Probing solute and solvent interactions within binary ionic liquid mixtures†

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In this communication, we explore solute–solvent and ion–ion interactions within binary ionic liquid mixtures. From the perspective of several solvatochromic reporter probes capable of a range of interactions, we have investigated the influence of mixture composition on the polarity, dielectric, hydrogen bonding interactions, and microfluidity within mixtures afforded by the ionic liquids 1-butyl-3-methylimidazolium bis(triflyl)imide, 1-ethyl-3-methylimidazolium bis(triflyl)imide, and 1-butyl-3-methylimidazolium hexafluorophosphate. Our results underscore the prevalence of hydrogen bond donor and competitive anion coordination effects, suggesting the possible use of such mixtures in the design and optimization of advanced media for separations or chemical processing.

Introduction

Having established clear potential as green(er) alternatives to existing solvents, room-temperature ionic liquids (RTILs) are receiving considerable global attention. By now, it is also clear that RTILs offer a unique environment for performing chemistry, biocatalysis, separations, materials synthesis, electrochemistry and electrodeposition.[1] Intriguingly, by systematic alteration in the parent ions or judicious coupling of cation and anion partners, one has the ability to, in principle, fine-tune solvent properties such as viscosity, melting point, density, refractive index, polarity, and water miscibility, creating 'designer solvents' at will. Far from being a panacea, however, it is becoming increasingly apparent that many solutes are poorly soluble or completely insoluble and some reactions take place sluggishly or not at all within common ionic liquids. Although serendipitous cation–anion combinations are sure to surface in this regard and significant progress has been made toward more rational design, as a research community our knowledge of the complex solvent interactions within RTILs is still quite elementary.

Aspects of solvent polarity are ubiquitous amongst chemistry and biology. As one of the simplest indicators of solvent strength, the polarity of pure RTILs and their admixtures remain of key interest. Not surprisingly, among those researchers who have begun probing the nature of solvation, interaction, structure, and dynamics within RTILs,[2–20] solvatochromic molecular probe-based polarity determinations have been the most popular. Polarity is a general term comprising the overall solvating capacity of a medium. However, within molecular solvents the term *polarity* eludes simple and tidy definition as manifold forces are involved, for example, hydrogen bonding, ionic/charge–charge, dipolar, π–π, n–π, and van der Waals interactions. While simple molecular solvents are frequently limited in the scope (both number and type) of interactions possible with dissolved solutes, RTILs, given their structure and diversity, are capable of multiple interactions. The scenario becomes even more complicated within RTILs as both the cation and anion can have their own distinct interactions; in this sense, a pure RTIL can be considered a binary mixture. While the response from a single probe is essentially an ensemble- or time-average of all possible solute–solvent interactions, the behavior is sometimes dominated by a specific type or class of interaction.

From its inability to dissect *polarity* into its unique individual contributions, the single-parameter approach has been the subject of some controversy. In fact, polarities are not simple numbers but are actually matrices whose solute × solvent product determine solvation energy. While an empirical polarity scale can be a dangerous oversimplification, it can also offer some very useful insight. For example, Dzyuba and Bartsch[5] observed a clear correlation between the polarity parameter $E_T(30)$ for a series of 1-X-3-methylimidazolium bis(triflyl)imide RTILs and the *endo*/*exo* ratio for Diels–Alder reaction between cyclopentadiene and methyl acrylate. However, as weighted averages, single-term polarities have not been definitive[6,7,9,16,19,20] with small changes in polarity reported among common RTILs.‡ Despite this difficulty in distinguishing ionic liquids merely on the basis of polarity, photophysical probe studies offer a versatile means to study the local microenvironment, dynamics, and organization within RTILs. Early efforts by our groups in this field[12–20] have focused on the local solvent microenvironment from the perspective of spectroscopic probes dissolved in neat RTILs[16,19,20] and (RTIL + water),[13,17–19] (RTIL + ethanol),[14] (RTIL + CO_2),[20] and (RTIL + water + ethanol) mixtures.[12] Most recently, we have also used these methods to study dynamic phenomena including solute diffusion kinetics[18] and transient solvation[17] within RTILs.

At the heart of many of these studies is the use of one or more solvatochromic probes to characterize the local

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† This paper is dedicated with congratulations to Professor Frank V. Bright, recipient of the 2003 New York SAS Gold Medal Award.

‡ Appropriate functional engineering of the 1-X-3-methylimidazolium cations of bis(triflyl)imides has been shown to result in a substantial increase in the observed range of polarity.[5]

environment (cybotactic zone) surrounding the probe. Of course, certain probe–solvent interactions may be favored causing various probes to 'perceive' differently the components of a solvent mixture.[21–25] For this reason, the observation of preferential solvation (*i.e.*, selective enrichment of certain solvent species within the probe's immediate environment relative to the bulk) is not uncommon. These local mole fraction excursions caused by 'solvent sorting' within the vicinity of a solute are of key importance in governing the efficiency, selectivity, and outcome of a chemical reaction, extraction, or separation. One must also realize that solvent molecules within the cybotactic zone are acted upon by the field of the solute itself. In this way, an indicator solute can both report on and influence its own environment. For instance, 'dielectric enrichment' is common in the neighbourhood of a dipolar solute.[21]

Preferential solvation exists whenever the solvation microsphere composition deviates from the bulk composition. Assuming ideality (*e.g.*, non-associating solvents), the expected spectral response of a solvatochromic probe (R_{ideal}) within a binary (A + B) solvent mixture, as given by eqn. (1), is a mole fraction (X_i) or volume fraction (V_i) weighted average of the probe's spectral responses in the two pure solvents (R_i) leading to linear $R_{\text{obs}}(X_i)$ plots.[26,27]

$$R_{\text{ideal}} = X_A R_A + (1 - X_A) R_B \tag{1}$$

In this way, deviations from ideality, expressed as excess functions ($R_{\text{obs}} - R_{\text{ideal}}$), for a given probe may reveal a local enrichment of a particular component or changes in solvent–solvent structure or cooperativity. By appropriate selection, such a probe may also serve as a surrogate or suitable stand-in for a target reagent, intermediate, or extractable species.

Attempts to optimize RTIL media for a given application have included the search for unorthodox ionic liquids as well as extensive use of co-solvents such as compressed CO_2 or aqueous ethanol. To date, however, the use of binary RTIL mixtures has not been studied. By preparing mixed RTIL solutions of two or more different RTILs (varying the cation, anion or both), the components, or latent properties thereof, may confer on the mixture improved properties for a specific application.

Seeking insight into solute-specific solvent effects, ion–ion interactions, and preferential solvation processes within binary RTIL mixtures, we have explored the influence of binary RTIL mixture composition on the local environment experienced by several solvent-sensitive indicators (*i.e.*, pyrene, pyrene-1-carboxaldehyde, Reichardt's betaine dye, 4-nitroaniline, *N*,*N*-dimethyl-4-nitroaniline, and 1,3-bis(1-pyrenyl)propane) dissolved therein. Binary mixtures formed from the ionic liquids 1-butyl-3-methylimidazolium bis(triflyl)imide [bmim][Tf_2N], 1-ethyl-3-methylimidazolium bis(triflyl)imide [emim][Tf_2N], and 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] were the subject of our preliminary studies. This RTIL selection was made on the basis of their popularity in the literature, the fact that these RTILs are mutually miscible in all proportions, and the prospect of studying a co-RTIL with a different cation, anion, or both: [emim][Tf_2N] + [bmim][Tf_2N], [bmim][Tf_2N] + [bmim][PF_6], or [emim][Tf_2N] + [bmim][PF_6].

Results and discussion

Pyrene polarity studies

Pyrene is one of the most popular fluorescent probes of polarity within organized media.[28–32] The pyrene polarity scale, defined by the ratio "I_I/I_{III}" of the monomer fluorescence intensities at bands *I* (0–0 band, *ca.* 373 nm) and *III* (*ca.* 384 nm), is a function of solvent dielectric (ε) and refractive index (*n*) *via* the dielectric cross term [$f(\varepsilon, n^2)$]. Acree and coworkers have shown that I_I/I_{III} within a binary solution of solvents becomes[33]

$$\frac{I_I}{I_{III}} = \frac{[Y_A \cdot I_{I,A} + (1 - Y_A) \cdot I_{I,B}]}{[Y_A \cdot I_{III,A} + (1 - Y_A) \cdot I_{III,B}]} \tag{2}$$

where Y_A and Y_B are the local mole fractions of solvents A and B.

Fig. 1 summarizes the effects of mixture composition on pyrene I_I/I_{III} values for the binary RTIL systems [bmim][Tf_2N] + [bmim][PF_6] (●), [emim][Tf_2N] + [bmim][PF_6] (□), and [emim][Tf_2N] + [bmim][Tf_2N] (○). In all three cases, I_I/I_{III} values above the predicted are observed suggesting an increased local dielectric relative to ideal mixing. Such results are quite unexpected given the fact that pyrene is an apolar solute. In fact, because in each case component "B" is the RTIL of lower polarity, monotonic decreases in I_I/I_{III} are actually expected. For example, for water–alcohol binary mixtures Kusumoto *et al.*[34] observed dramatic decreases in pyrene I_I/I_{III} as methanol, ethanol, or 1-propanol were added to water. The non-ideality of these mixtures increased with increasing alcohol chain length suggesting the importance of aliphatic chain–pyrene hydrophobic interactions. Similarly, we noted a decline in pyrene I_I/I_{III} as a [bmim][PF_6] sample was subjected to increasing CO_2 pressure (0–70 bar).[20] Earlier, we found that adding water below its solubility limit to [bmim][PF_6] had no effect on I_I/I_{III}.[13] Similarly, ethanol addition to the same RTIL has no effect on I_I/I_{III} up to 40 mol%.[14]

Although the [emim][Tf_2N] + [bmim][Tf_2N] (○) system behaves most ideally, there is still a statistically meaningful positive deviation from ideality at low X_B with a maximal excess (*ca.* 0.03) at a [bmim][Tf_2N] mole fraction of 0.25. Since these mixed cations may be expected to behave similarly one possible explanation for the observed behavior may simply be the more efficient packing possible between the [emim]$^+$ and [bmim]$^+$ cations resulting in greater charge density at the site of pyrene solubilization. Consider the scenario where the pyrene neighbourhood in these mixtures is crowded by these cation partners which attempt to orient their lipophilic groups toward the probe. The greatest deviation at low X_B is in line with this possibility.

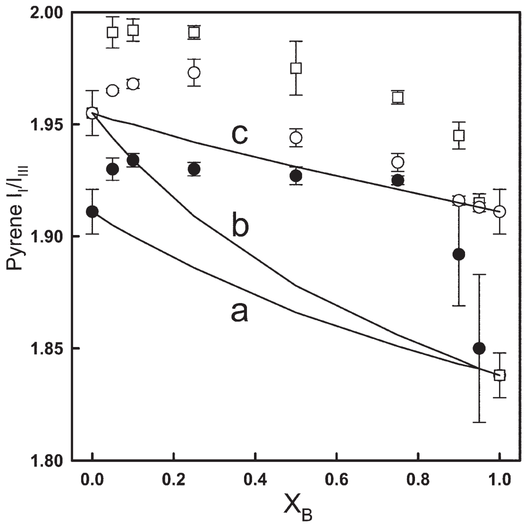

Fig. 1 Experimental pyrene I_I/I_{III} values for the binary (A + B) ionic liquid systems [bmim][Tf_2N] + [bmim][PF_6] (●), [emim][Tf_2N] + [bmim][PF_6] (□), and [emim][Tf_2N] + [bmim][Tf_2N] (○). X_B denotes the mole fraction for the component "B" in the bulk. Solid lines a–c are the corresponding ideal curves for these mixtures generated from eqn. (2).

More dramatic deviation from the theoretical curve is seen for the mixed anion RTIL binary system [bmim][Tf$_2$N] + [bmim][PF$_6$] (●). Here, a maximum deviation of 0.074 is observed for $X_B = 0.75$. We postulate that the increases in local polarity experienced by pyrene are due to solvent–solvent (ion–ion) interactions. Specifically, because the negative charge is localized across the S–N–S moiety,[35] [Tf$_2$N]$^-$ is a more strongly coordinating/nucleophilic anion than [PF$_6$]$^-$. Thus, the [bmim]$^+$ loosely associated with [PF$_6$]$^-$ may interact more strongly with the π-system of pyrene to result in a higher apparent dielectric. Of course, this should result in a higher I/III value for [bmim][PF$_6$] and this is not the case. One possibility then is that in the presence of [Tf$_2$N]$^-$ strong interaction with [bmim]$^+$ actually frees [PF$_6$]$^-$ for greater association with pyrene relative to neat [bmim][PF$_6$]. In addition, since pyrene acts on the basis of changes in the solvent dielectric cross term, $f(\varepsilon,n^2)$, changes in local dielectric and refractive index may also perturb this value although not enough in this case to explain the nonideality alone.

The most prominent departure from ideality is observed for the binary RTIL mixture [emim][Tf$_2$N] + [bmim][PF$_6$] (□) (*i.e.*, a RTIL mixture containing different cations *and* anions). A significant maximum excess of 0.106 again results at 0.75 X_B. We postulate a combination of both anion coordination effects and packing considerations to explain this synergy. One commonly evokes two solute-dependent phenomena to explain the occurrence of preferential solvation within mixtures: (i) 'dielectric enrichment' which entails a solute/probe selectively sequestering dipolar components of a solution due to dipole–dipole interactions between probe and solvent; (ii) specific probe–solvent interactions, most importantly, H-bonding. Non-ideal behavior can also result from *solvent microheterogeneity* whereby one component of a mixed solvent prefers a species of the same kind (auto-association) leading to clusters. Such effects are not probe-induced but instead result from dissolution within a 'cavity' pre-formed by bulk solvent demixing. While dielectric enrichment is consistent with the positive deviation in the I_I/I_{III} *versus* X_B profiles, the necessary underlying interactions are not possible for the apolar pyrene which likely only interacts *via* extremely weak quadrupole forces. Likewise, pyrene cannot participate in hydrogen bonding. Taken together, these results are consistent with pyrene detecting the existence of microheterogeneity or self-association resulting from strong solvent–solvent interactions within these RTIL mixtures.

Pyrene-1-carboxaldehyde dielectric (ε) studies

Another fluorescent probe that has found utility in studies of solution and interfacial polarity is pyrene-1-carboxaldehyde (PyCHO). PyCHO has two types of closely-lying excited singlet states (n–π* and π–π*), both of which show emission in fluid solution. In nonpolar solvents such as *n*-hexane, the emission from PyCHO is highly structured and weak ($\phi_F < 0.001$) arising from the n–π*state. On increasing the polarity of the medium, however, the π–π* state is brought below the n–π* state *via* solvent relaxation to become the emitting state. This is manifested by a broad, reasonably intense emission (*e.g.*, $\phi_F \approx 0.15$ in MeOH) that red-shifts with increasing solvent dielectric.[36]

Results for PyCHO emission energies (expressed in kK units, kK = 1000 cm^{-1}) within the binary RTIL mixtures [bmim][Tf$_2$N] + [bmim][PF$_6$], [emim][Tf$_2$N] + [bmim][PF$_6$], and [emim][Tf$_2$N] + [bmim][Tf$_2$N] are provided in Fig. 2. Two points are readily apparent given the data. First, within the experimental uncertainty (40–60 cm^{-1}), the emission energy for PyCHO changes in a completely predictable manner as the composition for each binary RTIL mixture changes. As a result, the emission changes are very small across all three mixtures. For example, the average emission maximum for PyCHO in [bmim][Tf$_2$N] + [bmim][PF$_6$] (●) across all mole fractions is 423.3 ± 0.5 nm compared with 423 nm and 424 nm for neat [bmim][Tf$_2$N] and [bmim][PF$_6$], respectively. In the same fashion, the PyCHO emission maxima for [emim][Tf$_2$N] + [bmim][PF$_6$] (□) and [emim][Tf$_2$N] + [bmim][Tf$_2$N] (○) blue shift slightly (3 and 4 nm, respectively) upon addition of the second RTIL. Second, it is interesting to note that the PyCHO emission maxima observed for all binary ionic liquid mixtures span the range 423–427 nm, suggesting a dielectric constant always below 10. These results are in accord with earlier observations by Bonhôte *et al.*[11] using PyCHO as well as a pyrene–PRODAN mixed probe study from one of our groups.[20]

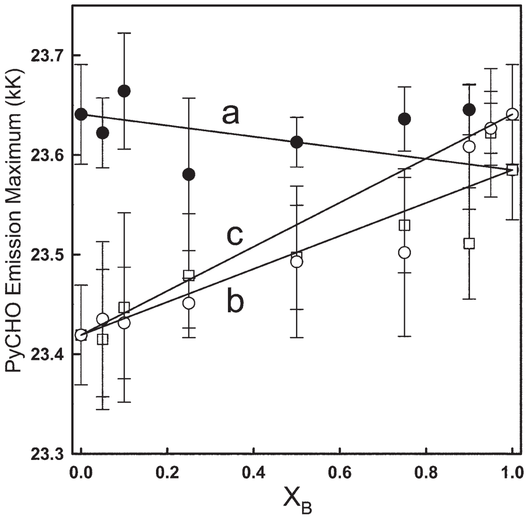

Fig. 2 Experimental pyrene-1-carboxaldehyde emission maxima for the binary ionic liquid systems [bmim][Tf$_2$N] + [bmim][PF$_6$] (●), [emim][Tf$_2$N] + [bmim][PF$_6$] (□), and [emim][Tf$_2$N] + [bmim][Tf$_2$N] (○). The solid lines a–c are the corresponding ideal curves resulting from eqn. (1).

The above results contrast with earlier studies of binary [bmim][PF$_6$] + water[13] and [bmim][PF$_6$] + ethanol[14] mixtures. In these cases (see Fig. 3), addition of a protic co-solvent resulted in strong preferential solvation of PyCHO by the co-solvent as evidenced by marked increases in λ_{max}.

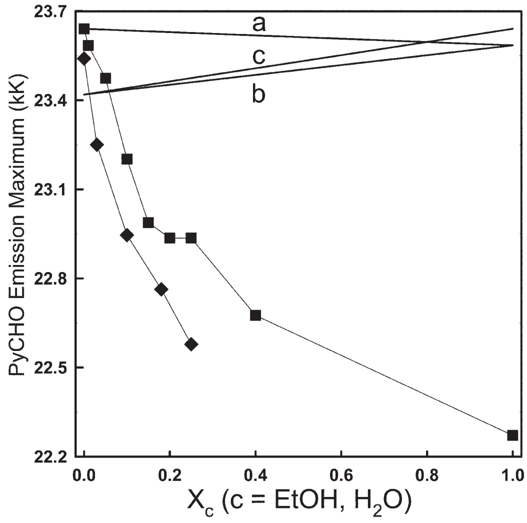

Fig. 3 Variation in PyCHO emission maximum as ethanol (■) or water (◆) are added to [bmim][PF$_6$] (data are taken from refs. 13 and 14, respectively). The ideal probe responses from Fig. 2 are included as benchmarks.

Dimroth–Reichardt $E_T(30)$ parameters

The E_T scale is among the most widely quoted empirical scales of solvent polarity. Most commonly, the Dimroth–Reichardt $E_T(30)$ scale based on the dye 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenolate is employed. A ground state zwitterion, a 'giant dipole' of sorts, this compound exhibits an extremely large negative solvatochromic shift in its intramolecular π–π^* charge transfer (CT) absorption band resulting from changes in polarity. The molar transition energy of the CT absorption may be calculated from λ_{max} using the relationship: $E_T(30)/\text{kcal mol}^{-1} = 28\,591.5/(\lambda_{max}/\text{nm})$.[19,37] The position of the CT band is strongly influenced by the hydrogen bond donor (HBD) ability of the solvent to the phenoxide oxygen atom. In fact, Taft and Kamlet estimated that roughly two-thirds of the shift in transition energy results from specific interactions involving the highly basic phenoxide oxygen atom while the remaining influence reflects solvent dipolarity/polarizability effects.[38]

The measured $E_T(30)$ values for the RTIL mixtures studied here are shown in Fig. 4. Because many researchers in the preferental solvation field have speculated on the solvation of solutes by a putative A–B mixed solvent pair (it is not clear whether this is a discrete physical species or a synergy resulting from structure or cooperativity), we expected the biggest deviations from regular solution behavior to result from [emim][Tf$_2$N] + [bmim][PF$_6$] (□) which is effectively a four-component mixture (*i.e.*, 6 pairwise interactions are possible *versus* 3 for a three-component mixture). We were surprised that this was not the case but, in fact, while all mixtures showed clear synergy, the [bmim][Tf$_2$N] + [bmim][PF$_6$] and [emim][Tf$_2$N] + [bmim][Tf$_2$N] systems were *highly* non-ideal.

In the [bmim][Tf$_2$N]-rich region, the [bmim][Tf$_2$N] + [bmim][PF$_6$] mixture (●) exhibits a maximum excess polarity [$\Delta E_T(30)$] of 1.64 at 5 mol% [bmim][PF$_6$]. The results for [emim][Tf$_2$N] + [bmim][Tf$_2$N] (○) mirror these observations. That is, an excess polarity of 1.43 is seen in the [bmim][Tf$_2$N]-rich region (5 mol% [emim][Tf$_2$N]). Although highly speculative, we postulate that the behavior for [bmim][Tf$_2$N] + [bmim][PF$_6$] again results from the lower coordination strength of [PF$_6$]$^-$ relative to [Tf$_2$N]$^-$. That is, [PF$_6$]$^-$ 'frees up' some fraction of otherwise [Tf$_2$N]$^-$ associated [bmim]$^+$ which then acts as a HBD solvent to the probe *via* the acidic C2 hydrogen. Further addition of [bmim][PF$_6$] results in a steady increase in $E_T(30)$ and a decrease in non-ideality as the probe environment gradually becomes saturated in [bmim][PF$_6$]. As an aside, it is interesting to note that while E_T studies suggest a higher polarity for [bmim][PF$_6$] relative to [bmim][Tf$_2$N],[7] the reverse was observed by Carmichael and Seddon[9] using the probe Nile Red.

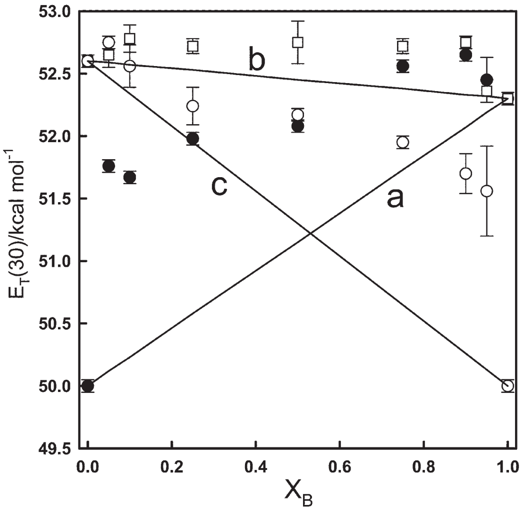

Fig. 4 Experimental $E_T(30)$ values for the binary ionic liquid systems [bmim][Tf$_2$N] + [bmim][PF$_6$] (●), [emim][Tf$_2$N] + [bmim][PF$_6$] (□), and [emim][Tf$_2$N] + [bmim][Tf$_2$N] (○). Solid lines a–c, respectively, are the corresponding ideal curves generated from eqn. (1).

The [emim][Tf$_2$N] + [bmim][Tf$_2$N] (○) results are more difficult to explain. One possible explanation is that inductive and steric/packing/orientation effects produce a more 'naked' proton in [emim]$^+$ resulting in stronger [emim]$^+$ – [Tf$_2$N]$^-$ association. Although this goes a long way toward explaining the observed synergy, we simply offer this as food for thought and do not assert that such a scenario is operative. The biggest skepticism for this explanation is the fact that on these grounds one expects the [emim][Tf$_2$N] + [bmim][PF$_6$] mixture to exhibit the largest $E_T(30)$ values as well as the greatest overall synergy. Of course, only the former is true. We note that while pronounced synergy was seen for [bmim][PF$_6$] + ethanol[14] and [bmim][PF$_6$] + ethanol + water,[12] a complete lack of preferential solvation was noted for [bmim][PF$_6$] + water.[13,19]

Kamlet–Taft parameters (π^*, β, α)

Additional insight into these mixed RTIL systems can be provided using Kamlet-Taft solvatochromic indicators of solvent dipolarity/polarizability (π^*), hydrogen bond donor strength (α), and hydrogen bond acceptor strength (β).[19,38,39]

The π^* parameters were estimated from the absorption maximum (ν_{DENA}, in kK) of *N*,*N*-diethyl-4-nitroaniline, a non-hydrogen bond donor solute, using:

$$\pi^* = 8.649 - 0.314\nu_{DENA} \tag{3}$$

β values were determined from the enhanced solvatochromic shift of 4-nitroaniline relative to its homomorph *N*,*N*-diethyl-4-nitroaniline, $-\Delta\nu(\text{DENA–NA})/\text{kK}$, resulting in eqn. (4).

$$\beta = -0.357\nu_{NA} - 1.176\pi^* + 11.12 \tag{4}$$

α parameters were in turn calculated from $E_T(30)$ and π^* values which were obtained as discussed above.

$$\alpha = 0.061E_T(30) - 0.885\pi^* - 1.633 \tag{5}$$

Using these methods, Kamlet-Taft parameters were determined for several organic solvents as a check of our reagents and general procedures.

Kamlet–Taft parameters for the binary RTIL systems [bmim][Tf$_2$N] + [bmim][PF$_6$], [emim][Tf$_2$N] + [bmim][PF$_6$], and [emim][Tf$_2$N] + [bmim][Tf$_2$N] are provided in Fig. 5. Although the average deviation for π^* ranges from -0.0014 to -0.0023, given the imprecision (~0.01), these deviations are statistically insignificant.

α values, on the other hand, show clear evidence for synergy. As expected from eqn. (5), these results track the results from $E_T(30)$ perfectly. Fig. 6 provides a head-to-head comparison of excess polarities determined from α-parameters *versus* the $E_T(30)$ response. From these reduced data, it is abundantly clear that the *N*-(4-oxidophenyl)pyridinium dye used in the determination of $E_T(30)$ "senses" only changes in solvent HBD ability.

Results for β within RTIL + RTIL systems do not show any systematic trends with changes in mixture composition. In fact, while all β values fall within the range from 0.204–0.268 the average β for all data is 0.228 ± 0.016 ($n = 27$). Thus, the hydrogen bond acceptor (HBA) basicity remains virtually unchanged across all mole fractions. This is in line with our earlier observations that addition of water to [bmim][PF$_6$] did not significantly affect β values.[19] Although some scatter in the data exists (such as that for a X_B of 0.95 for [emim][Tf$_2$N] + [bmim][Tf$_2$N]) the data do not support the existence of non-ideality in mixing. It is noteworthy that among common polar organic solvents only anisole has similarly poor HBA abilities.[19]

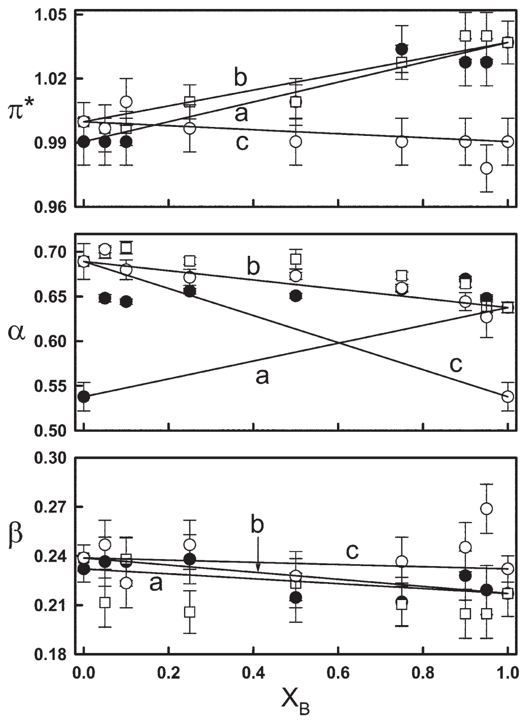

Fig. 5 Experimental Kamlet–Taft parameters for the binary ionic liquid systems [bmim][Tf$_2$N] + [bmim][PF$_6$] (●), [emim][Tf$_2$N] + [bmim][PF$_6$] (□), and [emim][Tf$_2$N] + [bmim][Tf$_2$N] (○). Solid lines a–c denote the respective ideal responses in the absence of preferential solvation.

1,3-Bis(1-pyrenyl)propane studies of fluidity

A 'molecular bolo' formed from a flexible alkane or polymer chain labeled at each end with an identical fluorophore forms the basis for a widely useful paradigm in the photophysical sciences. Upon electronic excitation of one fluorophore, cyclization may result in the collision of this species with its unexcited counterpart forming an intramolecular excited-state dimer or excimer.[40] Such excimer formation is revealed by dual emission resulting from the emergence of a new unstructured band at lower energy from, and in addition to, the familiar monomer vibronic fine structure. The relative spectroscopic populations of monomer and excimer species then allow one to address questions relating to solvent quality including the estimation of microviscosity over a broad dynamic range (*e.g.*, 1–300 cP). Provided suitable analogs exist, such an approach may also offer invaluable insight into reaction mechanisms. For example, by replacing the terminal alkenes with pyrenyl moieties we found an excellent correlation between ring closing metathesis yield for a 16-membered diene dissolved in supercritical carbon dioxide and the excimer-to-monomer ratios for a pyrene-labeled mimic.[41]

In this study, we used 1,3-bis(1-pyrenyl)propane (1,3-BPP) as our substrate to probe changes in fluidity within mixed RTIL solutions. Fig. 7 presents results for 1,3-bis(1-pyrenyl)-propane dissolved in [bmim][Tf$_2$N] + [bmim][PF$_6$], [emim]-[Tf$_2$N] + [bmim][PF$_6$], and [emim][Tf$_2$N] + [bmim][Tf$_2$N]. The predicted I_M/I_E profiles for 1,3-BPP were generated from eqn. (2) using I_M and I_E in place of I_I and I_{III}.

Several trends emerge following close scrutiny of the data in Fig. 7. First, the [emim][Tf$_2$N] + [bmim][Tf$_2$N] behavior is virtually ideal at $X_B \geq 0.1$. The departure from the predicted behavior at $X_B = 0.05$ may arise from more efficient cation packing at low [bmim]$^+$ levels (*vide supra*) resulting in an increased local microviscosity. The other two systems show more significant excursions from ideal mixing. Quite suprisingly, as [bmim][PF$_6$] is initially added to [bmim][Tf$_2$N] the observed fluidity actually *increases*. In fact, from a [bmim]-[PF$_6$] mole fraction of 0.05–0.75 a negative deviation from an ideal response persists and for an equimolar [bmim]-[Tf$_2$N] + [bmim][PF$_6$] mixture the microviscosity experienced by 1,3-bis(1-pyrenyl)propane is the same as that for neat [bmim][Tf$_2$N] within the experimental uncertainty. The origin of this behavior likely results from the effects of the weakly coordinating [PF$_6$]$^-$. At still higher mole fractions of [bmim]-[PF$_6$] this behavior is reversed. The origin of this behavior is not clear (*vide infra*).

The results for the [emim][Tf$_2$N] + [bmim][PF$_6$] are somewhat reminiscent of those for the system just discussed, however, the deviations are much less pronounced. Again, reduced friction ('lubrication) at low [bmim][PF$_6$] may be explained by the weaker ion–ion interactions within the RTIL mixture. As for the [bmim][Tf$_2$N] + [bmim][PF$_6$] mixture, at 95 mol% [bmim][PF$_6$] there is again an anomalously reduced fluidity. While efficient packing seems an obvious explanation, this is unlikely to be operative in the case of [bmim][Tf$_2$N] + [bmim][PF$_6$] where the deviation is more exaggerated. At this point, we simply offer that high [PF$_6$]$^-$ levels seem a necessary condition for this increased local microviscosity.

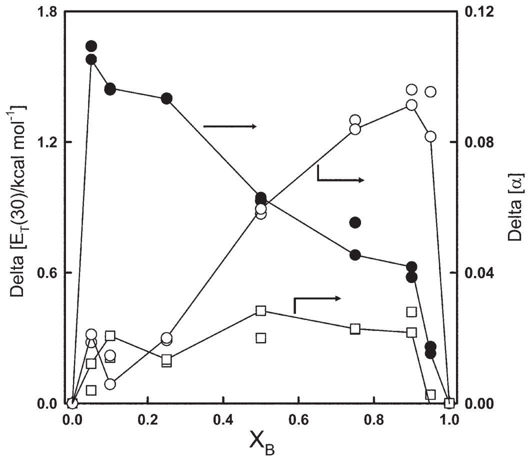

Fig. 6 Comparison of $E_T(30)$ and α-based excess polarities for [bmim][Tf$_2$N] + [bmim][PF$_6$] (●), [emim][Tf$_2$N] + [bmim][PF$_6$] (□), and [emim][Tf$_2$N] + [bmim][Tf$_2$N] (○). For clarity, solid lines connect data for excess α.

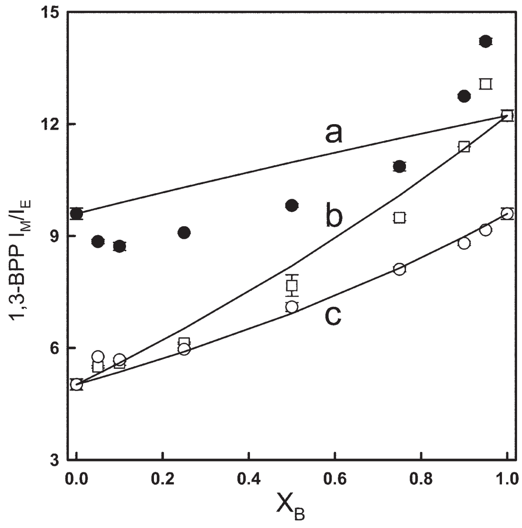

Fig. 7 Experimental 1,3-bis(1-pyrenyl)propane monomer-to-excimer intensity ratios for the binary ionic liquid systems [bmim][Tf$_2$N] + [bmim][PF$_6$] (●), [emim][Tf$_2$N] + [bmim][PF$_6$] (□), and [emim]-[Tf$_2$N] + [bmim][Tf$_2$N] (○). Solid lines a–c are the predicted results.

Our results suggest that mixing and matching ionic liquids may be a viable approach in the design and modification of these green solvent systems toward specific ends. Because mixtures often exhibit 'emergent' properties not readily apparent from those of the individual components, further exploration may reveal niche areas where binary (or higher) systems perform where the associated unary RTIL systems fail. For example, it may be possible for one component of an RTIL + RTIL mixture or a cooperative interaction to act as an *antisolvent* to aid in controlled extraction and recycling efforts. This possibility and others are currently being pursued within our laboratories.

Experimental

Materials

Pyrene was obtained from AccuStandard, Inc.; 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's betaine dye 30), pyrene-1-carboxaldehyde (99%), and 4-nitroaniline were purchased from Sigma–Aldrich; *N*,*N*-diethyl-4-nitroaniline was from Frinton Laboratories. These chemicals were recrystallized several times from methanol or another appropriate solvent system prior to preparation of stock solutions. 1,3-Bis(1-pyrenyl)propane was purchased in high purity from Molecular Probes, Inc. and used without further purification. All stock solutions were prepared by dissolution in ethanol stored over microwave-activated 4 Å molecular sieves and stored at 4 °C in pre-cleaned amber glass vials. All ionic liquids used were recently purchased in the highest purity available (electrochemical grade, 99% purity) from Covalent Associates, Inc. and shipped under argon. All transfers from these primary stocks, as well as storage, were handled in a dry box under argon. All samples were further dried *in vacuo* at room temperature for 72 h. Following this treatment, for a sample pre-equilibrated with D_2O, no water overtones were detectable by NIR absorbance spectroscopy for a 1 cm path sealed cell. Water contents determined by Karl-Fischer titration (Mettler Toledo DL31) using anhydrous methanol or AquaStar solvent KN revealed operationally dry materials (50–100 ppm water) in accord with our earlier observations.[19,20]

To prepare a given mixture, an appropriate volume (5–20 μL) of an ethanolic probe stock solution was micropipetted into a pre-cleaned quartz cuvette (Starna GL14-S) equipped with a stirring flea. After residual ethanol removal on a vacuum line, RTIL mixtures were gravimetrically prepared (±0.05%) and the sample immediately sealed with a screw-cap containing a fresh PTFE–silicone septum. The sample was stirred overnight with further evacuation on a Schlenk line. Samples remained sealed under vacuum for all experiments. Phase equilibrium was confirmed by time invariant spectra upon further stirring. Final probe concentrations were $0.5–2.0 \times 10^{-5}$ mol dm^{-3}

Methods

Steady-state fluorescence measurements were made with a PTI QuantaMaster Model C-60/2000 L-format scanning spectrofluorometer with a 75 W xenon lamp and single-grating monochromators. Excitation wavelengths/excitation slit widths/emission slit widths used: pyrene 337/2/1 nm; PyCHO 365/2/2 nm; 1,3-BPP 337/2/1 nm. Raw emission spectra were background corrected using appropriate solvent blanks.§ Absorption spectra were recorded on a Agilent Hewlett-Packard 8453 diode array spectrophotometer (±1 nm accuracy). All measurements were made at ambient temperature.

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§ Although all RTIL combinations showed weak backgrounds relative to samples containing fluorescent probe (no more than 1–2% of the total integrated intensity), the intrinsic ultraviolet emission from these RTILs should be considered *substantial* relative to more dilute or less fluorescent samples.

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