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Study on Ion Pair and Triple Ion Formation of an Ionic Liquid [(EMIM)(TOS)] in Different Solvents with the Manifestation of Solvation Consequence

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ABSTRACT

Solution behaviour of 1-ethyl-3-methyl imidazolium tosylate (IL) and some industrially important solvents (dimethylformamide, tetrahydrofuran and 1,4-dioxane) have been studied by electrolytic conductivity, density (ρ) and viscosity (η) study. The limiting molar conductivities (λ_0), association constants (K_A), and the distance of closest approach (R) of the ions have been measured using the Fuoss and Fuoss-Krass theory. The observed molar conductivities were explained by the formation of ion pairs and triple ions. Ion-solvent interactions have been interpreted in terms of apparent molar volumes and viscosity B-coefficients. Tetrabutylammonium tetraphenylborate [Bu_4NBP_4] was measured as “reference electrolyte” to estimate the limiting ionic conductivity ($\lambda_0^\pm$) of the ions along with the numerical appraisal of ion-pair formation constant.

1. Introduction

Ionic liquids (ILs) having combination of organic-organic and organic-inorganic cations/anions are of great interest in the current chemical field. Their intrinsic physicochemical properties make them “designer solvents” or “green solvent”, such as the favourable solubility of organic and inorganic compounds, negligible vapour pressures, low melting points, high thermal stability, solvated many organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical stability. In addition, along with these exceptional properties, ILs are used as heat transfer materials for processing biomass and electrically transport liquids as electrochemical tool in electrochemistry. Imidazolium cation based ILs are highly thermally stable, larger commercial available prominent bio-applications [1-5]. ILs having large anions are also susceptible to additional interactions with polar solvents.

N,N-dimethylformamide (DMF) is used in the production of acrylic fibers and plastics. It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings. 1,4-Dioxane (DO) is a trace contaminant of some chemicals used in cosmetics, detergents, and shampoos. Tetrahydrofuran (THF) is used as a precursor to polymers. The other main application of THF is an industrial solvent for PVC and in vernishes.

In the present work, herein we report conductivity, density, viscosity to ascertain the molecular interaction and ion association of the IL in the above solvents at 293.15 K, 303.15 K and 313.15 K respectively.

2. Experimental Methods

2.1 Source and Purity of Materials

1-Ethyl-3-methyl imidazolium tosylate (IL) ionic liquid selected for this work was of pure grade and procured from Sigma-Aldrich, Germany and it was used as purchased. The mass purity of the IL was ≥ 0.99 .

All the spectroscopic grade solvents were obtained from Sigma-Aldrich, Germany, and used as purchased. The purities of the solvents have been checked by measuring their densities and viscosities, which were in good accordance with the earlier work and are shown in Table 1.

Table 1 Density (ρ), viscosity (η) and relative permittivity (ϵ) of the different solvents dimethyl formamide (DMF), tetrahydrofuran (THF) and 1,4 dioxane (DO) at different temperatures

Solvents	Temp. (K)	ρ $10^{-3}/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	ϵ at T=298.15 K
DMF	293.15	0.93680	0.923	36.71
	303.15	0.93343	0.871	
	313.15	0.92908	0.726	
THF	293.15	0.88074	0.463	7.58
	303.15	0.87731	0.381	
	313.15	0.87179	0.369	
DO	293.15	0.96002	1.541	2.21
	303.15	0.95836	1.522	
	313.15	0.95374	1.509	

2.2 Apparatus and Procedure

Experimental Stock solutions of the IL in the different solvents were prepared by mass using Mettler Toledo AG-285 weighing machine having a precision of ± 0.0003 g. The uncertainty of molality of different solutions was estimated to ± 0.0001 mol kg $^{-1}$. Conductivity of the stock solution carried out in dilution method, i.e., addition of the pure solvent in a fixed concentration of IL solution of the same solvent.

Density (ρ , in g cm $^{-3}$) of the studied solution measured by Anton Paar digital density meter (DMA 4500M) with an accuracy of ± 0.00005 g cm $^{-3}$ at 293.15, 303.15 and 313.15 K and maintaining ± 0.01 K of the temperature deviation in each studied temperature. Calibration of the instrument was completed by triply distilled water and by passing dry air.

Viscosities of the experimental solution (η , mPa s) were measured by Brookfield DV-III Ultra Programmable Rheometer having a spindle size-42 with an accuracy of $\pm 1\%$. The particulars about the viscometer have previously been depicted earlier.

Specific conductivity of the IL in solutions was performed in Systronics-308 conductivity meter of working frequency 1 kHz and an accuracy of $\pm 1\%$. All the experimental solutions were positioned in a dip-type immersion conductivity (CD-10) cell, having a cell constant of approximately (0.1 ± 0.001) cm $^{-1}$. The Cell was connected with a temperature controlled water bath to maintain the experimental temperature. The cell constant was determined using the method suggested by Lind et al.

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3. Results and Discussion

The concentrations and molar conductances (Λ) of IL in DMF, DO and THF in different temperatures are given in Table 2.

Table 2 The concentration (c) and molar conductance (Λ) of [emim][TfSO₄] in DMF, DO and THF at 293.15, 303.15, 313.15 K respectively

$c \cdot 10^4 /$ mol dm ⁻³	$\Lambda \cdot 10^4 /$ Sm ² mol ⁻¹	$c \cdot 10^4 /$ mol dm ⁻³	$\Lambda \cdot 10^4 /$ Sm ² mol ⁻¹	$c \cdot 10^4 /$ mol dm ⁻³	$\Lambda \cdot 10^4 /$ Sm ² mol ⁻¹
293.15 K					
DMF		THF		DO	
3.8672	142.54	4.57	53.41	3.97	32.31
4.4641	142.5	5.34	52.31	4.74	31.21
5.235	142.46	6.12	51.41	5.52	30.31
6.26	142.41	6.81	50.6	6.21	29.50
7.1203	142.37	7.42	50.3	6.82	29.20
7.8984	142.33	7.81	50	7.21	28.90
8.7254	142.29	8.44	49.6	7.84	28.50
9.5721	142.27	8.88	49.1	8.28	28.00
10.6188	142.25	9.6	47.5	9.00	26.40
11.6422	142.25	10.05	46.6	9.45	25.50
12.4578	142.25	10.84	45.8	10.24	24.70
13.7642	142.27	11.62	44.21	11.02	23.11
14.7129	142.28	12.5	44	11.90	22.90
16.00	142.31	13.5	43.9	12.90	22.80
16.9106	142.34	15.58	43.1	14.98	22.00
303.15 K					
DMF		THF		DO	
3.8672	145.54	4.57	57.41	3.97	36.31
4.4641	145.5	5.34	55.31	4.74	34.21
5.235	145.46	6.12	53.41	5.52	32.31
6.26	145.41	6.81	52.6	6.21	31.50
7.1203	145.37	7.42	51.3	6.82	30.20
7.8984	145.33	7.81	51	7.21	29.90
8.7254	145.29	8.44	49.6	7.84	28.50
9.5721	145.27	8.88	49.1	8.28	28.00
10.6188	145.25	9.6	47.5	9.00	26.40
11.6422	145.25	10.05	46.6	9.45	25.50
12.4578	145.25	10.84	45.8	10.24	24.70
13.7642	145.27	11.62	44.21	11.02	23.11
14.7129	145.28	12.5	44	11.90	22.90
16.00	145.31	13.5	43.9	12.90	22.80
16.9106	145.34	15.58	43.1	14.98	22.00
313.15 K					
DMF		THF		DO	
3.8672	149.54	4.57	59.41	3.97	38.31
4.4641	149.5	5.34	59.31	4.74	38.21
5.235	149.46	6.12	59.41	5.52	38.31
6.26	149.41	6.81	59.6	6.21	38.50
7.1203	149.37	7.42	59.1	6.82	38.20
7.8984	149.33	7.81	50	7.21	28.90
8.7254	149.29	8.44	49.6	7.84	28.50
9.5721	149.27	8.88	49.1	8.28	28.00
10.6188	149.25	9.6	49.5	9.00	28.40
11.6422	149.25	10.05	49.6	9.45	28.50
12.4578	149.25	10.84	49.8	10.24	28.70
13.7642	149.27	11.62	49.21	11.02	28.11
14.7129	149.28	12.5	50	11.90	28.90
16.00	149.31	13.5	49.9	12.90	28.80
16.9106	149.34	15.58	49.1	14.98	28.00

The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation.

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

Linear conductance curve (Λ versus $\sqrt{c}$) were obtained for the electrolyte in DMF extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductance for the electrolyte.

3.1 Ion-Pair Formation

The ion-pair formation in case of conductometric study of IL in DMF analysed using the Fuoss conductance equation [6]. With a given set of conductivity values ($c_j, \Lambda_j; j = 1, \dots, n$), three adjustable parameters, i.e., Λ_0 , K_A and R have been 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 centre to centre distance

between the ions in the solvent separated ion-pairs. There is no precise method [7] 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 [8],

$$d = 1.183 (M / \rho)^{1/3} \quad (2)$$

where, M is the molecular mass and ρ is the density of the solvent.

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

$$\Lambda = \Lambda_0 [(1 + R_x) + E_L] \quad (3)$$

$$P = 1 - \alpha(1 - \gamma) \quad (4)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (5)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (6)$$

$$\beta = e^2 / (\epsilon_r k_B T) \quad (7)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (8)$$

where, Λ_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, ϵ is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarities 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, 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 were performed using the program suggested by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [9] Input for the program is the no. 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, molar masses, M_1 and M_2 along with c_j , Λ_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 Λ_0 and α which minimize the standard deviation, δ , whereby

$$\delta^2 = \sum [A_j(\text{cal}) - A_j(\text{obs})]^2 / (n - m) \quad (9)$$

for a sequence of R values and then plotting δ against R , the best-fit R corresponds to the minimum of the δ - 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 δ - R curves, thus R values is assumed to be $R = a + d$, with terms having usual significance. Finally, the corresponding limiting molar conductance (Λ_0), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation for IL in DMF at 293.15 K, 303.15 K and 313.15 K respectively are given in Table 3.

Table 3 Limiting molar conductance (Λ_0), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation for 1-ethyl-3-methylimidazolium tosylate in DMF at 293.15, 303.15, 313.15 K respectively

Solvent	$\Lambda_0 \cdot 10^4 / \text{Sm}^2 \text{mol}^{-1}$	$K_A / \text{dm}^3 \text{mol}^{-1}$	$R / \text{\AA}$	Δ
293.15 K				
DMF	25.24	428.25	6.34	0.21
303.15 K				
DMF	27.47	433.27	6.56	0.16
313.15 K				
DMF	38.26	463.24	7.44	0.11

Table 4 Walden product ($\Lambda_0 \eta$) and Gibb's energy change (ΔG°) of 1-ethyl-3-methylimidazolium tosylate in DMF at 293.15 K, 303.15 K and 313.15 K respectively are given below

Solvent	$\Lambda_0 \eta \cdot 10^4 \text{ Sm}^2 \text{mol}^{-1} \text{mPa}$	$\Delta G^\circ / \text{kJmol}^{-1}$
293.15 K		
DMF	23.29	-14.77
303.15 K		
DMF	23.92	-15.30
313.15 K		
DMF	27.77	-15.98

Table 3 shows that K_A values increase with increasing temperature in case of DMF. As in case of DMF, with increasing temperature the number

of free ions per unit volume decreases and hence the tendency of ion pair formation enhances.

The standard Gibbs free energy change of solvation, ΔG° , for IL in DMF is given by the following equation [10].

$$\Delta G^\circ = -RT \ln K_A \quad (10)$$

It is observed from the Table 4, values of the Gibbs free energy is entirely negative for DMF solvent at all temperatures and it can be explained by considering the participation of specific covalent interaction in the ion-association process.

Table 5 Limiting Ionic Conductance ($\lambda_0^\pm$), Ionic Walden Product ($\lambda_0^\pm \eta$), Stokes' Radii (r_s), and Crystallographic Radii (r_c) of 1-ethyl-3-methylimidazolium tosylate in DMF at 293.15 K, 303.15 K and 313.15 K respectively are given below

Solvent	Ion	$\lambda_0^\pm$ (Sm ² mol ⁻¹)	$\lambda_0^\pm \eta$ (Sm ² mol ⁻¹ mPa)	r_s (Å)	r_c (Å)
293.15	emim ⁺	8.12	7.88	3.14	4.78
	TSO ₄ ⁻	17.12	15.40	1.32	1.56
303.15	emim ⁺	8.36	7.91	3.16	4.88
	TSO ₄ ⁻	19.11	16.01	1.34	1.68
313.15K	emim ⁺	10.17	8.44	3.24	5.17
	TSO ₄ ⁻	28.09	19.33	1.36	2.27

Table 5 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).

3.2 Triple-Ion Formation

But for the electrolyte in THF and DO, a deviation in the conductance curve were obtained and shows a decrease in conductance values up to a certain concentration reaches a minimum and then increases indicating triple-ion formation.

The conductance data for the electrolyte in THF and DO have been analysed using the classical Fuoss-Kraus equation [11] for triple-ion formation.

$$\Delta g(c) \sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^2 K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (11)$$

$$g(c) = \frac{\exp\{-2.303 \beta' (c\Lambda)^{0.5} / \Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5} / \Lambda_0^{1.5}\} (1 - \Lambda / \Lambda_0)^{0.5}} \quad (12)$$

$$\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5} \quad (13)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta (\epsilon T)^{0.5}} \quad (14)$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution; Λ_0^T is the sum of the conductances of the two triple ions emim⁺TSO₄⁻ and emim⁺(TSO₄)₂⁻. $K_p \approx K_A$ and K_T are the ion-pair and triple-ion formation constants. To make Eq.(2) applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted [12] and Λ_0 values for the studied electrolytes have been calculated [13]. Λ_0^T is calculated by setting the triple ion conductance equal to $2/3\Lambda_0$ [14].

The ratio Λ_0^T/Λ_0 was thus set equal to 0.667 during linear regression analysis of Eq.(2). Limiting molar conductance of triple-ions (Λ_0^T), slope and intercept of Eq.(2) for [emim][TSO₄] in THF and DO at different temperatures are given in Table 6.

Table 6 The calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductances of triple ion Λ_0^T , experimental slope and intercept obtained from Fuoss-Kraus equation for 1-ethyl-3-methylimidazolium tosylate in THF and DO at 293.15 K, 303.15 K and 313.15 K respectively

Solvents	$\Lambda_0 \cdot 10^4$ /Sm ² mol ⁻¹	$\Lambda_0^T \cdot 10^4$ /Sm ² mol ⁻¹	Slope $\times 10^{-2}$	Intercept $\times 10^{-2}$
293.15 K				
THF	57.83	38.57	0.07	0.22
DO	36.10	20.74	0.06	0.21
303.15 K				
THF	61.76	41.19	0.12	0.44
DO	39.83	26.56	0.15	0.34
313.15 K				
THF	63.62	42.43	0.13	0.46
DO	41.86	27.92	0.14	0.29

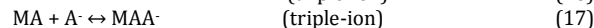
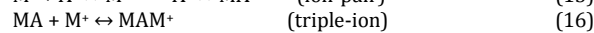
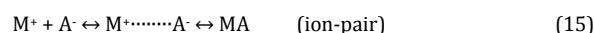
Linear regression analysis of Eq.(2) for the electrolytes with an average regression constant, $R^2 = 0.9653$, gives intercepts and slopes. These permit the calculation of other derived parameters such as K_p and K_T listed in Table 7.

Table 7 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-ethyl-3-methylimidazolium tosylate in THF and DO at 293.15 K, 303.15 K and 313.15 K respectively

Solvents	$C_{min} \cdot 10^4$ / mol dm ⁻³	$\log C_{min}$	$K_p \cdot 10^{-5}$ / (mol dm ⁻³) ⁻¹	K_T / (mol dm ⁻³) ⁻¹	K_T / K_p 10 ⁵	$\log K_T / K_p$
293.15 K						
THF	8.16	-3.088	1.74	64.34	36.97	-3.43215
DO	5.24	-3.280	1.22	80.68	66.13	-3.17960
303.15 K						
THF	8.26	-3.083	1.78	66.56	37.39	-3.42724
DO	5.34	-3.272	1.26	84.77	67.27	-3.17217
313.15 K						
THF	8.37	-3.077	1.82	69.78	38.34	-3.41634
DO	5.46	-3.263	1.31	90.75	69.27	-3.15945

It is observed that Λ 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).

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 become minimum. This results in the formation of triple-ion, which acquire the charge of the respective ions in the solution [15], i.e.,



where M^+ and A^- are respectively emim⁺ and TSO₄⁻. The effect of ternary association 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 THF and DO.

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 [emim][TSO₄] in THF and DO using the following relations:[16].

$$\alpha = 1 / (K_p^{1/2} \cdot c^{1/2}) \quad (18)$$

$$\alpha_T = (K_T / K_p^{1/2}) c^{1/2} \quad (19)$$

$$C_p = c(1 - \alpha - 3\alpha_T) \quad (20)$$

$$C_T = (K_T / K_p^{1/2}) c^{3/2} \quad (21)$$

where α and α_T are the fractions of ion-pairs and triple-ions present in the salt-solutions respectively and are given in Table 8. Thus, the values of C_p and C_T also given in Table 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 (α), triple-ion fraction (α_T), ion-pair concentration (C_p) and triple-ion concentration (C_T) have also been calculated over the whole concentration range of [emim][TSO₄] in THF and DO and are provided in Table 8.

Table 8 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-ethyl-3-methylimidazolium tosylate in THF and DO at 293.15 K, 303.15 K and 313.15 K respectively

Solvents	$C_{min} \cdot 10^4$ / mol dm ⁻³	$\alpha \cdot 10^{-5}$	$\alpha_T \cdot 10^3$	$C_p \cdot 10^{-4}$ / mol dm ⁻³	$C_T \cdot 10^{-6}$ / mol dm ⁻³
293.15 K					
THF	8.16	8.39	4.87	7.55	2.7
DO	5.24	12.50	5.57	6.98	3.6
303.15 K					
THF	8.26	8.24	4.92	7.64	2.6
DO	5.34	12.19	5.64	7.06	3.5
313.15K					
THF	8.37	8.10	4.95	7.73	2.5
DO	5.46	11.82	5.77	7.14	3.4

From Table 7, it has been observed with increasing temperature the number of free ions per unit volume decreases resulting in the increase of K_p and K_T values.

3.3 Apparent Molar Volume

The measured values of densities of IL in DMF, THF and DO at 293.15, 303.15 and 313.15 K are reported in Table 1. The densities of the electrolytes in different solvents increase linearly with the concentration at the studied temperatures. For this purpose, the apparent molar volumes ϕ_V were determined from the solutions densities using the following equation and the values are given in Table 9.

$$\phi_V = M / \rho - (\rho - \rho_0) / m \rho_0 \rho \quad (22)$$

where M is the molar mass of the solute, m is the molality of the solution, ρ and ρ_0 are the densities of the solution and solvent, respectively.

Table 9 Concentration, c , density, ρ , apparent molar volume, ϕ_V , limiting apparent molar volume ϕ_V^0 and experimental slope for 1-ethyl-3-methylimidazolium tosylate in THF and DO at 293.15 K, 303.15 K and 313.15 K respectively

Solvents	$c / \text{mol dm}^{-3}$	$\rho \cdot 10^{-3} / \text{kg m}^{-3}$	$\phi_V \cdot 10^6 / \text{m}^3 \text{mol}^{-1}$	$\phi_V^0 \cdot 10^6 / \text{m}^3 \text{mol}^{-1}$	$S_V^* \cdot 10^6 / \text{m}^3 \text{mol}^{-3/2} \text{dm}^{3/2}$
293.15 K					
DMF	0.010	0.95109	229.7438	223.34	-65.41
	0.025	0.95167	232.9002		
	0.040	0.95369	240.2651		
	0.055	0.95462	242.2379		
	0.070	0.95545	244.4737		
	0.085	0.95619	246.7438		
THF	0.010	0.89002	229.8142	224.51	-50.90
	0.025	0.89076	232.0633		
	0.040	0.89216	235.4370		
	0.055	0.89347	238.2484		
	0.070	0.89475	240.0758		
	0.085	0.89601	241.3971		
DO	0.010	1.03728	233.0668	228.11	-48.34
	0.025	1.03765	234.9957		
	0.040	1.03832	237.6479		
	0.055	1.03893	239.4964		
	0.070	1.03944	241.6262		
	0.085	1.03986	243.7721		
303.15 K					
DMF	0.010	0.94133	232.1275	225.92	-62.12
	0.025	0.94192	234.7851		
	0.040	0.94299	239.0373		
	0.055	0.94395	241.8721		
	0.070	0.94469	243.5269		
	0.085	0.94579	245.9471		
THF	0.010	0.88002	233.5627	227.94	-59.68
	0.025	0.88074	236.4060		
	0.040	0.88209	240.3867		
	0.055	0.88338	242.8509		
	0.070	0.88459	245.2204		
	0.085	0.88582	246.4146		
DO	0.010	1.02264	237.3807	232.61	-45.29
	0.025	1.02301	238.8480		
	0.040	1.02368	241.2936		
	0.055	1.02422	244.2284		
	0.070	1.02477	245.5734		
	0.085	1.02527	246.8696		
313.15 K					
DMF	0.010	0.93168	233.4619	228.14	-51.43
	0.025	0.93222	235.6798		
	0.040	0.93344	238.5637		
	0.055	0.93451	240.9804		
	0.070	0.93548	243.5314		
	0.085	0.93643	245.2767		
THF	0.010	0.86971	235.1858	230.44	-46.08
	0.025	0.87045	237.4875		
	0.040	0.87186	240.6523		
	0.055	0.87321	242.8581		
	0.070	0.87449	244.9679		
	0.085	0.87581	245.7735		
DO	0.010	1.01198	238.8960	234.47	-39.37
	0.025	1.01237	239.8845		
	0.040	1.01309	241.8617		
	0.055	1.01374	243.6740		
	0.070	1.01431	245.5688		
	0.085	1.01479	247.5953		

The apparent molar volumes ϕ_V were found to decrease with increasing molality (m) of IL in different solvents and increase with increasing temperature for the system under study. The limiting apparent molar volumes ϕ_V^0 were calculated using a least-squares treatment to the plots of ϕ_V versus $\sqrt{c}$ using the following Masson equation [17]

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

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

The plots of ϕ_V against the square root of the molar concentration $\sqrt{c}$ were found to be linear with negative slopes. The values of ϕ_V^0 and S_V^* are reported in Table 9. From Table 3 it is observed that ϕ_V^0 values for this electrolyte are generally positive for all the solvents and is highest in case of IL in DO. This indicates the presence of strong ion-solvent interactions and the extent of interactions increases from DMF to DO.

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 DO and is lowest in DMF. Owing to a quantitative comparison, the magnitude of ϕ_V^0 are much greater than S_V^* , in every solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions. The values of ϕ_V^0 also support the fact that higher ion-solvent interaction in DO, leads to lower conductance of IL in it than THF and DMF, discussed earlier.

3.4 Temperature Dependent Limiting Apparent Molar Volume

The variation ϕ_V^0 with the temperature of the IL in different solvents can be expressed (Fig.1).

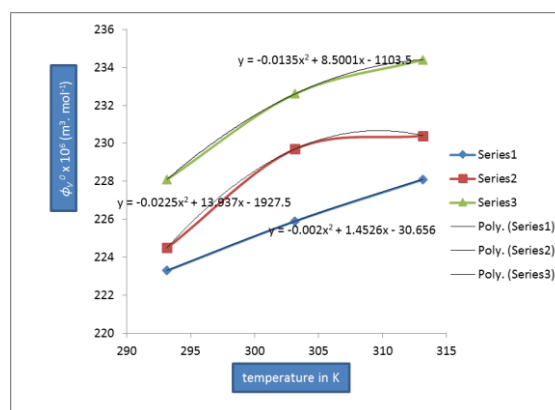


Fig. 1 Variation of ϕ_V^0 with temperature in K of the IL in DO (green line), THF (red line) and DMF (blue line)

By the general polynomial equation as follows,

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \quad (24)$$

where a_0 , a_1 , a_2 are the empirical coefficients depending on the solute, mass fraction (w_1) of the co solute IL, and T is the temperature range under study in Kelvin.

The values of these coefficients of the above equation for the IL in DMF, THF and DO are reported in Table 10.

Table 10 Values of empirical coefficients (a_0 , a_1 , and a_2) obtained from density data for IL in different solvents (DMF, THF and DO) at 293.15 K to 313.15 K respectively

Solvent mixture	$a_0 \cdot 10^6 / \text{m}^3 \text{mol}^{-1}$	$a_1 \cdot 10^6 / \text{m}^3 \text{mol}^{-1} \cdot \text{K}^{-1}$	$a_2 \cdot 10^6 / \text{m}^3 \text{mol}^{-1} \cdot \text{K}^{-2}$
DMF+IL			
293.15	-30.65	1.452	-0.002
303.15	-30.65	1.452	-0.002
313.15	-30.65	1.452	-0.002
THF+IL			
293.15	-275	3.023	-0.004
303.15	-275	3.023	-0.004
313.15	-275	3.023	-0.004
DO+IL			
293.15	-1103	8.5	-0.13
303.15	-1103	8.5	-0.13
313.15	-1103	8.5	-0.13

The limiting apparent molar expansibilities, ϕ_E^0 , can be obtained by the following equation,

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T \right)_p = a_1 + 2a_2 T \quad (25)$$

The limiting apparent molar expansibilities, ϕ_E^0 , change in magnitude with the change of temperature. The values of ϕ_E^0 for different solutions of the studied IL at 293.15, 303.15, and 313.15 K are reported in Table 11.

Table 11 Limiting apparent molal expansibilities (ϕ_E^0) IL in different solvents (DMF, THF and DO) at 293.15 K to 313.15 K respectively

solvent mixture	$\phi_E^0 \cdot 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$			$(\partial \phi_E^0 / \partial T)_p \cdot 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-2}$
DMF+IL				
T/K	293.15	303.15	313.15	
	0.36	0.2394	0.1994	-0.004
THF+IL				
T/K	293.15	303.15	313.15	
	0.6778	0.5978	0.5178	-0.008
DO+IL				
T/K	293.15	303.15	313.15	
	0.70221	0.6181	0.3581	-0.026

Table 12 Concentration, c , viscosity, η , viscosity A and B coefficients for 1-ethyl-3-methylimidazolium tosylate in THF and DO at 293.15 K, 303.15 K and 313.15 K respectively

Salts	$c / \text{mol dm}^{-3}$	$\eta / \text{mPa} \cdot \text{s}$	$\frac{(\eta_r - 1)}{\sqrt{c}}$	$B \text{ dm}^3 \text{mol}^{-1}$	$A \text{ dm}^{3/2} \text{mol}^{-1/2}$
293.15 K					
DMF	0.010	0.9041	0.028	0.156	0.011
	0.025	0.9059	0.034		
	0.040	0.9126	0.050		
	0.055	0.9159	0.056		
	0.070	0.9194	0.062		
	0.085	0.9216	0.078		
THF	0.010	0.4775	0.067	0.686	0.006
	0.025	0.4816	0.109		
	0.040	0.4885	0.149		
	0.055	0.4949	0.177		
	0.070	0.5016	0.203		
	0.085	0.5073	0.219		
DO	0.010	1.2994	0.005	0.701	-0.061
	0.025	1.3061	0.040		
	0.040	1.3202	0.082		
	0.055	1.3358	0.116		
	0.070	1.3493	0.137		
	0.085	1.3639	0.158		
303.15 K					
DMF	0.010	0.7668	0.027	0.172	0.010
	0.025	0.7685	0.035		
	0.040	0.7717	0.046		
	0.055	0.7745	0.052		
	0.070	0.7777	0.060		
	0.085	0.7805	0.065		
THF	0.010	0.3843	0.081	0.775	0.005
	0.025	0.3873	0.113		
	0.040	0.3936	0.162		
	0.055	0.3999	0.200		
	0.070	0.4060	0.229		
	0.085	0.4109	0.245		
DO	0.010	1.0946	0.012	0.777	-0.065
	0.025	1.1003	0.045		
	0.040	1.1128	0.089		
	0.055	1.1272	0.126		
	0.070	1.1415	0.155		
	0.085	1.1562	0.181		
313.15 K					
DMF	0.010	0.6848	0.0263	0.185	0.008
	0.025	0.6864	0.0352		
	0.040	0.6894	0.0468		
	0.055	0.6921	0.0542		
	0.070	0.6949	0.0614		
	0.085	0.6975	0.0668		

THF	0.010	0.2915	0.097	1.058	-0.003
	0.025	0.2946	0.144		
	0.040	0.3014	0.219		
	0.055	0.3071	0.259		
	0.070	0.3132	0.299		
	0.085	0.3185	0.325		
DO	0.010	0.9534	0.002	1.095	-0.106
	0.025	0.9598	0.049		
	0.040	0.9748	0.113		
	0.055	0.9918	0.165		
	0.070	1.0078	0.202		
	0.085	1.0265	0.242		

The table reveals that ϕ_E^0 is positive for IL in all the studied solvents and studied temperatures. This fact can be ascribed to the absence of caging or packing effect for the IL in solutions.

During the past few years it has been emphasized by different workers that S_V^* is not the sole criterion for determining the structure-making or -breaking nature of any solute. Hepler [18] developed a technique of examining the sign of $(\delta \phi_E^0 / \delta T)_p$ for the solute in terms of long-range structure-making and -breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$(\delta \phi_E^0 / \delta T)_p = (\delta^2 \phi_V^0 / \delta T^2)_p = 2a_2 \quad (26)$$

If the sign of $(\delta \phi_E^0 / \delta T)_p$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker [19]. As is evident from Table 7 the $(\delta \phi_E^0 / \delta T)_p$ values for IL in all the solvents are positive under investigation are predominantly structure makers in all of the experimental solutions.

3.5 Viscosity Calculation

Another transport property of the solution is viscosity has been studied for comparison and conformation of the solvation of the electrolyte in the chosen solvents. The viscosity data has been analyzed using Jones-Dole equation [20]

$$(\eta / \eta_0 - 1) / \sqrt{c} = A + B \sqrt{c} \quad (27)$$

where η and η_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 (Fig. 2) $(\eta / \eta_0 - 1) / \sqrt{c}$ against $\sqrt{c}$ which are reported in Table 12.

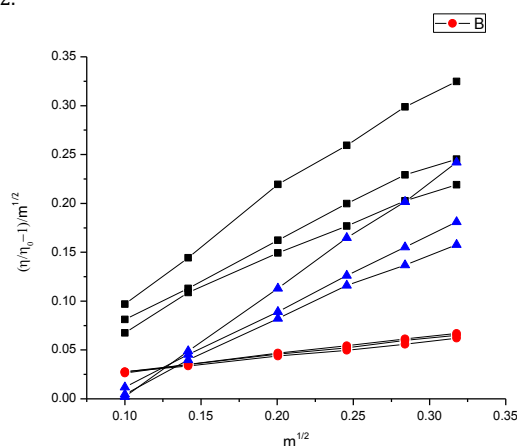


Fig. 2 Variation of $(\eta / \eta_0 - 1) / \sqrt{m}$ with $\sqrt{m}$ of the IL in DO (■); THF (Δ); DMF (◆)

The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 12, it is evident that the values of the B -coefficient are positive, thereby suggesting the presence of strong ion-solvent interactions, and strengthened with an increase in the solvent viscosity value, are agreement with the results obtained from ϕ_V^0 values discussed earlier. The values of the A -coefficient are found to increase slightly with temperature and with the increase in mass of IL in the solvent mixture. These results designate the presence of very weak solute-solute interactions. These results are in excellent arrangement with those obtained from S_V^* values.

The extent of solute-solvent interaction in the solution calculated from the viscosity B -coefficient [21] gives valuable information regarding the

solvation of the solvated solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules in the solutions. From Table 12, it is evident that the values of the *B*-coefficient are positive and much higher than *A*-coefficient, thereby suggesting the solute-solvent interactions are dominant over the solute-solute interactions. The higher *B*-coefficient values for higher viscosity values is due to the solvated solutes molecule associated by the solvent molecules all round to the formation of associated molecule by solute-solvent interaction, would present greater resistance, and this type of interactions are strengthened with a rise in temperature. These results are in good agreement with those obtained from ϕ_V^0 values discussed earlier.

Thus, the trend of ion-solvent interaction is DO > THF > DMF. The viscosity *A*- and *B*-coefficients are in excellent agreement with the results drawn from the volumetric studies.

4. Conclusion

The extensive study of IL, [emim][TfO₄] in DMF, DO and THF leads to the conclusion that, the salt is more associated in DO than the other two solvents. It can also be seen that in the conductometric studies in THF and DO, the IL mostly remains as triple-ions than ion-pairs but in DMF remains as ion-pairs. There is more ion-solvent interaction in DO than THF. The experimental values obtained from the volumetric, viscometric studies suggest that in solution here is more ion-solvent interaction than the ion-ion interaction and the extent of ion-solvent interaction of IL in DO, THF and DMF respectively.

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