_T \times 10^4$		$K_P \times 10^{-6}$		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	3.63	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
Hept$_4$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	0.08	0.03	0.08	0.10	85.30	28

*   Maximum concentrations at which calculations have been made;

[a]Ref. 12;   [b]Ref. 7;   [c]Ref. 18
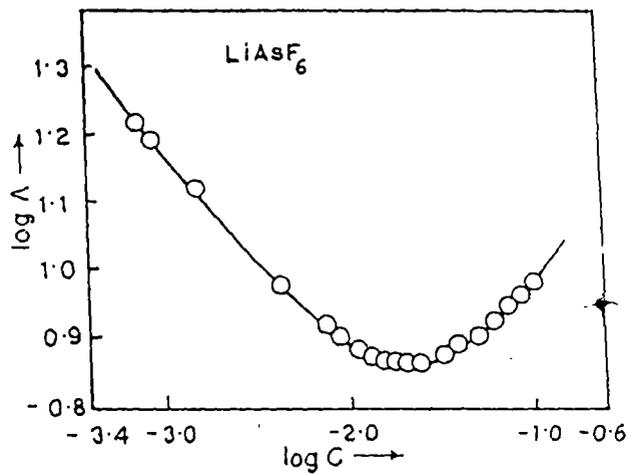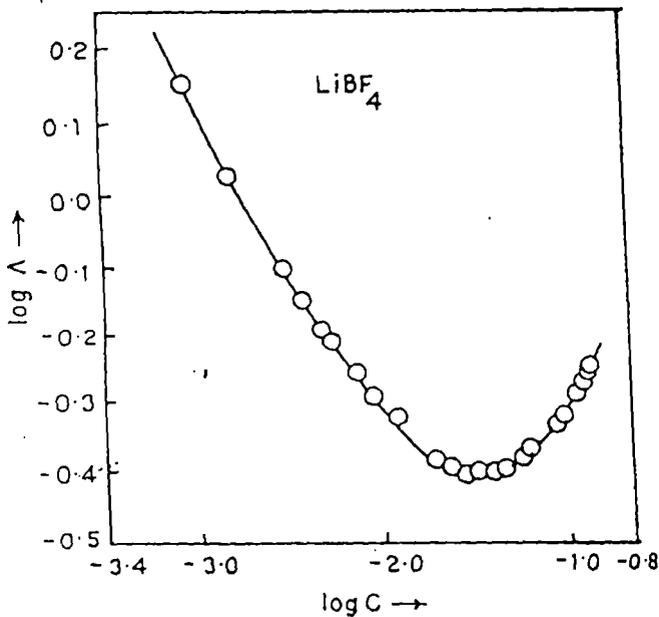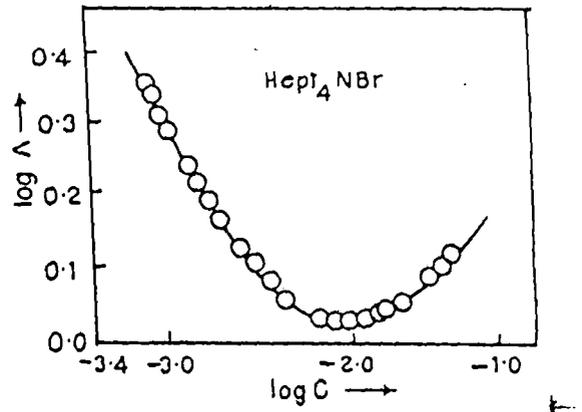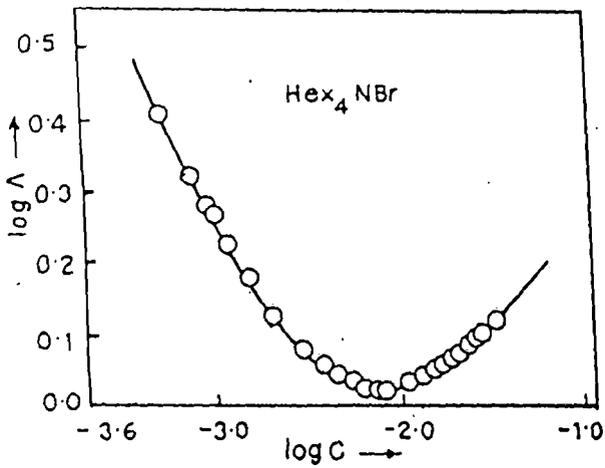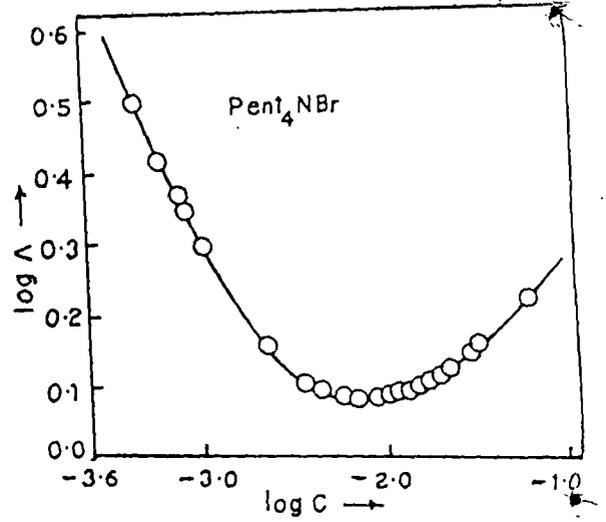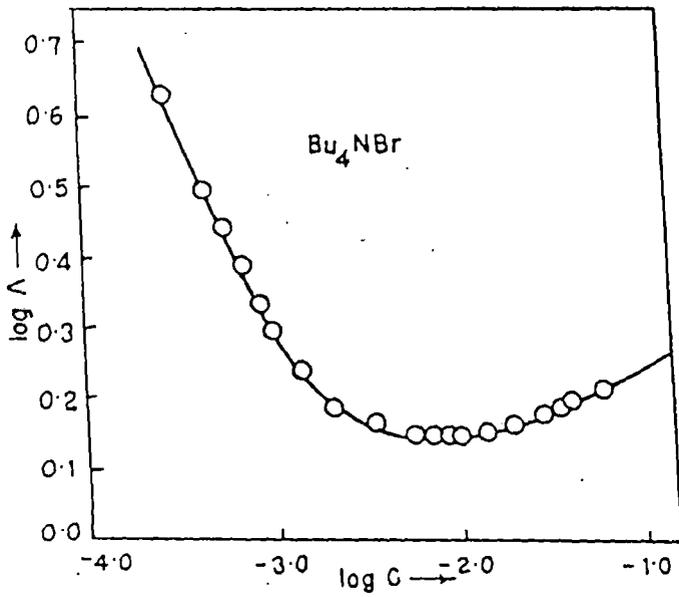
Fig.1. Plot of log Λ versus log c for Bu$_4$NBr, Pent$_4$NBr, Hex$_4$NBr, Hept$_4$NBr, LiBF$_4$ and LiAsF$_6$ in THF at 25° C.
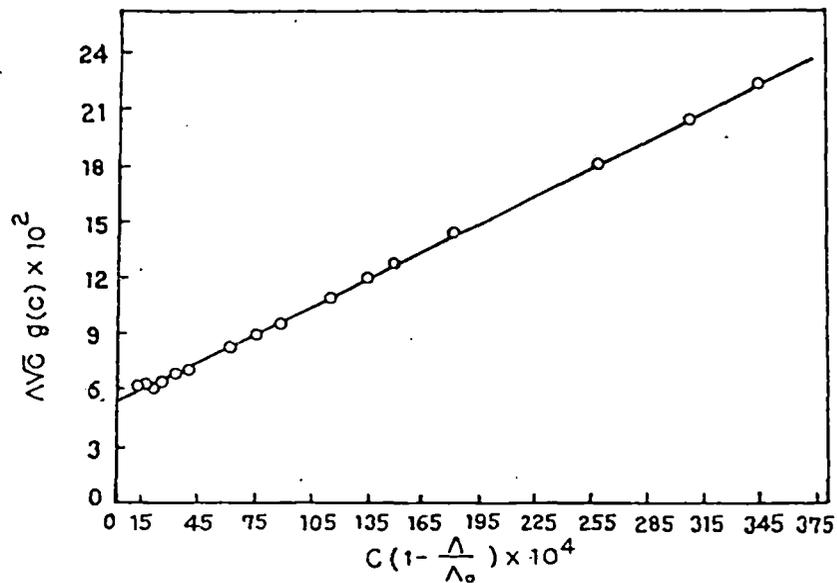
FIG. 2. Representative plot of $\Lambda\, g(c)c^{\frac{1}{2}}$ versus $C(1-\frac{\Lambda}{\Lambda_0})$ for $Hept_4NBr$ in THF at $25°C$.