

# Ion-pair and Triple-ion Formation of Lithium Salts in Non-aqueous Solvents at 25<sup>0</sup>C

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**Abstract**—The electrical molar conductivities of solutions of LiCl and LiNO<sub>3</sub> in pure non-aqueous solvents such as methylamine(CH<sub>3</sub>NH<sub>2</sub>), dichloromethane(CH<sub>2</sub>Cl<sub>2</sub>) and 1,4-dioxolane(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) were measured at 298.15K. Minima in the conductometric curves ( $\Lambda$  vs.  $\sqrt{c}$ ) were observed for electrolyte concentrations which depend upon both electrolyte and solvent. The observed molar conductivities were explained by the formation of ion-pairs ( $\text{Li}^+ + X^- \leftrightarrow \text{LiX}$ , where  $X = \text{Cl}^-$  or  $\text{NO}_3^-$ ) and triple-ions ( $2\text{Li}^+ + X^- \leftrightarrow \text{Li}_2\text{X}^+$ ;  $\text{Li}^+ + 2X^- \leftrightarrow \text{LiX}_2^-$ ). The experimental data were interpreted by Fuoss-Kraus equation leading to the values of the ion-pair formation constant ( $K_p$ ) and triple-ion formation constant ( $K_T$ ). A linear relationship between the triple-ion formation constants [ $\log(K_T/K_p)$ ] and the salt concentrations at the minimum conductivity ( $\log C_{\min}$ ) was given for all the salts in various solvents. The formation of triple-ion is attributed to the ion sizes in non-aqueous solvents in which Coulombic interactions and covalent bonding forces act as the main forces between the ions ( $\text{Li}^+ \dots X^-$ ).

**Keywords:** Conductivity data, Fuoss-Kraus equation, ion-pair, triple-ion, solvents, lithium salts.

## 1. INTRODUCTION

The branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance is termed as solution chemistry [1]. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. Solvent properties such 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. Understanding the state of association of the electrolytes and their interaction with the solvent molecules is important for selecting the solvent and electrolyte. Conductometric measurement has been used for studying the electrolytic solutions in various organic solvents.

We have come out with a modern technique [2-5] to study Li<sup>+</sup> ion solvation in various organic solvents from conductometric measurements. In this work, conductometric studies have been carried out for lithium chloride (LiCl) and lithium nitrate (LiNO<sub>3</sub>) in 100% mass fraction of methylamine, dichloromethane and 1,3 dioxolane. The lithium salts used in

this work when mixed with various organic solvents are very good electrolytes in lithium-ion batteries. Lithium-ion batteries are widely used in products such as portable consumer electronic devices. Therefore, by studying the behaviour of these lithium salts in various organic solvents, it will help in the production of more useful and cost effective batteries. Carefully, this would give a reasonable idea for selecting an important electrolyte in battery construction.

## 2. EXPERIMENTAL

The lithium salts selected for the present work puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of the lithium salts was  $\geq 0.99$ . Methylamine, Dichloromethane (DCM) and 1,3 Dioxolane was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of the solvent was  $\geq 0.995$ . The solutions of different concentrations ( $1 \times 10^{-4}$  M) were carefully prepared by dissolving requisite amount of the sample in conductivity solvent of low specific conductance ( $< 2 \times 10^{-6}$  S cm<sup>-1</sup>) and conductivity measurements were carried out over the temperature range of 25<sup>0</sup> C. All the dielectric constants and viscosities were obtained from literature [6-8]. The temperature control in the range of 25<sup>0</sup>C was made by using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg). All calculations were done on computer program using a Fuoss-Kraus technique. The observed conductivities were corrected for the conductivity of the solvent. The accuracy of the temperature of the thermostat was  $\pm 0.01^{\circ}\text{C}$

## 3. RESULTS AND DISCUSSIONS

The concentrations and molar conductances ( $\Lambda$ ) of LiCl and LiNO<sub>3</sub> in 100% mass fraction of Methylamine, Dichloromethane and 1,3 Dioxolane are given in Table 1. The molar conductance ( $\Lambda$ ) has been obtained from the specific conductance ( $k$ ) value using the following equation [9]

$$\Lambda = (1000 k) / c \quad \dots (1)$$

**Table 1: Molar conductance ( $\Lambda$ ) and the corresponding concentration (C) of the studied LiCl and LiNO<sub>3</sub> in different solvents at T = 298.15K.**

$c \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )	$\Lambda \times 10^4$ (mol mol <sup>-3</sup> )	$c \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )	$\Lambda \times 10^4$ (mol mol <sup>-3</sup> )	$c \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )	$\Lambda \times 10^4$ (mol mol <sup>-3</sup> )
<b>LiCl</b>					
CH <sub>3</sub> NH <sub>2</sub>		CH <sub>2</sub> Cl <sub>2</sub>		C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	
2.988	28.41	2.512	25.48	2.405	18.92
3.486	26.75	2.669	24.42	2.491	15.89
3.652	25.67	2.826	23.54	2.580	13.35
3.818	24.58	2.983	22.72	2.666	11.41
3.984	23.79	3.140	22.00	2.752	9.82
4.150	23.24	3.297	21.40	2.838	8.59
4.316	22.87	3.454	20.82	2.924	7.87
4.482	22.67	3.611	20.41	3.010	7.94
4.648	22.71	3.768	20.10	3.096	8.56
4.814	22.81	3.925	19.77	3.182	9.86
4.980	23.08	4.082	19.81	3.268	12.08
5.146	23.45	4.239	20.24	3.354	14.62
<b>LiNO<sub>3</sub></b>					
CH <sub>3</sub> NH <sub>2</sub>		CH <sub>2</sub> Cl <sub>2</sub>		C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	
2.160	26.42	1.727	23.83	1.548	16.43
2.320	25.00	2.041	22.55	1.720	13.13
2.490	23.68	2.198	21.69	1.978	10.56
2.656	22.59	2.355	21.07	2.147	8.73
2.822	21.88	2.512	20.44	2.233	7.35
2.988	21.19	2.669	19.85	2.319	6.43
3.154	20.94	2.826	19.24	2.405	6.20
3.320	20.76	2.983	18.70	2.491	6.25
3.486	20.79	3.140	18.24	2.580	6.78
3.652	20.82	3.297	18.26	2.666	7.92
3.818	20.96	3.454	18.28	2.752	9.79
3.984	21.46	3.611	18.59	2.838	12.43

Non linear conductance curve ( $\Lambda$  vs  $\sqrt{c}$ ) was obtained for the lithium salts in pure methylamine, dichloromethane and 1,3 dioxolane which shows that, the electrolyte (Li<sup>+</sup>...X) follows the same trend, i.e. the conductance value decreases with increasing concentration, reach a minimum and then increases. Due to the deviation of the conductometric curves from linearity in case of lithium salts (Li<sup>+</sup>...X) in methylamine ( $\epsilon_r = 9.35$ ), dichloromethane ( $\epsilon_r = 8.93$ ) and 1,3 dioxolane ( $\epsilon_r = 7.31$ ) the conductance data have been analyzed by the classical Fuoss-Kraus theory of triple-ion formation [10] in the form

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

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

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

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

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

In the above equations,  $\Lambda_0$  is the sum of the molar conductance of the simple ions LiX at infinite dilution,  $\Lambda_0^T$  is the sum of the conductance value of the two triple-ions LiX<sub>2</sub><sup>-</sup> and Li<sub>2</sub>X<sup>+</sup> for the lithium salts, where X= Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>;  $K_P \approx K_A$  and  $K_T$  are the ion-pair and triple-ion formation constants respectively and  $S$  is the limiting Onsager coefficient. To make equation (3) applicable, the symmetrical approximation of the two possible formation constants of triple-ions equal to each other has been adopted [11] and  $\Lambda_0$  values for the studied electrolyte have been calculated using the following scheme as suggested by B.Z. Krumgalz [12]  $\Lambda_0^T$  has been calculated by setting the triple-ion conductance equal to 2/3  $\Lambda_0$  [13]. The calculated values are listed in Table 23.

The ratio  $\Lambda_0^T / \Lambda_0$  was thus set equal to 0.667 during linear regression analysis of equation (2). Table 2 shows the calculated limiting molar conductance of simple ion ( $\Lambda_0$ ), limiting molar conductance of triple ion ( $\Lambda_0^T$ ), slope and intercept of equation (2) for lithium salts (Li<sup>+</sup>...X) in methylamine, dichloromethane and 1,3 dioxolane at 298.15K. The linear regression analysis of equation (2) for the electrolytes with an average regression constant,  $R^2 = 0.9689$ , gives intercept and slope. These values permit the calculation of other derived parameters such as  $K_P$  and  $K_T$  listed in Table 3. A perusal of Table 3 shows that the  $K_P$  is larger than  $K_T$ , indicate the major portion of the electrolytes (Li<sup>+</sup>...X) exists as ion-pairs with a minor portion as triple-ions. The tendency of triple ion formation with respect to ion-pair, can be judged from the  $K_T/K_P$  ratio and  $\log(K_T/K_P)$ . The ratios suggest that strong ion-association between the ions and solvent 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 and his groups [14]. At very low permittivity of the solvent, i.e.,  $\epsilon_r < 10$ , electrostatic ionic interactions are very large. So 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.

**Table 2: The calculated limiting molar conductance of ion-pair ( $\Lambda_0$ ), limiting molar conductance of triple-ion ( $\Lambda_0^T$ ), slope and intercept of equation 2 of lithium salts in methylamine, dichloromethane and 1,3 dioxolane at 298.15K**

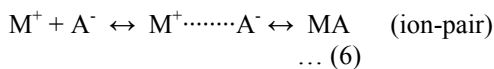
Solvents	$\Lambda_0 \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_0^T \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )	Slope x 10 <sup>2</sup>	Intercept x 10 <sup>-2</sup>
LiCl				

CH <sub>3</sub> NH <sub>2</sub>	139.10	93.20	1.82	0.96
CH <sub>2</sub> Cl <sub>2</sub>	116.51	78.06	2.05	0.75
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	101.50	68.00	2.25	0.49
LiNO <sub>3</sub>				
CH <sub>3</sub> NH <sub>2</sub>	128.77	86.28	1.97	0.78
CH <sub>2</sub> Cl <sub>2</sub>	104.55	70.05	2.48	0.52
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	90.01	60.31	2.88	0.38

**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 lithium salts in methylamine, dichloromethane and 1,3 dioxolane at 298.15K.**

	LiCl		
Solvents	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>
$c_{min} \times 10^4$ (mol dm <sup>-3</sup> )	4.482	3.925	2.924
log $c_{min}$	-3.35	-3.41	-3.53
$K_p \times 10^4$ (mol.dm <sup>-3</sup> ) <sup>-1</sup>	25.31	28.74	30.67
$K_T \times 10^4$ (mol.dm <sup>-3</sup> ) <sup>-1</sup>	18.45	21.29	23.68
$K_T/K_p \times 10^4$	728.96	740.78	772.09
log $K_T/K_p$	-1.14	-1.13	-1.11
	LiNO <sub>3</sub>		
$c_{min} \times 10^4$ (mol dm <sup>-3</sup> )	3.320	3.140	2.405
log $c_{min}$	-3.48	-3.50	-3.62
$K_p \times 10^4$ (mol.dm <sup>-3</sup> ) <sup>-1</sup>	23.63	26.43	28.98
$K_T \times 10^4$ (mol.dm <sup>-3</sup> ) <sup>-1</sup>	15.78	20.34	22.29
$K_T/K_p \times 10^4$	667.79	769.58	769.15
log $K_T/K_p$	-1.17	-1.12	-1.10

These results in the formation of triple-ions, which acquires the charge of the respective ions, attracted from the solution bulk [15] i.e.;



where M<sup>+</sup> and A<sup>-</sup> are [Li]<sup>+</sup> and X<sup>-</sup> (where X= Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>) respectively. The effect of ternary association [16] 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 lithium salts in methylamine, dichloromethane and 1,3 dioxolane.

Furthermore, the ion-pair and triple-ion concentrations, C<sub>p</sub> and C<sub>T</sub>, respectively, have also been calculated using the following equations [17]

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

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

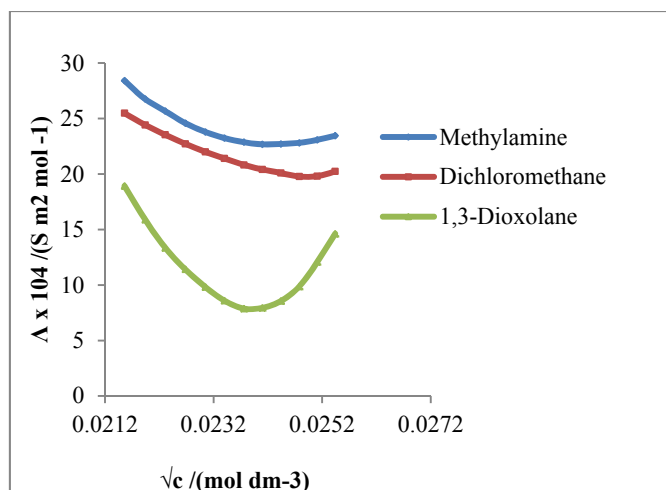
$$C_p = c(1 - \alpha - 3\alpha_T) \quad \dots (11)$$

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

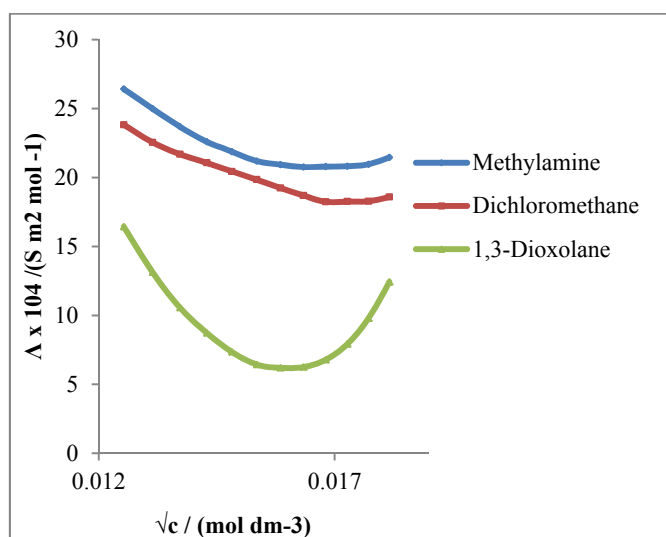
Here,  $\alpha$  and  $\alpha_T$  are the fraction of ion-pairs and triple-ions present in the salt-solutions are given in Table 4. Thus the values of C<sub>p</sub> and C<sub>T</sub> given in Table 4, indicates that the major portion ions are present as ion-pair even at high concentration and a small fraction exist as triple-ion. It is also observed that after a certain concentration the fraction of the triple-ions in the solution increases with the increasing concentration, in the studied solution media [Li]<sup>+</sup> and X<sup>-</sup> (where X= Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>) + methylamine, dichloromethane and 1,3 dioxolane.

**Table 4: Salt concentration ( $c_{min}$ ) at the minimum conductivity ( $\Lambda_{min}$ ), the ion-pair fraction ( $\alpha$ ), triple-ion fraction ( $\alpha_T$ ), ion-pair concentration ( $C_p$ ) and triple-ion concentration ( $C_T$ ) of ionic liquids in methylamine, dichloromethane and 1,3 dioxolane  $T = 298.15 \text{ K}$**

	LiCl		
Solvents	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>
$c_{min} \times 10^4$ (mol dm <sup>-3</sup> )	4.482	3.925	2.924
$\Lambda_{mn} \times 10^4$	22.67	19.77	7.87
$\alpha \times 10^2$	9.38	9.42	10.56
$\alpha_T \times 10^2$	3.60	3.86	4.31
$C_p \times 10^5$ (mol dm <sup>-3</sup> )	8.59	7.84	6.57
$C_T \times 10^5$ (mol dm <sup>-3</sup> )	1.61	1.75	2.49
	LiNO <sub>3</sub>		
$c_{min} \times 10^4$ (mol dm <sup>-3</sup> )	3.320	3.140	2.405
$\Lambda_{mn} \times 10^4$	20.76	18.24	6.20
$\alpha \times 10^2$	11.31	10.99	12.00
$\alpha_T \times 10^2$	3.97	4.08	4.52
$C_p \times 10^5$ (mol dm <sup>-3</sup> )	7.38	6.98	5.89
$C_T \times 10^5$ (mol dm <sup>-3</sup> )	2.02	2.25	2.81



**Fig.1** Plot of molar conductance ( $\Lambda$ ) vs. the square root of molar concentration ( $\sqrt{c}$ ) for LiCl in methylamine, dichloromethane and 1,3-dioxolane at T = 298.15K



**Fig. 2** Plot of molar conductance ( $\Lambda$ ) vs. the square root of molar concentration ( $\sqrt{c}$ ) for LiNO<sub>3</sub> in methylamine, dichloromethane and 1,3-dioxolane at T = 298.15K

The present work reveals an extensive study on the ion-solvation behaviour of the lithium salts [Li]<sup>+</sup> and X<sup>-</sup> (where X= Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>) in 100% mass fraction of methylamine, dichloromethane and 1,3 dioxolane through the conductometric. It becomes clear that the all the studied lithium salts exists as triple-ion in 100% mass fraction of methylamine, dichloromethane and 1,3 dioxolane at 298.15K. The tendency of the ion-pair and triple-ion formation depends on the size the charge distribution of the anions (Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>)

for the common cation (Li<sup>+</sup>), and structural aspects (functional group of the solvents).

#### 4. ACKNOWLEDGEMENTS

One of the authors (N. Mohondas Singh) thanks the Science and Engineering Research Board (SERB), New Delhi (vide no. SB/EMEQ-336/2014 dated 04.02.2016).

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