

## CHAPTER-V

---

### **Essential foundation of triple-Ion and ion-Pair formation of tetraheptylammonium iodide ( $\text{Hept}_4\text{NI}$ ) salt in organic solvents investigated by physicochemical approach**

---

#### **V.1. INTRODUCTION**

Behaviour of electrolytic solutions can be obtained by studying their thermodynamic and transport properties. The molecular interactions within the electrolytic solution can be studied in a better way by varying the properties of the solvents such as dielectric constant or viscosity. A number of conductometric [1] and related studies of different electrolytes in non-aqueous solvents, have been done in relation to the use of the electrolyte in high-energy batteries [2] and for understanding organic reaction mechanisms [3]. The formation of triple-ion in media having low permittivity ( $\epsilon < 10$ ) [4] have been investigated from the conductivity studies of  $\text{Hept}_4\text{NI}$  [5,6]. The minima observed in conductometric curves ( $\Lambda$  versus  $\sqrt{c}$ ) in this type of solvents were interpreted by the formation of  $\text{M}_2\text{X}^+$  and  $\text{MX}_2^-$  triple-ion species [7].

Volumetric and viscometric studies also render an insight into the molecular interactions prevailing in solution and helps in the better understanding of the behavior of electrolytic solutions. Studies on the apparent and limiting apparent molar volumes of the electrolyte and the dependence of viscosity on the concentration of salt have been employed as a function of studying ion-ion and ion-solvent interactions [8].

In this paper, conductometric, volumetric and viscometric studies have been carried out for  $\text{Hept}_4\text{NI}$  in o-Toluidine, o-Xylene and 2-Nitrotoluidine.  $\text{Hept}_4\text{NI}$  used in this study has a number of applications such as it employed as phase transfer catalyst, it is also used as osmolytes. The solvent o-Toluidine used in the production of dyes. o-Xylene and 2-Nitrotoluidine solvents are largely used in the production of phthalic anhydride and pigments, antioxidants respectively.

## V.2. EXPERIMENTAL

### V.2.1 Materials

Hept<sub>4</sub>NI of puriss grade was procured from Sigma Aldrich, Switzerland. It was used as purchased as the purity assay of the salt was ≥99%. o-Toluidine procured from Merck, India; o-Xylene procured from Sisco Research Laboratory Pvt. Ltd. Bombay, India and 2-Nitrotoluene procured from Sisco Chem. Industries, India. The solvents were purified using standard methods [9].

### V.2.2 Apparatus and Procedure

A stock solution for the electrolyte was prepared by mass (Mettler Toledo AG285 with uncertainty 0.0003 g), and the working solutions were obtained by mass dilution at 298.15 K. The uncertainty of molarity of different solutions was evaluated to ± 0.0001 mol dm<sup>-3</sup>.

The density ( $\rho$ ) was measured by means of vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of ± 0.00005 g·cm<sup>-3</sup>. It was calibrated by double-distilled water and dry air [10]. The temperature was automatically kept constant within ± 0.01 K.

The viscosity was also measured with the help Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 having an accuracy of ± 1.0% range with displayed test data and fitted to a Brookfield Digital Bath TC-500.

The conductance measurements were carried out in a Systronic-308 conductivity meter (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm<sup>-1</sup>. 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. [11] The conductance data were reported at a frequency of 1 kHz and the accuracy was ±0.3%.

### V.3. RESULTS AND DISCUSSION

The solvent properties are given in Table V.1. The concentrations and molar conductances ( $\Lambda$ ) of o-Toluidine, o-Xylene, and 2-Nitrotoluidine are given in Table V.2. The molar conductance ( $\Lambda$ ) has been obtained from the specific conductance ( $\kappa$ ) value using the following equation.

$$\Lambda = (1000 \kappa) / c \quad (1)$$

Linear conductance curve ( $\Lambda$  versus  $\sqrt{c}$ ) was obtained for the electrolyte in 2-Nitrotoluene, extrapolation of  $\sqrt{c} = 0$  evaluated the starting limiting molar conductance for the electrolyte. But for the electrolyte in o-Xylene and o-Toluidine, a deviation in the conductance curve was obtained and shows a decrease in conductance values upto a certain concentration reaches a minimum and then increases indicating triple-ion formation.

The conductance data for the electrolyte in o-Xylene and o-Toluidine have been analysed using the classical Fuoss-Kraus equation [12] for triple-ion formation

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

$$g(c) = \frac{\exp\{-2.303 \beta' (c\Lambda)^{0.5} / \Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5} / \Lambda_0^{1.5}\}(1 - \Lambda / \Lambda_0)^{0.5}} \quad (3)$$

$$\beta' = 1.8247 \times 10^6 / (\varepsilon T)^{1.5} \quad (4)$$

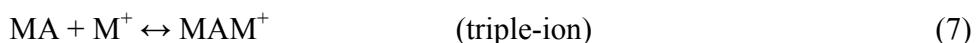
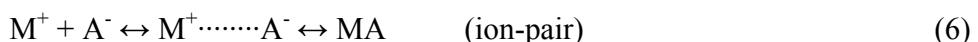
$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\varepsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \quad (5)$$

In the above equations,  $\Lambda_0$  is the sum of the molar conductance of the simple ions at infinite dilution;  $\Lambda_0^T$  is the sum of the conductances of the two triple ions  $[(\text{Hept})_4\text{N}]_2^+$  and  $(\text{Hept})_4\text{N(I)}_2^-$ .  $K_p \approx K_A$  and  $K_T$  are the ion-pair and triple-ion formation constants. To make equation (2) applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted [13] and  $\Lambda_0$  values for the studied electrolytes have been calculated [14].  $\Lambda_0^T$  is calculated by setting the triple ion conductance equal to  $2/3\Lambda_0$  [15].

The ratio  $\Lambda_0^T/\Lambda_0$  was thus set equal to 0.667 during linear regression analysis of equation (2). A perusal of Table V.3, Figure V.1 and V.2 show that the limiting molar conductance ( $\Lambda_0$ ) of Hept<sub>4</sub>NI is higher in o-Toluidine than o-Xylene. Limiting molar conductance of triple-ions ( $\Lambda_0^T$ ), slope and intercept of Eq. (2) for Hept<sub>4</sub>NI in o-Toluidine and o-Xylene are given in Table V.3.

Linear regression analysis of equation (2) for the electrolytes with an average regression constant,  $R^2 = 0.9653$ , gives intercepts and slopes. These permit the calculation of other derived parameters such as  $K_P$  and  $K_T$  listed in Table V.4. It is observed from Figure V.1 and V.2 that  $\Lambda$  passes through a minimum as  $c$  increases. The  $K_P$  and  $K_T$  values predict that major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions (neglecting quadrupoles). The value of  $\log(K_T/K_P)$  is found to be higher in o-Xylene than in o-Toluidine. This shows that o-Xylene has higher tendency to form triple-ion than o-Toluidine [16].

At very low permittivity of the solvent ( $\epsilon < 10$ ) electrostatic ionic interactions are very large. So the ion-pairs attract the free +ve and -ve ions present in the solution medium as the distance of the closest approach of the ions becomes minimum. These results in the formation of triple-ions, which acquire the charge of the respective ions in the solution [17] i.e.



Where  $M^+$  and  $A^-$  are Hept<sub>4</sub>N<sup>+</sup> and I<sup>-</sup> respectively. The effect of ternary association [18] thus removes some non-conducting species, MA, from solution, and replaces them with triple-ions which increase the conductance manifested by non-linearity observed in conductance curves for the electrolyte in o-Toluidine and o-Xylene.

Furthermore, the ion-pair and triple-ion concentrations,  $c_P$  and  $c_T$  respectively of the electrolyte have also been calculated at the minimum conductance concentration of Hept<sub>4</sub>NI in o-Toluidine and o-Xylene using the following relations [19].

$$\alpha = 1 / (K_P^{1/2} \cdot c^{1/2}) \quad (9)$$

$$\alpha_T = (K_T / K_P^{1/2}) c^{1/2} \quad (10)$$

$$c_P = c(1 - \alpha - 3\alpha_T) \quad (11)$$

$$c_T = (K_T / K_P^{1/2}) c^{3/2} \quad (12)$$

Here  $\alpha$  and  $\alpha_T$  are the fractions of ion-pairs and triple-ions present in the salt-solutions respectively and are given in Table V.5. Thus, the values of  $C_P$  and  $C_T$  also given in Table V.5 indicate that the ions are mainly present as ion-pairs even at high concentration and a small fraction existing as triple-ions. The ion-pair fraction ( $\alpha$ ), triple-ion fraction ( $\alpha_T$ ), ion-pair concentration ( $C_P$ ) and triple-ion concentration ( $C_T$ ) have also been calculated over the whole concentration range of [Hept<sub>4</sub>NI] in o-Tolidine and o-Xylene and the data are provided in Table V.5.

The ion-pair formation in case of conductometric study of Hept<sub>4</sub>NI in 2-Nitrotoluene was analysed using the Fuoss conductance equation [20]. With a given set of conductivity values ( $c_j, \Lambda_j; j = 1 \dots n$ ), three adjustable parameters, i.e.,  $\Lambda_0$ ,  $K_A$  and  $R$  have been derived from the Fuoss equation. Here,  $\Lambda_0$  is the limiting molar conductance,  $K_A$  is the observed association constant and  $R$  is the association distance, i.e., the maximum centre to centre distance between the ions in the solvent separated ion-pairs. There is no precise method [21] 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 and  $d$  is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance,  $d$  is given by:

$$d = 1.183 (M / \rho)^{1/3} \quad (13)$$

where,  $M$  is the molar mass and  $\rho$  is the density of the solvent.

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

$$\Lambda = P \Lambda_0 [(1 + R_x) + E_L] \quad (14)$$

$$P = 1 - \alpha(1 - \gamma) \quad (15)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (16)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (17)$$

$$\beta = e^2 / (\varepsilon_r k_B T) \quad (18)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (19)$$

where,  $\Lambda_0$  is the limiting molar conductance,  $K_A$  is the observed association constant,  $R$  is the association distance,  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic counter current,  $k$  is the radius of the ion atmosphere,  $\varepsilon$  is the relative permittivity of the solvent mixture,  $e$  is the electron charge,  $c$  is the molarity of the solution,  $k_B$  is the Boltzmann constant,  $K_S$  is the association constant of the contact-pairs,  $K_R$  is the association constant of the solvent-separated pairs,  $\gamma$  is the fraction of solute present as unpaired ion,  $\alpha$  is the fraction of contact pairs,  $f$  is the activity coefficient,  $T$  is the absolute temperature and  $\beta$  is twice the Bjerrum distance.

The computations were performed using the program suggested by Fuoss. The initial  $\Lambda_0$  values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [22]. Input for the program is the no. of data,  $n$ , followed by  $\varepsilon$ ,  $\eta$  (viscosity of the solvent mixture), initial  $\Lambda_0$  value,  $T$ ,  $\rho$  (density of the solvent mixture), mole fraction of the first component, molar masses,  $M_1$  and  $M_2$  along with  $c_j$ ,  $\Lambda_j$  values where  $j = 1, 2, \dots, n$  and an instruction to cover preselected range of  $R$  values.

In practice, calculations are performed by finding the values of  $\Lambda_0$  and  $\alpha$  which minimize the standard deviation,  $\delta$ , whereby

$$\delta^2 = \sum [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n - m) \quad (20)$$

for a sequence of  $R$  values and then plotting  $\delta$  against  $R$ , the best-fit  $R$  corresponds to the minimum of the  $\delta$ - $R$  versus  $R$  curve. So, an approximate sum is made over a fairly wide range of  $R$  values using 0.1 increment to locate the minimum but no significant minima is found in the  $\delta$ - $R$  curves, thus  $R$  values is assumed to be  $R = a + d$ , with terms having usual

significance. Finally, the corresponding  $\Lambda_0$  and  $K_A$  values are obtained which are reported in Table V.6 along with  $R$  and  $\delta$  for the all the solutions.

Limiting molar conductance ( $\Lambda_0$ ), association constant ( $K_A$ ), co-sphere diameter ( $R$ ) and standard deviations of experimental  $\Lambda$  ( $\delta$ ) obtained from Fuoss conductance equation for Hept<sub>4</sub>NI in 2-Nitrotoluene at 298.15 K are given in Table V.6.

The Gibb's energy change of solvation,  $\Delta G^\circ$ , for Hept<sub>4</sub>NI in 2-Nitrotoluene is given by the following equation [23]

$$\Delta G^\circ = -RT \ln K_A \quad (21)$$

It is observed from the Table V.7 that the value of the Gibb's free energy is entirely negative for 2-Nitrotoluene and it can be explained by considering the participation of specific covalent interaction in the ion-association process.

Table V.8 shows the value of ionic conductance ( $\lambda_0^\pm$ ) and ionic Walden product ( $\lambda_0^\pm \eta$ ) (product of ionic conductance and viscosity of the solvent) along with Stokes' radii ( $r_s$ ) and Crystallographic Radii ( $r_c$ ) of Hept<sub>4</sub>NI in 2-Nitrotoluene .It is seen from this table that I<sup>-</sup> has higher ionic conductance and Walden product than Hept<sub>4</sub>N<sup>+</sup> and in case of Stokes' radii and Crystallographic Radii reverse order of value is observed for I<sup>-</sup> and Hept<sub>4</sub>N<sup>+</sup> of Hept<sub>4</sub>NI.

The measured values of densities of Hept<sub>4</sub>NI in o-Tolidine, o-Xylene and 2-Nitrotolidine at 298.15 K are listed in Table V.9. The densities and viscosities of the electrolytes in different solvents increase linearly with the concentration at the experimental temperature. For this purpose, the apparent molar volumes  $\phi_V$  given in Table V.9 were determined from the solution densities using the following equation [24]

$$\phi_V = M / \rho_o - 1000(\rho - \rho_o) / c \rho_o \quad (22)$$

where  $M$  is the molar mass of the solute,  $c$  is the molarity of the solution,  $\rho$  and  $\rho_o$  are the densities of the solution and solvent, respectively. The limiting apparent molar volumes  $\phi_V^0$  were calculated using a least-squares treatment to the plots of  $\phi_V$  versus  $c^{1/2}$  using the following Masson equation [25]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \quad (23)$$

where  $\phi_V^0$  is the limiting apparent molar volume at infinite dilution and  $S_V^*$  is the experimental slope.

The plots of  $\phi_V$  against the square root of the molar concentration  $c^{1/2}$  were found to be linear with negative slopes. The values of  $\phi_V^0$  and  $S_V^*$  are reported in Table V.9. The variation of  $\phi_V^0$  for this electrolyte with the solvents is shown in Figure V.4. From Table V.9 it is seen that  $\phi_V^0$  values for this electrolyte are generally positive for all the solvents and is highest in case of Hept<sub>4</sub>NI in 2-Nitrotoluene. This indicates the presence of strong ion-solvent interactions and the extent of interactions increases from o-Toluidine to 2-Nitrotoluene.

On the contrary, the  $S_V^*$  indicates the extent of ion-ion interaction. The values of  $S_V^*$  shows that the extent of ion-ion interaction is highest in case of o-Toluidine and is lowest in 2-Nitrotoluene. A quantitative comparison of the magnitude of  $\phi_V^0$  values is much greater in magnitude than  $S_V^*$  values, for the solutions. This suggests that ion-solvent interactions dominate over ion-ion interaction in all the solutions. The values of  $\phi_V^0$  also support the fact that higher ion-solvent interaction in 2-Nitrotoluene, leads to lower conductance of Hept<sub>4</sub>NI in it than o-Toluidine and o-Xylene.

The viscosity data has been analysed by the Jones-Dole equation [26]

$$(\eta / \eta_0 - 1) / \sqrt{c} = A + B \sqrt{c} \quad (24)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the solution and solvent respectively. The values of  $A$ -coefficient and  $B$ -coefficient are obtained from the straight line by plotting  $(\eta / \eta_0 - 1) / \sqrt{c}$  against  $\sqrt{c}$  which are reported in Table V.10.

An assessment of Table V.10 and Figure V.5 shows that the values of the  $A$ -coefficient are either very small positive or negative for the solutions under investigation

at all solvents indicating the presence of weak ion-ion interactions, and these interactions further decrease from o-Toluidine to 2-Nitrotoluene. The viscosity *B*-coefficient reflects the quantitative ion-solvent interactions in the solution and the values of viscosity *B*-coefficient for  $\text{Hept}_4\text{NI}$  in the solvent systems studied are positive [27,28], thereby suggesting the presence of strong ion-solvent interaction. The trends in *B*-coefficient values support the results discussed earlier on the basis of  $\phi_V$ . This shows that with the increase in the viscosity *B*-coefficient of the solvent the mobility of the ions of the electrolyte solvated decrease [29] and hence the conductance also decreases. That is why,  $\text{Hept}_4\text{NI}$  salt is more solvated in 2-Nitrotoluene than the other two solvents.

The viscosity *A*-coefficient and *B*-coefficient values are in excellent agreement with the results drawn from the volumetric studies. The trend of ion-solvent interaction is o-Toluidine<o-Xylene<2-Nitrotoluene.

#### V.4. CONCLUSION

The extensive study of  $\text{Hept}_4\text{NI}$  in o-Toluidine, o-Xylene and 2-Nitrotoluene leads to the conclusion that, the salt more associated in 2-Nitrotoluene than the other two studied solvents. It can also be seen that in the conductometric studies in o-Toluidine and o-Xylene the  $\text{Hept}_4\text{NI}$  remains as triple-ions and ion-pairs and the extent of triple-ion formation is higher in o-Xylene than o-Toluidine. But in 2-Nitrotoluene the  $\text{Hept}_4\text{NI}$  remains as only ion-pairs. The experimental values obtained from the volumetric and viscometric studies suggest that in solution there is more ion-solvent interaction than the ion-ion interaction and the extent of ion-solvent interaction of  $\text{Hept}_4\text{NI}$  is highest in 2-Nitrotoluene.

**TABLES****Table V.1.** Density ( $\rho$ ), viscosity ( $\eta$ ) and relative permittivity ( $\epsilon$ ) of the different solvents o-Toluidine, o-Xylene and 2-Nitrotoluene.

Solvents	$\rho \cdot 10^{-3}/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	$\epsilon$
o-Toluidine	0.998	0.339	6.14
o-Xylene	0.87557	0.759	2.6
2-Nitrotoluene	1.163	2.218	26.1

**Table V.2.** Concentration ( $c$ ) and molar conductance ( $\Lambda$ ) of o-Toluidine, o-Xylene and 2-Nitrotoluene at 298.15 K.

$c \cdot 10^4/$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4/$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$c \cdot 10^4/$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4/$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$c \cdot 10^4/$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4/$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
Hept <sub>4</sub> NI					
o-Toluidine		o-Xylene		2-Nitrotoluene	
3.5044	14.82	3.3672	44.54	3.9720	56.31
4.4521	14.77	3.9641	44.50	4.7394	54.21
5.1938	14.72	4.7350	44.46	5.5180	52.31
5.8081	14.69	5.7600	44.41	6.2078	51.50
6.2001	14.68	6.6203	44.37	6.8164	50.20
6.9169	14.64	7.3984	44.33	7.2146	49.90
7.7841	14.60	8.2254	44.29	7.8414	48.50
8.7557	14.55	9.0721	44.27	8.2770	48.00
9.6534	14.51	10.1188	44.25	9.0000	46.40
10.6406	14.48	11.1422	44.25	9.7032	45.50
11.8542	14.44	11.9578	44.25	10.2400	44.70
13.3810	14.40	13.2642	44.27	11.0224	43.11

15.0777	14.38	14.2129	44.28	11.9025	42.90
16.4106	14.39	15.5000	44.31	12.9025	42.80
17.7241	14.42	16.4106	44.34	14.6459	42.00

**Table V.3.** Calculated limiting molar conductance of ion-pair ( $\Lambda_0$ ), limiting molar conductances of triple ion  $\Lambda_0^T$ , experimental slope and intercept obtained from Fuoss-Kraus Equation for Hept<sub>4</sub>NI in o-Toluidine and o-Xylene at 298.15 K.

Solvents	$\Lambda_0 \cdot 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	$\Lambda_0^T \cdot 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	Slope $\times 10^{-2}$	Intercept $\times 10^{-2}$
Hept <sub>4</sub> NI				
o-Toluidine	69.12	46.10	0.20	0.15
o-Xylene	60.34	40.25	0.11	0.45

**Table V.4.** Salt concentration at the minimum conductivity ( $C_{\min}$ ) along with the ion-pair formation constant ( $K_P$ ), triple ion formation constant ( $K_T$ ) for Hept<sub>4</sub>NI in o-Toluidine and o-Xylene at 298.15 K.

Solvents	$C_{\min} \cdot 10^4 /$ mol·dm <sup>-3</sup>	$\log C_{\min}$	$K_P \cdot 10^{-5} /$ (mol·dm <sup>-3</sup> ) <sup>-1</sup>	$K_T /$ (mol·dm <sup>-3</sup> ) <sup>-1</sup>	$K_T / K_P \cdot 10^5$	$\log K_T / K_P$
Hept <sub>4</sub> NI						
o-Toluidine	9.92	-3.0034	0.36	48.96	136.4	-2.86
o-Xylene	9.24	-3.0343	0.32	75.33	235.4	-2.62

**Table V.5.** Salt concentration at the minimum conductivity ( $c_{\min}$ ), the ion pair fraction ( $\alpha$ ), triple ion fraction ( $\alpha_T$ ), ion pair concentration ( $c_P$ ) and triple-ion concentration( $c_T$ ) for Hept<sub>4</sub>NI in o-Toluidine and o-Xylene at 298.15 K.

Solvents	$c_{\min} \cdot 10^4 /$ mol·dm <sup>-3</sup>	$\alpha \cdot 10^5$	$\alpha_T \cdot 10^3$	$c_P \cdot 10^4 /$ mol·dm <sup>-3</sup>	$c_T \cdot 10^6 /$ ·dm <sup>-3</sup>
Hept <sub>4</sub> NI					
O-Toluidine	9.92	16.6	8.13	9.68	8.1
O-Xylene	9.24	6.91	12.88	9.10	8.9

**Table V.6.** Limiting molar conductance ( $\Lambda_0$ ), association constant ( $K_A$ ), co-sphere diameter ( $R$ ) and standard deviations of experimental  $\Lambda$  ( $\delta$ ) obtained from Fuoss conductance equation for Hept<sub>4</sub>NI in 2-Nitrotoluene at 298.15 K.

Solvent	$\Lambda_0 \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$K_A / \text{dm}^3 \cdot \text{mol}^{-1}$	$R/\text{\AA}$	$\delta$
Hept <sub>4</sub> NI				
2-Nitrotoluene	34.67	453.24	8.54	0.16

**Table V.7.** Walden product ( $\Lambda_0 \cdot \eta$ ) and Gibb's energy change ( $\Delta G^\circ$ ) of Hept<sub>4</sub>NI in 2-Nitrotoluene at 298.15 K.

Solvent	$\Lambda_0 \cdot \eta \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \text{mPa}$	$\Delta G^\circ /$ $\text{kJ} \cdot \text{mol}^{-1}$
Hept <sub>4</sub> NI		
2-Nitrotoluene	76.90	-15.16

**Table V.8.** Limiting Ionic Conductance ( $\lambda_0^\pm$ ), Ionic Walden Product ( $\lambda_0^\pm \eta$ ) , Stokes' Radii ( $r_s$ ), and Crystallographic Radii ( $r_c$ ) of Hept<sub>4</sub>NI in 2-Nitrotoluene at 298.15 K.

Solvent	ion	$\lambda_0^\pm$ (S·m <sup>2</sup> ·mol <sup>-1</sup> )	$\lambda_0^\pm \eta$ (S·m <sup>2</sup> ·mol <sup>-1</sup> mPa)	$r_s$ (Å)	$r_c$ (Å)
2-Nitrotoluene	Hept <sub>4</sub> N <sup>+</sup>	10.15	22.51	3.64	5.88
	I <sup>-</sup>	21.71	48.15	1.70	2.16

**Table V.9.** Concentration,  $c$ , density,  $\rho$ , apparent molar volume,  $\phi_V$ , limiting apparent molar volume  $\phi_V^0$  and experimental slope for Hept<sub>4</sub>NI in o-Xylene, o-Toluidine and 2-Nitrotoluene at 298.15 K.

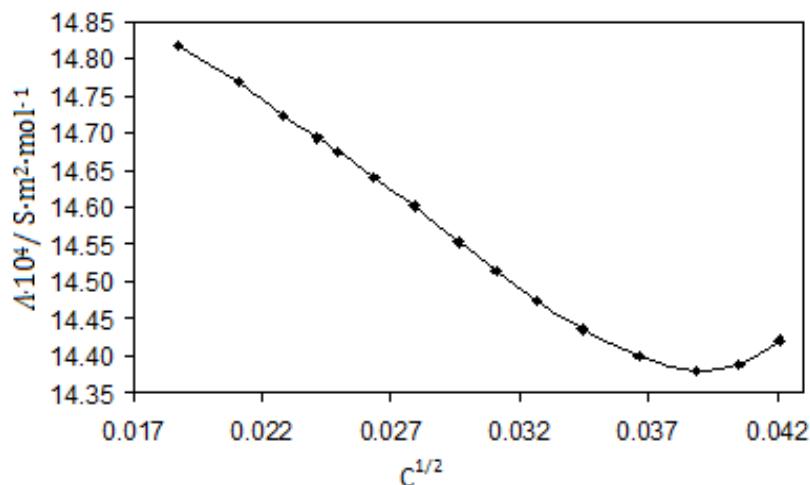
Solvents	$c/$ mol·dm <sup>-3</sup>	$\rho \cdot 10^{-3}/$ kg m <sup>-3</sup>	$\phi_V \cdot 10^6/$ m <sup>3</sup> ·mol <sup>-1</sup>	$\phi_V^0 \cdot 10^6/$ m <sup>3</sup> ·mol <sup>-1</sup>	$S_V^* \cdot 10^6/$ m <sup>3</sup> · mol <sup>-3/2</sup> ·dm <sup>3/2</sup>
Hept <sub>4</sub> NI					
o-Toluidine	0.005	0.99849	440.58	442.7	-29.47
	0.020	1.00000	438.58		
	0.035	1.00155	437.15		
	0.050	1.00312	436.17		
	0.065	1.00472	435.19		
	0.080	1.00634	434.32		
o-Xylene	0.005	0.87629	449.65	454.5	-69.97
	0.020	0.87854	444.51		
	0.035	0.88086	441.49		
	0.050	0.88324	438.91		
	0.065	0.88566	436.82		
	0.080	0.88814	434.66		

2-Nitrotoluene	0.005	1.16303	457.18	464.6	-103.60
	0.020	1.16328	450.30		
	0.035	1.16369	445.39		
	0.050	1.16421	441.53		
	0.065	1.16484	438.00		
	0.080	1.16550	435.47		

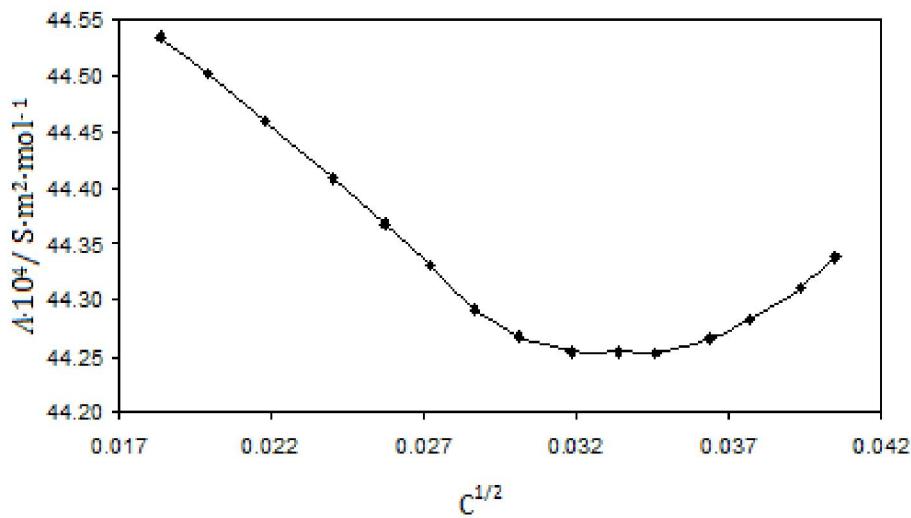
**Table V.10.** Concentration,  $c$ , viscosity,  $\eta$ ,  $\frac{(\eta_r - 1)}{\sqrt{c}}$ , viscosity  $A$  and  $B$  coefficients for Hept<sub>4</sub>NI in o-Xylene, o-Toluidine and 2-Nitrotoluene at 298.15 K.

Salts	$c$ /mol·dm <sup>-3</sup>	$\eta$ /mPa · s	$\frac{(\eta_r - 1)}{\sqrt{c}}$	$B$ /dm <sup>3</sup> · mol <sup>-1</sup>	$A$ /dm <sup>3/2</sup> · mol <sup>-1/2</sup>
Hept <sub>4</sub> NI					
o-Toluidine	0.005	0.34	0.13	1.9305	0.0032
	0.020	0.35	0.26		
	0.035	0.36	0.36		
	0.050	0.37	0.46		
	0.065	0.38	0.50		
	0.080	0.39	0.57		
o-Xylene	0.005	0.77	0.13	2.1570	-0.0006
	0.020	0.79	0.28		
	0.035	0.81	0.39		
	0.050	0.84	0.47		
	0.065	0.86	0.53		
	0.080	0.89	0.60		

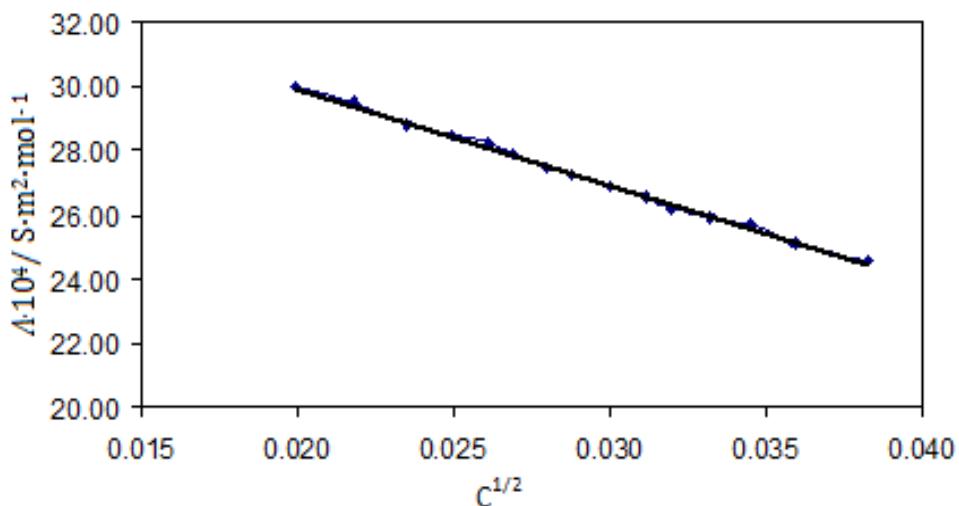
2-Nitrotoluene	0.005	1.57	0.23	3.8380	-0.0537
	0.020	1.65	0.48		
	0.035	1.74	0.66		
	0.050	1.82	0.80		
	0.065	1.91	0.93		
	0.080	2.00	1.04		

**FIGURES**

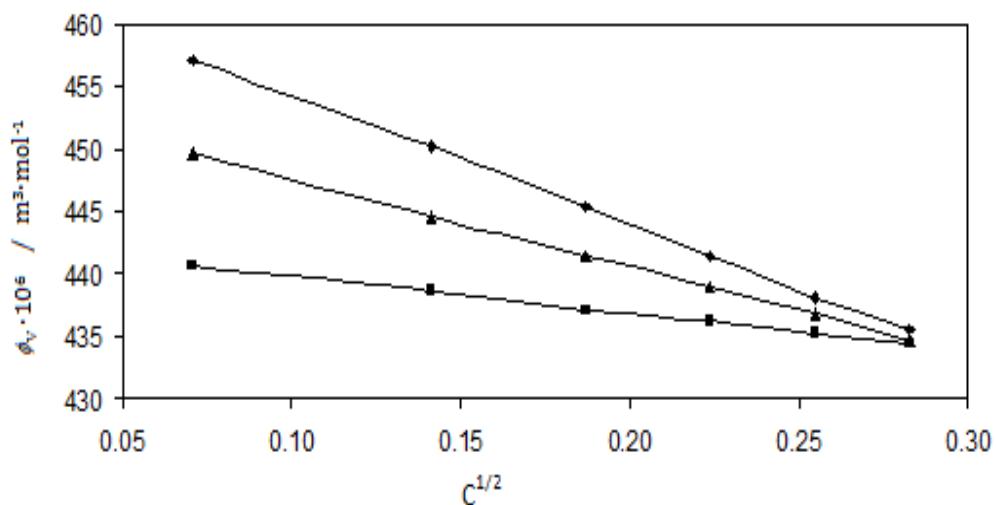
**Figure V.1.** Plot of molar conductance ( $\Lambda$ ) versus  $C^{1/2}$  for Hept<sub>4</sub>NI in o-Toluidine at 298.15 K.



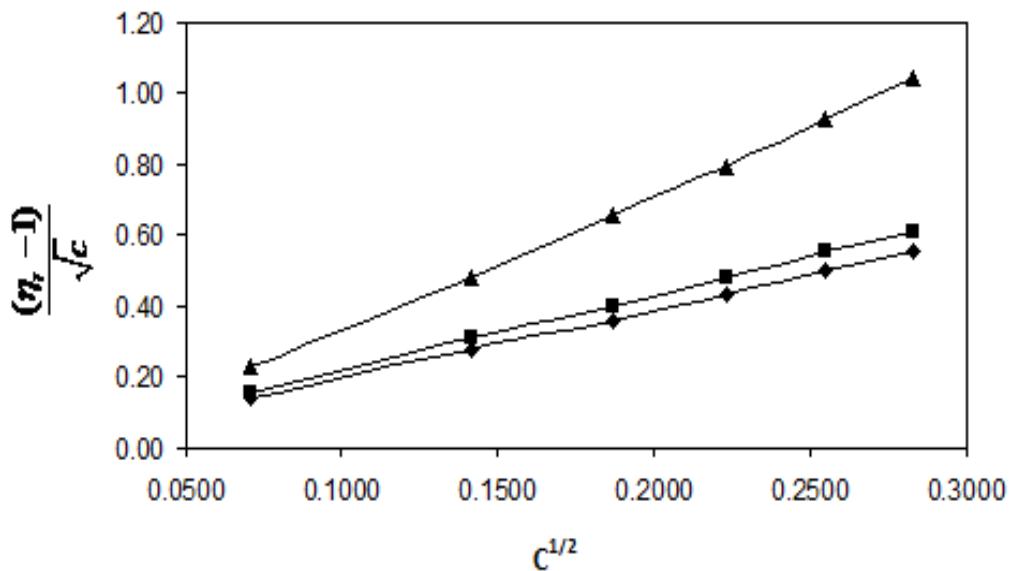
**Figure V.2.** Plot of molar conductance ( $\Lambda$ ) versus  $C^{1/2}$  for Hept<sub>4</sub>NI in o-Xylene at 298.15 K.



**Figure V.3.** Plot of molar conductance ( $\Lambda$ ) versus  $C^{1/2}$  for  $\text{Hept}_4\text{NI}$  in 2-Nitrotoluene at 298.15 K.



**Figure V.4.** Plot of  $C^{1/2}$  versus Limiting apparent molar volume ( $\phi_V^0$ ) for  $\text{Hept}_4\text{NI}$  in o-Toluidine (—■—), o-Xylene (—▲—) and 2-Nitrotoluene (—◆—) at 298.15 K.



**Figure V.5.** Plot of  $C^{1/2}$  versus  $\frac{(\eta_r - 1)}{\sqrt{c}}$  for Hept<sub>4</sub>NI in o-Toluidine (—♦—), o-Xylene (—■—) and 2-Nitrotoluene (—▲—) at 298.15 K.