



Ion-Pair and Triple-Ion Formation of Ammonium Iodide and Potassium Iodide Salts in Two Different Organic Solvents at 298.15 K

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In present work, the ion pair and triple ion formation of ammonium iodide (NH₄I) and potassium iodide (KI) have been studied at 298.15 K. The work has been done using the two different solvents *viz.* *o*-xylene and *o*-toluidine. The limiting molar conductance (Λ_0), limiting molar conductance of triple ion (Λ_0^T) at infinite dilution in the pure solvent, association constant (K_p) and triple ion constant (K_T) at a particular temperature was studied by using the Fuoss-Kraus technique for the chosen salts. At smaller concentrations, ion pair concentration (C_p), triple ion concentration (C_T), ion-pair fraction (α) and triple ion fraction (α_T), respectively were examined by using K_p , K_T and to compare $K_{p,s}$ as well as $K_{T,s}$ values for the chosen salts.

Keywords: Ammonium iodide, Potassium iodide, Association constant, Triple ion constant, Fuoss-Kraus technique.

INTRODUCTION

The electrical conductivity of electrolytes in solvents mainly depends upon the electrolytic concentration and also upon the viscosity of the solvent [1-3]. Simple electrostatic theory shows that a system of two charged spheres placed symmetrically on each side of an oppositely charged sphere, all three being of the same size, has energy 50% greater than that of two oppositely charged spheres. Thus, there is reason to believe that triple ions (+ - +) or (- + -) might be formed in solvent of low dielectric constant. The following treatment is taken from Fuoss-Kraus [4]. It must be noted that by selecting a solvent of such low dielectric constant the calculation has been capable of simplification by neglecting the interionic effects. For a solvent of a higher dielectric constant, the interionic forces are no longer negligible and the computation is not so straightforward. They were able to carry the argument one stage further: by treating the approach of a negative ion towards the positive ion of an ion-pair, subject to Coulomb forces only, they were able to show that there is a certain value of the distance which is critical: once the approaching ion is within this critical distance it is to be regarded as forming a triple ion [5].

Fuoss & Kraus [5] had examined the triple ion formation concept from a uni-univalent electrolyte with the help of Bjerrum

theory, to illustrate the relationship between equivalent conductivity (Λ) and concentration (C) of the agglomeration of ionic species in low-dielectric media is a well-known phenomenon. Both ion-pairs and triple-ions were found to behave differently in terms of conductance. The ion-pair is uncharged so it cannot react to the externally applied field; whereas, the triple-ions is charged so it easily reacts to the externally applied field thereby adding to the conductance. The degree to which the formation of ion-pair takes place is monitored by the equilibrium created among the ion-pairs and free ions [6]. As a result, aggregation increases with the increase of stoichiometric concentration thereby formation of both ion-pair and triple-ion become greater.

EXPERIMENTAL

Chemicals used for the studies are ammonium iodide and potassium iodide with $\geq 99\%$ purity (Sigma-Aldrich), *o*-toluidine *o*-xylene (Merck) were used as solvents. The Orion StarTM A112 Conductivity Benchtop meter had measured the specific conductivities which was linked to epoxy 2 cell ($K = 1.0$). Preparation of the salt solutions with the distinct value of their concentrations (1.00×10^{-3} M) was simply done by adding the various amount of sample to the water, where the

specific conductance was less than $2.00 \times 10^{-6} \text{ S cm}^{-1}$ *i.e.*, conductivity water or double distilled water. The dielectric constant and viscosity of the chosen solutions were obtained from the literature [7]. The temperature control of a particular temperature (298.15 K) was made by using a water bath and thermometer. Weight measurements had been performed with the help of METTER Balance, model TB-214 (max = 210g; d = 0.1mg). All the measured experimental data of conductance were calculated according to the Fuoss-Kraus technique.

RESULTS AND DISCUSSION

Table-1 shows the molar conductance (Λ) and concentration of both *o*-xylene and *o*-toluidine. The relationship between molar conductance (Λ), specific conductance (κ) and concentration (c) is given by the following equation:

$$\Lambda = \frac{1000\kappa}{c} \quad (1)$$

The non-linear curve for conductance, *i.e.* the plot between Λ and \sqrt{c} was found for both electrolytes NH_4I and KI in *o*-toluidine and *o*-xylene (Fig. 1a-b), which revealed that these two electrolytes follow almost the same trend, *i.e.* the decrease in conductance value with increasing the concentration, it

reaches a minimum and then increases indicating the formation of triple-ions.

Due to the variation of the conductometric curves from linearity in case NH_4I and KI in *o*-toluidine ($\epsilon_r = 6.14$) and *o*-xylene ($\epsilon_r = 2.60$) for each salt separately (Fig. 1a-b), the conductance data have been investigated by the classical Fuoss-Kraus theory [4] is given in the following equation of triple-ion formation:

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

where $g(c)$ represents the factor that integrates all the terms of interaction and mathematically it can be illustrated as

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

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

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

TABLE-1
MOLAR CONDUCTANCE (Λ) AND THE CORRESPONDING CONCENTRATION (C) OF THE STUDIED 1:1 IN DIFFERENT SOLVENTS AT 298.15 K FOR NH_4I AND KI SALTS

NH_4I				KI			
<i>o</i> -Toluidine		<i>o</i> -Xylene		<i>o</i> -Toluidine		<i>o</i> -Xylene	
$C \times 10^4$ (mol dm ⁻³)	$\Lambda \times 10^4$ (Sm ² mol ⁻¹)	$C \times 10^4$ (mol dm ⁻³)	$\Lambda \times 10^4$ (Sm ² mol ⁻¹)	$C \times 10^4$ (mol dm ⁻³)	$\Lambda \times 10^4$ (Sm ² mol ⁻¹)	$C \times 10^4$ (mol dm ⁻³)	$\Lambda \times 10^4$ (Sm ² mol ⁻¹)
1.476	34.37	1.352	31.37	1.472	32.97	1.352	29.87
1.527	30.82	1.398	28.07	1.525	29.42	1.398	26.57
1.578	27.60	1.463	25.50	1.562	26.20	1.463	24.00
1.629	25.18	1.538	23.67	1.629	23.78	1.538	22.17
1.680	22.91	1.571	21.97	1.680	21.51	1.534	20.47
1.731	21.72	1.649	20.84	1.731	20.32	1.636	19.34
1.781	20.35	1.695	20.14	1.759	18.95	1.682	18.64
1.832	19.29	1.743	20.15	1.808	17.89	1.732	18.65
1.883	18.79	1.752	20.94	1.875	17.39	1.750	19.44
1.934	18.88	1.827	22.31	1.917	17.48	1.821	20.81
1.985	19.85	1.864	24.53	1.962	18.45	1.864	23.03
2.036	22.30	1.926	27.07	2.021	20.90	1.926	25.57

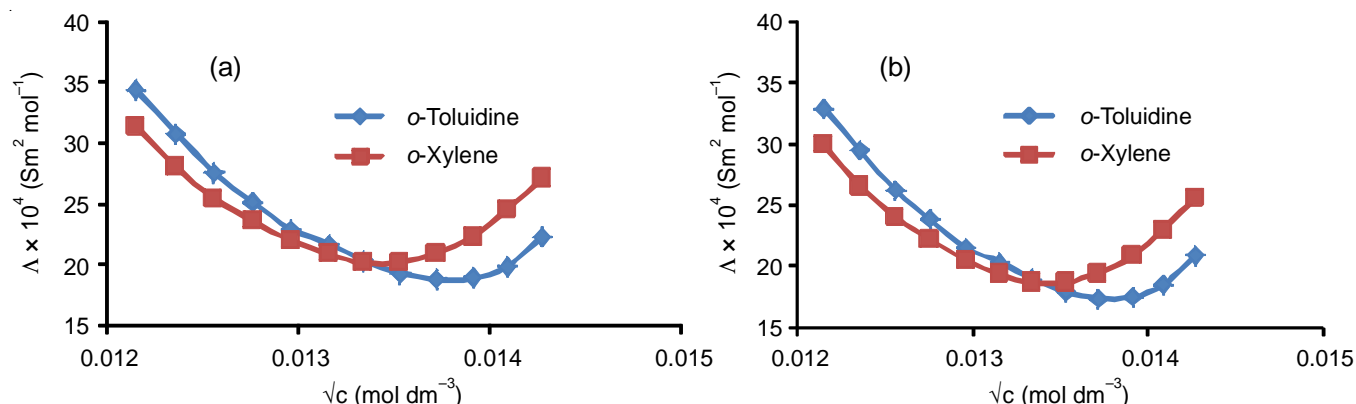


Fig. 1. Plot of molar conductance (Λ) vs. the square root of molar concentration (\sqrt{c}) for (a) NH_4I and (b) KI in *o*-toluidine and *o*-xylene at 298.15 K

where Λ_0 denotes the summation of molar conductance of ions at infinite dilution, Λ_0^T represents the summation of conductance of 2 triple ions, and K_p , K_T denote the constants for the formation of ion-pair and triple-ion, respectively and S is the limiting Onsager coefficient. Λ_0^T has been evaluated by putting the triple-ion conductance value equal to $2/3\Lambda_0$ [8].

Moreover, the concentrations of ion-pair (C_p) and triple-ion (C_T) were determined using the following equations [8,9]:

$$\alpha = \frac{1}{(K_p^{1/2} \cdot c^{1/2})} \quad (6)$$

$$\alpha_T = \left(\frac{K_T}{K_p^{1/2}} \right) c^{1/2} \quad (7)$$

$$C_p = c(1 - \alpha - 3\alpha_T) \quad (8)$$

$$C_T = \left(\frac{K_T}{K_p^{1/2}} \right) c^{3/2} \quad (9)$$

where both α and α_T denote the fraction of ion-pairs and triple-ions.

Table-1 observes that Λ values of NH₄I are greater than KI in both solvents, due to the KI is having more density than NH₄I and hence the movement of ions has restricted [10]. The ratio Λ_0^T/Λ_0 was 0.667 in the course of analysis of linear regression (eqn.1) [11]. Table-2 demonstrates the ion-pair limiting molar conductance of simple ion (Λ_0), limiting molar conductance of triple ion (Λ_0^T), intercept and slope of eqn. 2 for NH₄I and KI in *o*-toluidine and *o*-xylene at 298.15 K. Eqn. 2 for the electrolytes with regression constant, $R^2 = 0.9579$, gives intercepts and slopes, respectively. The calculation of K_p and K_T are given in Table-3. The K_p is larger than K_T , which shows

that both electrolytes (NH₄I and KI) exist as ion-pairs and minimum as triple-ions are given in Table-3. The impulse of formation of the triple-ions concerning ion-pair can be inspected from both K_T/K_p ratio and $\log(K_T/K_p)$. The ratios suggest strong ion-association between the ions and solvent which is because of the coulombic interactions and covalent forces in the solution. It agrees with the results of Roy *et al.* [12]. The electrostatic ionic interactions are greater at smaller permittivity of solvent, *i.e.* $\epsilon_r < 10$ [13]. Therefore, the ion-pairs tend to attract the free ions towards it when the distance of the closest approach of the ions is too less. Due to this, triple-ions acquire the charge of respective ions [14] *i.e.*



Due to the effect of ternary association [15], some non-conducting species, *i.e.*, MA, get eliminated from the solution and replaces with triple-ions which rise the conductance.

The higher K_p values in the case of NH₄I as compared to KI may be attributed to the more short-range interaction between the cation and anion [16,17]. α and α_T denote the fraction of ion-pairs and triple-ions respectively which are given in Table-4. So the values of C_p and C_T showed in Table-4, indicate that the maximum ions exist as ion-pair even at greater concentrations and minimum ions are present as triple-ion. Moreover, it is also noticed that after a certain concentration the portion of triple-ions increases with the rise of concentration.

Conclusion

The order of limiting molar conductance (Λ_0) and association constant (K_p) was found that ammonium iodide (NH₄I)

TABLE-2
CALCULATED ION-PAIR LIMITING MOLAR CONDUCTANCE (Λ_0), TRIPLE-ION LIMITING MOLAR CONDUCTANCE (Λ_0^T), SLOPE AND INTERCEPT OBTAINED FROM FUOSS-KRAUS EQUATION FOR 1:1 IN DIFFERENT SOLVENTS AT 298.15 K

Solvents	NH ₄ I				KI			
	$\Lambda_0 \times 10^4$ (S m ² mol ⁻¹)	$\Lambda_0^T \times 10^4$ (S m ² mol ⁻¹)	Slope $\times 10^{-2}$	Intercept $\times 10^{-2}$	$\Lambda_0 \times 10^4$ (S m ² mol ⁻¹)	$\Lambda_0^T \times 10^4$ (S m ² mol ⁻¹)	Slope $\times 10^{-2}$	Intercept $\times 10^{-2}$
<i>o</i> -Toluidine	98.62	66.07	34.92	2.37	90.01	60.31	35.17	2.31
<i>o</i> -Xylene	81.42	54.55	39.21	2.20	68.50	45.89	39.73	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 IN DIFFERENT SOLVENTS AT 298.15 K

Solvents	$c_{min} \times 10^4$ (mol dm ⁻³)		log c_{min}		$K_p \times 10^4$ (mol dm ⁻³) ⁻¹		$K_T \times 10^4$ (mol dm ⁻³) ⁻¹		$(K_T/K_p) \times 10^4$		log (K_T/K_p)	
	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI
<i>o</i> -Toluidine	1.883	1.875	-3.72	-3.73	61.47	59.26	37.25	34.21	605.99	577.29	-3.22	-3.24
<i>o</i> -Xylene	1.695	1.682	-3.77	-3.78	68.32	62.17	39.87	35.22	583.58	566.51	-3.23	-3.25

TABLE-4
SALT CONCENTRATION AT THE MINIMUM CONDUCTIVITY (c_{min}), THE ION-PAIR FRACTION (α), TRIPLE -ION FRACTION (α_T), ION-PAIR CONCENTRATION (c_p) AND TRIPLE-ION CONCENTRATION (c_T) FOR 1:1 IN DIFFERENT SOLVENTS AT 298.15 K

Solvents	$c_{min} \times 10^4$ (mol dm ⁻³)		$\Lambda_{min} \times 10^4$		$\alpha \times 10^2$		$\alpha_T \times 10^2$		$c_p \times 10^5$ (mol dm ⁻³)		$c_T \times 10^3$ (mol dm ⁻³)	
	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI	NH ₄ I	KI
<i>o</i> -Toluidine	1.883	1.875	18.79	17.39	9.31	9.55	6.51	6.04	0.52	0.50	0.13	0.12
<i>o</i> -Xylene	1.695	1.682	20.14	18.64	9.39	9.62	6.57	6.46	0.46	0.41	0.19	0.15

is greater than potassium iodide. The observed K_p is larger than K_T , which indicates that both electrolytes (NH_4I and KI) were present as compared to ion-pairs with minimum triple-ions. The course of formation of the triple-ions concerning ion-pair can be achieved from K_T/K_p and $\log(K_T/K_p)$. These ratios deliver that effective ion association among the ions and solvent due to the coulombic or electrostatic forces and covalent forces of attraction. At very low permittivity of the solvent, *i.e.* $\epsilon_r < 10$, the electrostatic ionic interactions-electrostatic attraction between 2 opposite charges are enormous. The ion-pairs tend to attract the free ions towards it when the distance of the closest approach of the ions is too less. Table-4 shows the fraction of ion-pairs (α) and the fraction of triple-ions (α_T) of the solution. Therefore, the ion-pair concentration (C_p) and triple-ions concentration (C_T) tell that the maximum ions exist as ion-pair even at greater concentration and minimum ions are present as triple-ion. It has also been noticed that after a certain concentration, the portion of triple-ions increases with the rise of concentration.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- M.N. Roy, D. Ekka and R. Dewan, *Fluid Phase Equilib.*, **314**, 113 (2012); <https://doi.org/10.1016/j.fluid.2011.11.002>
- V.V. Shcherbakov, Y.M. Artemkina, I.A. Akimova and IM. Artemkina, *Materials*, **14**, 5617 (2021); <https://doi.org/10.3390/ma14195617>
- W. Zhang, X. Chen, Y. Wang, L. Wu and Y. Hu, *ACS Omega*, **5**, 22465 (2020); <https://doi.org/10.1021/acsomega.0c03013>
- R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933); <https://doi.org/10.1021/ja01333a026>
- R.A. Robinson and R.H. Stokes, Butterworth & Co. Publishers Ltd., Ed.: 2, pp. 404-405 (2002).
- G. Emilsson, E. Röder, B. Malekian, K. Xiong, J. Manzi, F.-C. Tsai, N.-J. Cho, M. Bally and A. Dahlin, *Front Chem.*, **7**, 1 (2019); <https://doi.org/10.3389/fchem.2019.00001>
- <http://www.rafoeg.de/20>, Dokumentenarchiv/20, Daten/dielectric chart. Pdf.
- M. Delsignore, H. Farber and S. Petrucci, *J. Phys. Chem.*, **89**, 4968 (1985); <https://doi.org/10.1021/j100269a017>
- R. Chanda and M.N. Roy, *Fluid Phase Equilib.*, **269**, 134 (2008); <https://doi.org/10.1016/j.fluid.2008.04.001>
- N.M. Singh, G.C. Bag, N.R. Singh and N.R. Singh, *Chemical Environ. Res.*, **11**, 117 (2002).
- D. Aurbach, Non-aqueous electrochemistry, Marcel Dekker: New York (1999).
- M.N. Roy, D. Nandi and D.K. Hazra, *J. Indian Chem. Soc.*, **70**, 123 (1993).
- A.K. Covington and T. Dickinson, Physical Chemistry of Organic Solvent Systems. New York (NY), Plenum (1973).
- R.M. Fuoss and E. Hirsch, *J. Am. Chem. Soc.*, **82**, 1013 (1960); <https://doi.org/10.1021/ja01490a001>
- A. Sinha and M.N. Roy, *J. Phys. Chem. Liq.*, **45**, 67 (2007); <https://doi.org/10.1080/00319100601153830>
- G.C. Bag, N.M. Singh and N.R. Singh, *Indian J. Chem.*, **40A**, 500 (2001).
- N.M. Singh, T.D. Singh, N. Yaiphaba and N.R. Singh, *Asian J. Chem.*, **20**, 1750 (2008).