

CHAPTER-C

C.1: Conductometric Study of Some Alkali Metal Halides in Dimethyl Sulfoxide + Acetonitrile mixtures at 298.15 K

C.1.1. Introduction

Dimethylsulfoxide (DMSO), a typical aprotic solvent having both polar and nonpolar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells^{1,2}.

Dimethylsulfoxide (DMSO) was chosen in this experiment because of its wide range of applicability as a solvent in chemical and biological processes, involving both plants and animals. Furthermore, DMSO is also widely used in pharmaceutical applications, enzyme-catalyzed reactions, veterinary medicine, dermatology, experimental immunology, and microbiology³. The main pharmacological use of DMSO is as a vehicle for drugs such as idoxuridine: it aids in penetration of the drug into the skin, possibly enhancing the drug's effect. Other reported activities of DMSO include membrane penetration, anti-inflammatory effects, local analgesia, weak bacteriostasis, diuresis, vasodilatation, dissolution of collagen, and free-radical scavenging^{4,6}. In the sector of veterinary medicine, it is used in therapy category, in treatment of interstitial cystitis and scleroderma, and topically to reduce swelling due to trauma^{5,6}. DMSO is also a very important solvent for many organic compounds including fats, carbohydrates, dyes, resins, and polymers.

DMSO exhibits strong self-association, it is a highly polar aprotic solvent because of its S=O group. In case of acetonitrile, on the other hand there is a lack of strong specific intermolecular forces, while dipole-dipole forces predominate.

The conductivity of the electrolyte solution is very much influenced by the permittivity and the viscosity of the solvent. The permittivity is related to dissociation of the salt and the viscosity affects the motion of ions. So, studies of mixed systems consisting of two solvents, i.e., a high permittivity solvent and a low viscosity solvent have been assumed important because of their application in modern technology^{7,8}.

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In view of the complex nature of DMSO – acetonitrile mixtures, it is of interest to investigate the influence of the solvent composition on the ionic association and the solvation behavior of some alkali metal halides using conductance measurements. Several systematic investigations⁹⁻¹¹ on the conductivity of alkali metal halides in the mixed solvent systems have been carried out by workers to reveal the nature of ionic association and mobility of ions. In the present study the solubility of alkali metal halides MX (M= Li, Na, K ; X= Cl⁻, Br⁻, I⁻) in 20 mass%, 40 mass% and 60 mass% of DMSO in DMSO + Acetonitrile mixtures at 298.15 K have been reported. Here an attempt has been made to ascertain the nature of ion-solvent interactions of alkali metal halides in DMSO + Acetonitrile mixtures using the conductometric technique.

C.1.2. Experimental Section

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. Dimethylsulfoxide (SRL Extrapure) was kept for several days over anhydrous CaSO₄ and refluxed for 4 hr. over CaO. Finally, it was distilled according to the procedure described earlier². Purity of the solvents was checked by comparing their viscosity and density values with the literature values^{2,12}. Metal salts were obtained from Loba Chemie/S.D.Fine/E.Merck, India/Aldrich Chem and purified in the manner given in the literature^{9,11,13,14}. Tetrabutylammonium bromide (Bu₄NBr) was purified by recrystallization from acetone, and the crystallized salt was dried in vacuo for 48 hrs. Sodium tetraphenylborate (NaBPh₄) was recrystallized three times from acetone and then dried under vacuum for 72 hrs. Water was doubly-distilled and then passed through a column containing mixed resin (anion-cation exchange).

The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, having cell constant 1.11 cm⁻¹. Measurements were made in a thermostated water bath maintained at 298.15 ± 0.01 K. Solutions were prepared by weight precise to ± 0.02 %. The weights were taken on a Mettler electronic analytical balance (AG 285). Determination of cell constant was based on 0.1 (M) aqueous KCl solution. The cell was calibrated by the method of Lind et al^{13,15}. The entire conductance data were reported at 1 KHz and was found to be ± 0.3 % precise. Due correction was made for the specific conductance of the solvent and solvent mixtures. The relative permittivity of DMSO and Acetonitrile are 46.7 and 35.95 respectively.

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Densities (ρ) were measured at 298.15 K with an Ostwald-Sprengel type pycnometer having bulb volume of about 25 cm³ and an internal diameter of the capillary of about 1 mm. Viscosities (η) were measured by means of a suspended Ubbelohde type viscometer^{16,17,18}. Calibration was done at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. The details of the methods and techniques for determination of the parameters were described earlier^{19,20}.

C.1.3. Results and Discussion

The salts LiBr, LiI, NaBr, NaI, KI, Bu₄NBr and NaBPh₄ are freely soluble in all the proportion of DMSO + Acetonitrile mixtures at 298.15 K, the salts NaCl, KCl and KBr are insoluble in three proportions, whereas the salt LiCl is soluble in 60% of DMSO and insoluble in 20 and 40 mass % of DMSO. Physical properties of different solvent mixtures are given in Table 1.

The experimental values of the molar conductance, Λ against the respective concentration, c for different alkali metal halide salts in different binary solvent mixtures of DMSO + Acetonitrile at 298.15 K are recorded in Table 2.

The conductance data have been analyzed by the Fuoss conductance-concentration equation^{21,22}. For a given set of conductivity values ($c_j, A_j, j = 1 \dots, n$), three adjustable parameters, the limiting molar conductivity (Λ_0), the association constant (K_A) and the association diameter (R) are derived from the following set of equations:

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

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

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

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

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

$$K_A = \frac{K_R}{(1 - \alpha)} = K_R (1 + K_S) \quad (6)$$

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where R_X is the relaxation field effect, E_L is the electrophoretic countercurrent, \bar{K}^{-1} is the radius of the ion atmosphere, D is the dielectric constant of the solvent, e is the electronic charge, k_B is the Boltzmann constant, K_S is the association constant of contact pairs, K_R is the association constant of solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, c is the molarity of the solution, f is the activity coefficient, T is the absolute temperature, and β is twice the Bjerrum distance.

The computations were performed using the program suggested by Fuoss. The initial $\tilde{\Lambda}_0$ values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set $(c_j, A_j; J = 1, \dots, n)$, n , D , η , T , initial values of $\tilde{\Lambda}_0$, and an instruction to cover a preselected range of R values.

In practice, calculations are performed by finding the values of $\tilde{\Lambda}$ and α which minimize the standard deviation,

$$\sigma = \sum \frac{[\Lambda_j(\text{calcd}) - \Lambda_j(\text{obs})]^2}{n-2} \quad (7)$$

for a sequence of R values and then plotting σ against R ; the best fit R corresponds to the minimum of the σ versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increments to locate the minimum but no significant minima were found in the σ - R curves for all the salts studied here; thus, R values are assumed to be $R = a + d$, 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 (10 nm) is given by

$$d = 1.183 \left(\frac{M}{\rho} \right)^{1/3} \quad (8)$$

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

$$M_{av} = M_1M_2 / (W_1M_2 + W_2M_1) \quad (9)$$

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where W_1 is the mass fraction of the first component of molar mass M_1 . The values of $\tilde{\Lambda}_0$, K_A and R obtained by this procedure are reported in Table 2.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the limiting molar salt conductances into their ionic components. In the absence of accurate transference data for these systems we have used the "reference electrolyte" method. Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was used as the "reference electrolyte"^{13,20}. The $\Lambda_0(\text{Bu}_4\text{NBPh}_4)$ was obtained from the Λ_0 values of tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate (NaBPh_4), and sodium bromide (NaBr) in the appropriate solvent mixture using the relation,

$$\Lambda_0(\text{Bu}_4\text{NBPh}_4) = \Lambda_0(\text{Bu}_4\text{NBr}) + \Lambda_0(\text{NaBPh}_4) - \Lambda_0(\text{NaBr}) \quad (10)$$

Ionic divisions were accomplished through the following relationships^{23,24}:

$$\Lambda_0(\text{Bu}_4\text{NBPh}_4) = \lambda_0(\text{Bu}_4\text{N}^+) + \lambda_0(\text{BPh}_4^-) \quad (11)$$

$$\lambda_0(\text{Bu}_4\text{N}^+) = 0.517 \Lambda_0(\text{Bu}_4\text{NBPh}_4) \quad (12)$$

The limiting ionic conductances calculated from the above equation are recorded in table-4.

The Walden's product, $\Lambda_0\eta$ ²⁵ of an ion is also calculated for the various solvent compositions and the results have been depicted in Fig. 1.

Fig. 2 predicts the nature of the curves for the Gibbs' energy of ion-pair formation, ΔG° for the binary mixtures studied here. which is given by the relationship²⁶,

$$\Delta G^\circ = -R T \ln K_A \quad (13)$$

and presented in Table 3.

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Inspection of the data of Table 2 shows that the values of Λ of all salts decrease as the concentration of DMSO in the mixtures increases. The trends in Λ_0 can be discussed through another characteristic function called the Walden product, $\Lambda_0\eta$. Although Λ_0 decreases as the concentration of DMSO increases; $\Lambda_0\eta$ (Table 3) increases due to the increase of the viscosity (η). The decrease in Λ with increase of concentration of DMSO in the mixture can probably be interpreted as an expansion of the solvent sheath (which envelops an ion and moves by ion-solvent interactions, *i.e.*, the expansion of a solvated ion) because of the activation of solvent molecules forming the sheath.

From Table 3, we see that Λ_0 values of alkali metal salts of common anions and cations follow the sequence: $\text{Li} < \text{Na} < \text{K}$ and $\text{MCl} > \text{MBr} > \text{MI}$ respectively in DMSO-rich region. The trend of variation of Λ_0 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: $\text{Li} > \text{Na} > \text{K}$. For anions this order is $\text{Cl}^- < \text{Br}^- < \text{I}^-$ in the region containing higher concentration of DMSO in the mixture. This shows that Li^+ is the most solvated and K^+ is the least one in any mass% of DMSO.

The above findings show that the solvation behavior of alkali metal halides in DMSO + Acetonitrile mixture is quite similar to that observed in Acetonitrile + DMF²⁷ and water + DMSO¹⁰ but is different from that observed in DMSO + dioxane²⁸.

There are marked characteristic behavior in the K_A values. K_A for all salts increases as the concentration of DMSO increases in the mixture which support significant association. This also explains the increase in σ values as acetonitrile content in the mixture decreases.

The Walden products $\Lambda_0\eta$ of the ions are also included in Table 4, which are usually employed to discuss the interactions of the ions with the solvent medium. From this table, we see that the Walden product of cations decrease in the order, $\text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Bu}_4\text{N}^+$. And, for the electrolyte taken as a whole, it follows the same sequence. This is justified as the Walden product of an ion or solute is inversely proportional to the effective radius (r) of the ion or solute in a particular solvent²⁹,

$$\Lambda_0\eta = 1 / 6 \Pi r T \quad (14)$$

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This points out that the electrostatic ion-solvent interaction is strong in these cases. The variation of the Walden product reflects the change of solvation^{29,30}. Though the variation of the Walden product with solvent composition (fig. 1) is difficult to interpret quantitatively, still its variation with solvent composition can be explained by preferential solvation^{31,32} of alkali metal ions by DMSO and acetonitrile molecules respectively. At low concentration of DMSO, these ions are preferentially solvated by acetonitrile than DMSO and the viscosity of the solvent in the vicinity of these ions is lower than that of the bulk solvent. Since the bulk viscosity value is used in the calculation of $\Lambda_0\eta_0$, 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 product indicates the preferential solvation of alkali metal ions by DMSO in DMSO + acetonitrile mixtures. However this decrease may be due to the Zwanzig³³ solvent relaxation effect.

The starting point for most evaluations of ionic conductances is Stokes' law which states that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant. In Table 4, we have calculated the Stokes' radii r_s of these ions in these different solvent mixtures. For lithium, sodium and potassium ions, the Stokes' radii are much higher than their crystallographic radii suggesting that these ions are significantly solvated in these solvent mixtures. The Stokes' radii of the halide ions are, however, found to be either very close to or smaller than their corresponding crystallographic radii. This observation indicates that these halide ions are scarcely solvated in different solvent mixtures.

Figure 2 points out the nature of curve for the Gibbs energy for ion-pair formation, ΔG° which clearly predicts that the tendency for ion-pair formation decreases significantly with an increase in the association factor for the alkali metal halides in DMSO-Acetonitrile medium. The ΔG° curve in Fig. 2 along with the other parameters mentioned above are quite in accordance with the results observed by Barthel et al²⁶ and Hazra et al^{30,34}.

C.1.4. Conclusion:

It may thus be concluded that these electrolytes remain slightly associated in solvent mixtures and are very much solvated by DMSO than acetonitrile and that solvation of the ions is weakened as soon as the ion pair is formed. The cations are found to be substantially solvated in

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solvent mixtures whereas the anions appear to have weak interactions with the solvent molecules. The results further indicate that the Coulombic forces play a major role in the ion association processes. These electrolytes solutions, in general, show an increase in the association constant values with an increase in concentration of DMSO in the solvent mixtures. Further, the effect of concentration of DMSO on limiting equivalent conductances of alkali metal ions is more pronounced as compared to that of tetraalkylammonium ion in the present mixed solvent media.

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Table 1. Physical properties of different DMSO + Acetonitrile mixtures containing 20,40,60 mass% of DMSO at 298.15 K.

Mass% of DMSO	Density ($\text{g}\cdot\text{cm}^{-3}$)	Viscosity ($\text{mPa}\cdot\text{s}$)	Dielectric constant (ϵ)
20	0.8293	0.4196	38.10
40	0.8833	0.5249	40.25
60	0.9456	0.7147	42.41

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Table 2. Equivalent conductances and corresponding molarities of electrolytes in DMSO(1) + Acetonitrile mixtures containing 20,40,60 mass% of DMSO at 298.15 K.

20% DMSO		40% DMSO		60% DMSO	
LiBr					
$C \times 10^4$ (mol·dm ⁻³)	Λ (S·cm ² ·mol ⁻¹)	$C \times 10^4$ (mol·dm ⁻³)	Λ (S·cm ² ·mol ⁻¹)	$C \times 10^4$ (mol·dm ⁻³)	Λ (S·cm ² ·mol ⁻¹)
19.39	122.70	14.40	106.25	19.75	75.56
20.54	122.00	16.75	105.00	22.21	74.19
22.23	121.14	18.29	103.88	25.84	73.06
23.33	120.49	20.56	102.54	28.22	71.88
24.97	119.50	22.04	101.80	31.72	70.75
27.61	118.18	24.23	100.52	34.01	69.75
30.17	116.76	25.66	99.73	37.38	68.56
32.64	115.80	27.77	98.65	39.59	67.69
35.03	114.60	29.15	97.88	42.84	66.94
37.35	113.80	31.19	96.91	44.98	65.94
LiI					
7.16	132.75	13.96	103.68	18.30	67.06
8.53	131.06	15.70	102.06	20.59	66.17
10.54	129.44	18.26	100.50	23.95	65.37
11.85	127.81	19.94	99.29	26.15	64.48
13.79	127.13	22.41	97.93	29.39	63.21
15.06	126.63	24.03	96.86	31.52	61.88
16.93	124.94	26.42	95.75	34.64	61.04
18.15	124.06	27.98	94.72	36.69	60.23
19.95	122.88	30.28	94.06	39.71	59.5
21.13	121.88	31.78	92.56	41.68	58.8
NaBr					
7.08	135.9	49.58	93.04	29.43	78.41
8.43	134.2	52.55	92.40	33.08	76.72
10.42	132.7	55.44	91.67	35.47	75.83
11.72	131.8	58.24	91.07	38.99	74.85
13.64	130.5	60.96	90.20	41.29	73.95
14.89	129.6	63.60	89.54	44.69	72.98
16.73	128.4	66.16	88.74	46.91	72.25
17.94	127.5	68.64	87.97	50.19	71.32
19.72	126.1	73.41	87.09	52.34	70.52
20.89	125.5	77.92	86.08	55.51	69.54
NaI					
6.93	152.45	59.59	95.93	60.18	71.54
8.25	151.50	62.16	94.75	64.59	70.58
10.20	150.17	64.67	94.11	68.86	69.72
11.47	149.40	67.10	93.67	73.00	69.05

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20% DMSO		40% DMSO		60% DMSO	
13.34	148.26	71.76	92.91	77.01	68.23
14.57	147.83	76.16	91.82	80.90	67.52
16.38	146.80	80.34	90.68	84.67	66.71
17.56	146.33	84.30	89.93	88.34	66.04
19.30	145.44	88.06	89.14	91.89	65.40
20.44	144.97	91.64	88.45	95.35	64.75
KI					
7.73	168.47	26.62	113.14	20.27	90.52
9.20	167.60	28.81	112.22	23.59	89.08
11.37	166.57	30.24	111.79	25.75	88.46
12.79	165.96	32.35	110.76	28.95	87.16
14.89	165.14	33.74	110.27	31.04	86.36
16.25	164.70	35.78	109.56	34.11	85.22
18.27	163.93	37.12	109.02	36.13	84.72
19.59	163.45	39.09	108.48	39.10	83.89
21.53	162.57	42.30	107.25	41.05	83.43
22.80	162.13	45.40	106.27	43.92	82.24
Bu₄NBr					
25.10	99.58	25.05	77.51	25.82	56.98
26.18	99.33	27.54	76.72	29.02	56.08
27.76	98.93	29.16	76.37	31.11	55.61
28.80	98.64	31.56	75.72	34.20	54.76
30.33	98.24	33.13	75.36	36.22	54.33
32.82	97.77	35.45	74.88	39.20	53.71
35.23	97.21	36.97	74.51	41.15	53.29
37.56	96.65	39.20	74.09	44.03	52.76
39.81	96.21	40.67	73.69	45.91	52.36
41.74	95.75	42.83	73.24	48.69	51.85
NaBPh₄					
25.71	86.11	25.18	61.72	26.59	45.71
26.81	85.80	26.67	61.41	35.23	44.13
28.43	85.47	28.86	60.87	37.31	43.78
29.49	85.26	30.30	60.51	40.38	43.27
31.06	84.99	32.41	60.26	42.39	42.76
33.61	84.51	33.80	59.84	45.35	42.37
36.07	84.01	35.85	59.49	47.29	42.05
38.46	83.57	37.19	59.17	50.16	41.73
40.77	83.15	39.17	58.73	52.03	41.46
43.01	82.77	45.48	57.77	54.80	41.02
LiCl 60% DMSO					
		44.47	75.97		
		46.38	75.23		
		49.18	74.32		
		51.02	73.71		
		53.74	73.06		

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20% DMSO	40% DMSO	60% DMSO
	58.14	72.46
	62.41	71.47
	66.53	70.57
	70.53	69.77
	78.16	68.48

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Table 3. Derived conductivity parameters and standard Gibbs energy changes for the ion association process of electrolytes in DMSO (1) + Acetonitrile (2) mixtures containing 20,40,and 60 mass% of DMSO at 298.15 K.

Mass% of DMSO	Λ^0 ($S \cdot cm^2 \cdot mol^{-1}$)	K_A ($dm^3 \cdot mol^{-1}$)	R (Å)	ΔG^0 ($kJ \cdot mol^{-1}$)	Σ
LiCl					
20	-	-	-	-	-
40	-	-	-	-	-
60	97.66	94.43	7.05	-11.27	0.19
LiBr					
20	141.30	88.20	7.04	-11.10	0.08
40	121.61	111.07	7.11	-11.68	0.12
60	91.65	136.01	7.19	-12.18	0.19
LiI					
20	141.91	88.69	7.25	-11.12	0.34
40	119.77	129.76	7.32	-12.06	0.22
60	81.82	147.74	7.41	-12.38	0.33
NaBr					
20	144.93	83.89	7.39	-10.98	0.19
40	121.71	91.59	7.46	-11.19	0.16
60	100.43	134.57	7.55	-12.15	0.14
NaI					
20	159.24	45.71	7.60	-9.48	0.09
40	126.56	83.66	7.67	-10.97	0.19
60	101.34	115.06	7.76	-11.76	0.13
KI					
20	174.61	26.70	7.98	-8.14	0.09
40	131.33	70.58	8.05	-10.55	0.07
60	103.87	82.85	8.14	-10.95	0.12
Bu₄NBr					
20	109.72	40.59	11.38	-9.18	0.04
40	87.91	60.95	11.45	-10.19	0.05
60	68.37	99.23	11.54	-11.39	0.03
NaBPh₄					
20	94.83	38.88	10.24	-9.07	0.02
40	70.89	68.21	10.31	-10.46	0.07
60	54.94	95.82	10.39	-11.31	0.06

Conductometric Study in Acetonitrile mixtures at 298.15 K

Table 4. Limiting ionic conductances, ionic Walden products and ionic Stokes radii (r_s) in different DMSO (1) + Acetonitrile (2) mixtures containing 20,40,and 60 mass% of DMSO at 298.15 K.

Ion	λ_{\pm}° (S·cm ² ·mol ⁻¹)	$\eta \lambda_{\pm}^{\circ}$ (S·cm ² ·mol ⁻¹ ·Pa·s)	r_s (Å)
20 mass% of DMSO			
Li ⁺	62.40	26.19	3.13
Na ⁺	66.03	27.71	2.96
K ⁺	81.40	34.16	2.40
Br ⁻	78.91	33.11	2.48
I ⁻	93.21	39.11	2.10
40 mass% of DMSO			
Li ⁺	52.88	27.76	2.96
Na ⁺	52.98	27.82	2.95
K ⁺	57.75	30.31	2.71
Br ⁻	68.73	36.08	2.27
I ⁻	73.58	38.62	2.12
60 mass% of DMSO			
Li ⁺	35.11	25.09	3.27
Na ⁺	43.89	31.37	2.61
K ⁺	46.42	33.17	2.47
Cl ⁻	62.55	44.71	1.84
Br ⁻	56.54	40.41	2.03
I ⁻	57.45	41.06	2.01

Conductometric Study in Acetonitrile mixtures at 298.15 K

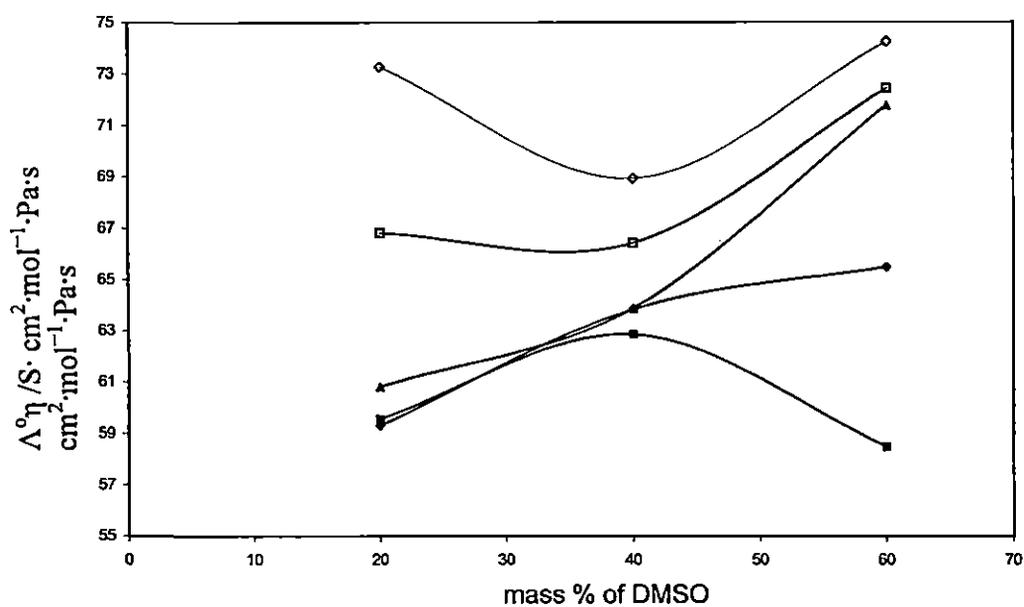


Fig. 1 Plot of Walden product, $\Lambda^{\circ}\eta$ of LiBr (◆), LiI (■), NaBr(▲), NaI(□), and KI (◇) in different DMSO + Acetonitrile mixtures containing 20, 40, and 60 mass% of DMSO at 298.15K.

Conductometric Study in Acetonitrile mixtures at 298.15 K

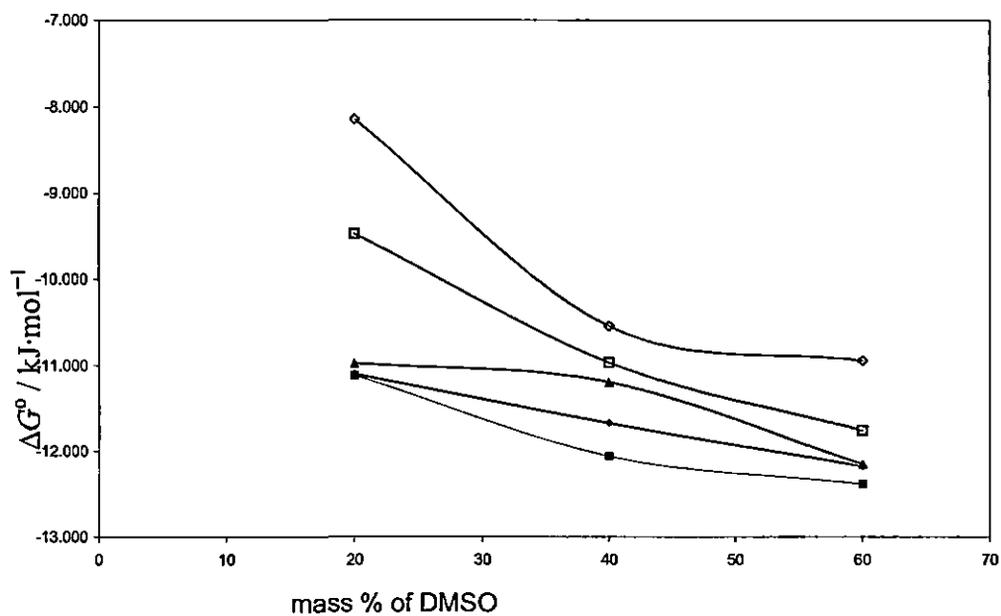


Fig. 2. Plot of standard Gibbs energy change, ΔG° of LiBr (♦), LiI (■), NaBr(▲), NaI(□), and KI (○) in different DMSO + Acetonitrile mixtures containing 20, 40, and 60 mass% of DMSO. at 298.15 K

C.2: Ion-Pair and Triple-Ion Formation by Some Tetraalkyl ammonium Iodides in Binary Mixtures of 1,4-Dioxane +Tetrahydrofuran

C.2.1. Introduction

Progress in battery technology using the lithium electrolytes in ethereal solution¹ has occurred largely in the last decade. Recently, there has been a renewed interest,² in the study of association or dimerisation of electrolytes in the media of low permittivity. In media of low permittivity, salts are generally so associated that the states of the ionic species in solutions are most difficult to elucidate. A number of conductometric³ and related studies of different electrolytes in non-aqueous solvents-specially mixed solvents have been made for their optimal use in high energy batteries⁴ and for understanding organic reaction mechanisms⁵ Ionic association of salts in solution depends upon the mode of solvation of its ions⁶⁻¹⁰, which in its turn depends on the nature of the solvent or solvent mixtures. 1,4-dioxane (DO) and tetrahydrofuran (THF) are polar aprotic solvents of low permittivity, each with great present-day synthetic and industrial importance. They are frequently used in electrical conductance studies^{3,4,11,12} and in high-energy batteries^{3,4,11,12}. Tetraalkylammonium salts are characterized by their low surface charge density and they are little or not solvated in solution^{12,13}. Hence in this paper we reported the electrical conductances of some tetraalkylammonium iodides, R₄NI (R=Pentyl to heptyl) in low-permittivity mixtures containing 10, 20 and 30 mass% of 1,4-dioxane in tetrahydrofuran (THF).

C.2.2. Experimental Section

C.2.2.1 Materials

1,4-dioxane and tetrahydrofuran were purchased from Merck, India and purified as reported earlier^{13,14}. The salts Pen₄NI, Hex₄NI and Hep₄NI of prouss grade were purchased from Aldrich, Germany and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium¹⁵. After filtration, the salts were dried in oven for few hours.

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C.2.2.2 Apparatus and Procedure

Binary solvent mixtures have been prepared by mixing required volume of 1,4-dioxane and tetrahydrofuran with earlier conversion of required mass of each liquid into volume at 298.15 K using literature densities¹⁶. A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The conversion of molality into molarity was accomplished using density values. The uncertainty of molarity of different salt solutions is evaluated to $(0.0001 \text{ mol} \cdot \text{dm}^{-3})$. The values of dielectric constant (ϵ) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner¹⁷.

Densities (ρ) were measured with an Ostwald –Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene¹⁸. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at $\pm 0.01 \text{ K}$ of the desired temperature. The pycnometer was then removed from the thermostat, properly dried and weighed in an electronic balance with a precision of $\pm 0.01 \text{ mg}$. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The density values were reproducible to $\pm 3 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature¹⁹⁻²¹. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to $\pm 0.01 \text{ K}$. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to $\pm 0.1 \text{ s}$. At least three repetitions of each data reproducible to $\pm 0.1 \text{ s}$ were taken to average the flow times. The accuracy of the viscosity measurements, based on our work on several pure liquids, was $\pm 0.003 \text{ mPa} \cdot \text{s}$. The details of the methods and measurement techniques had been described elsewhere¹³⁻¹⁴. The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy $\pm 0.01\%$) using a dip-type immersion conductivity cell, CD-10 having cell constant $0.1 \pm 10\%$. Measurements were made in a water bath maintained within $298.15 \pm 0.01 \text{ K}$ and the cell was calibrated by Lind et. at method.²² The conductance data were reported at a frequency of 1 KHz and the precision was $\pm 0.3\%$.

C.2.3. Results and discussion

The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. The concentrations (c) and equivalent conductances (Λ) of R_4NI (R=Pentyl to heptyl) in different binary solvent mixtures of 1,4-dioxane and tetrahydrofuran are given in Table 2.

Figure 1-3 represents the plots of equivalent conductance (Λ) versus square root of salt concentration (\sqrt{c}) for the salts under investigations at 298.15 K in different binary mixtures of 1,4-dioxane and tetrahydrofuran. A minimum has been found for all the electrolytes suggesting the possible formation of triple-ions in these solutions. Fuoss and Krauss as early as in 1933 introduced the concept of triple ion formation from uni-univalent electrolytes to explain the minima in the relation between the equivalent conductance and the concentration of tetraisoamylammonium nitrate in 1,4-dioxane + water mixture ($\epsilon < 12$). The classical Fuoss-Kraus theory of triple ion²³ formation can be presented by the eqn^{24,25}.

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

with, β' where is the Debye-Huckel activity coefficient term, defined by $\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5}$ is the Debye-Huckel term of the activity coefficient,

$$f = \exp \left[- \left(\frac{2.303}{\Lambda_0^{1/2}} \right) \beta' (c\Lambda)^{1/2} \right], \text{ and } S \text{ is the Onsager conductance term of the conductance}$$

equation, $\Lambda = \Lambda_0 - S \left(\frac{c\Lambda}{\Lambda_0} \right)^2$, defined by

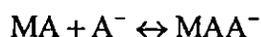
$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\epsilon T)^{0.5}}$$

where the units of Λ_0 and η are $S \cdot cm^2 \cdot mol^{-1}$ and poise, respectively. Also, Λ_0 is the sum of the equivalent conductance of the simple ions at infinite dilution and Λ_0^T is the sum of the conductances of the two triple ions $R_4N(I_2)^-$ and $(R_4N)_2I^+$ for R_4NI salts, K_P and K_T are the ion-pair and triple-ion formation constants. To make eq. 1 applicable, the symmetrical approximation of the two possible constant of triple ions equal to each other has been adopted²

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and Λ_0 values for the studied electrolytes has been calculated following the scheme as suggested by B. S. Krumgalz.¹²

The calculated values have been listed in Table 3. Linear regression analysis of eq. 1 gives intercept and slope; the values have been listed in Table 3. The K_p and K_T thus evaluated are listed in Table 4. A perusal of Table 4 shows that the major portion of the electrolytes exist as ion-pairs with only a negligible portion as triple ions. The observed difference in K_p and K_T values can be explained by molecular scale model:^{26,27}



It is likely possible that association of R_4N^+ cations with solvent components shifts the above equilibrium towards left, thus decreasing K_p values and increasing K_T values. The ion-pair and triple-ion concentrations (C_p and C_T , respectively) of the electrolytes at the highest electrolyte concentration have been derived using eqs²⁵⁻²⁷ 3 to 6 and listed in Table 4.

$$\alpha = (K_p c)^{-0.5} \quad (3)$$

$$\alpha_T = \frac{K_T}{\sqrt{K_p}} c^{0.5} \quad (4)$$

$$C_p = c(1 - \alpha - 3\alpha_T) \quad (5)$$

$$C_T = \frac{K_T}{\sqrt{K_p}} c^{1.5} \quad (6)$$

It was observed that dielectric constants of the binary solvent mixtures decreased as the amount of 1,4-dioxane increased in the solvent mixtures. The concomitant increase in K_T and C_T values suggests that R_4N^+ cations are preferable more solvated by 1,4-dioxane than by tetrahydrofuran. On the contrary, the steric hindrance caused by the CH_2 - group adjacent to the ethereal group of the cyclic ethers may cause solvation hindrance favouring the anion I^- as a

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competitor for the first coordination shell of R_4N^+ cations. This may shift the above equilibrium towards right increasing K_p values.

Table 4 shows that for a particular solvent mixture i. e., for a particular value of dielectric constant of the solvent mixture, K_p values are in the order: $Pen_4NI > Hex_4NI > Hep_4NI$ and that of K_T values is: $Pen_4NI < Hex_4NI < Hep_4NI$. This suggests that smaller R_4N^+ cations tend to remain more as ion-pairs than larger ones, which in their turn has greater capacity to form triple ions. This also supports our earlier view of preferential solvation¹⁰ of R_4N^+ cations by 1,4-dioxane in the electrolyte solutions.

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Table 1. Density ρ , viscosity η , and dielectric constant ϵ , of different binary mixtures of 1,4-DO and THF at $T = 298.15$ K

Solvent Mixture	$\rho \times 10^{-3} / \text{kg} \cdot \text{m}^{-3}$		$\eta / \text{mPa} \cdot \text{s}$		ϵ
	Exp.	Lit.	Exp.	Lit.	
0 mass% of DO	0.8807	0.8807 ¹⁶	0.4630	0.4630 ¹⁶	7.58 ¹¹
10 mass% of DO	0.8941	-	0.0049	-	7.04 ^a
20 mass% of DO	0.9071	-	0.0051	-	6.51 ^a
30 mass% of DO	0.9190	-	0.0053	-	5.96 ^a
100 mass% of DO	1.0305	1.0305 ¹⁶	1.2000	1.2000 ¹⁶	2.21 ¹¹

^a Calculated using the scheme given at ref. no 17.

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Table 2. The concentrations c and equivalent conductances Λ of R_4NI (R=Pentyl to heptyl) in different binary solvent mixtures of 1,4-DO and THF at $T = 298.15$ K

$c \times 10^4$ /mol·dm ⁻³	Λ /S·cm ² ·mol ⁻¹	$c \times 10^4$ /mol·dm ⁻³	Λ /S·cm ² ·mol ⁻¹	$c \times 10^4$ /mol·dm ⁻³	Λ /S·cm ² ·mol ⁻¹
10 mass% of DO					
Pen₄NI		Hex₄NI		Hep₄NI	
0.8046	7.02	0.6367	8.12	0.3419	12.27
0.8138	6.86	0.6469	8.04	0.3754	11.64
0.8294	6.60	0.6541	7.98	0.4052	11.13
0.8385	6.46	0.6631	7.91	0.4319	10.77
0.8549	6.26	0.6696	7.88	0.4559	10.48
0.8674	6.46	0.6754	7.89	0.4776	10.52
0.8702	6.52	0.6806	7.93	0.4973	10.84
0.8726	6.59	0.6851	7.98	0.5153	11.33
20 mass% of DO					
0.4957	4.94	0.5460	3.98	0.6037	6.38
0.5016	4.83	0.5518	3.94	0.6142	4.94
0.5077	4.74	0.5598	3.88	0.6288	3.03
0.5122	4.76	0.5646	3.85	0.6376	1.94
0.5197	4.90	0.5694	3.83	0.6456	1.00
0.5229	4.98	0.5736	3.84	0.6541	0.55
0.4788	5.21	0.5764	3.86	0.6625	1.63
0.4839	5.12	0.5808	3.90	0.6672	2.53
30 mass% of DO					
0.2156	2.77	0.3125	4.97	0.5589	2.74
0.2564	2.70	0.3247	3.71	0.5675	2.30
0.2906	2.64	0.3420	2.13	0.5749	1.92
0.3481	2.56	0.3536	1.13	0.5813	1.63
0.3827	2.53	0.3657	0.35	0.5869	1.49
0.3986	2.53	0.3758	1.23	0.5917	1.62
0.4124	2.55	0.3819	2.13	0.5962	1.86
0.4274	2.58	0.3868	2.96	0.6001	2.09
0.4406	2.62				
0.4508	2.65				

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Table 3. The calculated limiting conductance Λ_0 , slope and intercepts of eq. 1 for R_4NI (R=Pentyl to heptyl) in different binary solvent mixtures of 1,4-DO and THF at $T = 298.15$ K

Solvent mixture	Λ_0 /S · cm ² · mol ⁻¹	Slope	Intercept
10 mass% of DO		Pen₄NI	
	199.21	0.0064 (±0.0003)	-0.011 (±0.002)
		Hex₄NI	
	195.57	0.0346 (±0.0002)	-0.029 (±0.003)
		Hep₄NI	
	193.34	0.0974 (±0.0001)	-0.050 (±0.001)
20 mass% of DO		Pen₄NI	
	192.20	0.1315 (±0.0002)	-0.108 (±0.001)
		Hex₄NI	
	188.68	0.2975 (±0.0002)	-0.225 (±0.002)
		Hep₄NI	
	186.53	1.4633 (±0.0001)	-0.837 (±0.002)
30 mass% of DO		Pen₄NI	
	185.92	5.1354 (±0.0003)	-1.042 (±0.002)
		Hex₄NI	
	182.52	0.3102 (±0.0001)	-0.173 (±0.003)
		Hep₄NI	
	180.44	0.5852 (±0.0004)	-0.585 (±0.006)

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Table 4. Maximum concentration c , ion-pair constant K_p , triple-ion constant K_T , ion-pair concentration C_p , and triple-ion concentration C_T for R_4NI (R=Pentyl to heptyl) in different binary solvent mixtures of 1,4-DO and THF at $T = 298.15$ K

Salt	$c^* \times 10^4$ /mol·dm ⁻³	$K_p \times 10^5$ /mol·dm ⁻³	K_T /mol·dm ⁻³	$C_p \times 10^{-5}$ /mol·dm ⁻³	$C_T \times 10^{-10}$ /mol·dm ⁻³
10 mass% of DO					
Pen₄NI	0.8726	3316.37	0.883	8.71	0.40
Hex₄NI	0.6851	450.34	1.783	6.72	1.51
Hep₄NI	0.5153	132.90	2.753	4.95	2.81
20 mass% of DO					
Pen₄NI	0.4839	31.55	1.823	4.81	3.98
Hex₄NI	0.5805	7.03	1.983	4.92	6.16
Hep₄NI	0.6672	0.50	2.622	3.85	13.40
30 mass% of DO					
Pen₄NI	0.4508	0.32	7.389	3.50	4.25
Hex₄NI	0.3868	11.12	2.688	3.25	6.64
Hep₄NI	0.6001	1.26	1.728	3.77	23.50

*Maximum concentrations at which calculations have been performed.

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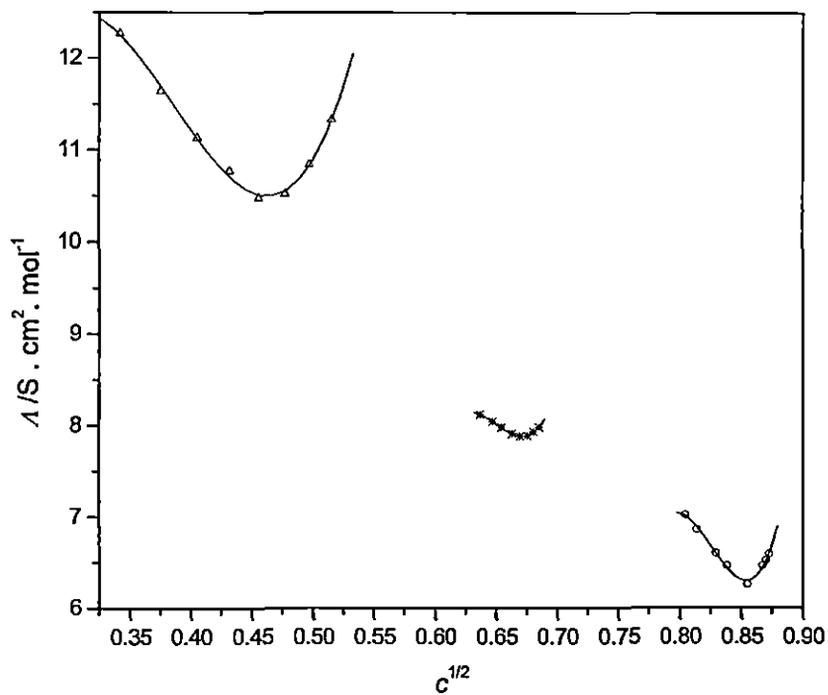


Figure 1. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at $T = 298.15$ K in 10 mass% of DO + THF solutions. O, Tetrapentylammonium iodide; *, Tetrahexylammonium iodide; Δ , Tetrheptylammonium iodide.

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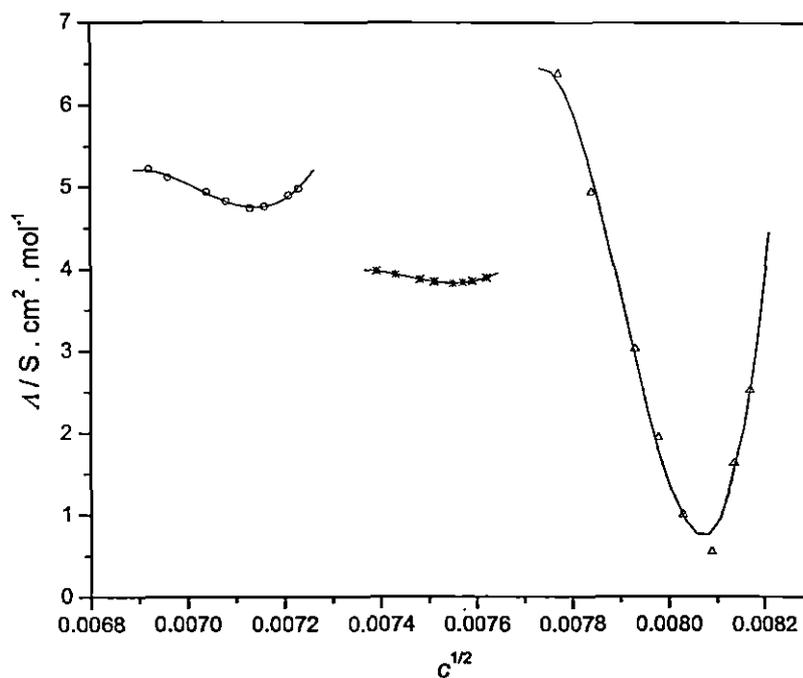


Figure 2. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at $T = 298.15$ K in 20 mass% of DO + THF solutions. O, Tetrapentylammonium iodide; *, Tetrahexylammonium iodide; Δ , Tetrheptylammonium iodide.

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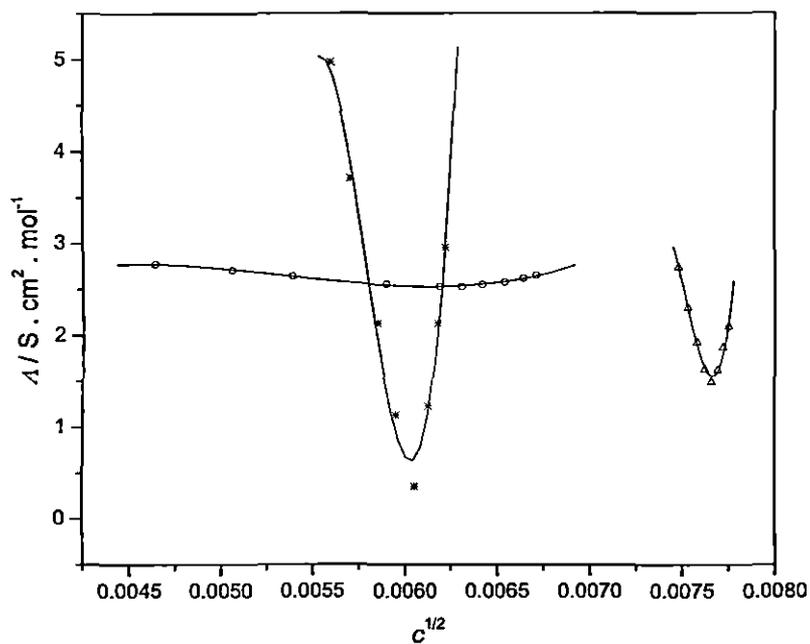


Figure 3. The plots of equivalent conductance (Λ) versus square root of salt concentration ($c^{1/2}$) for the salts under investigations at $T = 298.15$ K in 30 mass% of DO + THF solutions. O, Tetrapentylammonium iodide; *, Tetrahexylammonium iodide; Δ , Tetrheptylammonium iodide.