

CHAPTER-VI

B. Ion Association and Solvation Behavior of Tetraalkylammonium Iodides in Binary Mixtures of Dichloromethane + N, N-Dimethylformamide Probed by a Conductometric Study

VI-B.1. Introduction

Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore the ion-ion and ion-solvent interactions can be better studied. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration-dependence of the electrolyte conductivity. Consequently a number of conductometric [1] and related studies of different electrolytes in non-aqueous solvents, specially mixed organic solvents, have been made for their optimal use in high energy batteries [2] and for understanding organic reaction mechanisms [3]. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions [4-8], which in its turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Thus extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years [9-13] to examine the nature and magnitude of ion-ion and ion-solvent interactions. The study of electrolyte solutions in DMF is of interest in organic electrolyte batteries, photo electrochemical cells, electro deposition, wet electrolyte capacitors or electro organic synthesis. DCM is a very interesting solvent with appreciable industrial use in pharmaceutical industry, as a paint stripping agent, aerosols and as adhesives etc. and also as it is a solvent exhibiting high density and low viscosity. Also tetraalkylammonium salts are characterized by their low surface charge density and they show little or no solvation in solution [14, 15] as

such they are frequently selected as desired electrolytes in conductance studies. In continuation of our investigation on electrical conductance [8,10,11] the present work deals with the conductance measurements of some tetraalkylammonium iodides, R₄NI (R = n-butyl to n-heptyl) in binary mixtures of DCM - a non polar aprotic liquid and DMF polar aprotic liquid at 298.15 K.

VI-B.2. Experimental Section

DCM and DMF were purchased from Merck, India and purified by standard methods [16]. The salts n-Bu₄NI (*N,N,N*-tributyl-1-butaminium iodide, CAS: 311-28-4), n-Pen₄NI (*N,N,N*-tripentyl-1-pentaminium iodide, CAS: 2498-20-6), n-Hex₄NI (*N,N,N*-trihexyl-1-hexaminium iodide, CAS: 2138-24-1) and n-Hept₄NI (*N,N,N*-triheptyl-1-heptaminium iodide, CAS: 3535-83-9) of puriss grade were purchased from Aldrich, Germany and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium [16]. After filtration, the salts were dried in an oven for few hours.

Binary solvent mixtures were prepared by mixing required volume of DCM and DMF with earlier conversion of required mass of each liquid into volume at 298.15 K using experimental densities. 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 $\pm 0.0001 \text{ mol}\cdot\text{dm}^{-3}$.

The values of relative permittivity (ϵ_r) of the solvent mixtures were obtained by interpolation of the solvent permittivity data from the literature [17] by cubic spline fitting. The physical properties of the binary solvent mixtures at 298.15 K are listed in **Table 1**. Density measurements of ternary mixtures were performed at atmospheric pressure at $T = (298.15, 308.15, \text{ and } 318.15)$ K by means of vibrating-tube densimeter (Anton Paar, DMA 4500) which was calibrated with distilled water and air. The uncertainty in the density measurement was $\pm 0.0002 \text{ g}\cdot\text{cm}^{-3}$. The temperature was automatically kept constant within ± 0.01 K. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water.

Solvent viscosities were 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 literature [18-20]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa·s. The details of the methods and measurement techniques had been described elsewhere^[11,21]. The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10 having cell constant 0.1 ± 10 %. Measurements were made in a water bath maintained within $T = (298.15 \pm 0.01)$ K and the cell was calibrated by the method proposed by Lind *et al.* [22]. The conductance data were reported at a frequency of 1 KHz and were uncertain to ± 0.3 %.

VI-B.3. Results and Discussions

The concentrations and molar conductances A of R₄NI (R = n-butyl to n-heptyl) in different binary solvent mixtures of DCM (w_1) and DMF (w_2) are given in **Table 2**.

For the solvent mixtures in the range of higher to moderate relative permittivity ($\epsilon_r = 36.71$ -14.49), the conductance curves (A versus \sqrt{c}) were linear and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductances for the electrolytes. However, as the relative permittivity ϵ_r dropped to 8.93 for the 100 mass % of DCM, nonlinearity (**Figure 4**) was observed in conductance curves.

The conductance results have been analyzed by the Fuoss conductance-concentration equation [23,24]. For a given set of conductivity values ($c_j, A_j, j = 1, \dots, n$), three adjustable parameters, the limiting molar conductivity (A_0), the

association constant K_A , and the association diameter R are derived from the following set of equations:

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

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

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

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

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

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

where, R_x is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radius of the ion atmosphere, ϵ is the relative permittivity of the solvent or solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall pairing 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, f is the activity coefficient, T is the absolute temperature, and β is twice the Bjerrum distance.

The computations are performed on a computer using the program suggested by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [25,26]. Now, we input for the program, the number of data, n , followed by ϵ , η (viscosity of the solvent mixture), initial Λ_0 value, T , ρ (density of the solvent mixture), mole fraction of the first component,

molecular weights, M_1 and M_2 along with c_j , Λ_j values where $j = 1, 2, \dots, n$ and an instruction to cover pre-selected range of R values.

In practice, calculations are performed by finding the values of Λ_0 and σ which minimize the standard deviation,

$$\sigma^2 = \sum_{j=1}^n \frac{[\Lambda_j(\text{calc}) - \Lambda_j(\text{obs})]^2}{n-m} \quad (7)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two parameter fit ($m = 2$). As for the electrolytes studied in the solvent mixtures ($w_1 = 0.20 - 0.80$) no significant minima observed in the σ versus R curves and the R values were arbitrarily preset at the centre to centre distance of solvent-separated pair [8];

$$R = a + d \quad (8)$$

where a is the sum of the crystallographic radii of the cation and anion and d is the average distance corresponding to the side of a cell occupied by a solvent molecule.

The distance, d is given by [24],

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

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

$$M_{av} = \frac{M_1 M_2}{W_1 M_2 + W_2 M_1}$$

where W_1 is the weight fraction of the first component of molecular weight M_1 . The values of Λ_0 , K_A and R obtained by this procedure are reported in **Table 3**.

The Walden's product, $\Lambda_0 \eta_0$ [27] of an ion is also calculated for the various solvent compositions and the results have been depicted in **Figure 1**.

Figure 2 predicts the nature of the curves for the Gibbs' energy of ion-pair formation, ΔG^0 for the binary mixtures studied here. ΔG^0 is given by the relationship [28],

$$\Delta G^0 = -RT \ln K_A$$

The limiting molar conductivity values (Λ_0) of tetra-n-butylammonium iodide are always found to be higher than those of its higher homologues (see **Figure 1**). This means that the mobility of the (n-Bu₄N⁺) is greater than that of the (n-Pen₄N⁺), (n-Hex₄N⁺), (n-Hept₄N⁺) (anion being common) in all of the mixed solvent media. Now, a comparison of this trend in mobility with the crystallographic sizes of these ions, which is in the order [29] n-Bu₄N⁺ < n-Pen₄N⁺ < n-Hex₄N⁺ < n-Hept₄N⁺, shows that the larger the size of the bare ion, the smaller is its ionic mobility. This indicates that the relative actual sizes of these ions as they exist in solutions follow the order: n-Bu₄N⁺ < n-Pen₄N⁺ < n-Hex₄N⁺ < n-Hept₄N⁺. This observation clearly demonstrates that the electrostatic ion-solvent interaction is very weak for these ions in DCM +DMF solutions, which is to be expected because of their large crystallographic radii [18] and hence low surface charge density. Had these interactions been very strong in this medium, the limiting molar conductivity values should have been in the reverse order: n-Bu₄N⁺ < n-Pen₄N⁺ < n-Hex₄N⁺ < n-Hept₄N⁺, because a smaller ion with greater surface charge density is expected to associate more solvent molecules thus resulting in a bigger solvodynamic entity, which is obviously not the case here. A similar trend in the Walden products, $\Lambda_0\eta_0$ (**Table 3**), also points to the same conclusion.

Table 3 reveals that the limiting molar conductances (Λ_0) for the electrolytes decreases with the increase of DCM content in the solvent mixtures. This fact is in line with the decrease of the relative permittivity (ϵ_r) of the solvent mixtures [14,30]. Although, the decreasing trend of viscosity for the solvent mixtures with increasing content of DCM suggests concomitant increase in limiting molar conductances [14,30] for the electrolytes, but we observed an opposite trend. This

trend suggests predominance of relative permittivity (ϵ_r) over the solvent viscosity (η_0) in effecting the electrolytic conductances in these media.

In a particular solvent mixture the limiting molar conductances (Λ_0) of the electrolytes under investigation decreases as the size of the alkyl group increases, in contraposition to the conductance behaviour of the alkali metal cations, as tetraalkylammonium salts are characterized by their low surface charge density [14, 15].

There is a marked characteristic behaviour in the K_A values. The K_A for all salts increases as the concentration of DCM increases in the mixture, which supports significant association.

The decreasing trend of Walden products ($\Lambda_0\eta_0$) in **Table 3** is mainly in accordance with the concomitant decrease of both the solvent viscosity and limiting molar conductance of the electrolytes.

This is justified as the Walden product of an ion or solute is inversely proportional to the effective radius of the ion, or solute in a particular solvent, r [31].

$$\Lambda_0\eta_0 = \frac{1}{6\pi r T}$$

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 [6,32]. Though the variation of the Walden product with solvent composition (**Figure 1**) is difficult to interpret quantitatively, still its variation with solvent composition can be explained by preferential salvation [1,33] of tetraalkylammonium ions by DCM and DMF molecules, respectively. At low concentration of DCM, these ions are preferentially solvated by DMF rather than by DCM. 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 $\Lambda_0\eta_0$ go, the calculated values of $\Lambda_0\eta_0$ go are high up to 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 tetraalkylammonium ions by DCM in (DCM+DMF). However this decrease may be due to the Zwanzig [34] solvent relaxation effect.

The starting point for most evaluations of ionic conductance 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. The ionic conductances (λ_0^\pm) for the various cations (R= n-butyl to n-heptyl) in different solvent mixtures ($w_1= 0.20$ to 0.80) were calculated using tetrabutylammonium tetraphenyl borate ($Bu_4N\text{BPh}_4^-$) as a reference electrolyte following the scheme as suggested by B. Das *et al.* [35]. We calculated its limiting molar conductances (λ_0^\pm) in our solvent compositions by interpolation of conductance data from literature [18] using cubic spline fitting. The values were in turn utilizing for the calculation of Stoke's radii (r_s) according to the classical expression [36],

$$r_s = \frac{F^2}{6\pi N_A \eta_0 \lambda_0^\pm} \quad (9)$$

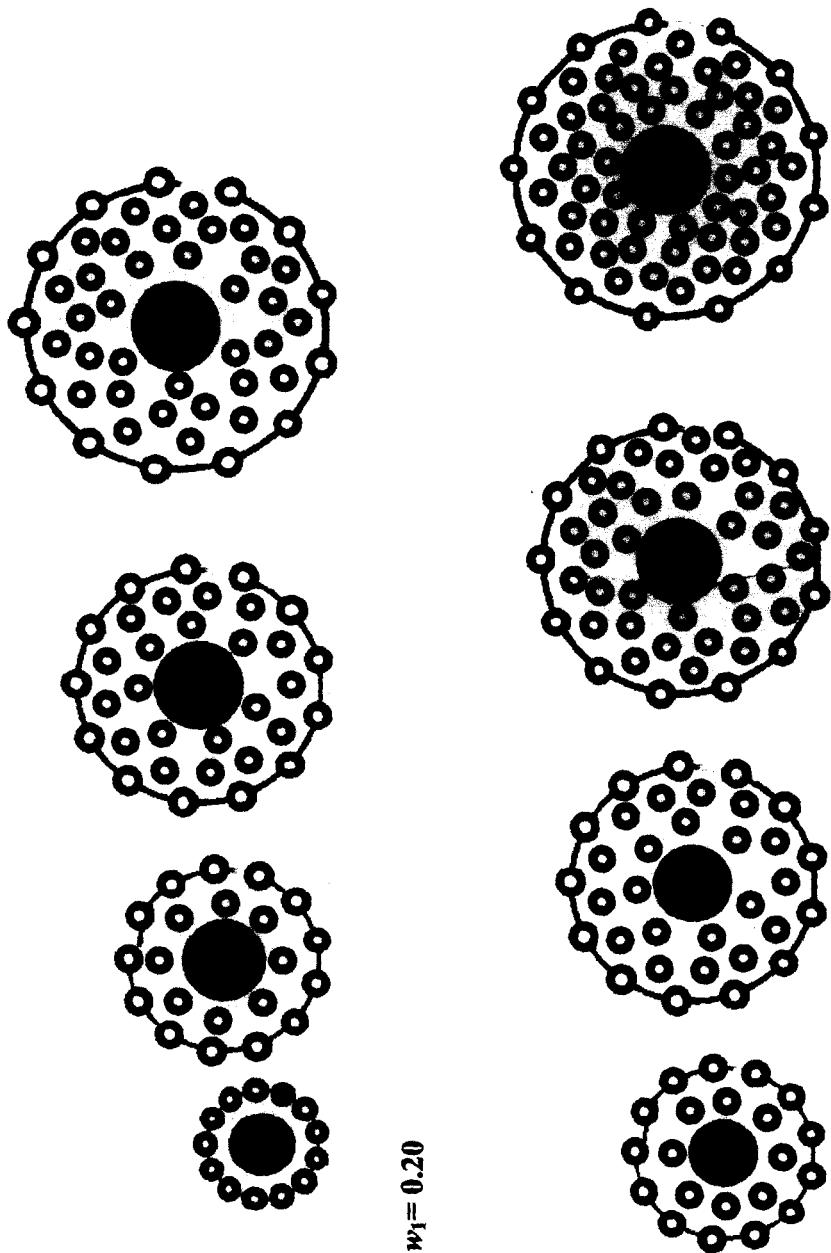
Limiting molar conductances (λ_0^\pm), Ionic Walden products ($\lambda_0^\pm \eta_0$), Stoke's radii (r_s) and crystallographic radii (r_c) are presented in **Table 4**. The trend in ionic Walden products ($\lambda_0^\pm \eta_0$) just mimics the trend in Walden product ($\Lambda_0 \eta_0$) for all electrolytes in the solvent mixtures ($w_1= 0.20$ to 0.80). The position of the curves in **Figure 1** and **Figure 2** ($\Lambda_0 \eta_0$ and $\lambda_0^\pm \eta_0$ versus w_1) suggest a relationship n-Bu₄NI < n-Pen₄NI < n-Hex₄NI < n-Hept₄NI for Stokes' radius, just similar to their ionic radii order. For tetraalkylammonium ions, the Stokes' radii are lower or comparable to their crystallographic radii (r_c), particularly for smaller ions. This suggests that these ions are comparatively less solvated than alkali metal ions due to their intrinsic low surface charge density. Since the ions are often far from being spherical and since they are of the same order of magnitude as the solvent molecules, it is questionable whether the retarding effect of the later can be accurately described by the macroscopic viscosity as has been done in the derivation of the Stokes law.

Hence, the Stokes law cannot be considered quantitatively reliable. Such failure of this law has also been observed earlier in other solvent media [37,38].

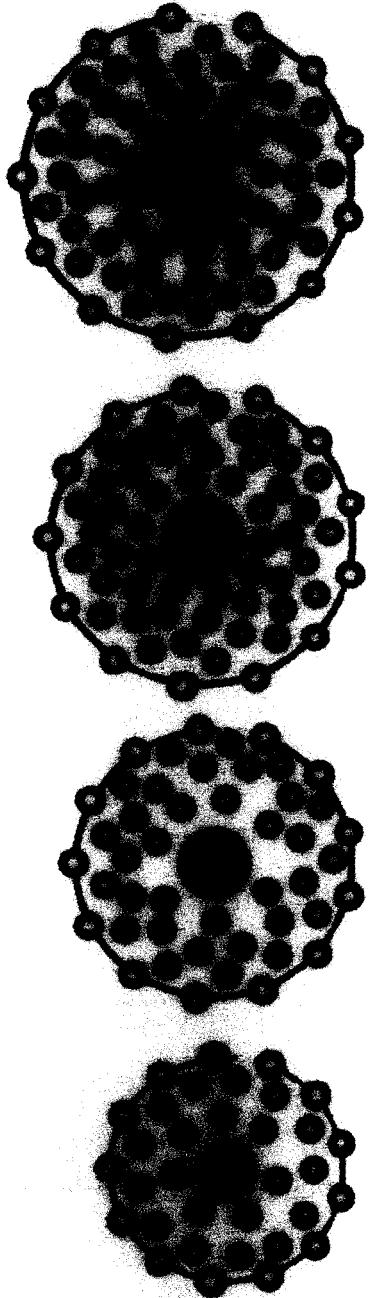
Figure 3 points out the nature of curve for the Gibbs free energy for ion-pair formation, ΔG^0 , which clearly predicts that the tendency for ion-pair formation decreases significantly with an increase in the association factor for the tetraalkylammonium halides in (DCM +DMF) medium. The ΔG^0 curve in **Figure 3** along with the other parameters mentioned above are in accordance with the results observed by Barthel *et al.* [28] and Hazra *et al.* [6,39].

The plausible diagram of solvation of ions, at a particular concentration, in the solvent mixtures studied here in view of various derived parameters is given below. Here C-4, C-5, C-6 and C-7 refer to n-Bu₄NI, n-Pen₄Ni, n-Hex₄Ni, n-Hept₄Ni respectively and the red circles refer to the DCM (w_1) and DMF (w_2) solvent mixture.

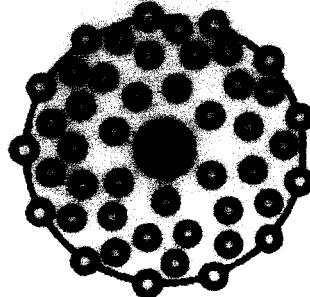
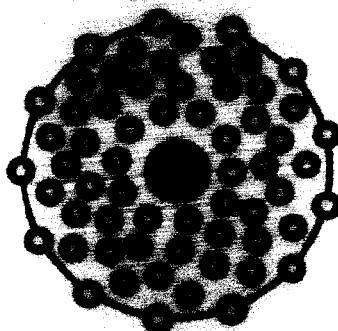
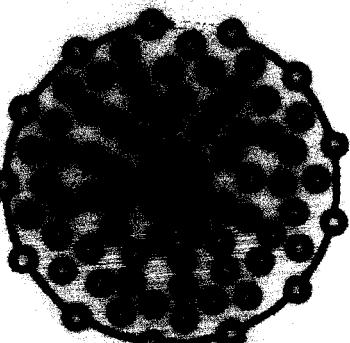
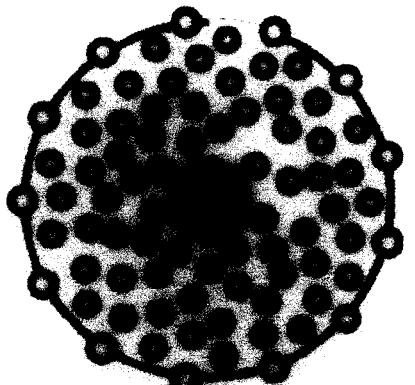
Here, as the size of the alkyl group increases the limiting molar conductances (Λ_0) of the electrolytes under investigation decreases. This is depicted in the above figure which suggests that as the size of the alkyl group increases, at a particular concentration of DCM, solvation of ions in the solvent mixtures also increases and hence the decrease in limiting molar conductances (Λ_0). Similar trend is observed with increasing concentration of DCM.



$w_1 = 0.40$



$w_1 = 0.60$



$w_1 = 0.80$

The experimental values of the molar conductances, Λ against the respective concentration, c of the tetraalkylammonium iodide in 100 mass % of DCM are presented in **Table 5**. **Figure 4** gives a representative plot for Λ vs. \sqrt{c} . All the salts follow the same trend, i.e., Λ decreases with increasing concentration, reaches a minimum and then increases.

The conductance data for all the electrolytes in 100 mass % of DCM ($\epsilon_r = 8.93$) was analyzed by the classical Fuoss-Kraus theory of triple ion formation in the form [40, 41] :

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (10)$$

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by:

$$g(c) = \frac{\exp\{-2.303 \beta' (c\Lambda)^{0.5} / \Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5} / \Lambda_0^{1.5}\}(1 - \Lambda / \Lambda_0)^{0.5}} \quad (11)$$

$$\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5} \quad (12)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\epsilon T)^{0.5}} \quad (13)$$

In the above equations, Λ_0 is the sum of the molar 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 $(R_4N)_2^+I^-$ for R_4NI salts, $K_p \approx K_A$ and K_T are the ion-pair and triple-ion formation constants. To make Eq. (10) applicable, the symmetrical approximation of the two possible constant of triple ions equal to each other has been adopted [42] and Λ_0 values for the studied electrolytes has been calculated following the scheme as suggested by B. S. Krumgalz [15]. The calculated values have been listed in **Table 5**. Linear regression analysis of Eq. (10) gives intercept and slope; the values have been listed in **Table 5**. In solving Eq. (10), Λ_0^T , the triple ion conductance, was set equal to $2/3 \Lambda_0$. This has specially been done so for relative comparison of K_T values for the same electrolyte in different solvent

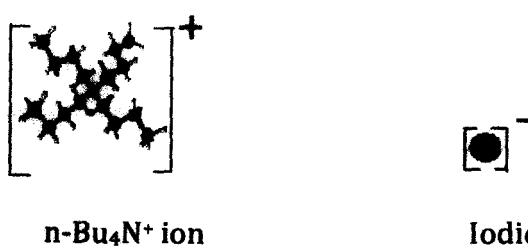
mixtures. Applying the Fuoss-Kraus equation, we obtain K_p, K_T , which are presented in **Table 5.**

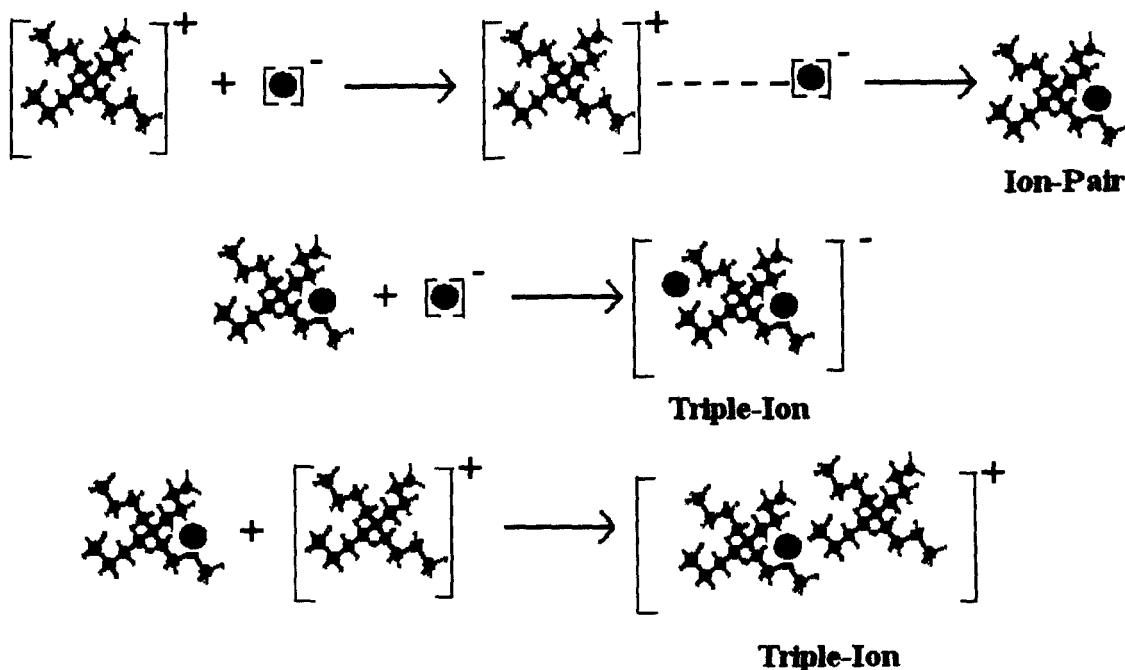
A perusal of **Table 5** shows that the major portion of the electrolytes exists as ion-pairs with a minor portion as triple ions. The tendency of triple ion formation can be judged from the K_T/K_p ratios, which is highest for Hept₄NI. These ratios suggest that strong association between the ions is due to the coulombic interactions as well as to covalent forces in the solution. These results are in good agreement with those of Hazra *et al.* [43]. At very low permittivity of the solvent ($\epsilon_r < 10$) [31], electrostatic interactions are very strong permitting the ion-pair to attract free anions/cations from solution bulk and form triple ions [40,44] which acquire the charge of the combining ion, i.e.,:



The effect of ternary association [32] thus removes some non-conducting species MA from solution and replace them by triple-ions which increase the conductance manifested by non-linearity observed in conductance curves for the electrolytes in 100 mass % of DCM.

Schematically, the picture of triple-ion formation in pure DCM can be depicted as given below for n-Bu₄NI as an example:





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 Eqs. [43] (17) to (20) and are listed in **Table 5**.

$$\alpha = (K_p c)^{-0.5} \quad (17)$$

$$\alpha_t = \frac{K_t}{\sqrt{K_p}} c^{-0.5} \quad (18)$$

$$C_p = c(1 - \alpha - 3\alpha_t) \quad (19)$$

$$C_t = \frac{K_t}{\sqrt{K_p}} c^{1.5} \quad (20)$$

While highest C_p value is for Bu_4NI , Hept_4NI has the highest C_t value and our results supports the general view that the tendency of ion-pair and triple-ion formation depends on the size and the charge distribution of the ions as well as on the solvent polarity.

VI-A.4. Conclusion

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 DCM in the solvent mixtures. Further, the effect of concentration of DCM on limiting equivalent conductance of tetraalkylammonium ions is less pronounced as compared to that of the alkali metal ion in the present mixed solvent media.

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Table 1. Density (ρ), viscosity (η), and dielectric constant (ε_r) of DCM (1) + DMF (2) at $T = 298.15$ K.

Solvent Mixture	$\rho \times 10^{-3}$ (kg·m ⁻³)	η (mPa·s)	ε_r
	Exp.	Exp.	
$w_1 = 0.00$	0.9443 [14]	0.801 [14]	36.71 [14]
$w_1 = 0.20$	1.0141	0.752	31.54 ^b
$w_1 = 0.40$	1.0832	0.684	25.60 ^b
$w_1 = 0.60$	1.1576	0.577	20.04 ^b
$w_1 = 0.80$	1.2363	0.493	14.49 ^b
$w_1 = 1.00$	1.3161 [44]	0.406 [45]	8.93

^b Obtained by interpolation of literature data from Ref. No [17].

Table 2. The concentrations (c) and molar conductances (Λ) of R_4Ni (R = n-butyl to n-heptyl) in different binary solvent mixtures of DCM (1) + DMF (2) at 298.15 K.

n-Bu ₄ Ni		n-Pen ₄ Ni		n-Hex ₄ Ni		n-Hept ₄ Ni	
$c \times 10^4$ (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)	$c \times 10^4$ (mol·dm ⁻³)	Λ (S cm ² mol ⁻¹)
$w_1 = 0.00$							
A*	A*	9.90	73.66			9.90	69.73
		18.14	72.84			18.15	68.85
		25.12	72.29			25.13	68.20
		31.10	71.95			31.12	67.67
		36.29	71.57	A*	A*	36.30	67.28
		40.82	71.27			40.84	66.93
		44.83	71.00			44.84	66.65
		48.38	70.84			48.40	66.44
		51.57	70.62			51.59	66.29
		54.43	70.47			54.45	66.03
$w_1 = 0.20$							
6.05	67.26	6.08	64.41	6.06	62.19	6.05	61.13
11.10	64.39	11.14	61.62	11.11	59.01	11.10	57.61
15.37	62.15	15.43	59.31	15.39	57.01	15.37	55.10
19.03	60.44	19.10	57.64	19.05	55.55	19.03	53.76
22.20	59.17	22.28	56.34	22.23	54.30	22.20	52.23
24.98	58.08	25.07	55.29	25.01	53.01	24.97	51.50
27.42	57.17	27.53	54.34	27.46	52.08	27.42	50.48
29.60	56.35	29.71	53.58	29.64	51.32	29.60	49.89
31.55	55.62	31.67	52.85	31.59	50.59	31.54	49.17
33.30	54.95	33.42	52.17	33.34	50.21	33.30	48.56
$w_1 = 0.40$							

3.39	66.57	3.36	63.91	3.36	61.05	3.36	60.33
6.21	63.66	6.16	60.97	6.16	57.92	6.15	56.86
8.60	61.36	8.53	58.40	8.53	55.82	8.52	54.29
10.65	59.64	10.57	57.26	10.56	54.46	10.55	52.91
12.43	58.46	12.33	56.16	12.32	53.21	12.31	51.47
13.98	57.56	13.87	55.04	13.86	51.89	13.85	50.72
15.35	56.67	15.23	54.12	15.22	50.99	15.21	49.78
16.57	55.51	16.44	53.32	16.42	50.14	16.41	49.14
17.66	54.92	17.52	52.78	17.50	49.45	17.49	48.27
18.64	54.26	18.49	51.82	18.48	49.17	18.46	47.76
<i>w₁ = 0.60</i>							
1.61	64.98	1.61	62.53	1.61	60.11	1.61	59.46
2.96	62.45	2.96	59.05	2.95	56.78	2.96	55.64
4.10	60.29	4.09	57.28	4.09	54.65	4.10	53.04
5.07	58.53	5.07	55.75	5.06	53.47	5.07	51.16
5.92	57.13	5.91	54.26	5.90	52.19	5.92	49.74
6.65	56.05	6.65	53.52	6.64	50.81	6.66	48.86
7.31	55.21	7.31	52.66	7.29	49.85	7.31	47.89
7.89	54.49	7.89	51.87	7.87	49.14	7.89	47.35
8.41	53.78	8.40	51.24	8.39	48.43	8.41	46.72
8.87	53.04	8.87	50.42	8.86	48.23	8.88	46.11
<i>w₁ = 0.80</i>							
0.61	63.88	0.61	61.38	0.61	58.97	0.61	57.71
1.13	61.04	1.12	58.27	1.13	55.74	1.13	54.52
1.56	58.67	1.55	56.13	1.56	53.61	1.56	52.31
1.93	56.92	1.92	54.60	1.93	52.16	1.93	50.71
2.25	55.60	2.24	53.11	2.25	50.95	2.25	49.29
2.54	54.36	2.52	52.00	2.54	49.77	2.54	48.41
2.78	53.50	2.77	51.27	2.78	48.89	2.78	47.44
3.00	52.51	2.99	50.55	3.00	48.07	3.00	46.90
3.20	52.05	3.18	49.73	3.20	47.32	3.20	46.27
3.38	51.52	3.36	49.27	3.38	46.99	3.38	45.66

$w_1 = 1.00$							
0.91	8.11	0.96	10.67	0.97	10.85	0.98	11.06
0.96	7.89	1.01	10.46	1.01	10.64	1.02	10.89
1.00	7.72	1.04	10.29	1.05	10.46	1.07	10.66
1.04	7.55	1.09	10.08	1.09	10.27	1.12	10.50
1.08	7.38	1.13	9.91	1.13	10.13	1.15	10.36
1.12	7.25	1.17	9.77	1.17	9.98	1.19	10.20
1.16	7.15	1.20	9.63	1.20	9.84	1.22	10.08
1.19	7.07	1.23	9.52	1.24	9.75	1.26	10.02
1.22	7.11	1.27	9.56	1.27	9.81	1.28	10.07
1.26	7.21	1.29	9.62	1.29	9.89	1.31	10.13

A* indicates raw values of c & Λ for the salts n-Bu₄NI, n-Hex₄Ni are not given since Λ_0 values for those salts are provided in the literature [46].

Table 3. Limiting molar conductance (Λ_0), association constant (K_A), co-sphere diameter (R), standard deviations of experimental Λ from Eq. (1) and Walden products ($\Lambda_0\eta_0$) for the electrolytes in different binary solvent mixtures of DCM (1) + DMF (2) at 298.15 K.

w_1	$\Lambda_0 /$ (S cm ² mol ⁻¹)	K_A	$R / (\text{\AA})$	$\Lambda_0\eta_0 /$ (S cm ² mol ⁻¹ mPa s)	$\Delta G^0 /$ (kJ·mol ⁻¹)	σ
n-Bu ₄ NI						
0.00	78.00 [46]	11.1 [46]	12.17	62.48	-5.97	0.05
0.20	74.29	166.6	12.07	55.87	-12.68	0.23
0.40	73.65	301.8	12.01	50.38	-14.15	0.26
0.60	72.20	634.5	11.95	41.66	-16.00	0.32
0.80	71.57	1864.6	11.89	35.28	-18.67	0.29
n-Pen ₄ NI						
0.00	75.81	11.41	12.49	60.72	-6.03	0.04
0.20	71.54	178.2	12.42	53.80	-12.85	0.24
0.40	70.56	305.4	12.36	48.26	-14.18	0.26
0.60	69.18	661.9	12.30	39.92	-16.10	0.27
0.80	68.65	1898.5	12.24	33.84	-18.71	0.23
n-Hex ₄ NI						
0.00	73.67 [46]	14.5 [46]	12.80	59.01	-6.63	0.05
0.20	69.09	184.8	12.73	51.96	-12.94	0.24
0.40	68.09	344.7	12.67	46.57	-14.48	0.26
0.60	67.17	741.7	12.61	38.76	-16.38	0.27
0.80	66.19	2001.4	12.55	32.63	-18.84	0.23
n-Hept ₄ NI						
0.00	71.99	15.72	13.08	57.66	-6.83	0.03
0.20	68.39	201.9	13.01	51.43	-13.16	0.13
0.40	67.49	378.9	12.95	46.16	-14.72	0.15
0.60	66.85	889.8	12.89	38.57	-16.83	0.15
0.80	64.99	2104.3	12.83	32.04	-18.97	0.14

Table 4. Limiting ionic conductance (λ_0^\pm), ionic Walden product ($\lambda_0^\pm \eta_0$), Stokes' radii (r_s) and crystallographic radii (r_c) at 298.15 K.

Ion	$\lambda_0^\pm /$ (S cm ² mol ⁻¹)	$\lambda_0^\pm \eta_0 /$ (S cm ² mol ⁻¹ mPa s)	$r_s(\text{\AA})$	$r_c(\text{\AA})$
$w_1 = 0.20$				
n-Bu ₄ N ⁺	27.94	21.01	3.90	4.94
n-Pen ₄ N ⁺	25.19	18.94	4.33	5.29
n-Hex ₄ N ⁺	22.73	17.09	4.80	5.60
n-Hept ₄ N ⁺	22.04	16.57	4.95	5.88
I ⁻	46.35	34.86	2.35	2.16
$w_1 = 0.40$				
n-Bu ₄ N ⁺	28.71	19.64	4.18	4.94
n-Pen ₄ N ⁺	25.62	17.52	4.68	5.29
n-Hex ₄ N ⁺	23.15	15.83	5.18	5.60
n-Hept ₄ N ⁺	22.55	15.42	5.32	5.88
I ⁻	44.94	31.11	2.64	2.16
$w_1 = 0.60$				
n-Bu ₄ N ⁺	29.13	16.81	4.88	4.94
n-Pen ₄ N ⁺	26.11	15.07	5.45	5.29
n-Hex ₄ N ⁺	24.10	13.91	5.90	5.60
n-Hept ₄ N ⁺	23.78	13.72	5.98	5.88
I ⁻	43.07	24.26	3.38	2.16
$w_1 = 0.80$				
n-Bu ₄ N ⁺	29.89	14.74	5.57	4.94
n-Pen ₄ N ⁺	26.97	13.30	6.17	5.29
n-Hex ₄ N ⁺	24.51	12.08	6.79	5.60
n-Hept ₄ N ⁺	23.31	11.49	7.14	5.88
I ⁻	41.68	19.83	4.14	2.16

Table 5. The calculated limiting molar conductance (Λ_0), slope and intercepts of Eq. (10), maximum concentration (c), ion-pair formation constant K_p , triple-ion formation constant K_T , ion-pair concentration C_p , and triple-ion concentration C_T for R₄NI (R = n- butyl to n-heptyl) in 100 mass % of DCM at 298.15 K.

$\Lambda_0 /$ (S cm ² mol ⁻¹)	Slope	Intercept	$c^a \times 10^4$ (mol·dm ⁻³)	$K_p \times 10^5$	K_T	$\frac{K_T}{K_p} \times 10^5$	$\log(\frac{K_T}{K_p})$	$C_p \times 10^4$ (mol·dm ⁻³)	$C_T \times 10^6$ (mol·dm ⁻³)
n-Bu ₄ NI									
136.40	4.587	0.209	1.26	4.25	32.87	7.73	-4.114	1.14	0.07
n-Pen ₄ NI									
130.49	8.681	0.277	1.29	2.22	47.00	21.2	-3.674	1.04	0.15
n-Hex ₄ NI									
126.06	15.922	0.275	1.29	2.09	86.74	41.3	-3.384	0.81	0.28
n-Hep ₄ NI									
123.85	20.663	0.278	1.31	1.96	111.40	56.6	-3.247	0.66	0.38

^aMaximum concentrations for which calculations have been performed

Figure 1. Walden products ($A_0\eta_0$) for electrolytes versus w_1 of DCM (1) + DMF (2) mixtures at 298.15 K. ■, n-Bu₄NI; □, n-Pen₄NI; ▲, n-Hex₄NI; Δ, n-Hept₄N.

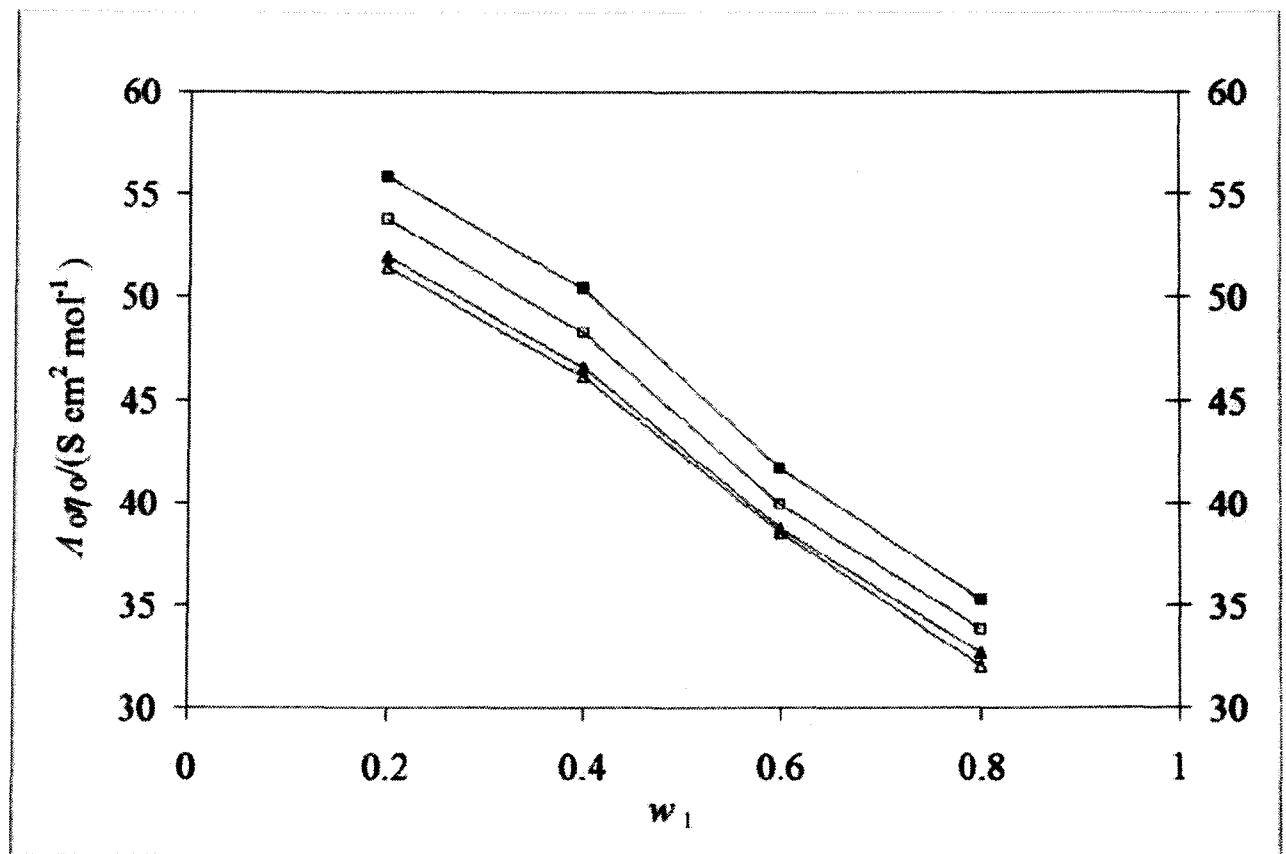


Figure 2. Plot of ionic Walden product ($\lambda_0^{\pm}\eta_0$) for electrolytes versus w_1 of DCM (1) + DMF (2) mixtures at 298.15 K. ■, n-Bu₄NI; □, n-Pen₄NI; ▲, n-Hex₄NI; Δ, n-Hept₄N.

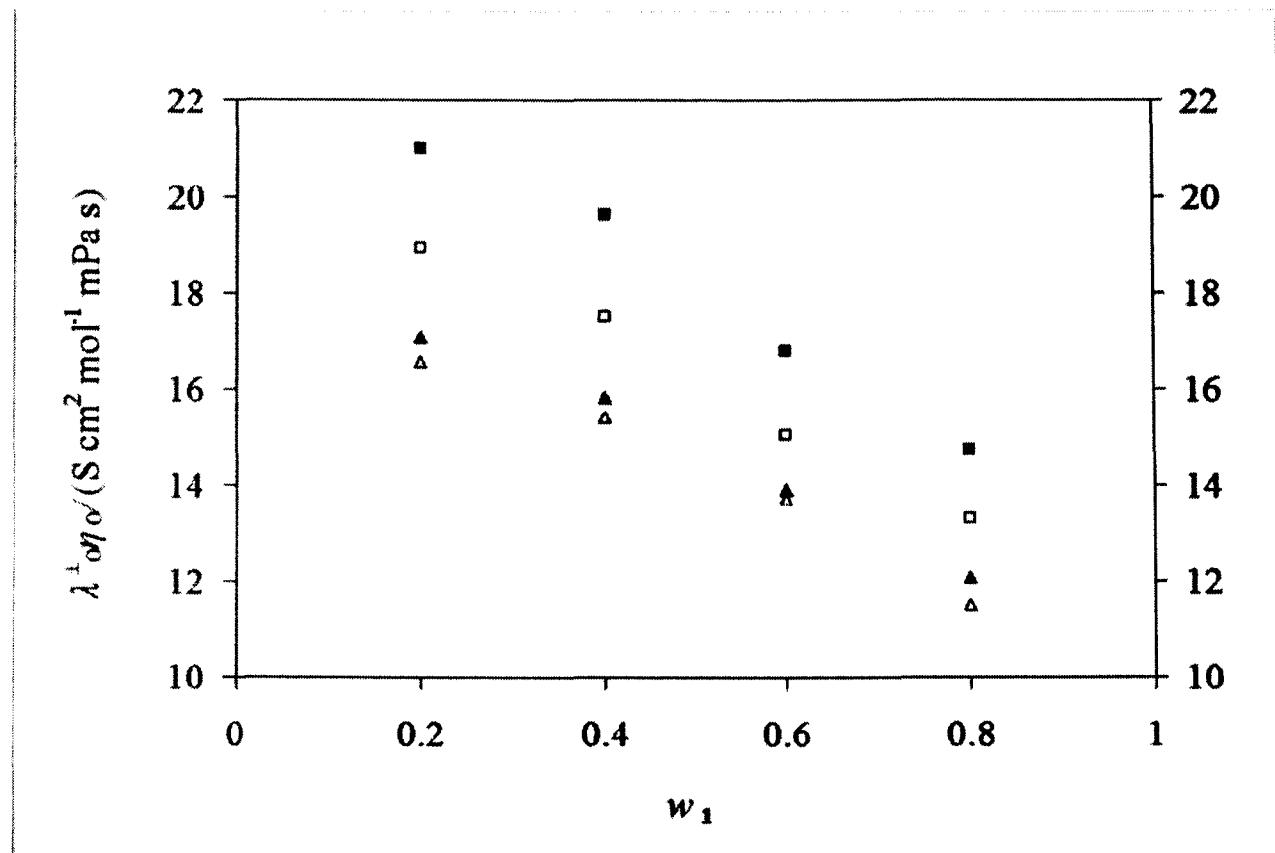


Figure 3. Plot of standard Gibbs free energy change, ΔG^0 versus w_1 of DCM (1) + DMF (2) mixtures at 298.15 K. ■, n-Bu₄NI; □, n-Pen₄NI; ▲, n-Hex₄NI; Δ, n-Hept₄N.

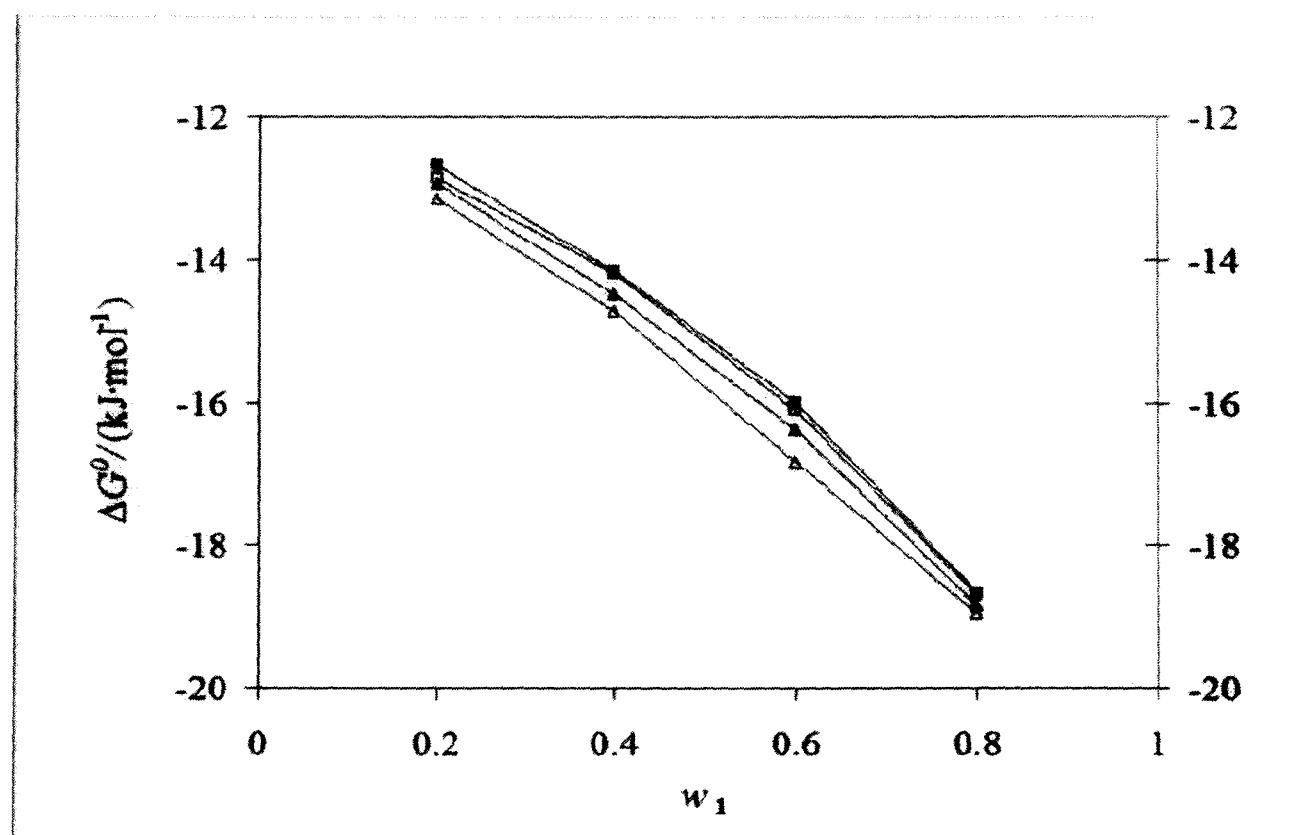


Figure 4. Plots of molar conductance, Λ , versus square root of salt concentration, $c^{1/2}$, in $w_1 = 1.00$ of DCM (1) + DMF (2) at $T = 298.15$ K. ■, n-Bu₄NI; □, n-Pen₄NI; ▲, n-Hex₄NI; Δ, n-Hept₄N.

