

# ION ASSOCIATION OF TETRABUTYLAMMONIUM SALTS IN DIFFERENT SOLVENTS BY FUOSS- KRAUSS METHOD

N. Mohondas Singh\* and A. Bimoti Devi

Department of Chemistry, School of Physical Sciences,  
Mizoram University Aizawl-796004, Mizoram, India  
E-mail: \*nmdas08@rediffmail.com

**Abstract**—Quantitative analysis of molecular interactions prevailing in two ionic liquids, i.e., tetrabutylammonium bromide and tetrabutylammonium iodide - organic solvents at  $T = 298.15\text{K}$  have been evaluated using ionic conductance. The conductometric curves ( $\Lambda$  vs.  $\sqrt{c}$ ) deviated from linearity for  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$  and  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{I}^-$  in dichloromethane and tetrahydrofuran and their mixtures showed the formation of triple-ion, consequently the electrical conductance data have been analysed by the Fuoss–Kraus equation. The experimental molar conductance data have been determined for the formation of ion-pair  $((\text{C}_4\text{H}_9)_4\text{N}^+ + \text{X}^- \leftrightarrow (\text{C}_4\text{H}_9)_4\text{N}^+\text{X}^-$  where  $\text{X}=\text{Br}$  and  $\text{I}$ ) and the formation of triple-ion  $(2(\text{C}_4\text{H}_9)_4\text{N}^+ + \text{X}^- \leftrightarrow [(\text{C}_4\text{H}_9)_4\text{N}]_2\text{X}]^+$ ,  $(\text{C}_4\text{H}_9)_4\text{N}^+ + 2\text{X}^- \leftrightarrow (\text{C}_4\text{H}_9)_4\text{N}^+\text{X}_2^-$ ). The triple-ion formation exhibited the ionic sizes in non-aqueous solvents where coulombic interaction and molecular bonding forces played an important role between the ions, i.e.,  $(\text{C}_4\text{H}_9)_4\text{N}^+$  and  $\text{X}^-$ .

**Keywords:** Electrical conductance, Fuoss-Kraus equation, ion-pair, triple-ion, solvents, tetrabutylammonium salts.

## 1. INTRODUCTION

Ionic liquids (ILs) are a new class of solvent, i.e., purely ionic, salt-like materials that remain as liquid at relatively low temperatures (below  $100^\circ\text{C}$  or at ambient temperature). ILs are preferred over to molecular solvents in the studies of potential chemical applications, with kinetics and thermodynamics of reactions accomplished in ILs are quite different from those of conventional Molecular solvents. ILs commonly consist of organic cationic and inorganic/inorganic anionic species of having no measurable vapour pressure and so can emit no volatile organic compounds [2]. ILs are capable of dissolving a variety of different chemicals, vast liquid range, high ionic conductivity, thermal stability and immense chemical windows and are described as designer solvents.

A chemical interaction in which ions of opposite electrical charge combine in solution resulting in definite chemical entity is term as ion-association. The number of ions that pair together and the nature of chemical species are classified as ion-associates. Dielectric constant of the solvent is the most significant factor for determining the extent of ion-pair. The idea of ion-pair formation has been introduced by Bjerrum [1]. Study of ion-solvation is an important tool for understanding any salt application in the modern technology. Hence, conduct

metric data and various investigations of electrolytes in non-aqueous solvents and the concomitant ionic conductance are studied to gain a better understanding in high energy batteries [3] and in mechanistic pathways for organic reactions [4]. In ionic association studies, the nature of the solvent + solvent mixtures plays a very important role in the mode of electrolytic solution. The properties of solvents such as viscosity and relative permittivity are taken into account for the determination of the nature electrolytes in solutions.

The triple ion formation in a medium having very low permittivity, i.e., ( $\epsilon < 10$ ) [6] has been studied based on the observed conductance data of Tetrabutylammonium salts [6, 7] using Fuoss–Kraus theory [8]. The minimum value of experimental molar conductance values in a particular solvent has been investigated for the triple-ion formation [9]. In non-aqueous solvents, tetraalkylammonium salts has been found to exhibit the best solubility attributes.

## 2. EXPERIMENTAL

The tetrabutylammonium salts i.e.,  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$  and  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{I}^-$  were purchased from Sigma-Aldrich, Germany. Purity of tetrabutylammonium salts were 97%. For the experimental work, distilled water of specific conductance of order  $< 1 \times 10^{-6} \text{ Scm}^{-1}$  at  $298.15\text{K}$  was used. The non-aqueous solvents were purchased from Sigma-Aldrich, Germany. The purity of dichloromethane are 98%, and tetrahydrofuran is  $\geq 99.6\%$ . The values of their viscosity, dielectric constant and density were obtained from the literature [10-12]. Orion Star A112 Conductivity Benchtop meter, a dip type immersion conductivity cell were used for measuring electrical conductance with Epoxy 2 cell ( $K=1.0$ ) at particular temperature at  $25^\circ\text{C}$ . Water circulator bath - Cole-Palmer, Polystat R6L and graduated thermometer were used for controlling the temperature range at  $25^\circ\text{C}$ . By using a METTER Balance, model TB 214(max=210g; d=0.1mg), the weight of the sample was accurately measured.

3. RESULT AND DISCUSSION

The electrical conductance values were taken at different solvents. The equivalent conductance at a particular solvents were calculated through equation[13]

$$\Lambda = 1000 \kappa / C \tag{1}$$

where C is the concentration of the solution in moles per cubic metre and  $\kappa$  is specific conductance

**Table 1: Molar conductance ( $\Lambda$ ) and the corresponding concentration, C of the studied 1:1 salts (Bu<sub>4</sub>NI and Bu<sub>4</sub>Br) in different solvents at T = 298.15K.**

C x 104 (mol dm-3)	$\Lambda$ x 104 (Sm2mol-1)	C x 104 (mol dm-3)	$\Lambda$ x 104 (Sm2mol-1)
<b>(C4H9)4NBr</b>			
<b>Dichloromethane</b>		<b>Tetrahydrofuran</b>	
2.198	29.73	2.153	26.48
2.355	28.45	2.304	25.2
2.512	27.59	2.491	24.34
2.669	26.87	2.587	23.52
2.826	26.24	2.778	22.79
2.983	25.55	2.976	22.24
3.14	25.14	3.072	21.8
3.297	24.66	3.264	21.28
3.454	24.35	3.360	20.93
3.611	24.02	3.552	20.77
3.768	24.06	3.648	20.81
3.925	24.49	3.744	21.24
<b>(C4H9)4NI</b>			
<b>Dichloromethane</b>		<b>Tetrahydrofuran</b>	
2.041	28.53	2.016	24.71
2.198	27.25	2.112	23.43
2.355	26.39	2.208	22.57
2.669	25.77	2.491	21.85
2.805	25.13	2.682	21.22
2.961	24.45	2.880	20.63
3.126	23.91	2.976	20.12
3.140	23.46	3.072	19.64
3.297	23.05	3.168	19.23
3.454	22.82	3.360	19
3.611	22.86	3.552	19.04
3.908	23.29	3.648	19.47

Nonlinear representation for (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NI salts in pure dichloromethane and tetrahydrofuran explained as the conductance value decreases with increasing concentration, and attained a minimum and subsequently increase (fig. 1 and 2). The electrical conductance value were analyzed by the classical Fuoss-Kraus theory of triple-ion formation as a result of their deviation of the conductometric curves from linearity of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NI salts in dichloromethane ( $\epsilon_r = 8.93$ ) and tetrahydrofuran ( $\epsilon_r = 7.58$ ) [14]

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

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

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

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

Therefore,  $\Lambda_0$  is the molar conductance of the (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NX<sup>-</sup> ion at infinite dilution,  $\Lambda_0^T$  is the molar conductance value of the two triple-ions (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NX<sub>2</sub><sup>-</sup> and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NX<sup>+</sup> for the (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NX salts, where X= Br, I,  $K_P \approx K_A$  and  $K_T$  are the ion-pair and triple-ion formation constants respectively and S is the limiting Onsager coefficient. The symmetrical approximation of the two possible formation constants of triple-ions equal to each other was adopted [8] to make equation (2) applicable and as suggested by Krumgalz [15]  $\Lambda_0$  values for the (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NX salts was calculated. From the value 2/3  $\Lambda_0$ , [16]  $\Lambda_0^T$  was calculated. The results are given in Table 2.

During linear regression analysis, the ratio (eqn 2),  $\Lambda_0^T / \Lambda_0$  was thus set equal to 0.667. The limiting molar conductance of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NX ion ( $\Lambda_0$ ), limiting molar conductance of triple ion ( $\Lambda_0^T$ ), slope and intercept of (eq 2) for [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>...X] salts in dichloromethane and tetrahydrofuran at 298.15K were showed in Table 2. Intercept and slope were obtained from the linear regression analysis of eq 2 for the electrolytes with an average regression constant,  $R^2 = 0.9689$ . Also  $K_P$  and  $K_T$  were calculated from the above value obtained shown in Table 3. From the given value  $K_P$  is larger than  $K_T$ , therefore most of the [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>...X] salts appear as ion-pairs. The  $K_T/K_P$  ratio and  $\log(K_T/K_P)$  can be determined from triple ion formation with respect to ion-pair. From the ratio, it may be suggested that due to their coulombic interactions and covalent forces, strong ion-association occurs between the ions and solvent. These results confirm that the results are in accordance with Hazra et al. [17]. The ion-pairs attract the free cations or anions present in the solution medium as the distance of the closest approach of the ions becomes minimum, this is due to their very low permittivity(i.e.,  $\epsilon_r < 10$ ), resulting in relatively large interactions.

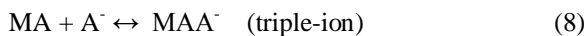
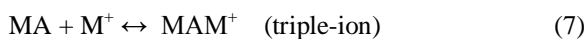
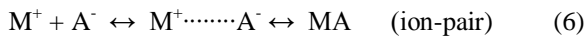
**Table 2: The calculated ion – pair limiting molar conductance ( $\Lambda_0$ ), triple – ion limiting molar conductance ( $\Lambda_0^T$ ), slope and intercept obtained from Fuoss – Kraus equation for 1:1 salts (Bu<sub>4</sub>NI and Bu<sub>4</sub>NBr) in different solvents at 298.15K.**

Solvents	$\Lambda_0$ x 104 (S m2 mol-1)	$\Lambda_0^T$ x 104 (S m2 mol-1)	Slope x 10-2	Intercept x 10-2
<b>(C4H9)4NBr</b>				
<b>Dichloromethane</b>	85.45	57.25	34.68	2.48
<b>Tetrahydrofuran</b>	61.96	41.51	37.21	2.25
<b>(C4H9)4NI</b>				
<b>Dichloromethane</b>	80.53	53.96	35.32	2.37
<b>Tetrahydrofuran</b>	55.18	36.97	37.84	2.18

**Table 3: Salt concentration at the minimum conductivity ( $c_{min}$ ) along with the ion – pair formation constant ( $K_p$ ), triple – ion formation constant ( $K_T$ ) for 1:1 salts( $Bu_4NI$  and  $Bu_4NBr$ ) in different solvents at 298.15K.**

Solvents	$c_{min}$ . 104/ (mol.dm-3)	log cmin n	$K_P \times 10^{-4}$ (mol.dm-3) <sup>-1</sup>	$K_T \times 10^{-4}$ (mol.dm-3) <sup>-1</sup>	$(K_T/K_P) \times 10^4$	log ( $K_T/K_P$ )
<b>(C4H9)4NBr</b>						
Dichloromethane	3.611	-3.44	68.36	41.65	609.27	-3.21
Tetrahydrofuran	3.552	-3.47	72.57	46.18	636.35	-3.19
<b>(C4H9)4NI</b>						
Dichloromethane	3.454	-3.46	66.29	36.75	554.38	-3.23
Tetrahydrofuran	3.360	-3.50	68.38	43.63	638.05	-3.20

These form triple-ion formation, obtaining the charge of the respective ions, attracted from the solution bulk [18] i.e.;



where  $M^+$  and  $A^-$  are  $[(C_4H_9)_4N]^+$  and  $X^-$  (where  $X= Br, I$ ) respectively. Due to their ternary association [19] some non-conducting species, MA, from solution are taken away and replaced with triple-ions which increase the conductance manifested by the non-linearity observed in the observed conductance curves for the tetrabutylammonium salts.  $C_p$  and  $C_T$  are obtained using the following equations [20]

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

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

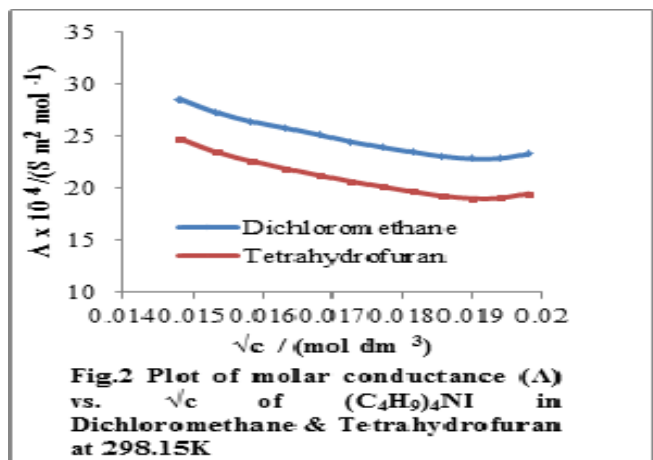
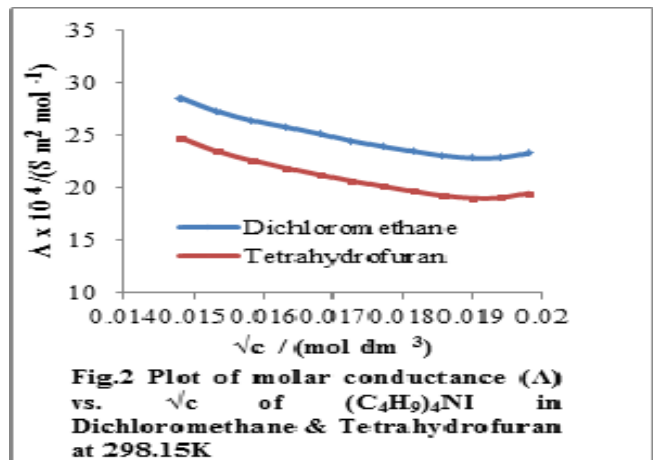
$$C_p = c(1 - \alpha - 3\alpha_T) \quad (11)$$

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

The fraction of  $\alpha$  and  $\alpha_T$  are present in the salt-solutions as given in Table 4. Major portion of ions are present as ion-pair even at high concentration however a small fraction exist as triple-ion as indicated by Table 4. The fraction of triple-ions in the solution increases with the increasing concentration of solutes in the solution medium.

**Table 4: 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 1:1 salts( $Bu_4NI$  and  $Bu_4NBr$ ) in different solvents at 298.15K.**

Solvents	$c_{min}$ . 104/ (mol.dm-3)	$\alpha_{min} \times 10^4$	$\alpha_T \times 10^2$	$C_p \times 10^5$ (mol dm-3)	$C_T \times 10^5$ (mol dm-3)
<b>(C4H9)4NBr</b>					
Dichloromethane	3.611	24.02	6.36	1.30	0.34
Tetrahydrofuran	3.552	20.77	6.43	1.28	0.36
<b>(C4H9)4NI</b>					
Dichloromethane	3.454	22.82	6.61	1.19	0.29
Tetrahydrofuran	3.360	19.00	6.65	1.16	0.32



#### 4. CONCLUSION

The present work shows important results on the ion association of  $(C_4H_9)_4NX$  salts in dichloromethane and tetrahydrofuran solutions through the conductometric measurements. Depending on their ionic size and charge distribution, ion-pair and triple-ion association were occurred.  $(C_4H_9)_4NX$  salts interact through hydrogen bonding and ion-dipole interactions in the non-aqueous solvents. It is possible ion-solvent interactions may dominate over ion-ion interactions. Consequently, the maximum amount of triple-ions formed was found in tetrahydrofuran.

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