

CHAPTER VII

CONDUCTOMETRIC, REFRACTOMETRIC AND FT-IR SPECTROSCOPIC STUDY OF [EMIM]NO₃, [EMIM]CH₃SO₃, AND [EMIM]OTS IN N, N-DIMETHYL FORMAMIDE, N, N-DIMETHYL ACETAMIDE AND DIMETHYL SULPHOXIDE

7.1. INTRODUCTION

The appearance of the new class of solvents “Ionic Liquid” or “Green Liquid” has newly charmed attention of the chemists due to its amiable properties with multiple exciting applications in areas of basic science and applied technology. As they are made up of at least two components which can be varied (the anion and cation), the solvents can be premeditated with a meticulous end use in mind, or to possess a meticulous set of properties. Hence, the term “designer solvents” has come into common use [1-2]. They are also used as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells) [3-5].

We have here studied the thermodynamic, optical and the transport properties of ionic liquids in industrially important solvents. These properties provide important information about the nature and potency of intermolecular forces operating among assorted components. FT-IR measurements have also been done as it is one of the most convenient methods for investigating the molecular interactions in electrolytic solutions [6-8].

In continuation with our investigation on understanding the behaviour of ionic liquids in organic solvents by physico-chemical techniques[9-12] we have studied the conductance, refractive index and FT-IR measurements of 1-ethyl-3-methylimidazolium nitrate [EMIm]NO₃, 1-ethyl-3-methylimidazolium methanesulfonate [EMIm]CH₃SO₃ and 1-ethyl-3-methylimidazolium tosylate [EMIm]OTs in N, N-dimethyl formamide (DMF), N, N-dimethyl acetamide (DMA) and dimethyl sulphoxide (DMSO) at 298.15K.

7.2. EXPERIMENTAL SECTION

7.2.1. Source and Purity of Sample

1-ethyl-3-methylimidazolium nitrate [EMIm]NO₃, 1-ethyl-3-methylimidazolium methanesulfonate [EMIm]CH₃SO₃ and 1-ethyl-3-methylimidazolium tosylate [EMIm]OTs of puriss grade were obtained from Aldrich, Germany. The mass fraction purity of [EMIm]NO₃, [EMIm]CH₃SO₃, and [EMIm]OTs was ≥ 0.99 , 0.98, and 0.98 respectively. The ionic liquids were stored in a CaO desiccator for 48 hours in a dark place and necessary precaution had been taken during the work. All the solvents of spectroscopic grade were procured from Thomas Baker, India and were sanitized using model techniques [13].

All the solvents of spectroscopic grade were procured from Sigma-Aldrich, Germany and were used as procured. The purities of N, N-dimethyl formamide (DMF), N, N-dimethyl acetamide (DMA) and dimethyl sulphoxide (DMSO) solution were 0.99, ≥ 0.995 and ≥ 0.99 respectively. The sample description has been given in Table 1.

7.2.2. Apparatus and Procedure

Stock solutions for the three electrolytes in three different solvents were prepared by mass (Mettler Toledo AG285 with uncertainty 0.0003 g), and the working solutions were obtained by mass dilution at 298.15K. The uncertainty of molality of different solutions was estimated to ± 0.0001 mol kg⁻¹. The density (ρ) was measured by means of vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of 0.0005 g·cm⁻³. It was standardized by double-distilled water and dry air.

The viscosities (η) were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The viscosities were obtained using the following equation

$$\eta = \left(\frac{100}{RPM} \right) \times TK \times torque \times SMC$$

where *RPM*, *TK* (0.09373) and *SMC* (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The instrument was calibrated against the standard viscosity samples supplied with the instrument, water and aqueous CaCl₂

solutions. [14] The temperature was maintained to within $\pm 0.01^\circ\text{C}$ using Brookfield Digital TC-500 thermostat bath. The viscosities were measured with an accuracy of $\pm 1\%$. Each measurement reported herein is an average of triplicate reading with a precision of 0.3 %.

The conductance measurement was measured in a Systronic-308 conductivity meter (accuracy 1.0 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately $0.1 \pm 0.001 \text{ cm}^{-1}$. Measurement was completed in a water bath sustained within $T = 298.15 \pm 0.01 \text{ K}$ and the cell was calibrated by the method planned by Lind et al. [15]. The electrical conductance experiments were carried out using an alternating current source.

Refractive index was measured with the help of a Digital Refractometer Mettler Toledo. The light source was LED, $\lambda=589.3\text{nm}$. The refractometer was calibrated twice using distilled water and calibration was checked after every few measurements. The uncertainty of refractive index measurement was ± 0.0002 units.

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have formerly been described [8].

7.3. RESULTS AND DISCUSSION

The solvent properties are given in Table 2. The concentrations and molar conductances Λ of [EMIm]NO₃, [EMIm]CH₃SO₃ and [EMIm]OTs in DMF, DMA and DMSO are given in Table 3. Linear conductance curves (Λ versus \sqrt{c}) were obtained and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductances for the electrolytes. The plot for the concentration versus molar conductance of [EMIm]NO₃ in DMF, DMA and DMSO is given in Figure 1 and the plots for other ionic liquids in the studied solvents have been given as supporting information. The conductance data for ion-pair formation have been analysed using the Fuoss conductance equation [16].

So with a given set of conductivity values ($c_j, \Lambda_j; j = 1, \dots, n$), three adaptable 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[17] for determining the R value but in order to treat the data in our system, R value is thought 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:

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

where M is the molar mass and ρ is the density of the solvent. For mixed solvents, M is replaced by the mole fraction average molar mass (M_{av}) which is given by,

$$M_{av} = M_1 M_2 / (W_1 M_2 + W_2 M_1) \quad (2)$$

where w_1 is the weight fraction of the first component of molar mass M_1 . Thus, the Fuoss conductance equation is given as follows:

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

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

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

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

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

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

where, Λ_0 is the limiting molar conductance, K_A is the experimental 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 molarity 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 [18]. 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

$$\delta^2 = \sum [\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n - m) \quad (9)$$

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 Λ_0 and K_A values are obtained which are reported in Table 4 along with R and δ for the all the solutions.

A review of Table 4 and Figure 2 shows that the limiting molar conductance (Λ_0) of all the electrolytes studied is highest in case of DMF and lowest in case of DMSO among the studied solvents. The trend of the Λ_0 of the electrolytes in three different solvents is enhanced by the following order:



The trend shows the molecules as well as ions are restricted to free move in DMSO. This shows that the electrolytes are solvated more by DMSO. The viscosity values of the solvents also support the same fact, i.e., the electrolytes are more solvated in highest viscous solvent of among the studied solvents. We can also see that with the increase in the size of the anion (for the common cation) the extent of solvation also increases. The trend in the extent of solvation of the anions (for common cation) of the electrolytes is as follow



The highest ion-solvent interaction leading to very high solvation is seen in case of [EMIm]OTs and DMSO which is evident from the K_A values given in Table 4 and Figure 2. The weakest ion-solvent interaction is in between [EMIm]NO₃ and the lowest viscous solvent DMF.

The Gibbs energy change of solvation, ΔG° , is given by the following equation [19] and given in Table 5.

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

It is observed from the Table 5 that the values of the Gibbs free energy are all negative entirely all over the solutions and the negativity increases from DMF to DMSO. This result indicates the extent of solvation enhanced by the following order:



It is also observed that among the three ionic liquids the value of Gibbs free energy of [EMIm]OTs is the most negative signifying the greatest ion-solvent interaction. The Walden's Product ($\Lambda_0 \cdot \eta_0$) have also been obtained and reported in Table 5.

The initial point for most evaluations of ionic conductance is Stokes' law which states that the limiting Walden product ($\lambda_0^{\pm} \eta_0$), (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant. The ionic conductance λ_0^{\pm} for the cation [EMIm]⁺ and the anion (NO₃⁻, CH₃SO₃⁻, OTs⁻) in all the solvents were calculated using tetrabutylammonium tetraphenylborate (Bu₄NBPh₄) as a 'reference electrolyte' following the scheme as suggested by B. Das et al [20]. The ionic limiting molar conductance λ_0^{\pm} for [EMIm]⁺ X⁻ (X⁻= NO₃⁻, CH₃SO₃⁻, OTs⁻) in all the solvents have been calculated by interpolation of conductance data from the literature[21] using cubic spline fitting. The λ_0^{\pm} values were in turn utilized for the calculation of Stokes' radii (r_s) according to the traditional expression [22]

$$r_s = \frac{F^2}{6\pi N_A \lambda_0^{\pm} r_c} \quad (11)$$

where, r_s is the Stokes' radii, r_c is the crystallographic radii, N_A is the Avogadro's no., λ_0^{\pm} is the limiting ionic conductance and F is the Faraday Constant.

Ionic limiting molar conductance λ_0^{\pm} , Ionic Walden product $\lambda_0^{\pm} \eta$, Stokes' radii r_s , and crystallographic radii r_c are presented in Table 6.

The ionic conductance values given in Table 6 shows that the greater share of the conductance values comes from the anions (NO₃⁻, CH₃SO₃⁻, OTs⁻) than the cation (EMIm⁺) except for that in the case of [EMIm]OTs in DMF were the cations conduct

more than the anion. The ionic conductance values also decrease from DMF to DMSO for the studied electrolytes.

The diffusion coefficient (D) is obtained using the Stokes-Einstein Relation[23]

$$D = \frac{k_B T}{6\pi\eta_0 r_s} \quad (12)$$

where k_B is the Boltzmann's constant, T is the temperature, η_0 is the solvent viscosity and r_s is the Stoke's radii.

The ionic mobility is obtained using the following equation [23]:

$$i = \frac{z^+ F}{RT} D \quad (13)$$

The values of the diffusion coefficient and ionic mobility are given in Table 7. The diffusion coefficient of the anions are more than the cation in all the solvents except in case of DMF where the cation diffuses more than the anion in case of [EMIm]OTs⁻. The diffusion coefficient reduces from DMF to DMSO as indicated in Table 6 for both the cation and the anions showing greater diffusion of the ions in DMF. At the same time the ionic mobility values also shows that the mobility of anions are higher than that of cation apart from that in the case of [EMIm]OTs⁻ in DMF where the trend is opposite. Hence the greater share of the conductance comes from the anions than the cation except for [EMIm]OTs⁻ in DMF. A graphical comparison of D and i for the different anions are given in Figure 3 and 4 respectively.

The molar refraction, R_M can be evaluated from Lorentz-Lorenz relation [24]

$$R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\}(M/\rho) \quad (14)$$

where R_M , n_D , M and ρ are the molar refraction, refractive index, molar mass and density of solution respectively. 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. As stated by Deetlefs *et al* [25] the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. Hence a review of Table 8 shows that the refractive indices (n_D) and molar refractions (R_M) of all the electrolytes are highest in

DMSO and lowest in case of DMF among the three solvents. The trend of n_D and R_M of the three ionic liquids in three different solvents is as follows:



As R_M is directly proportional to molecular polarizability, it is evident from Table 8 that the overall polarizability of all the electrolytes is highest in case of DMSO in comparison to the other solvents. A graphical representation of molar refraction (R_M) of studied ionic liquids in different solvents is given in Figure 5.

It is also found that the refractive index (n_D) and molar refraction (R_M) of [EMIm]OTs are highest in all the solvents studied and the greatest interaction is seen in case of [EMIm]OTs and DMSO. So, according to the statement of Deetlefs *et al* it is concluded that the molecules of [EMIm]OTs are most tightly packed among the three electrolytes in all the studied solvents and the packing is greatest in DMSO. The packing is least in the case of [EMIm]NO₃ in DMF.

With the help of FT-IR spectroscopy the molecular interaction existing between the solute and the solvent can be studied. At first the IR spectra of the pure solvents were studied. The stretching frequencies of the key groups are given in Table 9.

In case of DMF a sharp peak is obtained at 1654.4cm⁻¹ for C=O which shifts to 1670.2 cm⁻¹, 1687.1 cm⁻¹ and 1705.1 cm⁻¹ due to the addition of the electrolytes [EMIm]NO₃, [EMIm]CH₃SO₃ and [EMIm]OTs respectively due to the interaction of [EMIm]⁺ with the C=O dipole showing ion-dipole interaction which is formed due to the disruption of H-bonding interaction in DMF molecules [26].

Similar types of interactions are observed in case of DMA where the sharp peak for C=O shifts from 1672.2cm⁻¹ to 1684.1 cm⁻¹, 1693.1 cm⁻¹ and 1712.1 cm⁻¹ in case of [EMIm]NO₃, [EMIm]CH₃SO₃ and [EMIm]OTs respectively due to ion-dipole interaction between [EMIm]⁺ and C=O dipole.

The FT-IR spectra of the ionic liquids in DMSO show that the peak for S=O at 1022cm⁻¹ shifts to 1041.5 cm⁻¹, 1076.3 cm⁻¹ and 1099.3 cm⁻¹ for [EMIm]NO₃, [EMIm]CH₃SO₃ and [EMIm]OTs respectively due to the disruption of weak H-bonding interaction between the two DMSO molecules[27] leading to the formation of ion-dipole interaction between [EMIm]⁺ and S=O dipole.

7.4. Conclusion

Methodical conductivity analysis of [EMIm]NO₃, [EMIm]CH₃SO₃ and [EMIm]OTs in DMF, DMA and DMSO explains that the conductance for all the electrolytes are highest in case of DMF and lowest in case of DMSO. Among the three electrolytes [EMIm]OTs is associated most with the studied solvents and the highest association is observed between [EMIm]OTs and DMSO. The ionic conductivity values suggest the fact that the anions conduct more than the cation except in case of [EMIm]OTs in DMF. The diffusion coefficient and the ionic mobility also shows that in studied ionic liquids the anions diffuse more due to high ionic mobility compared to the cation in all the solvents except for the above mentioned case. The molar refraction values also support the above fact that the highest ion-solvent interaction is seen in case of [EMIm]OTs and DMSO. In all the solvents the electrolyte forms ion-dipole interactions as evident from the FT- IR studies.

TABLES:**Table 1:** Sample description

Chemical name	Source	Initial mass fraction purity	Purification Method	Final mass fraction purity
[EMIm]NO ₃ , [EMIm]CH ₃ SO ₃ , [EMIm]OTs	Aldrich, Germany	0.99 0.98 0.98	Used as procured	0.99 0.98 0.98
DMSO		0.99		0.99
DMA	Thomas Baker	0.995	Used as procured	0.995
DMF		0.99		0.99

Table 2. Experimental and literature [28] values of density (ρ), viscosity (η_0), relative permittivity (ϵ) and refractive index (n_D) of the solvents at 298.15K and 0.101MPa pressure

Solvents	$\rho \cdot 10^{-3} / \text{kg} \cdot \text{m}^{-3}$		$\eta_0 / \text{mPa} \cdot \text{s}$		n_D		ϵ
	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	
DMF	0.9445	0.9437	0.794	0.79	1.4282	1.4279	36.71
DMA	0.9368	0.9359	0.923	0.92	1.4356	1.4351	37.78
DMSO	1.0960	1.0953	1.946	1.96	1.4775	1.4773	46.70

Uncertainty of the density $u(\rho) = 0.0005 \text{ g} \cdot \text{cm}^{-3}$; viscosity $u(\eta) = 0.01 \text{ mPa} \cdot \text{s}$; refractive index $u(n_D) = 0.0002$; temperature $u(T) = 0.01 \text{ K}$; pressure $u(P) = 0.01 \text{ MPa}$

Table 3. The concentration (m) and molar conductance (Λ) of [EMIm]X (where X=NO₃, CH₃SO₃, OTs) in DMF, DMA and DMSO at 298.15K and 0.101MPa pressure

$m \cdot 10^4 /$ mol·kg ⁻¹	$\Lambda \cdot 10^4 /$ S·m ² ·mol ⁻¹	$m \cdot 10^4 /$ mol·kg ⁻¹	$\Lambda \cdot 10^4 /$ S·m ² ·mol ⁻¹	$m \cdot 10^4 /$ mol·kg ⁻¹	$\Lambda \cdot 10^4 /$ S·m ² ·mol ⁻¹
[EMIm]NO ₃ in DMF		[EMIm] NO ₃ in DMA		[EMIm] NO ₃ in DMSO	
11.06	86.20	22.54	45.31	18.70	36.66
20.27	84.31	31.20	44.40	26.83	35.70
28.06	83.01	38.63	43.76	34.27	35.06
34.73	81.98	45.06	43.28	47.45	34.06
40.51	81.24	50.67	42.77	58.74	33.26
45.56	80.80	55.63	42.44	68.52	32.58
50.01	80.27	60.02	42.14	77.07	32.06
53.95	79.74	63.96	41.85	84.60	31.60
57.48	79.41	67.49	41.70	91.29	31.26
63.54	78.79	70.68	41.47	94.35	31.16
66.16	78.54	73.59	41.27	97.24	31.01
72.75	77.79	78.69	41.03	105.13	30.46
79.42	77.08	86.69	40.56	111.92	30.16
84.45	76.71	93.94	40.23	119.66	29.81
92.28	76.11	100.19	39.83	126.19	29.62
[EMIm]CH ₃ SO ₃ in DMF		[EMIm]CH ₃ SO ₃ in DMA		[EMIm]CH ₃ SO ₃ in DMSO	
10.35	59.82	12.07	38.41	18.92	29.69
18.98	58.01	22.14	36.39	34.67	27.50
26.28	56.82	30.65	35.91	48.02	25.90
32.51	56.16	37.94	35.20	59.44	25.30
37.93	55.26	44.26	34.51	69.34	24.20
42.65	54.76	49.77	34.11	77.99	23.50
46.82	54.32	54.64	33.99	85.63	23.20
53.84	53.47	58.96	33.49	92.40	22.90

56.82	53.14	66.31	32.98	98.47	22.40
59.52	52.88	74.96	32.45	103.92	21.94
66.27	52.32	81.59	32.16	108.83	21.87
69.90	51.99	88.38	31.74	113.33	21.40
75.68	51.56	95.72	31.41	117.40	21.20
81.05	51.15	101.67	31.13	121.09	21.20
85.78	50.53	106.46	30.82	127.71	20.80
[EMIm]OTs in DMF		[EMIm]OTs in DMA		[EMIm]OTs in DMSO	
10.39	51.34	11.03	37.30	21.03	19.21
19.06	49.50	20.22	35.60	38.57	35.23
26.39	48.84	27.99	34.73	53.40	48.78
32.66	48.02	34.65	33.91	66.12	60.39
38.09	47.45	40.42	33.56	77.14	70.45
42.84	46.99	45.48	32.88	86.78	79.25
47.03	46.43	49.92	32.51	95.29	87.01
50.74	45.92	57.41	32.35	102.86	93.91
54.06	45.38	63.47	31.78	109.63	100.09
57.05	45.15	68.48	31.32	115.72	105.62
62.21	44.40	76.27	31.06	121.23	110.62
70.17	44.20	82.04	30.69	126.24	115.16
75.99	43.30	88.37	30.30	135.00	123.10
80.43	42.70	94.13	30.12	142.42	129.84
85.43	42.50	98.15	29.85	148.78	135.58

Standard uncertainties u are: $u(m) = 2 \times 10^{-6} \text{ mol}\cdot\text{kg}^{-1}$, $u(\Lambda) = 1 \times 10^{-6} \text{ S}\cdot\text{m}^2\cdot\text{mol}^{-1}$, $u(T) = 0.01 \text{ K}$ and pressure $u(P) = 0.01 \text{ MPa}$

Table 4. Limiting molar conductance (Λ_0), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental (δ) of [EMIm]X (where X=NO₃, CH₃SO₃, OTs) in DMF, DMA and DMSO at 298.15K and 0.101MPa pressure

Solvents	$\Lambda_0 \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$K_A / \text{dm}^3 \cdot \text{mol}^{-1}$	$R / \text{\AA}$	Δ
[EMIm]NO ₃				
DMF	90.08	27.27	8.86	0.0807
DMA	49.10	35.55	9.18	0.0319
DMSO	39.86	40.97	8.72	0.0757
[EMIm]CH ₃ SO ₃				
DMF	64.14	44.70	9.70	0.0835
DMA	40.74	53.04	10.02	0.1547
DMSO	34.16	86.81	9.41	0.1372
[EMIm]OTs				
DMF	54.87	54.66	10.03	0.2711
DMA	39.55	59.15	10.35	0.1617
DMSO	31.46	189.67	9.89	0.3110

Table 5. Walden product ($\Lambda_0 \cdot \eta_0$) and Gibbs energy change (ΔG°) of [EMIm]X (where X=NO₃, CH₃SO₃, OTs) in DMF, DMA and DMSO at 298.15K and 0.101MPa pressure

Solvents	$\Lambda_0 \cdot \eta_0 \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \text{mPa} \cdot \text{s}$	$\Delta G^\circ \cdot 10^{-3} / \text{kJ} \cdot \text{mol}^{-1}$
[EMIm]NO ₃		
DMF	71.71	-8.19
DMA	45.32	-8.85
DMSO	78.25	-9.20
[EMIm]CH ₃ SO ₃		
DMF	51.06	-9.42
DMA	37.61	-9.84
DMSO	67.06	-11.06
[EMIm]OTs		

DMF	43.68	-9.92
DMA	36.50	-10.11
DMSO	61.76	-13.00

Table 6. Ionic limiting molar conductance (λ^{\pm_0}), ionic Walden product ($\lambda^{\pm_0}\eta_0$), crystallographic radii (r_c) and Stoke's radii (r_s) [EMIm]⁺ and X⁻(NO₃,CH₃SO₃,OTs) DMF, DMA and DMSO at 298.15K and 0.101MPa pressure

Solvents	$\lambda^{\pm_0}\cdot 10^4/$ S·m ² ·mol ⁻¹		$\lambda^{\pm_0}\eta_0\cdot 10^4/$ S·m ² ·mol ⁻¹ mPa·s		$r_c/\text{Å}$		$r_s/\text{Å}$	
	[EMIm] ⁺	NO ₃ ⁻	[EMIm] ⁺	NO ₃ ⁻	[EMIm] ⁺	NO ₃ ⁻	[EMIm] ⁺	NO ₃ ⁻
DMF	31.1	58.98	24.57	46.59	1.33	1.99	3.34	1.76
DMA	20.16	28.94	18.55	26.62	1.33	1.99	4.42	3.08
DMSO	14.43	25.43	28.28	49.84	1.33	1.99	2.90	2.64
	[EMIm] ⁺	CH ₃ SO ₃ ⁻	[EMIm] ⁺	CH ₃ SO ₃ ⁻	[EMIm] ⁺	CH ₃ SO ₃ ⁻	[EMIm] ⁺	CH ₃ SO ₃ ⁻
DMF	30.3	33.84	23.91	26.73	1.33	2.83	3.42	3.07
DMA	19.03	21.71	17.51	19.97	1.33	2.83	4.68	4.10
DMSO	13.25	20.91	25.97	40.98	1.33	2.83	3.16	2.99
	[EMIm] ⁺	OTs ⁻	[EMIm] ⁺	OTs ⁻	[EMIm] ⁺	OTs ⁻	[EMIm] ⁺	OTs ⁻
DMF	30.46	24.41	24.06	19.28	1.33	3.16	3.41	4.25
DMA	19.44	20.11	17.88	18.50	1.33	3.16	4.58	4.43
DMSO	13.73	17.73	26.91	34.75	1.33	3.16	3.04	3.36

Table 7. Diffusion Coefficient (D) and ionic mobility (i) of [EMIm]⁺ and X⁻ (NO₃,CH₃SO₃,OTs) in DMF, DMA and DMSO at 298.15K and 0.101MPa pressure

Solvents	$D \cdot 10^{10} / (\text{m}^2 \cdot \text{s}^{-1})$		$i \cdot 10^8 / (\text{m}^2 \text{ s}^{-1} \text{ volt}^{-1})$	
	[EMIm] ⁺	NO ₃ ⁻	[EMIm] ⁺	NO ₃ ⁻
DMF	8.29	15.70	3.23	6.12
DMA	5.38	7.72	2.09	3.00
DMSO	3.85	6.78	1.50	2.64
Solvents	[EMIm] ⁺	CH ₃ SO ₃ ⁻	[EMIm] ⁺	CH ₃ SO ₃ ⁻
	DMF	8.11	9.05	3.16
DMA	5.11	5.83	1.99	2.27
DMSO	3.57	5.63	1.39	2.19
Solvents	[EMIm] ⁺	OTs ⁻	[EMIm] ⁺	OTs ⁻
	DMF	8.15	6.53	3.17
DMA	5.22	5.4	2.03	2.10
DMSO	3.70	4.78	1.44	1.86

Table 8. Experimental densities, refractive indices and molar refractions of [EMIm]X (where X=NO₃, CH₃SO₃, OTs) in DMF, DMA and DMSO at 298.15K and 0.101MPa pressure

Solvents	$m / \text{mol} \cdot \text{kg}^{-1}$	$\rho \cdot 10^{-3} / \text{kg} \cdot \text{m}^{-3}$	n_D	$R_M / \text{m}^3 \cdot \text{mol}^{-1}$
[EMIm]NO ₃				
DMF	0.0532	0.9486	1.4310	47.25
DMA	0.0537	0.9403	1.4373	48.27
DMSO	0.0459	1.0968	1.5257	48.43
[EMIm]CH ₃ SO ₃				
DMF	0.0532	0.9500	1.4318	56.29
DMA	0.0537	0.9415	1.4386	57.57
DMSO	0.0460	1.0978	1.5385	58.81

[EMIm]OTs				
DMF	0.0533	0.9524	1.4323	76.94
DMA	0.0538	0.9433	1.4391	78.74
DMSO	0.0461	1.0984	1.5390	80.53

Uncertainty of the density $u(\rho) = 0.0005 \text{ g}\cdot\text{cm}^{-3}$; refractive index $u(n_D) = 0.0002$; temperature $u(T) = 0.01\text{K}$; $u(m) = 0.0002 \text{ mol}\cdot\text{kg}^{-1}$, and $u(p) = 0.01\text{MPa}$.

Table 9. Stretching frequencies of the functional groups present in the pure solvent and change of frequency of [EMIm]X (where X=NO₃, CH₃SO₃, OTs) in DMF, DMA and DMSO.

Solvents	Stretching frequencies(cm^{-1})			
	Pure Solvent	Solvent + [EMIm]NO ₃	Solvent+ [EMIm]CH ₃ SO ₃	Solvent + [EMIm]OTs
DMF	C=O (1675)	C=O (1721.2)	C=O (1745)	C=O (1763)
DMA	C=O (1670)	C=O (1695.4)	C=O (1725.1)	C=O (1755.1)
DMSO	S=O (1050)	S=O (1071.5)	S=O (1093.3)	S=O (1123.3)

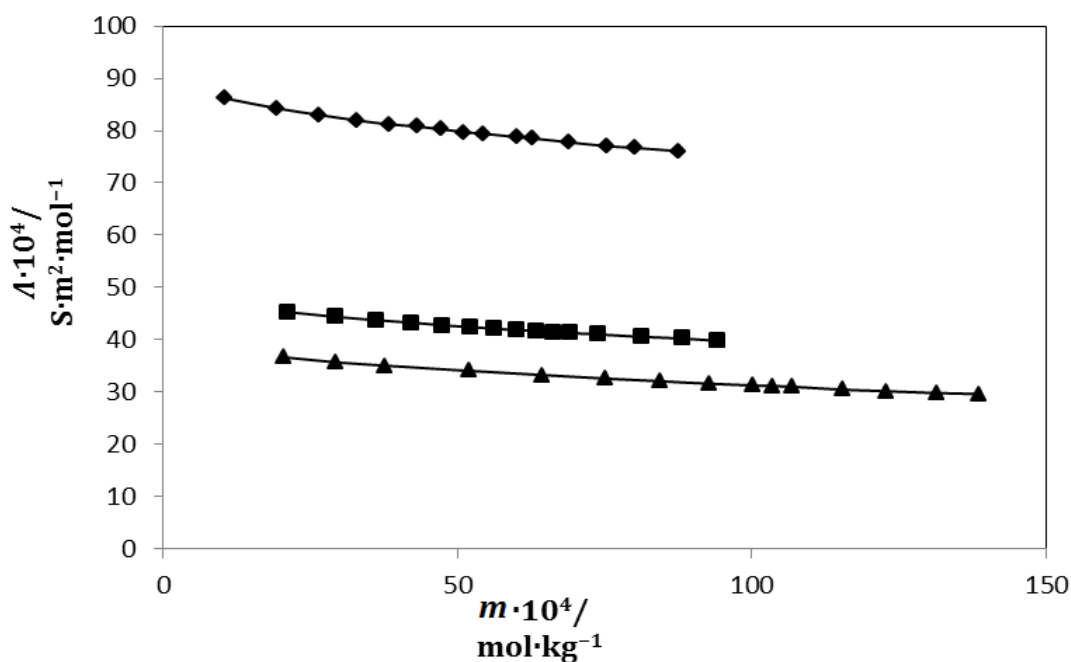
FIGURES:


Figure 1: Plot of molar conductance (Λ) versus concentration (c) of [EMIm] NO_3 , in DMF (—◆—), DMA (—■—) and DMSO (—▲—) at 298.15K.

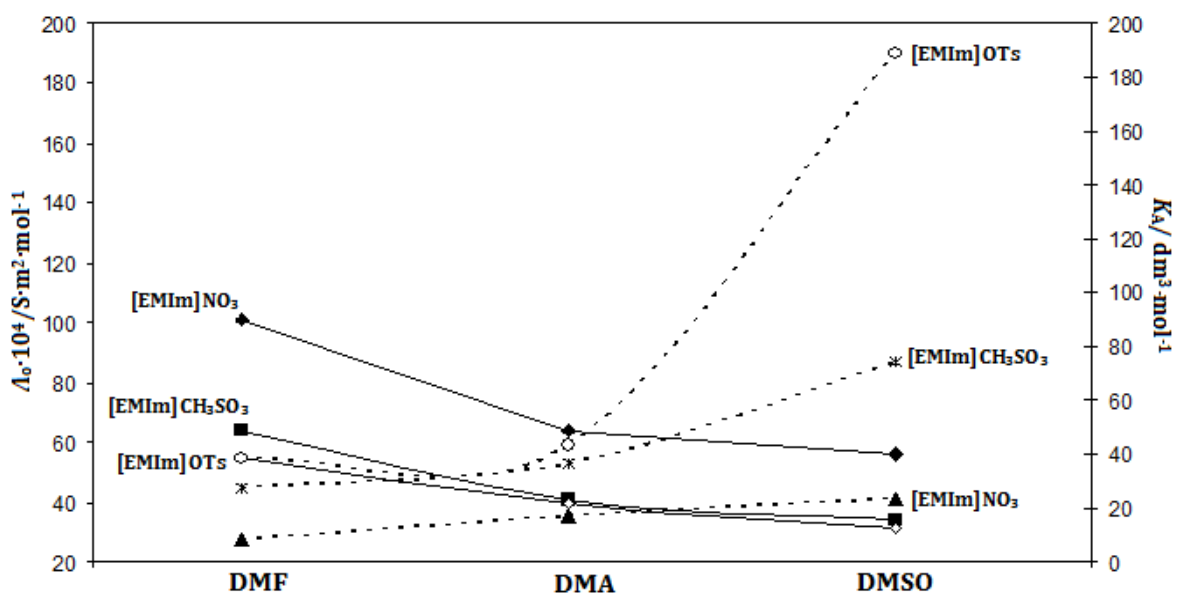


Figure 2: Plot of Limiting molar conductance (Λ_0) of [EMIm] NO_3 (—◆—), [EMIm] CH_3SO_3 (—■—), [EMIm] OTs (—◇—) and association constant (K_A) of [EMIm] NO_3 (---▲---).

---),[EMIm] CH₃SO₃ (---*---),[EMIm] OTs (---○---) in DMF, DMA and DMSO respectively at 298.15K

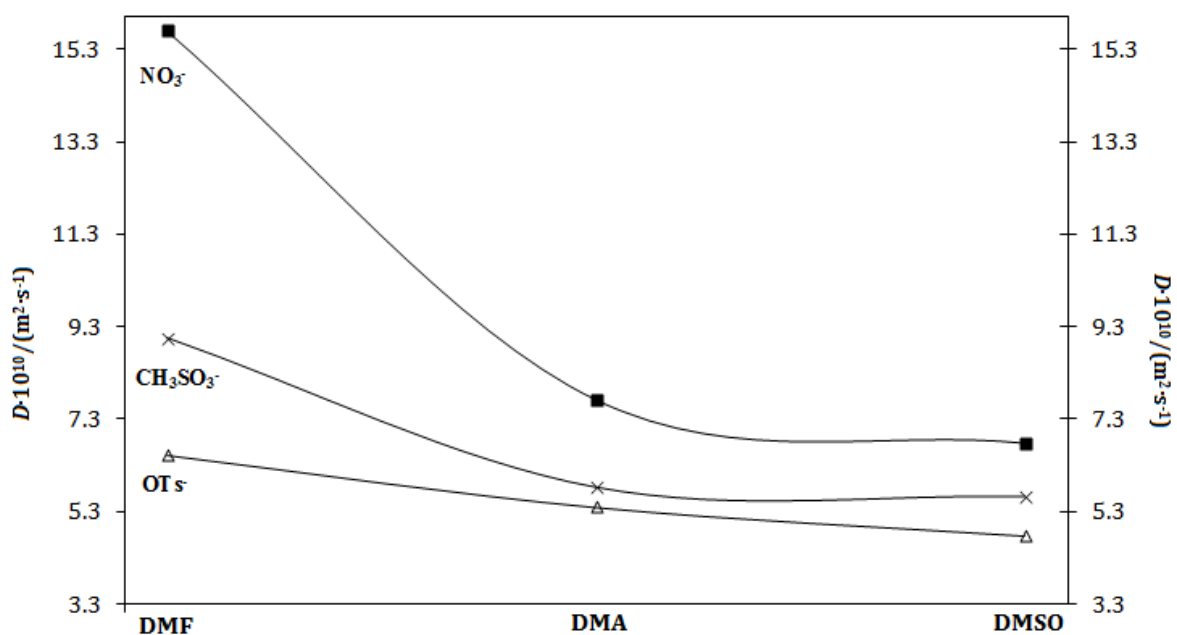


Figure 3. Plot of Diffusion Coefficient (D) of NO₃⁻ (—■—),CH₃SO₃⁻ (—x—) and OTs⁻ (—Δ—) in different studied solvents at 298.15K

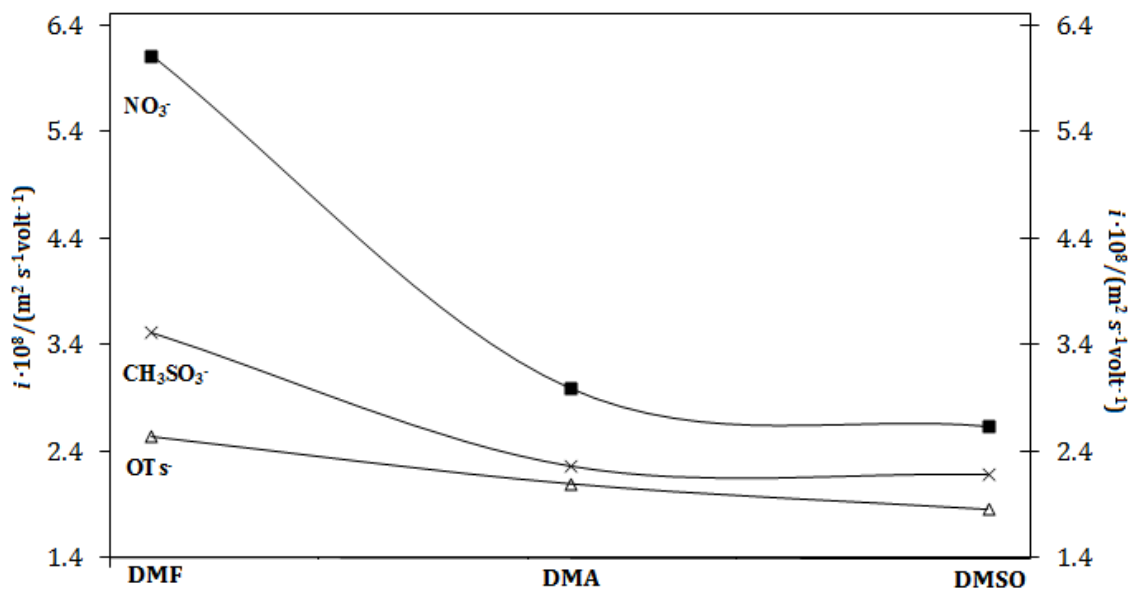


Figure 4. Plot of ionic mobility (i) of NO₃⁻ (—■—),CH₃SO₃⁻ (—x—) and OTs⁻ (—Δ—) in different studied solvents at 298.15K

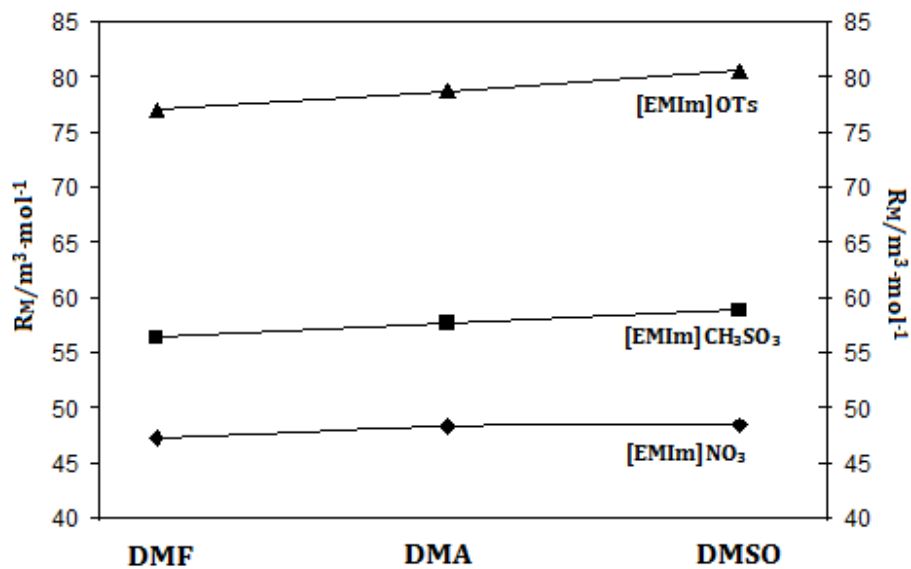


Figure 5: Plot of Molar Refraction (R_M) of [EMIm]NO₃ (—◆—), [EMIm] CH₃SO₃ (—■—), [EMIm] OTs (—▲—) in DMF, DMA and DMSO respectively at 298.15K.