

## CHAPTER IV

### CONDUCTOMETRIC INVESTIGATIONS OF ION-SOLVENT INTERACTIONS OF AN IONIC LIQUID {[EMIM]CH<sub>3</sub>SO<sub>3</sub>} IN PURE N-ALKANOLS

#### 4.1. INTRODUCTION

An ionic liquid (IL) is an electrolyte in the liquid state or phase, whose melting point is below some arbitrary temperature, such as 100°C. In general, ionic liquids (ILs) are liquid electrolytes that consist of combinations of organic–organic or organic–inorganic cation/anions. Because of their unique physicochemical properties, such as the favorable solubility of organic and inorganic compounds, low vapor pressures, low melting points, high thermal stability, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, non-flammability and high ionic conductivity, ionic liquids have generated significant interest in wide range of industrial applications [1].

Ionic association of electrolytes in solution depends upon the mode of solvation of its ions which in turn depends on the nature of the solvent/solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties helps in determining the extent of ion association and the ion-solvent interactions. The association and solvation behavior of ions in solution is obtained from the Conductance Measurement. Along with our investigation on electrical conductance of electrolyte the present work deals with the transport and thermodynamic properties of 1-ethyl-3-methylimidazolium methanesulfonate in n-propanol, n-butanol and n-pentanol at 298.15 K. Study on the transport properties of electrolytes in different solvent media are of great importance to obtain information about the solvation and association behavior of ions in solutions. The electrical conductivity of electrolytes in solvents mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent.

## 4.2. Experimental

### 4.2.1. Materials

1-ethyl-3-methylimidazolium methanesulfonate [emim]CH<sub>3</sub>SO<sub>3</sub> of puriss Grade was procured from Aldrich, Germany and was used as purchased as the purity assay of the salt was  $\geq 98.0\%$ . All the solvents of spectroscopic grade were procured from Sd. Fine Chemicals. The purity of the solvents were  $>99.5\%$ . The solvents were dried using standard methods [2].

### 4.2.2. Apparatus and procedure

A stock solution for the electrolyte was prepared by mass (Mettler Toledo AG285 with uncertainty  $\pm 0.0003$  g), and the working solutions were obtained by mass dilution at 298.15 K. The uncertainty of molarity of different solutions was evaluated to  $\pm 0.0001$  mol dm<sup>-3</sup>.

The density was measured by means of vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of  $\pm 0.0005$  g cm<sup>-3</sup>. It was calibrated by double-distilled water and dry air.

The viscosity was also measured with the help Brookfield DVIII Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500.

The conductance measurements were carried out in a Systronic-308 conductivity meter (accuracy  $\pm 0.01$  %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately  $(0.1 \pm 0.001)$  cm<sup>-1</sup>. Measurements were made in a water bath maintained within  $T = (298.15 \pm 0.01)$  K and the cell were calibrated by the method proposed by Lind et al. [12]. The conductance data were reported at a frequency of 1 kHz with the accuracy of  $\pm 0.3\%$ .

Digital Refractometer Mettler Toledo was utilized to measure the refractive index. The light source was LED,  $\lambda = 589.3$  nm. Distilled water was introduced to

calibrate the refract meter twice and each was checked after every few measurements. The uncertainty of the value of refractive index measurement was  $\pm 0.0002$ .

### 4.3. Results and Discussion

The experimental values of physical properties of the pure solvents were in good agreement with those found in the literature, as in Table 1 where appropriate corrections were made by the specific conductance of the solvents at that temperature. The specific conductance ( $\kappa$ ,  $\text{mS cm}^{-1}$ ) of the electrolytes (ILs) solutions under investigation with a molar concentration within the range of  $1.13 \times 10^{-4} - 1.04 \times 10^{-3}$  (M) in different solvents were measured. The molar conductances ( $\Lambda$ ) for all studied solution system have been calculated using the appropriate equation [3].

The values of equivalent conductance ( $\Lambda_0$ ) at various concentrations are represented in Table 2 and the conductance data for 1-ethyl-3-methyl imidazolium methanesulfonate in n-propanol, n-butanol, n-pentanol have been investigated using the Fuoss conductance equation [4]

Three adjustable parameters namely the limiting molar conductance  $\Lambda_0$ , the association constant ( $K_A$ ) and the distance of closest approach of ions ( $R$ ) are derived for a given set of conductivity values ( $c_j, \Lambda_j, j=1, \dots, n$ ) from the following set of equations,

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

$$P = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (4)$$

$$\beta = e^2 / (\epsilon_r k_B T) \quad (5)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (6)$$

where the relaxation field effect is denoted by  $R_x$ ,  $E_L$  represents the electrophoretic counter current,  $k$  is the radius of the ion atmosphere,  $e$  is the electron charge,  $\epsilon_r$  is the

relative permittivity of the solvent mixture,  $k_B$  is the Boltzmann constant,  $c$  is the molarity of the solution,  $K_A$  is the overall pairing constant,  $K_R$  is the association constant of the solvent separated Pairs,  $K_S$  is the association constant of the contact-pairs,  $\gamma$  is the fraction of solute present as unpaired ion,  $\alpha$  is the fraction of contact pairs,  $\beta$  is twice the Bjerrum distance,  $f$  is the activity coefficient and  $T$  is the absolute temperature. The computations were done by virtue of using a program suggested by Fuoss. The initial  $\Lambda_0$  values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set  $(c_j, \Lambda_j, j = 1, \dots, n), n, \epsilon, \eta, T$ , initial values of  $\Lambda_0$ , and an instruction to cover a pre-selected range of  $R$  values. The best value of a parameter is the one when equations is best fitted to the experimental data corresponding to minimum standard deviation  $\delta$  for a sequence of predetermined  $R$  values, and standard deviation  $\delta$  was calculated by the following equation

$$\delta^2 = \sum_{j=1}^n [\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n - m) \quad (7)$$

where  $n$  is the number of experimental points and  $m$  is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach  $R$  with two parameter fit ( $m = 2$ ). As for the studied ionic liquid (IL) in solvents (n-propanol, n-butanol and n-pentanol), no significant minima were observed in the  $\delta$  versus  $R$  curves, whereas the  $R$  values were arbitrarily preset at the centre to centre distance of solvent-separated ion pair. Thus,  $R$  values are assumed to be

$$R = a + d \quad (8)$$

where  $a = (r_+ + r_-)$  is the sum of the crystallographic radii of the cation ( $r_+$ ) and anion ( $r_-$ ) and  $d$  is the average distance corresponding to the side of a cell occupied by a solvent molecule. This distance  $d$  is given by

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

where  $M$  is the molar mass of the solvent and  $\rho$  is its density. The values of  $\Lambda_0$ ,  $K_A$  and  $R$  attained by this procedure are reported in Table 3. The Table 3 also reveals that the association constant ( $K_A$ ) of the ionic liquids (ILs) is just reverse of the limiting molar conductance, lower in n-propanol and higher in n-pentanol, which is in following order;

n-pentanol > n-butanol > n-propanol

Hence the ion-solvent interaction or ion-association increases from n-propanol to n-pentanol among the chosen solvents, leading to a lower conductance of ionic liquid. From the Table 1 and 3, we can see that the association constant values follow the same trend as viscosity value of the solvents, thus the viscosity values also support the above facts, i.e.; the electrolyte (IL) in the lower viscous solvent, the  $\Lambda_0$  value should increase.

This implies that lowering of conductance of [emim]CH<sub>3</sub>SO<sub>3</sub> is found to be highest in n-pentanol and lowest in n-propanol. The lowest viscosity of n-propanol also supports the above observation because with lowering of viscosity the  $\Lambda_0$  value should increase [5].

The above trend in  $\Lambda_0$  values may be verified through another characteristic function called the Walden product,  $\Lambda_0 \eta$  given in Table 4. Although the viscosity of n-pentanol is more than that of n-butanol and n-propanol, the  $\Lambda_0 \eta$  is found to attain a decreasing order from n-propanol to n-pentanol which points out the predominance of  $\Lambda_0$  over  $\eta$ .

The Gibbs energy change of solvation,  $\Delta G^\circ$ , is given by the following equation [6] and given in Table 4.

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

It is observed from the Table 4 that the values of the Gibbs free energy are all negative entirely all over the solutions and the negativity increases from n-propanol to n-pentanol. This result indicates the extent of solvation enhanced by the following order:

n-pentanol > n-butanol > n-propanol

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting Walden product ( $\lambda_0^\pm \eta$ ), (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 conductances  $\lambda_0^\pm$  for the cation [emim]<sup>+</sup> and the anion (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>) in all the solvents were calculated using tetrabutylammonium tetraphenylborate (Bu<sub>4</sub>NBPh<sub>4</sub>) as a 'reference electrolyte'

following the scheme as suggested by B. Das et al. [7]. From the examination of the observed values (Table 6), of the limiting ionic conductance of both the cation and anion are higher in propanol than other two investigated solvent systems, show that higher the movement of the ions in propanol is higher as well as leads weaker the ion-solvent interaction. More over from the same table higher the  $\lambda_o^\pm$  value for [emim]<sup>+</sup> ion than (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>) also suggests weaker ion-solvent interaction of [emim]<sup>+</sup> with the investigated solvents in comparison with (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>).

The ionic limiting molar conductances  $\lambda_o^\pm$  for [emim]<sup>+</sup> X<sup>-</sup> (X<sup>-</sup>= CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>) in all the solvents have been calculated by interpolation of conductance data from the literature [8] using cubic spline fitting. The  $\lambda_o^\pm$  values were in turn utilized for the calculation of Stokes' radii ( $r_s$ ) according to the classical expression [9].

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

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

Even though the viscosity increases from n-propanol to n-pentanol the decrease in conductance value is comparatively more than the increase in viscosity value leading to higher Walden product of salt in propanol compare to other two solvents.

Limiting ionic conductance  $\lambda_o^\pm$ , Ionic Walden product  $\lambda_o^\pm \eta$ , Stokes' radii  $r_s$ , and crystallographic radii  $r_c$  are presented in Table 6. Plot of limiting ionic conductance ( $\lambda_o^\pm$ ) of [emim] CH<sub>3</sub>SO<sub>3</sub>, ionic Walden product ( $\lambda_o^\pm \eta$ ) of [emim]<sup>+</sup> and (CH<sub>3</sub>SO<sub>3</sub>)<sup>-</sup> is represented in figure 1.

The diffusion coefficient ( $D$ ) is obtained using the Stokes-Einstein Relation [10].

$$D = \frac{kT}{6\pi\eta r_s} \quad (12)$$

where  $k$  is the Boltzmann's constant,  $T$  is the temperature,  $\eta$  is the solvent viscosity and  $r_s$  is the Stoke's radii.

The ionic mobility is obtained using the following equation

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

The values of the diffusion coefficient and ionic mobility are given in Table 5. The diffusion coefficient of the cation is more than the anion in all the solvents which indicates that [emim]<sup>+</sup> ion diffuses more through the solvents. The diffusion coefficient decrease from n-propanol to n-pentanol. At the same time the ionic mobility values also shows that the mobility of cation is higher than that of anion indicating greater share of conductance by [emim]<sup>+</sup> ions mentioned earlier. The observation indicates the diffusion coefficient ( $D_{\pm}$ ) is directly proportional to the ionic mobility ( $i_{\pm}$ ) and these are the driving force to conduct electricity by ILs or ions in solutions. Hence the greater share of the conductance comes from the cation than the anion. The results are inverse to the density and viscosity of the solvents. Lower the diffusivity and mobility higher the ion-solvent interaction or ion-solvation, which is evident from the association constant values, reported in Table3. A graphical comparison of  $D$  and  $i$  for the different ions are given in Figure 2.

The molar refraction,  $R_M$  can be evaluated from Lorentz-Lorenz relation [11],

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

where  $R_M$ ,  $n_D$ ,  $M$  and  $\rho$  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.* [12], 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 perusal of Table 5 shows that the refractive indices ( $n_D$ ) and molar refractions ( $R_M$ ) of all the electrolytes (0.05M) are highest in n-pentanol and lowest in case of n-propanol among the three solvents. The trend of  $n_D$  and  $R_M$  of the ionic liquid in three different solvents is as follows:

n-pentanol > n-butanol > n-propanol

As  $R_M$ , is directly proportional to molecular polarizability, it is evident from Table 7 that the overall polarizability of the electrolyte is highest in case of n-pentanol in comparison to the other solvents. A graphical representation of molar refraction ( $R_M$ ) of studied ionic liquid in different solvents is given in Figure 3.

#### 4.4. Conclusion

Thorough conductivity study of [emim]CH<sub>3</sub>SO<sub>3</sub> in n-propanol, n-butanol and n-pentanol shows that the conductance for the electrolyte is highest in case of n-propanol and lowest in case of n-pentanol. The molar refraction values also support the above fact that the highest ion-solvent interaction is seen in case of [emim]CH<sub>3</sub>SO<sub>3</sub> and n-pentanol. The diffusion coefficient ( $D_{\pm}$ ) and the ionic mobility ( $i_{\pm}$ ) decrease from n-propanol to n-pentanol for ions [emim]<sup>+</sup>, {CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>} showing greater ion-solvent interaction in n-pentanol than the other studied solvents. The derived parameters obtained by analyzing various equations supplemented with experimental data sustain the same finale as discussed and explained in this manuscript demanding the uniqueness of the work.

## TABLES

**Table 1. Density ( $\rho$ ), viscosity ( $\eta$ ), refractive index ( $n_D$ ) and dielectric constant ( $\epsilon$ ) of different pure solvents at 298.15 K**

Solvents	$\rho \cdot 10^{-3}$ (kg·m <sup>-3</sup> )		$\eta$ (mPa·s)		$n_D$		$\epsilon$
	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	
n-propanol	0.79970[13]	0.79985	1.9450[13]	1.95	1.3835[17]	1.3834	20.10
n-butanol	0.80575[14]	0.80580	2.5710[14]	2.56	1.3973[18]	1.3960	18.03
n-pentanol	0.81100[15]	0.81128	3.5100[16]	3.51	1.4090[19]	1.4070	13.90

**Table 2. Molar conductance ( $\Lambda$ ) and the corresponding concentration ( $c$ ) of the studied IL (1-ethyl-3-methyl imidazolium methanesulfonate) in different solvents at  $T = 298.15$  K**

$c \cdot 10^4$ (mol dm <sup>-3</sup> )	$\Lambda \cdot 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )	$c \cdot 10^4$ (mol dm <sup>-3</sup> )	$\Lambda \cdot 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )	$c \cdot 10^4$ (mol dm <sup>-3</sup> )	$\Lambda \cdot 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> )
n-propanol		n-butanol		n-pentanol	
1.67	27.30	1.38	18.11	1.18	12.31
3.07	25.84	2.07	17.66	1.63	12.06
4.25	25.11	2.76	17.10	1.96	11.82
5.26	24.31	3.53	16.77	2.72	11.48
6.91	23.55	4.45	16.22	3.53	11.13
7.59	23.03	5.43	15.88	4.04	11.01
8.19	22.88	6.50	15.33	4.49	10.77
8.73	22.50	7.64	14.88	5.42	10.42
9.65	22.23	8.35	14.57	6.25	10.21
10.41	22.08	8.88	14.30	7.07	9.94
11.05	21.84	9.86	14.05	8.29	9.55
11.60	21.74	11.02	13.79	9.12	9.39
12.84	21.10	12.18	13.47	10.36	9.08
14.14	20.70	13.32	13.24	11.83	8.66
14.81	20.50	14.52	12.88	13.72	8.24

**Table 3. Limiting molar conductance ( $\Lambda_0$ ), association constant ( $K_A$ ), co-sphere diameter ( $R$ ) and standard deviations of experimental  $\Lambda$  ( $\delta$ ) obtained of [emim]CH<sub>3</sub>SO<sub>3</sub> in different solvents at 298.15 K.**

Solutions	$\Lambda_0 \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$K_A / \text{dm}^3 \cdot \text{mol}^{-1}$	$R / \text{\AA}$	$\delta$
[emim]CH <sub>3</sub> SO <sub>3</sub> in propanol	29.95	569.33	9.15	0.09
[emim]CH <sub>3</sub> SO <sub>3</sub> in butanol	20.35	811.39	9.50	0.11
[emim]CH <sub>3</sub> SO <sub>3</sub> in pentanol	14.26	1961.13	9.80	0.12

**Table 4. Walden product ( $\Lambda_0 \cdot \eta$ ) and Gibb's energy change ( $\Delta G^\circ$ ) of [emim] CH<sub>3</sub>SO<sub>3</sub> in different solvents at 298.15 K**

Solutions	$\Lambda_0 \cdot \eta \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \text{mPa} \cdot \text{s}$	$\Delta G^\circ / \text{kJ} \cdot \text{mol}^{-1}$
[emim]CH <sub>3</sub> SO <sub>3</sub> in propanol	58.19	-1.57
[emim]CH <sub>3</sub> SO <sub>3</sub> in butanol	52.20	-1.66
[emim]CH <sub>3</sub> SO <sub>3</sub> in pentanol	50.07	-1.88

**Table 5. Diffusion Coefficient ( $D$ ) and ionic mobility ( $i$ ) of [emim]<sup>+</sup> and X<sup>-</sup> (CH<sub>3</sub>SO<sub>3</sub>) in n-Propanol, n-Butanol and n-Pentanol at 298.15K**

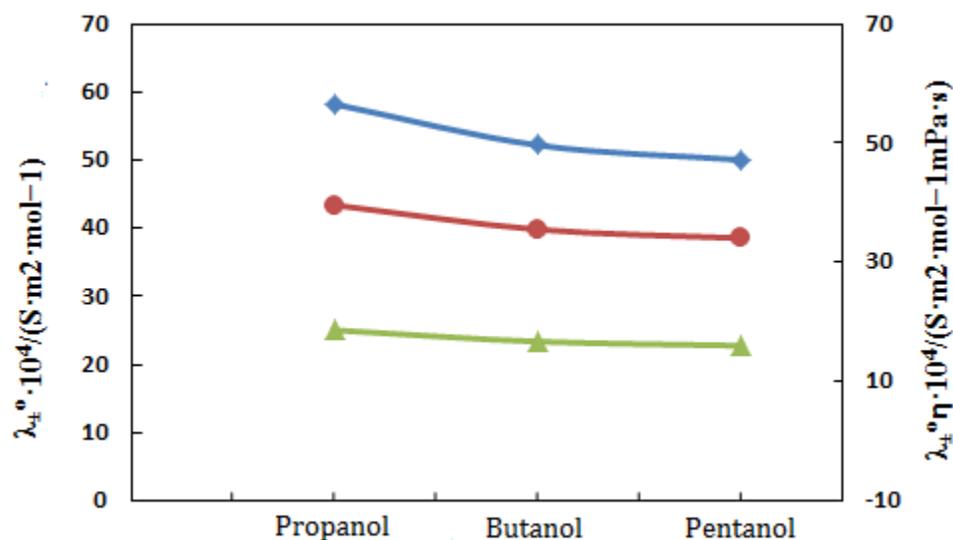
Solvents	$D \cdot 10^{10} / (\text{m}^2 \cdot \text{s}^{-1})$		$i \cdot 10^8 / (\text{m}^2 \text{ s}^{-1} \text{ volt}^{-1})$	
	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub>
propanol	0.54	0.26	2.11	0.99
butanol	0.37	0.17	1.43	0.67
pentanol	0.26	0.12	1.00	0.47

**Table 6. Limiting ionic conductance ( $\lambda^{\circ}$ ), ionic Walden product ( $\lambda^{\circ}\eta$ ), crystallographic radii ( $r_c$ ) and Stoke's radii ( $r_s$ ) [emim]<sup>+</sup> and X<sup>-</sup>(CH<sub>3</sub>SO<sub>3</sub>) n-Propanol, n-Butanol and n-Pentanol at 298.15 K**

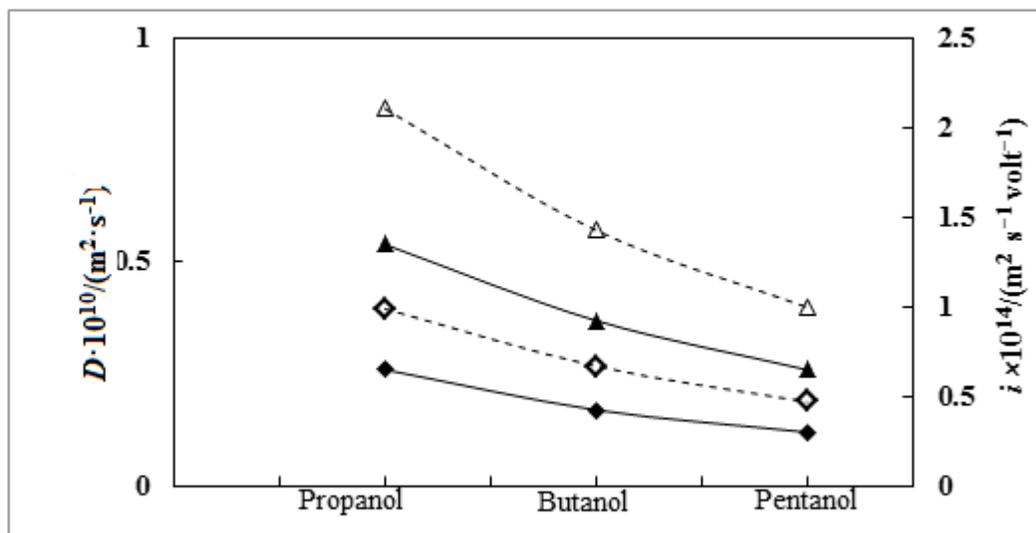
Solvents	$\lambda^{\circ}\cdot 10^4 /$ S·m <sup>2</sup> ·mol <sup>-1</sup>		$\lambda^{\circ}\eta\cdot 10^4 /$ S·m <sup>2</sup> ·mol <sup>-1</sup> mPa·s		$r_c / \text{Å}$		$r_s / \text{Å}$	
	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>
propanol	20.37	9.58	39.59	18.60	1.33	2.83	2.07	4.40
butanol	13.84	6.51	35.51	16.69	1.33	2.83	2.31	4.91
pentanol	09.70	4.56	34.05	16.00	1.33	2.83	2.41	5.12

**Table 7. Experimental densities, refractive indices and molar refractions of 0.05(M) concentration [emim]X (where X= CH<sub>3</sub>SO<sub>3</sub>) in n-Propanol, n-Butanol, n-Pentanol at 298.15K.**

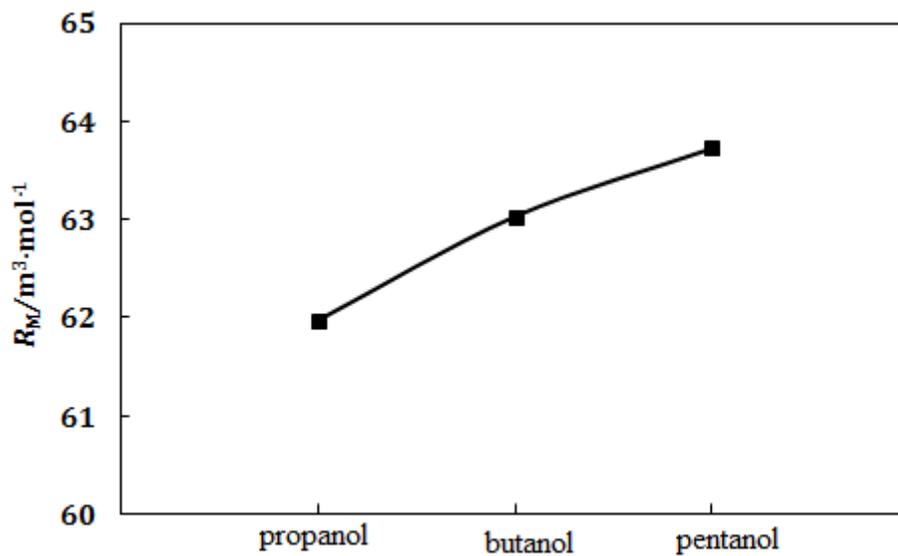
Solutions	$\rho\cdot 10^{-3} / \text{kg}\cdot \text{m}^{-3}$	$n_D$	$R_M / \text{m}^3\cdot \text{mol}^{-1}$
[emim]CH <sub>3</sub> SO <sub>3</sub> in propanol	0.80885	1.4011	61.97
[emim]CH <sub>3</sub> SO <sub>3</sub> in butanol	0.81522	1.4125	63.03
[emim]CH <sub>3</sub> SO <sub>3</sub> in pentanol	0.82113	1.4211	63.72

**FIGURES:**


**Fig 1.** Plot of limiting ionic conductance ( $\lambda_{\pm}^0$ ) of [emim]<sup>+</sup> CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> (◆), ionic Walden product ( $\lambda_{\pm}^0\eta$ ) of [emim]<sup>+</sup> (●) and (CH<sub>3</sub>SO<sub>3</sub>)<sup>-</sup> (▲) in n-Propanol, n-Butanol and n-Pentanol respectively at 298.15 K



**Fig 2.** Plot of Diffusion Coefficient ( $D$ )(solid line) of [emim]<sup>+</sup>(▲) and (CH<sub>3</sub>SO<sub>3</sub>)<sup>-</sup> (◆) and ionic mobility ( $i$ )(dotted line) of [emim]<sup>+</sup>( Δ) and (CH<sub>3</sub>SO<sub>3</sub>)<sup>-</sup> (ϕ) in n-Propanol, n-Butanol and n-Pentanol respectively at 298.15K.



**Fig 3:** Plot of Molar Refraction ( $R_M$ ) of [emim]CH<sub>3</sub>SO<sub>3</sub> (—■—), in n-Propanol, n-Butanol and n-Pentanol respectively at 298.15K