Indian Journal of Chemistry
Vol. 55A, May 2016, pp. 544-553

Tuning the physicochemical properties of protic-aprotic ionic liquids upon reciprocal binary mixing

Pankaj Bharmoria[a], Tushar J Trivedi[a], Naved I Malek[b,]* & Arvind Kumar[a,c,]*

[a]AcSIR, CSIR-Central Salt and Marine Chemicals Research Institute, GB Marg, Bhavnagar 364 002, India
[b]Applied Chemistry Department, Sardar Vallabhbhai National Institute of Technology, Surat 395 007, India
[c]Salt and Marine Chemicals Division, CSIR-Central Salt and Marine Chemicals Research Institute, GB Marg, Bhavnagar 364 002, India
Email: arvind@csmcri.org/mailme_arvind@yahoo.com

Received 17 September 2015; revised and accepted 27 April 2016

The alterations in properties of protic/aprotic (2-hydroxyethylammonium formate)/ 1-butyl-3-methylimidazolium methyl sulfate) ionic liquids (ILs), based on reciprocal binary mixing concept ([A][B][X][Y]) have been investigated by studying the density, speed of sound, and viscosity of mixtures as a function of temperature. The volume of mixing, isentropic compressibility, excess molar isentropic compressibilities and activation energy of viscous flow have been derived, which indicate a very high level of non-ideality in the mixtures desired to take advantage of improved solvent properties. FTIR spectral analysis and solvatochromic parameters (normalized Reichardt's parameter, dipolarity/polarizibility, hydrogen bond donor and acceptor coefficients) determined through the solvatochromic probes have been utilized to examine the hydrogen bonding and ion-ion interactions prevailing in the studied systems. Although significant alterations in hydrogen bonding and ion-ion interactions are observed, dispersion type interactions dominate over chemical interactions as indicated by a high positive deviations in the volumes of mixing.

Keywords: Solution chemistry, Ionic liquids, Protic ionic liquids, Aprotic, Reciprocal binary mixing

Ionic liquids (ILs) have huge potential as a solvent for an array of applications.[1-4] The desired properties of ILs can be attained by (1) tuning the structure of cation/anions (2) direct synthesis of so called "Double Salt Ionic Liquids (DSILs)" through direct mixing of multiple ions,[5] or (3) by mixing two or more ionic liquids at different mole fractions. Chatel *et al.*[5] have defined DSILs as "salts composed of more than two types of ions, liquid at low temperature (<373 K), where each unique combination of ion types and ion ratios constitutes a unique DSIL, leading to properties specific to that combination". On the other hand, in binary mixtures of ILs the identities of the individual components are retained. Therefore, mixing the ILs containing ions of diverse nature and different sizes and a highly non-ideal mixture with improved properties can be synthesized for specific application. IL mixtures have been classified into binary ([A][X][Y] or [A][B][X]), reciprocal binary ([A][B][X][Y]), ternary ([A][X][Y][Z] or [A][B][C][X]) and reciprocal ternary ([A][B][X][Y]) on account of number of components and constituents.[1] Considering these conventions the [HEA][HCOO] +[C_4mim][C_1OSO_3] mixture studied in this article is a reciprocal binary type. Recently, Niedermeyer *et al.*[1] and Chatel *et al.*[5] have systematically reviewed studies on IL mixtures and found that large part of these investigations are focussed on mixtures having combinations of aprotic cations and hydrophobic anions or either cation/anion in common.[6-20] Khupse *et al.*[21] have analysed the temperature dependence of viscosity of a binary mixture of [C_4mim][BF_4]+[[C_4mim][PF_6] and [C_6mim][BF_4]+[[C_6mim][PF_6] mixtures in light of Vogel-Fulcher-Tammann (VFT) equation and showed the importance of mixture for chemical processes. Binary IL mixtures involving a common cation, [C_4mim] and commonly used anions (Cl, Br, [BF_4], [PF_6] or [NTf_2]) have also been investigated by means of IR spectroscopy and a good molecular mixing without a nanosegregation of domains has been reported.[22] Fletcher *et al.*[23] have studied the solvatochromic behaviour in terms of hydrogen bond donor capacity and competitive anion coordination effects in the binary mixtures of [C_4mim][Tf_2N]+[C_4mim][PF_6],[C_2mim][Tf_2N] +[C_4mim][Tf_2N] and [C_2mim][Tf_2N]+[C_4mim][PF_6]. Kagimoto *et al.*[24] have also determined the Kamlet-

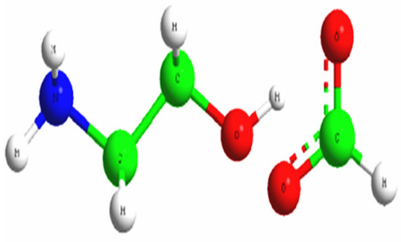
Taft parameters of some polar and low viscosity amino acid-based ILs as a function of ionic composition.

As can be seen from literature the mixing studies in ILs are largely restricted towards examining the changes in thermo-physicochemical properties of aprotic binary combinations and lacks molecular level investigations using spectroscopic/microscopic techniques with ions of diverse chemical nature, which can results in improved properties with clear understanding of structure property relationship. Therefore, in the present article the alteration in macroscopic properties in relation to changes in the microscopic structure of IL has been investigated for a reciprocal binary mixture containing a protic ionic liquids (PIL), 2-hydroxyethylammonium formate ([HEA][HCOO]) with an aprotic ionic liquid (APIL) viz., 1-butyl-3-methylimidazolium methylsulfate ($[C_4mim][C_1OSO_3]$). The primary physical properties such as density (ρ), speed of sound (u), viscosity (η) at different mole fractions at 298.15, 308.15 and 318.15 K were measured and used to derive excess volumes (V_m^E), isentropic compressibility (κ_s) and the activation energy of viscous flow (E_a). Various chemical interactions in the system were observed by comparing the FT-IR spectra of mixtures at different mole fraction. The solvatochromic parameters, E_T^N (normalized Reichardt's parameter), π^* (dipolarity/polarizability coefficient), β (hydrogen bond acceptor coefficient) and α (hydrogen bond donor coefficient) were determined through UV measurements at 298.15 K.

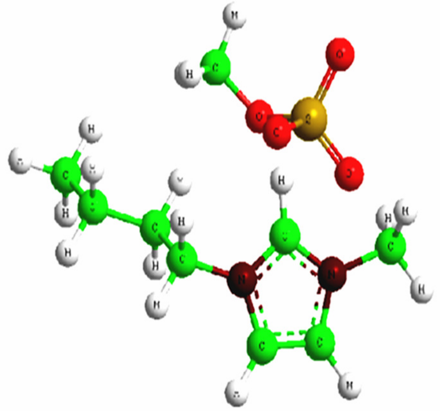
Materials and Methods

2-Hydroxyethylammonium formate (HEA][HCOO]) was synthesized in our laboratory according to the procedure published elsewhere[25] and characterized for purity using ^{1}H-NMR, ^{13}C-NMR and mass spectrometry. The purity of the synthesized IL was higher than 98% mass fraction. 1-Butyl-3-methylimidazolium methylsulfate ($[C_4mim][C_1OSO_3]$) with >98% mass fraction was purchased from Solvent Innovation, Germany. All the ILs used were dried as described in our earlier publication[26] and water content as measured from Karl Fischer titration was < 200 and 170 ppm respectively for [HEA][HCOO] and $[C_4mim][C_1OSO_3]$. Binary mixtures of ILs at different mole fractions were prepared by weight using an analytical balance with a precision of ±0.0001 g (Denver Instrument APX-200) in a glove box in nitrogen atmosphere. Reichardt's dye and 4-nitroaniline were procured from Sigma-Aldrich, while N,N-diethyl-4-nitroaniline was purchased from Oakwood Products. Inc.

Density (ρ) and speed of sound (u) of various IL mixtures were measured using an Anton Paar (model DSA5000) vibrating tube density meter with a resolution of 5×10^{-6} g cm^{-3} and 0.01 m s^{-1}. The temperature of the apparatus was controlled to within ±0.01 K by a built-in Peltier device that corresponds to an uncertainty in density of ±0.0002% and speed of sound ±0.1%. Dried and degassed samples kept in desiccators were directly injected through a syringe in the measuring cell. The reproducibility of the results was confirmed by performing at least three experiments for each sample in the entire temperature range. Observed and literature values of physical properties are compared in Table S1 (Supplementary Data). Viscosity (η) measurements were made using an Anton Paar Automated Microviscometer (AVMn) which is based on falling ball principle. The temperature of the apparatus was controlled to within ±0.1K by a built-in Peltier device. Uncertainty



(HEA[HCOO])



($[C_4mim][C_1OSO_3]$)

in viscosity measurements was ±0.001%. Fourier transform infrared (FT-IR) spectra of the samples at 298.15 K were recorded on Nicolet 6700 FT-IR spectrometer in a demountable cell using BaF_2 window with a Teflon spacer. The optical path length was 0.02 mm. Temperature was controlled to within ±0.1K with an inbuilt Peltier device. For each spectrum, 32 scans were made with a selected resolution of 4 cm^{-1}. Solvatochromic parameters were determined by measuring the maximum absorption wavelength (λ_{max}) of solvatochromic probes (Reichardt's dye, 4-nitroaniline and N-N-diethyl-4-nitroaniline) at 298.15 K, with a concentration of about 10 μ*M*, in IL mixtures, using a UV 3600 Shimadzu UV-vis-NIR spectrophotometer with a thermocell attached to it. The stock solutions of 1 m*M* of the probes were prepared in absolute methanol. For each measurement 0.016 g of the probe solution was taken in a quartz cuvette (path length 1 cm), evaporated under vacuum and diluted to 1.6 g with various IL mixtures to make the final concentration 10 μ*M*. For complete mixing, the solutions were stirred for 12 h on a magnetic stirrer in a glove box and stored in a vacuum desiccator containing P_2O_5 for 24 h before measurements.

Results and Discussion

Physical properties

Experimental variation in density (ρ) of [HEA][HCOO](x_1)+[C_4mim][C_1OSO_3](x_2) mixture at temperatures 298.15 K, 308.15 K and 318.15 K is plotted in Fig. 1(a) and corresponding values are tabulated in Table S2 (Supplementary Data). A decrease in density was observed with increase in temperature due to loosening of bonds because of enhanced thermal motion of molecules. The density plots were fitted using third order polynomial equation with a standard deviation of 0.005 at 298.15 K. Accuracy of the fitting was indicated by correlation coefficient (R^2) value > 0.99 in all the cases. The density of an ionic liquid depends upon the packing of ions in a given volume which is controlled by size and shape of the ions along with prevailing interactions among the ions.[27] The ρ of mixtures decreased non-linearly as a function of x_1 at all the temperatures, thus indicating non-ideal mixing. The non-ideality in a mixture arises due to spacing among the ions because of improper packing. The extent of nonideality in a mixture can be estimated from the extent of molecular level interactions among ions from the excess molar volume (V_m^E), which can be calculated from the experimental ρ using Eq. (1),

$$V_m^E = V_m - V_m^{id} = \frac{(x_1M_1 + x_2M_2)}{\rho} - \left[\frac{x_1M_1}{\rho_1^*} + \frac{x_2M_2}{\rho_2^*}\right] \quad \ldots(1)$$

where V_m and V_m^{id} are the real and ideal molar volumes of the solutions; ρ, ρ_1^* and ρ_2^* are the densities of a

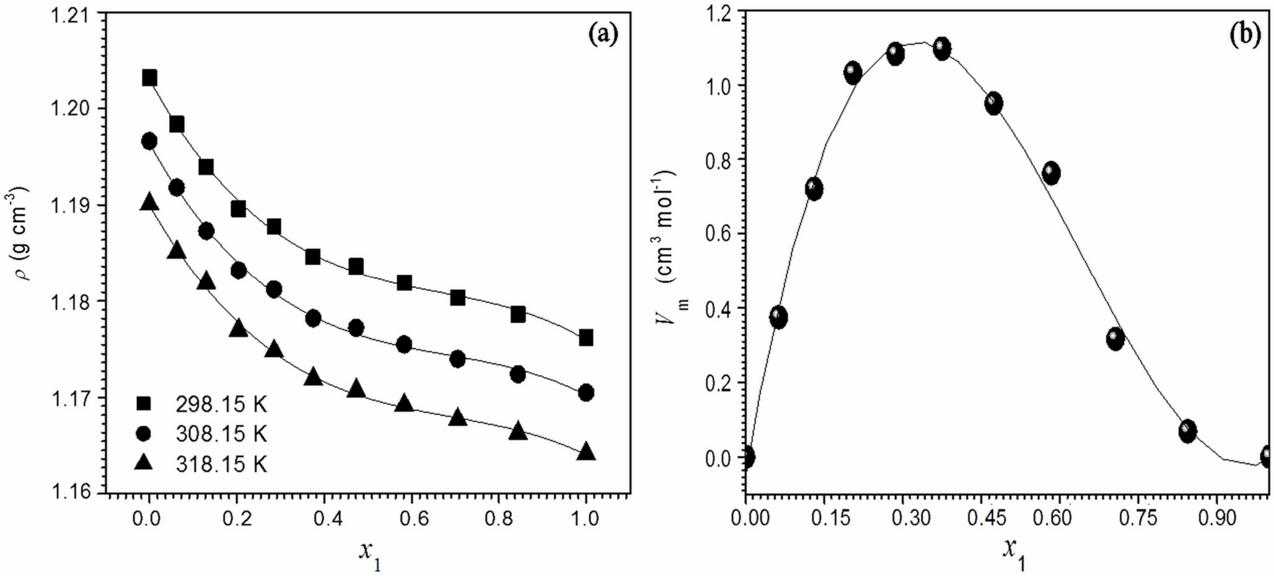


Fig. 1—Plots showing (a) variation in density at different temperatures, and, (b) excess molar volume (V_m^E) at 298.15 K of [HEA][HCOO](x_1) + [C_4mim][C_1OSO_3](x_2) mixture at different mole fractions.

mixture comprising component 1 and component 2; M_1, M_2 and x_1, x_2 are the molar masses and mole fractions of component 1 and component 2 respectively. V_m^E, calculated at 298.15 K, is plotted in Fig. 1(b). A third order polynomial equation indicated a standard deviation of 0.002. A large positive deviation in V_m^E has been observed as compared to that of reported binary mixtures of imidazolium or pyridinium ILs containing either cation or anion in common.[10-13] The large positive V_m^E indicates expansion of volumes upon mixing, which can be accounted to the inefficient packing of ions in the [HEA][HCOO](x_1)+[C$_4$mim][C$_1$OSO$_3$] mixture, due to the large difference in size and dominance of physical interactions over the chemical/specific interactions between unlike ions.[14]

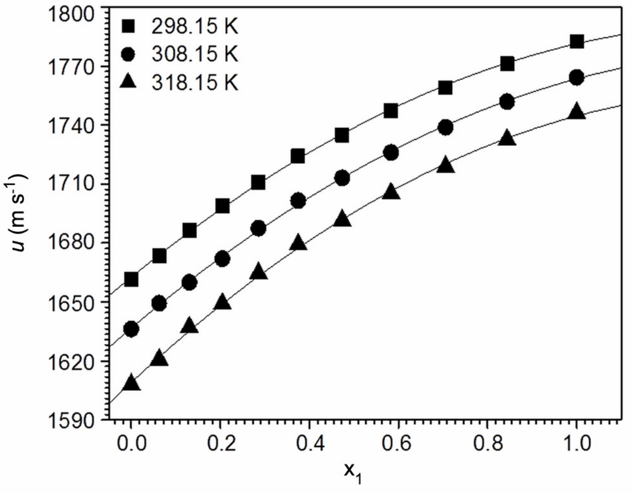


Fig. 2—Plots showing variation in speed of sound of [HEA][HCOO] (x_1)+[C$_4$mim][C$_1$OSO$_3$] (x_2) mixture at 298.15, 308.15, and 318.15 K at different mole fractions.

Therefore, we further looked into the rigidity of solution mixtures which is controlled by various non-covalent interactions by measuring the isentropic compressibility (κ_s). The κ_s was calculated using Newton-Laplace equation[29] ($\kappa_s = 1/u^2\rho$) from experimental ρ and speed of sound (u) data (third order polynomial equation gives a standard deviation of 0.8 at 298.15 K). The u value increased with an increase in x_1 (Fig. 2 and Table S3), indicating that solution rigidity increases as the speed of sound is increases upon moving from loosely packed to tightly packed structures. These observations were further supported by isentropic compressibility results plotted in Fig. 3(a). At the studied temperatures, [C$_4$mim][C$_1$OSO$_3$] is more compressible than [HEA][HCOO]. With the increase in concentration of x_1, the solutions became less compressible as indicated by the decrease in κ_s. The increase in rigidity of the solution can be ascribed to the increase in hydrogen bonding in the solution microstructure (discussed later), since [HEA][HCOO] has a hydrogen bond donor protic cation and good hydrogen acceptor [HCOO] anion. An increase in κ_s

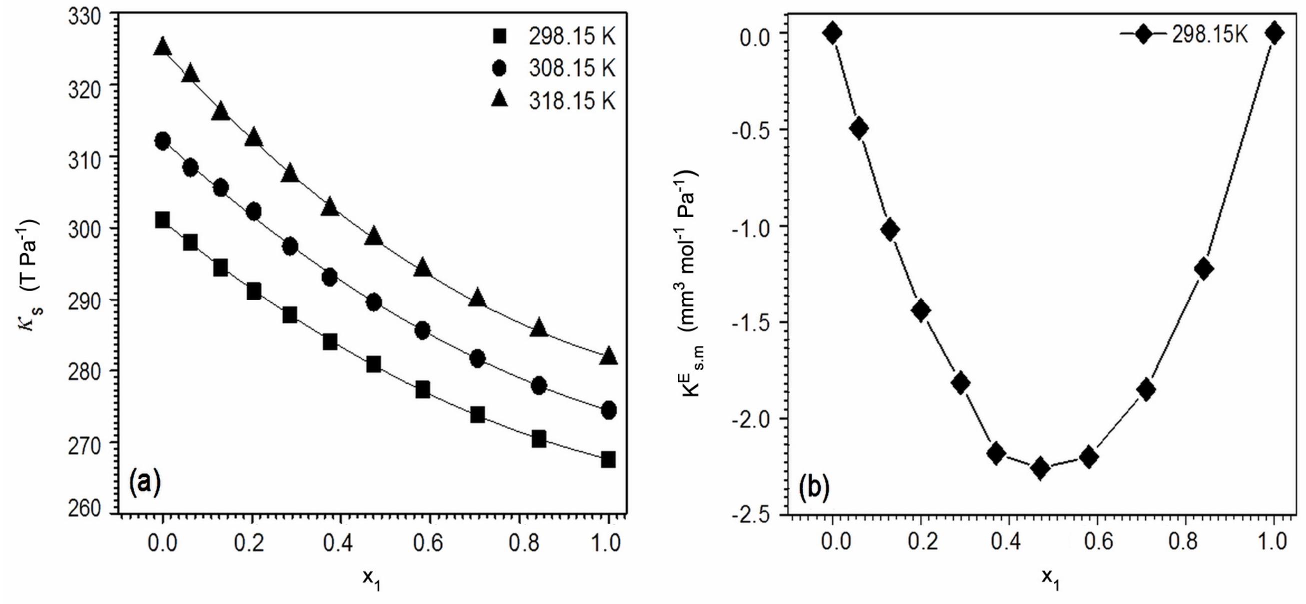


Fig. 3—Plots showing (a) variation in isentropic compressibility (κ_s), and (b), excess molar isentropic compressibilities ($K_{s,m}^E$) of [HEA][HCOO] (x_1)+[C$_4$mim][C$_1$OSO$_3$] (x_2) mixtures at different mole fractions at 298.15, 308.15 and 318.15 K.

with rise in temperature from 298.15 K to 318.15 K occurs due to the weakening of bonding interactions assisted by increased thermal motions. Excess molar isentropic compressibilities $K_{s,m}^{E}$ at 298.15 K were calculated from differences of real molar isentropic compressibilities ($K_{s,m}$) and ideal molar isentropic compressibilities ($K_{s,m}^{id}$)[30,31]. Standard deviation in fitting of $K_{s,m}^{E}$ to third degree polynomial was 0.0095. $K_{s,m}^{E}$ is negative over the entire range of mole fraction, Fig. 3 (b). This behaviour is similar to that of V_m^E, but with opposite sign. Negative $K_{s,m}^{E}$ indicates that the mixture is less compressible than the corresponding ideal mixture.

Since flow property of liquids defines their applications as medium for various processes to be carried out, we measured the alterations in viscosity (η) of ILs upon mixing. The experimental η versus x_1 plots at 298.15 to 318.15 K are shown in Fig. 4 and corresponding values are tabulated in Table S4 (Supplementary Data). Standard deviation in fitting of η versus x_1 to fifth degree polynomial was 1.20 at 298.15 K. The η decreases as a function of x_1, attains a minimum value at x_1 = 0.47 and increases further at higher mole fractions. On account of the unsymmetrical nature of cations of both the ILs, we fitted the temperature dependence of η at different mole fractions using an Arrhenius-like law.[27,32]

$$\ln\eta = \ln\eta_\infty - E_a/RT \quad \ldots(2)$$

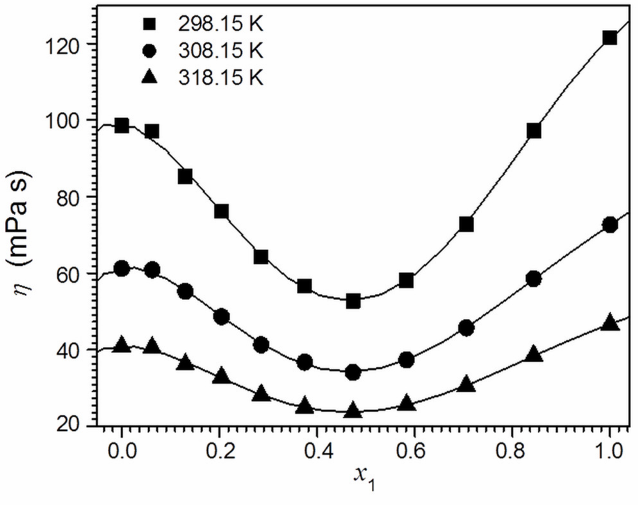


Fig. 4—Plots showing variation in viscosities (η) of [HEA][HCOO] (x_1)+[C_4mim][C_1OSO_3] (x_2) at 298.15 K, 308.15 K, and 318.15 K.

In Eq. (2), η is viscosity, E_a is activation energy of viscous flow, R is universal gas constant and T is working temperature of the system in Kelvin. The Arrhenius fits of lnη versus 1/T of [HEA][HCOO](x_1)+[C_4mim][C_1OSO_3](x_2) mixture at various mole fractions are shown in Fig. 5(a). With the increase in temperature, the η values decrease at all the mole fractions due to the loss of interionic forces causing an increase in velocity gradient of different layers in the solution mixture. We also calculated the activation energy of viscous flow (E_a) from the slope of Arrhenius fits. The plot of E_a versus x_1 is shown in Fig. 5(b). E_a is found to be minimum near the equi-molar concentration (x_1 = 0.47). These results show that viscosity of IL solution can be easily altered as required by diffusion dependent processes such as electrochemistry,[33] gas absorption[34] and biochemical reactions.[35]

Solution structure and solvatochromic behaviour

The utility of ILs as solvents depends upon their solution structure and solvatochromic characteristics. Being differentially polar solvents, ILs are composed of different polar/non-polar domains kept intact by electrostatic, hydrogen bonding and van der Waal's interactions.[36] Since the mixtures contain ions having capability of hydrogen bonding along with obvious electrostatic interactions, we have examined the solution microstructure from FT-IR measurements. FT-IR spectra have been recorded at different mole fraction over the entire composition range and are shown in Fig. 6. For better clarity, the spectra have been divided into two frequency regions: 1480–1800 cm^{-1} and 2500–3800 cm^{-1}. Different peaks assigned to the pure spectra of ILs used are provided in the Table S5 (Supplementary Data). Vibrational shifts in the characteristic frequency of ILs upon mixing are plotted as a function of mole fraction and are shown in Fig. S1 (Supplementary Data).

In the FT-IR spectra, a blue shift of 28 cm^{-1} for the peak at 3287 cm^{-1} (ν O-H of HEA) was observed upon addition of [C_4mim][C_1OSO_3] up to x_2 = 0.52 (Fig. 6 (b) and Fig. S1(a)). It is to be noted that protic ILs ethylammonium nitrate (EAN) and propyl ammonium nitrate (PAN) have been reported to form three-dimensional hydrogen bonding network by Fumino *et al.*[37] Therefore, structure of the protic part of the mixture, [HEA][HCOO], is maintained by strong C–O$^-\cdots$H–O and C–O$\cdots$H–N$^+$ hydrogen bonding interactions. It is due to these interactions

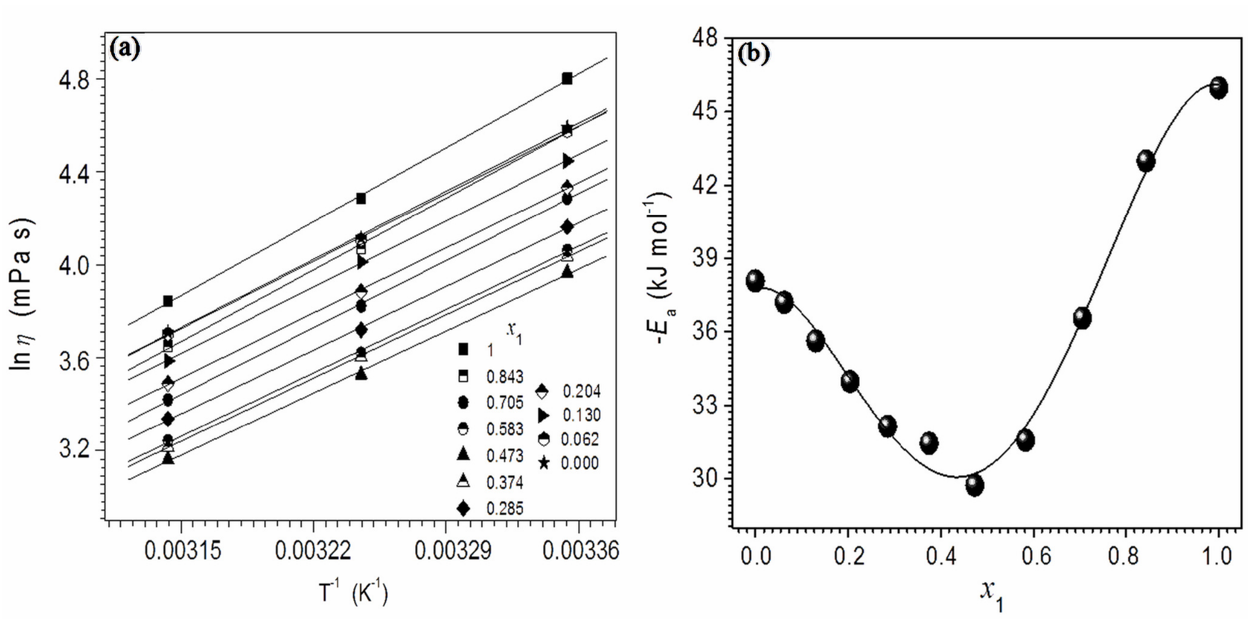


Fig. 5—(a) Arrhenius plots (lnη versus T^{-1}) showing variation in viscosity as a function of temperature, and, (b) variation in activation energy of viscous flow (E_a) of [HEA][HCOO](x_1)+[C_4mim][C_1OSO_3](x_2) mixture at different mole fractions.

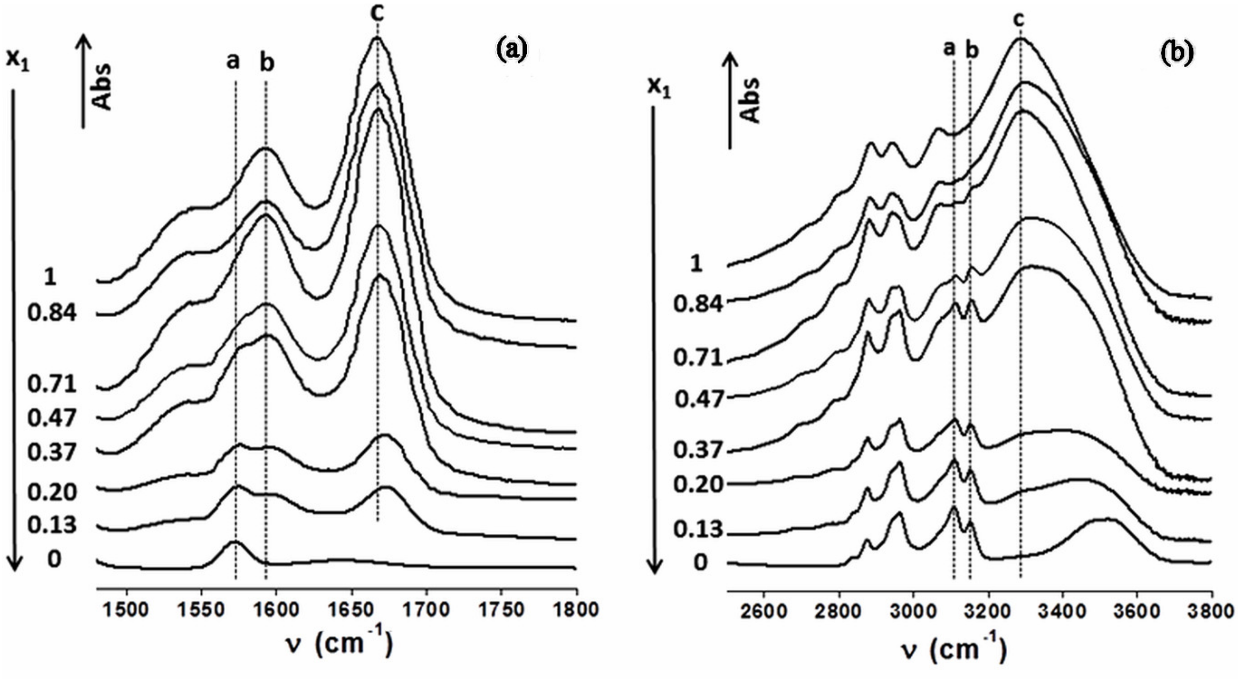
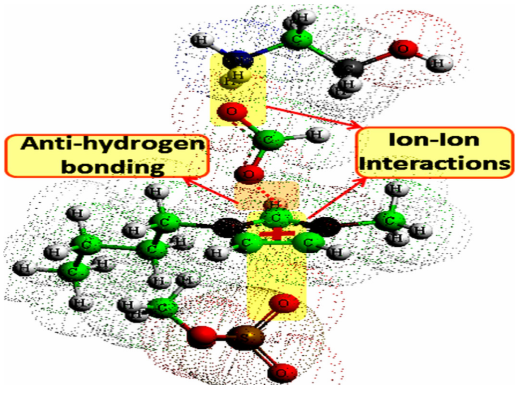


Fig. 6—FT-IR spectra of [HEA][HCOO](x_1)+[C_4mim][C_1OSO_3] (x_2) mixtures at different mole fractions in the (a) mid and (b) high frequency regions.

that highest rigidity was observed for [HEA][HCOO]. The blue shift in the overlapped νN-H, νO–H band of HEA$^+$ at 3287 cm^{-1} upon increasing the mole fraction of [C$_4$mim][C$_1$OSO$_3$] indicates the breakage of the hydrogen bonding network of [HEA][HCOO]. Moreover, in the [C$_4$mim][C$_1$OSO$_3$] rich region the absorption can be accounted to the quaternary nitrogen of imidazolium.(+NR$_4$). The C(2)H band of [C$_4$mim]$^+$ at 3151 cm^{-1} undergoes a blue shift of 17 cm^{-1} on addition of [HEA][HCOO] up to $x_1 = 0.84$, Fig. 6(b) and Fig. S1(b), which may be ascribed to the formation of a weak C(2)H···O=C hydrogen bond due to strengthening of C–H bond. A blue shift usually occurs due to weak or anti-hydrogen bonding arising due to the dominance of ion-ion interactions over prevailing hydrogen bonding interaction.[38] C–H···O weak or anti- hydrogen bonding has been studied extensively in the crystals of organic molecules and mixture of organic liquids and very recently in ILs.[39-41] The electron density transfer from proton acceptor (a Brønsted base) to the remote part of proton donor has been cited as the most probable reason for this phenomenon.[39-41] A red shift of 2 cm^{-1} in the asymmetric stretching band of C=O of HCOO (1387 cm^{-1}) and blue shift of 2 cm^{-1} in the symmetric stretching band of C=O of HCOO (1593 cm^{-1}) was observed with the addition of [C$_4$mim][C$_1$OSO$_3$] up to $x_2 = 0.87$, Fig. 6(a) and Fig. S1(c). Red shift in symmetric (1593 cm^{-1}) and blue shift in asymmetric (1387 cm^{-1}) stretching vibrational bands of O–C–O indicate a balance of forces between the ions upon mixing. The ion-ion interaction in the mixture is depicted in Scheme 1. Izgorodina *et al.*[41] have reported that the ion-ion interactions in [C$_2$mim][Cl] are most favourable when Cl$^-$ approaches the C$_2$mim$^+$ from above or below the plane of C$_4$mim$^+$ ring. Therefore, we propose that in the present systems, HCOO$^-$ approaches the C$_4$mim$^+$ from above or below the plane of ring for ion-ion interactions.



Possible arrangement of ions in the reciprocal binary mixture

Scheme 1

The polarity of a solution plays a key role in its solvating ability by various specific and non-specific interactions with solute molecules. Therefore, the solvatochromic behaviour has been measured from Kamlet-Taft solvatochromic parameters, E_T^N, $E_T(30)$, π^*, α and β using Reichardt's dye (RD), nitroanilone (4NA) and N-N-diethyl-4-nitroaniline (DENA) as solvatochromic probes. The experimental solvatochromic parameters plotted as a function of [HEA][HCOO] mole fraction (x_1) are shown in Fig. 7 and corresponding values are tabulated in Table S6 (Supplementary Data). The maximum wavelength ($\lambda_{\max}$) values of the different dyes in the IL mixtures at various mole fractions are tabulated in Table S7 (Supplementary Data) and corresponding UV-vis spectra are shown as Fig. S2 (Supplementary Data). On comparison with literature values, the calculated values of π^*, α and β of the pure ILs are within the experimental error.[42] In Fig. S2, for [C$_4$mim][C$_1$OSO$_3$], the literature value of α, i.e., 0.53 has been used.[43]

The E_T^N (kcal mol^{-1}) the normalized Reichardt's parameter (indicates solute-solvent interactions and polarity of the solution) was calculated from the maximum absorption wavelength of Reichardt's dye

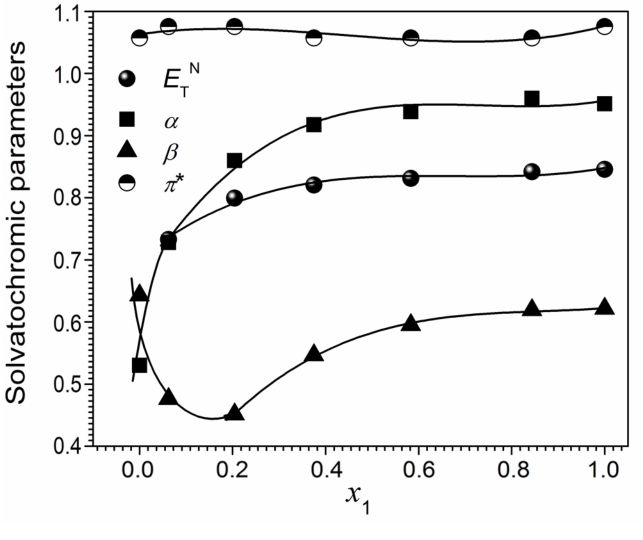


Fig. 7—Plots showing variation of solvatochromic parameters (E_T^N, α, β, π^*) of [HEA][HCOO] (x_1)+[C$_4$mim][C$_1$OSO$_3$] (x_2) mixture at different mole fractions.

using Eq. (3).[42]

$$E_T^N = (E_T(30) - 30.7)/32.4 \qquad ...(3)$$

where the parameter $E_T(30) = 28591/\lambda_{\max}(\mathrm{RD})$ is the Dimroth-Reichardt parameter which indicates both dipolarity/polarizibility and acidity of the solvent.[42] The E_T^N has been found to increase with an increase in x_1, which indicates that the polarity of the mixture increases in moving from $[C_4mim][C_1OSO_3]$ to [HEA][HCOO]. This effect can be attributed to the presence of non-polar butyl chain in the imidazolium cation in $[C_4mim][C_1OSO_3]$ whose magnitude decreases with decrease in concentration of $[C_4mim][C_1OSO_3]$.

The parameter π^* was calculated from the changes in maximum absorption energy of the dye which induced the local electric field generated by the solvent. It is affected by the dye-solvent interaction with the increase in mole fraction of one of the components.[44] It indicates the dipolarity/polarizability of solvent, and was calculated by measuring the $\lambda_{\max}$ of dye, N-N-diethyl-4-nitroaniline in different IL mixtures using Eq. (4).[45-47]

$$\pi^* = (27.52 - \nu_{\mathrm{DENA}})/3.183 \qquad ...(4)$$

The calculated values of π^* for all the studied mixtures were ≥1, which indicates that the mixtures are highly polarizable solvents. This behaviour may be due to the large sizes and polar/nonpolar domains and ionic nature of IL used.[46] It is to be noted that high polarizibility in a mixture arises due to the presence of molecular ions having delocalized electrons.[42] The presence of molecular ions having delcolized electrons in both ILs demonstrates the high polarizilbity of the mixtures.

The parameters, α and β indicate the hydrogen bond donor capacity (HBD) and hydrogen bond acceptor capacity (HBA) of solvents and were calculated by measuring the variation in $\lambda_{\max}$ of Reichardt's dye (RD), N-N-diethyl-4-nitroaniline and nitroaniline (4NA) in ILs mixture using Eqs (5)[48,49] and (6).[47,50]

$$\alpha = E_T(30) - 14.6(\pi^* - 0.23) - 30.31/16.5 \qquad ...(5)$$

$$\beta = 1.035 \cdot \nu_{\mathrm{DENA}} - \nu_{\mathrm{4NA}} + 2.64/2.8 \qquad ...(6)$$

In Eqs (5) and (6), ν_{DENA} (kilokeyser, 10^{-3} cm^{-1}) = $10000/\lambda_{\max}$ and ν_{NA} (kilokeyser, 10^{-3} cm^{-1}) = $10000/\lambda_{\max}$ are the wave numbers corresponding to maximum absorption wavelengths of the dyes, DENA and 4NA in the ionic liquid mixtures.

An increase in α as a function of [HEA][HCOO] was observed, which indicates the increase in hydrogen bond donor capacity of the mixture. The maximum deviation from linearity in α is seen at x_1 ~0.40, where the activation energy of viscous flow is also quite low and electrostatic interactions among ions are suggested to be significantly reduced in the mixture. At higher mole fractions ($x_1 \geq 0.40$), the values of α at saturation are close to that of pure [HEA][HCOO] showing that there is very little change in the hydrogen bonding donor capacity due to the imidazolium cation in [HEA][HCOO] rich region of the mixture.

The β value decreased initially with the increase in x_1 and attained a minimum value (x_1=0.21), and increased thereafter in a non-linear fashion. The decrease in β indicates the decrease in hydrogen bond accepting ability and solvent strength of the mixture. In both systems, a sharp increase in HBD (α) was observed till x_1 ~0.40 and a nearly constant value was reached thereafter. Since the β parameter depends upon the nature of the anion, the initial decrease in β may be due to competition between $[C_1OSO_3]$ and [HCOO] anions (having similar hydrogen bond acceptor oxygen atom) for hydrogen bond donor site of [HEA]. The increase in β above x_1 = 0.21 is due to more site specific interactions in the system.

Conclusions

The present study shows that the desired physicochemical properties pertaining to specific application can be easily achieved by mixing two ionic liquids exhibiting different properties. Reciprocal binary mixing has the additional advantage of all the four ions exhibiting different properties, each of which can be tuned by changing the mixing ratios. Experimental evidences obtained from different physicochemical and spectroscopic analysis of the reciprocal binary mixtures of [HEA][HCOO]+ $[C_4mim][C_1OSO_3]$ have demonstrated the feasibly of this concept. A significant departure from ideality in volume of mixing and excess molar isentropic compressibilities compared to binary mixtures containing common cation or anions indicate different macroscopic behaviour of such mixtures. The viscosity of mixtures show a minima at equimolar composition which can be ascribed to the decrease in electrostatic interactions among the ions. This behaviour is also evident from the behaviour of activation energy of viscous flow. Low viscous IL mixtures can be utilized for diffusion dependent applications such as gas absorption, electrochemistry and biochemical reactions. At the microscopic level, anti-hydrogen bonding (C(2)···H···O–C) was observed at the C(2)–H position of [C_4mim] cation due to the dominance of ion-ion interactions between ions of different ILs. The dominance of ion-ion interactions was also evident from the breaking of the hydrogen bonding network of [HEA][HCOO] upon mixing with [C_4mim][C_1OSO_3]. The solvatochromic properties of mixtures showed that the mixtures are highly polar throughout the composition range and the microenvironment of ILs around the probe remains nearly the same as that of the bulk of the mixture. Good hydrogen bond basicity and polarity of mixtures support their candidature as solvents for biopolymer processing.

Acknowledgement

PB and NIM acknowledge Department of Science and Technology, Govt of India, New Delhi, India, for financial support from the projects (SB/S1/PC-104/2012) and (SR/FT/CS-014/2010) respectively. TJT is thankful for financial assistance by Council of Scientific and Industrial Research, Govt of India, New Delhi, (EMR-II/2545/2011). The Analytical Division of CSIR-CSMCRI is acknowledged for sample characterization.

Supplementary Data

Supplementary data associated with this article, i.e., synthesis procedure of [HEA][HCOO], Figs S1-S2 and Tables S1-S7, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(05)544-553_SupplData.pdf.

References

1 Niedermeyer H, Hallett J P, Villar-Garcia I J, Hunt P A & Welton T, *Chem Soc Rev*, 41 (2012) 7780.
2 Holbrey J D & Rogers R D, *Technol Rev*, 118 (2002) 446.
3 Singh G & Kumar A, *Indian J Chem,* 49A (2008) 495.
4 Khupse N D & Kumar A, *Indian J Chem,* 49A (2010) 635.
5 Chatel G, Pereira J F B, Debbeti V, Wang H & Rogers R D, *Green Chem,*16 (2014) 205.
6 Stoppa A, Buchner R & Hefter G, *J Mol Liq,* 153 (2010) 153, 46.
7 Annat G, Forsyth M & MacFarlane D R, *J Phys Chem B*, 116 (2012) 8251.
8 Pint A M, Rodríguez H, Colón Y J, Arce, Jr A, Arce A & Soto A, *Ind Eng Chem Res,* 52 (2013) 5975.
9 Navia P, Troncoso J & Romaní L, *J Solution Chem,* 37 (2008) 677.
10 Lopes J N C, Cordeiro T C, Esperança J M S S, Guedes H J R, Huq S, Rebelo L P N & Seddon K R, *J Phys Chem B*, 109 (2005) 3519.
11 Oliveira M B, Domínguez-Pérez M, Freire M G, Llovell F, Cabeza O, Lopes-da-Silva J A, Vega L F & Coutinho J A P, *J Phys Chem B,* 116 (2012) 12133.
12 Navia P, Troncoso J & Romań L, *J Chem Eng Data,* 52 (2007) 1369.
13 Larriba M, García S, Navarro P, García J & Rodríguez F, *J Chem Eng Data,* 57 (2012) 1318.
14 Fox E T, Weaver J E F & Henderson W A, *J Phys Chem C,* 116 (2012) 5270.
15 Bharmoria P, Damarla K, Trivedi T J, Malek N I & Kumar A, *RSC Adv,* 5 (2015) 99245.
16 Pereiro A B J, Araújo M M, Oliveira F S, Bernardes C E S, Esperança J M S S, Lopes J N C, Marrucho I M & Rebelo L P N, *Chem Commun,* 48 (2012) 3656.
17 Xiao D, Rajian J R, Hines Jr L G, Li S, Bartsch R A & Quitevis E L, *J Phys Chem B*, 112 (2008) 13316.
18 Castiglione F, Raos G, Appetecchi G B, Montanino M, Passerini S, Moreno M, Famularia A & Mele A, *Phys Chem Chem Phys*, 12 (2010) 1784.
19 Brüssel M, Brehm M, Voigt T & Kirchner B, *Phys Chem Chem Phys*, 13 (2011) 13617.
20 Aparicio S & Atilhan M, *J Phys Chem B,* 116 (2012) 2526.
21 Khupse N D, Kurolikar S R & Kumar A, *Indian J Chem,* 49A (2010) 727.
22 Andanson J M, Beier M J & Baiker A, *J Phys Chem Lett,* 2 (2011) 2959.
23 Fletcher K A, Baker S N, Baker G A & Pandey S, *New J Chem,* 27 (2003) 1706.
24 Kagimoto J, Noguchi K, Murata K, Fukumoto K, Nakamura N & Ohno H, *Chem Lett*, 37 (2008) 1026-1027.
25 Bicak N A, *J Mol Liq,* 116 (2004) 15.
26 Singh T & Kumar A, *J Phys Chem B,* 112 (2008) 4079.
27 Jacquemin J, Husson P, Padua A A H & Majer V, *Green Chem,* 8 (2006) 172.
28 Trivedi S & Pandey S, *Indian J Chem,* 49A (2010) 731.
29 Onori G, *Acoustics Lett,* 14 (1990) 7.
30 Douhéret G, Salgado C & Davis M I, *Thermochim Acta,* 207 (1992) 313.
31 Douhéret G, Pal A & Davis M I, *J Chem Thermodyn,* 22 (1990) 99.
32 Seddon K R, Stark A S & Torres M J, *Viscosity and Density of 1-alkyl-3-methylimidazolium ionic liquids,* edited by R D Rogers, K R Seddon, *Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities*, *ACS Symposiom Series* 901, Washigton DC, 2004.
33 Naoki T & Masayoshi W, *J Vac Soc Jpn,* 56 (2013) 67.
34 Pint A M, Rodríguez H, Colón Y J, Arce, Jr A, Arce A & Soto A, *Ind Eng Chem Res,* 52 (2013) 5975.
35 Zhao H, Jones C L & Cowins J V, *Green Chem,* 11 (2009), 1128.
36 Hayes R, Warr G G & Atkin R, *Chem Rev,* 115 (2015) 6357.
37 Fumino K, Wulf A & Ludwig R, *Angew Chem Int,* 48 (2009) 3184.
38 Izgorodina E I & MacFarlane D R, *J Phys Chem B,* 115 (2011) 14659.

39 Desiraju G R & Steiner T, *The Weak Hydrogen Bond* (Oxford University Press, Oxford) 1999.

40 Hobza P & Havlas Z, *Chem Rev,* 100 (2000) 4253.

41 Chang H, Jiang J, Tsai W, Chen G & Lin S H, *J Phys Chem B,* 110 (2006) 3302.

42 Jessop P G, Jessop D A, Fu D & Phan L, *Green Chem,* 14 (2012) 1245.

43 Rani M A A, Brant A, Crowhurst L, Dolan A, Lui M, Hassan N H, Hallett J P, Hunt P A, Welton T & Wilding R, *Phys Chem Chem Phys* 13 (2011) 16831.

44 Khodadadi-Moghaddam M, Habibi-Yangjeh A & Gholami M R, *Monat Chem,* 140 (2009) 29.

45 Kamlet M J, Abboud J L & Taft R W, *J Am Chem Soc,* 99 (1977) 6027.

46 Lopes J N C, Gomes M F C, Husson P, Pádua A A H, Rebelo L P N, Sarraute S & Tariq M, *J Phys Chem B*, 115 (2011) 6088.

47 Crowhurst L, Mawdsley P R, Perez-Arlandis J M, Salter P A & Welton T, *Phys Chem Chem Phys,* 5 (2003) 2790.

48 Taft R & Kamlet M J, *J Am Chem Soc,* 98 (1976) 2886.

49 Lee J, Ruckes S & Prausnitz J M, *J Phys Chem B,* 112 (2008) 1473.

50 Kamlet M J & Taft R W, *J Am Chem Soc,* 98 (1976) 377.