

# CHAPTER VII

## INVESTIGATION OF SOLUTION BEHAVIOUR OF AN IONIC LIQUID IN DIVERSE CELLOSOLVES BY PHYSICOCHEMICAL CONTRIVANCE

### 6.1. 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” [1], 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 [2]. 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 [3,4]. Imidazolium cation based ILs are highly thermally stable, larger commercial available prominent bio-applications [5]. ILs having large anions are also susceptible to additional interactions with polar solvents.

Alkoxy-alkanols (or cellosolves) are very interesting solvents having the ability to form intra- and intermolecular hydrogen bonds with various electrolytes (viz., ILs) [6-7]. They are the most well-known solvents with protic and self-associated properties [8-13]. Upon interaction of ILs with these cellosolve generate interesting properties due to specific interactions, hydrogen bond effects, ion-dipole interaction [14], etc. A detailed understanding of the nature of interaction of simultaneous presence of the ether (-O-) and hydroxyl (-OH) groups in the same solvent and the corresponding alkoxy alcohols with ILs are of immense

important from both the practical and fundamental view points. Alkoxy alcohols are used as solvents for enormous purposes such as varnishes, dyes, and resin industries.

In the present work, herein we report conductivity, density, viscosity and FT-IR spectroscopy to ascertain the molecular interaction and ion association of the IL in the congener series of cellosolves (methoxy, ethoxy and propoxy alcohol) at 293.15K, 303.15K and 313.15K respectively.

### **6.2.0. Experimental Section:**

#### **6.2.1 Source and purity of Materials**

The room temperature 1, 3-dimethylimidazolium methyl sulfate ionic liquid selected for this work was of puriss grade and procured from Sigma-Aldrich, Germany and it was used as purchased. The mass purity of the IL was  $\geq 0.99$ .

All the spectroscopic grade solvents were obtained from Sigma-Aldrich, Germany, and used as purchased. The mass fraction purities of 2-methoxy ethanol (ME) is 0.97, 2-ethoxy ethanol (EE) is 0.99 and 2-propoxy ethanol (PE) is 0.99 (Table 1).

The purities of the alkoxy alcohols have been checked by measuring their densities and viscosities, which were in good accordance with the supplemented literature values [7-13] and are shown in Table 2.

#### **6.2.2 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  $\pm 0.0003$  g. The uncertainty of molality of different solutions was estimated to  $\pm 0.0001$  mol  $\text{kg}^{-1}$ . 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 ( $\rho$ , in  $\text{g cm}^{-3}$ ) of the studied solution measured by Anton Paar digital density meter (DMA 4500M) with an accuracy of  $\pm 0.00005$   $\text{g cm}^{-3}$  at 293.15, 303.15 and 313.15K and maintaining  $\pm 0.01$  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 ( $\eta$ , mPas) 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 [15].

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  $(0.1 \pm 0.001) \text{ cm}^{-1}$ . 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. [16].

Infrared Spectra of the pure solvents and IL in presence of pure solvents were recorded by 8300 FTIR spectrometer (Shimadzu, Japan). The details about this instrument discussed earlier [17].

### 6.3. Results and discussion

#### 6.3.1 Conductivity:

The concentrations and molar conductance ( $\Lambda$ ,  $\text{S m}^2 \text{ mol}^{-1}$ ) of the IL in 2-methoxy ethanol (ME), 2-ethoxy ethanol (EE) and 2-propoxy ethanol (PE) at different temperatures are given in Table 3. The molar conductance ( $\Lambda$ ) has been obtained from the specific conductance ( $k$ ) value using the following equation:

$$\Lambda = (1000k) / C \quad (\text{VII.1})$$

Linear conductivity curves ( $\Lambda$  vs.  $C$ ) were obtained for the electrolyte in ME, EE and PE and extrapolation of  $\sqrt{c} = 0$  was used to evaluate the starting limiting molar conductance for the IL.

#### 6.3.2 Ion Pair formation:

Ion-Pair formation of an IL in the studied solvent can be achieved from the

conductometric investigation. All the selected solvents have higher and moderate relative permittivity ( $\epsilon_r \geq 10$ ), thus the conductance data obtained for the IL in various studied solvents systems have been analyzed using the Fuoss conductance equation [18,19] for the formation of ion-pair [20] and it was introduced by Bjerrum in 1926. For a given set of conductivity data ( $c_{j;j=1,\dots,n}$ ) the three adjustable parameters are obtained from Fuoss equation. In which,  $\Lambda_0$ ,  $K_A$  and  $R$  are the limiting molar conductance, association constant and distance of closest approach of ions, i.e., the maximum centre-to-centre distance between the ions in the solvent separated ion-pairs respectively. The value of  $R$  is assumed to be  $R = a + d$ , here,  $a$  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 value of  $d$  obtained from the given equation (2), where  $M$  is the molecular mass and  $\rho$  is the density of the solvents [21].

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

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

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

$$g = 1 - K_A c \gamma^2 f^2$$

$$-\ln f = \beta k / 2(1 + kR) \quad (\text{VII.3-VII.8})$$

$$\beta = e^2 / (e_r k_B T)$$

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

All the symbols used in the above equations signify the usual meanings [22]. The initial  $\Lambda_0$  values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [23]. Input for the program to perform computation is the number of data,  $n$ , followed by  $\epsilon$ ,  $\Lambda_0$ ,  $T$ ,  $\rho$ , mole fraction of the first component, molar masses,  $M_1$  and  $M_2$  along with  $C_j$ ,  $\Lambda_j$  values where  $j = 1, \dots, n$  and an instruction followed to maintain the range of  $R$  values. The minimum standard deviation  $\delta$  was calculated by the given equation (VII.9);

$$\delta^2 = \sum_{j=1}^n [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n - m) \quad (\text{VII.9})$$

Where,  $n$  is the number of experimental points and  $m$  is the number of fitting parameters. Thus by fixing of  $R$  value with two parameter fit ( $m = 2$ ), the conductance data were analyzed. For the studied IL in every studied solvent (from ethoxy ethanol to propoxy ethanol), no significant minima in the curves of  $\delta$  vs  $R$  were obtained, whereas the  $R$  values were arbitrarily preset at the center to center distance of solvent-separated ion pair.

The values of  $\Lambda_0$  ( $S\ m^2\ mol^{-1}$ ),  $KA$  ( $dm^3\ mol^{-1}$ ), and  $R$  ( $\text{\AA}$ ) obtained by this procedure are represented in Table 4. Perusal of Table 4 reveals that the limiting molar conductance ( $\Lambda_0$ ,  $S\ m^2\ mol^{-1}$ ) for the electrolyte (IL) gradually decreases from 2-methoxy ethanol to 2-propoxy ethanol of the studied solvents.

The Table 4 also reveals that the association constant of the IL is opposite of the limiting molar conductance, which is in order;

2-propoxyethanol > 2-ethoxyethanol > 2-methoxyethanol

Hence the ion-solvent interaction or ion-association increases from lower alkoxy-alcohol to higher alkoxy-alcohols among the chosen solvents, leading to a lower conductivity of IL.

If we consider the effect of solvent properties (such as viscosity and relative permittivity), the discrepancy of conductance data depends upon not only depends upon the relative permittivity of the solvents but also vary with the solvent viscosity. From the Table 3 and 4, we can support the above facts from the viscosity values, as following; the limiting molar conductivity for the IL in are linearly vary with reciprocal of the solvent viscosity ( $1/\eta$ ) (or fluidity,  $\eta^{-1}$ , ( $mPa\ s$ ) $^{-1}$ ), i.e.; the electrolyte (IL) in the lower viscous solvent, the  $\Lambda_0$  ( $S\ m^2\ mol^{-1}$ ) value should increase[24,25] which suggested that the solvents viscosity ( $\eta$ ,  $mPa\ s$ ) is predominant over the relative permittivity ( $\epsilon$ ), in effecting the electrolytic conductance of the electrolyte (IL) under the studied solvent conditions.

The ion-association of the electrolyte (IL) in pure solvent can also be explained through the important characteristics function termed as Walden product. The product,  $\Lambda_0\eta$ , is the Walden product ( $\Lambda_0\eta$ ,  $S\ m^2\ mol^{-1}\ mPa$ ) and it is a constant at a particular condition, are tabulated in Table 5. Walden product decreases

arbitrarily from ME to PE and then slightly increases in PE at higher temperatures. The decreasing tendency is for the increase of  $\eta$  and decrease of  $\Lambda_0$  values of the IL in the solvents, but the slight increase in case of PE at higher temperatures is obviously due to effect of the high viscosity. This is realistic because of the effective solvated radius,  $r_{\text{eff}}$ , (Å) of the ions of IL is inversely proportional to the Walden product of the ions of IL in the various solvent systems [26,27],

$$\Lambda_0 \eta = \frac{1}{6\pi r_{\text{eff}} T} \quad (\text{VII.10})$$

The solvation of molecule (IL) as well as ions in the chosen solvents can be explain by

(i) Solvation efficiency of IL among the three alcohols:

By consideration of the conductivity and ion-pair formation constant value of IL in different solvents, we can conclude that the IL mostly prefers the 2-propoxy ethanol solvent than other two lower member alkoxy ethanol.

(ii) Structural influence aspect of the IL and solvents:

All the alkoxy alcohols have terminal –OH group and ethereal (-O-) moiety. IL has imidazolium cation and methyl sulphate anion. The terminal –OH functional group of alcohols interact on the  $N^+$  centre of imidazolium ring through ion – dipole interaction (scheme 1). Another contributing factor in the alkoxy alcohols is the ethereal (-O-) atom. The lone pair donating tendency of ethereal oxygen increases with the increase in alkoxy group (i.e. methoxy, ethoxy and propoxy) of the studied solvents. It may be due to the +I effect of alkyl group present in the alcohols and thus +I effect in 2-propoxy ethanol is maximum than the other two alcohols. Hence, the interaction is more prominent in 2-propoxy ethanol (PE) due to the presence of more lone pair availability of oxygen atom, making it stronger interaction with IL (Scheme 2).

The preliminary point for evaluations of ionic conductance is Stokes' law which states that the limiting ionic Walden product ( $\lambda_0 \eta$ ,  $S \text{ m}^2 \text{ mol}^{-1} \text{ mPa s}$ ) (the product of the limiting ionic conductance and solvent viscosity) 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  $\lambda_0^\pm$  ( $\text{S m}^2 \text{ mol}^{-1}$ ) in different solvents, were calculated using tetrabutylammonium tetraphenylborate ( $\text{Bu}_4\text{NBPh}_4$ ) as a 'reference electrolyte' following the scheme as suggested by B. Das et al. [28]. We have calculated the limiting ionic conductivities  $\lambda_0^\pm$  ( $\text{S m}^2 \text{ mol}^{-1}$ ) in our solvent compositions by interpolation of conductance data from the literature [29] using cubic spline fitting. Ionic conductivity values given in Table 6 shows that the greater share of the conductivity come for the cation than the anion. The Table 6 shows that the contribution of ionic conductance values also decrease from ME to PE for the ionic liquid (IL). The  $\lambda_0^\pm$  ( $\text{S m}^2 \text{ mol}^{-1}$ ) values were used for the calculation of Stokes' radii ( $r_s$ , Å) according to the classical expression [30].

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

Ionic Walden products  $\lambda_0^\pm \eta$  ( $\text{S m}^2 \text{ mol}^{-1} \text{ mP s}$ ), Stokes' radii  $r_s$  (Å), and crystallographic radii  $r_c$  (Å) are presented in Table 6. The trends in Walden products  $\Lambda_0 \eta$  and ionic Walden products  $\lambda_0^\pm \eta$  for the electrolyte in the solvents are depicted in Table 6. It shows that both the ionic Walden products  $\lambda_0^\pm \eta$  and Walden products  $\Lambda_0 \eta$  for the electrolyte randomly decreases from ME to PE. The Stokes' radii  $r_s$  (Å) are higher or comparable to their crystallographic radii  $r_c$  (Å), this suggests that the ion are solvated in the studied solvent medium and this may be due to the low surface charge density. The distance parameter  $R$  (Å) is the minimum distance that two free ions can approach before they combine to form an ion-pair.

The nature of the curve for the Gibb's energy changes for ion-pair formation;  $G^\circ$  ( $\text{kJ mol}^{-1}$ ) clearly depicts the tendency for ion-pair formation. The Gibb's energy change is given by the following relationship [31] and is given in Table 5.

$$G^\circ = -RT \ln K_A \quad (\text{VII.12})$$

The negative values of  $G^\circ$  ( $\text{kJ mol}^{-1}$ ) can be ascribed by considering the participation of specific interaction in the ion-association process. It is observed from the Table 5 that the values of the Gibb's free energy are all negative, entire

all over the solutions and the negativity suggests the ion-solvent interaction increases from ME to PE.

#### 6.4.1 Apparent Molar volume:

The densities of the IL in different solvents increase linearly with the concentration at the studied temperatures. For this purpose, the apparent molar volumes ( $\Phi_v$ ) were determined from the solution densities using the following equation

$$\Phi_v = M / \rho - (\rho - \rho_0) / m \rho_0 \rho \quad (\text{VII.13})$$

where  $M$  is the molar mass of the solute,  $m$  is the molality of the solution, and  $\rho$  and  $\rho_0$  are the densities of the solution and solvent, respectively. The apparent molar volumes,  $\Phi_v$ , were found to decrease with increasing molality ( $m$ ) of the IL in different solvents and increase with increasing temperature for the system under study. The limiting apparent molar volumes were obtained using the following Masson equation [32].

$$\Phi_v = \Phi_v^0 + S_v^* \sqrt{c} \quad (\text{VII.14})$$

Where, all the symbols have usual meanings. The values of  $\Phi_v^0$  and  $S_v^*$  are reported in Table 7. From Table 7 it is clear that  $\Phi_v^0$  values are normally positive for all the solvents and is highest in case of IL in PE. This indicates the presence of strong ion-solvent interactions and the extent of interactions increases from ME to PE. On the contrary,  $S_v^*$  indicates the extent of ion-ion interactions. The values of  $S_v^*$  show that the extent of ion-ion interaction is highest in the case of PE and is lowest in the case of ME. Quantitatively the magnitudes of  $\Phi_v^0$  are much greater than  $S_v^*$ , for all solutions.

This observation suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions. The values of  $\Phi_v^0$  also signifies the fact that a higher ion-solvent interaction in PE leads to lower conductance of IL in it than in EE and ME.

#### 6.4.2 Temperature-dependent limiting apparent molar volume.

The variation of  $\Phi_v^0$  with the temperature of the IL in different solvents can be expressed by the general polynomial equation as follows:

$$\Phi_v^0 = a_0 + a_1T + a_2T^2 \quad (\text{VII.15})$$

where  $a_0$ ,  $a_1$ ,  $a_2$  are empirical coefficients depending on the solute and mass fraction of the co solute IL, and T is the Kelvin Temperature and their values in ME, EE and PE reported in Table 8.

The limiting molar expansibilities can also be estimated from the following equations:

$$\delta\Phi_E^0 = (\delta\Phi_v^0 / \delta T)_P = a_1 + 2a_2T \quad (\text{VII.16})$$

The limiting apparent molar expansibility,  $\Phi_E^0$  is the change in magnitude with a change of temperature at fixed pressure. The values of  $\Phi_E^0$  for different solutions of the studied IL at 293.15, 303.15, and 313.15 K are reported in Table 8. The table shows that  $\Phi_E^0$  is positive for IL in all the studied alcohols and studied Kelvin temperatures. This fact can be attributed to the absence of caging or packing effect for the IL in solutions. Recently it has been proved by different scientists that,  $S_V^*$  is not the sole criterion for determining the structure-making or breaking nature of any solute. For that purpose, Hepler[33] developed a technique for the solute in terms of long-range structure-making and -breaking capacity of the solute in mixed solvent systems using the following equation:

$$(\delta\Phi_E^0 / \delta T)_P = (\delta^2\Phi_v^0 / \delta T^2)_P = 2a_2 \quad (\text{VII.17})$$

The sign of  $(\delta\Phi_E^0 / \delta T)_P$ , is positive or a small negative value, then the molecule is a structure maker; otherwise, it is a structure breaker [34]. As is evident from Table 9 the values for IL in all the solvents under investigation are positive so are mostly structure makers in all the solvent systems.

### 6.5. Viscosity calculation:

Viscosity is an important transport property for the electrolyte to determine the ion – solvent interaction in various investigated solvents. The viscosity data have been estimated by Jones-Donner equation:

$$(\eta / \eta_0 - 1) / \sqrt{c} = A + B\sqrt{c} \quad (\text{VII.18})$$

Where,  $\eta$  and  $\eta_0$  are the viscosities of the solution and solvent respectively. The values of A-coefficient and B-coefficient are obtained from the plots of  $(\eta / \eta_0 - 1)$  Vs  $\sqrt{c}$  which are reported in Table 10. From Table 10 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 the solvent viscosity value, in accordance with the results obtained from  $\Phi_v^0$  values explained earlier. The values of the A-coefficient are found to very small as compared to B-coefficients. These results indicate the presence of very weak solute-solute interactions. These results are in outstanding agreement with those obtained from  $S_V^*$  values. The extent of solute-solvent interaction obtained from the B-coefficient and occurs into the local vicinity of the solute molecules in the solutions. Values of the B-coefficient are positive and much higher than those of the A-coefficient, thereby suggesting the solute-solvent interactions are leading over the solute-solute interactions. The higher B-coefficient values for higher viscosity values is due to the solvated solute molecules associated by the solvent molecules all round to the formation of associated molecule by solute-solvent interactions. Further, these types of interactions are strengthened with rise in temperatures. Therefore, the trend of ion-solvent interaction is PE > EE > ME (Figure1.).

### 6.6. FT-IR spectroscopy:

From the help of FT-IR spectroscopic investigation the molecular interaction existing between the IL and the solvent can be interpreted. The IR spectra of the pure solvents and IL in presence of solvents were studied. The stretching

pure solvents and IL in presence of solvents were studied. The stretching frequencies of the key groups are given in Table 11.

In the case of ME, a sharp peak is observed at  $3414.27\text{ cm}^{-1}$  for O-H which shifts to  $3409.05\text{ cm}^{-1}$  on addition of 0.05M of the ionic liquid, [MMIm] MSO<sub>4</sub>, due to the interaction of [MMIm]<sup>+</sup> or [MSO<sub>4</sub>]<sup>-</sup> with the O-H dipole showing ion-dipole interaction which is formed due to the disruption of intra-molecular H-bonding interaction in ME molecules.

Similar types of interactions are observed in the case of EE and PE where the sharp peak for O-H group shifts on addition of [MMIm]MSO<sub>4</sub> due to the formation of ion-dipole interaction between [bmmim]<sup>+</sup> or [MSO<sub>4</sub>]<sup>-</sup> with O-H group of solvents. Consequently, the disruption of weak H-bonding interaction occurs in the pure solvent systems [22, 36]. Therefore, the molecular interaction existing in these solvent systems can successfully ascribe from the shifting of stretching frequency (Table 11).

### 6.7. Conclusion

Extensive study reveals that the investigated IL in these industrial solvents mainly exists as Ion pair.  $\Lambda$  values suggest molecular interaction increases from ME to PE. The results of  $K_A$  indicate IL is more associated in the PE than the other two solvents.  $G^\circ$  values imply the overall process for ion-dipole interaction and ion-association of the IL in the studied solvents are feasible. Density and viscosity measurements provide the information about ion-dipole interaction, and show the solute-solvent interaction for this system is higher than the solute-solute interaction. FT-IR studies definitely recommend the ion-dipole interaction in each binary system (IL+alkoxy alcohols). Formation of Ion pair was confirmed and well established from the transport, volumetric and spectroscopic studies.

### 4.5. REFERENCES

References of CHAPTER VI are given in BIBLIOGRAPHY (Page No.298-299)

## Tables

**Table1.** Sample descriptions.

Chemical name	Source	CAS No.	Purification method	Final mass Purity*
1,3-dimethylimidazolium methylsulfate	Sigma-Aldrich, Germany	97345-90-9	Used as procured	≥0.99
2-methoxy ethanol (ME)	Sigma-Aldrich, Germany	109-86-4	Used as procured	≥0.97
2-ethoxy ethanol (EE)	Sigma-Aldrich, Germany	110-80-5	Used as procured	≥0.99
2-propoxy ethanol (PE)	Sigma-Aldrich, Germany	2807-30-9	Used as procured	≥0.99

Described by the supplier\*

**Table2.** Experimental and literature values of density ( $\rho$ ), viscosity ( $\eta_0$ ) and relative permittivity ( $\epsilon$ ) of the solvents at 293.15 K, 303.15K and 313.15K temperatures and 0.101M Pa pressure.

Solvents	$\rho \times 10^{-3} / \text{kg.m}^{-3}$		$\eta_0 \times 10^3 / \text{mPa}$		$\epsilon$
	Lit.	Exp.	Lit.	Exp.	
	293.15K				
ME	0.96465[7]	0.96461	1.99[11]	1.99	17.38[13]
EE	0.92954[7]	0.92955	2.07[11]	2.08	14.25[13]
PE	0.91151[7]	0.91152	2.57[12]	2.58	11.76[13]
	303.15K				
ME	0.95554[7]	0.95553	0.37[11]	1.38	16.56[13]
EE	0.92045[7]	0.92046	1.61[11]	1.62	13.76[13]
PE	0.90273[7]	0.90274	2.12[12]	2.13	11.19[13]
	313.15K				
ME	0.94629[8]	0.94628	0.94[11]	0.95	15.77[13]
EE	0.91370[9]	0.91371	1.24[11]	1.25	13.07[13]
PE	-	0.89642	-	1.78	10.62[13]

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

**Table3.**The concentration (c) and molar conductivity ( $\Lambda$ ) of IL in 2-methoxy ethanol (ME), 2-ethoxy ethanol (EE) and 2-propoxy ethanol (PE) at 293.15, 303.15 and 313.15K respectively and 0.101MPa Pressure.

m x10 <sup>4</sup> /mol.kg <sup>-3</sup>	$\Lambda$ x10 <sup>4</sup> /Sm <sup>2</sup> mol <sup>-1</sup>	m x10 <sup>4</sup> /mol.kg <sup>-3</sup>	$\Lambda$ x10 <sup>4</sup> /Sm <sup>2</sup> mol <sup>-1</sup>	m x10 <sup>4</sup> /mol.kg <sup>-3</sup>	$\Lambda$ x10 <sup>4</sup> /Sm <sup>2</sup> mol <sup>-1</sup>
ME		EE		PE	
293.15K					
1.56	26.3	1.33	16.78	1.11	11.57
2.96	25.55	2.01	16.42	1.53	11.35
4.14	25.01	2.46	16.13	1.76	11.21
5.15	24.53	3.34	15.76	2.57	10.87
6.8	23.66	4.27	15.36	3.48	10.48
7.48	23.31	5.13	15.03	3.87	10.35
8.08	23.09	6.44	14.66	4.23	10.13
8.62	22.81	7.36	14.36	5.11	9.81
9.54	22.39	8.17	14.01	6.05	9.46
10.3	22.01	8.74	13.78	7.85	8.89
10.94	21.76	9.56	13.48	8.84	8.47
11.49	21.54	10.89	13.06	9.19	8.37
12.73	21.01	11.68	12.66	10.58	7.88
14.03	20.38	12.35	12.45	11.35	7.56
14.67	20.04	13.82	11.97	12.57	7.11
303.15K					
1.56	29.15	1.33	18.58	1.11	13.67
2.96	28.36	2.01	18.23	1.53	13.41
4.14	27.75	2.46	18.01	1.76	13.31
5.15	27.21	3.34	17.68	2.57	12.94
6.8	26.34	4.27	17.45	3.48	12.54
7.48	26.04	5.13	17.02	3.87	12.41
8.08	25.77	6.44	16.46	4.23	12.14
8.62	25.44	7.36	16.12	5.11	11.92
9.54	25.01	8.17	15.91	6.05	11.53
10.3	24.61	8.74	15.58	7.85	10.85
10.94	24.29	9.56	15.25	8.84	10.57
11.49	24.14	10.89	14.82	9.19	10.34

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12.73	23.53	11.68	14.58	10.58	9.84
14.03	22.85	12.35	14.18	11.35	9.58
14.67	22.48	13.82	13.54	12.57	9.12
		313.15K			
1.56	32.04	1.33	20.88	1.11	15.68
2.96	31.38	2.01	20.61	1.53	15.45
4.14	30.82	2.46	20.34	1.76	15.28
5.15	30.37	3.34	19.86	2.57	14.94
6.8	29.58	4.27	19.34	3.48	14.51
7.48	29.27	5.13	19.05	3.87	14.31
1.56	32.04	1.33	20.88	1.11	15.68
2.96	31.38	2.01	20.61	1.53	15.45
4.14	30.82	2.46	20.34	1.76	15.28
5.15	30.37	3.34	19.86	2.57	14.94
6.8	29.58	4.27	19.34	3.48	14.51
7.48	29.27	5.13	19.05	3.87	14.31
8.08	28.94	6.44	18.54	4.23	14.18
8.62	28.74	7.36	18.16	5.11	13.81
9.54	28.31	8.17	17.88	6.05	13.51
10.3	27.98	8.74	17.58	7.85	12.79
10.94	27.73	9.56	17.15	8.84	12.46
11.49	27.41	10.89	16.75	9.19	12.32

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

**Table4.** Limiting molar conductance ( $\Lambda_0$ ), association constant ( $K_A$ ), co-sphere diameter(R) and standard deviations of experimental  $\Lambda(\delta)$  obtained from Fuoss conductance equation for IL in ME, EE and PE at 293.15, 303.15, and 313.15 K respectively and 0.101MPa pressure

Solvents	$\Lambda_0 \times 10^4 / \text{Sm}^2 \text{mol}^{-1}$	$K_A / \text{dm}^{-3} \text{mol}^{-1}$	R/Å	$\Lambda(\delta)$
293.15 K				
ME	29.47	481.54	4.66	0.35
EE	19.14	707.27	4.69	0.28
PE	14.20	1661.21	4.71	0.33
303.15 K				
ME	32.93	415.10	4.56	0.40
EE	21.06	580.51	4.67	0.34
PE	16.13	1075.87	4.69	0.31
313.15K				
ME	35.24	299.19	4.48	0.40
EE	23.56	528.74	4.58	0.29
PE	18.07	712.56	4.68	0.29

**Table5.** Walden product ( $\Lambda_0 \eta$ ) and Gibbs energy change ( $G^\circ$ ) of IL in ME.EE and PE at 293.15 K to 313.15 K temperatures and 0.101MPa pressure.

Solvents	$\Lambda_0 \eta \times 10^4 / \text{S m}^2 \text{mol}^{-1} \text{mPa.s}$	$G^\circ / \text{kJ mol}^{-1}$
293.15K		
ME	58.67	-15.05
EE	39.75	-15.99
PE	36.56	-18.07
303.15K		
ME	45.67	-15.19
EE	33.94	-16.03
PE	34.26	-17.59
313.15K		
ME	33.19	-14.84
EE	29.21	-16.32
PE	32.16	-17.10

**Table 6.** Ionic limiting molar conductance ( $\lambda_{\infty}^{\pm}$  /S m<sup>2</sup> mol<sup>-1</sup>), ionic Walden product ( $\lambda_{\infty}^{\pm}\eta$ / S m<sup>2</sup> mol<sup>-1</sup> mPa s), crystallographic radii ( $r_c/\text{\AA}$ ) and Stoke's radii ( $r_s/\text{\AA}$ ) of IL (having [MMIm]<sup>+</sup> cation and [MSO<sub>4</sub>]<sup>-</sup> anion) in ME,EE and PE at various Kelvin and 0.101 MPa pressure

Solvents	$\lambda_{\infty}^{\pm} \times 10^4$		$\lambda_{\infty}^{\pm}\eta \times 10^4$		$r_c/\text{\AA}$		$r_s/\text{\AA}$	
	/S m <sup>2</sup> mol <sup>-1</sup>		/S m <sup>2</sup> mol <sup>-1</sup> mPa s		[MSO <sub>4</sub> ] <sup>-</sup> [MMIm] <sup>+</sup>		[MSO <sub>4</sub> ] <sup>-</sup> [MMIm] <sup>+</sup>	
					[MMIm] <sup>+</sup> [MSO <sub>4</sub> ] <sup>-</sup>			
293.15K								
ME	19.28	10.19	38.37	20.30	1.32	2.83	1.61	3.05
EE	12.52	6.62	26.00	13.75	1.32	2.83	1.62	3.07
PE	9.22	4.98	23.74	12.82	1.32	2.83	1.65	3.06
303.15K								
ME	21.34	11.59	27.61	18.06	1.33	2.84	1.45	3.11
EE	13.54	7.52	22.59	11.35	1.33	2.84	1.55	3.12
PE	10.41	5.72	20.38	13.88	1.33	2.84	1.56	3.13
313.15K								
ME	22.68	12.56	24.33	8.86	1.34	2.85	1.33	3.15
EE	14.35	9.21	21.52	7.69	1.34	2.85	1.39	3.19
PE	11.97	6.10	18.24	13.92	1.34	2.85	1.47	3.21

**Table 7.** Concentration,  $m$ , density,  $\rho$ , apparent molar volume,  $\Phi_v$ , limiting apparent molar volume  $\Phi_v^0$ , and exponential slope ( $S_v^*$ ) for IL in ME, EE and PE at 293.15K, 303.15K and 313.15K respectively and 0.101 MPa pressure.

Solvents	$m$ /mol.kg <sup>-1</sup>	$\rho \times 10^{-3}$ /kg.m <sup>-3</sup>	$\Phi_v \times 10^6$ /m <sup>3</sup> mol <sup>-1</sup>	$\Phi_v^0 \times 10^6$ /m <sup>3</sup> mol <sup>-1</sup>	$S_v^* \times 10^6$ /m <sup>3</sup> mol <sup>3/2</sup> kg <sup>3/2</sup>
<b>293.15K</b>					
ME	0.010	0.96489	180.64		
	0.025	0.96545	178.57		
	0.040	0.96606	176.75		
	0.055	0.96675	174.42	186.30	-49.88
	0.070	0.96745	172.94		
	0.085	0.96825	170.76		
EE	0.010	0.92977	200.35		
	0.025	0.93015	198.20		
	0.040	0.93058	196.32		
	0.055	0.93108	194.09	205.70	-47.55
	0.070	0.93158	192.82		
	0.085	0.93218	190.73		
PE	0.010	0.91161	211.99		
	0.025	0.91181	209.14		
	0.040	0.91204	207.60		
	0.055	0.91231	206.11	216.60	-43.60
	0.070	0.91263	204.47		
	0.085	0.91299	202.89		
<b>303.15K</b>					
ME	0.010	0.95587	182.34		
	0.025	0.95642	180.67		
	0.040	0.95702	178.94		
	0.055	0.95771	176.45	188.60	-52.14
	0.070	0.95845	174.27		
	0.085	0.95925	172.12		

EE	0.010	0.92068	202.33		
	0.025	0.92109	198.85		
	0.040	0.92155	196.62		
	0.055	0.92208	194.23	208.30	-57.11
	0.070	0.92265	192.24		
	0.085	0.92322	190.95		
PE	0.010	0.90284	212.95		
	0.025	0.90307	209.40		
	0.040	0.90333	207.68		
	0.055	0.90362	206.30	218.10	-47.98
	0.070	0.90399	204.24		
	0.085	0.90436	202.91		
		<b>313.15K</b>			
ME	0.010	0.94662	184.13		
	0.025	0.94721	180.74		
	0.040	0.94785	178.58		
	0.055	0.94855	176.44	189.20	-51.44
	0.070	0.94925	175.22		
	0.085	0.94999	173.93		
EE	0.010	0.91393	203.82		
	0.025	0.91435	199.88		
	0.040	0.91485	196.71		
	0.055	0.91544	193.48	210.8	-67.30
	0.070	0.91599	192.25		
	0.085	0.91662	190.43		
PE	0.010	0.89654	213.33		
	0.025	0.89677	210.43		
	0.040	0.89709	207.19		
	0.055	0.89744	205.12	219.30	-56.01
	0.070	0.89788	202.49		
	0.085	0.89816	202.90		

Uncertainty of the density  $u(\rho) = 0.0005 \text{ g cm}^{-3}$ ; temperature  $u(T) = 0.01 \text{ K}$ ;  $u(m) = 0.0002 \text{ mol kg}^{-1}$ , and  $u(p) = 0.010 \text{ MPa}$ .

**Table8.** Values of empirical coefficients ( $a_0$ ,  $a_1$ , and  $a_2$ ) of temperature dependent apparent molar volume for IL in different solvents (ME,EE, PE) at 293.15 K to 313.15 K and 0.101MPa pressure.

Solvent mixtures	$a_0$ / $\text{m}^3 \text{mol}^{-1}$	$a_1$ / $\text{m}^3 \text{mol}^{-1}\text{K}^{-1}$	$a_2$ / $\text{m}^3 \text{mol}^{-1}\text{K}^{-2}$
293.15K			
ME+IL	-636.5	5.298	-0.008
EE+IL	85.04	0.558	-0.0005
PE+IL	39.32	1.044	-0.001
303.15K			
ME+IL	-636.5	5.298	-0.008
EE+IL	85.04	0.558	-0.0005
PE+IL	39.32	1.044	-0.001
313.15K			
ME+IL	-636.5	5.298	-0.008
EE+IL	85.04	0.558	-0.0005
PE+IL	39.32	1.044	-0.001

**Table9.** Limiting apparent molal expansibilities for IL in different solvents (ME, EE, PE) at 293.15 K to 313.15 K and 0.101MPa pressure

Solvent mixtures	$\Phi_E^0 \times 10^6$ / $\text{m}^3 \text{mol}^{-1}\text{K}^{-1}$	$(\delta\Phi_E^0 / \delta T)_P \times 10^6$ / $\text{m}^3 \text{mol}^{-1}\text{K}^{-2}$
293.15K		
ME+IL	0.6076	-0.016
EE+IL	0.2648	-0.001
PE+IL	0.4577	-0.002
303.15K		
ME+IL	0.4476	-0.016
EE+IL	0.2548	-0.001
PE+IL	0.4377	-0.002
313.15K		
ME+IL	0.2876	-0.016
EE+IL	0.2448	-0.001
PE+IL	0.4177	-0.002

**Table 10.** Concentration,  $c$ , viscosity,  $\eta$ ,  $(\eta/\eta_0-1)/\sqrt{c}$ , viscosity A- and B-coefficients for IL in ME, EE and PE at 293.15 K, 303.15 K and 313.15 K respectively and 0.101MPa pressure.

Solvents	$m$ /mol.kg <sup>-1</sup>	$\eta \times 10^{-3}$ /MPa.s	$(\eta/\eta_0-1)/\sqrt{c}$ /m <sup>3</sup> mol <sup>-1</sup>	B /kg <sup>3</sup> mol <sup>-1</sup>	A /kg <sup>3/2</sup> mol <sup>-1/2</sup>	
<b>293.15K</b>						
ME	0.010	2.01	0.100			
	0.025	2.03	0.127			
	0.040	2.05	0.150			
	0.055	2.07	0.171	0.555	0.041	
	0.070	2.09	0.189			
EE	0.085	2.11	0.206			
	0.010	2.10	0.096			
	0.025	2.12	0.121			
	0.040	2.14	0.144			
	0.055	2.16	0.163	0.581	0.031	
PE	0.070	2.18	0.181			
	0.085	2.21	0.213			
	0.010	2.60	0.077			
	0.025	2.63	0.122			
	0.040	2.65	0.135			
	0.055	2.67	0.148	0.588	0.020	
	0.070	2.70	0.175			
ME	0.085	2.73	0.199			
	<b>303.15K</b>					
	0.010	1.40	0.145			
	0.025	1.42	0.183			
	0.040	1.44	0.217			
	0.055	1.46	0.246	0.798	0.060	
	0.070	1.48	0.273			
	0.085	1.50	0.297			
	EE	0.010	1.64	0.123		

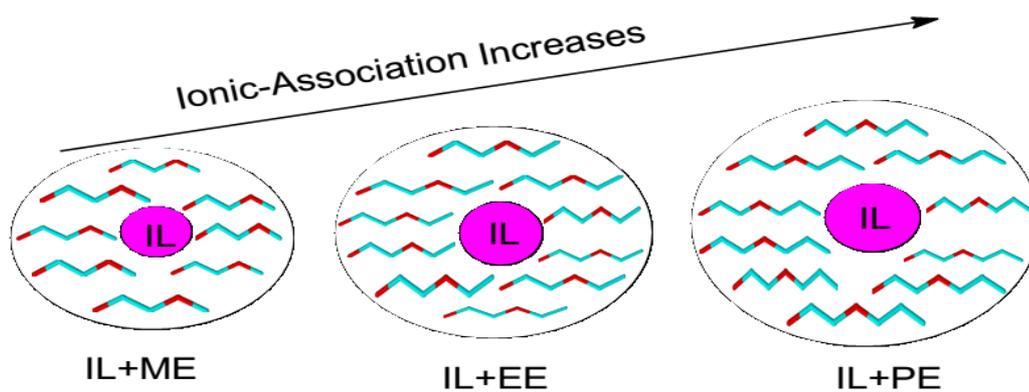
	0.025	1.66	0.156		
	0.040	1.68	0.185		
	0.055	1.71	0.236	0.826	0.033
	0.070	1.73	0.255		
	0.085	1.75	0.274		
PE	0.010	2.15	0.094		
	0.025	2.18	0.148		
	0.040	2.21	0.187		
	0.055	2.24	0.220	0.877	0.009
	0.070	2.27	0.248		
	0.085	2.29	0.257		
		<b>313.15K</b>			
ME	0.010	0.97	0.210		
	0.025	0.99	0.266		
	0.040	1.01	0.315		
	0.055	1.03	0.358	1.154	0.088
	0.070	1.05	0.396		
	0.085	1.07	0.431		
EE	0.010	1.27	0.160		
	0.025	1.29	0.202		
	0.040	1.32	0.279		
	0.055	1.34	0.306	1.214	0.027
	0.070	1.37	0.361		
	0.085	1.39	0.382		
PE	0.010	1.81	0.168		
	0.025	1.84	0.213		
	0.040	1.88	0.280		
	0.055	1.91	0.310	1.225	0.033
	0.070	1.95	0.360		
	0.085	1.99	0.403		

Uncertainty of the viscosity  $u(\eta) = 0.01$  mPa s; temperature  $u(T) = 0.01$  K;  $u(m) = 0.0002$  mol kg<sup>-1</sup>, and  $u(p) = 0.01$  MPa.

**Table11.** Stretching frequencies of the functional groups present in the pure solvent and change of frequency of IL in ME, EE and PE.

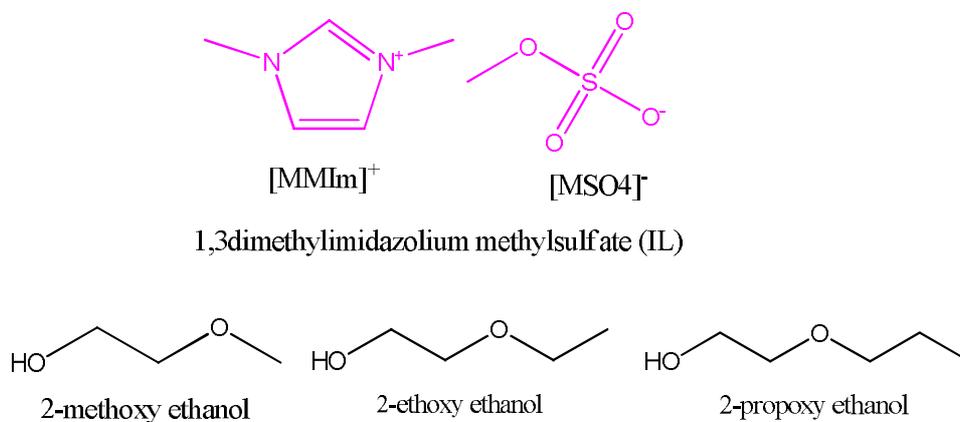
Solvents	Stretching frequencies(cm <sup>-1</sup> )			
	Functional groups	Range	Pure solvents	IL+ Solvent
ME	O-H	3200-3600	3414.27	3409.05
EE	O-H	3200-3600	3421.17	3416.39
PE	O-H	3200-3600	3423.53	3417.05

## Figure

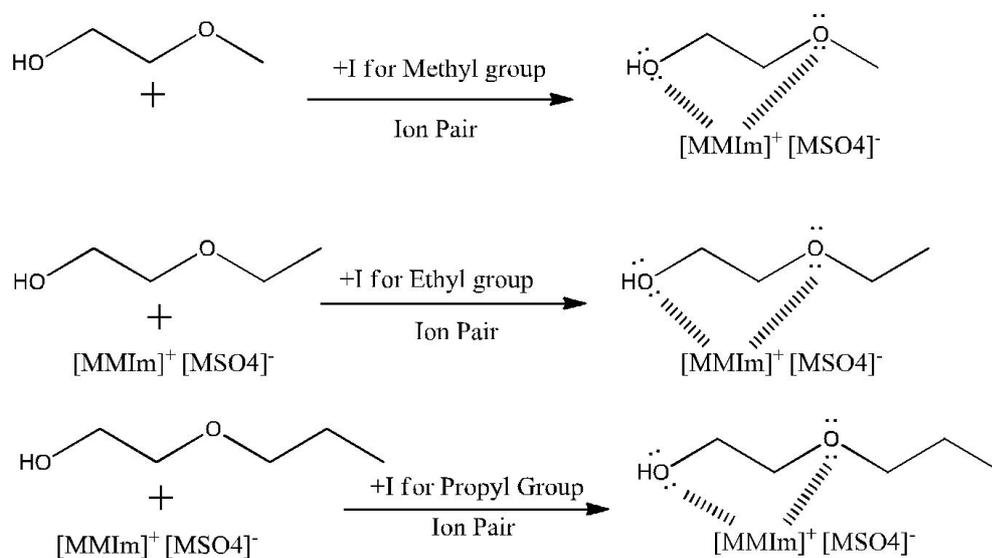


**Figure 1.** Extent of solvation consequences of an IL with diverse cellosolves

## Schemes



**Scheme 1.** Molecular structures of IL and studied solvents.



**Scheme2.** Schematic representation of ion-dipole interaction for the IL in studied solvents (+I denote; Inductive effect on operates ethereal oxygen on ME, EE, and PE).