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Comparative Investigation of the Ionicity of Aprotic and Protic Ionic Liquids in Molecular Solvents by using Conductometry and NMR Spectroscopy

Sachin Thawarkar, Nageshwar D. Khupse, and Anil Kumar*[a]

Electrical conductivity (σ), viscosity (η), and self-diffusion coefficient (D) measurements of binary mixtures of aprotic and protic imidazolium-based ionic liquids with water, dimethyl sulfoxide, and ethylene glycol were measured from 293.15 to 323.15 K. The temperature dependence study reveals typical Arrhenius behavior. The ionicities of aprotic ionic liquids were observed to be higher than those of protic ionic liquids in these solvents. The aprotic ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, [bmIm][BF_4], displays 100% ionicity in both water and ethylene glycol. The protic ionic liquids in both water and ethylene glycol are classed as good ionic candidates, whereas in DMSO they are classed as having a poor ionic nature. The solvation dynamics of the ionic species of the ionic liquids are illustrated on the basis of the ^{1}H NMR chemical shifts of the ionic liquids. The self-diffusion coefficients D of the cation and anion of [HmIm][CH_3COO] in D_2O and in [D_6]DMSO are determined by using ^{1}H nuclei with pulsed field gradient spin-echo NMR spectroscopy.

1. Introduction

Ionic liquids are composed of organic cations as well as either inorganic or organic anions, and they possess interesting physical properties such as low vapor pressure, high thermal stability, wide electrochemical window, and large liquid range. These properties render ionic liquids useful to employ in many applications in several fields[1,2] such as a solvent in organic synthesis, catalysis, separation and extraction processes, electrochemical cells, and solar energy cells.[3,4] In view of great need to develop clean and renewable energy sources, ionic liquids have also been explored as electrolytes for energy conversion devices such as lithium-ion batteries and fuel cells.[5] However, the high viscosity of ionic liquids reduces the optimum performance in many electrochemical devices that employ such compounds as electrolytes. The effect is further complicated by the high sensitivity of viscosity not only to the choice of constituent ions but also to the presence of impurities and cosolvents.[6] In particular, the addition of co-solvents such as water or methanol can strongly affect the physical and chemical properties of ionic liquids such as viscosity, electrical conductivity (σ), and reactivity as well as solvation and solubility properties.[7] Water and ethylene glycol are protic solvents that are useful for enhancing electrical conductivity. Previous investigations by our group have revealed a drastic reduction in the viscosity of ionic liquids upon the addition of small amounts of co-solvent.[8] Recently, several binary ionic liquids/co-solvent systems have been shown to perform better than the pure ionic liquids, and such systems have been used in many applications.[9,10]

To use such binary mixtures in applications, it is essential to study fundamental properties such as the thermal behavior of the mixture, and the conductivity, viscosity, and self-diffusion coefficients, etc. of ionic liquid solutions. Knowledge of such fundamental properties and of ion–ion and ion–solvent systems in a solution will help to achieve the maximum efficiency of a system by tuning the nature and amount of cations, anions, and solvent. It is essential to elucidate the properties of mixtures that are very different from those of pure ionic liquids and molecular solvents. In binary mixtures, the structural organization of ions differs from those of pure ionic liquids. The effective use of binary mixtures in electrolytic systems remains limited because of the lack of experimental data on physical properties such as conductivity, viscosity, and diffusion, and because of a lack of understanding on the molecular level of interactions present in the system. Ionic liquids possess unique characteristics because of their ionic nature; however, obtaining an estimate of the ionicity of such liquids through conductivity measurements is very important for their use as an electrolyte. Previous reports have shown that many pure ionic liquids lie below the reference line indicating incomplete ionization of ionic liquids, which was explained on the basis of the Walden plot.[11–13] An adjusted Walden plot that allows for differences in ionic size was shown to offer an improvement to this approach for a series of ionic liquids. Some ionic liquids studied by the authors showed ionicity values that were close to ideal, which was described in terms of a model in which the ion correlations had similar influence on both the diffusive and conductive motions. It was established by the authors that the ionicity was not essentially a measure of ion availability in the chemical sense.[12] The group of MacFarlane has demonstrated

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[a] S. Thawarkar, N. D. Khupse, Dr. A. Kumar
Physical and Materials Chemistry Division,
CSIR-National Chemical Laboratory,
Pune 411 008 (India)
E-mail: a.kumar@ncl.res.in

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that there is a clear distinction between the behavior of simple primary versus tertiary amines. Proton transfer is more complete in primary amines than in tertiary amines. This effect was attributed to the hydrogen-bonding ability of the ammonium ions to provide a good solvating environment for the ions produced by the proton transfer.[13] Ionicity provides information on molecular interactions between ions and ion–solvent interactions.[14] A literature survey suggests that the data on ionicities are available for only pure ionic liquids. Krossing et al. described the ionicities of imidazolium and ammonium based ionic liquids.[15] Rebelo et al. investigated ways to generate high ionicity by adding inorganic salts to pure ionic liquids.[16] Mu et al. studied the ionicity of acetate-based protic ionic liquids.[17] Unfortunately, a survey of the literature reveals that available data on the ionicities of ionic liquids in molecular solvents are very limited. Buchner et al. compared the ionic association behavior of different classes of ionic liquids in acetonitrile.[18] Sagara et al. measured the temperature dependent transport properties of ionic liquids.[19] Watanabe et al. illustrated the ionicity and proton transfer mechanism of binary protic ionic liquid mixtures for fuel cell reactions.[20] However, there remains a lack of data on the role of molecular level interactions on iconicity in different solvent systems for seeking their better applications.

The present work is focused on temperature-dependent transport properties: electrical conductivity (σ), viscosity (η), and self-diffusion coefficient (D) of nine protic and aprotic ionic liquids. The aprotic ionic liquids investigated were 1-butyl-3-methylimidazolium bromide ([bmIm]Br), 1-hexyl-3-methylimidazolium bromide ([hmIm]Br), 1-octyl-3-methylimidazolium bromide ([omIm]Br), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmIm][BF_4]), and 1-octyl-3-methylimidazolium tetrafluoroborate ([omIm][BF_4]). The protic ionic liquids employed in the investigation were 1-methylimidazolium formate ([HmIm][HCOO]), 1-methylimidazolium acetate ([HmIm][CH_3COO]), 1-methylimidazolium propionate ([HmIm][CH_3CH_2COO]), and 1-butylimidazolium acetate ([HbIm][CH_3COO]), where H indicates a proton. Water, dimethyl sulfoxide (DMSO), and ethylene glycol were used as molecular solvents. These ionic liquids were selected for study based on the nature and structural arrangement of cations and anions. The molecular solvents were selected on the basis of their properties: polarity, relative permittivity (ε), hydrogen-bond donating (α) and hydrogen-bond accepting ability (β), and viscosity (η).[21]

As part of our ongoing investigation on ionic liquids systems,[22–27] we now measured three transport properties: electrical conductivity, viscosity, and self-diffusion coefficient of binary mixture of ionic liquids with solvents. According to Angell and co-workers,[11,28] ionic systems can be classified as super ionic, good ionic, poor ionic, and nonionic on the basis of Walden plots. Deviation from the ideal line represents the ionicity in a binary mixture of ionic liquids and solvents, which can be used to classify the systems as super ionic, good ionic, or poor ionic.[11] A departure from the reference KCl line indicates the existence of ion pairs or ionic aggregates. High ionicity indicates less ionic aggregation whereas poor ionicity indicates high ionic aggregation.

2. Results and Discussion

2.1. Electrical Conductivity of Aprotic Ionic Liquids

Conductivity values σ have been measured for all the systems at atmospheric pressure and in the temperature range of 293.15 to 313.15 K. The σ values mainly depend on temperature, concentration of ions in solution, and the mobility of the ion. As expected, the σ values of all the aprotic ionic liquids in molecular solvents increase with increased temperature from 293.15 to 313.15 K. The plot of $\ln\sigma$ against $1/T$ is shown in Figure S1. Now, we consider the specific concentration of ionic liquids throughout all the system; however, the production of the ions depends on solvent properties and on the structure of the ionic liquids. Finally, the mobility of ions plays a major role in electrical conductivity, which depends on the viscosity of the medium and on solute–solvent interactions present in the system. Here, we focus on a comparative study of the σ values of ionic liquids, [bmIm]Br, [hmIm]Br, [omIm]Br, [bmIm][BF_4], and [omIm][BF_4] in water, DMSO, and ethylene glycol at 298.15 K (Table 1). The σ value is higher in water than in either DMSO or ethylene glycol for all aprotic ionic liquids and follows the order water > DMSO > ethylene glycol. Furthermore, for each solvent, the σ values are observed to be [bmIm]Br > [hmIm]Br > [omIm]Br, which is imparted due to an increase in alkyl chain length. The [BF_4]$^-$ based ionic liquids show higher σ values than those of [Br]$^-$ based ionic liquids. In the series of [RmIm]Br (R is alkyl chain length) aprotic ionic liquids, the σ value of [bmIm]Br is higher than that of [hmIm]Br and [omIm]Br in each of the solvents, and [bmIm][BF_4] has a higher σ value than [omIm][BF_4].

Table 1. Electrical conductivity (σ) of aprotic ionic liquids in molecular solvents at 298.15 K.

Solvent	Ionic liquid σ [mScm^{-1}] [bmIm]Br	[hmIm]Br	[omIm]Br	[bmIm][BF_4]	[omIm][BF_4]
water	8.05	7.69	7.43	9.93	7.51
DMSO	2.65	2.36	2.28	3.44	2.50
ethylene glycol	0.50	0.47	0.44	0.77	0.46

The change in the σ values of ionic liquids in different molecular solvents depends on the solvent properties and structure of the ionic liquids. In previous work, we have also described the effect of solvent properties and the structure of ionic liquids on the limiting molar conductivity.[25] Herein, solvent properties such as relative permittivity (ε), solvatochromic parameters [i.e. polarity (E_T^N)], hydrogen-bond donating ability (α), hydrogen-bond accepting ability (β), and viscosity (η) of solvents are shown to play a major role in determining the σ values of systems.

2.2. Effect of Relative Permittivity (ε)

The σ values of all the aprotic ionic liquids were higher in water than in either DMSO or ethylene glycol because of the very high relative permittivity of water (78.4) followed by those of DMSO (46) and ethylene glycol (37.7). The high relative permittivity means that the columbic interactions between cations and anions of ionic liquids are reduced, leading to higher dissociation of cations and anions. Higher numbers of free ions available to carry the electric current in water–ionic liquid systems thus become available. Figure 1 shows the decrease in σ values for all ionic liquids from water to ethylene glycol because of the decrease in relative permittivity from water to ethylene glycol. This indicates that higher ionic association is present in DMSO and ethylene glycol systems than in water.

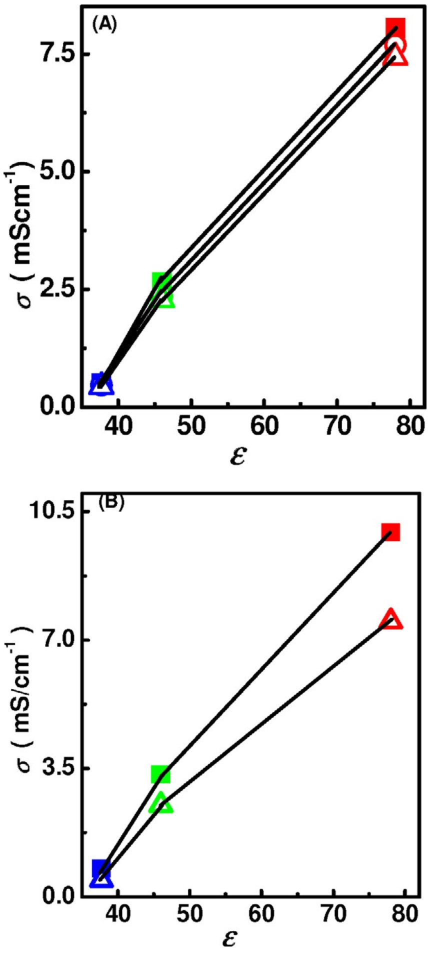

Figure 1. Plots of the electrical conductivity σ of ionic liquids vs. relative permittivity (ε) of solvents A) [bmIm]Br (solid square), [hmIm]Br (hollow circle), [omIm]Br (hollow triangle); B) [bmIm][BF_4] (solid square) and [omIm][BF_4] (hollow triangle) in water (red), DMSO (green) and ethylene glycol (blue) at 298.15 K.

2.3. Effect of Solvatochromic Parameters

Polarity is a general term that refers to all the interaction forces between molecules, and is composed of several specific and nonspecific interacting components, including columbic interactions, the various dipole–dipole interactions, hydrogen-bonding and electron-pair donor–acceptor interactions.[29–31] The solvatochromic parameters $E_T(30)$ or E_T^N, α and β explain the solvent dependent phenomena at the molecular level and give information about the solvation ability of the medium.[21] The values of E_T^N, and the α and β parameters for molecular solvents water, DMSO, and ethylene glycol are given in Table 2.

Table 2. Solvent properties of molecular solvents: E_T^N, α, β, η, and ε at 298.15 K.[21]

No.	Solvent	Properties E_T^N	α	β	ε	η [cP]
1	water	1.00	1.12	0.50	78	0.89
2	DMSO	0.44	0.00	0.76	46	1.99
3	ethylene glycol	0.79	0.90	0.52	37.7	16.9

As shown in Figure 2, the effect of the E_T^N values of molecular solvents on σ of aprotic ionic liquids [bmIm][BF_4] and [omIm][BF_4] does not show any correlation. Here, water and ethylene glycol are polar protic solvents whereas DMSO is a polar aprotic solvent. The E_T^N values for water, ethylene glycol, and DMSO solvents are 1, 0.79, and 0.44, respectively. In the case of polar protic solvents water and ethylene glycol, the σ values for all aprotic ionic liquids decrease in accordance with the E_T^N value (Table 2). However, in the case of DMSO, the σ values are observed to be higher than in ethylene glycol for all aprotic ionic liquids, even though the E_T^N is smaller for DMSO than for ethylene glycol. This contradicts the generalized correlation on the basis of E_T^N. Similar correlations like those of the E_T^N values are observed for the α values of water and ethylene glycol with those of the σ values of aprotic ionic liquids (Table 2). Hence, the ability of water and ethylene glycol to form hydrogen bonds plays a dominant role in the solvation of the ions of aprotic ionic liquids independently. A smaller effect is observed in the case of the β parameter of water and ethylene glycol with σ in the case of aprotic ionic liquids. Thus, E_T^N, hydrogen-bond donor ability of water and ethylene glycol helps the dissociation of cation and anions in aprotic ionic liquids, which dominates the columbic attraction force between cations and anions in ionic liquids. This effect is limited to polar protic solvents. However, in the case of polar aprotic solvent DMSO, the effect of solvatochromic parameters E_T^N, α, and β on the σ of all aprotic ionic liquids is observed to be weak. The effect of solvatochromic parameters on σ of [bmIm]Br, [hmIm]Br, and [omIm]Br in molecular solvents are given in Figure S3.

Importantly, the σ values for all aprotic ionic liquids in ethylene glycol are smaller than in DMSO, although the E_T^N and α values are higher for ethylene glycol. These values arise because of the higher viscosity of ethylene glycol (16.90 cP) compared with DMSO (1.99 cP). The high viscous drag opposes the mobility of ions in a binary mixture of ionic liquids with ethylene glycol; this aspect is discussed further in Section 2.4.

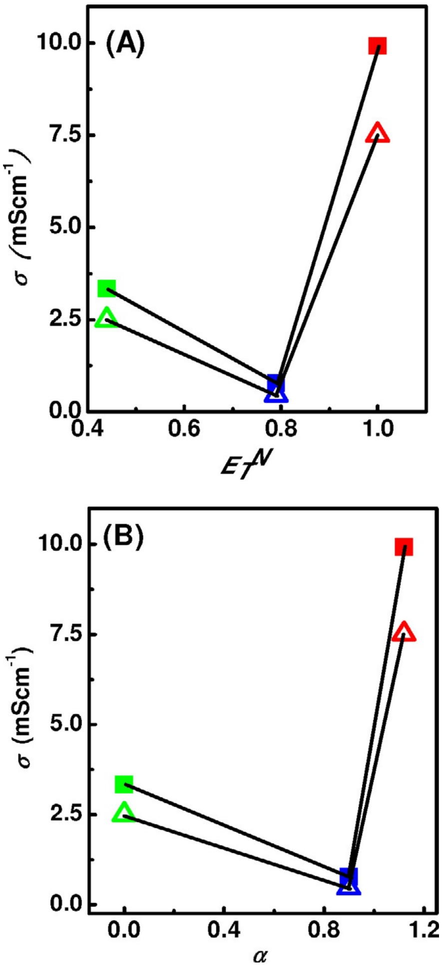

Figure 2. A) Plots of σ vs. E_T^N; B) Plots of σ vs. α for [bmIm][BF$_4$] (solid square) and [omIm][BF$_4$] (hollow triangle) in water (red), DMSO (green), and ethylene glycol (blue) at 298.15 K.

2.4. Effect of Viscosity on σ

Figure 3 shows a plot of the η values of solvents versus the σ values for the aprotic ionic liquids in solvent. The results show that the σ values of aprotic ionic liquids decreases with increasing η values of the solvents. The bulk η values of water, ethylene glycol, and DMSO are 0.89, 1.99, and 16.9 cP, respectively. Thus, the higher the viscosity of the medium, the lower will be the σ value of the system. The σ values of aprotic ionic liquids decrease with molecular solvents in the order water > DMSO > ethylene glycol. The σ values of aprotic ionic liquids decrease drastically from water to DMSO although the change in viscosity is observed to be very small; however, a small decrease in the σ values of aprotic ionic liquids from DMSO to ethylene glycol is observed but the corresponding viscosity change is significant. Thus, in addition to the viscosity of medium, other factors are important for the solvation dynamics of the ions of ionic liquids. This effect is similar to the effect of relative permittivity of the medium on the σ values of aprotic ILs. Thus, in the case of aprotic ILs, only bulk properties of viscosity η and dielectric constant ε play dominant roles in determining the σ values of aprotic ILs.

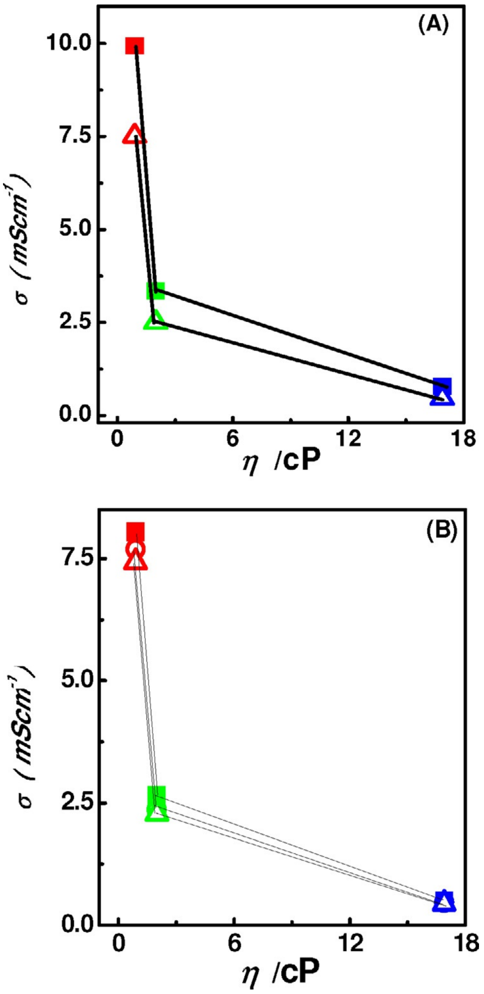

Figure 3. Plots of viscosity (η) vs. electrical conductivity (σ) of A) [bmIm][BF$_4$] (solid square) and [omIm][BF$_4$] (hollow triangle), and B) [bmIm]Br (solid square), [hmIm]Br (hollow circle), and [omIm]Br (hallow triangle) in water (red), DMSO (green), and ethylene glycol (blue) at 298.15 K.

2.5. Structure of Cations and Anions in Aprotic Ionic Liquids

Comparing the σ values of [bmIm]Br, [hmIm]Br, [omIm]Br, [bmIm][BF$_4$], and [omIm][BF$_4$] in water, DMSO, and ethylene glycol reveals an inverse linear relationship between the σ values with an increase in the number of carbon atoms in the alkyl chain of the cations of the aprotic ionic liquids. An increase in alkyl chain length from butyl to octyl and the associated increase in the size of cation, decreases the mobility of ions in all studied systems. The effect of the nature of the cations on σ values is shown in Figure 4. Similarly, the experimental results shows that the σ values of [BF$_4$]$^-$ based ionic liquids are higher than those of the respective [Br]$^-$ based ionic liquids in each of the molecular solvents examined. The σ values of [bmIm]Br and [bmIm][BF$_4$], with the same cation, are 8.05 and 9.93 mScm^{-1} in water, respectively, and for [omIm]Br and [omIm][BF$_4$] the values are 2.28 and 2.50 mScm^{-1}, respectively.

Given that the size of the [BF$_4$]$^-$ anion is larger than that of the [Br]$^-$ anion,[21] the electrostatic interactions and hydrogen-bonding ability of [Br]$^-$ anion with [bmIm]$^+$ cation is stronger than that of the [BF$_4$]$^-$ anion with the [bmIm]$^+$ cation, which

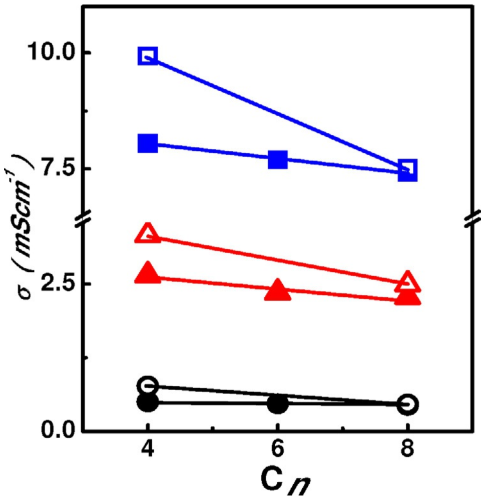

Figure 4. Plots of σ versus alkyl chain length, C_n of $[C_nmIm][BF_4]$ (hollow) and $[C_nmIm]Br$ (solid) in water (blue), DMSO (red), and ethylene glycol (black) at 298.5 K.

reduces the ionic strength of the ionic liquids. The separation of cations and anions in $[BF_4]^-$ based ionic liquids means that larger numbers of free ions are available than for $[Br]^-$ based ionic liquids.

2.6. Electrical Conductivity of Protic Ionic Liquids

The conductivity of [HmIm][HCOO], $[HmIm][CH_3COO]$, $[HmIm][CH_3CH_2COO]$, and $[HbIm][CH_3COO]$ in water, DMSO, and ethylene glycol are shown in Table 3. For all the studied protic ionic liquids, the σ values decrease in the order $[HmIm][HCOO] > [HmIm][CH_3COO] > [HmIm][CH_3CH_2COO] > [HbIm][CH_3COO]$ in water, DMSO, and ethylene glycol. The σ values of the protic ionic liquids in DMSO and ethylene glycol are smaller than in water. Thus, the order of σ values for protic ionic liquids in molecular solvents is water > ethylene glycol > DMSO. However, these results for all protic ionic liquids contracts to the role of viscosity and relative permittivity. Here, the effect of the ε and η values of the medium show a relationship with the σ values of the protic ionic liquids in water and DMSO systems, and water and ethylene glycol systems; however, the correlation of σ values of aprotic ionic liquids contradicts the correlation of σ values with the η and ε values of the medium in the case of DMSO and ethylene glycol systems. For example, the σ value for $[HmIm][CH_3COO]$ is higher in water (6.461) than in DMSO (0.163) and ethylene glycol (0.42), which is due to the high ε (78) and η (0.89 cP) values of water, whereas DMSO and ethylene glycol have low values of both ε (46 and 37.7, respectively) and η (1.99 and 16.9 cP, respectively).

Table 3. Electric conductivities (σ) of protic ionic liquids in molecular solvents at 298.15 K.

Solvent	Ionic liquid σ [mScm^{-1}]			
	[HmIm] [HCOO]	[HmIm] $[CH_3COO]$	[HmIm] $[CH_3CH_2COO]$	[HbIm] $[CH_3COO]$
water	6.461	6.143	5.732	4.379
DMSO	0.163	0.012	0.010	0.010
ethylene glycol	0.421	0.252	0.238	0.203

Interestingly, the σ values for all the protic ionic liquids in ethylene glycol are higher than those in DMSO, although DMSO posses higher ε and low η than ethylene glycol. This contradicts the correlation of σ of all protic ionic liquids with ε and η of the medium. Thus, it is important to consider the microscopic properties rather than bulk or macroscopic properties of the medium to fully understand the factors affecting the σ values of protic ionic liquids. Thus, here we have considered microscopic parameters such as solvatochromic parameters E_T^N, α and β, which are found to be more specific compared with ε and η. The parameters E_T^N, α, and β for water, DMSO, and ethylene glycol are given in Table 2. Figure 5 shows plots of the σ values of protic ionic liquids as a function of E_T^N and α for water, ethylene glycol, and DMSO. Here, the

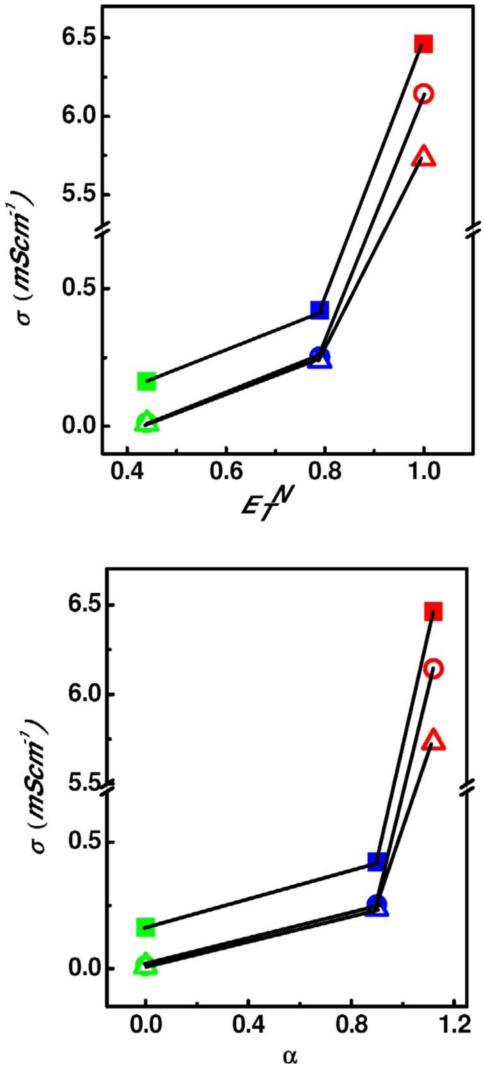

Figure 5. A) Plots of σ vs. E_T^N; B) plots of σ vs. α for [HmIm][HCOO] (solid square), $[HmIm][CH_3COO]$ (hollow circle), and $[HmIm][CH_3COO]$ (hollow triangle) in water (red), DMSO (green), and ethylene glycol (blue) at 298.15 K.

σ values for all protic ionic liquids decrease with E_T^N, and α decreases in the order water > ethylene glycol > DMSO. Thus, the role of the hydrogen-bond donor ability of the solvent plays a crucial role in the solvation of cations and anions, irrespective of the nature of the protic ionic liquids. Similarly, β values of the medium affect the conduction behavior in protic ionic liquids to some extent. This is because the Grotthuss-type mechanism[32] occurs in binary mixtures of protic ionic liquids with water and ethylene glycol. Here, the σ value of protic ionic liquids is higher in ethylene glycol than in DMSO, as a result of the proton hopping mechanism in protic ionic liquids. Given that protic ionic liquids are more polar than aprotic ionic liquids,[33] the properties of protic ionic liquids are more sensitive towards the surrounding medium or solvents at the microscopic level. Thus, microscopic parameters determine the conductivity of protic ionic liquids whereas macroscopic properties determine the conductivity of aprotic ionic liquids.

Figure 6 shows the plot of σ versus alkyl chain length of anions of [Hmim][HCOO], [Hmim][CH_3COO], and [Hmim][CH_3CH_2COO] in water, DMSO, and ethylene glycol. From the results it has been concluded that the σ value of protic ionic liquids has an inverse relationship with alkyl chain length of anions in water, DMSO, and ethylene glycol. With an increase in the number of carbon atoms in the structure of the anions from [HmIm][HCOO] to [HmIm][CH_3CH_2COO], the value of σ decreases from 6.461, 6.143 and 5.732, to 0.163, 0.012 and 0.010, to 0.421, 0.252 and 0.238 $mScm^{-1}$ in water, DMSO, and ethylene glycol, respectively. An increase in the alkyl chain length of the anions is associated with an increase in the size of the anions from [HmIm][HCOO] to [HmIm][CH_3CH_2COO] as 0.158, 0.159, and 0.162 nm, respectively.[21] The mobility of [CH_3CH_2COO]$^-$ is slower because of its larger size and hence the conductivity of [HmIm][CH_3CH_2COO] is lower in all the solvents studied. The decrease in the σ values of protic ionic liquids in water is nearly linear with an increase in alkyl chain length; however, there is sharp of decrease in the σ value of protic ionic liquids in DMSO and ethylene glycol from [HmIm][HCOO] to [HmIm][CH_3COO] and a gradual decrease for [HmIm][CH_3CH_2COO]. Similarly, we have examined the role of cations, which were changed from [HmIm]$^+$ to [HbIm]$^+$ with common anion [CH_3COO]$^-$, in determining the σ values in water, DMSO, and ethylene glycol (Table 3).

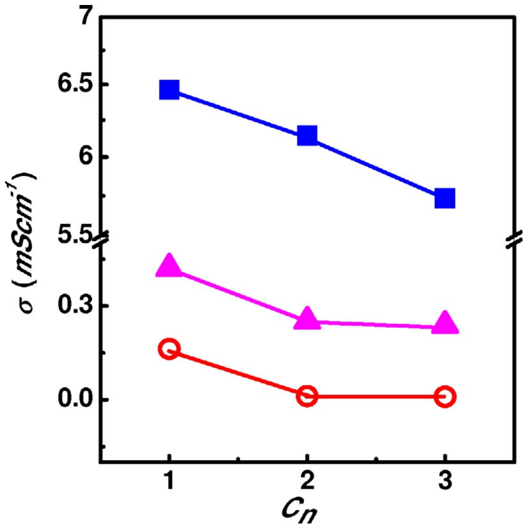

Figure 6. Plots of σ vs. alkyl chain length (C_n) of anions of [Hmim][HCOO], [Hmim][CH_3COO] and [Hmim][CH_3CH_2COO] in water (■), ethylene glycol (▲), and DMSO (○) at 298.15 K.

The σ values decrease from 6.143, 0.012, and 0.252 $mScm^{-1}$ for [HmIm][CH_3COO] to 4.379, 0.010, and 0.203 $mScm^{-1}$ for [HbIm][CH_3COO] in water, DMSO, and ethylene glycol, respectively. This is due to the increase in alkyl chain length from one carbon atom to four carbon atoms on the imidazolium cation ring.

2.7. Interactions between Cations and Anions of Ionic Liquids

Cations and anions are held together by electrostatic and hydrogen-bond interactions. The electrostatic and hydrogen-bond interactions primarily depend on charge density, the size of the ions, and availability of protons on the ions. Here, we have considered three ionic liquids [bmIm]Br, [bmIm][BF_4], and [HbIm][CH_3COO] in which the size of the cations are almost identical but ionic radii of the anions differ for [BF_4]$^-$, Br^-, and [CH_3COO]$^-$ as 0.232, 0.195, and 0.159 nm, respectively. Thus, an increase in the ionic radii of anions from [CH_3COO]$^-$ to Br^- to [BF_4]$^-$, leads to an increase in the σ values of the ionic liquids in all the molecular solvents studied. Here, the *e/r* ratio (where *e* is the charge on the molecule and *r* is the radius of the molecule) increases from [BF_4]$^-$ to [CH_3COO]$^-$ and charge density decreases from [CH_3COO]$^-$ to [BF_4]$^-$.[21] The value of *e/r* for [BF_4]$^-$, Br^-, and [CH_3COO]$^-$ is 4.31, 5.12, and 6.28, respectively.

Protic ionic liquids [HbIm][CH_3COO] show stronger interactions between cations and anions because of the large electrostatic interactions between cations and anions and also because of the strong hydrogen-bonding ability of the proton on the cation with the anion. This leads to a decrease in the number of free ions in solution. This effect is clear in Figure 7, which shows that the σ values decrease slowly from [BF_4]$^-$ to Br^- but decrease sharply from Br^- to [CH_3COO]$^-$. The order of electrical conductivity is [bmIm][BF_4] > [bmIm][Br] > [HbmIm][CH_3COO] in water, DMSO, and ethylene glycol. Thus, aprotic ionic liquids exhibit higher σ values than protic ionic liquids because of the stronger attraction of ions in protic ionic liquids.

2.8. Solvation Effects

Here, we illustrate the solvation of ions by using the ^1H NMR chemical shift (δ) of the C-2 proton of imidazolium cations of ionic liquids. The chemical shift of the C-2 proton is more sensitive than the C-4 and C-5 protons because it is located between two nitrogen atoms of the imidazolium ring.[34–37] If the concentration of the ionic liquids in solution is the same, the chemical shift of the C-2 proton should be dependent on the solvent. The experimental δ value for the C-2 proton of neat

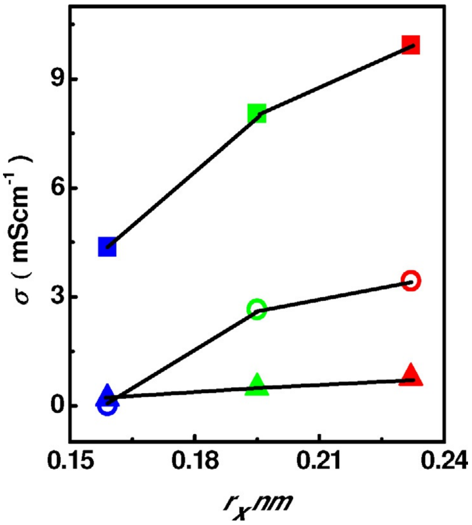

Figure 7. Plots of σ vs. ionic radii r_x of anions for [bmIm][BF$_4$] (red), [bmIm]Br (green), and [HbIm][CH$_3$COO] (blue) in water (■), DMSO (○), and ethylene glycol (▲) at 298.15 K.

[bmIm][BF$_4$] is 8.71 ppm and for neat [bmIm]Br is 9.67 ppm, which indicates that the interaction of the C-2 proton with the smaller and less polarizable Br$^-$ anion is greater than that with the [BF$_4$]$^-$ anion, which larger and more polarizable.

The δ shifts of the C-2 proton of the imidazolium ring of [bmim]Br and [bmIm][BF$_4$] in 0.1 M D_2O and [D$_6$]DMSO are given Table S7. The δ values of [bmIm]Br in D_2O and [D$_6$]DMSO are 8.61 and 9.19 ppm and for [bmIm][BF$_4$] in D_2O and [D$_6$]DMSO are 8.62 and 9.11 ppm, respectively. The lower δ values of [bmIm]Br and [bmIm][BF$_4$] in D_2O show the stronger solvation of ions in water (D_2O) than in DMSO ([D$_6$]DMSO). Thus, there is an increase in the σ values for [bmIm]Br and [bmIm][BF$_4$] in water compared with those in DMSO. The upfield shift in δ is a direct consequence of weakening of the hydrogen bond between cations and anions and the interaction with solvent molecules. Figure 8 shows that the δ value of the C-2 proton is strongly affected by the polarity of the solvent, and it is reported that higher polarity leads to lower δ values of the C-2 proton.[38–40] In the case of [HmIm][CH$_3$COO], we have explained the solvation of ions on the basis of the δ value of CH$_3$- proton of anions [CH$_3$COO]. Given that the N-H proton is more acidic than the C-2 proton of protic ionic liquids and that it resonates at a more downfield position, we consider the CH$_3$- proton of the anion for analysis. The δ value of the CH$_3$-proton in D_2O (1.78 ppm) is lower than that in [D$_6$]DMSO (1.93 ppm). This indicates that there is a larger increase in the solvation of the ions of protic ionic liquids in water than in DMSO, which leads to higher σ values for protic ionic liquids in water than in DMSO.

2.9. Diffusion Coefficients (*D*) and Hydrodynamic Radius

The temperature dependence of diffusion coefficients of cations and anions was obtained from PGSE-NMR measurements (Figure S4). Both cationic and anionic diffusion coefficient, *D*, were measured from the ^{1}H nucleus. Fitting was performed with the Stejskal–Tanner equation.[41,22] The data show that cationic diffusion coefficients of [HmIm][CH$_3$COO] (0.1 M) in D_2O solution is higher than the anionic diffusion coefficients. The coefficient values of the cation and anion of [HmIm][CH$_3$COO] increase with increased temperature. From these results, it is observed that at higher temperature the rate of diffusion of the cation is higher than that of the anion. The temperature dependence of the diffusion coefficients of the binary system of [HmIm][CH$_3$COO] with D_2O can be fitted by using the Arrhenius equation [Eq. (1)].[42]

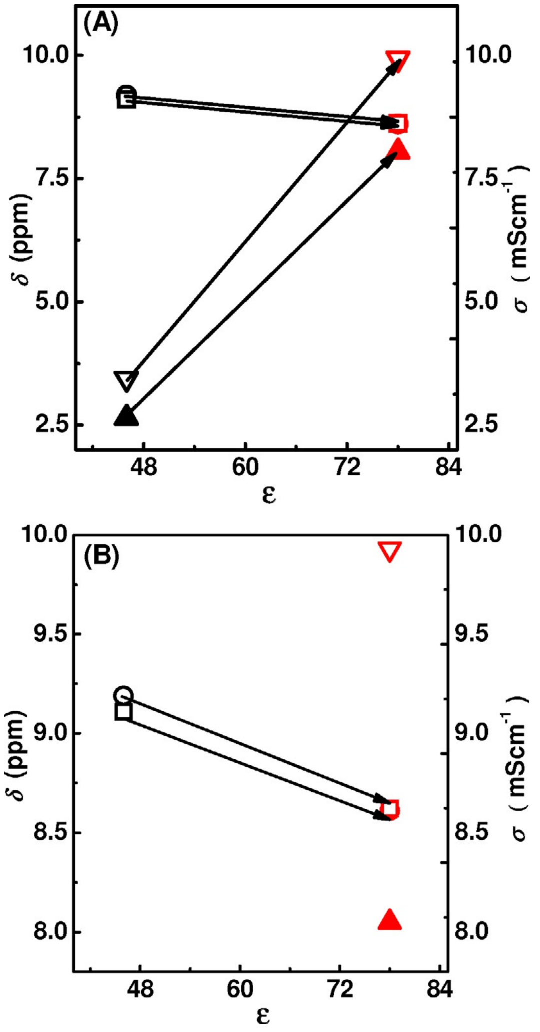

Figure 8. A) Plots of ε vs. A) chemical shift (δ) for [bmIm]Br in DMSO (○) and D_2O (○) and for [bmIm][BF$_4$] in [D$_6$]DMSO (□) and D_2O (□) and conductivity (σ) for [bmIm]Br in [D$_6$]DMSO (▲) and D_2O (▲) and for [bmIm][BF$_4$] in [D$_6$]DMSO (▽) and D_2O (▽). B) Enlarged plot between 7.5 to 10 ppm of δ at 298.15 K.

$$D = D_o \exp^{-\frac{E_a}{RT}}$$

or (1)

$$\ln D = \ln D_o - \frac{E_a}{RT}$$

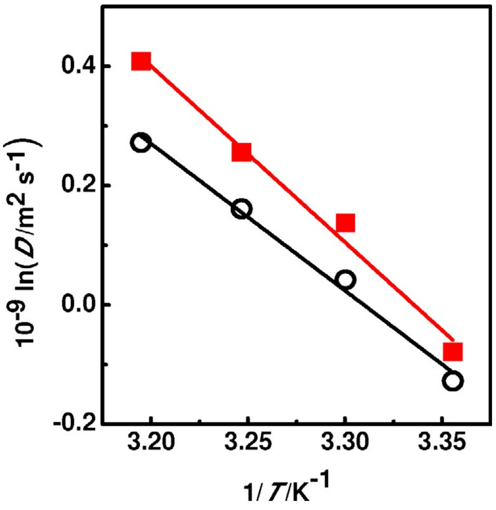

Figure 9. The Arrhenius plots of cationic and anionic self-diffusion coefficients based on PGSE-NMR measurements for [HmIm][CH_3COO] vs. 1/T for [HmIm]$^+$ (■) and [CH_3COO]$^-$ (○) in D_2O at 298.15 K.

where, E_a is the activation energy for diffusion of ions and D_o is the maximum diffusion coefficient. The plot of ln$D$ versus 1/T give straight lines, as shown in Figure 9.

Furthermore, we have determined the hydrodynamic radii from the Stoke–Einstein equation [Eq. (2)].[15]

$$D = \frac{kT}{C\pi\eta R_H} \qquad (2)$$

where, D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, and η the viscosity of the solvent. R_H is the hydrodynamic radius. The C factor is a constant that is influenced by the strength of the interactions between the diffusing species and the solvent medium. It is generally taken as 6 but can be reduced to 4. To determine the hydrodynamic radius we gave C the value 6. The D values of the cation and anion in D_2O and [D_6]DMSO are consistent with the σ values of [HmIm][CH_3COO] in water and DMSO. The D values of the cation and anion of [HmIm][CH_3COO] in D_2O is almost 1.5 times greater than in [D_6]DMSO but the σ value in D_2O is much greater than that noted in [D_6]DMSO. Thus, it is clear that some additional factor is also responsible for the electric current in water. As mentioned in Section 2.6, water—being a polar protic solvent—is responsible for the Grotthuss-type mechanism.[32] The hydrodynamic radii (R_H) of [HmIm]$^+$ and [CH_3COO]$^-$ in D_2O are 265 and 278 pm and for [D_6]DMSO are 178 and 230 pm, respectively, calculated from the Stokes–Einstein equation. The radii R_H of [HmIm]$^+$ and [CH_3COO]$^-$ are greater in D_2O than in [D_6]DMSO, which suggests that solvation of ions occurs to a greater extent in water.

To discuss the ionicity of binary mixtures of ionic liquids with solvents in more qualitative and quantitative detail, we measured the self-diffusion coefficients of all protons in the cation and anion of [HmIm][CH_3COO] individually, using the PGSE-NMR method. The molar conductivity (Λ_{NMR}) of binary mixtures can be determined from the Nernst–Einstein [Eq. (3)] by using the self-diffusion coefficient.[43,44]

$$\Lambda_{NMR} = \frac{N_A e^2}{kT}\,(D_+ + D_-) \qquad (3)$$

where N_A is Avogadro's number, e is the electronic charge, k is the Boltzmann constant, T is the absolute temperature, and D_+ and D_- are the self-diffusion coefficient of the cation and anion of [HmIm][CH_3COO], respectively.

The values of Λ_{imp} are less than Λ_{NMR}, indicating that not all of the diffusive species contribute to the conduction of electric current because of the formation of neutral ion pair species in molecular solvents. If the Λ_{NMR} calculated from Equation 3 and the molar conductivity, obtained from the electrical conductivity Λ_{imp}, are equal then all the ions participate in ionic conduction.

In the case of ionic association, the molar conductivities, Λ_{NMR} and Λ_{imp} are different, and the ratio of $\Lambda_{imp}/\Lambda_{NMR}$ [45] represents the ionicity of the binary mixtures. The values for the ionicity of [HmIm][CH_3COO] are lower than unity, confirming the presence of ionic association in these binary systems (Figure 10).

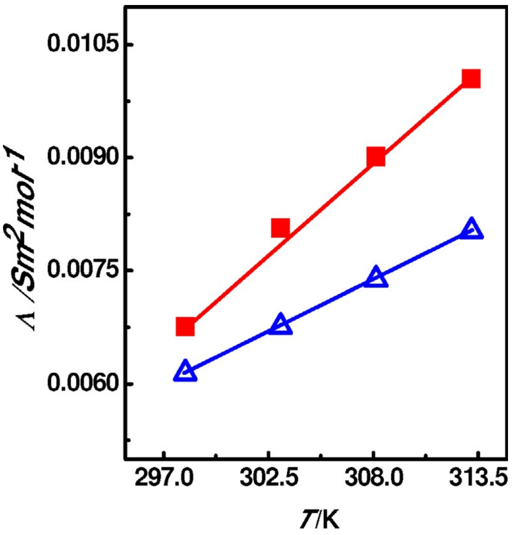

Figure 10. Plots of molar conductivity (Λ_m) vs. temperature (T) of [HmIm][CH_3COO] in water for Λ_{imp} (△), Λ_{NMR} (■) at 298.15 K.

The Λ_{imp} and Λ_{NMR} values for [HmIm][CH_3COO] are 61.43 and 67.62 Scm^2 mol^{-1} in water and D_2O, respectively. On the other hand, the Λ_{imp} and Λ_{NMR} values for [HmIm][CH_3COO] are noted as 0.12 and 40.82 Scm^2 mol^{-1} in DMSO ([D_6]DMSO), respectively. The ionicity values of [HmIm][CH_3COO] calculated from the Walden plot are 61.6 and 0.003 % and ionicity values from $\Lambda_{imp}/\Lambda_{NMR}$ are 90 and 0.003 % in water (D_2O) and DMSO ([D_6]DMSO), respectively, at 298.15 K. The effect of temperature on the rate of increase of Λ_{NMR} is greater than on Λ_{imp}. Thus, it is clear that temperature does not have a significant effect on the dissociation of ions in [HmIm][CH_3COO] with water.

Temperature dependent ionic transference numbers t have been determined by using the self-diffusion coefficients of each ion; the ionic transference number t_i is defined as by Equation (4):[46,47]

$$t_i = \frac{x_i D_i}{\sum x_i D_i} \tag{4}$$

where x_i is the i^{th} ion molar fraction and D_i is the i^{th} ion diffusion coefficient.

From Table S6, it is observed that the t^+ values for all protic ionic liquids are higher than the t^-values in D_2O and [D_6]DMSO. The cationic transport number t^+ for $[HmIm]^+$ is higher than 0.5, whereas the anionic transport number $t^-[CH_3COO]^-$ is less than 0.5, suggesting $[HmIm]^+$ carries more than half of the current and less than half is carried by the $[CH_3COO]^-$, because $[HmIm]^+$ is able to move or diffuse faster than anions. These results are analogous with our previous work and with other reports.[25,43] At higher temperature, t^+ increases and t^- decreases, which is consistent with the self-diffusion coefficient of ions (Figure S4).

2.10. Ionicity in Protic and Aprotic Ionic Liquids

Herein, we approximately quantify the ionicity of the binary mixture on the basis of the Walden plot of $\log \Lambda_m$ against $\log \eta^{-1}$ with ideal 0.1 M KCl as a reference line. The relation between molar conductivity and viscosity can be demonstrated by Equation (5):[48,49]

$$\log \Lambda_m = \log C + \oslash \log \eta^{-1} \tag{5}$$

The ø value is the slope of the line in the Walden plot, which reflects the dissociation of the ions. The value of the ø parameter reveals the difference of the activation energies of the ionic conductivity and viscosity. In the present investigation, all ø values of binary mixtures are smaller than unity ($ø < 1$), indicating that the ionic conductivities of binary mixture is, to some extent, reduced as a result of ion-pair formation.

The fitted ø values of binary mixtures are given in Table 4. Another method that can be used to obtain similar values of ø is the ratio of the temperature-dependent activation energies for viscosity and molar conductivity, $E_{a,\Lambda}/E_{a,\eta}$.[46]

Table 4 compares the ø values obtained from the slopes of the Walden plots in Figure 11 with those calculated from the activation energies and are in very good agreement. The ionicities for all protic and aprotic ionic liquids are calculated from the Walden plot of $\log \Lambda_m$ against $\log \eta^{-1}$ with KCl as reference ideal line. The vertical distance measured from the KCl ideal line to the point of the ionic liquid binary mixture is called ΔW (deviation). The distance (ΔW) and ionicity calculated as %Ionicity $= 10^{(-\Delta W)} \times 100$, and data of ionicities for all systems are given in Table 5.

The binary system of aprotic ionic liquids [bmIm]Br, [hmIm]Br, [omIm]Br with water, DMSO, and ethylene glycol falls in the region of good ionic binary mixtures. The order of ionicity of aprotic ionic liquids is ethylene glycol > water > DMSO. However, the σ values of aprotic ionic liquids in water are higher than those in DMSO and ethylene glycol as per their relative permittivity. The fluidity of ethylene glycol is lower than that of water and DMSO, which is the dominant factor for the ionicity in the aprotic ionic liquids. According to the classification by Angell et al.,[11,28] the plot for [bmIm][BF_4] with water and ethylene glycol are on the ideal KCl line and other plots are located below the reference KCl line. The [bmIm][BF_4] with water and ethylene glycol shows ideal ionicity or 100% ionic characters. Furthermore, the binary systems of [omIm][BF_4] with water, DMSO, and ethylene glycol are in the region of a good ionic class but still lower than the ionic region of [bmIm][BF_4].

Table 4. Linear fit parameters from the Walden Plot.

Ionic liquid	Solvent[a]	φ	$\log C$ [$S \cdot cm^2 \cdot mol^{-1}$]	$E_{a,\Lambda}/E_{a,\eta}$
[bmIm]Br	water	0.7940	0.3301	0.8094
	DMSO	0.7955	0.0969	0.7926
	EG	0.8013	0.0912	0.8013
[hmIm]Br	water	0.8008	0.2919	0.8110
	DMSO	0.8384	0.0146	0.8387
	EG	0.8035	0.0867	0.8034
[omIm]Br	water	0.8088	0.2667	0.8242
	DMSO	0.8759	−0.0520	0.8764
	EG	0.9662	−0.0868	1.0240
[bmIm][BF_4]	water	0.7259	0.5606	0.7306
	DMSO	0.7902	0.2565	0.7907
	EG	0.9195	0.0787	0.9205
[omIm][BF_4]	water	0.7386	0.4162	0.7439
	DMSO	0.8191	0.0646	0.8192
	EG	0.8176	0.0420	0.8175
[HmIm][HCOO]	water	0.8110	0.1879	0.8126
	DMSO	0.4341	−0.4855	0.4340
	EG	0.7625	0.0072	0.7626
[HmIm][CH_3COO]	water	0.7738	0.2431	0.7740
	DMSO	0.6519	−1.9843	0.6520
	EG	0.6596	−0.0953	0.6594
[HmIm][CH_3CH_2OO]	water	0.6858	0.3963	0.7046
	DMSO	0.7060	−2.1209	0.7063
	EG	0.6487	−0.1310	0.6488
[HbIm][CH_3COO]	water	0.8900	−0.1262	0.8905
	DMSO	0.5982	−1.8568	0.5983
	EG	0.6825	−0.2255	0.6864

[a] EG: Ethylene glycol.

In the case of protic ionic liquids, the binary systems of [HmIm][HCOO], [HmIm][CH_3COO], [HmIm][CH_3CH_2COO], and [HbIm][CH_3COO] with water and ethylene glycol fall in the region of good a ionic class. The systems of [HmIm][HCOO], [HmIm][CH_3COO], [HmIm][CH_3CH_2COO], and [HbIm][CH_3COO] with DMSO are in the poor ionic region. These deviations from the ideal line are observed to depend on the structures of the ionic liquids and on the properties of the molecular solvents.

Ionicity in protic ionic liquids was observed to depend on microscopic properties such as solvatochromic parameters E_T^N and α, as noted above in the case of σ.

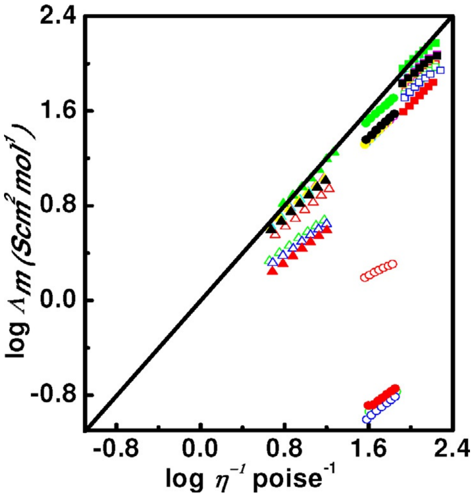

Figure 11. Walden plot of log Λ_m against log η^{-1} The binary systems of ionic liquids with solvents: (□), water-[Hmlm][HCOO]; (○), DMSO-[Hmlm][HCOO]; (△), EG-[Hmlm][HCOO]; (□), water-[Hmlm][CH_3COO]; (○), DMSO-[Hmlm][CH_3COO]; (△), EG-[Hmlm][CH_3COO]; (□), water-[Hmlm][CH_3CH_2COO]; (○), DMSO-[Hmlm][CH_3CH_2COO]; (△) EG-[Hmlm][CH_3CH_2COO]; (□), water-[bmlm]Br; (○), DMSO-[bmlm]Br; (△), EG-[bmlm]Br; (□), water-[hmlm]Br; (○), DMSO-[hmlm]Br; (△), EG-[hmlm]Br; (■), water-[omlm]Br; (●), DMSO-[omlm]Br; (▲),EG-[omlm]Br; (■), water-[Hblm][CH_3COO]; (●),DMSO-[Hblm][CH_3COO]; (▲), EG-[Hblm][CH_3COO]; (■), water-[bmlm][BF_4]; (●), DMSO-[bmlm][BF_4]; (▲), EG-[bmlm][BF_4]; (■), water-[omlm][BF_4]; (●), DMSO-[omlm][BF_4]; (▲), EG-[omlm][BF_4]from 293.15 to 313.15 K.

The order of ionicity for protic ionic liquids in solvents was found to be water > ethylene glycol > DMSO, and E_T^N and α parameters also decrease in the same way, which is due to the individual solvation of ions through hydrogen bonding.

The lower ionicity is due to the stronger ionic interaction exhibited by the protic ionic liquids, which possess higher polarity compared with aprotic ionic liquids. Deviation (ΔW) from the ideal KCl line and ionicities for all of the systems have been calculated at 298.15 K. The calculated data are presented in Table 5.

The ionicity in aprotic ionic liquids can be classified by considering the following factors. (1) The increase in alkyl chain length of the cation in [Rmlm]Br (R = alkyl chain length); the ionicity of binary mixture ionic liquids in water and ethylene glycol decreases in the order [bmlm]Br > [hmlm]Br > [omlm]Br, whereas in the case of DMSO, the ionicity is nearly equal for all three ionic liquids [bmlm]Br ≈ [hmlm]Br ≈ [omlm]Br. (2) The ionicities of [bmlm]Br, [hmlm]Br, and [omlm]Br in each molecular solvent is observed in the order ethylene glycol > water > DMSO. (3) The ionicities of $[Br]^-$ based ionic liquids are ca. 80% for water, ca. 56% for DMSO, and greater than 80% for ethylene glycol. This means that nearly 20% of the ions are not available for charge transport in water and ethylene glycol, and nearly 44% of the ions in DMSO, indicating the occurrence of ion pairing or ion aggregation.

Similarly, in the case of protic ionic liquids (1) as the alkyl chain length of anions of protic ionic liquids increase, the order of ionicity of the ionic liquids in each molecular solvent is [Hmlm][COO] > [Hmlm][CH_3COO] > [Hmlm] [CH_3CH_2COO]. (2) The ionicity of protic ionic liquids in each solvent is in the order water > ethylene glycol > DMSO. (3) Upon changing the cations from $[Hmlm]^+$ to $[Hblm]^+$ with the common anion $[CH_3COO]^-$, the ionicity of [Hblm][CH_3COO] decreases in each of the molecular solvents. Thus, it is concluded from the data of ionicities that 35–55% of ion pairs (or ion aggregation) are present in protic ionic liquids in water. Similar results are obtained in the case of ethylene glycol, but nearly all ions are in paired or aggregated form for DMSO. The cations and anions for protic ionic liquids in molecular solvents are strongly bound together. The ionicity obtained according to the Walden plot and from $\Lambda_{imp}/\Lambda_{NMR}$ by measuring the σ and ion self-diffusion coefficient, show moderate interaction between cations and anions for water; in DMSO, the cation and anions are held strongly to form ion pair and clustered ions with non-charge-neutral ion clusters.

Table 5. Deviation (ΔW) from ideal KCl line and ionicity of binary mixtures of ionic liquids with molecular solvents at 298.15 K.

Ionic liquid	Solvent	ΔW	Ionicity [%]
[bmlm]Br	water	0.08	83.1
	DMSO	0.25	56.2
	EG	0.05	89.1
[hmlm]Br	water	0.11	77.6
	DMSO	0.24	57.4
	EG	0.08	83.0
[omlm]Br	water	0.11	77.6
	DMSO	0.25	56.2
	EG	0.10	79.0
[bmlm][BF_4]	water	–	ca. 99.0
	DMSO	0.08	83.1
	EG	–	ca. 99.0
[omlm][BF_4]	water	0.10	79.0
	DMSO	0.24	57.5
	EG	0.10	79.0
[Hmlm][HCOO]	water	0.18	66.0
	DMSO	1.39	4.07
	EG	0.19	64.5
[Hmlm][CH_3COO]	water	0.21	61.6
	DMSO	2.52	0.003
	EG	0.35	44.6
[Hmlm][CH_3CH_2COO]	water	0.24	57.5
	DMSO	2.55	0.0028
	EG	0.41	38.9
[Hblm][CH_3COO]	water	0.34	45.7
	DMSO	2.50	0.0031
	EG	0.48	33.1

3. Conclusions

In this work, we have investigated the ionicities of five aprotic ionic liquids and four protic ionic liquids in three different molecular solvents, water, ethylene glycol, and DMSO, by analyzing conductivity, viscosity, and self-diffusion coefficients through the application of PGSE-NMR techniques. Our study reveals that (1) the σ values for protic and aprotic ionic liquids are reflected through the systematic variation in the structure of cation and anions and also through the size of the anions. (2) The σ values of aprotic ionic liquids is determined by macroscopic or bulk properties such as relative permittivity and viscosity the of molecular solvent, whereas the σ values in protic ionic liquids are determined by the microscopic properties of solvents, solvatochromic parameters, E_T^N, α. (3) The use of PGSE-NMR spectral techniques clarifies the association of cations and anions of ionic liquids in molecular solvents, which explains the σ values. For example, the degree of association of ions is less in water than in DMSO. (4) Aprotic ionic liquids are observed to be a better class of ionic salts (in solvents the order is ethylene glycol > water > DMSO) than protic ionic liquids (water > ethylene glycol > DMSO). (5) Ionicities obtained from the Walden plots offer information on the ionicity of binary mixtures readily, whereas the molar conductivity ratio ($\Lambda_{imp}/\Lambda_{NMR}$) approach estimates the ionicity more precisely. (6) The Stokes–Einstein radius $[HmIm]^+$ and $[CH_3COO]^-$ in water and DMSO calculated from the self-diffusion coefficient are consistent with the experimental values of ionic conductivity. The transference number of $[HmIm]^+$ and $[CH_3COO]^-$ is consistent with the results obtained by using PGSE-NMR techniques.

Experimental Section

Chemicals

1-Methylimidazole (99%), 1-butylimidazole (99%), 1-bromobutane, 1-bromohexane, 1-bromooctane, formic acid, acetic acid, propionic acid were purchased from Sigma–Aldrich and used as obtained. The molecular solvents, DMSO and ethylene glycol of high purity were purchased from Merck, India. Milli Q water with specific conductivity 5.5×10^{-6} mScm^{-1} was used throughout the experiment.

Synthesis of Ionic Liquids

Protic ionic liquids [HmIm][HCOO], [HmIm][CH_3COO], [HmIm][CH_3CH_2COO], and [HbIm][CH_3COO] were synthesized and purified according to the reported procedure.[50] The protic ionic liquids were synthesized by neutralization of acids such as formic acid, acetic acid and propanoic acid with bases methylimidazolium and butylimidazolium. Dropwise addition of base to acid was carried out in an ice bath to avoid heat generation due to the exothermic reaction. The reaction mixture of acid and base in the molar ratio of 1:1 was stirred for 6 h at RT. Water was removed by using a rotavapor at 80 °C under reduced pressure. These protic ionic liquids were further dried under vacuum at 70 °C for 10 h. Aprotic ionic liquids were synthesized according to the reported procedure,[51] using the quarternization reaction between 1-methylimidazole and 1-bromoalkane to form a salt [RmIm]Br. In a second step, [RmIm]BF_4 was synthesized by using the metathesis reaction of $NaBF_4$ with [RmIm]Br in dichloromethane under inert atmosphere at RT. The characterization and determination of purities were performed by ^{1}H NMR spectroscopic analysis the data were in agreement with reported values. The ionic liquids were dried under vacuum to remove excess water; the water content of the ionic liquids was measured before making the solution by a Karl–Fischer coulometer and did not exceed 50 ppm for all ionic liquids.

Table 6. The w/w ratios of the ionic liquid to molecular solvent used in the current study.

Ionic liquid	Water	DMSO	EG
[bmIm][BF_4]	0.020	0.021	0.023
[omIm][BF_4]	0.026	0.026	0.029
[bmIm]Br	0.020	0.020	0.022
[hmIm]Br	0.022	0.023	0.025
[omIm]Br	0.025	0.026	0.028
[HmIm][HCOO]	0.011	0.012	0.012
[HmIm][CH_3COO]	0.013	0.013	0.014
[HmIm][CH_3CH_2COO]	0.014	0.014	0.015
[HbIm][CH_3COO]	0.017	0.017	0.018

The w/w ratios of a given ionic liquid to water, DMSO, and ethylene glycol used in the above work are given in Table 6.

Conductivity Measurements

The specific conductivities σ were measured with a Synchrotron 306 conductometer at 1 kHz. The conductivity meter was calibrated by using a 0.1 M potassium chloride (KCl) solution.[52] The cell constant was determined with standard aqueous solutions of KCl. A 0.1 M solution of ionic liquids was prepared and σ was measured at a temperature range from 293.15 to 348.15 K with constant stirring. The molar conductivity was calculated by using the equation $\Lambda_m = (\sigma/c)\times1000$, where σ is the specific conductivity and c is the concentration in mole per liter. The uncertainties were estimated to be ±0.1% for concentration and 1% for σ, respectively. The temperature of the jacket was maintained with a JULABO thermostat with an accuracy of ±0.01 K.

Viscosity Measurements

All the experiments were performed with a Brookfield-ultra rheometer with a cone plate. The viscosity was measured with a 0.1 M solution of binary systems of ionic liquids with molecular solvents at temperatures from 293.15 to 323.15 K. Temperatures of the systems were monitored with a JULABO thermostat bath with an accuracy of ±0.01 K. The calibration of the instrument was performed by taking the reported viscosity data of aqueous solutions of NaCl and KCl with different concentration. The accuracy of the instrument was determined to be ±1%.[52]

PGSE-NMR Measurements

The pulsed-field gradient spin-echo (PGSE) NMR technique was used to measure the self-diffusion coefficients of both the cation and anion species by observing ^{1}H nuclei. The PGSE-NMR measurements were performed with a Bruker Avance 400 ultra shield spectrometer with a 9.4 T superconducting magnet. The spectrometer was equipped with a 2D sequence for diffusion measurement. The self-diffusion coefficients were measured by using a stimulated echo sequence, longitudinal-eddy-current delay (LED), and bipolar gradient pulses to improve the self-diffusion coefficient measurements.[53] The experiment was carried out at 0.1 M solution and at four temperatures ranging from 298.15 to 313.15 K with an increment of 5 K. Self-diffusion coefficients, D, were calculated by using Equation (6):[54]

$$I = I_o \exp\left[-\gamma 2\, g\, 2\delta\, 2D\, (\Delta - \delta/3)\right] \qquad (6)$$

where I is the measured intensity with field gradient g, and I_0 is the equilibrium intensity; δ, Δ, γ and D are the effective gradient pulse, diffusion time, gyromagnetic ratio, and diffusion coefficient, respectively. The samples were thermally equilibrated at each temperature for 30 min before measurements were performed.

1D ^{1}H NMR Measurements

^{1}H NMR spectra were obtained with a Bruker 200 MHz spectrometer at ambient temperature, and chemical shift values are given in parts per million (ppm) relative to respective solvent and TMS signals as internal standards.

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Keywords: conducting materials · electrochemistry · electrostatic interactions · ionic liquids · ion pairs

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