

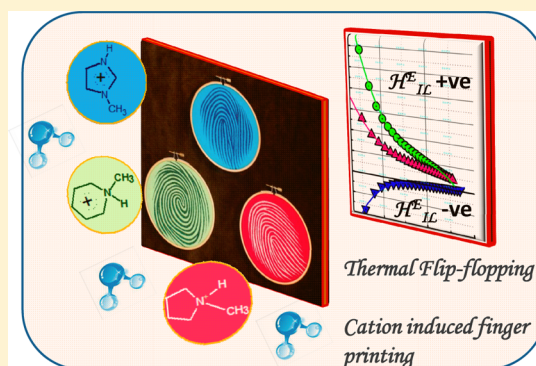
Elucidation of Ionic Interactions in the Protic Ionic Liquid Solutions by Isothermal Titration Calorimetry

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S Supporting Information

ABSTRACT: The strong hydrogen-bonded network noted in protic ionic liquids (PILs) may lead to stronger interactions of the ionic entities of PILs with solvents (water, methanol, ethylene glycol, dimethylsulfoxide (DMSO), *N,N'*-dimethylformamide (DMF)) as compared with those of aprotic ionic liquids (APILs). The PILs used in this work are 1-methylimidazolium tetrafluoroborate, 2-methylpyridinium tetrafluoroborate, and *N*-methylpyrrolodinium tetrafluoroborate in comparison to 1-butyl-3-methylimidazolium tetrafluoroborate, which is classified as an APIL. In this work, the excess partial molar enthalpy, H^E_{IL} , obtained from isothermal calorimetric titrations at 298.15 K is used to probe the nature of interactions of the PIL cations with solvent molecules against those present in APIL–solvent systems. This work also reports interesting flip-flopping in the thermal behavior of these PIL–solvent systems depending upon the structure of the cationic ring of a PIL. In some cases, these flip-flops are the specific fingerprints for specific PILs in a common solvent environment. The excess partial molar enthalpy at infinite dilution, $H^{E,\infty}_{IL}$, of these PILs bears a critical dependence on the solvent properties. An analysis of relative apparent molar enthalpies, ϕ_L , of the PIL solutions by the ion interaction model of Pitzer yields important information on ionic interactions of these systems.



INTRODUCTION

Because of several unique properties like low vapor pressure, chemical stability at higher temperatures, miscibility with polar and nonpolar solvents, recyclability, etc., ionic liquids (ILs) find their utility in a variety of industrial applications.^{1–9} An ionic liquid when mixed with a solvent offers some interesting properties that merit investigation in view of its potential applications. The fine-tuning of properties of an IL can lead to the improvement in the efficiency of a process by adding a cosolvent (another IL or molecular solvent).^{10–14} A cosolvent is a very small amount of solvent that can be added to a pure IL of interest to tailor its physicochemical properties for achieving optimum conditions for synthesis of compounds, extractions, separations, etc. Thus, in view of their importance, it would be of great interest to understand the effect of a small amount of solvent added (or impurities) on the physical properties of different ILs. In addition, it would also be interesting to understand the ion–solvent interactions due to an IL in the presence of an excess amount of the solvent in the system.

ILs can be divided into two broad categories, i.e., aprotic ionic liquids (APILs) and protic ionic liquids (PILs). It was recently demonstrated for the first time that APILs in water exhibit a shift from endothermal to exothermal (excess partial molar enthalpy) profiles upon increasing alkyl chain length from $-C_2H_5$ to $-C_8H_{17}$ attached to the imidazolium ring.^{15–17} These studies confirmed that the behavior of some APIL–solvent systems were not only governed by Coulombic

interactions but also by interactions emerging from the van der Waals forces operating between the hydrophobic parts of the cation and the solvent dipole. These weaker interactions become more formidable, as there is an increase in the hydrophobicity of the APIL cation in terms of the length of alkyl chains.^{18–20} In recent years, experimental determination of enthalpies of the APIL solutions has been investigated.²¹ For example, the partial molar excess enthalpies have been obtained from activity coefficients at infinite dilutions of APILs.²² The molar solution enthalpies of some APILs have been reported.²³ Rebelo and workers have investigated the excess molar enthalpies of ionic liquid systems and presented simple methodologies for calculating excess properties of aqueous ionic liquids.²⁴ The excess partial molar enthalpies of APILs have also been measured and the interaction parameters obtained using an empirical approach.²⁵ Excess enthalpy of mixing of ionic liquid solutions has also been reported.^{26–28} The CHELPG atomic charges obtained during the study were consistent with the observed trends in excess enthalpy of mixing.²⁶ Effort has been made to model the pyridinium-based ionic liquids and their mixtures with the help of a soft statistical associating fluid theory, called the SAFT equation of state.²⁹ The model is shown to be successful in predicting high pressure densities and second order derivative properties of the systems.

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The soft SAFT equations can also describe the phase behavior in the CO₂ and SO₂ containing systems. Recently, Paduszynski and Domanska have presented an exhaustive approach called perturbed-chain statistical soft statistical associating fluid theory (PC-SAFT) combined with modified UNIFAC (Dortmund) for modeling ionic liquids and their mixtures with solvents.³⁰ An excellent summary of the efforts carried out in the past for using different models to estimate/correlate/predict properties of the ionic liquids is also described in the article. The application of PC-SAFT has led to accurate prediction of heats of mixing data (both endothermal and exothermal) of the ionic liquid–solvent systems. Domanska et al. also measured excess enthalpy of mixing using an isothermal titration calorimeter (TAM III) for the binary mixtures containing isoquinolinium ionic liquids with good comparison with those estimated/predicted by the use of PC-SAFT.³¹ Very recently, molar excess enthalpies of mixing of two piperidinium-based ionic liquids in ethanol and 1-propanol have been measured. These data have been accurately reproduced with the help of the PC-SAFT equation of state.³²

The literature dealing with the enthalpy-related work on the APIL solutions described above is by no means exhaustive. Important developments have however been discussed. On the contrary, the ionic interactions in the PIL–solvent systems have not been investigated to date. In this article, we attempt to elucidate the interactions operating between PILs with molecular solvents of varied nature in terms of their excess partial molar enthalpy (H_{IL}^E) and the derived thermal properties. Herein, we attempt to resolve two major issues: (1) How do the interactions of a PIL with a solvent differ from those of an APIL with a solvent, and how are these interactions modulated from one solvent to another solvent? (2) How do the structural features of PIL cation regulate the PIL–solvent interactions? In other words, we report an interesting flip-flopping in the thermal behavior of these systems arising out of changing the ring structure of the cations of PILs.

In the present study, we have selected the imidazolium-, pyridinium-, and pyrrolidinium-based PIL cations, which are aromatic and nonaromatic in nature, whereas [BF₄][−] is kept common as the anion. The results are compared with those obtained for aqueous solutions of 1-methyl-3-butylimidazolium tetrafluoroborate abbreviated as [BMIM][BF₄] and classified as APIL. Therefore, the PILs selected in these investigations are [MIM][BF₄] (1-methylimidazolium tetrafluoroborate), [hPY][BF₄] (2-methylpyridinium tetrafluoroborate), and [hPYRR][BF₄] (N-methylpyrrolodinium tetrafluoroborate) (see Figure 1). The solvents chosen are water, methanol, ethylene glycol, dimethylsulfoxide (DMSO), and *N,N'*-dimethylformamide (DMF).

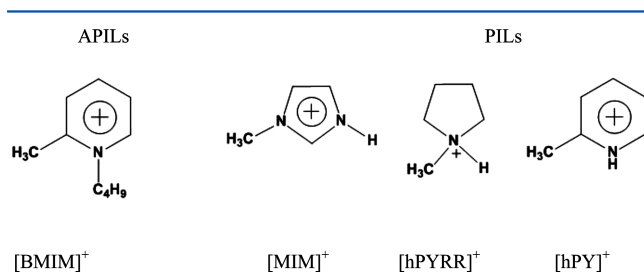


Figure 1. Different cations used in the present study.

EXPERIMENTAL SECTION

Materials. The Brønsted bases, i.e., 1-methylpyrrolidine, 1-methylpyridine, and 1-methylimidazole (all procured from Sigma-Aldrich, >99%), used for preparing the employed PILs in the present study were distilled prior to their use. The solvents employed in the present study were of spectroscopic grade and were procured from Spectrochem Pvt. Ltd. All of the solvents were dried over molecular sieves (3 Å) in order to avoid even the minimal amount of water contents. The deionized water (specific conductance $<0.055 \times 10^{-6} \text{ S cm}^{-1}$) was used for aqueous PIL systems.

Synthesis of PILs. PILs were synthesized by a single step atom economic reaction with an equimolar mixture of acid and base. Drop-wise addition of the desired base to tetrafluoroboric acid solution (50 wt % in H₂O) was carried out in a round-bottom flask over ice in order to avoid heat generation.³³ The reaction mixture was then stirred at room temperature for 6–8 h. Water was removed by putting the reaction mixture into the rotavapor at 80 °C for 10 h. The final product was typically hygroscopic and further required vacuum-drying prior to use for another 24 h at <0.01 Torr pressure. All the PIL samples were characterized and checked for their purity with the help of their ¹H NMR spectra.^{34,35} The ¹H NMR spectra of these PILs are given in the Supporting Information.

Before each experiment, the freshly prepared ionic liquids were dried for 24 h and the water content was determined by using Karl Fischer coulometric titration performed using a Metrohm-831 KF coulometer. The water content of the ionic liquid sample was less than 30 ppm.^{34,36}

The excess partial molar enthalpy, H_{IL}^E , of the ionic liquid in its solution in a solvent was determined with the help of an Isothermal Titration Calorimeter (ITC; MicroCal LLC, VP-ITC 2000) controlled by the VP-Viewer 2000 software. The concentration of each PIL solution investigated in the current work was $0.0326 \pm 0.0005 \text{ mol kg}^{-1}$. Before the real time experiments, the instrument was checked for its baseline by using the Y-axis calibration. In this method, the DP (differential power between the reference and the sample cell) calibration pulse is administered by using a relatively large pulse of $> \pm 5$ mcal/min, which exposes the DP calibration errors that are greater than 1%. The instrument was calibrated by performing the water–water titrations and also against the known H^E data of the aqueous 1-propanol system at 298.15 K.³⁷ Other specific details of the calibration and experimental methods are described elsewhere.¹⁵ In practice, the solution of the ionic liquid was titrated against a pure solvent. The accuracy of the instrument was within $\pm 5\%$ and goes as high as 8% for the systems studied in a very dilute range. The selection of the correct peaks for determining the correctness of the measurements is given in the Supporting Information (Figure S1). Other details are also given in the Supporting Information. The temperature was maintained at $298.15 \pm 0.05 \text{ K}$, and the stirring speed for the mixing was kept constant at a recommended value of 310 rpm.

The excess partial molar enthalpy, H_{IL}^E , was obtained by $H_{IL}^E = DH/n_{IL}$, with DH being the differential heat as recorded by ITC upon addition of the number of moles, n_{IL} , of the ionic liquid.

RESULTS AND DISCUSSION

The H_{IL}^E values (Supporting Information, Tables S1–S15) can provide a starting point for understanding the ion–solvent and

ion–ion interactions. In order to compare the effect of different cationic rings [MIM], [hPY], and [hPYRR] with a common BF_4^- species for these PILs in water, the H_{IL}^{E} versus m plots for these systems are shown in Figure 2.

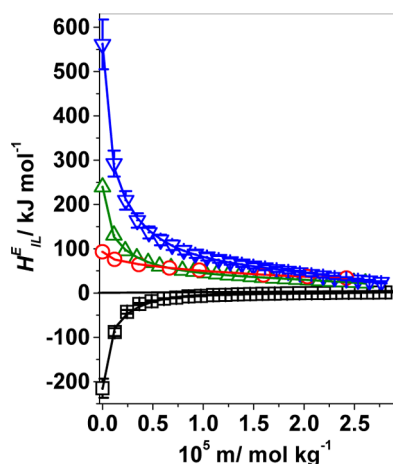


Figure 2. Comparison of the H_{IL}^{E} values between the aqueous PIL and APIL systems: (∇) [hPYRR][BF_4], (\triangle) [hPY][BF_4], (\square) [MIM][BF_4], and (\circ) [BMIM][BF_4] systems.

It is seen from Figure 2 that the H_{IL}^{E} values for [MIM][BF_4] are negative, i.e., the exothermic effect, while the positive H_{IL}^{E} values (endothermic) are noted for both [hPY][BF_4] and [hPYRR][BF_4].

Protic ionic liquids apart from having a number of unique properties possess an induced network structure because of the extended hydrogen bonding. It has been suggested that this PIL-network structure in some respect mimics the 3D hydrogen-bonded network of water.^{36,38,39} As seen in Figure 2, a change in the structure of the cationic ring of PILs induces a visible thermal change. The $H_{\text{IL}}^{\text{E}}-m$ plots for three different PILs shown in the drawing suggest that the interactions of [MIM][BF_4] with water are energetically most favored (exothermic). We are not sure whether the recently noted hyperpolarity of PILs has any influence on the quantum and sign of H_{IL}^{E} .^{40,41} These data can also be analyzed in terms of the hydrogen bond acidity denoted by α and considered mainly to be the cation dependent of [BMIM]⁺ and [BMPY]⁺. According to the work from Welton et al., hydrogen bond acidity of [BMIM]⁺ ($\alpha = 0.615$) is much higher than that of [BMPY]⁺ ($\alpha = 0.560$).⁴² This can be analogically applied on the actual cations, i.e., [MIM]⁺ and [hPY]⁺. Further, the polarity possessed by an imidazole ring is 3.61 D while by pyridine is 2.2 D. This is in agreement with the exothermic behavior due to stronger cation–water hydrogen bonds of the [MIM]⁺ based ionic liquid and endothermic behavior (weaker cation–water hydrogen bonds) of the [hPY]⁺ one.⁴³ The interactions are less favored in the case of [hPYRR][BF_4], which exhibits endothermic behavior.

The process of mixing a PIL and a solvent can be understood on the basis of the cavity formation and ion–solvent interactions.^{44,45} In the aromatic class of PILs, the smaller size of [MIM]⁺ allows more solute molecules to fit into the cavities of the solvent. During this process, the Coulombic interactions between [MIM]⁺ and BF_4^- are weakened. Further, these loosely bonded ion pairs are dissociated to form free ionic species separated by the solvent molecules. The

process of accommodating ionic entities into these solvent cavities is endothermic. This process is the least endothermic for [MIM][BF_4] and most endothermic for [hPYRR][BF_4] owing to their different sizes.

The interactions between the ionic species of a given ionic liquid and solvent molecules depend upon the nature, polarity in particular, of the solvents. In the case of a polar solvent like water, the water molecules will mainly reside near the polar region of the ionic liquids, while the molecules of apolar solvents like hexane, diethyl ether, etc., will try to solvate at the nonpolar domains of ionic liquids. The reported data suggest that that water or other polar solvents interact with ionic liquids by mainly electrostatic interactions through hydrogen bonding. Depending upon the polarity and availability of apolar groups in the solvent molecules, the interactions between ionic species and the solvent molecules may shift from predominant electrostatic nature to van der Waals type weak interactions.^{11,38c,39} The group of Rebelo has shown that different types of interactions, like specific, nonionic types, may exist in the solutions of the imidazolium ionic liquids in aromatic solvents like benzene.^{46,47} Therefore, it is safer to state that the interactions in the solutions of ionic liquids in the solvents with different polarities may not always be electrostatic in nature.

The gain in the enthalpy as a result of the insertion of [hPYRR]⁺ into water cannot be compensated due to weak interactions between the ion and solvent, leading to the destabilization of the [hPYRR][BF_4]–water system. Thus, the whole process of the dissolution of [hPYRR][BF_4] in water is endothermic. Both the [hPY]⁺ and [MIM]⁺ cations having aromatic ring structures do not vary significantly in their sizes from each other. Hence, it is the interaction of these ions with water that results in a change in their thermal behavior. [hPY]⁺ is more hydrophobic as compared to [MIM]⁺, and because of this, the interactions between [hPY]⁺ cation and solvent are weak.⁴⁶ Thus, the mixing process remains endothermic for [hPY][BF_4], as the system does not spend the same or more amount of energy gained by way of the bond formation. It may be noted that aromatic hydrocarbons are considered less hydrophobic than cyclic hydrocarbons with the same number of carbon atoms. In the former case, the reduced hydrophobicity is less due to its π – π electrons which lead to stronger van der Waals attraction to water molecules.^{48,49}

In Figure 2 are also plotted the H_{IL}^{E} values for an APIL, i.e., [BMIM][BF_4], with those obtained for [MIM][BF_4], [hPY][BF_4], and [hPYRR][BF_4] in water. It is seen that the interactions prevailing in PIL–solvent systems are considerably stronger as compared to those in the imidazolium-based APIL. Comparing both [MIM]⁺ and [BMIM]⁺, it is obvious that the mechanisms of interactions of both of the cations with water are different in both cases. [MIM][BF_4] exhibits the exothermal behavior with water, whereas [BMIM][BF_4] shows an endothermic trend. The hydrophobic hydration with respect to cations of APIL has been assigned a key role.^{15,50–53} The extent of hydrophobicity is either extremely small or absent in the imidazolium-based PIL, and the cation undergoes hydration in the presence of an excess amount of water.⁵¹ A comparison of the H_{IL}^{E} data of [MIM][BF_4] with a strong electrolyte like NaCl in water reveals that the mode of interactions in PILs is vastly different from that in strong electrolytes. The calculations of $H_{\text{NaCl}}^{\text{E}}$ were carried out on the basis of the data reported in the literature.⁵⁴ As compared to the cations of APILs, the charge is more centrally located on the cation of PIL. However, the cation of PILs may involve some weaker interactions in

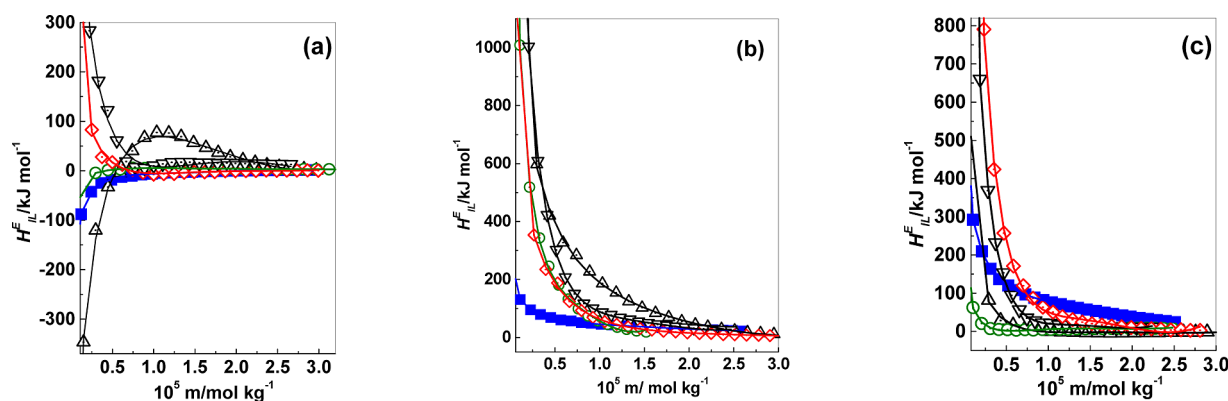


Figure 3. The solvent dependency of H^E_{IL} for (a) [MIM][BF₄], (b) [hPY][BF₄], and (c) [hPYRR][BF₄] in (▽) DMSO, (◇) DMF, (○) ethylene glycol, (■) water, and (△) methanol.

addition to the electrostatic ones, which are completely absent in aqueous strong electrolytes. In strong electrolytes like NaCl, Na⁺ orients water molecules around itself due to its smaller size and strong electric field. This effect is significant in the first hydration layer, which subsequently weakens.^{15,44,55} This also clearly brings out the H^E values resulting from the hydrophobic hydration and hydrophilic hydration.

This solvent dependent thermal behavior of PILs is shown in Figure 3. In the case of [MIM][BF₄] (Figure 3a), water displays an exothermic effect (with negative H^E values). On the other hand, the H^E values for this ionic liquid in methanol are highly exothermic in extremely dilute solutions but become endothermic at higher concentrations covered in this study. The interactions of [MIM][BF₄] with DMF and with DMSO are accompanied by positive H^E_{IL} values, i.e., endothermic in nature. However, the interactions of [MIM][BF₄] with ethylene glycol are mildly exothermic throughout.

The interactions of [hPY][BF₄] with the solvents undertaken in this work are represented by the endothermic effect. Out of all the solvents studied herein, water displays the weakest endothermal behavior.

There was no specific trend of H^E_{IL} at finite concentrations with the molecular properties like the hydrogen bond donating acidity (α), hydrogen bond accepting basicity (β), Hildebrand solubility parameter (δ), normalized Dimorth–Reichardt polarity parameter (E_T^N), and polarity index (π^*) of the solvents. We make some comments on the interactions of DMSO and of water with [hPY][BF₄]. DMSO is known to be a good cationic solvator, but it does not solvate the anions.^{55,56} This enhances the possibility of the intact ion pairs in [hPY][BF₄]. The energy required to keep the ion pairs solvated is too large, and hence, the PIL–DMSO system becomes highly endothermic. In addition, pure [hPY][BF₄] contains a set of complex interactions such as π – π ones operating between [hPY]⁺–[hPY]⁺ cations, which adds to the cost of dissolution.⁵⁷ Due to these factors, the process of dissolving [hPY][BF₄] makes the PIL solvation more energy consuming, which is reflected through the endothermic behavior of the [hPY][BF₄] PIL–water system. Compared to DMSO, water supports the solvation of both of the ionic species, rendering [hPY][BF₄] to experience more stabilization arising from the hydration of ions. However, the π – π interactions screen the thermal behavior of this system that leads to mild endothermic behavior as noted above.^{56,57}

The ionic liquid [hPYRR][BF₄] when titrated against the solvents studied in this work produces endothermal effects in

terms of positive H^E . The variations of H^E with the concentrations of the ionic liquid in the protic polar solvents including water, methanol, and ethylene glycol show an increase in the order of increasing ability of solvents to donate protons to the solute for hydrogen bonding (for properties of solvents, see Supporting Information Table S16). However, the H^E values for [hPYRR][BF₄] with the aprotic dipolar solvents including DMSO and DMF suggest hydrogen bond donating ability seems ineffective to explain the trend. The H^E_{IL} values increase in the order of decreasing hydrogen bond accepting ability of the solvent. It suggests that those solvents which can donate the H-atoms for the purpose of bonding stabilize the system to the maximum extent for [hPYRR][BF₄], whereas solvents having H-bonding acceptor tendency destabilize it. All the solvents showing endothermal behavior suggest that the cost of dissolution of [hPYRR][BF₄] is much higher as compared to the energy released during the bond formation between PIL and the solvent molecules during its solvation.

The probable interpretation of the enthalpy data originated from the interactions between PILs and nonaqueous solvents is given in the Supporting Information together with relevant information and drawings (Figures S2–S4, Supporting Information). We do realize that the spectroscopic data dealing with ionic liquids in a nonaqueous medium are not available in the literature.

In order to better understand the ion–solvent interactions in extremely dilute solutions, the H^E_{IL} data of the ionic liquids were fitted to the polynomial expression of the form

$$H^E_{IL} = H^{E,\infty}_{IL} + a_1\sqrt{m} + a_2m + a_3m^{1.5} \quad (1)$$

where $H^{E,\infty}_{IL}$ is the limiting excess partial molar enthalpy and a_1 , a_2 , and a_3 are the adjustable parameters, the values of which were obtained using a least-squares fitting program. The $H^{E,\infty}_{IL}$ values of PILs in different solvents are listed in Table 1, while the values of adjustable parameters, i.e., a_1 , a_2 , and a_3 , are listed in the Supporting Information (Table S17).⁵⁸ The $H^{E,\infty}_{IL}$ values in our case are the standard molar enthalpy of the solution, as the ionic liquid is already dissolved in a solvent in order to make a clear solution. Hence, $H^{E,\infty}_{IL}$ is a combination of standard molar enthalpy of dissolution and molar enthalpy of solution.

The $H^{E,\infty}_{IL}$ values listed in Table 1 suggest that [MIM][BF₄] requires much less energy to dissolve them in the solvent ($H^{E,\infty}_{IL}$ indicates the energy required to dissolve 1 mol of cation and anion in a solvent). Interestingly, the $H^{E,\infty}_{IL}$ values are reported highest for the pyridinium-based PIL, surpassing

Table 1. The Limiting Excess Partial Molar Enthalpies, $H_{\text{IL}}^{\text{E},\infty}$ (kJ mol^{-1}), of [MIM][BF₄], [hPY][BF₄], and [hPYRR][BF₄] in Different Solvents

solvents	[MIM][BF ₄]	[hPY][BF ₄]	[hPYRR][BF ₄]
water	-215 ± 11^a	239 ± 5	561 ± 123
methanol	-1202 ± 37	1561 ± 59	365 ± 31
ethylene glycol	433 ± 4	2885 ± 138	175 ± 13
DMF	387 ± 27	1182 ± 32	3100 ± 169
DMSO	1285 ± 61	3700 ± 129	2670 ± 102

^aThe values given after \pm indicate standard errors in the $H_{\text{IL}}^{\text{E},\infty}$ values

that of the pyrrolidinium-based PILs with maximum cationic size. As discussed above, the presence of the π – π stacking interactions in the pyridinium-based PILs provide additional stability to the solute. Hence, the pyridinium-based PIL shows the maximum values of $H_{\text{IL}}^{\text{E},\infty}$.

These $H_{\text{IL}}^{\text{E},\infty}$ values indicating the ion–solvent interactions in the PIL solutions were also correlated with the solvent properties of molecular solvents using linear solvation energy relations (LSERs).⁵⁹ The LSER has been used to correlate and predict a wide variety of solvent effects as well as to provide an analysis in terms of theoretical concepts of molecular structural effects. This model makes use of several solvent properties like the hydrogen bond donating acidity (α), hydrogen bond accepting basicity (β), Hildebrand solubility parameter (δ), normalized Dimorth–Reichardt polarity parameter (E_{T}^{N}), and polarity index (π^*) to state a few. The selection of the solvent properties is made upon the characteristics of both the solute and the solvent. In this multiparameter approach, the properties are so chosen to offer the best fit of the quantity of interest. A rigorous examination suggests that the difference in the behavior of the PILs having different ring structures in their solutions also depends upon the solvent properties. The relevant solvent properties for these solvents taken from the literature⁵⁴ are compiled in Table S16 (Supporting Information). For the [MIM][BF₄] and [hPy][BF₄] systems, a combination of α , δ , and E_{T}^{N} is effective in representing the $H_{\text{IL}}^{\text{E},\infty}$ values as shown by

For [MIM][BF₄], correlation coefficient = 0.991:

$$H_{\text{IL}}^{\text{E},\infty} = -0.494 \pm 0.031 - 2.93 \pm 0.18\alpha - 1.38 \pm 0.10\delta + 1.16 \pm 0.08E_{\text{T}}^{\text{N}} \quad (2)$$

For [hPy][BF₄], correlation coefficient = 0.971:

$$H_{\text{IL}}^{\text{E},\infty} = -1.06 \pm 0.06 - 9.70 \pm 0.67\alpha - 3.01 \pm 0.03\delta + 2.89 \pm 0.17E_{\text{T}}^{\text{N}} \quad (3)$$

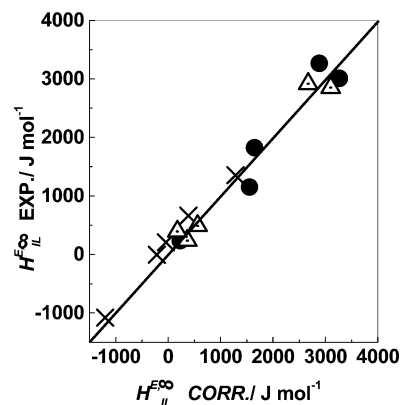
For [hPYRR][BF₄], correlation coefficient = 0.923:

$$H_{\text{IL}}^{\text{E},\infty} = -0.098 \pm 0.004 - 0.174 \pm 0.009\beta + 1.110 \pm 0.058\delta + 5.52 \pm 0.28\pi^* \quad (4)$$

The regression of data was carried out according to the procedure given in the original papers.⁵⁹ Though the coefficients given on the right-hand side of the above correlations do not bear any physical significance, they essentially assist us in understanding the strength of the correlation as discussed in the literature.⁶⁰

Success of such a correlation of $H_{\text{IL}}^{\text{E},\infty}$ with the solvent properties can be verified by comparing the $H_{\text{IL}}^{\text{E},\infty}$ values obtained from the experiments ($H_{\text{IL}}^{\text{E},\infty}$) with those from the

correlation ($H_{\text{IL,CORR}}^{\text{E},\infty}$) for the studied PIL–solvent systems (Figure 4). There was a very good agreement found between

**Figure 4.** A comparison between the $H_{\text{IL,EXP}}^{\text{E},\infty}$ and $H_{\text{IL,CORR}}^{\text{E},\infty}$ values for (x) [MIM][BF₄], (●) [hPY][BF₄], and (△) [hPYRR][BF₄] in different solvents.

the two quantities, suggesting that the solvent properties can offer insights into our understanding of the ionic liquid–solvent interactions.

To further probe the ion–solvent and ion–ion interactions, we calculated the relative apparent molar enthalpy ϕ_{L} using standard thermodynamic relationships (Supporting Information, Tables S1–S15).⁶⁰ The ϕ_{L} of a solute in its solution can be defined as the heat that can be attributed to 1 mol of solute in solution if it is assumed that the solvent contribution is the same enthalpy it has in its pure state. The ϕ_{L} values of the PIL solutions were analyzed using the ion–interaction model developed by Pitzer.⁶¹ The Pitzer model is an effective tool to analyze the equilibrium thermodynamic properties of electrolyte solutions.⁶²

The basic Pitzer equation for expressing excess free energy is

$$G^{\text{ex}}/W_{\text{w}}RT = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} + \dots \quad (5)$$

where W_{w} is the number of kilograms of water and I , the ionic strength, is given by

$$I = 0.5 \sum_i m_i z_i^2 \quad (6)$$

with z being the number of charges on an ion. $f(I)$ includes the Debye–Hückel limiting law, which is presented as an extended form chosen for empirical effectiveness. $f(I)$ depends upon the ionic strength and not on individual molalities of ions. $\lambda_{ij}(I)$ and μ_{ijk} denote binary and ternary interactions, respectively.

The working Pitzer equation for correlating ϕ_{L} and m for the solution of ionic liquid is given below:

$$\phi_{\text{L}} = (A_{\text{L}}/b) \ln(1 + bm_{\text{IL}}^{0.5}) - 2RT^2 m_{\text{IL}} (\beta^{(0)\text{L}} - 2\beta^{(1)\text{L}} [1 - (1 + 2m_{\text{IL}}^{0.5}) \exp(-am_{\text{IL}}^{0.5})] / (am_{\text{IL}}^{0.5})^2 - C^{\text{L}} m_{\text{IL}}) \quad (7)$$

The first term on the right-hand side of eq 7 indicates the long-range interactions as depicted by a Debye–Hückel term, which includes A_{L} , the modified Pitzer–Debye–Hückel limiting slope. The values of A_{L} for different solvents at

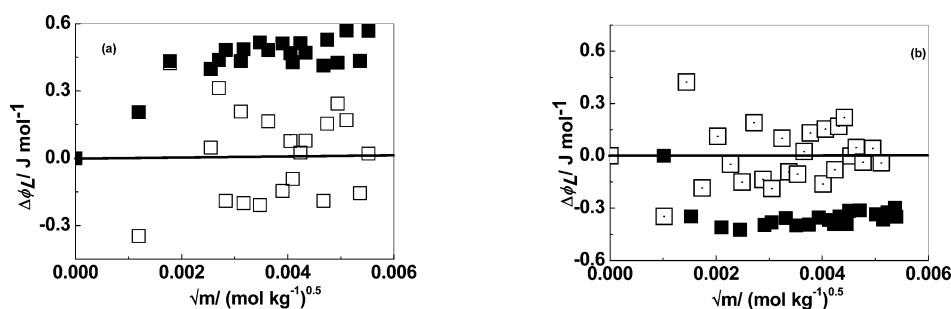


Figure 5. The difference between the experimental and correlated ϕ_L ($\Delta\phi_L$) plotted against \sqrt{m} for the (a) [MIM][BF₄]-methanol and (b) [hPYRR][BF₄]-ethylene glycol systems. The solid symbols show $\Delta\phi_L$ obtained from the fits carried out using eq 7 with $C^L = 0$, while the hollow symbols those with $C^L \neq 0$.

298.15 K are listed in the previous work.¹⁶ In the Pitzer equations, the values of constants, i.e., α and b , are set to 2.0 and $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, respectively. Pitzer and co-workers recommended these values after analyzing equilibrium thermodynamic properties of numerous electrolytes. However, these values in the case of the solutions of ionic liquids in organic solvents may require a revision once an adequate database becomes available. New optimal values of these constants in these solutions can be established in the future using the analysis of activity and activity coefficient data. Most of the ionic liquids synthesized so far are 1:1 with a few divalent ionic liquids reported recently. Once osmotic coefficients of a large number of the ionic liquid solutions in different solvents become available in the literature, it will be possible to analyze the measured osmotic coefficients using Pitzer equations to collect full information on the values of α and b . It will then be possible for us or others to recommend the optimum values of both α and b . The second term on the right-hand side of eq 7 provides short-range interactions in which $\beta^{(0)L}$ and $\beta^{(1)L}$ are the virial coefficients to quantify the binary interactions between the opposite and like charges and C^L is the virial coefficient accounting for ternary interactions.

The ϕ_L - m data for the solutions of PILs were subjected to the Pitzer equation (eq 7) using a nonlinear fitting program to evaluate $\beta^{(0)L}$, $\beta^{(1)L}$, and C^L coefficients. In order to check the importance of the virial coefficient terms for these systems, we first set C^L to be zero but allowed both $\beta^{(0)L}$ and $\beta^{(1)L}$ to vary. This led to a systematic deviation particularly at higher concentrations between the experimental ϕ_L and the fitted ones. Next, all three $\beta^{(0)L}$, $\beta^{(1)L}$, and C^L coefficients were allowed to vary, resulting in the best fits, i.e., minimum standard deviations. The importance of C^L in the Pitzer equations as applied to the PIL solutions (for instance, [MIM][BF₄]-methanol and [hPYRR][BF₄]-ethylene glycol systems) is shown in Figure 5, in which the $\Delta\phi_L$ ($\phi_{L,\text{exp}} - \phi_{L,\text{COR}}$) obtained by eq 7 is without (shown by solid symbol) and with (shown by hollow symbol) the C^L coefficient. This shows that a higher order virial coefficient (C^L) was required for obtaining an accurate fitting of ϕ_L of these PIL-solvent systems even in the dilute range. It could be correlated to the poor ionicity data of these PILs resulting in higher order interactions due to incomplete dissociation.⁶³

The values of these coefficients together with standard errors are given in Table 2. The average standard deviation (σ) for all 15 PIL-solvent systems was noted to be $\pm 0.53 \text{ kJ mol}^{-1}$.

For all the systems studied herein, the random distribution of the $\Delta\phi_L$ values noted in other systems confirms the application of the Pitzer equations in analyzing the ϕ_L data. It is seen that

Table 2. The Evaluated Pitzer Coefficients by Using eq 7 for the PIL-Solvent Systems

PIL/solvent	Pitzer coefficients		
	$\beta^{(0)L}$ ($\text{kg mol}^{-1} \text{ K}^{-1}$)	$\beta^{(1)L}$ ($\text{kg mol}^{-1} \text{ K}^{-1}$)	C^L ($\text{kg}^2 \text{ mol}^{-2} \text{ K}^{-1}$)
[MIM][BF ₄]			
water	-1.08 ± 0.02^a	-1.22 ± 0.02	3.15 ± 0.14
methanol	-4.13 ± 0.05	-4.42 ± 0.05	-18.4 ± 0.4
ethylene glycol	-1.30 ± 0.02	-1.46 ± 0.02	5.60 ± 0.17
DMF	0.333 ± 0.060	0.254 ± 0.061	13.58 ± 0.44
DMSO	7.54 ± 0.21	7.78 ± 0.22	46.6 ± 1.7
[hPYRR][BF ₄]			
water	-0.394 ± 0.010	-0.434 ± 0.011	7.22 ± 0.11
methanol	-0.663 ± 0.033	-0.794 ± 0.032	7.38 ± 0.21
ethylene glycol	-1.21 ± 0.04	-1.36 ± 0.04	9.86 ± 0.32
DMF	0.28 ± 0.06	0.20 ± 0.06	28.8 ± 0.5
DMSO	3.55 ± 0.13	3.63 ± 0.14	65 ± 1
[hPY][BF ₄]			
water	-0.233 ± 0.022	-0.275 ± 0.02	6.26 ± 0.14
methanol	0.395 ± 0.060	0.313 ± 0.070	31.2 ± 0.5
ethylene glycol	1.46 ± 0.14	1.42 ± 0.15	54.89 ± 1.22
DMF	-0.054 ± 0.05	-0.144 ± 0.051	21.37 ± 2.31
DMSO	2.69 ± 0.09	2.75 ± 0.10	44.1 ± 0.2

^aThe values given after \pm are the standard errors in the coefficients.

the Pitzer equations can accurately correlate both endo- and exothermic behavior as well as the different nature of cationic parent rings of PILs and solvents.

From the Pitzer coefficients noted in Table 2, it appears that, as the carbon content in the cationic rings increases, the magnitude of virial coefficients ($\beta^{(0)L}$ and $\beta^{(1)L}$) also increases almost linearly, suggesting enhanced ion-solvent and ion-ion interactions. However, in the case of the higher order coefficient C^L , this increase is not as sharp as in the case of lower order coefficients. It may be due to some leveling effect of different interactions, which are noticed for [hPY][BF₄] and [hPYRR][BF₄].

As the number of hydrogen bond donating sites on the PIL cations is enhanced (Supporting Information, Figure S5), it results in enhanced interactions between the cation and solvent. These interactions are very strong in the presence of DMSO, as seen from both $\beta^{(0)L}$ and $\beta^{(1)L}$ values. Both DMSO and methanol show very high values of $\beta^{(0)L}$ and $\beta^{(1)L}$ but with signs opposite to each other. This observation suggests that the interactions offered by the two solvents, i.e., methanol and DMSO, to the PIL cations during their solvation and dissolution (introduction of solute) in the solvent system are

entirely different from each other. As discussed earlier, the methanol system being a loosely bound system can be disrupted at a lesser expense of energy and further intense hydrogen bonding between the PIL cations and the methanol molecules makes the whole process exothermic. However, in DMSO, the solute insertion is expensive and the anion solvation is not supported. Hence, the process becomes endothermic which is evident from both H_{IL}^{E} data and the Pitzer analysis. Thus, the above study suggests that a varying degree of strong interactions prevails between PIL cations and the solvent molecules. We are beginning to collect thermodynamic data on new ionic liquid systems with a view to create a global generalization of the PC SAFT and other relevant models.

CONCLUSIONS

From the above study, it can be concluded that (1) the solvation plays a key role in determining the nature of interactions of PILs with solvents especially water, (2) in the case of APILs, hydrophobic hydration arising due to the hydrophobic groups attached to the cations of APIL cations is a contributory factor toward ion–solvent interactions, and (3) the variation in the ring structures of the PIL cations alters the course of solvation in different solvents. In water, upon changing the ring structure from imidazolium to pyrrolidinium, the solvation behavior shifts to exothermic from endothermic behavior, and (4) the central finding of this work demonstrates a thermal flip-flop behavior in PIL systems emerging from the structural alterations in PIL cations.

In view of the poor ionicity of PILs, the development of a model accounting for both un-ionized and ionized species to accurately represent equilibrium thermodynamic properties is highly desirable. It is hoped that, once accurate enthalpy data on a variety of ionic liquids is analyzed with the help of the advanced modeling technique like that recently described by the group of Domanska, our understanding of ion–solvent interactions in the ionic liquid solutions will be greatly enhanced.

ASSOCIATED CONTENT

Supporting Information

^1H NMR spectra of the ionic liquids, additional information on experimental work, a drawing showing the peaks of ITC experiments, 15 tables of the H_{IL}^{E} data for PILs in different solvents (Tables S1–S15), comments on the interactions (Figures S2–S4) showing possible interactions between a PIL and solvent, one table (Table S16) showing the solvent properties, one table (Table S17) containing the values of adjustable parameters, and a drawing (Figure S5) showing the variation in Pitzer coefficients with n_{H} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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