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Solvent-Mediated Molar Conductivity of Protic Ionic Liquids

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Abstract

The molar conductivity, A_m of protic ionic liquids (PILs) in molecular solvents is measured at 298.15 K. The decrease in the A_m values of PILs is observed with an increase in concentration of PILs. The limiting molar conductivities, A_m were obtained for each PIL in different molecular solvents using a least squares method. The A_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_ and transport number, t were determined, which were consistent with the A_m values of PILs in water. The A_m and D_ 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 A_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 properties1, 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 techniques13-18 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

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][C1] 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 ethanol32 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, A_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 (A_m) are determined for all these systems. These data of A_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.

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† Electronic supplementary information (ESI) available: Plots of A_m vs. concentration for [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] in water, methanol, ethanol, dimethyl sulfoxide, acetonitrile and nitrobenzene.
Table 1: Tabulated data of $A_m^0$ for PILs obtained from eq. 1 in different molecular solvents at 298.15 K

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Relative permittivity</th>
<th>$A_m^0/(Scm^2mol^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[HmIm][HCOO]</td>
</tr>
<tr>
<td>1 Water</td>
<td>78.00</td>
<td>115.06</td>
</tr>
<tr>
<td>2 Methanol</td>
<td>32.70</td>
<td>64.71</td>
</tr>
<tr>
<td>3 Ethanol</td>
<td>24.50</td>
<td>10.93</td>
</tr>
<tr>
<td>4 Dimethyl sulfoxide</td>
<td>46.70</td>
<td>9.26</td>
</tr>
<tr>
<td>5 Acetonitrile</td>
<td>37.50</td>
<td>6.38</td>
</tr>
<tr>
<td>6 Nitrobenzene</td>
<td>34.82</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The jacket was maintained using JULABO thermostat.

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 $5.5 \times 10^{-6}$ Sm$^{-1}$) was used throughout the experiments.

2.2 Synthesis of protic ILs

The protic ionic liquids, [HmIm][HCOO], [HmIm][CH$_3$COO], [HmIm][CH$_3$CH$_2$COO] were synthesized and purified according to the reported procedure from our research group. 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 $^3$H NMR spectroscopy in agreement with the reported values.

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 $A_m = (k/c)^*1000$. The uncertainties were estimated within to be ±0.1% for concentration and 1 % for conductivity, respectively. The temperature of the

3. Results and discussion

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

The $A_m$ 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 $A_m$ of the imidazolium-based PILs [HmIm][HCOO] with different molecular solvents such as water, methanol, ethanol, dimethyl sulfoxide, acetonitrile and nitrobenzene. The behaviour of $A_m$ of [HmIm][CH$_3$COO] and [HmIm][CH$_3$CH$_2$COO] 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 (LeCM). Ismail and co-workers have proposed an equation 1 for analyzing conductivity data.

$$A = A_0 exp (B_1 c + C_1 c^2)$$

where $A_0$, $B_1$, and $C_1$ 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 $A_0$ is considered as limiting molar
conductivity denoted as $A_m^0$. 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 $A_m^0$ obtained from equation 1 and that from LcCM. For example, Buchner et al.\textsuperscript{31} reported $A_m^0$ for [BMM][BF$_4$] is 121.84 Scm$^2$mol$^{-1}$ at 298.15 K from LcCM, while using equation 1 for same data of [BMM][BF$_4$] and $A_m^0$ is observed to be 117 Scm$^2$mol$^{-1}$. However, there is inconsistency in the $A_m^0$ 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 ($\varepsilon$) on limiting molar conductivities

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

Table 1 shows the $A_m^0$ for all three PILs in polar protic solvents (A) water, methanol, ethanol and polar aprotic solvents (B) dimethyl sulfoxide, acetonitrile, nitrobenzene molecular solvents. The $A_m^0$ values for PILs possesses higher in polar protic solvents compared to polar aprotic solvents. Fig. 2 shows the plots of $A_m^0$ of PILs [HmIm][HCOO], [HmIm][CH$_3$COO], [HmIm][CH$_3$CH$_2$COO] vs relative permittivity ($\varepsilon$) of polar protic solvents. In all above cases, the $A_m^0$ for PILs in molecular solvents increases with an increase $\varepsilon$ 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 $A_m^0$ are seen in water, while in ethanol the ion remain associated and hence showing lower $A_m^0$. A difference between $A_m^0$ 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 $A_m^0$ of PILs with dielectric medium in polar aprotic solvents; dimethyl sulfoxide, acetonitrile, and nitrobenzene are shown in Fig. 3. The $A_m^0$ 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 $A_m^0$ 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 Grothuss type mechanism in polar protic solvents.\textsuperscript{60} Similarly, we have also observed that in other PILs system, the $A_m^0$ 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 $A_m^0$ increases with increase in dielectric constant of the solvents but to small extent.

![Fig. 3 Plots of $A_m^0$ vs relative permittivity ($\varepsilon$) of dimethyl sulfoxide, acetonitrile, nitrobenzene for [HmIm][HCOO] (■), [HmIm][CH$_3$COO] (○), [HmIm][CH$_3$CH$_2$COO] (▲) at 298.15K.](image)

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 $A_m^0$ 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 $A_m^0$ 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.](image)

Comparing the values of $A_m^0$ for [HmIm][HCOO],
[HmIm][CH₃COO] and [HmIm][CH₂CH₂COO] in polar protic solvents water, methanol and ethanol reveal an inverse linear relationship between the $A_{m0}^a$ with increase in carbon atoms in the alkyl chain of anion of PILs. However, we did not observe any correlation of $A_{m0}^a$ for [HmIm][HCOO], [HmIm][CH₂COO] and [HmIm][CH₂CH₂COO] in polar aprotic solvents dimethyl sulfoxide, acetonitrile, nitrobenzene.

Table 2: Limiting molar conductivities $A_{m0}^a$ and transport numbers $t'$ and $t$ of cations and anions of PILs in water at 298.15 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$A_{m0}^c$ (Scm$^{-1}$mol$^{-1}$)</th>
<th>$A_{m0}^a$ (Scm$^{-1}$mol$^{-1}$)</th>
<th>$t'$</th>
<th>$t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HmIm][HCOO]</td>
<td>60.46</td>
<td>54.60</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>[HmIm][CH₂COO]</td>
<td>50.12</td>
<td>40.20</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>[HmIm][CH₂CH₂COO]</td>
<td>47.44</td>
<td>35.80</td>
<td>0.57</td>
<td>0.43</td>
</tr>
</tbody>
</table>

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][CH₂CH₂COO] in water and methanol is higher as compared to that in [HmIm][HCOO] and [HmIm][CH₂COO]. In ethanol, all three PILs show comparable association of cation and anion. The decrease in $A_{m0}^a$ for PILs with each methyl group shows association of cation and anion in water. Further, we have determined $A_{m0}^a$ 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 $A_{m0}^a$. The total $A_{m0}^a$ of PILs is a contribution of individual cation and anion each ions as

$$A_{m0}^a = \lambda_{m0}^+ + \lambda_{m0}^-.$$  

where, $\lambda_{m0}^+$ and $\lambda_{m0}^-$ are the limiting molar conductivities of cation and anion, respectively. The $\lambda_{m0}^+$ of [HCOO$^-$], [CH₂COO$^-$] and [CH₂CH₂COO$^-$] anions in water are 54.6, 40.2 and 35.8 Scm$^{-1}$mol$^{-1}$, respectively at 298.15 K, which are reported in the literature. The calculated $\lambda_{m0}^+$ for the [HmIm]$^-$ cation for each PIL decrease from [HCOO$^-$] to [CH₂CH₂COO$^-$] (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][CH₂CH₂COO] in solvents. It is due to the fact that [CH₂CH₂COO$^-$] is less stabilised as compared to [HCOO$^-$] and [CH₂COO$^-$] anions, as high inductive effect is observed in [CH₂CH₂COO$^-$] 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.

$$t' = \lambda_{m0}^+ / \lambda_{m0}^- \quad \text{and} \quad t = \lambda_{m0}^- / \lambda_{m0}^+.$$  

Table 3: The $E_{\alpha}$, $\alpha$, $\beta$ values of the PILs and molecular solvents at 298.15 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_{\alpha}$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HmIm][HCOO]</td>
<td>0.78</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>[HmIm][CH₂COO]</td>
<td>0.61</td>
<td>0.50</td>
<td>0.85</td>
</tr>
<tr>
<td>[HmIm][CH₂CH₂COO]</td>
<td>0.50</td>
<td>-0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>Water</td>
<td>1.0</td>
<td>1.12</td>
<td>0.50</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.76</td>
<td>1.05</td>
<td>0.63</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.65</td>
<td>0.83</td>
<td>0.75</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>0.44</td>
<td>0.00</td>
<td>0.76</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.45</td>
<td>0.19</td>
<td>0.40</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.32</td>
<td>0.00</td>
<td>0.39</td>
</tr>
</tbody>
</table>

The solvatochromic parameter $E_{\alpha}$, $E_{\beta}$, electronic transition energy, $\alpha$ hydrogen bond donor ability (HBD) and $\beta$ 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 interations at molecular level. The values of \( E_a \) and parameters for PILs and molecular solvents are shown in Table 3. Figure 5 (a) displays the effect of \( E_a \) values of molecular solvents on \( A_{\infty} \) of PILs, which shows that the \( A_{\infty} \) of PILs increases with increasing \( E_a \) value of molecular solvents. The effect is more pronounced in polar protic solvent compared to polar aprotic solvents. The \( E_a \) values for polar protic solvent decreases from water to methanol to ethanol as 1 to 0.652 which decreases \( A_{\infty} \) from 115.06 to 10.93 for [HmIm][HCOO], 91.12 to 10.53 for [HmIm][CH2COO] and 83.24 to 9.09 for [HmIm][CH3CH2COO]. However, the smaller effect is observed in polar aprotic solvents. This is because of the \( E_a \) of PILs is lies between the \( E_a \) 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 (\( \alpha \)) of molecular solvents and PILs. The HBD (\( \alpha \)) values for [HmIm][HCOO], [HmIm][CH2COO] and [HmIm][CH3CH2COO] are observed to be 0.81, 0.51 and -0.06, respectively, which are smaller than the \( \alpha \) values for water, methanol and ethanol 1.12, 1.05 and 0.83, respectively. The \( \alpha \) 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. All three PILs shows higher values of \( A_{\infty} \) in water. This is because of higher \( \alpha \) of water, which increases the interaction of anions with water through hydrogen bonding and hence more dissociation of PILs. Methanol and ethanol possesses \( \alpha \) values smaller than water. The fact that methanol and ethanol differs from water by the presence of only a methyl and an 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 \( A_{\infty} \) in water than of methanol and ethanol. The effect of \( \alpha \) of each polar protic solvent on \( A_{\infty} \) PILs shows as [HmIm][HCOO] > [HmIm][CH2COO] > [HmIm][CH3CH2COO] (Fig. 5B). In the case of polar aprotic solvents, dimethyl sulfoxide, acetonitrile and nitrobenzene possesses very small \( \alpha \) values compared to polar protic solvents leading to lower in \( A_{\infty} \). However, we did not observed any correlation of \( A_{\infty} \) on the basis of \( \beta \) of basicity of molecular solvents. The correlation of \( \alpha \) values with \( A_{\infty} \) of PILs in all solvents is similar to \( E_a \) which indicate \( \alpha \) is dominant factor contributing to solvation dynamic of ions of PILs compared to \( \beta \). Thus for given PILs, the ionic association was affected significantly by ionic solvation through polarity parameters \( E_a \) and \( \alpha \) 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 equation 4.

\[
D_{\text{PIL}} = \frac{RT}{6 \pi \eta R_H} \frac{\Lambda_+ \Lambda_-}{\Lambda_+ + \Lambda_-} \tag{4}
\]

where \( D_{\text{PIL}} \) 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. \( \Lambda^+ \) and \( \Lambda^- \) are the infinite dilution conductivities of the cation and anion, respectively.

#### Table 4: Diffusion coefficient of ILs \( D^\alpha \) and cation \( D^\alpha \) and anion \( D^\alpha \) of ILs in aqueous solution and hydrodynamic radius of anion \( R_H \) at 298.15K.

<table>
<thead>
<tr>
<th>S</th>
<th>N</th>
<th>Protonated Ions Liquids</th>
<th>( D^\alpha , (10^{-5}) ) cm²/s</th>
<th>( D^\alpha , (10^{-5}) ) cm²/s</th>
<th>( D^\alpha , (10^{-5}) ) cm²/s</th>
<th>( R_H ) pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[HmIm][HCOO]</td>
<td></td>
<td>1.527</td>
<td>1.609</td>
<td>1.453</td>
<td>168</td>
</tr>
<tr>
<td>2</td>
<td>[HmIm][CH2COO]</td>
<td></td>
<td>1.187</td>
<td>1.334</td>
<td>1.070</td>
<td>229</td>
</tr>
<tr>
<td>3</td>
<td>[HmIm][CH3CH2COO]</td>
<td></td>
<td>1.086</td>
<td>1.263</td>
<td>0.953</td>
<td>257</td>
</tr>
</tbody>
</table>

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 [Pyr][HSO4] and [Pyr][CF2COO] which were determined from conductivity and NMR studies. It is also possible to determine the diffusion coefficient of cation and anion from the equation 5a and 5b as

\[
D^\alpha_+ = \frac{RT}{6 \pi \eta R_H} \frac{\Lambda_+}{z_+} \tag{5a}
\]

\[
D^\alpha_- = \frac{RT}{6 \pi \eta R_H} \frac{\Lambda_-}{z_-} \tag{5b}
\]

The diffusion of PILs in water decreases from [HCOO]⁻ to [CH3CH2COO]. These results are consistent with \( A_{\infty} \) 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 \( \eta \) the viscosity of solvents.

The hydrodynamic radius of anion varies as [HmIm][HCOO] < [HmIm][CH2COO] < [HmIm][CH3CH2COO]. 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 [CH3CH2COO]⁻ ion is due to larger hydrodynamic radius of 257 pm than [HCOO]⁻ of 168 pm and [CH2COO]⁻ 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 $\Lambda_a$ vs log $\eta^2$ is a suitable method for measuring the ionicity of electrolytic solutions. Walden rule of relation between conductivity and viscosity is given by equation

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

(7)

where, $\lambda$, $\eta$ 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.²⁴, ³⁵ have described a qualitative approach about the Walden rule for different neat ILs. The plot of log $\Lambda_a$ vs log $\eta^2$ predicts a straight line that passes through the origin for ideal solution. The solution of 0.01 M 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 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$_2$COO] and [HmIm][CH$_3$CH$_2$COO]. The dissociation of PILs is consistent with hydrogen bonding model described as earlier section 3.3. Thus from the $\Delta W$, 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

<table>
<thead>
<tr>
<th>S</th>
<th>Protic Ionic Liquids</th>
<th>$\Lambda_a$ (Scm$^2$mol$^{-1}$)</th>
<th>$\eta$ (cP)</th>
<th>$\Delta W$</th>
<th>Ionicity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[HmIm][HCOO]</td>
<td>47.92</td>
<td>1.23</td>
<td>0.23</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>[HmIm][CH$_2$COO]</td>
<td>34.93</td>
<td>1.40</td>
<td>0.31</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>[HmIm][CH$_3$CH$_2$COO]</td>
<td>31.14</td>
<td>1.54</td>
<td>0.33</td>
<td>46</td>
</tr>
</tbody>
</table>

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 $\Lambda_a$ 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

$$HA + B \rightarrow BH^+ + A^-$$

(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 $\Delta pK_a$ values of the acid and the base. If the $\Delta pK_a$ values are more than 2, it is sufficient to transfer the proton frequently from acid to base. In our systems, the $\Delta pK_a$ values are 3.34, 2.34 and 2.22 for [HmIm][HCOO], [HmIm][CH$_2$COO] and [HmIm][CH$_3$CH$_2$COO], 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 $[\text{HmIm}][\text{HCOO}] > [\text{HmIm}][\text{CH}_2\text{COO}] > [\text{HmIm}][\text{CH}_2\text{CH}_2\text{COO}]$ leading to the lower $\alpha$ values, which are far beyond the $\alpha$ values for pure HCOOH, CH$_2$COOH and CH$_2$CH$_2$COOH 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. The PILs used herein were synthesized with 1:1 ratio in PILs were observed to be $[\text{HmIm}][\text{HCOO}] > [\text{HmIm}][\text{CH}_2\text{COO}] > [\text{HmIm}][\text{CH}_2\text{CH}_2\text{COO}]$. 

Acknowledgements

Hydrogen bond

Dissociation:
Polar Protic solvent
Polar Aprotic solvent

83x42mm (96 x 96 DPI)