SOLVATOCHROMIC PROBE BEHAVIOR WITHIN NEAT AND COSOLVENT ADDED ROOM-TEMPERATURE IONIC LIQUID SOLUTIONS

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ABSTRACT

Room-temperature ionic liquids (RTILs) show tremendous promise as replacements to toxic and volatile organic solvents for many applications. Before the full utilization of RTILs can be achieved, more information about their physical properties needs to be understood. Towards this end, we have employed the solvatochromic probes pyrene, 1-pyrenecarboxaldehyde, 1,3-bis-(1-pyrenyl)propane, and Reichardt’s betaine dye to investigate the solvent properties of neat and cosolvent-added RTILs. The solvent properties of neat 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF6), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimIM) and 1-ethyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide (emimIM) were investigated. Because of the hygroscopic nature of most RTILs, the preferential solvation of the bmimPF6 + water solvent system was studied. Furthermore, there is a desire to tune the specific solvent properties of RTILs to meet the needs of a particular application through the addition of green cosolvents, therefore the preferential solvation of the bmimPF6 + ethanol solvent system was also investigated.

INTRODUCTION

Room-temperature ionic liquids (RTILs) have shown tremendous promise as replacements for traditional organic solvents in a variety of industrially important chemical processes (1,2). With no measurable vapor pressure, RTILs have the potential to act as an environmentally benign, green solvent media. Before the full utilization of this class of compounds can be realized, much more information related to their physical properties needs to be understood. Furthermore, the addition of cosolvents to a RTIL can alter its physical properties to better suit a particular application of interest. Our research group has undertaken a two-part investigation of the physicochemical properties of select RTILs.

Initially we were interested in determining the relative solvent properties of select RTILs through the use of solvatochromic probes. However, it became clear to us that it is also extremely important to determine the relative solvent properties of RTILs when cosolvents are present. Establishing the relative solvent properties of RTILs under the influence of added cosolvents or impurities can serve multiple purposes. First, removing all impurities from the RTIL following synthesis is often difficult and can be quite expensive. In addition, several RTILs have been shown to be hygroscopic in nature.

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making it virtually impossible to eliminate all the water (3-8). Also, RTILs are effective solvents in extraction and separation processes that place the RTIL in physical contact with another solvent. Completely separating the RTIL from this solvent is not likely to occur, leading to a mixed solvent system. Finally, and most importantly, it could be desirable to tune the physical properties of the RTIL to meet the specific needs of an application through the use of added cosolvents (3,4). Keeping in mind the green nature of RTILs, we thought it would be most instructive to begin our investigation of the preferential solvation of select solvatochromic probes by introducing incremental amounts of water or ethanol to one of the most widely used RTILs, 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆).

EXPERIMENTAL

Chemicals and Reagents

Pyrene (99%) was obtained from AccuStandard, Inc., while 1-pyrenecarboxaldehyde (99%), Reichardt's betaine dye, and 4-nitroaniline were obtained from Aldrich Chemical Co. 1,3-Bis(1-pyrenyl)propane was purchased in high purity from Molecular Probes, Inc. N,N-Diethyl-4-nitroaniline was purchased from Frinton Laboratories. All these probes were used as received. Stock solutions of all probes were prepared by dissolving in ethanol in pre-cleaned amber glass vials and stored at ~4°C. 1-Butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (emimIM), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimIM) (electrochemical grade, 99.99+%) were stored under argon and used as received from Covalent Associates, Inc. Karl-Fisher titrations showed no detectable presence of water in freshly purchased bmimPF₆, bmimIM or emimIM. Spectroscopic grade high purity ethanol was obtained from Fisher Scientific and used as received. All other chemicals were of highest purity grade.

Methods

Samples for spectroscopic studies were prepared as follows: appropriate aliquots of solvatochromic probe stock solutions were transferred into 1-cm² quartz cuvettes and evaporated under argon. For the neat RTIL investigation, two mLs of the fresh sample of RTIL were added to the cuvette, mixed thoroughly and allowed to equilibrate for sufficient time in a moisture-free environment. For the preferential solvation studies, two mL of the fresh sample of bmimPF₆ and the required amount of water or ethanol were added to the cuvette, mixed thoroughly and allowed to equilibrate for sufficient time in a moisture-free environment. 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. All fluorescence data were measured in a 1-cm² quartz cuvette at 25°C and 1 atm pressure. Absorption spectra were recorded on an Agilent Hewlett-Packard 8453 Photo-Diode Array spectrophotometer in the usual manner with a 1-cm² quartz cuvette at 25°C.
RESULTS AND DISCUSSION

Neat RTIL Studies

The use of solvatochromic probes can provide important information about solvent parameters related to polarity (9) (static dielectric constant, refractive index, the hydrogen-bond donating ability, etc.) as well as viscosity. Because the dipolarity of a solvent is not readily described by one or two microscopic properties, several probes describing one or two interactions in solution must be employed in order to obtain a better idea of the relative dipolarity of the solvent. The solvatochromic probes used in the current study are pyrene, 1-pyrenecarboxaldehyde, 1,3-bis-(1-pyrenyl)propane, and Reichardt's betaine dye (see Figure 1 for structures). The RTILs investigated are bmimPF$_6$, emimIM, and bmimIM, see Figure 2 for molecular structures. Results obtained in the RTILs are compared with select traditional organic solvents in order to determine the relative dipolarity of the RTILs.

Pyrene. Pyrene, constituted of four fused benzene rings with no other functional groups, is one of the most widely used neutral fluorescence probes (10-12). The pyrene polarity scale is defined as the $I_{II}/I_{III}$ 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 (12). The $I_I/I_{III}$ emission intensity ratio increases with increasing solvent polarity.

A careful examination of Table I reveals the relative dipolarity of pyrene in bmimPF$_6$ is less than bmimIM that, in turn, is less dipolar in nature than emimIM. This makes sense because the larger butyl chain should impart more nonpolar character to the RTIL than the ethyl chain. Also, the hexafluorophosphate anion is considered to resemble a hard sphere, whereas the bis(trifluoromethylsulfonyl)imide anion is larger and more polarizable. Relative to traditional organic solvents, the dipolarity of bmimPF$_6$ is slightly lower than acetonitrile, emimIM appears to be remarkably similar to water, and the dipolarity of bmimIM is very near that of dimethylsulfoxide. In an analogous study, Bonhôte et al. utilized pyrene to assess the polarity of RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethyl)imide (emimTf$_2$N) (13). They report a pyrene $I_I/I_{III}$ value for emimTf$_2$N similar to ethanol. Therefore, it appears that the anion plays an important role in determining the pyrene $I_I/I_{III}$ emission intensity ratio.

1-Pyrenecarboxaldehyde. The solvent-dependent characteristics of the 1-pyrenecarboxaldehyde emission spectra are manifested through two types of closely spaced excited states (14). In nonpolar solvents a $n-n^*$ transition occurs and the fluorescence spectra are highly structured with fairly low quantum yields (<0.001). As the polarity of the surrounding medium is increased and the static dielectric constant increases past ~10, the $n-n^*$ transition becomes more energetically favorable. When this occurs a broad, structureless fluorescence band of moderate intensity is observed, with the peak maximum shifting to longer wavelengths as the static dielectric constant increases. For this reason, 1-pyrenecarboxaldehyde has been an effective solvatochromic probe in various isotropic and complex solubilizing media.

Table I tabulates the observed peak maxima for 1-pyrenecarboxaldehyde in bmimPF$_6$, emimIM, bmimIM as well as select traditional organic solvents at 25°C and 1 atm pressure. The peak maxima for all three RTILs included in this study are very near that of dimethylsulfoxide. The wavelength maxima for bmimPF$_6$ and bmimIM are nearly identical at 423 – 424 nm, while the wavelength maximum of emimIM is slightly red-shifted to 427 nm. Bonhôte et al. report the emission maximum of 1-pyrenecarboxaldehyde in emimTf$_2$N at 20°C appeared at 431 nm (13). Based upon the results of these limited studies, it appears that the primary factor affecting the static dielectric constant is the length of the alkyl side chain, where a shorter alkyl chain leads to a higher static dielectric constant; the choice of anion does not seem to significantly affect the positioning of the fluorescence maximum.

1,3-Bis-(1-pyrenyl)propane. It is well established that, in addition to a usual structured monomer fluorescence band, the emission spectra of dipyrenylalkanes exhibit a broad, structureless band with maximum intensity in the vicinity of 450 – 500 nm due to fluorescence from an intramolecular excimer (15,16). Pyrene is especially suitable for this purpose primarily because of the large stabilization energy of pyrene excimers as well as the fact that pyrene and its derivatives possess long fluorescence lifetimes that allow a suitable configuration to be achieved for excimer formation (15). Intramolecular excimer emission is strongest for dipyrenylpropane, which has been used as a fluorescence probe for micellar interiors (17). In a low-viscous solvent the two pyrenes easily fold together to form an intramolecular excimer. As the microviscosity...
surrounding the probe increases, the efficiency of excimer formation decreases and a corresponding reduction in the intensity of the excimer band is observed.

Table I presents monomer-to-excimer emission intensity ratios \( (I_M/I_E) \) for 1,3-bis-(1-pyrenyl)propane solubilized in bmimPF₆, emimIM and bmimIM, as well as select organic solvents. A close inspection of the data reveals that the viscosity of the RTIL decreases as the length of the alkyl chain decreases. Also, the hexafluorophosphate-based RTIL is more viscous than the imide-based RTIL. Our observed results are consistent with viscosity measurements reported by Covalent Associates, Inc (18).

Table I. Behavior of various solvatochromic probes solubilized in neat RTILs bmimPF₆, bmimIM and emimIM and organic solvents. Reported uncertainties are determined by measuring data for three separate analyses with three scans for each analysis.

| Solvent        | Pyrene [Iₐ/Iₐ] | 1-Pyrene-carboxaldehyde | 1,3-Bis-(1-pyrenyl)propane [Iₐ/Iₐ] | Reichardt’s Dye [λₐb₁/μₐ₃] | Eₜ(30) |
|----------------|----------------|-------------------------|----------------------------------|---------------------------|--------|
| bmimPF₆         | 1.83 (± 0.01)  | 423 ± 1                 | 12.2 ± 0.1                        | 547                        | 52.3   |
| bmimIM          | 1.91 (± 0.01)  | 423 ± 1                 | 9.6 ± 0.3                         | 572                        | 50.0   |
| emimIM          | 1.96 (± 0.01)  | 427 ± 1                 | 5.0 ± 0.1                         | 544                        | 52.6   |
| Cyclohexane     | 0.64 (± 0.01)  | highly structured       | not determined                    | not determined             | not determined |
| Dichloromethane | 1.45 (± 0.01)  | 416 ± 1                 | not determined                    | 700                        | 40.8   |
| Ethanol         | 1.37 (± 0.01)  | 449 ± 1                 | 1.2 ± 0.1                         | 546                        | 52.4   |
| Methanol        | 1.50 (± 0.01)  | 453 ± 1                 | 1.0 ± 0.1                         | 515                        | 55.1   |
| Acetonitrile    | 1.88 (± 0.01)  | 416 ± 1                 | 1.3 ± 0.1                         | 630                        | 45.4   |
| Diethylsulfoxide| 1.90 (± 0.01)  | 418 ± 2                 | 1.5 ± 0.1                         | 630                        | 45.4   |
| Ethylene glycol | 1.55 (± 0.02)  | 460 ± 2                 | 4.7 ± 0.1                         | 508                        | 56.3   |
| Water           | 1.96 (± 0.05)  | 475 ± 2                 | not determined                    | 456                        | 63.1   |

*Uncertainties associated with λₐb₁ values are ± 1 nm

Reichardt’s Betaine Dye. One of the most widely used empirical scales of solvent polarity is the \( E_T(30) \) scale based on the following expression:

\[
E_T(30) = \frac{a_{\text{absorbance}}}{\lambda_{\text{max}}} \tag{1}
\]

where \( E_T(30) \) has units of kcal mol⁻¹ and \( \lambda_{\text{max}} \) is the wavelength (in nm) of the maximum of the longest wavelength intramolecular charge transfer \( \pi-\pi^* \) absorption band of the zwitterionic 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridino)phenolate molecule (20-24). This compound, also known as Reichardt’s betaine dye, exhibits one of the largest observed solvatochromic effects of any known organic molecule (20,21). Because of its zwitterionic nature, the solvatochromic probe behavior of Reichardt’s dye is strongly affected by the hydrogen-bond donating ability of the solvent. Hydrogen-bond donating solvents stabilize the ground state more than the excited state shifting the charge-transfer band to lower wavelengths (20-22,25).

Table I tabulates the observed \( \lambda_{\text{max}} \) values and calculated \( E_T(30) \) values at 25°C and 1 atm pressure. In agreement with previous studies, the \( E_T(30) \) value of neat
bmimPF$_6$ is close to a short-chain alcohol (6,7,19,26). The E$_{fl}$(30) value of emimIM and bmimIM are 52.6 and 50.0, respectively. This indicates the hydrogen-bond donating ability of emimIM is similar to bmimPF$_6$.

**Preferential Solvation Studies**

Investigating physicochemical properties that depend on solute-solvent interactions is much more complex in mixed solvent systems than in pure solvents (27). For instance, the solute may be preferentially solvated by any of the solvents present in the mixture, or solvent-solvent interactions can have a dramatic affect on solute-solvent interactions. Solvatochromic probes can provide a simple and convenient method to study solute-solvent interactions.

When solubilized in a multi-component solvent system, the solute molecule may experience preferential solvation. Preferential solvation arises whenever the bulk mole fraction solvent composition is different from the solvent composition in the cybotactic region (the solvent region immediately surrounding the probe molecule). Since the response of spectroscopic probes depends on the composition of the cybotactic region, these molecules can provide a convenient means to determine the degree of preferential solvation.

Most spectroscopic probe techniques assume the idealized solution where solvent-solvent interactions can be neglected, and the measured spectral response, R, in a binary solvent mixture is given by (28-33)

$$ R = Y_A R_A^0 + (1 - Y_A) R_B^0 $$

[2]

a weighted mole fraction (shown here) or volume fraction average of the probe’s spectral response in the two pure solvents, $R_A^0$ and $R_B^0$. $Y_A$ and $(1-Y_A)$ refer to the solvation sphere mole fraction composition of solvent A and B, respectively, which in the case of preferential solvation may be quite different than the overall bulk liquid-phase composition, $X_A$ and $(1-X_A)$.

The solvatochromic probes pyrene, 1-pyrenecarboxaldehyde, 1,3-bis-(1-pyrenyl)propane, and Reichardt’s betaine dye were solubilized in bmimPF$_6$ and incremental amounts of water or ethanol were added to the bmimPF$_6$ + probe systems until the limit of solubility was reached. Due to the low solubility of water (3-8) and ethanol (3) in bmimPF$_6$, the maximum mole fraction water added was 0.25 and the maximum mole fraction ethanol added was 0.40.

**Pyrene.** Table II and Table III present pyrene $I_I/I_{III}$ emission intensity ratios in binary bmimPF$_6$ + water and binary bmimPF$_6$ + ethanol systems, respectively. A careful examination of the results reveals that pyrene $I_I/I_{III}$ does not change appreciably as water or ethanol is added to bmimPF$_6$. Furthermore, the observed pyrene $I_I/I_{III}$ values in the water-added or ethanol-added solutions are very similar to that obtained in neat bmimPF$_6$, even at the highest composition of water or ethanol, and very different from the $I_I/I_{III}$ ratio obtained in neat water or neat ethanol, respectively.
Acree and coworkers have shown that, in the case of pyrene, the $I_{I/III}$ emission intensity ratio in a binary solution of components A and B becomes \[ \frac{I_I}{I_{III}} = \frac{Y_{I, phaseB} I_{I, phaseB} + (1 - Y_{I}) I_{III, phaseB}}{Y_{III, phaseA} I_{III, phaseA} + (1 - Y_{III}) I_{I, phaseA}} \] \[ [3] \]
Calculations using equation [3] suggest that pyrene $I_{I/III}$ in binary bmimPF$_6$ + water solutions should remain essentially constant at 1.84 in going from neat bmimPF$_6$ to 0.25 mole fraction water in bmimPF$_6$. Because of the large uncertainty associated with the pyrene $I_{I/III}$ determined in water, we would speculate that if pyrene is preferentially solvated by bmimPF$_6$, it is slight at best. Using equation [3], the pyrene $I_{I/III}$ ratio should theoretically decrease from 1.84 to 1.65 as more ethanol is added to bmimPF$_6$ up to a maximum of 0.40 mole fraction ethanol. However, the observed pyrene $I_{I/III}$ value only changes from 1.84 in neat bmimPF$_6$ to 1.88 (0.40 mole fraction ethanol added). With an uncertainty of $\pm 0.02$ associated with each measurement, the apparent difference in $I_{I/III}$ as ethanol is added is insignificant. These results clearly indicate a strong preferential solvation of the excited-state pyrene moieties by bmimPF$_6$. It can be inferred from these results that a lack of the presence of any polar functional groups within the pyrene molecular structure may force pyrene to have a solvation sphere constituted primarily of bmimPF$_6$.

Table II. Behavior of pyrene, 1-pyrenecarboxaldehyde and 1,3-bis-(1-pyrenyl)propane in the presence of water when dissolved in RTIL bmimPF$_6$ (5). Reported uncertainties are obtained from measuring data for three separate analyses with three scans for each analysis.

| Mole Fraction Water, $X_w$ | Pyrene $[I_{I/III}]$ | 1-Pyrenecarboxaldehyde $[\lambda_{max}/\text{nm}]$ | 1,3-Bis-(1-pyrenyl)propane $[I_{I/III}]$ |
|---------------------------|---------------------|-----------------------------------------------|-----------------|
| 0.00                      | 1.84 (± 0.01)       | 424.8 (± 1.1)                                 | 13.7 (± 0.2)    |
| 0.03                      | 1.82 (± 0.01)       | 430.1 (± 1.2)                                 | 11.9 (± 0.4)    |
| 0.10                      | 1.83 (± 0.01)       | 435.8 (± 0.9)                                 | 9.9 (± 0.3)     |
| 0.18                      | 1.84 (± 0.02)       | 439.3 (± 1.0)                                 | 7.7 (± 0.2)     |
| 0.25                      | 1.83 (± 0.01)       | 442.9 (± 1.1)                                 | 6.5 (± 0.2)     |
| 1.00                      | 1.96 (± 0.05)       | 475.0 (± 2.0)                                 | not determined  |

1-Pyrenecarboxaldehyde. Table II and Table III tabulate the observed wavelength maximum for 1-pyrenecarboxaldehyde solubilized in varying compositions of bmimPF$_6$ + water and bmimPF$_6$ + ethanol solutions, respectively. In the water-added solutions, the observed spectral response shifted to higher wavelengths as incremental volumes of water were added. Using equation [2] and substituting $1/\lambda_{max}$ for the spectral response (9,28,33), R, the calculated solvation sphere mole fraction water, $Y_w$, of 0.12, 0.24, 0.31, and 0.39 compared to the bulk-phase water mole fraction, $X_w$, of 0.03, 0.10, 0.18, and 0.25, respectively, show a strong preferential solvation of 1-pyrenecarboxaldehyde by water. A similar trend was observed with the ethanol-added

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solutions. The calculated solvation sphere mole fraction ethanol, $Y_{E}$, values of 0.04, 0.13, 0.50, 0.52, and 0.69 show a clear preferential solvation by ethanol when compared with the bulk-phase mole fraction of ethanol, $X_{E}$, of 0.01, 0.05, 0.10, 0.15, 0.20, 0.25, 0.40, respectively. We believe the presence of the polar aldehyde functional group may induce an enrichment of water or ethanol over bmimPF$_6$ within the cybotactic region.

1,3-Bis-(1-pyrenyl)propane. Recently Sedden et al. presented their investigation concerning the decrease in viscosity of two RTILs, bmimPF$_6$ and bmimBF$_4$, in the presence of a variety of cosolvents (3). However, the effect of the presence of water on the viscosity was only reported for bmimBF$_4$. Table II and Table III list the observed monomer-to-excimer emission intensity ratio ($I_{m}/I_{e}$) for 1,3-bis-(1-pyrenyl)propane solubilized in bmimPF$_6$ + water and bmimPF$_6$ + ethanol solutions, respectively. Intramolecular excimer formation efficiency within 1,3-bis-(1-pyrenyl)propane depends on the viscosity of the probe solubilization site (vide supra). It is clear that the addition of water or ethanol decreases the viscosity of the resulting bmimPF$_6$ + cosolvent solution.

A determination of the extent of preferential solvation within the binary bmimPF$_6$ + water solvent systems is impossible due to the extremely low solubility of 1,3-bis-(1-pyrenyl)propane in neat water. For the ethanol-added study, a modification of equation [3] (i.e., replacing $I_{I}$ with $I_{M}$ and $I_{III}$ with $I_{E}$) allowed us to determine the solvation sphere surrounding the probe molecule is enriched with ethanol in comparison to the bulk-phase ethanol composition. While pyrene was observed to be preferentially solvated by bmimPF$_6$ (vide supra), the opposite is observed with 1,3-bis-(1-pyrenyl)propane.

Reichardt’s Betaine Dye. Reichardt’s dye gives an indication of the hydrogen-bond donating ability of the solvent. An evaluation of the entries in Table IV indicates the hydrogen-bond donating ability of the solution increases as more water is added to bmimPF$_6$. At first glance this behavior seems perfectly reasonable, and calculations based upon equation [2] (using $E_{T}(30)$ values for the spectral response (30)) indicate the lack of any preferential solvation. However, a close inspection of reported $\lambda^{a}_{m_{\text{absorbance}}}$ values listed in Table V for the ethanol-added RTIL solutions clearly indicate unusual solution behavior. The $\lambda^{a}_{m_{\text{absorbance}}}$ values for Reichardt’s dye in neat bmimPF$_6$ and ethanol are nearly identical, indicating a similar hydrogen-bond donating ability, and yet the observed $\lambda^{a}_{m_{\text{absorbance}}}$ values for the ethanol-added solutions decrease as more ethanol is added.
Table III. Behavior of pyrene, 1-pyrenecarboxaldehyde and 1,3-bis-(1-pyrenyl)propane in the presence of ethanol when dissolved in RTIL bmimPF₆ (34). Reported uncertainties are obtained from measuring data for three separate analyses with three scans for each analysis.

| Ethanol Mole Fraction, Xₑ | Pyrene $[I/I_{II}]^a$ | 1-Pyrene carboxaldehyde $[λ_{max}/nm]^b$ | 1,3-Bis-(1-pyrenyl)propane $[I_M/I_e]$ |
|---------------------------|----------------------|---------------------------------|-------------------------------|
| 0.00                      | 1.84                 | 423                             | 12.2 (± 0.2)                  |
| 0.01                      | 1.86                 | 424                             | 12.2 (± 0.2)                  |
| 0.05                      | 1.87                 | 426                             | 11.1 (± 0.2)                  |
| 0.10                      | 1.86                 | 431                             | 9.61 (± 0.2)                  |
| 0.15                      | 1.86                 | 435                             | 8.48 (± 0.2)                  |
| 0.20                      | 1.86                 | 436                             | 7.42 (± 0.1)                  |
| 0.25                      | 1.87                 | 436                             | 6.70 (± 0.1)                  |
| 0.40                      | 1.88                 | 441                             | 4.83 (± 0.1)                  |
| 1.00                      | 1.37                 | 449                             | 1.20 (± 0.1)                  |

* The uncertainties associated with each measurement are within ± 0.02 units.

b The uncertainties associated with each measurement are within ± 2 nm.

In order to further explore the unexpected observations in the ethanol-added study, we performed a Kamlet-Taft treatment of both water-added and ethanol-added data to determine the dipolarity/polarizability and the hydrogen-bond accepting and donating abilities of the solvent systems (20-22,35-37). The solvent dipolarity/polarizability, $\pi^*$, are estimated using $N,N$-diethyl-4-nitroaniline, a non-hydrogen bond donor solute with the following equation

$$\nu_{max} = \nu_0 + s\pi^*$$  \[4\]

where $\nu_{max}$ is the position of the absorbance maximum, $\nu_0$ is 27.52 kK, and $s$ is -3.182 (21,35-37). The hydrogen-bond accepting ability (HBA), $\beta$, for solvents can be determined using the enhanced solvatochromic shift ($-\Delta\nu(1-2)$) of 4-nitroaniline relative to the homomorphic $N,N$-diethyl-4-nitroaniline.

$$\beta = [1.035\nu(2)_{max} - \nu(1)_{max} + 2.64 \text{ kK}] / 2.80$$  \[5\]

Here $\nu(1)_{max}$ and $\nu(2)_{max}$ are the observed absorbance maxima for 4-nitroaniline and $N,N$-diethyl-4-nitroaniline, respectively (20-22,35-37). Finally, the hydrogen-bond donating ability (HBD), $\alpha$, of the solvent is calculated using the $E_T(30)$ and $\pi^*$ values

$$\alpha = [E_T(30) - 14.6(\pi^* - 0.236) - 30.31] / 16.5$$  \[6\]

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where $\delta$ is a polarizability correction term that is 0.0 for non-halogenated aliphatic solvents, 0.5 for polyhalogenated aliphatic solvents, and 1.0 for aromatics (20-22,35-37).

Table IV. Behavior of Reichardt’s Dye, N,N-diethyl-4-nitroaniline and 4-nitroaniline in the presence of water when dissolved in RTIL bmimPF$_6$. Reported uncertainties are obtained from measuring data for three separate analyses with three scans for each analysis.

| Mole Fraction Water, $X_w$ | Solvatochromic Probe | Response |
|---------------------------|----------------------|----------|
|                           | Reichardt’s Dye $^5$ | $\pi^{*}$ | $\beta^*$ | $\alpha^*$ |
|                           | [nm] | E$_T$(30) |           |           |           |
| 0.00                      | 545.7 (± 1.0) | 52.4 | 1.03 | 0.22 | 0.62 |
| 0.03                      | 541.7 (± 0.7) | 52.8 | 1.03 | 0.20 | 0.65 |
| 0.10                      | 535.6 (± 0.7) | 53.4 | 1.06 | 0.19 | 0.67 |
| 0.18                      | 526.0 (± 1.3) | 54.4 | 1.05 | 0.23 | 0.73 |
| 0.25                      | 521.2 (± 1.4) | 54.8 | 1.06 | 0.21 | 0.75 |
| 1.00                      | 453.0 (± 2) | 63.1 | 1.33 | 0.49 | 1.01 |

$^5$The uncertainties associated with each measurement are within ± 0.02 units.

Equation [4] indicates the solvent dipolarity/polarizability only depends on the absorbance maximum of N,N-diethyl-4-nitroaniline. The measured electronic absorbance of N,N-diethyl-4-nitroaniline dissolved in binary bmimPF$_6$ + water and bmimPF$_6$ + ethanol are listed in Table IV and Table V, respectively. In the water-added investigation, the position of the peak maximum shifted from ~412 nm (no water added) to ~415 nm (0.25 mole fraction water in bmimPF$_6$). This change indicates a very slight increase in dipolarity/polarizability on moving from neat bmimPF$_6$ to 0.25 mole fraction water in bmimPF$_6$. The absorbance maximum in neat water was at ~429 nm suggesting a relatively higher dipolarity/polarizability for this solvent compared to bmimPF$_6$. The HBA ability of a solvent depends on the absorbance maxima of both N,N-diethyl-4-nitroaniline and 4-nitroaniline (equation [5]). We observed an increase of only ~2 nm in the absorbance maxima of 4-nitroaniline in the range of neat bmimPF$_6$ to bmimPF$_6$ + 0.25 mole fraction water. This indicates a very slight increase in the HBA ability of the binary bmimPF$_6$ + water solutions. Calculated $\beta$ values indicate the HBA ability of water is substantially greater than neat bmimPF$_6$ or any bmimPF$_6$ + water solutions. The HBD ability of a solvent system, $\alpha$, depends on the measured E$_T$(30) as well as the $\pi^*$ values. The HBD ability of the bmimPF$_6$ + water system increases as more water is added, in agreement with the observed E$_T$(30) results.

Despite the fact that the calculated $\pi^*$ values for neat bmimPF$_6$ and neat ethanol are fairly different from each other, the position of the N,N-diethyl-4-nitroaniline peak maximum did not shift by more than ~1 nm from the neat bmimPF$_6$ position with each addition of ethanol, indicating the lack of any change in the dipolarity/polarizability of the bmimPF$_6$-ethanol solvent system. Furthermore, the HBA ability of ethanol is calculated to be nearly three times that of neat bmimPF$_6$ or any of the ethanol-added solutions, however only a fairly small increase in HBA ability of the binary bmimPF$_6$ +
ethanol solutions is observed as the ethanol mole fraction in bmimPF₆ is increased from 0 to 0.40. Because the calculated π* and β values do not change to a large extent as more ethanol is added, the primary factor determining the position of the Reichardt's dye charge-transfer band observed in the binary bmimPF₆ + ethanol solvent systems is the HBD ability of the solvent. In fact, Taft and Kamlet calculated that roughly 68% of the shift in the absorbance maximum of the Reichardt’s dye could be assigned directly to specific interactions involving the phenoxide oxygen (35). This suggests that the E₆(30) scale is largely, but not exclusively, a measure of the HBD ability of the solvent system (*vide supra*). We observe that the HBD ability of neat ethanol is greater than that of neat bmimPF₆, whereas the dipolarity/polarizability of bmimPF₆ is substantially greater than ethanol. As a consequence, in binary bmimPF₆ + ethanol solutions where π* is not changing significantly as the ethanol composition is increased, the observed increase in the HBD ability of the binary solutions as the ethanol composition is increased is manifested through the gradual decrease in the experimentally observed absorbance maximum of Reichardt's dye (i.e., an increase in the E₆(30) values).

**Table V.** Behavior of Reichardt’s Dye, N,N-diethyl-4-nitroaniline and 4-nitroaniline in the presence of ethanol when dissolved in RTIL bmimPF₆ (34). Reported uncertainties are obtained from measuring data for three separate analyses with three scans for each analysis.

| Ethanol Mole Fraction, Xₑ | Solvatochromic Probe [Response] | Reichardt’s Dye | π* | β | α | E₆(30) |
|--------------------------|--------------------------------|----------------|----|---|---|--------|
|                          |                               | λₑₘₑₙₙ nm       |     |   |   |        |
| 0.00                     |                               | 547            | 52.3| 1.03 | 0.21 | 0.63 |
| 0.01                     |                               | 544            | 52.6| 1.03 | 0.22 | 0.64 |
| 0.05                     |                               | 539            | 53.0| 1.03 | 0.24 | 0.68 |
| 0.10                     |                               | 534            | 53.5| 1.04 | 0.21 | 0.69 |
| 0.15                     |                               | 529            | 54.0| 1.03 | 0.23 | 0.73 |
| 0.20                     |                               | 525            | 54.4| 1.04 | 0.21 | 0.75 |
| 0.25                     |                               | 524            | 54.6| 1.04 | 0.23 | 0.75 |
| 0.40                     |                               | 518            | 55.2| 1.04 | 0.26 | 0.79 |
| 1.00                     |                               | 546            | 52.4| 0.75 | 0.68 | 0.84 |

* The uncertainties associated with each measurement are within ± 1 nm.

* The uncertainties associated with each measurement are within ± 0.02 units.

**CONCLUSION**

The relative dipolarity of a solvent is difficult to define by any single microscopic characteristics. Consequently many solvatochromic probes that define one or two solvent interactions need to be investigated in order to obtain an overall impression of the solvent polarity. The pyrene Iᵢ/Iᵢᵢᵢ ratios observed in neat bmimPF₆, bmimIM, and emimIM are similar to the Iᵢ/Iᵢᵢᵢ values determined in acetonitrile, dimethylsulfoxide, and water,
respectively. Furthermore, the static dielectric constants of bmimPF₆, bmimIM, and emimIM are very near to that of dimethylsulfoxide or acetonitrile where the static dielectric constants of bmimPF₆ and bmimIM are approximately equal and slightly less than emimIM. The microviscosity surrounding the probe molecule 1,3-bis-(1-pyrenyl)-propane is greatest in bmimPF₆ and the least in emimIM. And, the calculated Eₒ(30) value of bmimPF₆ is nearly equal to that of emimIM. The hydrogen-bond donating ability of bmimIM is less than bmimPF₆ and emimIM.

The use of equation [2] to get an idea about the preferential solvation of four solvatochromic probes within binary bmimPF₆ + water and bmimPF₆ + ethanol solutions neglects the effects of the interaction between the two solvent components. The unusual solvatochromic probe response observed in the binary solutions could be due to specific probe-solvent interactions as well as the altered solvent properties arising from any solvent-solvent interactions. The simple model used to investigate the extent of preferential solvation within bmimPF₆ + water and bmimPF₆ + ethanol solutions indicates that pyrene is preferentially solvated by bmimPF₆ while 1-pyrenecarboxaldehyde is preferentially solvated by water or ethanol, respectively. The response of 1,3-bis-(1-pyrenyl)propane demonstrated the reduction in viscosity of bmimPF₆ as water or ethanol was added, with a clear enrichment of the probe solvation sphere by ethanol. Reichardt's betaine dye shows no preferential solvation in the bmimPF₆ + water system, and the hydrogen-bond donating ability of the bmimPF₆ + ethanol is markedly greater than either neat bmimPF₆ or neat ethanol.

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