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Solvatochromic Absorbance Probe Behavior and Preferential Solvation in Aqueous 1-Butyl-3-methylimidazolium Tetrafluoroborate

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The hypothesis that aqueous, rather than pure, ionic liquids provide substantially altered physicochemical properties and versatile/increased solute solvation is addressed. Solvatochromic absorbance probes are utilized to gather information on aqueous solutions of a completely water-miscible ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$). A simplistic solvation model suggests possible preferential solvation of a water-soluble betaine dye by $bmimBF_4$. The lowest-energy electronic absorption band of this dye is further used to interpret dipolarity/polarizability and hydrogen-bond donating (HBD) acidity of aqueous $bmimBF_4$. On the basis of the responses of two other probes, *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline, dipolarity/polarizability, HBD acidity, and hydrogen-bond accepting basicity are separately assessed.

Introduction

During the past decade or so, ionic liquids as potential environmentally friendly solvents have been able to gather widespread interest and curiosity from the scientific and engineering community alike. The number of research publications on investigations of ionic liquids for properties, analysis, and applications has increased many fold.[1] Almost every named synthesis and many more organic/inorganic/organometallic reactions have been reported in ionic liquids.[2,3] Novel analytical applications of ionic liquids are emerging. Effective, and in some cases unique, utilization of ionic liquids as solvents has been demonstrated in a variety of techniques in electroanalysis, separation, spectrometry, and sensing.[1,4−10]

Though not reported explicitly, certain drawbacks have also emerged from the aforementioned detailed investigations with ionic liquids. Perhaps, the most striking and crucial is the *limited* solubility of a fairly large number of common solutes in many popular ionic liquids.[11] Among the approaches to enhance solute solubility in ionic liquids, addition of a cosolvent (preferably "green") or mixing two or more ionic liquids is both simple and effective.[12−18] Toward this end, we have previously reported our investigations on the effects of added water,[12,13] ethanol,[14] aqueous ethanol,[15] and other ionic liquids[16] on a common ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$). Miscibility of water and ethanol in $bmimPF_6$ is significantly low (in ambient conditions, ~2.1 and ~9.7 wt %, respectively).[19−23] As a consequence, ample modulation of the physicochemical properties of $bmimPF_6$ is difficult to achieve. Further, from the point of view of ionic liquid−cosolvent solution structural studies, these investigations are restricted in the sense that the whole concentration range cannot be explored.

To obtain information on structural and physicochemical properties of the aqueous ionic liquid solutions over the complete composition range, we have selected the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$), which shows complete miscibility in water at ambient conditions.[19] To obtain an understanding of the solute−solvent interactions within aqueous $bmimBF_4$, we have utilized solvatochromic absorbance probes.[24] Depending on the solute−solvent interaction(s), a solubilizing medium may exert a profound effect on the electronic transition. Many of such interactions, e.g., dipolarity/polarizability, hydrogen-bond donating ability, hydrogen-bond accepting ability, etc., are readily manifested through molecular absorbance spectra of a variety of solvatochromic probes.[25] Further, specific solute−solvent interaction(s) may result in preferential solvation of the solute by one of the components in the solution.[26] In this paper, we present the behavior of a variety of molecular absorbance probes when dissolved in aqueous $bmimBF_4$. On the basis of these probe responses, using empirical relationships established in the literature, the dipolarity/polarizability (π^*), hydrogen-bond donating ability (α), and hydrogen-bond accepting ability (β) of aqueous $bmimBF_4$ are calculated. Finally, the extent of preferential solvation, if any, is also explored.

Experimental Section

Materials. 2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate [$E_T(30)$] and 2,6-dichloro-4-(2,4,6-triphenyl-*N*-pyridino)phenolate [$E_T(33)$] were purchased from Aldrich Chemical Co. in the highest purity possible and Fluka (≥99 %, HPLC grade), respectively. 4-Nitroaniline (≥90 %) and *N*,*N*-diethyl-4-nitroaniline were purchased from Spectrochem Co. Ltd. and Frinton Laboratories, respectively. Ionic liquid $bmimBF_4$ was purchased from Solvent Innovation, Germany, in the highest purity possible and was further purified to render it water-free. HPLC grade water was obtained from Merck. Ethanol (99.9 %) was obtained from SD Fine-Chem. Ltd.

Method. All probe stock solutions were prepared in ethanol and stored in ambered glass vials at 4 ± 1 °C. The required amount of probes was weighed using a Mettler Toledo AB104-S balance with a precision of ±0.1 mg. Aqueous $bmimBF_4$ solutions were prepared by mass using an Ohaus AR2130 balance with a precision of ±1 mg. An appropriate amount of the probe solution from the stock was transferred to the quartz cuvette. Ethanol was evaporated using a gentle stream of high-purity nitrogen gas. A $bmimBF_4$, water, or aqueous $bmimBF_4$ solution was added to the cuvette to achieve the desired probe

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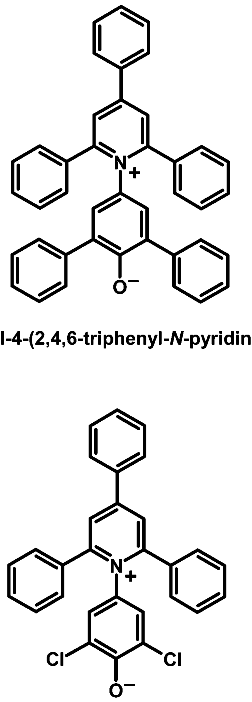
Scheme 1



2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate

2,6-Dichloro-4-(2,4,6-triphenyl-*N*-pyridino)phenolate

concentration. It is important to mention that all data were acquired immediately with freshly prepared bmimBF$_4$ + water samples to avoid any BF$_4^-$ hydrolysis. All data were acquired in 1 mM pH 7 phosphate buffer also to check any adverse effect on the data due to such a hydrolysis. Responses of all probes were found to be statistically similar. Further, in a control experiment, we observed insignificant hydrolysis after 30 min of sample preparation. Consequently, for all practical purposes, the effect of bmimBF$_4$ hydrolysis on the data presented can be deemed insignificant.

A Perkin-Elmer Lambdabio 20 double-beam spectrophotometer with variable bandwidth was used for acquisition of the UV−vis molecular absorbance data. All the data were acquired using 1 cm^2 path length quartz cuvettes. The spectral response from appropriate blanks was subtracted before data analysis. All the measurements were taken in triplicate and averaged. All data analysis was performed using Microsoft Excel and SigmaPlot 8.0 software.

Results and Discussion

Behavior of 2,6-Dichloro-4-(2,4,6-triphenyl-N-pyridino)-phenolate and E$_T$(33). 2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's dye) exhibits an unusually high solvatochromic band shift.[27−29] The lowest-energy intramolecular charge-transfer absorption band of Reichardt's dye is hypsochromically shifted by ca. 357 nm on going from relatively nonpolar diphenyl ether ($\lambda_{max} \sim 810$ nm) to water ($\lambda_{max} \sim 453$ nm). There is a considerable charge transfer from the phenolate to the pyridinium part of the zwitterionic molecule (see structure in Scheme 1). Because of its zwitterionic nature, the solvatochromic probe behavior of Reichardt's dye is strongly affected by the hydrogen-bond donating (HBD) acidity of the solvent; hydrogen-bond donating solvents stabilize the ground state more than the excited state.[30] Reichardt's dye is one of the most widely used probes of its kind; the empirical scale of solvent "polarity", E$_T$(30), is defined as the molar transition energy of the dye in kcal·mol^{-1} at room temperature and normal pressure according to the expression E$_T$(30) = 28591.5/λ_{max} in nm. However, in the present work, a derivative of Reichardt's dye, 2,6-dichloro-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Scheme 1, henceforth named E$_T$(33) because of historical reasons), is used due to certain advantages over Reichardt's dye. Specifically, the low solubility ($<10^{-6}$ M) of Reichardt's dye in water renders it somewhat unsuitable to investigate aqueous-based solutions.[17,31] E$_T$(33) has a pK_a value of 4.78 ± 0.05, and it remains unprotonated at physiological pH.

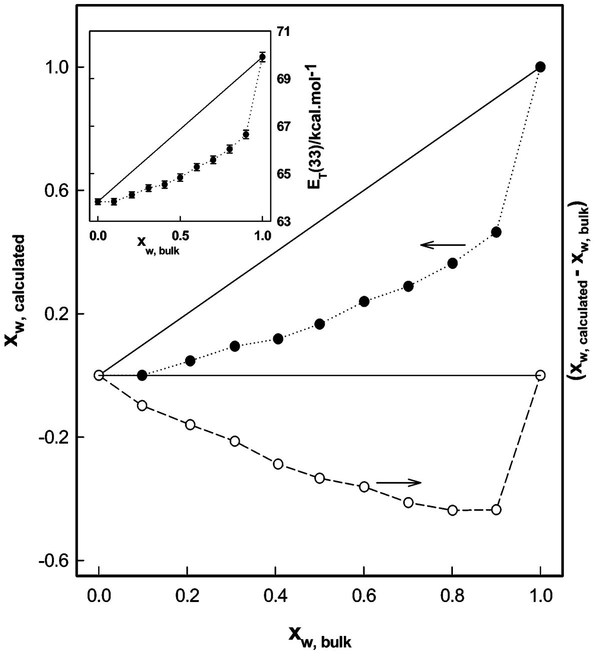


Figure 1. Variation in E$_T$(33) with the mole fraction of water in aqueous bmimBF$_4$ (inset). Solvation sphere composition in terms of the mole fraction of water ($x_{w,calcd}$) calculated from eq 1 and [$x_{w,calcd} - x_{w,bulk}$] vs the mole fraction of water in the bulk ($x_{w,bulk}$): ●, $x_{w,calcd}$; ○, [$x_{w,calcd} - x_{w,bulk}$]; —, ideal behavior.

Absorbance spectra of E$_T$(33) (~100 μM) were collected in aqueous bmimBF$_4$ at ambient conditions. The well-established empirical solvent "polarity" parameter, E$_T$(33) (the molar transition energy of the probe in kcal·mol^{-1}), was calculated from λ_{max} (absorption maxima of the lowest-energy intramolecular charge-transfer band) and is plotted in the inset of Figure 1. The E$_T$(33) in neat bmimBF$_4$ (64.7 ± 0.1 kcal·mol^{-1}) is very similar to that observed in methanol (64.8 ± 0.1 kcal·mol^{-1}) and close to that observed in formamide (64.1 ± 0.1 kcal·mol^{-1}). This is in agreement with what was reported earlier by many researchers.[9,12,14−17,20,30,32−34] Upon addition of water to bmimBF$_4$, as expected, a hypsochromic shift in λ_{max} [an increase in E$_T$(33)] is evident indicating an increase in the dipolarity/polarizability and/or HBD acidity of the solubilizing microenvironment (i.e., the cybotactic region) around this probe. It is apparent that, as water is added to bmimBF$_4$, the initial increase in E$_T$(33) is gradual; however, toward water-rich composition, the increase in E$_T$(33) becomes more dramatic (the change being most pronounced between $x_{w,bulk} \sim 0.9$ and 1.0). It appears that the addition of *small* amounts of bmimBF$_4$ to water may alter the dipolarity/polarizability and/or HBD acidity of the water to a significant degree. This may imply a substantially altered liquid structure of dilute aqueous solutions of bmimBF$_4$. We have observed a similar behavior with other ionic liquids, and detailed reports on such systems and their applications will be the basis of other future reports.

Our efforts to find a simple empirical relation between E$_T$(33) [and λ_{max}] and $x_{w,bulk}$ were futile. Perhaps the complex nature of the aqueous bmimBF$_4$ solutions forbids any such simple empirical relationships to be established. What is more surprising to us, however, is the fact that the increase in E$_T$(33) is gradual when water is added to bmimBF$_4$. One would expect both dipolarity/polarizability and HBD acidity to increase as the water is added to bmimBF$_4$. We address this issue in the next section.

Preferential Solvation as Indicated by E_T(33). The study of physicochemical properties that depend on solute−solvent interactions is much more complex in mixed solvent systems than in pure solvents.[26] 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 arises whenever the bulk mole fraction solvent composition 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. Most spectroscopic probe techniques assume an idealized situation where solvent−solvent interactions can be neglected, and the measured spectral response, *R*, in a binary solvent mixture is given by[26,14−16]

$$R = Y_A R_A^0 + (1 - Y_A) R_B^0 \tag{1}$$

which is a weighted local mole fraction of the probe's spectral response in the two pure solvents, R_A^0 and R_B^0. Here, Y_A and $(1 - Y_A)$ refer to the solvation sphere composition, which, in the case of preferential solvation, may be quite different from the overall bulk liquid-phase composition.

Considering the spectral response as E$_T$(33), we calculated the mole fractions of water ($x_{w,calcd}$) around the probe using eq 1. Figure 1 presents $x_{w,calcd}$ vs the mole fraction of water in bulk ($x_{w,bulk}$) for E$_T$(33) in aqueous bmimBF$_4$. It is clear that $x_{w,calcd} < x_{w,bulk}$ at all compositions. It can be inferred that the probe E$_T$(33) is significantly preferentially solvated by bmimBF$_4$. This observation implies a more favorable interaction between E$_T$(33) and bmimBF$_4$ than that between E$_T$(33) and water. It is conceivable that the structural similarities between the zwitterionic probe and ionic liquids are inducing this effect (see probe structure in Scheme 1). Differences in the solubility of E$_T$(33) in two neat solvents can contribute to these observations as well. Similar observations are reported previously by our group for several other absorbance and fluorescence probes in a different ionic liquid, bmimPF$_6$ + water,[12] + ethanol,[14] and + aqueous ethanol[15] systems. It is important to mention here the most significant difference between bmimPF$_6$ and bmimBF$_4$: although the latter shows complete miscibility with water, the former is almost immiscible with water (vide supra). The fact that bmimBF$_4$ is completely miscible with water and E$_T$(33) is still significantly preferentially solvated by bmimBF$_4$ in aqueous bmimBF$_4$ is certainly an unusual and important outcome.

Figure 1 also demonstrates that the extent of preferential solvation (i.e., $|x_{w,calcd} - x_{w,bulk}|$) increases gradually and reaches a maximum at $x_{w,bulk} \sim 0.9$. As the bulk environment becomes more and more water rich, E$_T$(33) is solvated more and more preferentially by the minor component bmimBF$_4$. Again, the origin of this observation can be conceived in the suitability of bmimBF$_4$ as a solvent toward solubilizing E$_T$(33) due to favorable interactions (e.g., $\pi-\pi$ between bmim cations and E$_T$(33), zwitterionic−ionic, among others). We conclude that in aqueous bmimBF$_4$ the microenvironment around this probe (i.e., the cybotactic region) is predominantly an ionic liquid type. This finding may be utilized in many synthetic and analytical applications where advantage may be taken of the fact that solutes of similar structure are solvated preferentially by ionic liquids in aqueous ionic liquid solutions.

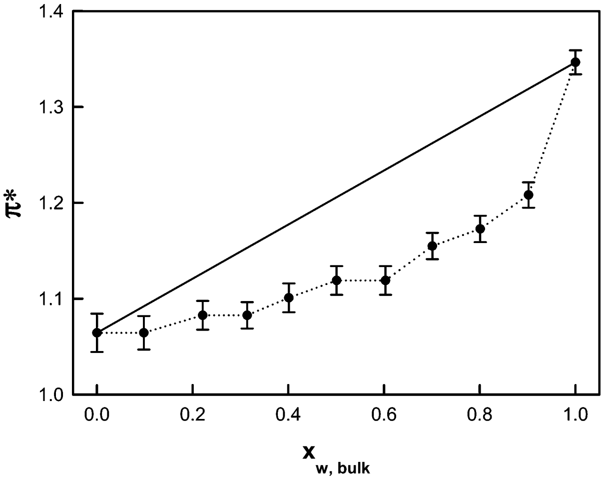


Figure 2. Dipolarity/polarizability (π^*) vs the mole fraction of water in the bulk ($x_{w,bulk}$) for aqueous bmimBF$_4$: ●, π^*; —, ideal π^* using bulk mole fractions.

Empirical Kamlet−Taft Parameters. Additional insight into the aqueous bmimBF$_4$ can be provided using empirical Kamlet−Taft solvatochromic indicators of solvent dipolarity/polarizability (π^*), HBD acidity (α), and hydrogen-bond accepting (HBA) basicity (β).[35] The π^* parameters were estimated from the absorption maximum (ν_{DENA}, in kK) of *N*,*N*-diethyl-4-nitroaniline (DENA), a non-hydrogen-bond donor solute, using:

$$\pi^* = 8.649 - 0.314\nu_{DENA} \tag{2}$$

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

$$\beta = -0.357\nu_{NA} - 1.176\pi^* + 11.12 \tag{3}$$

α parameters were in turn calculated from E$_T$(30) and π^* values.

$$\alpha = [E_T(30) - 14.6(\pi^* - 0.23\delta) - 30.31]/16.5 \quad \delta = 1.00 \tag{4}$$

E$_T$(30), in turn, was calculated from E$_T$(33). For this, both E$_T$(30) and E$_T$(33) were obtained in 20 different solvents and the following relationship is obtained from the linear regression analysis:

$$E_T(30) = 0.9953\ (\pm 0.0287)\ E_T(33) - 8.1132\ (\pm 1.6546)$$

$$R = 0.9926;\ \text{standard error of estimate} = 0.8320;\ n = 20 \tag{5}$$

Experimentally obtained π^* are presented in Figure 2. The dark line represents the ideal π^*. It is important to mention that, statistically, our π^* in neat bmimBF$_4$ and water, respectively, are similar to those reported earlier in the literature.[30,34,35] The key feature of our data is that π^* gradually increases upon addition of water to bmimBF$_4$; the measured π^* is always lower than the predicted ideal π^*. It is important to pinpoint that, in bmimBF$_4$ + water, the measured π^* follows the same trend as that in E$_T$(33). This is expected as the majority of the contribution toward E$_T$(33) is from dipolarity/polarizability of the solubilizing medium.[30] An important outcome of the data is that two structurally very different solvatochromic molecular absorbance probes (along with the fact that one shows negative solvatochromism and the other shows positive solvatochromism)

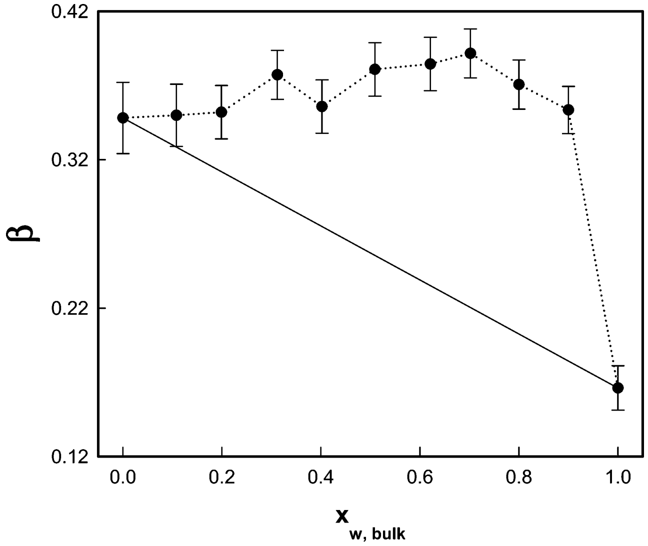


Figure 3. Hydrogen-bond accepting basicity (β) vs the mole fraction of water in the bulk ($x_{\mathrm{w,bulk}}$) for aqueous bmimBF$_4$: ●, β; —, ideal β using bulk mole fractions.

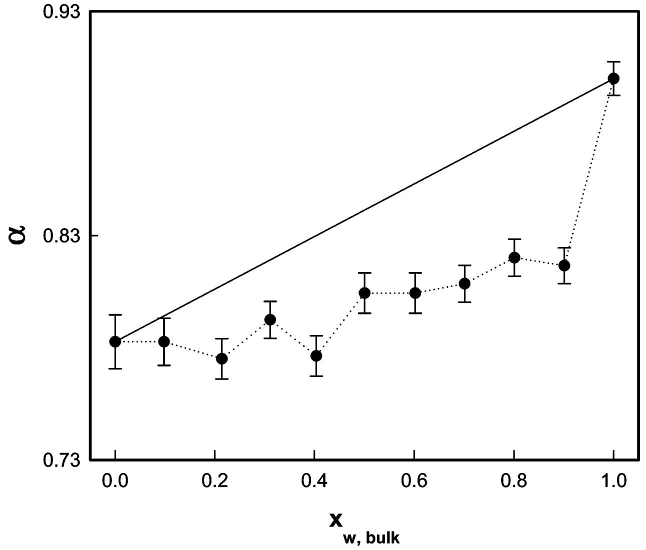


Figure 4. Hydrogen-bond donating acidity (α) vs the mole fraction of water in the bulk ($x_{\mathrm{w,bulk}}$) for aqueous bmimBF$_4$: ●, α; —, ideal α using bulk mole fractions.

provide information on a physicochemical property which are nicely in agreement. In accordance with the betaine dye results, the trend in π^* also indicates a possible preference toward solvation of the probe *N*,*N*-diethyl-4-nitroanile by the ionic liquid bmimBF$_4$.

HBA basicity (β) of the neat ionic liquid bmimBF$_4$ is higher than that in neat water (measured values of β are presented in Figure 3; the dark line represents the ideal β calculated on the basis of the mole fraction). Although the cations of ionic liquids may appear to contribute as well, the HBA basicity of ionic liquids is predominantly decided by the structure of the anions. In this context, neat bmimBF$_4$ has a much higher β than neat bmimPF$_6$.[30] It is clear from our data that the measured β increases ever-so-slightly when water is added to bmimBF$_4$ before decreasing eventually to its value in neat water. At all compositions investigated, the measured β was always found to be higher than that predicted from the ideal behavior (i.e., from mole fraction additivity). This again confirms the possible preferential solvation of the probe (4-nitroanile in this case) by the ionic liquid bmimBF$_4$.

Finally, the HBD acidity (α) was calculated for aqueous bmimBF$_4$ using eqs 4 and 5 (the values are reported in Figure 4 along with the mole fraction weighted ideal α which is indicated by a dark line). It is clear that α values do not increase as rapidly as ideally predicted upon addition of water to bmimBF$_4$. Instead, the change in α is very gradual. As a consequence, at compositions with a higher mole fraction in water, α is significantly lower than predicted ideally. It is well-established that HBD acidity of 1-alkyl-3-methylimidazolium ionic liquids stems from the ring hydrogens located on the imidazolium ring, with the hydrogen on C2 being the most acidic.[30] All previous studies on HBD acidity report α values for neat ionic liquids that are lower than those for water.[30,34] In this context, on the basis of data presented so far in this manuscript, preferential solvation by bmimBF$_4$ of the solute involved in hydrogen bonding with the milieu may be conveniently suggested.

The E$_T$ value for a solvent system is a manifestation of a combined effect of dipolarity/polarizability and HBD acidity (see eq 4). In these studies, dipolarity/polarizability are independently acquired using an absorbance probe DENA (vide supra). Further, the E$_T$(33) values are calculated directly from the response of a modified betaine dye. HBD acidity (α) is subsequently calculated using the independently obtained E$_T$(33) and π^*. As discussed before (see Figures 1 (inset) and 2), both π^* *and* E$_T$(33) show similar trends upon addition of water to bmimBF$_4$. In the composition range $0.1 \leq x_{\mathrm{w,bulk}} \leq 0.9$, both α and π^* gradually increase which subsequently results in an increase in E$_T$(33).

Conclusions

A water-soluble betaine dye shows a gradual increase in its charge-transfer electronic transition energy as water is added to the ionic liquid bmimBF$_4$. This may be due to the dye being preferentially solvated by the ionic liquid. However, a drastically altered aqueous ionic liquid structure cannot be ruled out. The dipolarity/polarizability of the solubilizing medium indicated by two structurally very different solvatochromic probes, betaine dye and *N*,*N*-diethyl-4-nitroanile, is in excellent agreement. Although the hydrogen-bond donating acidity is found to always be lower, the hydrogen-bond accepting basicity is always higher than that ideally predicted. It can be concluded that the probe behaviors of betaine dye, *N*,*N*-diethyl-4-nitroaniline, and 4-nitroanile are internally consistent and that the empirical parameters obtained from them—E$_T$(33), π^*, α, and β—hint toward possible preferential solvation of solutes by bmimBF$_4$ in aqueous bmimBF$_4$ solutions. The work presented here will help enhance the potential overall utility and applications of ionic liquids, specifically in improving solute solubility.

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