Solvent-Mediated Molar Conductivity of Protic Ionic Liquids

Sachin Thawarkar, Nageshwar D. Khupse, Anil Kumar*

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Abstract

The molar conductivity, Λ_m of protic ionic liquids (PILs) in molecular solvents is measured at 298.15 K. The decrease in the Λ_m values of PILs is observed with an increase in concentration of PILs. The limiting molar conductivities,Λ°_m were obtained for each PIL in different molecular solvents using a least squares method. The $\Lambda°_m$ data for PILs were correlated with the structural aspects of PILs and of solvent properties. The polar protic solvents show poor ionic association as compared to the polar aprotic solvents, which is discussed on the basis hydrogen bond donating ability (HBD) of solvents and PILs. The alkyl chain substitution of anion plays a significant role in ionic association of the PILs. The diffusion coefficient, D^o and transport number, t were determined, which were consistent with the $\Lambda°_m$ values of PILs in water. The $\Lambda°_m$ and D^o values are dependent on hydrodynamic radius of anion of these ionic liquids. The extent of ionic association for each PIL was discussed using temperature dependent Λ_m data of aqueous PILs systems in terms of Walden plot.

1. Introduction

In the last decade, ionic liquids (ILs) have received more and more attention because of their unique interesting physico-chemical properties and have been widely used in chemical reaction, electrochemical, separation, absorption, and transport processes etc.[1-8] Other recent interesting applications are in electrochemical processes, fuel cells, lithium batteries and solar cells.[9-12] Interestingly, the properties of ionic liquids can be tuned with the combination of different anion and cation, which provide the chances for designing and developing ILs with desired properties[1, 2] such as catalytic activity, viscosity, ionic conductivity, solubility, polarity, phase behavior, extraction ability etc. These properties are influenced by anion–cation and ion–solvent interactions. Many experimental methods like spectroscopic techniques[13-18] and isothermal titration calorimetry have been developed to explore the anion–cation and ion–solvent interactions of ILs.[19, 20] The theoretical studies have been receiving attentions because of its advantages in producing electronic structure, anion–cation binding energy, etc.[14, 21]A study of conductance of the solutions of ionic liquids is essential for learning the ionic interactions in these systems. The electrical conductivity of neat ILs is very low due to its high viscosity. To increase the conductivity of ILs, it is necessary to blend these ILs with other molecular solvents.[22-25] This is especially important because the addition of molecular solvents dramatically decreases the viscosity of ILs and hence it greatly enhances their electrical conductivity.[26, 27] The literature survey reveals that the data on electrical conductivity of ILs with molecular solvents are limited.[28, 29]

Physical & Materials Chemistry Division, CSIR- National Chemical Laboratory, Pune 411 008, India. E-mail: a.kumar@ncl.res.in; Fax: +912025902636.
† Electronic supplementary information (ESI) available: Plots of Λ_m vs. concentration for [HmIm][CH_3OO] and [HmIm][CH_3CH_2OO] in water, methanol, ethanol, dimethyl sulfoxide, acetonitrile and nitrobenzene.

Zhang *et. al.*[30] studied ionic conductivity of solutions of pyridinium based ionic liquids with different molecular solvents in different temperature range of 283.15 to 313.15 *K*. Buchner *et. al.* [31] compared the ionic association behaviour of [BMIM]Cl and [BMIM]BF_4 in methanol and dimethyl sulfoxide and used Low Concentration Chemical Model (LcCM) to analyse the conductivity data. The limiting molar conductivities of selected binary mixtures of the imidazolium ILs with molecular solvents show a correlation of solvent properties such as polarity, viscosity, relative permittivity, etc with the conductivity of ILs. The viscosity and ionic conductivity of binary mixtures of 1-alkyl-3-methylimidazolium tetrafluoroborate [RMIM]BF_4 with ethanol[32] have also been investigated and the relationship between viscosity and ionic conductivity is obtained from Walden plots.[33-35] As such the search of the literature shows that the data are available for aprotic ILs as refereed above. However no data exist regarding conductance of protic ionic liquids.

In this article, we report for first time the molar conductivity, Λ_m of three protic imidazolium-based ILs with different molecular solvents at 298.15 K. The molar conductivities were measured for binary mixtures of three PILs, 1-methylimidazolium formate [HmIm][HCOO], 1-methylimidazolium acetate [HmIm][CH_3COO], 1-methyl imidazolium propionate [HmIm][CH_3CH_2COO] in six molecular solvents, water, methanol, ethanol, dimethyl sulfoxide, nitrobenzene and acetonitrile at 298.15 K. The effect of molecular solvents on the molar conductivity of PILs was investigated. The experimental molar conductance data for these PILs in different solvents collected at 298.15 K are given in Electronic Supporting Information. The limiting molar conductivities (Λ°_m) are determined for all these systems. These data of Λ°_m are correlated with the properties of ILs and solvents. Further, the transport behaviour of cation and anion is investigated from transport number and diffusion coefficient. Walden plots are presented for three PILs in water as a function of temperature to explain the ionicity of PILs.

Table 1: Tabulated data of Λ_m^0 for PILs obtained from eq. 1 in different molecular solvents at 298.15 K

S N	Solvents	Relative permittivity (ε)	$\Lambda_m^0/(Scm^2mol^{-1})$		
			[HmIm][HCOO]	[HmIm][CH_3COO]	[HmIm][CH_3CH_2COO]
1	Water	78.00	115.06	91.12	83.24
2	Methanol	32.70	64.71	47.55	19.66
3	Ethanol	24.50	10.93	10.53	9.08
4	Dimethyl sulfoxide	46.70	9.26	9.06	9.09
5	Acetonitrile	37.50	6.38	8.47	4.42
6	Nitrobenzene	34.82	1.40	2.20	3.07

2. Experimental Section

2.1 Chemicals and Materials

1-Methylimidazole (99%), acetic acid, formic acid and propanoic acid were purchased from sigma Aldrich and used as obtained. The solvents dimethyl sulfoxide, nitrobenzene, acetonitrile, ethanol and methanol of high purity grade were purchased from Merck India. Milli-Q water (with its specific conductance 5.5 x 10^{-6} Sm^{-1}) was used throughout the experiments.

2.2 Synthesis of protic ILs

The protic ionic liquids, [HmIm][HCOO], [HmIm][CH_3COO], [HmIm][CH_3CH_2COO] were synthesized and purified according to the reported procedure from our research group.[36-38] The PILs were synthesized by neutralization reaction of acid and base. Dropwise addition of base to acid was carried out in an ice bath to avoid the heat generation due to exothermic reaction. The reaction mixture of acid and base in the molar ratio of 1:1 was stirred for 6 *h* at room temperature. Water was removed by using rotavapour at 80 *°C* under reduced pressure. These PILs were further dried under a vacuum at 70 *°C* for 10 *h*. The water content of PILs is analyzed by Karl-Fisher titration and is observed to be 50 ppm. The characterization and their purities were determined by ^1H NMR spectroscopy in agreement with the reported values.[37]

2.3 Conductivity measurement

The specific conductivities were measured using a Synchrotron 306 conductometer at 1 *kHz*. The calibration of conductivity meter was done by using a 0.1 M potassium chloride (KCl) solution. The cell constant was determined with standard aqueous solutions of KCl. Initially, 100 ml of solvent was accurately weighed into the jacket and conductivity measurement was made. The known amount of solution of PILs was added stepwise to the jacket to obtain required concentration (10^{-5} to 10^{-4} mol dm^{-3}) and conductivity was measured after each addition. The molar conductivity was calculated using equation $\Lambda_m = (k/c)*1000$. The uncertainties were estimated within to be ±0.1% for concentration and 1 % for conductivity, respectively. The temperature of the jacket was maintained using JULABO thermostat.

3. Results and discussion

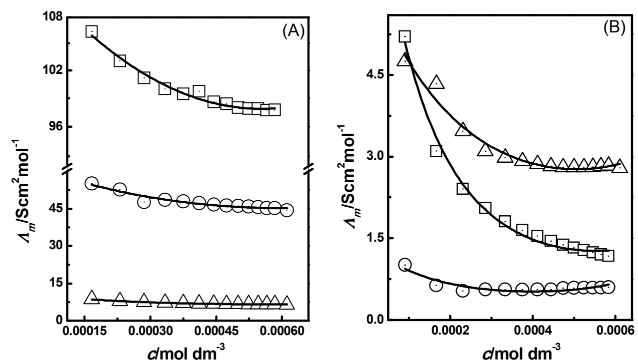

Fig. 1 The plots of Λ_m vs. Conc. (A) for [HmIm][HCOO] in water (□), methanol (○), ethanol (△), (B) for [HmIm][HCOO] in dimethyl sulfoxide (□), acetonitrile (○), nitrobenzene (△) at 298.15 K.

The Λ_m data for the PILs of the current interest are given in Table S1-S6 in Electronic Supporting Information. Fig. 1, shows comparative plots of the Λ_m of the imidazolium-based PILs [HmIm][HCOO] with different molecular solvents such as water, methanol, ethanol, dimethyl sulfoxide, acetonitrile and nitrobenzene. The behaviour of Λ_m of [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] with above molecular solvents shown in Fig. S1 and S2, respectively. The conductivity measurement was carried out for dilute concentrations of the PILs of the range 0.0001 to 0.0007 mol dm^{-3}. There are many reports available in the literature that interprets the molar conductivity data on the basis of low concentration chemical model (LcCM). Ismail and co-workers have proposed an equation 1 for analyzing conductivity data.[39]

$$\Lambda = A_\Lambda exp\,(B_\Lambda c + C_\Lambda c^2) \qquad (1)$$

where A_Λ, B_Λ, and C_Λ are the adjustable parameters and c is the molarity of solution expressed in mol dm^{-3}. The values of these parameters were obtained by a least-squares fitting method. In this case, the parameter A_Λ is considered as limiting molar conductivity denoted as Λ_m^0. We also applied this equation 1 for our binary systems of ILs with molecular solvents and compared with those fitted by LcCM equation. It was interesting to find that existence of greater close agreement between values of Λ_m^0 obtained from equation 1 and that from LcCM. For example, Buchner *et. al.*[31] reported Λ_m^0 for [BMIM][BF$_4$] is 121.84 Scm^{2}mol^{-1} at 298.15 K from LcCM, while using equation 1 for same data of [BMIM]BF$_4$] and Λ_m^0 is observed to be 117 Scm^{2}mol^{-1}. However, there is inconsistency in the Λ_m^0 of ILs due to either the use of different conductivity equations to describe the concentration dependence of the molar conductivities or the use of experimental data in a different concentration range to fit the conductivity equations. Our conductivity measurements were carried out in a low diluted concentration range.

3.1 Effect of relative permittivity (ε) on limiting molar conductivities

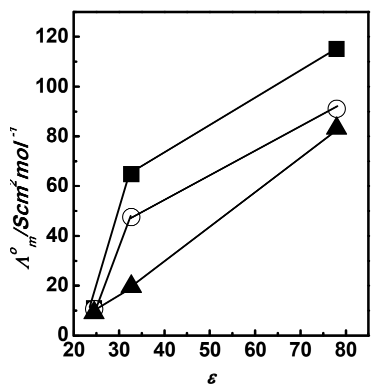

Fig. 2 Plots of Λ_m^0 with relative permittivity (ε) of water, methanol, ethanol for [HmIm][HCOO] (■), [HmIm][CH$_3$COO] (○), [HmIm][CH$_3$CH$_2$COO](▲) at 298.15 K.

Table 1 shows the Λ_m^0 for all three PILs in polar protic solvents (A) water, methanol, ethanol and polar aprotic solvents (B) dimethyl sulfoxide, acetonitrile, nitrobenzene molecular solvents. The Λ_m^0 values for PILs possesses higher in polar protic solvents compared to polar aprotic solvents. Fig. 2 shows the plots of Λ_m^0 of PILs [HmIm][HCOO], [HmIm][CH$_3$COO], [HmIm][CH$_3$CH$_2$COO] vs relative permittivity (ε) of polar protic solvents. In all above cases, the Λ_m^0 for PILs in molecular solvents increases with an increase ε of solvents. This suggests that cation and anion are less associated in the solvent possessing high dielectric constant due to independent solvation of ions. Thus, both cation and anion do not remain associated in water and hence higher values of Λ_m^0 are seen in water, while in ethanol the ion remain associated and hence showing lower Λ_m^0. A difference between Λ_m^0 of water and methanol is high as compared to that between methanol and ethanol. It suggests relative permittivity plays a significant role in dissociation of PILs in polar protic solvents. Further, we have also observed a trend in Λ_m^0 of PILs with dielectric medium in polar aprotic solvents; dimethyl sulfoxide, acetonitrile, and nitrobenzene are shown in Fig. 3. The Λ_m^0 values for [HmIm][HCOO] in dimethyl sulfoxide, acetonitrile and nitrobenzene are 9.26 Scm^2 mol^{-1}, 6.38 Scm^2 mol^{-1}and 1.40 S cm^2 mol^{-1}, respectively. These values of Λ_m^0 of PILs in polar aprotic solvents are very small compared to protic solvents even though the relative permittivities are in the comparable range. It may be due to the Grotthuss type mechanism in polar protic solvents.[40] Similarly, we have also observed that in other PILs system, the Λ_m^0 for [HmIm][CH$_3$COO] are 9.06 Scm^{2}mol^{-1}, 8.47 Scm^{2}mol^{-1} and 2.20 Scm^{2}mol^{-1}, while [HmIm][CH$_3$CH$_2$COO] and 9.09 Scm^{2}mol^{-1}, 4.42 Scm^{2}mol^{-1} and 3.07 Scm^{2}mol^{-1} in dimethyl sulfoxide, acetonitrile and nitrobenzene, respectively. In this case also we have observed that the Λ_m^0 increases with increase in dielectric constant of the solvents but to small extent.

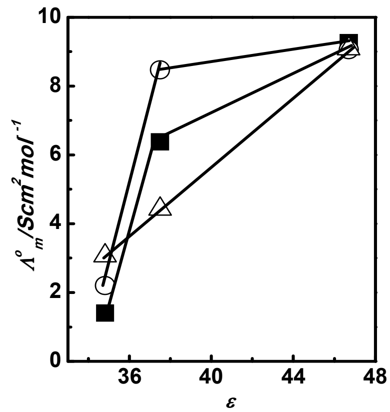

Fig. 3 Plots of Λ_m^0 vs relative permittivity (ε) of dimethyl sulfoxide, acetonitrile, nitrobenzene for [HmIm][HCOO] (■), HmIm][CH$_3$COO](○), [HmIm][CH$_3$CH$_2$COO] (△) at 298.15K.

However, in the case of polar protic solvent not only dielectric constant does play a significant role in the solvating the cation and anion independently compared to the polar aprotic solvents. This signifies that strong association of cation and anions of PILs is present in the polar aprotic solvents.

The viscosities of water, methanol, ethanol, dimethyl sulfoxide, acetonitrile and nitrobenzene are 0.89, 0.54, 1.10, 2.22, 0.38 and 1.8 mPa.s, respectively at 298.15K. An examination of the Λ^o_m values of PILs given in Table 1 did not offer any correlation with viscosities of these solvents.

3.2 Effect of anions on limiting molar conductivity

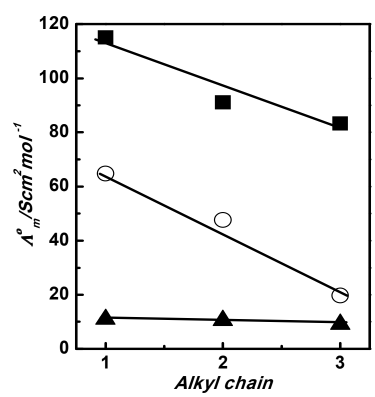

Fig. 4 Plots of Λ_m^0 vs alkyl chain length of the anions for [HmIm][HCOO],[HmIm][CH$_3$COO] and [HmIm][CH$_3$CH$_2$COO] in water (■), in methanol(○), and in ethanol (▲) at 298.15 K.

Comparing the values of Λ_m^0 for [HmIm][HCOO],

[HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] in polar protic solvents water, methanol and ethanol reveal a inverse linear relationship between the Λ_m^0 with increase in carbon atoms in the alkyl chain of anion of PILs. However, we did not observe any correlation of Λ_m^0 for [HmIm][HCOO], [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] in polar aprotic solvents dimethyl sulfoxide, acetonitrile, nitrobenzene.

Table 2: Limiting molar conductivities Λ_m^0 and transport numbers t^+ and t^- of cations and anions of PILs in water at 298.15 *K*.

S N	Protic Ionic Liquids	λ_m^{0+} Scm^2mol^{-1}	λ_m^{0-} Scm^2mol^{-1}	t^+	t^-
1	[HmIm][HCOO]	60.46	54.60	0.53	0.47
2	[HmIm] [CH_3COO]	50.12	40.20	0.55	0.45
3	[HmIm] [CH_3CH_2COO]	47.44	35.80	0.57	0.43

The representative results for PILs in polar protic solvents are shown in Fig. 4. It is observed that the ionic association of cation and anion for [HmIm][CH_3CH_2COO] in water and methanol is higher as compared to that in [HmIm][HCOO] and [HmIm][CH_3COO]. In ethanol, all three PILs show comparable association of cation and anion. The decrease in Λ_m^0 for PILs with each methyl group shows association of cation and anion in water. Further, we have determined Λ_m^0 of cation and anion to study the behaviour and contribution of individual ions in association process. The individual limiting molar conductivity of ions can be calculated from the total Λ_m^0. The total Λ_m^0 of PILs is a contribution of individual cation and anion each ions as

$$\Lambda_m^0 = \lambda_m^{0+} + \lambda_m^{0-} \quad (2)$$

where, λ_m^{0+} and λ_m^{0-} are the limiting molar conductivities of cation and anion, respectively. The λ_m^{0-} of $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ anions in water are 54.6, 40.2 and 35.8 $Scm^2\ mol^{-1}$, respectively at 298.15 K, which are reported in the literature.[41] The calculated λ_m^{0+} for the $[HmIm]^+$ cation for each PIL decrease from $[HCOO]^-$ to $[CH_3CH_2COO]^-$ (Table 2). This is due to an increase in ionic association of cations with anions of PILs. The ionic association is the highest for [HmIm][CH_3CH_2COO] in solvents. It is due to the fact that $[CH_3CH_2COO]^-$ is less stabilised as compared to $[HCOO]^-$ and $[CH_3COO]^-$ anions, as high inductive effect is observed in $[CH_3CH_2COO]^-$ anion leading to higher interactions between cations and anions and thus less dissociation.

The transport numbers for cation (t^+) and anion (t^-) of PILs were calculated by equation 3 and tabulated in Table 2.

$$t^+ = \lambda_m^{0+}/\lambda_m^0 \text{ and } t^- = \lambda_m^{0-}/\lambda_m^{0-} \quad (3)$$

where, t^+ and t^- are cationic and anionic transport numbers, respectively. From Table 2, it is observed that the t^+ values for all PILs are higher than that t^- in water. The cationic transport number t^+ for $[HmIm]^+$ is higher than 0.5, while the anionic transport number is less than 0.5. This indicate that $[HmIm]^+$ carries more than half of the current and less than half is carried by the anions, as $[HmIm]^+$ is able to move or diffuse faster than other anions.

Since the Λ_m^{0-} values decrease from $[HCOO]^-$ to $[CH_3CH_2COO]^-$ in polar protic solvents. This may be due to the diffusivity of ions of PILs being a function of the ion size and the interactions of ion with the solvents. Thus, $[HCOO]^-$ migrates faster as compared to $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ and hence shows larger Λ_m^{0-} values. This is also reflected to transport number t^- which is noted to be the highest for $[HCOO]^-$ while lowest for $[CH_3CH_2COO]^-$. This is due to the increase in van der Waal radii of anion from $[HCOO]^-$ to $[CH_3CH_2COO]^-$.

3.3 Effect of hydrogen bonding on solvation of anions

In section 3.1, we have discussed the effect of polarity through relative permittivity of medium on the Λ_m^0. Polarity is a general term that refers to all the interaction forces between molecules, both specific and nonspecific interaction and it is composed of several interacting components, including columbic interactions, the various dipole interactions, hydrogen-bonding and electron pair donor–acceptor interactions.[42, 43]

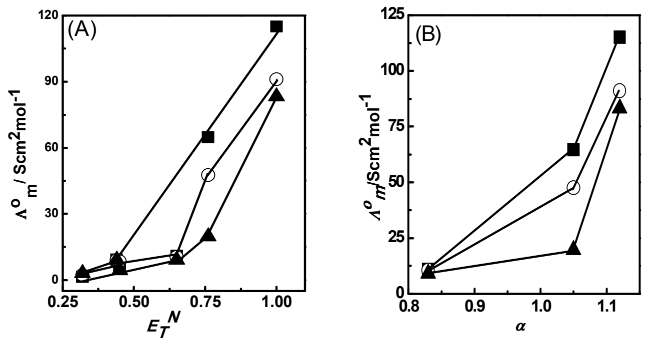

Fig. 5: Plots (A) Λ_m^0 *vs* E_T^N (B) Λ_m^0 *vs* α of solvents for [HmIm][HCOO](■), [HmIm][CH_3COO](○), [HmIm][CH_3CH_2COO](▲).

Table 3: The E_T^N, α, β values of the PILs and molecular solvents at 298.15 K[37, 42, 44]

S. No.	Protic Ionic Liquids / Solvents	E_T^N	α	β
1	[HmIm][HCOO]	0.78	0.81	0.81
2	[HmIm][CH_2COO]	0.61	0.50	0.85
3	[HmIm][CH_3CH_2COO]	0.50	-0.06	0.10
4	Water	1.0	1.12	0.50
5	Methanol	0.76	1.05	0.63
6	Ethanol	0.65	0.83	0.75
7	Dimethyl sulfoxide	0.44	0.00	0.76
8	Acetonitrile	0.45	0.19	0.40
9	Nitrobenzene	0.32	0.00	0.39

The solvatochromic parameter $E_T(30)$ or E_T^N, electronic transition energy, α hydrogen bond donor ability (HBD) and β hydrogen bond acceptor (HBA) parameter, which explains the solvent dependent phenomenon at molecular level and gives information about solvation ability of the medium. There are many reports available on the polarity of ILs and molecular solvents and explained the presence of different site of interactions at molecular level.[44-46] The values of E_T^N, α and β parameters for PILs and molecular solvents are shown in Table 3. Figure 5 (a) displays the effect of E_T^N values of molecular solvents on Λ^o_m of PILs, which shows that the Λ^o_m of PILs increases with increasing E_T^N value of molecular solvents. The effect is more pronounced in polar protic solvent compared to polar aprotic solvents. The E_T^N values for polar protic solvents decreases from water to methanol to ethanol as 1 to 0.652 which decreases Λ^o_m from 115.06 to 10.93 for [HmIm][HCOO], 91.12 to 10.53 for [HmIm][CH_3COO] and 83.24 to 9.09 for [HmIm][CH_3CH_2COO]. However, the smaller effect is observed in polar aprotic solvents. This is because of the E_T^N of PILs is lies between the E_T^N values of polar protic solvent and polar aprotic solvents. Thus polar protic solvent could strongly solvating the cation and anions of PILs through hydrogen bond donor (HBD)/acceptor (HBA) ability of solvents. To explain this we have also considered the role of hydrogen bond donor ability HBD (α) of molecular solvents and PILs. The HBD (α) values for [HmIm][HCOO], [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] are observed to be 0.81, 0.51 and -0.06, respectively,[37] which are smaller than the α values for water, methanol and ethanol 1.12, 1.05 and 0.83, respectively. The α values of aprotic solvents such as dimethyl sulfoxide, acetonitrile and nitrobenzene are 0, 0.19 and 0, respectively, which are very small than polar protic solvents.[43, 47] All three PILs shows higher values of Λ^o_m in water. This is because of highest α of water, which increases the interaction of anions with water through hydrogen bonding and hence more dissociation of PILs. Methanol and ethanol possesses α values smaller than water. The fact that methanol and ethanol differs from water by the presence of only a methyl and a ethyl group, respectively makes such a difference more relevant. A rational explanation is that the anion is strongly solvated by the hydrogen bonding interactions between the anion and water, methanol, ethanol. Therefore anion of PILs has more affinity towards polar protic solvents as compare to cations in solutions. Thus, PILs shows higher Λ^o_m in water than of methanol and ethanol. The effect of α of each polar protic solvents on Λ^o_m PILs shows as [HmIm][HCOO] > [HmIm][CH_3COO] > [HmIm][CH_3CH_2COO] (Fig. 5B). In the case of polar aprotic solvents, dimethyl sulfoxide, acetonitrile and nitrobenzene possesses very small α values compared to polar protic solvents leading to lower in Λ^o_m. However, we did not observed any correlation of Λ^o_m on the basis of basicity β of molecular solvents. The correlation of α values with Λ^o_m of PILs in all solvents is similar to E_T^N which indicate α is dominant factor contributing to solvation dynamic of ions of PILs compared to β. Thus for given PILs, the ionic association was affected significantly by ionic solvation through polarity parameters E_T^N and α of the molecular solvents. Thus strong solvation of the cation and/or anion weakens the ionic association which is observed in polar protic solvent, whereas weak ionic solvation enhances the ionic association of the PILs in molecular solvents, which is observed in polar aprotic solvents.

3.4 Diffusion coefficient and hydrodynamic radius

The diffusion of PIL in water a combination of diffusion of individual cation and anion can be determined by applying the Nernst-Haskell[48] equation 4.

$$D^{\circ}_{PIL} = \frac{RT}{F^2}\,\frac{|z_+|\,|z_-|}{|z_+ z_-|}\,\frac{\Lambda^{\circ}_+\Lambda^{\circ}_-}{\Lambda^{\circ}_+ + \Lambda^{\circ}_-} \tag{4}$$

where D°_{PIL} is the diffusion coefficient of PILs in water at infinite dilution, R the gas constant, T the absolute temperature, F Faradays constant and z_+ and z_- are the charge numbers on cation and anion, respectively. $\Lambda^{\circ+}$ and $\Lambda^{\circ-}$ are the infinite dilution conductivities of the cation and anion, respectively.

Table 4: Diffusion coefficient of ILs D°_{IL} and cation $D^{\circ+}$ and anion $D^{\circ-}$ of ILs in aqueous solution and hydrodynamic radius of anion R_H at 298.15K.

SN	Protic Ionic Liquids	D°_{IL} (10^{-5}) cm^2s^{-1}	$D^{\circ+}$ (10^{-5}) cm^2s^{-1}	$D^{\circ-}$ (10^{-5}) cm^2s^{-1}	R_H pm
1	[HmIm][HCOO]	1.527	1.609	1.453	168
2	[HmIm][CH_3COO]	1.187	1.334	1.070	229
3	[HmIm][CH_3CH_2COO]	1.086	1.263	0.953	257

The diffusion coefficients for PILs were obtained at infinite dilution in the case of aqueous solutions (Table 4). These values are comparable with the reported values of diffusion coefficient of PILs [Pyrr][HSO_4] and [Pyrr][CF_3COO] which were determined from conductivity and NMR studies.[49] It is also possible to determine the diffusion coefficient of cation and anion from the equation 5a and 5b as

$$D^{0+} = \frac{RT}{F^2}\,\frac{\lambda_m^{0+}}{|z|} \tag{5a}$$

$$D^{0-} = \frac{RT}{F^2}\,\frac{\lambda_m^{0-}}{|z|} \tag{5b}$$

The diffusion of PILs in water decreases from $[HCOO]^-$ to $[CH_3CH_2COO]^-$. These results are consistent with Λ^o_m of PILs of same system. From the Table 4, it is observed that the diffusion coefficient for cation is higher than the anion shows cation diffuse faster compared to anion. These results are consistent with transport number. Further we have determined hydrodynamic radii from Stoke-Einstein equation 6.

$$D = \frac{kT}{6\pi\eta R_H} \tag{6}$$

where, D diffusion coefficient, k Boltzmann constant, T temperature in K and η the viscosity of solvents.

The hydrodynamic radius of anion varies as [HmIm][HCOO] <[HmIm][CH_3COO] < [HmIm][CH_3CH_2COO]. This result is also consistent with molar conductivity of aqueous solution of PIL and diffusion coefficient of anion for each system. Thus lower mobility and diffusion of $[CH_3CH_2COO]^-$ ion is due to larger hydrodynamic radius of 257 pm than $[HCOO]^-$ of 168 pm and $[CH_3COO]^-$ of 229 pm.

3.5 Ionicity in protic ionic liquids

Ionicity in an electrolytic solution represents free ions present in a system. Walden plot of log Λ_m *vs* log η^{-1} is a suitable method for measuring the ionicity of electrolytic solutions. Walden rule of relation between conductivity and viscosity is given by equation 7

$$\lambda\eta = k \text{ (constant)} \qquad (7)$$

where, λ, η and k denote the conductivity, viscosity and a temperature dependent constant, respectively. From this, we obtain the formation of free ions, ion pairs and non charged aggregates in solution. Angell *et. al.*[34, 35] have described a qualitative approach about the Walden rule for different neat ILs. The plot of log Λ_m vs log η^{-1} predicts a straight line that passes through the origin for ideal solution. The solution of 0.01M KCl gives a helpful reference line on the Walden plot as shown in Fig. 6.[34] Interestingly, a linear relationship exists between the molar conductivities for each of the PILs and the reciprocal of the viscosity ($1/\eta$) of water as a function of temperature. This suggests that the fluidity of the medium played a predominant role in the ionic association of the PILs.

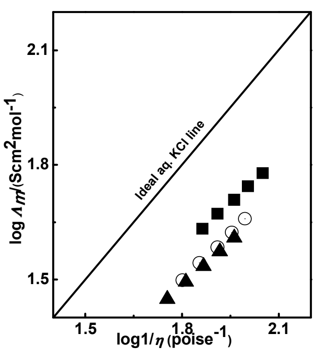

Figure 6: Walden plot of 1M aqueous solution of [HmIm][HCOO] (■), [HmIm][CH_3COO] (○) and [HmIm][CH_3CH_2COO] (▲) from 293.15 to 313.15 K

The deviation from the ideal line of KCl suggests the extent of ionicity in electrolyte solution. The Walden plot for [HmIm][HCOO], [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] in water are shown Fig. 6. These binary mixtures of PILs with water show a deviation from the aqueous solution of 0.01 M KCl in which KCl in water is fully dissociated. Angell have explained such deviations by measuring the vertical distance between the KCl line and PILs and is denoted by ΔW. Thus the % ionicity can be calculated from ΔW as,

$$\%\ \text{Ionicity} = 10^{(-\Delta W)}\ \text{X}100 \qquad (8)$$

For example, the value of $\Delta W = 1$ express 10% of ionicity of electrolytic solution with respect to the line for 0.01M KCl. In our system, the ΔW values and % ionicities for three PILs are tabulated in Table 5. The ΔW values for all PILs are less than 1, which significantly indicates that ionicity is very high and large ΔW indicate incomplete ionic dissociation. The distinction between three PILs assists in understanding the various effects that can be observed from the examination of the Walden plot. [HmIm][HCOO] with an ΔW of 0.23 represents an example of a close-to-ideal KCl. Remaining two [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] PILs are located by the distance of ΔW of 0.31 and 0.33, respectively. The calculated ionicity for PILs are 58%, 49% and 46% and follows order as [HmIm][HCOO] > [HmIm][CH_3COO] > [HmIm][CH_3CH_2COO]. A similar trend is observed in the case of molar conductivities and diffusion coefficient of same PILs. Thus from the data of ionicity, molar conductivity, viscosity, anion size and diffusion coefficient, it observed that the [HmIm][HCOO] is more dissociated as compared to [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO]. The dissociation of PILs is consistent with hydrogen bonding model described as earlier section 3.3. Thus from the ΔW, the PILs in water are not fully dissociated like ideal aqueous 0.01 M KCl solution. It may be due to strong ion association in cation and anions in PILs. This study may find applications in the modulation of the conductance performance of the ILs in molecular solvents.

Table 5: Data obtained from Walden plot of 1M aqueous solution of PILs at 298.15 K

S N	Protic Ionic Liquids	Λ_m *(Scm^2mol^{-1})*	η *(cP)*	$\triangle w$	Ionicity *(%)*
1	[HmIm][HCOO]	47.92	1.23	0.23	58 %
2	[HmIm][CH_3COO]	34.93	1.40	0.31	49 %
3	[HmIm][CH_3CH_2COO]	31.14	1.54	0.33	46 %

Many pure PILs lies below the reference line indicate that incomplete ionization in PILs compared to APILs on the basis of Walden plot.[34] This order of Λ^o_m for PILs of magnitude lower than APILs as a result of more ionic association in PILs.[31]The conductivity or ionicity in PILs depends to transfer of proton from Bronsted acid to HA to a Bronsted base B as

$$\text{HA} + \text{B} \rightarrow \text{BH}^+ + \text{A}^- \qquad (9)$$

The ionicity is adjustable in PILs by the virtue of different driving forces for the proton-transfers. However, the extent of proton transfer in PILs is not yet explained in details. There are reports available to explain the degree of proton transfer in PILs. First, it is estimated after considering the difference of ΔpK_a^{aq} values of the acid and the base. If the ΔpK_a^{aq} values are more than 2, it is sufficient to transfer the proton frequently from acid to base.[50, 51] In our systems, the ΔpK_a^{aq} values are 3.34, 2.34 and 2.22 for [HmIm][HCOO], [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO], respectively. These values indicate that proton transfer is effective in the environment of PILs. Also from our conductivity data of PILs, we observed that the cation and anion of PILs exhibit the conductivity, which is higher than the neutral species of the acid and the base. Conductivity values also represent the availability of cations and anions in binary system of water with PILs. From all above observations and spectral data of ^{1}H-NMR it is clear that the proton is predominately displaced from acid to base. Secondly, PILs form extensive hydrogen bonding, which stabilizes both cation and anion, resulting into the probability of reverse proton transfer becoming low. Due to these opposing phenomena, a very small proportion of neutral moiety exists along with the PILs [HmIm][HCOO]> [HmIm][CH_3COO]>[HmIm][CH_3CH_2COO] leading to the lower α values, which are far beyond the α values for pure HCOOH, CH_3COOH and CH_3CH_2COOH i.e. 1.23, 1.12 and 1.12, respectively. Thus due to the strong columbic interactions between ions, and the long range of the interaction, the vapor pressure over the PILs is very low than individual vapor pressure of pure acid and base indicating the free energy change in the proton transfer process is large. It is important to note that a possibility of formation of super anions in pure ionic liquids has been reported.[51] The PILs used herein were synthesized with 1:1 of acid and base. Further, our experiments were concerned in very dilute ionic liquid solutions. It is, however, not clear to state whether the formation of super anions is possible in our system unlike those prepared considering the composition of acid in excess compared to base.[51]

4. Conclusions

In this work, we have investigated the ionic association of PILs in different molecular solvents through conductivity measurement. The existence ion pairing in PILs is observed and depends on the presence of type cation and anion and solvent medium. In short, we learn: 1) that the limiting molar conductivity Λ^o_m of PILs is mostly directed by the dielectric properties of the solvents, 2) the solvatochromic parameters E_T^N and hydrogen bond donor ability, α of solvents dominantly affect the ionic association in PILs as compared to hydrogen bond acceptor ability, β of the solvents, 3) the diffusion coefficients and transport numbers of the individual cation and anion of PILs in aqueous systems can be correlated with solvent properties and structure of PILs and 4) the ionicity order in PILs were observed to be [HmIm][HCOO]> [HmIm][CH_3COO] > [HmIm][CH_3CH_2COO].

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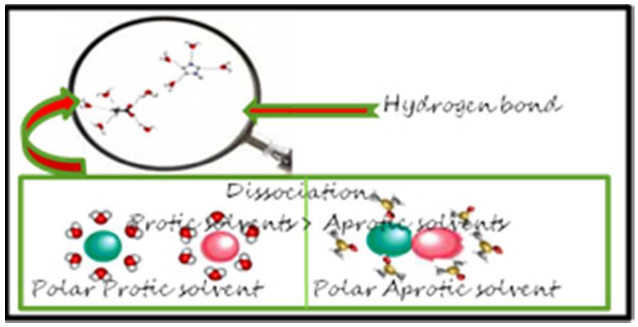

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