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# Solvatochromic Probe Behavior within Ternary Room-Temperature Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate + Ethanol + Water Solutions

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The solvatochromic probe behavior within ternary $BMIMPF_6$ + ethanol + water systems were investigated using four solvatochromic probes: pyrene, 1,3-bis(1-pyrenyl)propane, 1-pyrenecarboxaldehyde, and Reichardt's betaine dye ($BMIMPF_6$ [1-butyl-3-methylimidazolium hexafluorophosphate] is one of the most popular room-temperature ionic liquids [RTIL]). A simplified preferential solvation model based on the weighted mole fraction probe response shows that the pyrene cybotactic region is rich in $BMIMPF_6$ compared to the bulk. However, the 1,3-bis(1-pyrenyl)propane and 1-pyrenecarboxaldehyde solvation environments appear to be ethanol enriched. Although the aldehyde functional moiety on 1-pyrenecarboxaldehyde may explain an ethanol-rich cybotactic region, a significant decrease in bulk viscosity (more than that predicted from additivity) of $BMIMPF_6$ upon aqueous-ethanol addition may result in an increased intramolecular excimer formation efficiency of 1,3-bis(1-pyrenyl)propane. $E_T(30)$ values in ternary $BMIMPF_6$ + ethanol + water solutions are higher than those observed in neat $BMIMPF_6$ or aqueous ethanol, suggesting a local solvation environment rich in water. The results strongly suggest that the physicochemical properties of this RTIL can be modulated in a controlled fashion by adding appropriate amounts of aqueous ethanol.

## Introduction

One of the biggest problems posed to the chemical industry is to continuously deal with the fact that all chemical plants rely heavily on toxic, hazardous, and flammable organic solvents. Newly rediscovered (in their modified forms) room-temperature ionic liquids (RTILs), with no measurable vapor pressure, can be used as replacements for select organic solvents. RTILs are organic salts composed of anions and cations that are in the liquid state at ambient conditions. The new-generation RTILs have the potential to act as environmentally benign solvent media for many industrially important chemical processes.[1−3] Recently, these novel RTILs have shown promise toward important applications such as synthesis, catalysis, polymerization, separation, and extraction processes.[1−14] Some of the recent investigations of RTILs as novel solvent systems have been a part of this Journal.[15−18]

To expand the utility of RTILs and better tune their physicochemical properties, researchers have started to focus on RTIL-based mixed solvent systems. A part of the effort toward this end has been in the area where interesting RTILs are combined with other "green" solvents to tailor the physicochemical properties of the RTIL of interest in a favorable fashion.[19−23] Often, to increase the efficiency of a process (e.g., separation, extraction, synthesis, etc.), one wishes to "tune" a solvent or solvent mixture by addition of cosolvents. It is beneficial in many ways to understand how added cosolvents (or impurities) affect the physical properties of RTILs.

In our previous investigations, we examined the affect of added water and ethanol, respectively,[23] on the behavior of a variety of solutes when dissolved in a popular RTIL 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$). RTIL $BMIMPF_6$, however, is known to be hygroscopic in nature and removing the water impurity is a major concern.[19−26] Another factor that can impose limitations on the use of the binary $BMIMPF_6$ + water system in many applications is the fact that the solubility of water in $BMIMPF_6$ is very low.[19−26] Ethanol is the next choice as a "green" cosolvent that can be effectively used to "tune" the physicochemical properties of $BMIMPF_6$ and other RTILs.[19−21] However, although higher than water, the solubility of ethanol in $BMIMPF_6$ is also shown to be rather limited. Surprisingly, a binary mixture of ethanol + water was observed to be completely miscible in $BMIMPF_6$ in the composition range $X_{\text{ethanol}} \sim 0.5{-}0.9$.[19−21] This suggests that an ethanol−water mixture of appropriate composition can be used as a "green" cosolvent to effectively modify and tailor $BMIMPF_6$ physicochemical properties for specific analytical applications. To better understand any effect added ethanol−water mixtures may have on $BMIMPF_6$, we have investigated the behavior of several solvatochromic probes having different functionalities when solubilized in the ternary $BMIMPF_6$ + ethanol + water system.

Studying solute−solvent and solvent−solvent interactions by means of solvatochromic probes is both simple and convenient. Solvatochromic probe studies offer direct information on solvent properties such as dipolarity, hydrogen bond donating/accepting capabilities, etc., as experienced by the probe in its cybotactic region (a *cybotactic region* may be defined as the volume around a solute molecule in which the ordering of the solvent molecules has been influenced by the solute, including both the first solvation shell and the transition region).[27] The study of physicochemical properties that depend on solute−solvent and solvent−solvent interactions is much more complex in mixed solvent systems than in pure solvents.[28] On one hand, the solute can be preferentially solvated by any of the solvents present in the mixture; on the other, solvent−solvent interactions can strongly affect solute−solvent interactions. Preferential solvation may arise whenever the bulk mole fraction solvent composition

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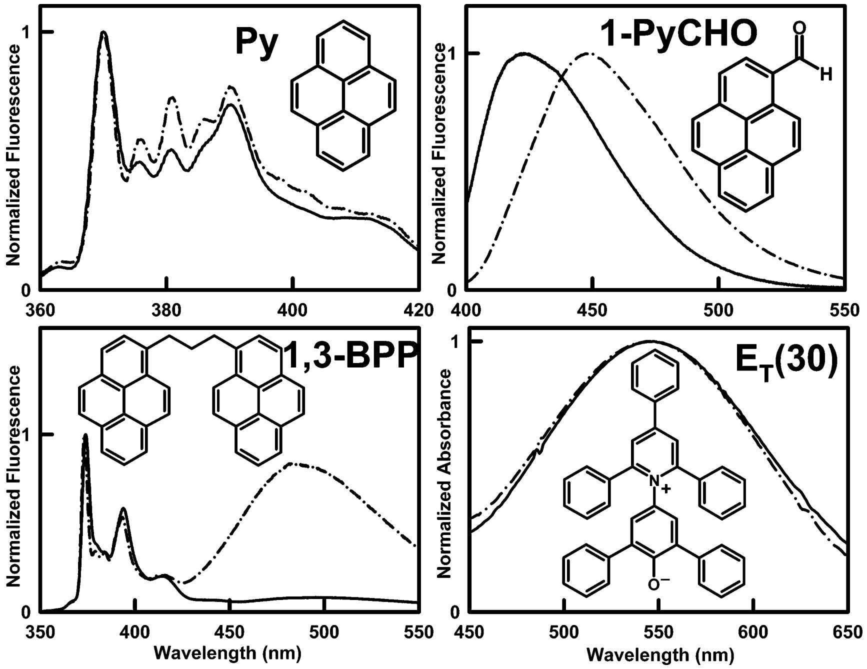

**Figure 1.** Chemical structures and the corresponding solvatochromic responses of the probes used in this study: Py, pyrene; 1-PyCHO, 1-pyrenecarboxaldehyde; 1,3-BPP, 1,3-bis(1-pyrenyl)propane; $E_T(30)$, Reichardt's dye. Solid and broken lines represent probe responses in neat $BMIMPF_6$ and ethanol, respectively.

is different from the solvation microsphere solvent composition. The response of spectroscopic probes is dependent upon the composition of the solvation microsphere and therefore provides a convenient means to measure the extent of preferential solvation.

It is important to mention that many research groups have used a variety of solvatochromic probes to gain information on the cybotactic region that these probes encounter when solubilized in different RTILs. In one of our earlier studies, we used pyrene, Reichardt's betaine dye, 1-pyrenecarboxaldehyde, Nile Red, and dansylamide to probe neat $BMIMPF_6$ at ambient conditions.[29] Muldoon et al. have also utilized Reichardt's dye along with [Cu(acac)(tmen)][X] (acac = acetylacetone, tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, X = $[BPh_4]G$ or $[ClO_4]G$) to investigate the solute−solvent interactions in many of the neat 1,3-dialkylimidazolium cation-based RTILs.[25] Carmichael and Seddon have performed polarity studies of some neat 1-alkyl-3-methylimidazolium-based RTILs with the solvatochromic dye Nile Red.[26] Recently, Baker et al. have investigated the effects of temperature and added carbon dioxide on the cybotactic region surrounding three fluorescent probes, pyrene, PRODAN (6-propionyl-2-(*N*,*N*-dimethylamino)naphthalene), and BTBP (*N*,*N*′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,-10-perylenedicarboximide), dissolved in neat $BMIMPF_6$.[30] In another study, the same group has reported on the temperature-dependent microscopic solvent properties of dry and wet $BMIMPF_6$ using $E_T(30)$ and Kamlet−Taft solvent polarity scales.[31] Most recently, these authors have used fluorescence correlation spectroscopy to determine the influence of water on the diffusion coefficients of several fluorescent probes dissolved within $BMIMPF_6$.[32]

In this paper, we present the behavior of four different solvatochromic probes dissolved in different compositions of the ternary $BMIMPF_6$ + ethanol + water solutions: pyrene, 1-pyrenecarboxaldehyde, 1,3-bis(1-pyrenyl)propane, and Reichardt's betaine dye (see Figure 1). It is important to note that all compositions studied are in the complete miscibility region of the ternary phase diagram.[19−21]

## Experimental Section

**Chemicals and Reagents.** Pyrene (99%) was obtained from AccuStandard, Inc., and 1-pyrenecarboxaldehyde (99%), Reichardt's dye, and 4-nitroaniline were obtained from Aldrich Chemical Co. 1,3-Bis(1-pyrenyl)propane was purchased from Molecular Probes, Inc., and *N*,*N*-diethyl-4-nitroaniline was purchased from Frinton Laboratories. All materials were of the highest purity available and were used as received. Stock solutions were prepared in ethanol and stored in precleaned amber glass vials at ~4 °C. $BMIMPF_6$ (electrochemical grade, 99.99+%) was stored under argon and used as received from Covalent Associates. Karl-Fisher titrations showed no detectable presence of water in freshly purchased $BMIMPF_6$. Alternatively, BMIMCl can be prepared by reaction of equimolar amounts of 1-methylimidazole and chlorobutane in a round-bottomed flask fitted with a reflux condenser by heating and stirring at 70 °C for 48−72 h. The resulting viscous liquid was cooled to room temperature followed by three washings with ethyl acetate. The remaining ethyl acetate was removed by heating to 70 °C under vacuum. To prepare $BMIMPF_6$, hexafluorophosphoric acid was slowly added to a mixture of BMIMCl in water. After stirring for ~12 h, the upper acidic aqueous layer was decanted and the lower ionic liquid layer was washed with water several times until the washings were no longer acidic. Thus obtained $BMIMPF_6$ was then heated under vacuum at 70 °C to remove any excess water.[20,21] Spectroscopic grade high-purity ethanol was obtained from Fisher Scientific and used as received. Doubly distilled deionized water was obtained from a Millipore, Milli-Q Academic water purification system.

**Methods.** Samples for spectroscopic studies were prepared as follows: appropriate aliquots of solvatochromic probe stock solutions were transferred into 1 $cm^2$ quartz cuvettes and evaporated under argon. Ethanol−water mixtures of appropriate compositions were prepared separately, and required amounts were added along with the appropriate amounts of the fresh sample of RTIL $BMIMPF_6$ directly to the cuvette, mixed thoroughly, and allowed to equilibrate for sufficient time in a

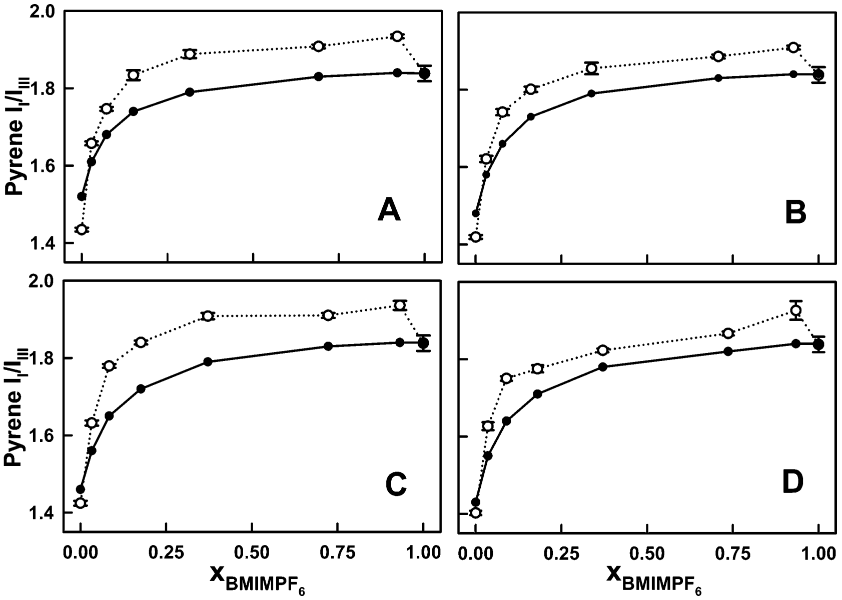

**Figure 2.** Pyrene $I_I/I_{III}$ (10 $\mu$M) in ternary BMIMPF$_6$ + ethanol + water: (A) BMIMPF$_6$ + 0.55 mole fraction ethanol in water; (B) BMIMPF$_6$ + 0.65 mole fraction ethanol in water; (C) BMIMPF$_6$ + 0.75 mole fraction ethanol in water; (D) BMIMPF$_6$ + 0.85 mole fraction ethanol in water, respectively. Key: (open circles, dotted lines) experimentally measured values; (filled circles, solid lines) predicted additive values.

moisture-free environment. All solutions were prepared on an analytical balance with ±0.1 mg accuracy. Steady-state emission experiments were performed with a PTI QuantaMaster Model C-60/2000 L-format scanning spectrofluorometer with a 75 W xenon arc lamp as the excitation source and single-grating monochromators as wavelength selection devices. All emission spectra were corrected for emission monochromator response and were background subtracted using appropriate blanks. Absorption spectra were recorded on an Agilent Hewlett-Packard 8453 photodiode array spectrophotometer.

## Results and Discussion

**Pyrene.** Pyrene is one of the most widely used neutral fluorescence probes.[33−35] The pyrene solvent polarity scale is defined as the $I_I/I_{III}$ emission intensity ratio, where band I corresponds to a $S_1(v = 0) \rightarrow S_0(v = 0)$ transition and band III is a $S_1(v = 0) \rightarrow S_0(v = 1)$ transition.[35] $I_I/I_{III}$ increases with increasing solvent polarity. It is important to mention here that we observed a pyrene $I_I/I_{III}$ in neat BMIMPF$_6$ that was significantly higher than that measured in neat ethanol ($I_I/I_{III} = 1.37 \pm 0.01$ in ethanol).[29] The only solvents with higher pyrene $I_I/I_{III}$ than observed in BMIMPF$_6$ were acetonitrile, dimethyl sulfoxide, and neat water, and among these three solvents only neat water showed a significant difference in the measured pyrene $I_I/I_{III}$ (1.96 for water versus 1.84 for BMIMPF$_6$).[29]

Our experimental pyrene $I_I/I_{III}$ (open circle, dotted lines) at ambient conditions is presented in Figure 2 (panels A−D show pyrene $I_I/I_{III}$ for BMIMPF$_6$ + 0.55, 0.65, 0.75, and 0.85 mole fractions of ethanol in water, respectively). The data clearly show higher pyrene $I_I/I_{III}$ in the higher BMIMPF$_6$ mole fraction region. At higher ethanol compositions where BMIMPF$_6$ and water mole fractions are low, as expected, the observed pyrene $I_I/I_{III}$ values are low. However, when the BMIMPF$_6$ concentration is low, increasing the water content in ethanol results in higher experimental pyrene $I_I/I_{III}$. To assess the extent of solute−solvent and solvent−solvent interactions present in a multicomponent system, a first-order spectroscopic approach assumes an idealized situation where solvent−solvent interactions can be neglected. Here, the additive spectral response, $R_{\text{additive}}$, a weighted measured (or observed) mole fraction, $X_i$, or volume fraction average of the probe's spectral response in pure solvents, $R_i^0$, is given by[36−39]

$$R_{\text{additive}} = \sum_i X_i R_i^0 \quad (1)$$

In the case of preferential solvation, however, the measured (or observed) mole fraction ($Y_i$) composition may differ substantially from the bulk. Acree and co-workers have shown that in the case of pyrene, $I_I/I_{III}$ in a ternary solution of components A−C, becomes[40]

$$\frac{I_I}{I_{III}} = \frac{[Y_A I_{I,A} + Y_B I_{I,B} + Y_C I_{I,C}]}{[Y_A I_{III,A} + Y_B I_{III,B} + Y_C I_{III,C}]} \quad (2)$$

Pyrene band I and III emission intensities are measured in the three pure solvents under identical conditions, and pyrene $I_I/I_{III}$ values for an additive ternary mixture are calculated using the bulk mole fractions, $X_i$, for each component. Data depicted as solid lines in each panel of Figure 2 represent this calculated probe behavior. A careful examination of Figure 2 reveals that (1) Experimental pyrene $I_I/I_{III}$ values deviate significantly from predicted additive values. (2) Although experimental pyrene $I_I/I_{III}$ values in aqueous ethanol are lower than predicted (the difference between experimental and predicted pyrene $I_I/I_{III}$ in aqueous ethanol decreases as the mole fraction of ethanol increases), the addition of BMIMPF$_6$ to the aqueous-ethanol mixture clearly shows increased experimentally observed pyrene $I_I/I_{III}$ values as compared to predicted additive values. (3) Except at extremely low BMIMPF$_6$ concentrations, the differences between experimental and predicted pyrene $I_I/I_{III}$ values are significant over the entire composition range.

Though our aqueous-ethanol pyrene $I_I/I_{III}$ data suggest preferential solvation of pyrene by the less polar ethanol, it is clearly not the case in the ternary BMIMPF$_6$ + ethanol + water system. The fact that experimental pyrene $I_I/I_{III}$ values are higher than predicted on the addition of BMIMPF$_6$ to aqueous ethanol may imply the possibility of favorable interaction(s) between pyrene and BMIMPF$_6$ rather than between pyrene and ethanol. It can be suggested that a lack of the presence of any polar

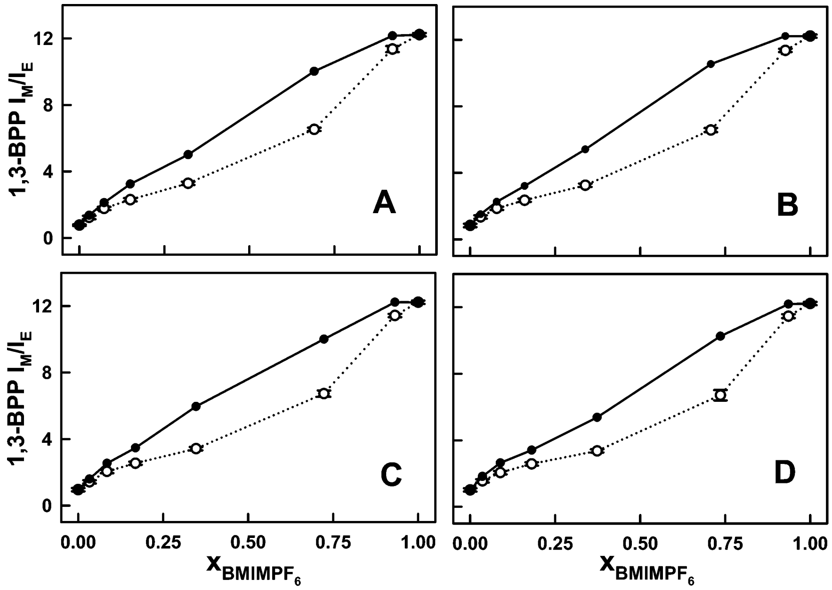

**Figure 3.** 1,3-Bis(1-pyrenyl)propane $I_M/I_E$ (10 $\mu$M) in ternary BMIMPF$_6$ + ethanol + water: (A) BMIMPF$_6$ + 0.55 mole fraction ethanol in water; (B) BMIMPF$_6$ + 0.65 mole fraction ethanol in water; (C) BMIMPF$_6$ + 0.75 mole fraction ethanol in water; (D) BMIMPF$_6$ + 0.85 mole fraction ethanol in water, respectively. Key: (open circles, dotted lines) experimentally measured values; (filled circles, solid lines) predicted additive values.

functionalities within the pyrene molecular architecture may force pyrene moieties to have a solvation sphere constituted primarily of BMIMPF$_6$. Further, these observations may also suggest the presence of interactions between the $\pi$-electron cloud on pyrene with the 1-butyl-3-methylimidazolium cation moiety. However, examination of the data presented in Figure 2 clearly indicates experimentally observed pyrene $I_I/I_{III}$ values that are higher than that observed in neat BMIMPF$_6$ (pyrene $I_I/I_{III}$ = 1.84 in neat BMIMPF$_6$). In our system, water is the only solvent in which the experimentally observed pyrene $I_I/I_{III}$ is higher than 1.84 (pyrene $I_I/I_{III}$ = 1.96 in neat water). Considering the molecular architecture and the associated hydrophobic nature of pyrene combined with its extremely low solubility in water ($<1$ $\mu$M), it is inconceivable to imagine a solvation microsphere composition surrounding excited-state pyrene that is rich in water. Further, the aqueous-ethanol results clearly indicate a situation quite contrary to this.

In a recent investigation using ATR and transmission IR spectroscopic techniques, Kazarian et al. have investigated the state of water within many RTILs, including BMIMPF$_6$.[41] Their results indicated that molecules of water are present in the "free" (not self-aggregated) state, bound via hydrogen-bonding with PF$_6^-$. Further, they also concluded that most of the water molecules exist in symmetric 1:2 type hydrogen-bonded complexes: PF$_6^-$...HOH...PF$_6^-$. A possible explanation of experimental pyrene $I_I/I_{III}$ values in BMIMPF$_6$ + ethanol + water that are higher than those observed in neat BMIMPF$_6$ could be due to the favorable interaction(s) between the probe and the RTIL; however, the presence of a hydrogen-bonded complex of the anion of the RTIL with water may increase the water composition within the cybotactic region of the excited-state pyrene probe. This will result in a higher experimentally observed pyrene $I_I/I_{III}$ than observed in neat BMIMPF$_6$.

**1,3-Bis(1-pyrenyl)propane.** A change in the viscosity of the immediate microenvironment surrounding a probe molecule is effectively manifested through 1,3-bis(1-pyrenyl)propane steady-state emission spectra.[42,43] It is well-established that, in addition to a usual structured monomer fluorescence band, the emission spectra of these compounds exhibit a broad and structureless band with maximum intensity in the vicinity of 450−500 nm due to fluorescence from an intramolecular excimer.[44] In a low-viscous solvent, the two pyrenes easily fold together to form an intramolecular excimer. As the microviscosity in the cybotactic region increases, the efficiency of the excimer formation decreases and a corresponding reduction in the intensity of the excimer band (band maximum ca. 450−500 nm) is observed.

Monomer-to-excimer emission intensity ratios ($I_M/I_E$) for 1,3-bis(1-pyrenyl)propane dissolved in ternary BMIMPF$_6$ + ethanol + water is presented in Figure 3 (panels A−D present 1,3-bis(1-pyrenyl)propane $I_M/I_E$ for BMIMPF$_6$ + 0.55, 0.65, 0.75, and 0.85 mole fraction of ethanol in water, respectively). A close inspection of Figure 3 reveals that, as expected, the $I_M/I_E$, or the microviscosity of the cybotactic region, decrease as the concentrations of the less viscous components in the mixture, ethanol and water, increase. We observed similar behavior from this probe dissolved in binary BMIMPF$_6$ + ethanol and BMIMPF$_6$ + water.[23] A modification of eq. 2 (i.e., replacing $I_1$ with $I_M$, and $I_{III}$ with $I_E$) allows us to calculate the additive $I_M/I_E$ at various compositions of the ternary mixture. The predicted additive probe responses $I_M/I_E$ are conveniently represented in Figure 3. It is important to mention here that the solubility of 1,3-bis(1-pyrenyl)propane in neat water is extremely low, and therefore it is impossible for us to measure any meaningful $I_M/I_E$ in neat water. As a consequence, the additive 1,3-bis(1-pyrenyl)propane $I_M/I_E$ in ternary BMIMPF$_6$ + ethanol + water are calculated using $I_M/I_E$ for binary aqueous ethanol and neat BMIMPF$_6$, respectively.

A careful examination of Figure 3 clearly implies that our measured $I_M/I_E$ does not show the predicted additive behavior upon addition of RTIL BMIMPF$_6$ to the aqueous-ethanol solution. For all aqueous-ethanol compositions investigated, the departure of 1,3-bis(1-pyrenyl)propane $I_M/I_E$ from additivity first increases and then decreases as the concentration of the BMIMPF$_6$ is increased. It seems that the deviation from additivity is considerably significant in the BMIMPF$_6$ mole fraction range ~0.30 to ~0.80. Further, lower experimental 1,3-bis(1-pyrenyl)propane $I_M/I_E$ than predicted from additivity initially suggests that the solvation sphere immediately surrounding 1,3-bis(1-pyrenyl)propane is enriched in low-viscosity component(s) of the mixture, i.e., either ethanol, water, or both,

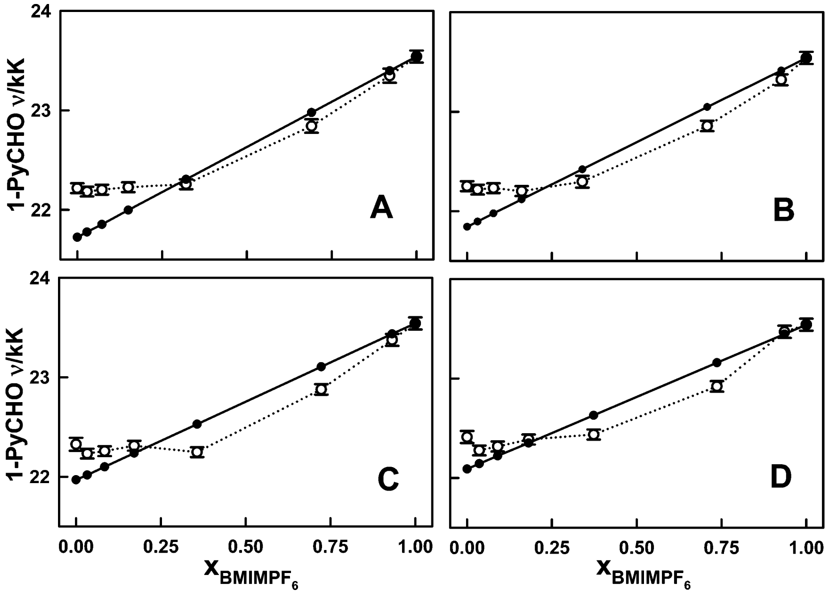

**Figure 4.** 1-Pyrenecarboxaldehyde (10 $\mu$M) lowest energy emission maxima in ternary $BMIMPF_6$ + ethanol + water: (A) $BMIMPF_6$ + 0.55 mole fraction ethanol in water; (B) $BMIMPF_6$ + 0.65 mole fraction ethanol in water; (C) $BMIMPF_6$ + 0.75 mole fraction ethanol in water; (D) $BMIMPF_6$ + 0.85 mole fraction ethanol in water, respectively. Key: (open circles, dotted lines) experimentally measured values; (filled circles, solid lines) predicted additive values.

in comparison to the bulk-phase composition (viscosity of $BMIMPF_6$ is reported to be 312 cP at 303 K).[45] This is in contrast to what is observed and suggested in the case of pyrene (vide infra). It is important to mention here that it is well-known that the addition of even small quantities of organic solvents to RTILs results in a significant decrease in the bulk viscosity of the medium.[22] It is possible that the observed changes in the $I_M/I_E$ arise principally from the decrease in the bulk viscosity of the $BMIMPF_6$ + ethanol + water solutions as compared to neat $BMIMPF_6$. This decrease in bulk viscosity of $BMIMPF_6$ on addition of aqueous ethanol can be envisioned as a consequence of solvent−solvent interactions, and as a result, the increased efficiency of intramolecular excimer formation may not be due to some specific solute−solvent interactions.

To further substantiate this reasoning, we measured the bulk viscosities of the $BMIMPF_6$ + water system at 27.6 °C in a separate preliminary investigation (a detailed report of these experiments and their interpretation will appear in a separate publication soon). For 0.03, 0.08, 0.19, and 0.26 mole fraction of water in $BMIMPF_6$ (0.26 mole fraction is close to the solubility limit of water in $BMIMPF_6$[23a]), the experimentally measured viscosities were significantly lower than those calculated from additivity (~8%, 30%, 98%, and 114% lower for 0.03, 0.08, 0.19, and 0.26 mole fraction added water, respectively). It is clear that this dramatic reduction in bulk viscosity (as compared to that obtained from additivity) results in increased intramolecular excimer formation efficiency in 1,3-bis(1-pyrenyl)propane.

**1-Pyrenecarboxaldehyde.** The spectral response of 1-pyrenecarboxaldehyde is known to be dependent on the static dielectric constant of the cybotactic region.[46] Bredereck et al. were the first to report on the solvent-dependent emission characteristics of this probe.[47] In nonpolar solvents, the fluorescence spectra of 1-pyrenecarboxaldehyde are highly structured and fluorescence quantum yields are fairly low. However, as the polarity of the surrounding medium is increased, the fluorescence emitting state changes and it is manifested through a broad, structureless, and moderately intense fluorescence behavior. The fluorescence maxima of 1-pyrenecarboxaldehyde is known to red-shift with increasing static dielectric constant of the surrounding milieu.[46,47] For this reason, 1-pyrenecarboxaldehyde has been used as a probe of solvent static dielectric constant in various isotropic and complex solubilizing media.

Figure 4 presents the lowest energy emission maxima of 1-pyrenecarboxaldehyde ($\nu$ in kK units) measured in ternary $BMIMPF_6$ + ethanol + water solutions (panels A−D present 1-pyrenecarboxaldehyde lowest energy emission maxima, $\nu$, for $BMIMPF_6$ + 0.55, 0.65, 0.75, and 0.85 mole fraction of ethanol in water, respectively). We have used eq 1 to determine the extent of preferential solvation (or lack thereof) by using lowest energy emission maxima of 1-pyrenecarboxaldehyde, $\nu$ in kK units, for spectral response, $R$, as suggested in the literature.[27,36,40] The calculated additive values are represented as filled circles and solid lines whereas the experimentally measured values are shown using open circles and dotted lines in Figure 4. A close examination of data presented in Figure 4 reveals interesting probe behavior. The 1-pyrenecarboxaldehyde probe response in aqueous-ethanol solutions strongly suggests a preferential solvation by ethanol. The more interesting fact is that there is no significant change in 1-pyrenecarboxaldehyde lowest energy emission maxima upon addition of up to ~0.35 mole fraction $BMIMPF_6$ to the aqueous-ethanol solutions. Further, as more $BMIMPF_6$ is added to the aqueous-ethanol solutions, $\nu$ for 1-pyrenecarboxaldehyde increases; nonetheless, the measured values are lower than those predicted from additivity. This overall behavior strongly suggests a preferential solvation of the excited-state 1-pyrenecarboxaldehyde by ethanol. It is interesting to observe, however, for very high $BMIMPF_6$ concentrations the departure from additivity for this probe is decreased. Our previous studies of 1-pyrenecarboxaldehyde behavior within binary $BMIMPF_6$ + ethanol and $BMIMPF_6$ + water suggested an augmented local concentration of ethanol and water (with respect to the bulk), respectively,[23] in the solvation microsphere surrounding the excited-state probe molecule. Although in our previous studies, 1-pyrenecarboxaldehyde probe behavior suggested the possibility of preferential solvation by water when solubilized within the $BMIMPF_6$ + water system, the extent of preferential solvation by ethanol was observed to be greater in the $BMIMPF_6$ + ethanol solvent system.[23] We believe the presence of the polar aldehyde

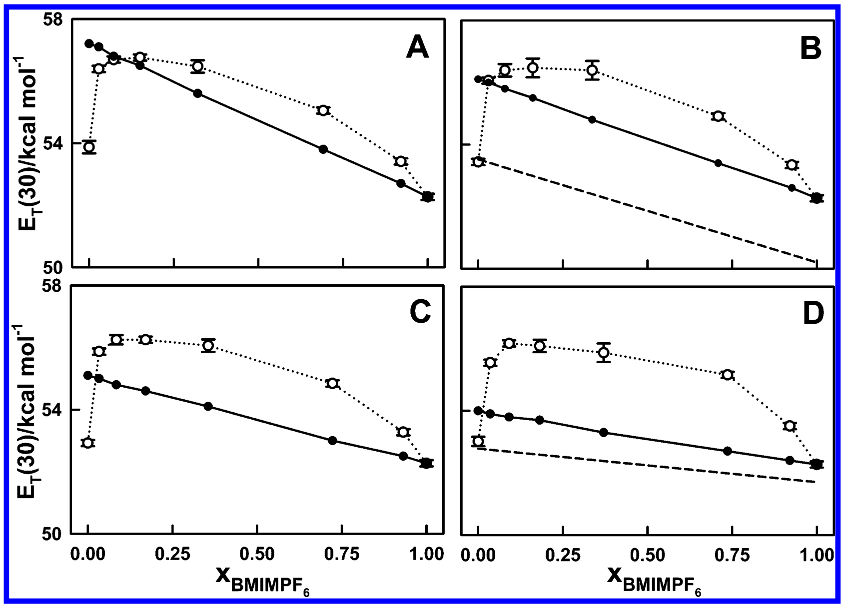

**Figure 5.** $E_T$(30) using lowest energy absorbance maxima of Reichardt's betaine dye (100 $\mu$M) in ternary BMIMPF$_6$ + ethanol + water: (A) BMIMPF$_6$ + 0.55 mole fraction ethanol in water; (B) BMIMPF$_6$ + 0.65 mole fraction ethanol in water; (C) BMIMPF$_6$ + 0.75 mole fraction ethanol in water; (D) BMIMPF$_6$ + 0.85 mole fraction ethanol in water, respectively. The corrected additive profiles are denoted in panels B and D as short-dashed lines (according to eq 3). Key: (open circles, dotted lines) experimentally measured values; (filled circles, solid lines) predicted additive values.

functional group may induce an enrichment of ethanol within the cybotactic region. Solubility constraints may restrict a similar affinity of this probe for water as the solubility of 1-pyrenecarboxaldehyde in water is significantly lower than that in ethanol.

**Reichardt's Betaine Dye.** One of the most widely used empirical scales of solvent polarities is the $E_T$(30) scale, where $E_T$(30) (in kcal mol$^{-1}$) = 28591/$\lambda_{\max}^{\text{abs}}$ (in nm).[48−50] $\lambda_{\max}^{\text{abs}}$ is the maximum wavelength of the lowest energy, intramolecular charge-transfer $\pi-\pi^*$ absorption band of the zwitterionic 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate molecule. This zwitterionic compound, also known as Reichardt's betaine dye, exhibits one of the larger observed solvatochromic effects of any known organic molecule. Because of its zwitterionic nature, solvatochromic probe behavior of Reichardt's dye is strongly affected by the hydrogen-bond donating acidity of the solvent; hydrogen-bond donating solvents stabilize the ground state more than the excited state.

It has been shown by our group and many others that the $E_T$(30) in dry BMIMPF$_6$ is similar to that observed in ethanol.[24,25,29,31] Figure 5 (panels A−D show $E_T$(30) for BMIMPF$_6$ + 0.55, 0.65, 0.75, and 0.85 mole fraction of ethanol in water, respectively) presents experimentally observed $E_T$(30) for Reichardt's dye in ternary BMIMPF$_6$ + ethanol + water solutions. The additive Reichardt's dye behavior in ternary BMIMPF$_6$ + ethanol + water mixtures was calculated using eq. 1. These predicted $E_T$(30) from additivity are presented as filled circles and solid lines in Figure 5. Examination of the experimental $E_T$(30) in Figure 5 reveals anomalous probe behavior in the ternary mixture. It is instructive to first consider the behavior of Reichardt's dye in aqueous-ethanol mixtures. We observe that the measured $E_T$(30) in aqueous ethanol, for the ethanol mole fraction range considered here, are lower than that predicted from additivity, the departure from additivity decreasing with increased ethanol mole fraction. These observations are in agreement with literature reports.[51] Most of these investigations explain such observations by suggesting the presence of a "third" solvent environment formed as a result of ethanol−water complexation. Though our previous investigation of Reichardt's dye solvation behavior in binary BMIMPF$_6$ + water revealed no preferential solvation, binary BMIMPF$_6$ + ethanol mixtures showed strong synergistic effects.[23] For ternary BMIMPF$_6$ + ethanol + water, contrary to what was observed for 1-pyrenecarboxaldehyde, experimental $E_T$(30) increases significantly as small amounts of BMIMPF$_6$ are added to aqueous ethanol and as aqueous ethanol is added to BMIMPF$_6$, the increase being more drastic for the former. Although the predicted curve for additive solvation suggests a linear decrease in $E_T$(30) with increasing BMIMPF$_6$ mole fraction, the experimentally observed values rapidly increase to a maximum near 0.10 mole fraction BMIMPF$_6$ falling off slowly thereafter. Because aqueous-ethanol mixtures do not follow additivity, one can generate a corrected additive curve for the ternary system using the expression

$$R_{\text{additive}} = \sum_i X_i R_i^0 + \Delta E_T(30) \tag{3}$$

where $\Delta E_T$(30), the "excess polarity", is the difference between the measured $E_T$(30) and that obtained from additivity for aqueous ethanol at a given ethanol mole fraction. The so-corrected curves for additive behavior for 0.65 and 0.85 mole fraction ethanol are included in Figure 5B,D. In this way, it becomes clear that Reichardt's dye is preferentially solvated by ethanol in ethanol−water mixtures whereas in BMIMPF$_6$ + ethanol + water mixtures preferential solvation by water occurs. This remarkable result may have important implications for chemical processing within RTIL + ethanol + water mixtures.

**Kamlet−Taft Treatment.** To further explore these observations, we performed Kamlet−Taft investigation of ternary BMIMPF$_6$ + ethanol + water system.[48−50,52−54] In this treatment, the solvent dipolarity/polarizability, $\pi^*$, is estimated using the response of *N*,*N*-diethyl-4-nitroaniline, a non-hydrogen bond donor solute by using

$$\pi^* = 0.314(27.52 - \nu_{\text{DENA,max}}) \tag{4}$$

where $\nu_{\text{DENA,max}}$ is the position of the absorbance maximum of *N*,*N*-diethyl-4-nitroaniline in kK units.[50,52−54] The hydrogen

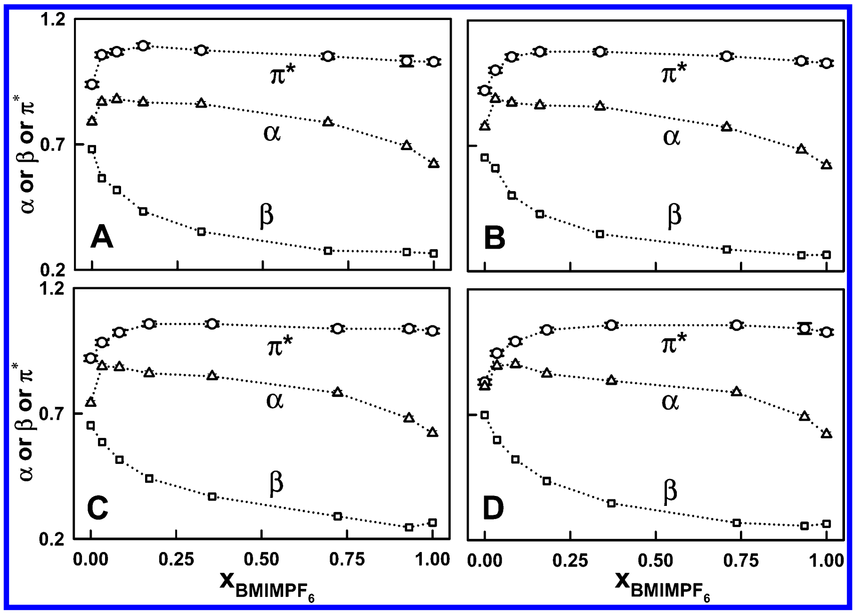

**Figure 6.** Dipolarity/polarizability ($\pi^*$, open circles), hydrogen-bond donating acidity, HBD (α, open triangles), and hydrogen-bond accepting basicity, HBA ($\beta$, open squares) in ternary BMIMPF$_6$ + ethanol + water: (A) BMIMPF$_6$ + 0.55 mole fraction ethanol in water; (B) BMIMPF$_6$ + 0.65 mole fraction ethanol in water; (C) BMIMPF$_6$ + 0.75 mole fraction ethanol in water; (D) BMIMPF$_6$ + 0.85 mole fraction ethanol in water, respectively.

bond accepting basicity (HBA), $\beta$, for solvents can be determined by using the enhanced solvatochromic shift of 4-nitroaniline relative to the homomorphic *N*,*N*-diethyl-4-nitroaniline and using the expression:

$$\beta = 0.358(31.10 - \nu_{\mathrm{NA,max}}) - 1.125\pi^* \qquad (5)$$

Here, $\nu_{\mathrm{NA,\ max}}$ is the observed absorbance maxima for 4-nitroaniline in kK units.[48−50,52−54] Finally, the hydrogen bond donating acidity (HBD), α, of the solvent is calculated using the $E_T(30)$ and $\pi^*$ values: [48−50,52−54]

$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \qquad (6)$$

For ternary BMIMPF$_6$ + ethanol + water, measured $\pi^*$ are presented (open circles) in Figure 6 (panels A−D show $\pi^*$ for BMIMPF$_6$ + 0.55, 0.65, 0.75, and 0.85 mole fractions of ethanol in water, respectively). It is clear that as BMIMPF$_6$ is added to aqueous ethanol, $\pi^*$ increases rapidly, reaches a maxima, and then gradually decreases to its value in neat BMIMPF$_6$. It is interesting to note that the position of the $\pi^*$ maxima shifts to higher BMIMPF$_6$ mole fraction as the concentration of ethanol is increased. It is evident from the data that the dipolarity/polarizability increases as BMIMPF$_6$ is added to aqueous-ethanol mixtures. The pyrene polarity scale (i.e., pyrene $I_I/I_{III}$) is known, in part, to depend on the dipolarity/polarizability of the solubilizing media. A comparison of data in Figure 2 and Figure 6 reveals that pyrene $I_I/I_{III}$ also increases rapidly as BMIMPF$_6$ is added to aqueous-ethanol mixtures. At higher BMIMPF$_6$ mole fractions, the change in pyrene $I_I/I_{III}$, for the most part, is not as drastic. However, the behavior of 1-pyrenecarboxaldehyde (Figure 4), which is largely dependent on the static dielectric constant of the probe cybotactic region, does not show any similarity with observed $\pi^*$ values of the medium. We propose that an enrichment of the cybotactic solvation microsphere of excited 1-pyrenecarboxaldehyde by ethanol (as suggested earlier) would not allow this probe to report on the bulk solvent characteristics. Similar trends between observed $E_T(30)$ and $\pi^*$ confirm the behavior of Reichardt's betaine dye (Figure 5) which, in part, depends on the dipolarity/polarizability of the solubilizing medium.

The HBA (i.e., $\beta$) ability of a solvent depends on the absorbance maxima of both *N*,*N*-diethyl-4-nitroaniline *and* 4-nitroaniline (eq 5). The $\beta$ for ternary BMIMPF$_6$ + ethanol + water are shown (open squares) in Figure 6 (panels A−D show $\beta$ for BMIMPF$_6$ + 0.55, 0.65, 0.75, and 0.85 mole fractions of ethanol in water, respectively). As expected, on addition of BMIMPF$_6$ to aqueous ethanol, the HBA of the solvent mixture decreases; the decrease is initially rapid but becomes more gradual at higher BMIMPF$_6$ mole fractions. Unlike ethanol and water, BMIMPF$_6$ lacks a genuine HBA moiety or site. $PF_6^-$ is known to have a compact structure possessing much weaker HBA basicity in comparison to ethanol or water.[41]

The HBD ability of a solvent system, α, depends on $E_T(30)$ *and* $\pi^*$ (eq 6). Kamlet and Taft calculated that approximately two-thirds of the shift in the absorbance maxima of the Reichardt's dye could be assigned directly to specific interactions involving the phenoxide oxygen (see Figure 1).[52] This suggests that the $E_T(30)$ scale is largely, albeit not exclusively, a measure of the HBD ability of the solvent system (vide supra). In light of these facts, it is clear that, as the composition of the ternary system is varied, any significant changes in the BMIMPF$_6$ + ethanol + water α values (and $\pi^*$, to a lesser extent) should be manifested through the observed $E_T(30)$. We remind the reader that the cybotactic region experienced by Reichardt's dye in this solvent mixture may differ from those observed by 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline due to the possibility of differential preferential solvation. For the ternary BMIMPF$_6$ + ethanol + water, measured α are presented (open triangle) in Figure 6 (panels A−D show α for BMIMPF$_6$ + 0.55, 0.65, 0.75, and 0.85 mole fractions of ethanol in water, respectively). A careful examination of the α clearly shows a sharp increase in HBD ability as very small amounts of BMIMPF$_6$ are added, followed by a gradual decrease as more BMIMPF$_6$ is added to aqueous-ethanol mixtures. A comparison of $E_T(30)$ (Figure 5) with α (Figure 6) for the same compositions of the ternary mixture demonstrates a very similar trend (refer to eq 6). Therefore, the surprising nature of $E_T(30)$ (i.e., the deviation from additivity, vide infra, Figure 5) may be attributed to the corresponding changes in the HBD acidity as well as the dipolarity/polarizability of the system as the composition of the ternary mixture is varied. It appears that the Kamlet–Taft treatment is able to explain, in part, the experimentally observed solvatochromic probe behavior (i.e., $E_T(30)$ and pyrene $I_I/I_{III}$) for ternary $BMIMPF_6$ + ethanol + water. A major part of the current efforts in our group is focused on identifying and/or developing preferential solvation models that may conform to our experimental solvatochromic probe data within RTIL-based multicomponent systems.

## Conclusion

The deviations between experimentally observed and predicted additive behavior of the probes could arise not only from specific solute–solvent interactions but also due the altered properties of the solution due to any solvent–solvent interactions. For most cases, the dipolarity of the ternary solution appears to be greater than that predicted from the simple solvation model used in the current study. Presumably, interactions between pyrene and the imidazolium cation and/or interactions between water molecules and the $PF_6^-$ anion account for these observations. Model predictions indicate 1,3-bis(1-pyrenyl)propane may be preferentially solvated by the lower-viscosity components in solution; however, these observations seem to result from a reduction in the bulk viscosity of $BMIMPF_6$ due to the presence of low-viscosity cosolvents. 1-Pyrenecarboxaldehyde appears to be preferentially solvated by ethanol; however, for $X_{BMIMPF6} < \sim 0.35$, the observed response of 1-pyrenecarboxaldehyde remains constant. As the composition of $BMIMPF_6$ increases past 0.35 mole fraction, the observed response of 1-pyrenecarboxaldehyde is lower than that obtained from additivity, indicating the static dielectric constant of the cybotactic region surrounding this probe in the ternary solvent system is lower than predicted. On the basis of the response of Reichardt's betaine dye, synergistic effects are again observed upon the addition of aqueous ethanol to $BMIMPF_6$. The dipolarity/polarizability and hydrogen-bond donating ability of the ternary solution first increase and then gradually decrease as the composition of $BMIMPF_6$ increases. The hydrogen-bond accepting ability decreases with increasing $BMIMPF_6$. The results of the current study indicate that one is able to significantly alter the physicochemical properties of $BMIMPF_6$ by simply adding appropriate amounts of ethanol and water.

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