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Probing Subsistence of Diverse Interplay of an Imidazolium Based Ionic Liquid Insight into Industrially Significant Solvent Environments

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ABSTRACT

Molecular interactions prevailing in ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF_4) in nitromethane, 1,3-dioxolane (DO) and dimethyl sulfoxide have been explored at 298.15 K. Investigations regarding electrolytic conductivities (Λ), densities (ρ), viscosities (η), refractive indices (n_D) and speed of sound (u) of the ionic liquid ([OMIM]BF_4) have been performed in the solvents at 298.15 K. The deviation of the conductometric curves (Λ vs. $\sqrt{c}$) linearity for the salt in DO indicates triple-ion formation, and conductance data have been analyzed by using the Fuoss–Kraus theory of triple-ions. Limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) derived from the masson equation, and viscosity A and B coefficients using the Jones–Dole equation have been interpreted in terms of ion-ion and ion solvent interactions respectively. Molar refraction (R_M) has been determined from Lorentz–Lorenz equation. Adiabatic compressibility (β_S) has been evaluated using the u values.

Key words: *1-methyl-3-octylimidazolium tetrafluoroborate, Nitromethane, 1,3-dioxolane, Dimethyl sulfoxide, Ion-solvent interaction.*

1. INTRODUCTION

Study on the transport properties of electrolytes in different solvent media is extremely important to obtain information regarding the solvation and association behavior of ions in solutions. The electrical conductivity of electrolytes in solvents mainly depends on the concentration of the electrolyte and the viscosity of the solvent. The application of the salt is well understood from the study of ionic solvation. Conductometric and related studies of electrolytes in non-aqueous solvents have been done in relation to the application of these types of electrolytes in high-energy batteries and for further making out of organic reaction mechanisms [1-3]. Volumetric, viscometric, refractometric and interferometric techniques also render an insight into the molecular interactions that are prevailing in solution and helps in the better understanding of the behavior of the salt with different solvents. Investigations 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 [4].

The solvents used in this study find wide industrial usage. 1,3-dioxolane (DO) is a good industrial solvent. It figures prominently in the high energy battery industries and finds application in organic synthesis as manifested from the physicochemical studies in this medium. DO and their derivatives exhibit a broad spectrum of biological activities such as antifungal, antibacterial, antineoplastic, antiviral, anesthetic and anticonvulsant ones [5-13].

Nitromethane (NM) is an aprotic solvent with high polarity, and it is used widely in the manufacture of pharmaceuticals, pesticides, explosives, fibers, and coatings. NM is used in the synthesis of NM derivatives used as pharmaceuticals, agricultural soil fumigants, and industrial antimicrobials [14]. It is also used as a fuel or fuel additive with methanol in racing cars, boats, and model engines. It is used as a chemical stabilizer to prevent decomposition of various halogenated hydrocarbons.

Dimethyl sulfoxide (DMSO) is a powerful broad spectrum solvent for a wide variety of inorganic and organic reactants. Having low toxicity, DMSO can be used in biology and medicine, especially for low-temperature preservation [15].

Viscosity, density and speed of sound help in understanding molecular interactions between the

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components of the mixture to develop new theoretical models and also for engineering applications [16].

An ionic liquid is a salt in the liquid state of melting point below some arbitrary temperature such as 373 K. They have specific intrinsic properties, such as negligible vapor pressure, high thermal stability, large liquid range, ability of dissolving a variety of chemicals, large electrochemical window. They are used as "designer solvents" and "green" replacements for volatile organic solvents used in reactions involving inorganic and biocatalytic reactions, etc. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells) [17-22].

In the modern technology, the application of the salt is well understood from the study of ionic solvation or ion association. Ionic association of electrolytes in solution depends on the mode of solvation of its ions that in turn depends on the nature of the solvent/solvent mixtures [23-26]. The association and solvation behavior of ions in solution is obtained from the conductance measurement. Moreover, solvent properties as viscosity and the relative permittivity help in determining the extent of ion association and the solvent-solvent interactions. The non-aqueous system has been of immense importance to the technologist and theoretician as many chemical processes occur in these systems. The volumetric, viscometric and interferometric behavior of solutes has been found to be very useful in elucidating the various interactions occurring in solutions [27,28].

In continuation of our investigation on electrical conductance the present work deals with the transport and thermodynamic properties of 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF_4) in NM, DO and DMSO at 298.15 K. Thermodynamic parameters are evaluated and discussed [29-31].

2. EXPERIMENTAL METHODS

2.1. *Source and Purity of Samples*

[OMIM]BF_4 of puriss grade was procured from Aldrich, Germany and was used as purchased. The solvents NM, DO and DMSO analytical reagent grade were procured from SD. Fine Chemicals and were purified using standard methods [32].

2.2. *Apparatus and Procedure*

A stock solution for [OMIM]BF_4 was prepared by mass and the working solutions were obtained by mass dilution at 298.15 K. The density (ρ) was measured by means of vibrating-tube Anton Paar density-meter (DMA 4500 M) with a precision of 0.00005 g/cm^3. It was calibrated by dry air and double-distilled water.

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [33-35].

A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ±0.01 K. After attainment of thermal equilibrium, a stopwatch was used to record the efflux times of flow being correct to ±0.1 s.

At least three repetitions of each data reproducible to ±0.1 s were taken to average the flow times. Viscosity of the solution, η, is given by the following equation:

$$\eta = \left(\mathrm{Kt} - \mathrm{L}/\mathrm{t}\right)\rho \tag{1}$$

where K and L are the viscometer constants, and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid respectively. The uncertainty in viscosity measurements is within ±0.003 mPas.

The conductance measurements were performed in a systronics-308 conductivity bridge (accuracy ±0.01%) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1±0.001). Measurements were made in a water bath maintained within T=(298.15±0.01) K and the cell were calibrated by the method proposed by Lind et al. [36]. The conductance data were reported at a frequency of 1 kHz and were uncertain to ±0.3%. Refractive index was measured with the help of a digital refractometer mettler toledo. The light source was light-emitting diode, λ=589.3 nm. The refractometer was calibrated twice using distilled water. The calibration was checked after every few measurements. The uncertainty of refractive index measurement was ±0.0002 units.

Speeds of sound were determined by multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 1 MHz, calibrated with water, methanol, and benzene at 298.15 K. The details of the methods and techniques have been described earlier [37,38]. The uncertainty of ultrasonic speed measurements is ±0.2 m.s^{-1}.

3. RESULTS AND DISCUSSION

3.1. *Electrical Conductance*

3.1.1. *Ion-pair formation*

The physical properties of the pure solvents were in good agreement with the values found in the literature, as reported in Table 1. The equivalent conductances (Δ) of electrolyte measured at the corresponding molar concentrations (c) in NM, DO and DMSO are given in Table 2. The conductance data for [OMIM]BF_4 in NM and DMSO have been analyzed using the Fuoss conductance equation [39-40]. For a given set of conductivity values ($c_j, \Lambda_j, j = 1,...n$) three

Table 1: Values of density (ρ), viscosity (η), refractive index (n_D), speed of sound (u), and dielectric constant (ε) of studied pure solvents at 298.15 K.

Solvent	ρ ($\times10^{-3}$ kg m^{-3})		η (mPa s)		n_D		(ms^{-1})		ε
	Expt	Lit	Expt	Lit	Expt	Lit	Expt	Lit	
NM	1.13039	1.13042 [55]	0.614	0.6140 [56]	1.3924	1.3920 [56]	1317.2	1317.0 [58]	35.87
DO	1.05872	1.05874 [59]	0.589	0.5886 [60]	1.3983	1.3980 [57]	1338.6	1338.8 [61]	7.34
DMSO	1.09538	1.09540 [62]	1.992	1.9910 [62]	1.4768	1.4770 [63]	1492.5	1493.0 [64]	34.82

NM: Nitromethane, DO: 1,3-dioxolane, DMSO: Dimethyl sulfoxide

Table 2: Molar conductance (Λ) and the corresponding concentration (c) of [OMIM]BF_4 in NM, DO and DMSO at 298.15 K.

NM		DO		DMSO	
C×10^4 (mol dm^{-3})	Λ×10^4 (S m^2 mol^{-1})	C×10^4 (mol dm^{-3})	Λ×10^4 (S m^2 mol^{-1})	C×10^4 (mol dm^{-3})	Λ×10^4 (S m^2 mol^{-1})
9.2073	114.70	0.0792	105.42	20.3691	35.35
16.8800	108.20	0.1451	96.36	37.3433	33.64
23.3723	103.97	0.2012	90.73	51.7062	32.87
28.9371	100.70	0.2489	87.67	64.0171	32.00
33.7600	98.34	0.2876	85.69	74.6867	31.20
37.9800	96.40	0.3269	84.05	84.0225	30.77
41.7035	94.70	0.3586	83.14	92.2600	30.44
45.0133	93.80	0.3989	82.96	99.5822	30.15
47.9747	92.50	0.4361	83.28	112.0300	29.68
50.6400	91.30	0.4758	84.06	122.2145	29.05
55.2436	89.30	0.5088	84.86	130.7017	28.72
59.0800	87.80	0.5503	85.78	137.8831	28.53
62.3262	86.70	0.5971	86.91	144.0386	28.29
66.3559	85.50	0.6328	88.03	154.0413	27.86
68.6090	84.40	0.6703	89.36	161.8211	27.58

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, NM: Nitromethane, DO: 1,3-dioxolane, DMSO: Dimethyl sulfoxide

adjustable parameters, the limiting molar conductance (Λ_o) the association constant (K_A) and the distance of closest approach of ions (R) are derived from the following set of equations.

$$\Lambda = P\Lambda_o[(1+R_X)+E_L] \tag{2}$$

$$P = 1-\alpha(1-\gamma) \tag{3}$$

$$\gamma = 1-K_A c\gamma^2 f^2 \tag{4}$$

$$-\ln f = \beta\kappa/2(1+\kappa R) \tag{5}$$

$$\beta = e^2/(\varepsilon k_B T) \tag{6}$$

$$K_A = K_R/(1-\alpha) = K_R/(1+K_S) \tag{7}$$

where R_X is the relaxation field effect, E_L is the electrophoretic counter current, k^{-1} is the radius of the ion atmosphere, ε 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_A is the overall paring 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 a program suggested by Fuoss. The initial Λ_o values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set $(c_j, \Lambda_j, j=1,...n), n, \varepsilon, \eta, T$, initial values of Λ_o, and instruction to cover a pre-selected range of R values.

In practice, calculations are performed by finding the values of Λ_o and α which minimize the standard deviation:

$$\delta^2 = \sum [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n-2) \qquad (8)$$

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, approximate runs are made over a fairly wide range of R-values using 0.1 increments to locate the minimum, but no significant minima were found in the δ-R curves for $[OMIM]BF_4$ in NM and DMSO; thus, R-values are 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

$$d(\text{Å}) = 1.183(M/\rho)^{1/3} \qquad (9)$$

where M is the molar mass of the solvent and ρ is its density. The values of Λ_o, K_A, and R obtained by this procedure are reported in Table 3.

Perusal of Table 3 shows that the limiting molar conductance Λ_o of $[OMIM]BF_4$ in NM is far greater than that in DMSO. The Table 3 also reveals that the association of the $[OMIM]BF_4$ is more in DMSO than in NM. Hence, this shows that there is more ion-solvent interaction in DMSO than NM leading to a lower conductance of $[OMIM]BF_4$ in the former than the latter. The lower viscosity of NM also supports the above fact because with lower viscosity the Λ_o value should increase.

The trend in Λ_o values can be discussed through another characteristic function called the Walden product, $\Lambda_o\,\eta$ given in Table 4. Even though the viscosity of DMSO is more than NM, the $\Lambda_o\,\eta$ is more in case of $[OMIM]BF_4$ in NM. This suggests the predominance of Λ_o overs η.

ΔG° is given by the following relationship and is given in Table 4 [41].

$$\Delta G^{o} = -RT\ln K_A \qquad (10)$$

The negative values of ΔG° can be explained by considering the participation of specific covalent interaction in the ion-association process. A decrease in the value of ΔG° of $[OMIM]BF_4$ in DMSO than NM shows that the greater degree of association in DMSO.

3.2. Triple-Ion Formation

Due to the deviation of the conductometric curves (Λ_o vs. √c) from linearity in case of $[OMIM]BF_4$ in DO, the conductance data have been analyzed by the classical Fuoss–Kraus theory of triple-ion formation [42,43] in the form

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

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

$$\beta^{/} = 1.8247\times10^{6}/(\varepsilon T)^{1.5} \qquad (13)$$

$$S = \alpha\,\Lambda_0 + \beta = \frac{0.8204\times10^{6}}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad (14)$$

In the above equations, Λ_o is the sum of the molar conductance of the simple ions at infinite dilution, Λ_0^T is the sum of the conductance of the two triple-ions $[OMIM][(BF_4)_2]^-$ and $[([OMIM])_2]^+BF_4^-$ for $[OMIM]BF_4$; $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants. To make equation (11) applicable, the symmetrical approximation of the two possible constants of triple-ions equal to each other has been adopted and Λ_o values for the studied $[OMIM]BF_4$ in DO have been calculated [44,45]. Λ_o^T is calculated by setting the triple-ion conductance equal to 2/3 Λ_0 [46].

The ratio $\Lambda_0^T = \Lambda_o$ was thus set equal to 0.667 during linear regression analysis of equation (11). Table 5

Table 3: Limiting molar conductivity (Λ_o), the association constant (KA) and the distance of closest approach of ions (R) of $[OMIM]BF_4$ in NM and DMSO at 298.15 K.

Solvent	Λo ($S\ m^2\ mol^{-1}$)	K_A ($dm^2\ mol^{-1}$)	R (Å)	δ
NM	129.7413	73.8202	7.12	0.5263
DMSO	38.5142	84.1212	7.56	0.1025

$[OMIM]BF_4$: 1-methyl-3-octylimidazolium tetrafluoroborate, NM: Nitromethane, DMSO: Dimethyl sulfoxide

Table 4: Walden product, $\Lambda_o\,\eta_o$ and free energy change, ΔG° of $[OMIM]BF_4$ in NM and DMSO at 298.15 K.

Solvent	$\Lambda_o\eta_o$ ($S\ m^2\ mol^{-1}$ mPa s)	$\Delta G^\circ\times10^{-4}$ ($kJ\ mol^{-1}$)
NM	79.6612	−10.6629
DMSO	75.7202	−10.9867

$[OMIM]BF_4$: 1-methyl-3-octylimidazolium tetrafluoroborate, NM: Nitromethane, DMSO: Dimethyl sulfoxide

Table 5: The calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductance of triple-ion (Λ_0^T) slope and intercept of Equation (11) of $[OMIM]BF_4$ in DO at 298.15 K.

$\Lambda_o\times10^4$ ($S\ m^2\ mol^{-1}$)	$\Lambda_o^T\times10^4$ ($S\ m^2\ mol^{-1}$)	Slope×10^3	Intercept×10^4
114.95	76.88	4.26	−5.09

$[OMIM]BF_4$: 1-methyl-3-octylimidazolium tetrafluoroborate, DO: 1,3-dioxolane shows the calculated limiting molar conductance of simple ion (Λ_o), limiting molar conductance of triple ion (Λ_0^T), slope and intercept of equation (11) for [OMIM] BF_4 in DO at 298.15 K. The linear regression analysis of equation (11) for the electrolytes with an average regression constant, R^2=0.9653, gives intercepts and slopes. These values permit the calculation of other derived parameters such as K_P and K_T listed in Table 6. It is observed from Figure 1 that Λ passes through a minimum as c increases. The value of log (K_T/K_P) has also been reported. At very low permittivity of the solvent, i.e., ε<10, electrostatic ionic interactions are very large. So the ion-pairs attract the free cations, and anions ions present in the solution medium as the distance of the closest approach of the ions becomes minimum. This result in the formation of triple-ions, which acquire the charge of the respective ions in the solution [47] depicted in the Scheme 1.

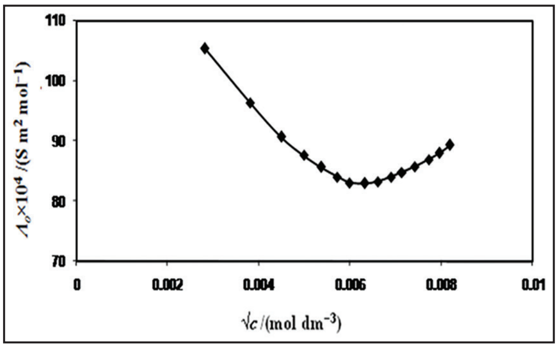
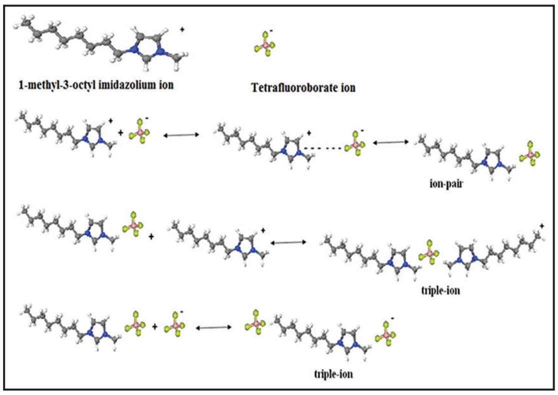


Figure 1: Plots of values of molar conductance (Λ) and the square root of concentrations (√c) of 1-methyl-3-octylimidazolium tetrafluoroborate in 1,3-dioxolane at 298.15 K.



Scheme 1: Schematic representation of ion-solvent interaction for the particular ion in the studied solutions (1-methyl-3-octylimidazolium tetrafluoroborate+solvents).

Furthermore, the ion-pair and triple-ion concentrations, C_P and C_T, respectively of the [OMIM]BF_4 in DO have also been calculated using the following relations [48].

$$\alpha = 1/\left(K_P^{1/2} \times C^{1/2}\right) \tag{15}$$

$$\alpha_T = \left(K_T / K_P^{1/2}\right) C^{1/2} \tag{16}$$

$$C_P = C\left(1-\alpha-3\alpha_T\right) \tag{17}$$

$$C_T = \left(K_T / K_P^{1/2}\right) C^{3/2} \tag{18}$$

Here, α and α_T are the fraction of ion-pairs and triple-ions and is given in Table 7. Thus, the values of C_P and C_T given in Table 7 indicate that the ions are mainly present as triple-ions and a small fraction existing as ion-pairs. The ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_P) have been also calculated over the whole concentration range of [OMIM]BF_4 in DO and the data are provided in Table 8. It is observed that the amount of the triple-ions in the solution increases with the increase in concentration.

3.3. Density Calculation

The measured value of densities of [OMIM]BF_4 in NM, DO and DMSO, as a function of concentration at 298.15 K is listed in Table 9. For the analysis of the interaction of [OMIM]BF_4 in NM, DO and DMSO limiting apparent molar volumes are important. For this purpose, the apparent molar volumes ϕ_V given in Table 9 were determined from the solution densities using the following equation

$$\phi_V = M/\rho_o - 1000\left(\rho-\rho_o\right)/c\rho_o \tag{19}$$

where M is the molar mass of the solute, c is the molarity of the solution, ρ and ρ_o are the densities of the solution and solvent, respectively. The limiting apparent molar volumes ϕ_V^0 were calculated using a least-squares treatment to the plots of ϕ_v versus √c using the following Masson equation [49].

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \tag{20}$$

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 √c were found to be linear with negative slopes that are shown in Figure 2. The values of ϕ_V^0

Table 6: Salt concentration at the minimum conductivity (c_{min}) along with the ion-pair formation constant (K_P), triple-ion formation constant (K_T) of [OMIM]BF_4 in DO at 298.15 K.

$c_{min}\times10^4$ (mol dm^{-3})	Log c_{min}	$K_P\times10^{-10}$ (dm^3 mol^{-1})	K_T (dm^3 mol^{-1})	$(K_T/K_P)\times10^{-10}$	Log (K_T/K_P)
0.3989	−0.3991	5.063	12.637	2.496	10.397

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, DO: 1,3-dioxolane

Table 7: 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 of [OMIM]BF_4 in DO at 298.15 K.

$C\times10^4$ (mol dm^{-3})	$\alpha\times10^4$	$\alpha_T\times10^7$	$c_P\times10^5$ (mol dm^{-3})	$c_T\times10^{11}$ (mol dm^{-3})
0.3989	7.0366	3.5471	3.9862	1.4149

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, DO: 1,3-dioxolane

Table 8: Salt concentration (c), the ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (c_P) and triple-ion concentration (c_T) of [OMIM]BF_4 in DO at 298.15 K.

$c\times10^4$ (mol dm^{-3})	$\alpha\times10^4$	$\alpha_T\times10^7$	$c_P\times10^5$ (mol dm^{-3})	$c_T\times10^{11}$ (mol dm^{-3})
0.0792	15.7919	1.5805	0.7907	0.1252
0.1451	11.6671	2.1393	1.4493	0.3104
0.2012	9.9079	2.5191	2.0100	0.5069
0.2489	8.9081	2.8019	2.4868	0.6974
0.2876	8.2871	3.0119	2.8736	0.8662
0.3269	7.7730	3.2111	3.2665	1.0497
0.3586	7.4215	3.3631	3.5833	1.2060
0.3989	7.0366	3.5471	3.9862	1.4149
0.4361	6.7298	3.7088	4.3581	1.6174
0.4758	6.4429	3.8739	4.7549	1.8432
0.5088	6.2305	4.0060	5.0848	2.0383
0.5503	5.9910	4.1662	5.4997	2.2927
0.5971	5.7514	4.3397	5.9676	2.5913
0.6328	5.5868	4.4676	6.3245	2.8271
0.6703	5.4283	4.5981	6.6994	3.0821

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, DO: 1,3-dioxolane

and S_V^* are reported in Table 9. ϕ_V^0 values indicate the extent of ion-solvent interaction. A perusal of Table 9 reveals that the ϕ_V^0 values are positive and is highest in case of [OMIM]BF_4 in DMSO, indicating that the ion-solvent interaction is more in case of [OMIM] BF_4 in DMSO than in DO than in NM shown in the Scheme 2 where I_1, I_2 and I_3 are the extent of ion-solvent interaction of [OMIM]BF_4 in NM, DO and DMSO respectively. The observed trend of ion-solvent interaction is,

$I_1<I_2<I_3$

On the contrary, the S_V^* indicates the extent of ion-ion interaction. The values of S_V^* show that the extent of ion-ion interaction is more in case of the NM. A quantitative comparison of the magnitude of ϕ_V^0 values

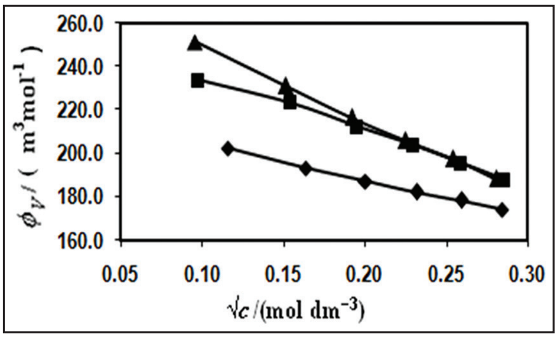
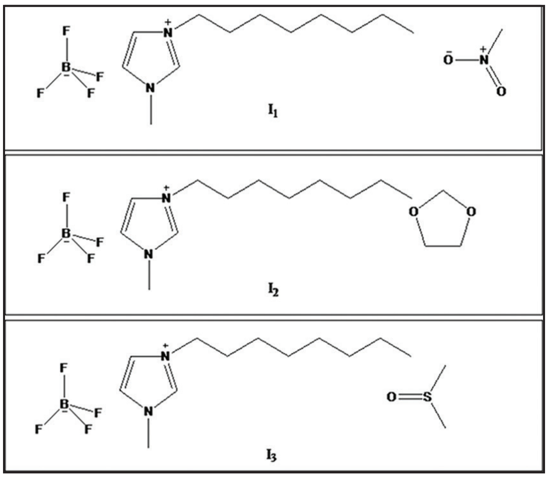


Figure 2: Apparent molar volume (ϕ_V), and the square root of concentrations (√c) for 1-methyl-3-octylimidazolium tetrafluoroborate in nitromethane (—♦—), 1,3-dioxolane (—■—), and dimethyl sulfoxide (—▲—) at 298.15 K.



Scheme 2: Schematic representation of the interaction occurring in pure solvent and (1-methyl-3-octylimidazolium tetrafluoroborate+solvents) together with the trend in the ion-solvation in the studied solvents following the order I1<I2<I3.

Nomenclature

ρ_o	Solvent density
η_o	Solvent viscosity
ρ	Solution density
η	Solution viscosity
n_D	Refractive index
u	Speed of sound
ε	Relative permittivity
c	Molarity
Λ	Equivalent conductance
Λ_o	Limiting molar conductance
K_A	Association constant
R	Association distance or co-sphere diameter
R_x	Relaxation field effect
E_L	Electrophoretic counter current

Nomenclature

k	Radius of the ion atmosphere
e	Electron charge
k_B	Boltzmann constant
K_S	Association constant of the contact-pairs
K_R	Association constant of the solvent-separated pairs
γ	Fraction of solute present as unpaired ion
α	Fraction of contact pairs
f	Activity coefficient
T	Absolute temperature
β	Twice the Bjerrum distance
ΔG^o	Gibbs energy of ion-association reaction
Λ_o^T	Conductance of the two triple ion
K_p	Ion-pair formation constant
K_T	Triple-ion formation constant
α	Fraction of ion-pairs
α_T	Fraction of triple-ions
C_P	Ion-pair concentration
C_T	Triple-ion concentration
ϕ_V	Apparent molar volume
ϕ_V^o	Limiting apparent molar volume
S_V^*	Experimental slopes
A	Constant
B	Constant
R_M	Molar refraction
β_o	Adiabatic compressibility of the solvent
β_s	Adiabatic compressibility of the solution
ϕ_K	Apparent molal adiabatic compressibility
S_K^*	Experimental slopes
ϕ_K^o	Apparent molal adiabatic compressibility

is much greater in magnitude than S_V^* values, for the 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 lower ion-solvent interaction in NM, leads to higher conductance of [OMIM]BF_4 in it than DO and DMSO.

3.4. *Viscosity Calculation*

The viscosity data have been analyzed using Jones–Dole equation [50].

$$(\eta / \eta_0 - 1) / \sqrt{c} = A + B\sqrt{c} \qquad (21)$$

where η_0 and η are the viscosities of the solvent and solution respectively. A and B are the constants estimated by a least-squares method and are reported in Table 10. The values of A and B are obtained from the straight line by plotting $(\eta/\eta_o-1)/\sqrt{c}$ against $\sqrt{c}$ as depicted in Figure 3 and reported in Table 10.

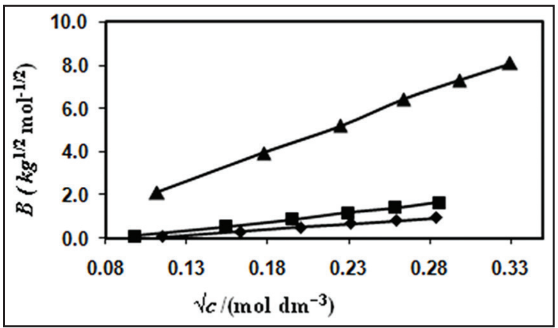


Figure 3: Plots of viscosity B-coefficient versus √c of 1-methyl-3-octylimidazolium tetrafluoroborate in nitromethane (—◆—), 1,3-dioxolane (—■—) and dimethyl sulfoxide (—▲—) at 298.15 K.

A perusal of Table 10 shows that the values of the A coefficient are generally negative for all of the solutions under investigation and indicates weak ion-ion interactions. The viscosity B coefficient reflects the effects of ion-solvent interactions [51]. Table 10 shows that the values of the viscosity B coefficient for [OMIM]BF_4 in NM, DO, and DMSO are positive, thereby suggesting the presence of strong ion-solvent interactions. The viscosity B-coefficient value is lowest for [OMIM]BF_4 in NM supporting the fact that the conductance of [OMIM]BF_4 in NM is highest.

3.5. *Refractive Index Calculation*

The molar refraction R_M can be evaluated from the Lorentz–Lorenz relation [52].

$$R_M = \left\{(n_D^2 - 1) / (n_D^2 + 2)\right\}(M / \rho) \qquad (22)$$

where R_M, n_D, M and ρ are the molar refraction, the refractive index, the molar mass and the density of the solution respectively. The refractive index of a substance is defined as the ratio c_o/c, where c is the speed of light in the medium and c_o the speed of light in vacuum. Stated more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted [53]. As stated by Deetlefs et al. the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser [54]. Hence, a perusal of Table 11 we found that the refractive index and the molar refraction are higher for [OMIM]BF_4 in DMSO indicating to the fact that the molecules are more tightly packed in the solution. This shows that [OMIM]BF_4 is more solvated in DMSO leading to low conductance value as indicated by the conductometric study.

3.6. *Ultrasonic Speed Calculation*

The adiabatic compressibility (β_s) was evaluated from the following equation:

$$\beta_S = 1 / u^2 \rho \qquad (23)$$

Table 9: Experimental values of molarity (c), densities (ρ), apparent molar volume (ϕ_v), limiting apparent molar volume (ϕ_v^o) and experimental slope (S_v^*) of [OMIM]BF_4 in NM, DO and DMSO at 298.15 K.

C (mol dm^{-3})	ρ(kg m^{-3})	φ_v (m^3 mol^{-1})	φ_v^o (m^3 mol^{-1})	S_v^* (m^3 mol$^{-3/2}$ L^{½})
NM				
0.0133	1.13119	202.41	220.8	−165.7
0.0267	1.13230	193.26		
0.0401	1.13357	187.07		
0.0537	1.13498	181.91		
0.0672	1.13645	178.11		
0.0809	1.13806	174.19		
DO				
0.0095	1.05907	233.42	259.4	−246.1
0.0237	1.05986	223.41		
0.0381	1.06101	212.41		
0.0525	1.06237	203.80		
0.0670	1.06399	196.45		
0.0816	1.06581	190.25		
DMSO				
0.0092	1.09545	251.17	282.5	−338.6
0.0230	1.09611	230.91		
0.0368	1.09719	216.25		
0.0508	1.09851	205.61		
0.0648	1.10001	197.18		
0.0789	1.10185	188.07		

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, NM: Nitromethane, DO: 1,3-dioxolane, DMSO: Dimethyl sulfoxide

Table 10: Experimental values of molarity (c), viscosities (η), (η/η$_o$-1)/√ c), viscosity A, B-coefficients of [OMIM]BF_4 in NM, DO and DMSO at 298.15 K.

C (mol dm^{-3})	η (mPa s)	(η/η$_o$-1)/√ c (kg$^{1/2}$ mol$^{-1/2}$)	A (L mol^{-1})	B (L$^{1/2}$mol$^{-1/2}$)
NM				
0.0133	0.6180	0.057	−0.542	5.195
0.0267	0.6452	0.311		
0.0401	0.6750	0.495		
0.0537	0.7072	0.655		
0.0672	0.7432	0.812		
0.0809	0.7772	0.934		
DO				
0.0095	0.5943	0.092	−0.729	8.279
0.0237	0.6371	0.530		
0.0381	0.6902	0.881		
0.0525	0.7464	1.166		
0.0670	0.8031	1.405		
0.0816	0.8665	1.651		
DMSO				
0.0092	2.4620	2.110	−0.981	27.72
0.0230	3.3864	3.944		
0.0368	4.3225	5.201		
0.0508	5.3809	6.439		
0.0648	6.3473	7.321		
0.0789	7.3140	8.103		

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, NM: Nitromethane, DO: 1,3-dioxolane, DMSO: Dimethyl sulfoxide

where ρ is the density of solution and u is the speed of sound in the solution. The apparent molar adiabatic compressibility (ϕ_K) of the solutions was determined from the relation,

$$\phi_K = M\beta_S / \rho + 1000\left(\beta_S \rho_o - \beta_o \rho\right) / c\rho \, \rho_o \qquad (24)$$

where β_0, β_S are the adiabatic compressibility of the solvent and solution respectively and c is the molarity of the solution. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were obtained by fitting ϕ_K against the square root of molarity ($\sqrt{c}$) of the electrolyte using the method of least squares.

$$\phi_K = \phi_K^0 + S_K^* \times \sqrt{c} \qquad (25)$$

The values of β_S and ϕ_K are reported in Table 12. Since the values of ϕ_K^0 and S_K^* are measures of ion-solvent and ion-ion interactions respectively, a perusal of Table 12 and Figure 4 shows that the values are in agreement with results drawn from the values of ϕ_V^0 and S_V^* discussed earlier.

Table 11: Experimental values of molarity (c), refractive index (n_D) and molar refraction (R_M) of [OMIM]BF_4 in NM, DO and DMSO at 298.15 K.

NM			**DO**			**DMSO**		
C (mol dm^{-3})	**n_D**	**R_M (m^3 mol^{-1})**	**C (mol dm^{-3})**	**n_D**	**R_M (m^3 mol^{-1})**	**C (mol dm^{-3})**	**n_D**	**R_M (m^3 mol^{-1})**
0.0133	1.3937	59.6195	0.0095	1.4007	64.6803	0.0092	1.4784	72.9549
0.0267	1.3939	59.5878	0.0237	1.4008	64.6463	0.0230	1.4785	72.9240
0.0401	1.3942	59.5612	0.0381	1.4011	64.6189	0.0368	1.4787	72.8783
0.0537	1.3946	59.5407	0.0525	1.4016	64.6073	0.0508	1.4792	72.8557
0.0672	1.3950	59.5171	0.0670	1.4022	64.5940	0.0648	1.4798	72.8342
0.0809	1.3954	59.4862	0.0816	1.4028	64.5686	0.0789	1.4806	72.8162

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, NM: Nitromethane, DO: 1,3-dioxolane, DMSO: Dimethyl sulfoxide

Table 12: Experimental values of molarity (c), speed of sound (u), adiabatic compressibility (β_s) and apparent molar adiabatic compressibility (ϕ_K), limiting apparent molar adiabatic compressibility (ϕ_K^o), and experimental slopes (S_K^*) of [OMIM]BF_4 in NM, DO and DMSO at 298.15 K.

C (mol dm^{-3})	**u (m s^{-1})**	**$\beta_s \times 10^{10}$ (Pa^{-1})**	**$\phi_K \times 10^{10}$ (m^3 mol^{-1} Pa^{-1})**	**$\phi_K^o \times 10^{10}$ (m^{3}mol^{-1}Pa^{-1})**	**$S_K^* \times 10^{10}$ (m^{3}mol$^{-3/2}$Pa^{-1} kg$^{1/2}$)**
NM					
0.0133	1322.6	5.053	−1.978	0.206	−18.750
0.0267	1331.1	4.984	−2.825		
0.0401	1342.1	4.897	−3.523		
0.0537	1355.8	4.793	−4.163		
0.0672	1371.2	4.680	−4.679		
0.0809	1388.3	4.558	−5.108		
DO					
0.0095	1342.8	5.236	−2.223	1.048	−33.510
0.0237	1354.7	5.141	−4.036		
0.0381	1372.2	5.005	−5.527		
0.0525	1394.1	4.843	−6.714		
0.0670	1419.7	4.663	−7.664		
0.0816	1448.8	4.469	−8.437		
DMSO					
0.0092	1502.7	4.042	−3.046	1.922	−44.899
0.0230	1537.9	3.857	−6.065		
0.0368	1591.5	3.598	−8.202		
0.0508	1666.6	3.277	−10.017		
0.0648	1767.0	2.912	−11.524		
0.0789	1899.7	2.515	−12.779		

[OMIM]BF_4: 1-methyl-3-octylimidazolium tetrafluoroborate, NM: Nitromethane, DO: 1,3-dioxolane, DMSO: Dimethyl sulfoxide

4. CONCLUSIONS

The extensive study of [OMIM]BF_4 in NM, DO and DMSO leads to the conclusion that, the salt more associated in DMSO than the other two solvents. From the conductometric investigation it becomes clear that [OMIM]BF_4 mostly remains as triple-ions in DO than ion-pairs, whereas it remains as ion-pairs in NM and DMSO. The values of the limiting apparent molar volume (ϕ_V^0), viscosity B-coefficients and limiting partial isentropic compressibility (ϕ_K^0) indicate the predominance of ion-solvent interaction than the ion-ion interaction (Scheme 3). The extent of ionic solvation is highest in DMSO and lowest in NM and DO renders an intermediacy between DMSO and NM. The derived parameters obtained by analyzing various equations supplemented with experimental data sustain the same finale as discussed and explained above.

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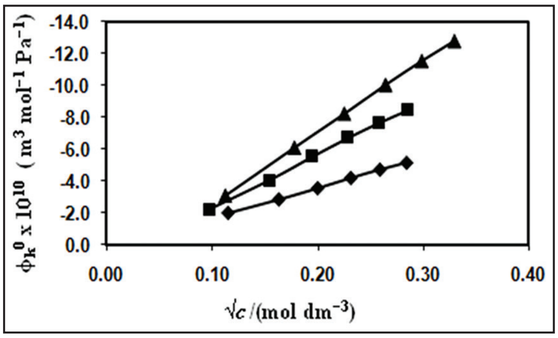
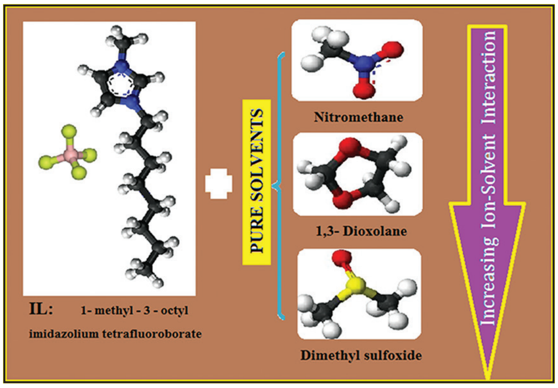


Figure 4: Apparent molar adiabatic compressibilities (ϕ_K) and the square root of concentrations (√c) of 1-methyl-3-octylimidazolium tetrafluoroborate in nitromethane (—♦—),1,3-dioxolane (—■—) and dimethyl sulfoxide (—▲—) at 298.15K.



Scheme 3: Trend of ion-solvent interaction between
AQ2 ionic liquid and pure solvents

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