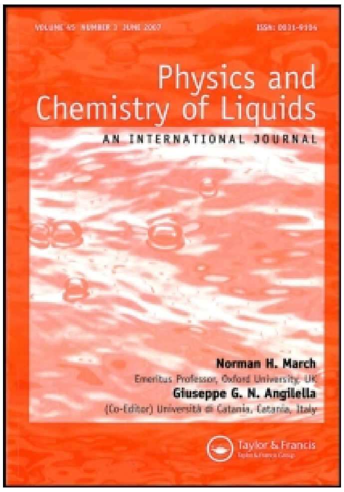

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Conductivity studies of sodium iodide in pure tetrahydrofuran and aqueous binary mixtures of tetrahydrofuran and 1,4-dioxane at 298.15 K

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Conductivity studies of sodium iodide in pure tetrahydrofuran and aqueous binary mixtures of tetrahydrofuran and 1,4-dioxane at 298.15 K

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Electrical conductance measurements are reported for sodium iodide (NaI) in water + tetrahydrofuran (THF) and water + 1,4-dioxane binary mixtures at 298.15 K. The conductance data have been analyzed by the Fuoss conductance–concentration equation in terms of the limiting molar conductance (Λ_0), the association constant (K_A) and the distance of closest approach of ions (R). Furthermore, the conductance data for pure THF have also been analyzed by the Fuoss–Kraus theory and the values of the ion-pair and triple-ion formation constants are calculated.

Keywords: Association constant; Walden product; Ion-pair; Triple-ion; Tetrahydrofuran; 1,4-dioxane

1. Introduction

Studies on ionic solvation of alkali metal ions in solvents of low permittivity are very few. Such studies have been assumed important because of their applications in modern technology [1]. Tetrahydrofuran (THF) and 1,4-dioxane (DO) are solvents of low permittivity which have applications in high energy batteries and organic syntheses as manifested from the physicochemical studies in these media [2,3]. Water–THF and water–DO binary mixtures are favorite solvent systems to study association and mobilities of ions, because the permitivities can be varied over a large range. Changes upon addition of these solvents to aqueous solutions are due to increasing ion–ion interaction at decreasing permittivity and to changes in ion-solvent and solvent–solvent interactions.

Several systematic investigations on the conductivity of alkali metal halides in water–THF [4,5] and water–DO [6–8] mixtures have been carried out by workers to reveal the nature of ionic association and mobility of ions in these mixed solvent systems.

After the classical work of Fuoss and Kraus [9] in the thirties, there has been a renewed interest in the study of association and dimerization of electrolytes in media of

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low permittivity [10]. This has been particularly important because knowledge of the state of association of the electrolytes along with the type and structure of the complex species in solution is essential for the optical choice of solvents and electrolytes. The formation of triple ions in media having low permittivity ($\varepsilon < 10$) [11] have been investigated from the conductivity studies of tetraalkylammonium, [12,13] alkali metals, [14,15] and ammonium salts [16] by fitting the Fuoss–Kraus equation.

In this article, a systematic conductivity study of sodium iodide (NaI) in water–THF and water–DO mixtures is presented at 298.15 K over the whole mole fraction range. We have also reported the formation of triple ions of NaI in pure THF ($\varepsilon = 7.58$) and the result is discussed herein.

2. Experimental

2.1. *Source and purity of samples*

THF (Tetrahydrofuran, C_4H_8O, LR grade) containing 0.1% water, and 0.005% peroxide was supplied as 99.5% pure and DO (1, 4-dioxane, $C_4H_8O_2$) containing 0.5% water, 0.02% nonvolatile matter was 99.0% pure. These were used after further purification by standard methods [17]. Sodium iodide salt (NaI, Merck, 99.0%) contained 3% moisture, 0.03% sulfate, and 0.1% potassium. It was dissolved in acetone, filtered and cooled to −20°C, the resulting yellow crystals being filtered off and heated in a vacuum oven at 70°C for 6 h to remove acetone. It was then crystallized from very dil. NaOH, dried under vacuum, and stored in a desiccator. The purity was detected by gas-liquid chromatography. Deionized water was used after further distillation having specific conductivity $1.99 \times 10^{-6}\,\Omega^{-1}\,\text{cm}^{-1}$. The purity of the liquids was checked by measuring their densities and viscosities at 298.15 K which were in good agreement with the literature values [5,18]. The materials finally obtained were found to be >99.5% pure.

2.2. *Method*

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 $1.11\,\text{cm}^{-1}$. Measurements were made in a thermostated water bath maintained at 298.15 K ± 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.* [19,20]. 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 water, THF, and DO are 78.54, 7.58, and 2.21, respectively. The concentration range of electrolytes was ~(1.48–968.95) × $10^{-4}\,\text{mol}\,\text{dm}^{-3}$ for water-THF mixture and ~(0.35–968.95) × $10^{-4}\,\text{mol}\,\text{dm}^{-3}$ for water–DO mixture.

Densities (ρ) were measured at 298.15 K with an Ostwald–Sprengel type pycnometer having bulb volume of about $25\,\text{cm}^3$ and an internal diameter of the capillary of about 1 mm. Viscosities (η) were measured by means of a suspended Ubbelohde type viscometer [21]. Calibration was done at 298.15 K with triply distilled water and purified THF using density and viscosity values from the literature. The details of the methods and techniques for determination of the parameters were described earlier [22,23]. The precision in the density and viscosity measurements are $\pm 2 \times 10^{-4}\,\mathrm{kg\,m^{-3}}$ and $\pm 3 \times 10^{-4}$ Poise, respectively.

3. Results and discussion

The physical properties of the pure liquids and the solvent mixtures are given in table 1.

3.1. *Treatment of data*

The experimental values of the molar conductances, Λ against the respective concentration, c for NaI salt in water–THF and water–DO binary mixtures over the whole mole fraction range at 298.15 K are recorded in table 2. The conductance data are analyzed using the Fuoss conductance equation [24]. So with a given set of conductivity values (c_j, Λ_j; $j = 1, \ldots, n$), three adjustable parameters, i.e., Λ_0, K_A, and R are derived from the Fuoss equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant, and R is the association distance, i.e., the maximum center to center distance between the ions in the solvent separated ion-pairs. There is no precise method [25] for determining the R value but in order to treat the data in our system, R value is assumed to be, $R = a + d$, where a is the sum of the crystallographic radii of the ions, which varies from 6 to 7 Å 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],

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

Table 1. Physical properties of pure solvents and the solvent mixtures.

		$\rho \times 10^{-3}$ (kg m^{-3})		$\eta \times 10^{2}$ (Poise)	
$x_{(\mathrm{THF/DO})}$	ε	Observed values	Literature values	Observed values	Literature values
THF + H_2O mixture					
0.0000	78.54	0.9973	0.9971 [12]	0.8904	0.8903 [12]
0.0588	57.25	0.9865	0.9867	1.4903	1.4900
0.1427	44.50	0.9666	0.9664	1.7323	1.7321
0.2725	32.00	0.9462	0.9460	1.4901	1.4904
0.4998	19.50	0.9157	0.9159	0.9234	0.9237
1.0000	7.58	0.8808	0.8807	0.4632	0.4630
DO + H_2O mixture					
0.0486	63.50	1.0145	1.0143 [17]	1.3003	1.3000 [17]
0.1199	44.40	1.0286	1.0284	1.7397	1.7400
0.2347	27.50	1.0358	1.0360	1.9803	1.9800
0.4498	12.10	1.0352	1.0350	1.7302	1.7300
1.0000	2.21	1.0271	1.0269	1.1963	1.1960

Table 2. Molar conductances, Λ and the corresponding concentration, c of NaI salt in THF + H_2O and DO + H_2O binary mixtures at 298.15 K.

$c \times 10^4$ (mol dm^{-3})	$\Lambda \times 10^4$ (S m^2 mol^{-1})	$c \times 10^4$ (mol dm^{-3})	$\Lambda \times 10^4$ (S m^2 mol^{-1})	$c \times 10^4$ (mol dm^{-3})	$\Lambda \times 10^4$ (S m^2 mol^{-1})
$x_{THF} = 0.0000$, $\varepsilon = 78.54$		$x_{THF} = 0.0588$, $\varepsilon = 57.25$		$x_{THF} = 0.1427$, $\varepsilon = 44.50$	
97.04	114.2	38.37	72.5	18.03	54.7
177.90	111.9	70.35	71.5	30.32	54.2
304.97	108.9	120.60	70.2	51.97	53.5
400.28	107.2	158.29	69.4	68.21	52.9
474.40	105.9	187.60	68.8	80.84	52.7
533.70	104.9	211.05	68.4	90.95	52.5
582.22	104.2	230.24	68.1	99.22	52.3
622.65	103.6	246.23	67.9	106.11	52.1
656.86	103.2	259.75	67.6	111.94	52.0
686.19	102.8	271.35	67.4	116.94	51.9
711.60	102.4	281.40	67.3	121.27	51.9
733.84	102.2	290.19	67.1	125.06	51.8
$x_{THF} = 0.2725$, $\varepsilon = 32.00$		$x_{THF} = 0.4998$, $\varepsilon = 19.50$		$x_{DO} = 0.0486$, $\varepsilon = 63.50$	
6.96	53.9	1.56	59.7	53.88	75.9
11.70	52.8	3.15	56.7	98.78	72.0
20.06	51.3	5.40	53.4	169.34	67.4
26.33	50.3	7.09	51.2	222.26	64.8
31.20	49.6	8.40	49.7	263.42	62.9
35.10	49.1	9.45	48.8	296.35	61.6
38.29	48.7	10.31	48.1	323.29	60.6
40.95	48.4	11.03	47.8	345.74	59.9
43.20	48.2	11.63	47.2	364.74	59.1
45.13	47.9	12.15	46.8	381.02	58.5
46.80	47.8	12.60	46.3	395.13	58.1
47.48	47.8	12.99	46.2	407.48	57.6
$x_{DO} = 0.1199$, $\varepsilon = 44.40$		$x_{DO} = 0.2347$, $\varepsilon = 27.50$		$x_{DO} = 0.4498$, $\varepsilon = 12.10$	
18.82	56.6	4.37	40.8	0.36	31.7
31.65	55.5	7.35	38.4	0.60	28.8
54.26	54.1	12.60	35.3	1.03	25.0
71.21	53.2	16.54	33.4	1.35	22.9
84.40	52.6	19.60	32.1	1.60	21.1
94.95	52.1	22.05	31.1	1.80	19.9
103.58	51.7	24.05	30.2	1.96	19.1
110.78	51.5	25.73	29.7	2.10	18.3
116.86	51.2	27.14	29.1	2.21	17.6
122.08	51.0	28.35	28.7	2.31	17.1
126.60	50.9	29.40	28.3	2.40	16.7
130.18	50.8	30.32	28.1	2.48	16.3

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,

$$M_{av} = \frac{M_1 M_2}{W_1 M_2 + W_2 M_1} \tag{2}$$

where W_1 is the weight fraction of the first component of molecular weight M_1.

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

$$\Lambda = p[\Lambda_0(1 + R_X) + E_L] \tag{3}$$

$$p = 1 - \alpha(1 - \gamma) \tag{4}$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \tag{5}$$

$$-\ln f = \frac{\beta k}{2(1 + kR)} \tag{6}$$

$$\beta = \frac{e^2}{\varepsilon k_B T} \tag{7}$$

$$K_A = \frac{K_R}{1 - \alpha} = K_R(1 + K_S) \tag{8}$$

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 [26,27]. 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 $j = 1, 2, \ldots, n$ and an instruction to cover pre-selected range of R values.

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

$$\sigma^2 = \sum \frac{[\Lambda_{j(\text{Calcd})} - \Lambda_{j(\text{obs})}]^2}{n - 2} \tag{9}$$

for a sequence of R values and then plotting σ against R, the best- fit R corresponds to the minimum in σ *versus* R curve. So an approximate sum is made over a fairly wide range of R values using a 0.1 increment to locate the minimum, but no significant minima is found in the $\sigma - R$ curves for the salt studied here, thus R values are assumed to be $R = a + d$, with terms having usual significance [24]. Finally, the corresponding Λ_0 and K_A values are obtained which are reported in table 3 along with R and σ for the two binary mixtures of NaI salt.

The Walden's product, $\Lambda_0\,\eta$ [28,29] 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° for the binary mixtures studied here. ΔG° is given by the relationship [30],

$$\Delta G^{\circ} = -RT \ln K_A. \tag{10}$$

Table 3. Derived conductance parameters for NaI in $THF + H_2O$ and $DO + H_2O$ binary mixtures at 298.15 K.

$x_{(THF/DO)}$	R^a (Å)	$\Lambda_0{}^b \times 10^4$ ($S\,m^2\,mol^{-1}$)	$K_A{}^c$ ($dm^3\,mol^{-1}$)	$\sigma(\%)$ ^{d}
$THF + H_2O$ mixture				
0.0000	6.23	122.87 ± 0.13	1.69 ± 0.04	0.13
0.0588	6.29	76.88 ± 0.09	1.94 ± 0.11	0.11
0.1427	6.39	57.68 ± 0.07	0.72 ± 0.22	0.08
0.2725	6.54	57.71 ± 0.05	33.9 ± 0.51	0.05
0.4998	6.87	66.29 ± 0.21	470 ± 11.14	0.17
$DO + H_2O$ mixture				
0.0486	6.26	85.78 ± 0.18	17.02 ± 0.24	0.14
0.1199	6.31	60.32 ± 0.04	10.03 ± 0.14	0.04
0.2347	6.41	49.31 ± 0.63	477.46 ± 28.13	0.36
0.4498	6.68	53.00 ± 0.19	30322 ± 39.62	0.89

[a] Association distance.
[b] Limiting molar conductance.
[c] Association constant.
[d] Standard deviation.

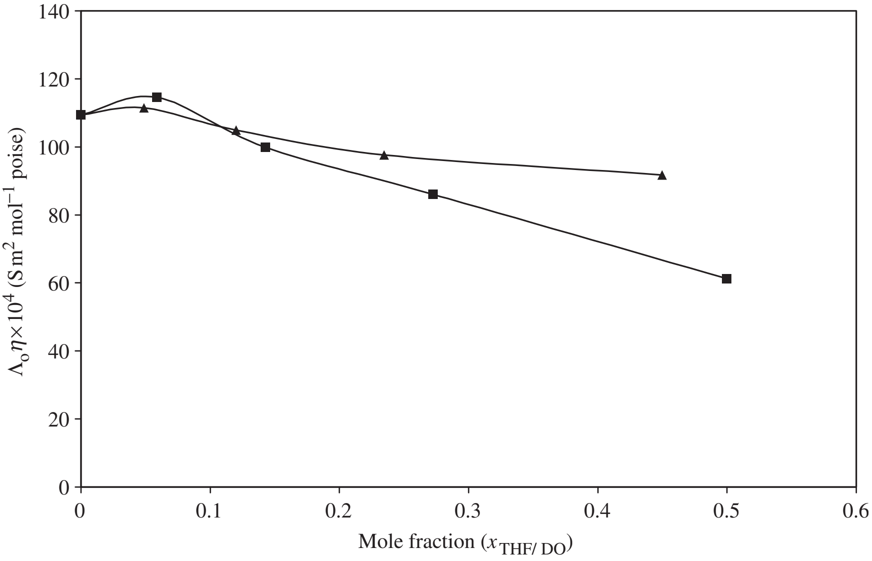

Figure 1. Walden product, $\Lambda_0\eta$ of NaI salt in $THF + H_2O$ (■) and $DO + H_2O$ (▲) binary mixtures at 298.15 K.

3.2. *Electrical conductivity of NaI in aqueous THF mixtures*

As observed from table 3, the molar conductance at infinite dilution i.e., Λ_0 is maximum in pure aqueous medium but it gradually decreases up to $x_{THF} = 0.14$ and then increases with the increase in the THF content of the mixture. The results are in good agreement with those obtained by Taniewska *et al*. [31]. The decrease in Λ_0 means decrease in mobility of the ions which is due to increase in viscosities of the mixtures and vice versa (table 1). Thus, the experimental results obtained here for the binary mixtures are in accordance with the Walden's rule. Pure water has maximum mobility

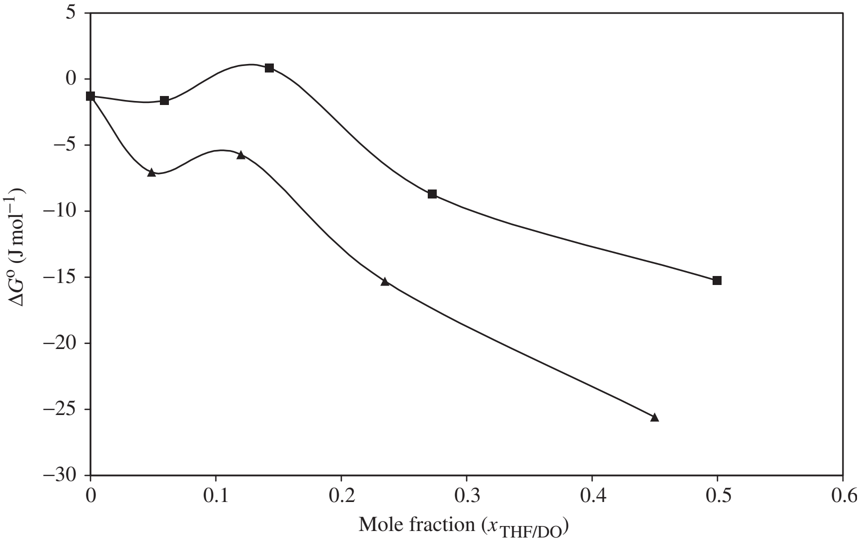

Figure 2. Gibbs energy of ion-pair formation, ΔG^o of NaI salt in THF + H_2O (■) and DO + H_2O (▲) binary mixtures at 298.15 K.

of the ions as pure liquids have easier flow than mixed solvents. Since, the resistance to the flow of liquid mixture becomes highest at $x_{THF} = 0.14$, we find minimum Λ_0 at this point.

The association constant, K_A for this binary mixture also follows the same trend as that of Λ_0. However, the association in pure water is less than that in $x_{THF} = 0.06$. The K_A values become minimum at $x_{THF} = 0.14$ but it increases significantly as the THF content in the mixture increases showing much larger deviations (σ), and thus pointing towards ionic association in pure THF which will be discussed later on.

Figure 1 shows that Walden product is maximum at $x_{THF} = 0.06$ and then decreases gradually for the mixture. 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 [32].

$$\Lambda_0 \eta = \frac{1}{6\Pi r T} \tag{11}$$

Figure 2 points out the nature of curve for the Gibbs energy of ion-pair formation, ΔG^o which clearly predicts that the tendency for ion-pair formation decreases significantly with an increase in the association factor for the electrolyte in aqueous-THF medium.

3.3. *Electrical conductivity of NaI in aqueous DO mixtures*

We observe that Λ_0 values decrease up to $x_{DO} = 0.23$ and then it shows an increase. At this minima, we have maximum viscosity of the DO mixture as seen in table 1, thus, indicating maximum resistance to the flow of the liquid mixture.

However, K_A value is lowest at $x_{DO} = 0.12$ but shows a significant increase at the higher mole fraction of DO owing to the very low permittivity ($\varepsilon = 2.21$) of the pure solvent in which there will be a significant association. This also explains the increase in σ values as water content in the mixture decreases.

The Walden product rises up to $x_{\mathrm{DO}} = 0.05$ and then there is a gradual fall in it as r increases with the increase in the mole fraction of DO in its aqueous mixture.

The ΔG^{o} curve in figure 2 for NaI in this binary mixture along with the other parameters mentioned previously are quite in accordance with the results observed by Barthel *et al.* [30].

3.4. *Comparison of the behavior of the electrolyte in the aqueous THF and aqueous DO mixtures*

The conductance of the ions is observed to be highest when water is considered. This is due to its large ε (78.54) which results in greater dissociation of the salt as compared to the solvents, THF and DO. Further, in the binary mixtures we get minimum Λ_0 at $x_{\mathrm{THF}} = 0.14$ and $x_{\mathrm{DO}} = 0.23$ owing to their maximum viscosities at these points. It is observed that depending on η, Λ_0 changes its nature in the respective solvent mixtures because the viscosity of the solvents increases to a maximum and then decreases (table 1).

The association constants show that NaI is almost completely dissociated in the water-rich mixtures but a perturbation by triple-ion formation is also expected at very high THF and DO content. The difference in the ε values for the solvents results in the different amounts of association, K_{A} as noticed here. However, NaI showed a larger association in aqueous DO mixture than in the THF medium. This is expected as DO has lower ε (2.21) than THF ($\varepsilon = 7.58$).

Figure 1 indicates that Walden's product is higher for NaI in water-DO mixtures. The variation of the Walden product reflects the change of solvation [33,34]. The solvation of NaI ions is weak in presence of DO molecules, but THF solvates the sodium ions specifically resulting in greater ion-solvent interaction. At lower mole fraction of THF and DO, the ions are preferentially solvated by water. The maxima is, however attained at the same mole fraction for both the mixtures i.e., at $x = 0.05$, but the maximum value is greater in THF mixture. The maximum point indicates preferential solvation of the ions by THF and DO in their respective aqueous mixtures.

Figure 2 compares ΔG^{o} for the binary mixtures. The aqueous-THF mixtures have higher ΔG^{o} than aqueous-DO mixtures. This indicates greater degree of ion-pair formation and lower extent of association in presence of THF molecules, attributing to its higher ε than DO. Similar works have been performed by Hazra *et al.* [35,36].

3.5. *Data analysis for pure THF*

Figure 3 presents the plot of Λ *versus* $\sqrt{c}$ for NaI in pure THF which is a curve showing a minima. The conductance data have been analyzed by the Fuoss–Kraus triple-ion theory [37] in the form as given below,

$$\Lambda g\sqrt{c} = \frac{\Lambda_0}{\sqrt{Kp}} + \frac{\Lambda_0^{\mathrm{T}} K_{\mathrm{T}}}{\sqrt{Kp}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \qquad (12)$$

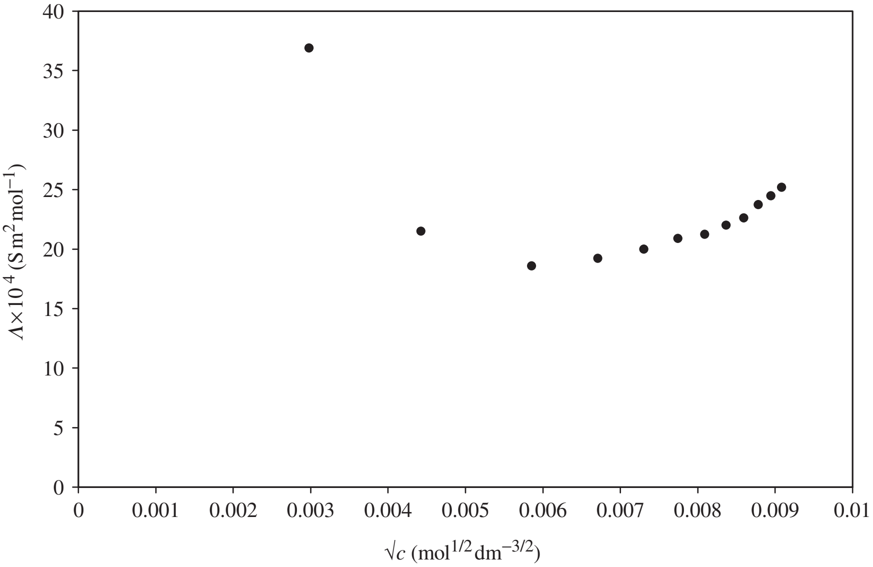

Figure 3. Plot of Λ *vs.* $\sqrt{c}$ of NaI in pure THF at 298.15 K.

$$g(c) = \frac{\exp\left\{\left(-\beta'/\sqrt{\Lambda_0}\right)\sqrt{c\Lambda}\right\}}{\left\{1-(S/\Lambda_0^{3/2})\sqrt{c\Lambda}\right\}\sqrt{1-(\Lambda/\Lambda_0)}} \tag{13}$$

$$\beta' = \frac{1.8247 \times 10^6}{(\varepsilon T)^{3/2}} \tag{14}$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8206 \times 10^6}{(\varepsilon T)^{3/2}}\Lambda_o + \frac{82.501}{\eta_o(\varepsilon T)^{1/2}}. \tag{15}$$

In the above equations, Λ_0 is the sum of the molar conductances of the simple ions at infinite dilution, Λ_0^{T} is the sum of the values for the two kinds of triple- ions, Kp and K_{T} are the ion-pair and triple-ion formation constants, respectively, S is the limiting Onsager coefficient. The symmetrical approximation of the two possible formation constant of triple ions equal to each other has been considered [38].

Neglecting, Λ/Λ_0, $(S/\Lambda_0^{3/2})(c\Lambda)^{1/2}$ and assuming $f_{\pm}=1$, lead to $g\ (c)=1$ in equation (12), we get,

$$\Lambda\sqrt{c} = \frac{\Lambda_0}{\sqrt{Kp}} + \frac{\Lambda_0^T K_{\mathrm{T}}}{\sqrt{Kp}}c. \tag{16}$$

But equation (16) becomes inadequate as a downward curvature is obtained when $\Lambda\sqrt{c}$ is plotted against c for NaI in THF. On the contrary, equation (12) gives a reasonably straight line. Λ_0 is obtained by applying the Walden's rule [29] as suggested by the work of Krumgalz [39].Λ_0^{T} is calculated by setting the triple-ion conductance as equal to 2/3 Λ_0 [40]. On running the Fuoss–Kraus equation, we get $Kp = 1.168 \times 10^7 (\mathrm{mol\,dm^{-3}})^{-1}$ and $K_\mathrm{T} = 39011.12\ (\mathrm{mol\,dm^{-3}})^{-1}$ while the slope = 1798.25 and intercept = 6.914×10^{-2}.

The values predict that major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions (neglecting quadrupoles). At very low permittivity of the solvent, i.e., $\varepsilon < 10$, electrostatic ionic interactions are very large. So the ion-pairs attract the free positive and negative ions present in the solution medium as the distance of the closest approach of the ions becomes minimum. This results in the formation of triple-ions which acquire the charge of the respective ions in the solution. [11,41] i.e.,

$$\mathrm{M^+ + A^- \leftrightarrow M^+ \cdots A^- \leftrightarrow MA} \tag{17}$$

$$\mathrm{MA + M^+ \leftrightarrow MA\,M^+} \tag{18}$$

$$\mathrm{MA + A^- \leftrightarrow MA\,A^-}. \tag{19}$$

Furthermore, the ion-pair and triple-ion concentrations, C_P and C_T, respectively of the electrolyte are also calculated at the highest concentration ($0.825 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) of THF using the following relations [13,42]

$$\alpha = \frac{1}{Kp^{1/2} \cdot c^{1/2}} \tag{20}$$

$$\alpha_\mathrm{T} = \left(\frac{K_\mathrm{T}}{Kp^{1/2}}\right) c^{1/2} \tag{21}$$

$$C_\mathrm{P} = c(1 - \alpha - 3 \cdot \alpha_T) \tag{22}$$

$$C_\mathrm{T} = \left(\frac{K_\mathrm{T}}{Kp^{1/2}}\right) c^{3/2}. \tag{23}$$

Here, α and α_T are the fraction of ion-pairs and triple-ions, respectively. Thus, $C_\mathrm{P} = 0.542 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ and $C_\mathrm{T} = 0.086 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ which indicate that the ions are mainly present as ion pairs even at high concentration of THF with a fraction existing as triple-ions. Since the effect of ternary association is to remove some nonconducting species MA from the solution and replace them by triple ions which contribute to the conductance, it is observed (figure 3) that Λ passes through a minimum as c increases. Similar type of work has been reported by Corti *et al.* [43].

The experimental work, however, could not be performed with pure DO as the salt was not completely soluble in the requisite amount for the measurements of conductance at 298.15 K. However, the results with pure water have been analyzed with Fuoss conductance equation as reported earlier in this work.

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References

[1] J. Barthel, H.G. Gores. *Top. Curr. Chem.*, **70**, 495 (1983).
[2] N. Inove, M. Xu, S. Petrucci. *J. Phys. Chem.*, **91**, 4628 (1987).
[3] A. Lewandowski. *Electrochim. Acta*, **31**, 59 (1986).
[4] R.E. Renard, J.C. Justice. *J. Solut. Chem.*, **3**, 633 (1974).
[5] M.N. Roy, D. Nandi, D.K. Hazra. *J. Indian Chem. Soc.*, **70**, 121 (1993).
[6] R.L. Kay, T.L. Broadwater. *Eletrochim. Acta*, **16**, 667 (1971).
[7] A.D. Aprano, F. Accasina, R.M. Fuoss. *J. Solut. Chem.*, **19**, 65 (1990).
[8] E. Rousset, J. Barthel, J.C. Justice. *J. Solut. Chem.*, **22**, 571 (1993).
[9] R.M. Fuoss, C.A. Kraus. *J. Am. Chem. Soc.*, **55**, 2387 (1933).
[10] Y. Harada, M. Salamon, S. Petrucci. *J. Phys. Chem.*, **89**, 2006 (1985).
[11] A.K. Covington, T. Dickinson. *Physical Chemistry of Organic Solvent Systems*, p. 564, Plenum, New York (1973).
[12] A.P. Abbott, D.J. Schiffrin. *J. Chem. Soc.*, *Faraday Trans. 1*, **86**, 1453 (1990).
[13] M.N. Roy, D. Nandi, D.K. Hazra. *J. Indian Chem. Soc.*, **70**, 305 (1993).
[14] S. Onishi, H. Farber, S. Petrucci. *J. Phys. Chem.*, **84**, 2922 (1980).
[15] D. Saar, S. Petrucci. *J. Phys. Chem.*, **90**, 3326 (1986).
[16] M. Hojo, T. Takiguchi, M. Hagiwara, H. Nagai, Y. Imai. *J. Phys. Chem.*, **93**, 955 (1989).
[17] D.D. Perrin, W.L.F. Armarego. *Purification of Laboratory Chemicals*, 3rd Edn, p. 164, Pergamon, Great Britain (1988), 284, 349.
[18] A.K. Covington, T. Dickinson. *Physical Chemistry of Organic Solvent Systems*, p. 19, Plenum, New York (1973).
[19] B. Das, A. Chatterjee. *J. Chem. Eng. Data*, **51**, 1352 (2006).
[20] J.E. Lind, J.J. Zwolenik, R.M. Fuoss. *J. Am. Chem. Soc.*, **81**, 1557 (1959).
[21] M.N. Roy, A. Jha, A. Choudhury. *J. Chem. Eng. Data*, **49**, 291 (2004).
[22] I. Gascon, S. Martin, B. Giner, M. Haro, C. Lafuente. *Can. J. Chem.*, **81**, 357 (2003).
[23] B. Das, P. Haldar. *Z. Phys. Chem.*, **218**, 1129 (2004).
[24] R.M. Fuoss. *J. Phys. Chem.*, **82**, 2427 (1978).
[25] B. Per. *Acta Chem. Scand. Ser. A*, **31**, 869 (1977).
[26] D.S. Gill, M.S. Chauhan. *Z. Phys. Chem. NF*, **140**, 139 (1984).
[27] G.C. Bag, N.M. Singh, N.R. Singh. *J. Ind. Chem. Soc.*, **78**, 294 (2001).
[28] D.D. Gupta, S. Das, D.K. Hazra. *J. Chem. Soc., Faraday Trans. 1*, **84**, 1057 (1988).
[29] P. Walden, H. Ulich, G. Busch. *Z. Phys. Chem.*, **123**, 429 (1926).
[30] J. Barthel, M.B. Rogac, R. Neueder. *J. Solut. Chem.*, **28**, 1071 (1999).
[31] S. Taniewska-Osinska, Z. Kozlowski, B. Nowicka, A. Bald, A. Szejgis. *J. Chem. Soc., Faraday Trans. 1*, **85**, 479 (1989).
[32] J.I. Bhat, P. Bindu. *J. Ind. Chem. Soc.*, **72**, 788 (1995).
[33] U.G.K. Raju, B. Sethuramam, T.N. Rao. *Bull. Chem. Soc. Jpn*, **55**, 293 (1982).
[34] R.L. Kay, T.L. Broadwater. *J. Solut. Chem.*, **5**, 57 (1976).
[35] D.K. Hazra, D. Das, B. Das. *Z. Phys. Chem.*, **218**, 341 (2004).
[36] D.K. Hazra, D. Das, B. Das. *J. Solut. Chem.*, **32**, 77 (2003).
[37] R.M. Fuoss, F. Accascina. *Electrolytic Conductance*, Interscience, New York (1959).
[38] H. Maser, M. Delsignore, M. Newstein, S. Petrucci. *J. Phys. Chem.*, **88**, 5100 (1984).
[39] B.S. Krumgalz. *J. Chem. Soc., Faraday Trans. 1*, **79**, 571 (1983).
[40] S. Boileau, P. Hemery. *Electrochim. Acta*, **21**, 647 (1976).
[41] E. Hirsch, R.M. Fuoss. *J. Am. Chem. Soc.*, **82**, 1018 (1960).
[42] D. Nandi, S. Das, D.K. Hazra. *Ind. J. Chem.*, **27(A)**, 574 (1988).
[43] H.R. Corti, D.L. Goldfarb, M.P. Longinotti. *J. Solut. Chem.*, **30**, 307 (2001).