Temperature-Dependent Solvatochromic Probe Behavior within Ionic Liquids and (Ionic Liquid + Water) Mixtures

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Spectroscopic responses of absorbance probes, betaine dye 33, *N*,*N*-diethyl-4-nitroaniline, and 4-nitroaniline, and fluorescence dipolarity probes, pyrene (Py) and pyrene-1-carboxaldehyde (PyCHO) within ionic liquids (ILs) 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), and aqueous mixtures of [bmim][BF_4] are used to assess the changes in important physicochemical properties with temperature in the range 10−90 °C. E_T^N obtained from betaine dye 33, indicating dipolarity/polarizability and/or hydrogen bond donating (HBD) acidity, decreases linearly with increasing temperature within the two ILs. Changes in Kamlet−Taft parameters dipolarity/polarizability (π^*), HBD acidity (α), and HB accepting (HBA) basicity (β) with temperature show interesting trends. While π^* and α decrease linearly with increasing temperature within the two ILs, β appears to be independent of the temperature. Similar to E_T^N and π^*, the first-to-third band intensity ratio of probe Py also decreases linearly with increasing temperature within the ILs. The lowest energy fluorescence maxima of PyCHO, though it decreases significantly within water as the temperature is increased from 10 to 90 °C, it does not change within the two ILs investigated. The temperature dependence of the dipolarity/polarizability as manifested via betaine dye 33 behavior is found to be more within the aqueous mixtures of [bmim][BF_4] as compared to that within neat [bmim][BF_4] or neat water. The sensitivity of π^* toward temperature increases as IL is added to water and that of α decreases. The temperature dependent Py behavior shows no clear-cut trend within aqueous mixtures of [bmim][BF_4]; insensitivity of the PyCHO response toward temperature change is reasserted within aqueous IL mixtures. All-in-all, the temperature-dependent behavior of solvatochromic probes within [bmim][PF_6], [bmim][BF_4], and aqueous mixtures of [bmim][BF_4] is found to depend on the identity of the probe.

Introduction

The newly rediscovered room-temperature ionic liquids (ILs), consisting entirely of ions that are molten at room temperature with negligible vapor pressure, are showing enormous potential as media with unusual properties.[1] Consequently, interest in investigating the properties of ILs has been intensified in many fields of science and technology.[2] They appear to be promising future replacements for volatile organic compounds (VOCs) though this proposition is yet to be established.[3] The fact that an IL is composed of ions alone and is still liquid at ambient conditions is reason enough to evoke curiosity among researchers as far as properties and applications are concerned. Further, the option of fine-tuning the physicochemical properties by an appropriate choice of cations and anions has stimulated much of the current excitement with respect to these compounds and has led to the term “designer solvents”.[4] Almost every named synthesis and many more organic/inorganic/organometallic reactions have been reported in ILs.[2a−c] Novel analytical applications of ILs are emerging day by day.[5] Due to the possibility of widespread applications in various fields, ILs are employed with other environmentally benign systems such as aqueous,[6] polymer,[7] and surfactant-based systems,[8] etc. ILs also play an important role in altering the behavior of dye probes and porphyrin aggregation within solution.[9]

As mentioned earlier, properties of ILs could be specific to the cation−anion combination; however, mixtures of ILs with other solvents have been proposed to possess altered (and in some cases, even improved) physicochemical properties.[10] Mixtures of ILs with water, in this respect, have garnered increased attention.[6] The major reason for this could be traced to the fact that aqueous mixtures of ILs may form a class of “hybrid green” system.[10] The fact that many ILs are hygroscopic in nature further contributes to the growing interest in understanding aqueous IL mixtures. Due to the possibility of strong intermolecular H-bonding interactions, among others, between water and the constituent ions of ILs,[6,11] addition of water may potentially alter the physicochemical properties of ILs in significant fashion. In this regard, though the investigation of structural features of the solution[12] as well as measurement of bulk physicochemical properties[13] of aqueous mixtures of ILs are of certain importance, understanding the behavior of solutes dissolved in such media may directly furnish crucial information on solute−solvent interactions(s). Key insights on physicochemical properties of aqueous mixtures of ILs along with the information on solute solvation within such systems would be obtained in the process.

Responses of solvatochromic absorbance and fluorescence probes usually change as a result of changes in the cybotactic

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region of the probe. The changes in the cybotactic region could be due to the changes in the specific solute−solvent interactions or they could be due to the changes in the properties of the milieu as a result of changing conditions, e.g., changing temperature and/or pressure. Depending on the solute−solvent interaction(s), a solubilizing medium may exert a profound effect on the electronic transition of a solute. In solvatochromic absorbance and fluorescence probes, such changes in electronic transitions are systematic with respect to some property of the medium. Many of such properties, e.g., dipolarity/polarizability, dipolarity, static dielectric constant, hydrogen-bond donating (HBD) acidity, hydrogen-bond accepting (HBA) basicity, etc., are readily manifested through molecular absorbance or fluorescence spectra of a variety of solvatochromic probes.[13]

To assess the temperature dependence of important physicochemical properties of ILs and aqueous mixture of ILs, we have chosen to observe the behavior of different solvatochromic absorbance and fluorescence probes as a function of temperature. Specifically, we have used three common electronic absorbance probes, betaine dye 33, *N*,*N*-diethyl-4-nitroaniline, and 4-nitroaniline, and two popular fluorescence probes, pyrene and pyrene-1-carboxaldehyde, for this purpose (structures of the probes are provided in Scheme S1, Supporting Information). While the behaviors of absorbance probes furnish information on empirical parameters of importance of a medium, the two fluorescence probes are common empirical polarity probes (vide infra). To understand the effect of temperature on solvatochromic probe behavior that may manifest in changes in important physicochemical properties of ILs as a function of ions constituting ILs, we have selected two ILs having the same cation but different anions: 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) (Scheme S1, Supporting Information). While [bmim][PF_6] is considered a “hydrophobic” IL with minimal aqueous solubility, “hydrophilic” IL [bmim][BF_4] is completely miscible with water.[14] Subsequently, temperature dependent probe behavior is investigated within aqueous mixtures of [bmim][BF_4] in the complete composition regime in the temperature range 10−90 °C.

It is well-established that temperature has a profound effect on the physicochemical properties of solutions.[15] Recently, El Seoud groups investigated thermosolvatochromism in binary mixtures of water and ILs (1-allyl-3-alkylimidazolium chlorides) to assess the relative importance of solute−solvent solvophobic interactions.[16a] Previously, the same group had reported thermosolvatochromic behavior of certain dyes in aqueous [bmim][BF_4] and compared it with behaviors of aqueous alcohols in the temperature range 10−60 °C.[11d] An earlier report on thermosolvatochromic behavior of chloronickel complexes in 1-hydroxyalkyl-3-methylimidazolium cation based ILs suggested changes in the structure of the complex as the temperature was changed.[16b] Interesting results were found by Kumar et al. by contrasting thermosolvatochromic trends in three series of ILs in the temperature range 298−353 K.[15m] The temperature dependent polarity of [bmim][PF_6] was studied by Baker et al. emphasizing that HBD strength of imidazolium cation was strongly temperature dependent but HBA abilities were weak functions of temperature and added water.[1k]

Experimental Section

Reagents and Supplies. 2,6-Dichloro-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (betaine dye 33), 4-nitroaniline, and *N*,*N*-diethyl-4-nitroaniline were purchased in the highest available purity from Fluka, Spectrochem. Co. Ltd., and Frinton Laboratories, respectively. Doubly distilled deionized water with >18.0 MΩ cm resistivity was obtained from a Millipore Milli-Q Academic water purification system. Pyrene and pyrene-1-carboxaldehyde were purchased in the highest purities available from Sigma-Aldrich. Ethanol was obtained from Merck.

ILs [bmim][BF_4] and [bmim][PF_6] were obtained from Merck (ultrapure, halide content <10 ppm, water content <10 ppm) and stored under dry argon. Alternatively, these ILs were synthesized and purified in our laboratories using the procedures provided in the literature.[17] Specifically, [bmim][BF_4] was synthesized from [bmim][Cl]. To obtain [bmim][Cl], a mixture of 1-methylimidazole (24.64 g, 0.3 mol), 1-chlorobutane (37.03 g, 0.4 mol), and acetonitrile (50 mL) was refluxed for 48 h, after which the solvent and an excess of 1-chlorobutane were removed. The remaining pale yellow oil was redissolved in 50 mL of acetonitrile and added dropwise to 200 mL of ethyl acetate under nitrogen with vigorous agitation. The mixture was cooled to −30 °C and kept at this temperature for 2 h; a white solid was formed. The supernatant was removed and the washing step was repeated to obtain [bmim][Cl].[17a] A solution of $NaBF_4$ (0.060 mol) in water (50 cm^3) was added slowly to a cooled, rapidly stirring solution of [bmim][Cl] (0.060 mol) in water (200 cm^3).[17b] The product precipitated as a waxy solid and was collected by filtration, dissolved in dichloromethane (300 cm^3), and washed with water (2 × 100 cm^3). The organic layer was collected, dried over $MgSO_4$, and filtered and the solvent was removed in vacuo to yield the tetrafluoroborate salt, which was recrystallized from methanol as a colorless product. The minimum volume of water was used to dissolve the chloride salts. The tetrafluoroborate salt did not initially separate from the aqueous phase but was preferentially extracted by dichloromethane.

To prepare [bmim][PF_6], hexafluorophosphoric acid (1.3 mol) was added (slowly to prevent the temperature from rising significantly) to a mixture of [bmim][Cl] (1 mol) in 500 mL of water. After stirring for 12 h, the upper acidic aqueous layer was decanted and the lower IL portion was washed with water (10 × 500) mL until the washings were no longer acidic. The IL was heated under vacuum at 70 °C to remove any excess water.[17c] We observed our results to be similar irrespective of whether the ILs were purchased or synthesized.

Methods. The required amount of probes was weighed using a Mettler Toledo AB104-S balance with a precision of ±0.1 mg. All absorbance and fluorescence probe stock solutions were prepared in absolute ethanol and stored in sealed ambered glass vials at 4 ± 1 °C. Aqueous [bmim][BF_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 precleaned quartz cuvette. Ethanol was evaporated using a gentle stream of high-purity dry, filtered nitrogen gas. [bmim][PF_6], [bmim][BF_4], water, or aqueous [bmim][BF_4] mixture was added to the cuvette to achieve the desired probe concentration.

A Varian Cary 100-bio double-beam spectrophotometer with variable bandwidth was used for the acquisition of the UV−vis molecular absorbance spectra. Steady-state fluorescence spectra were acquired on a Jobin-Yvon Fluorolog-3 (model FL-3-11) modular spectrofluorometer equipped with single grating Czerny−Turner monochromators as wavelength selection devices, a 450 W Xe arc lamp as the excitation source, and a photomultiplier tube as the detector. All absorbance and fluorescence data were acquired using 1 cm^2 quartz cuvettes. All spectroscopic measurements were performed in triplicate with samples prepared individually, and the results were averaged. All spectra were duly corrected by measuring the

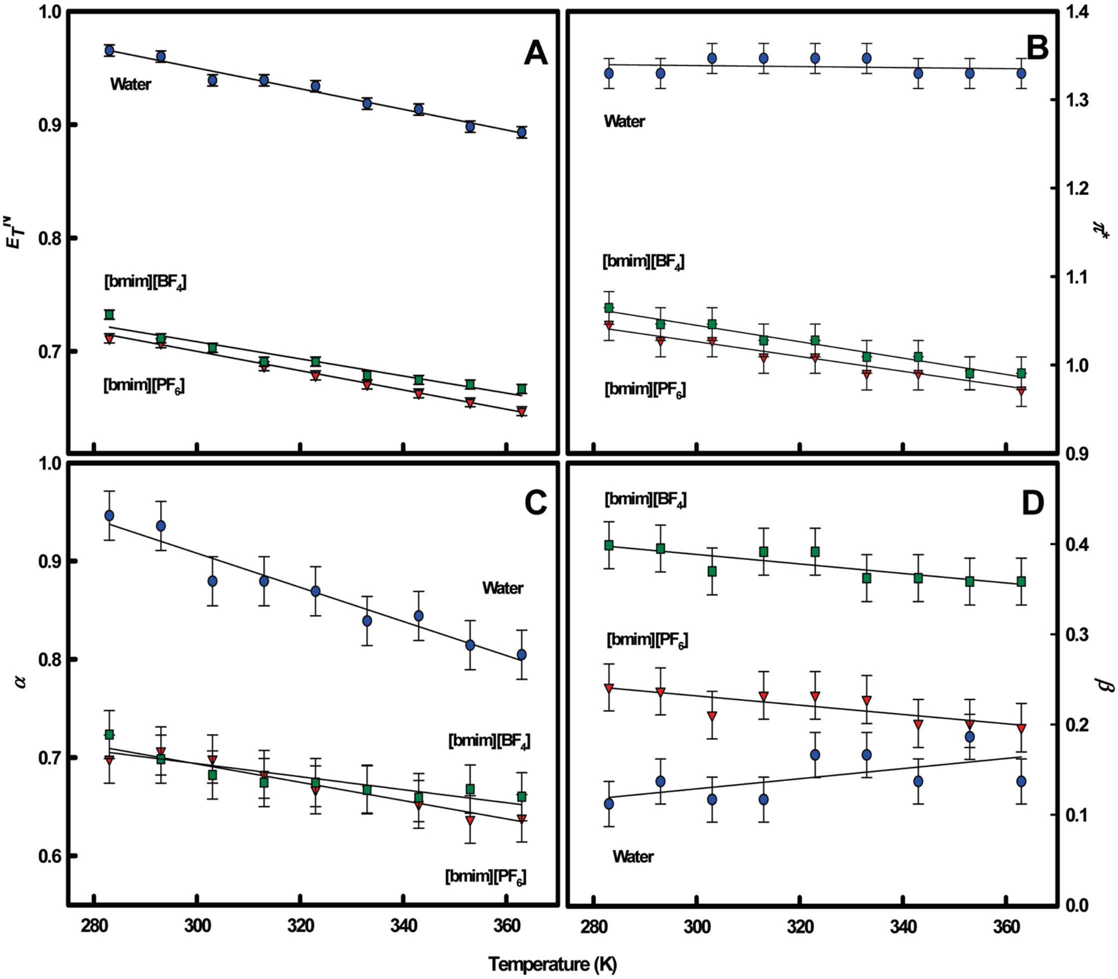

Figure 1. Variation of E_N^T (A), π^* (B), α (C), and β (D) with temperature in [bmim][PF$_6$] (▼), [bmim][BF$_4$] (■), and water (●). Lines show results of the linear regression analysis.

spectral responses from suitable blanks prior to data analysis and statistical treatment.

Results and Discussion

Temperature-Dependent Probe Behavior within Neat Ionic Liquids. We have utilized an effective UV−vis molecular absorbance probe 2,6-dichloro-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (betaine dye 33) (see structure in Scheme S1, Supporting Information) to assess its temperature dependence, which is subsequently manifested into the temperature dependence of dipolarity/polarizability and/or hydrogen bond donating (HBD) acidity of neat ILs as well as IL−water mixtures. The more popular 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (betaine dye 30) exhibits an unusually high solvatochromic band shift.[18] The lowest energy intramolecular charge-transfer absorption band of betaine dye 30 is hypsochromically shifted by ca. 357 nm on going from relatively nonpolar diphenyl ether (λ_{max} ~ 810 nm) to water (λ_{max} ~ 453 nm). There is a considerable charge transfer from the phenolate to the pyridinium part of the zwitterionic molecule. Because of its zwitterionic nature, the solvatochromic probe behavior of betaine dye 30 is strongly affected by the HBD acidity of the solvent; HBD solvents stabilize the ground state more than the excited state.[19] This 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 $E_T(30) = 28591.5/\lambda_{max}^{abs}$ (nm). However, in the present work betaine dye 33 [corresponding molar transition energy is subsequently termed as $E_T(33)$] is used due to certain advantages over betaine dye 30. Specifically, the low solubility ($<10^{-6}$ M) of betaine dye 30 in water renders it somewhat unsuitable to investigate aqueous-based solutions.[1k,20] Betaine dye 33 has a pK_a value of 4.78 ± 0.05, and it remains unprotonated at physiological pH. An established empirical relationship was used to convert $E_T(33)$ values to the more commonly employed $E_T(30)$,[10a] which was subsequently used to arrive at the corresponding E_T^N, as suggested in the literature.[21]

Figure 1A presents measured E_T^N within [bmim][PF$_6$], [bmim][BF$_4$], and water, respectively, in the temperature range 10−90 °C. A cursory examination reveals that an increase in temperature results in decrease in E_T^N within each of the solvents investigated. A decrease in E_T^N implies a decrease in the dipolarity/polarizability and/or the HBD acidity of the medium with increasing temperature. In general, "polarity" is suggested to usually decrease with increasing temperature due in major part to the increased average thermal reorientation of the dipoles.[22] This results in usually a decrease in dielectric constant with increasing temperature of polar liquids due partly to the destruction of the cooperative effect.[22] For example, the static dielectric constant of water is observed to decrease as the temperature is increased to 100 °C.[23] It is important to mention that the observed decrease in E_T^N with increasing temperature is similar to that observed by Baker et al. for [bmim][PF$_6$] using

TABLE 1: Slopes Recovered from the Linear Regression Analysis of E_T^N, π*, α, β, Pyrene I_1/I_3 (Py I_1/I_3) and Pyrene-1-carboxaldehyde Lowest Energy Fluorescence Maxima (PyCHO λ_{max}^{fluo}), Respectively, versus Temperature in [bmim][PF$_6$], [bmim][BF$_4$], and Water

	slope		
probe response	[bmim][PF$_6$]	[bmim][BF$_4$]	water
E_T^N	$-8.50\ (\pm 0.36) \times 10^{-4}\ K^{-1}$	$-7.55\ (\pm 0.79) \times 10^{-4}\ K^{-1}$	$-9.10\ (\pm 0.55) \times 10^{-4}\ K^{-1}$
π^*	$-8.37\ (\pm 0.78) \times 10^{-4}\ K^{-1}$	$-9.26\ (\pm 0.67) \times 10^{-4}\ K^{-1}$	$-0.57\ (\pm 0.02) \times 10^{-4}\ K^{-1}$
α	$-9.29\ (\pm 0.90) \times 10^{-4}\ K^{-1}$	$-6.64\ (\pm 1.35) \times 10^{-4}\ K^{-1}$	$-17.2\ (\pm 1.7) \times 10^{-4}\ K^{-1}$
β	$-5.15\ (\pm 1.43) \times 10^{-4}\ K^{-1}$	$-5.26\ (\pm 1.32) \times 10^{-4}\ K^{-1}$	$5.63\ (\pm 2.88) \times 10^{-4}\ K^{-1}$
Py I_1/I_3	$-4.24\ (\pm 0.70) \times 10^{-3}\ K^{-1}$	$-4.21\ (\pm 0.29) \times 10^{-3}\ K^{-1}$	$-2.99\ (\pm 0.33) \times 10^{-3}\ K^{-1}$
PyCHO λ_{max}^{fluo}	$-1.50\ (\pm 0.83) \times 10^{-2}$ nm K^{-1}	$3.33\ (\pm 1.91) \times 10^{-2}$ nm K^{-1}	$-9.50\ (\pm 1.79) \times 10^{-2}$ nm K^{-1}

betaine dye 30[1k] and by the El Seoud group for [bmim][BF$_4$][11d] and for 1-allyl-3-alkylimidazolium chlorides (alkyl being methyl, 1-butyl, and 1-hexyl, respectively)[16a] using different UV−vis absorbance-based probes. Linear regression analysis of E_T^N versus temperature for [bmim][PF$_6$], [bmim][BF$_4$], and water, respectively, reveals a decrease in E_T^N with increasing temperature to be linear in nature (Figure 1A and Table S1, Supporting Information). The temperature dependence of dipolarity/polarizability and/or HBD acidity as revealed by betaine dye 33 is represented by the slope of the E_T^N versus temperature best fit straight line (Table 1). Though the dipolarity/polarizability and/or HBD acidity decreases the most within water followed by that within ILs [bmim][PF$_6$] and [bmim][BF$_4$], the differences in slopes are statistically not very significant. It may be inferred that the decrease in dipolarity/polarizability and/or HBD acidity with increasing temperature within ILs [bmim][PF$_6$] and [bmim][BF$_4$], respectively, is not too different from that observed within water. Further, ILs constituted of the same bmim$^+$ cation but two different anions PF$_6$ and BF$_4$, furnishing contrasting aqueous solubilities to the two ILs ([bmim][PF$_6$] is "hydrophobic", while [bmim][BF$_4$] is "hydrophilic"), show similar decreases in dipolarity/polarizability and/or HBD acidity as the temperature is increased based on the behavior of betaine dye 33. It is concluded that the increased average thermal reorientations of the dipoles leading to the destruction of the cooperative effect resulting in decreased dielectric constant with increasing temperature for both the ILs [bmim][PF$_6$] and [bmim][BF$_4$] are very similar. The HBD acidity, which is decided in major part by the C2−H of bmim$^+$ of these ILs, may be assumed to change in a similar fashion with temperature as both the ILs possess the same cation (vide infra).

To assess separately the temperature dependence of dipolarity/polarizability, HBD acidity, and HBA basicity of ILs, we used a well-documented empirical procedure for the estimation of Kamlet−Taft parameters using UV−vis molecular absorbance probes *N*,*N*-diethyl-4-nitroaniline (DENA) and 4-nitroaniline (NA) (Scheme S1, Supporting Information).[24] We measured the wavelength of electronic absorbance maxima of DENA and NA, respectively, within each [bmim][PF$_6$], [bmim][BF$_4$], and water in the temperature range 10−90 °C, and by combining it with $E_T(30)$ (vide supra), we obtained empirical parameters π* (dipolarity/polarizability), α (HBD acidity), and β (HBA basicity).[24] It is important to mention at this point that π*, α, and β for the two ILs assessed by us at ambient temperature are in good agreement with those reported by other groups in the recent past.[1d,k,11e,19] Measured π* (panel B), α (panel C), and β (panel D) within [bmim][PF$_6$], [bmim][BF$_4$], and water, respectively, are presented in Figure 1, while the slopes recovered from the linear regression analysis of each of the parameter versus temperature are reported in Table 1. Some interesting inferences can clearly be drawn from our experimental outcomes. The extents of decrease in π* with an increase in temperature within the two ILs [bmim][PF$_6$] and [bmim][BF$_4$], respectively, are observed to be statistically similar, as evidenced from the two slope values, indicating two ILs to have similar temperature-dependent dipolarities/polarizabilities. However, the reduction in π* as the temperature is increased within each of the ILs is very different from that observed within water where the decrease in π* is almost insignificant. While the static dielectric constant of water is known to decrease with increasing temperature,[23] it is not manifested in the behavior of absorbance probe DENA. This may be attributed to the compensatory contributions from polarizability, although it is proposed that polarizabilities are only very slightly temperature dependent.[23] For IL [bmim][PF$_6$], Bright's group also observed a linear decrease in π* with increasing temperature.[1k] It is clear that, unlike water, the dipolarity/polarizability of ILs [bmim][PF$_6$] and [bmim][BF$_4$] decreases as the temperature is increased.

Variations in HBD acidity (α) with temperature within [bmim][PF$_6$], [bmim][BF$_4$], and water, respectively, however, are found to be different. The parameter α is observed to decrease with increasing temperature within each of [bmim][PF$_6$], [bmim][BF$_4$], and water. The extent of decrease in α with increasing temperature (represented by the slope of α versus temperature best fit straight lines, Table 1) is observed to be a maximum within water followed by that within [bmim][PF$_6$]; the extent is observed to be a minimum within IL [bmim][BF$_4$]. Bright's group has reported a similar decrease in α with increasing temperature within [bmim][PF$_6$].[1k] It is important to mention that while π* (and to a lesser extent E_T^N) of [bmim][BF$_4$] is slightly higher than that of [bmim][PF$_6$] in the temperatures range 10−90 °C, the α within the two ILs are very similar at lower temperatures and only start to become different at very high temperatures. It is easily conceivable as the C2−H of the bmim$^+$ is the major contributor to the HBD acidity of ILs constituted of bmim cation.[19,25] It appears that the anion of an IL has an insignificant effect on HBD acidity of ILs having the bmim cation. Only at higher temperatures may the other factors such as the interaction of bmim$^+$ with the anion start to play a role in HBD acidity of the bmim-type ILs. The temperature dependence of α is a little more pronounced within IL [bmim][PF$_6$] as compared to that within IL [bmim][BF$_4$].

HBA basicity (β) does not change in a distinct manner in any of [bmim][PF$_6$], [bmim][BF$_4$], or water as the temperature is changed (Figure 1D and Table 1). This is clearly represented by the high values of the standard deviations of the slopes; errors associated with each of the β measurements is also fairly significant. The linear regression analyses of β versus temperature data also result in not-so-good fits (Table S1, Supporting Information). Bright and co-workers have also reported β to be not a strong function of temperature between 10 and 70 °C.[1k] It appears that β within each of the IL decreases ever-so-slightly to a similar extent with increasing temperature, it appears to

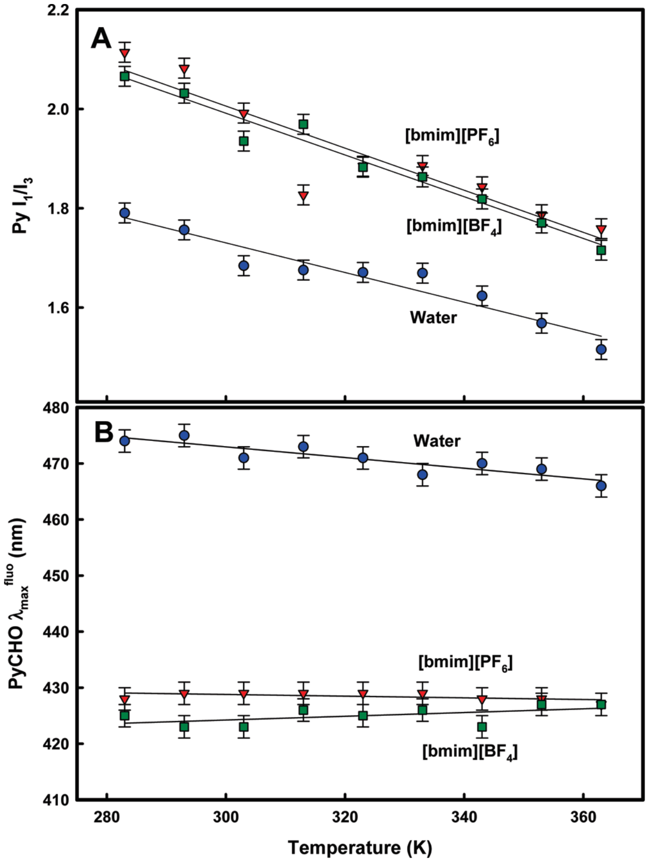

Figure 2. Variation of pyrene (1 μM) I_1/I_3 (A) and pyrene-1-carboxaldehyde (10 μM) lowest energy fluorescence maxima $\lambda_{\max}^{\text{fluo}}$ (B) with temperature in [bmim][PF$_6$] (▼), [bmim][BF$_4$] (■), and water (●) ($\lambda_{\text{excitation}} = 337$ and 365 nm, and excitation and emission slits are at 2/1 and 2/2 nms for pyrene and pyrene-1-carboxaldehyde, respectively). Lines show results of the linear regression analysis.

increase slightly with increasing temperature within water. It is reemphasized from other reports in the literature that IL [bmim][BF$_4$] possesses a significantly higher HBA basicity as compared to the case for IL [bmim][PF$_6$].[25c] This is obviously attributed to the different anions of the ILs, as the anion of an IL usually plays the major role in deciding the HBA basicity.[25c]

Molecular fluorescence from an appropriate fluorophore is well-suited to furnish information regarding complex systems owing to the high sensitivity and orthogonality of information inherent to fluorescence techniques.[18b,26] In some previous investigations, we have demonstrated the effectiveness of using a variety of fluorescence probes to obtain key insight into solute−solvent and solvent−solvent interactions within IL-based solvent mixtures.[1e,h,k,27] To further assess the temperature dependence of the properties via the probe behavior within ILs, we have utilized two valuable fluorescence polarity probes, pyrene and pyrene-1-carboxaldehyde. Pyrene (Scheme S1, Supporting Information) is one of the most widely used neutral fluorescence probes for polarity studies.[8,26,28] The pyrene solvent polarity scale (Py I_1/I_3) is defined by its I_1/I_3 emission intensity ratio, where I_1 is the intensity of the solvent-sensitive band arising from the $S_1(\upsilon=0) \rightarrow S_0(\upsilon=0)$ transition and I_3 corresponds to the solvent-insensitive $S_1(\upsilon=0) \rightarrow S_0(\upsilon=1)$ transition.[26,28] The I_1/I_3 ratio increases with increasing solvent dipolarity and is a function of both the solvent dielectric (ε) and the refractive index (n) via the dielectric cross term, $f(\varepsilon,n^2)$. Measured Py I_1/I_3 within [bmim][PF$_6$], [bmim][BF$_4$], and water, respectively, in the temperature range 10−90 °C are plotted in Figure 2A. Similar to the observations for E_T^N and π^*, the Py I_1/I_3 decreases with increasing temperature within each of the two ILs and water. Further, the slopes of Py I_1/I_3 versus temperature best fit straight lines (Table 1) representing the extent of temperature dependence is observed to be almost identical for the two ILs. Interestingly, this slope for water is observed to be lower. Dependence of Py I_1/I_3 on temperature, in this regard, is more similar to that observed for the parameter π^*. It is easy to comprehend as these two empirical parameters are supposed to represent dipolarity/polarizability of the medium in general. Two important inferences, that the dipolarities of the two ILs investigated here decrease more rapidly as compared to that of water and that these decreases are similar for both the ILs irrespective of their different anions, are reemphasized nonetheless.

The temperature-dependent behavior of another fluorescence probe pyrene-1-carboxaldehyde (PyCHO), a pyrene probe analog containing an aldehyde functionality (Scheme S1, Supporting Information), within the two ILs is found to be different from that observed for pyrene. PyCHO has two types of closely lying excited singlet states (n−π^* and π−π^*), both of which show emission in fluid solution. In nonpolar solvents, the emission from PyCHO is highly structured and weak ($\phi_F < 10^{-3}$ in hexane), arising exclusively from the n−π^*state. On increasing the polarity of the medium, however, the π−π^* state is brought below the n−π^* state via solvent relaxation to become the emitting state, manifested by broad, moderately intense emission ($\phi_F \approx 0.15$ in MeOH) that red shifts with increasing solvent dielectric.[1e,7f,26a,27c,e] Figure 2B presents experimental PyCHO $\lambda_{\max}^{\text{fluo}}$ within [bmim][PF$_6$], [bmim][BF$_4$], and water, respectively, in the temperature range 10−90 °C. A careful examination of the data reveals an interesting outcome: within each of the two ILs investigated, PyCHO $\lambda_{\max}^{\text{fluo}}$ appears to be insensitive to the temperature variations (the PyCHO $\lambda_{\max}^{\text{fluo}}$ between 10 and 90 °C are within the experimental error for both the ILs). Further, the resulting linear fits of the data between PyCHO $\lambda_{\max}^{\text{fluo}}$ and temperature are not satisfactory (Table S1, Supporting Information). It is noteworthy that in water, PyCHO $\lambda_{\max}^{\text{fluo}}$ does decrease significantly from 474(±1) nm at 10 °C to 466(±1) nm at 90 °C. This is in agreement with the decrease in static dielectric constant of water from 83.96 at 10 °C to 58.12 at 90 °C.[29] As PyCHO is known to be a probe of the static dielectric constant of the medium,[25b,26a,b,27c] it may be inferred that either the static dielectric constants of ILs [bmim][PF$_6$] and [bmim][BF$_4$] do not change significantly with a change in temperature in the range 10−90 °C or the temperature independence of PyCHO $\lambda_{\max}^{\text{fluo}}$ is specific to this probe, which may be a consequence of solute−solvent interactions between the aldehyde functionality of PyCHO and the constituents of ILs, rendering this probe unsuitable as a thermosolvatochromic probe.

Temperature-Dependent Probe Behavior within Aqueous Mixtures of [bmim][BF$_4$]. The temperature dependence of the properties of water mixtures of IL[bmim][BF$_4$] is acquired through the behavior of the probes used in the previous section at 0.1 mol fraction intervals in the temperature range 10−90 °C. IL [bmim][BF$_4$] is selected for this purpose, as this IL is completely miscible with water whereas IL [bmim][PF$_6$] shows limited solubility in water [only ∼2 wt % water (or [bmim][PF$_6$]) is miscible in [bmim][PF$_6$] (or water) at ambient conditions].[14]

Parameters E_T^N, π^*, α, β, Py I_1/I_3, and PyCHO $\lambda_{\max}^{\text{fluo}}$ were obtained at 10 deg intervals in the temperature range 10−90 °C at nine different compositions of aqueous [bmim][BF$_4$] mixtures in [bmim][BF$_4$] mole fraction range $X_{[\text{bmim}][\text{BF}_4]} = 0.1-0.9$ (Figures S1−S6, Supporting Information). Results of

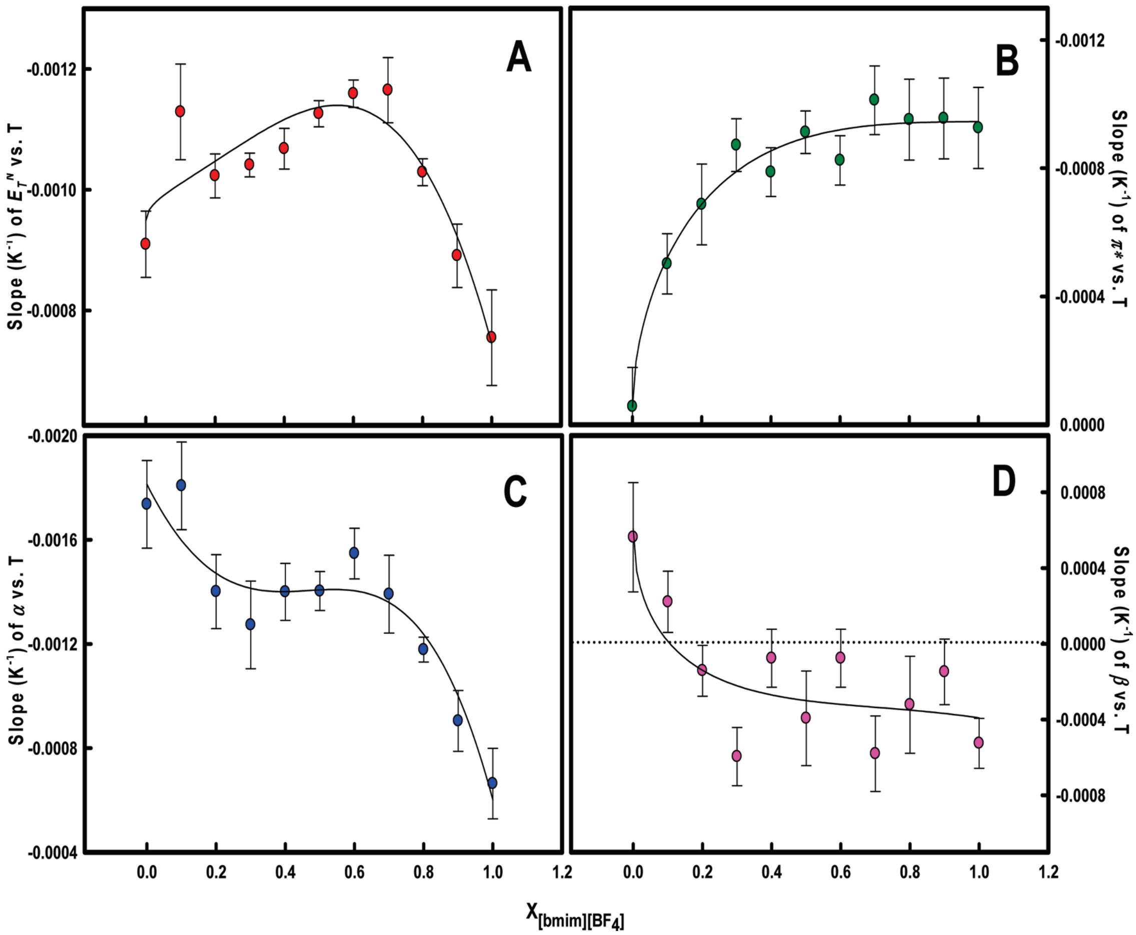

Figure 3. Slopes recovered from the linear regression analysis of $E_{\mathrm{N}}^{\mathrm{T}}$ (A), π^* (B), α (C), and β (D), respectively, versus temperature as function of [bmim][BF$_4$] mole fraction ($X_{[\mathrm{bmim}][\mathrm{BF}_4]}$) within aqueous [bmim][BF$_4$].

the linear regression analysis of the parameters versus temperature at each composition of aqueous [bmim][BF$_4$] mixtures are presented in Table S2 (Supporting Information) and are shown as dark lines in Figures S7−S12 (Supporting Information). It is important to mention that at ambient temperature the values of these parameters are similar to those reported earlier.[6d] Though from a careful examination of the data plotted in Figures S7−S12 (Supporting Information) and parameters reported in Table S2 (Supporting Information) it appears that the fit of the parameters versus the temperature data to a linear relationship may not be entirely satisfactory at all compositions for all parameters, we chose to demonstrate the slope as a function of $X_{[\mathrm{bmim}][\mathrm{BF}_4]}$ for all parameters. Figure 3 presents slopes of $E_{\mathrm{T}}^{\mathrm{N}}$ (panel A), π^* (panel B), α (panel C), and β (panel D), respectively, versus temperature at each composition within aqueous [bmim][BF$_4$] mixtures. It is clear from Figure 3A that, as suggested by betaine dye 33, dipolarity/polarizability and/or HBD acidity of aqueous mixtures of IL [bmim][BF$_4$] are more sensitive to the changes in temperature than that of IL [bmim][BF$_4$] alone—the decrease in dipolarity/polarizability and/or HBD acidity with temperature is more in [bmim][BF$_4$] + water mixtures. It is suggested by our data that the decrease in dipolarity/polarizability and/or HBD acidity with temperature is the most at $X_{[\mathrm{bmim}][\mathrm{BF}_4]} \sim 0.7$. It is interesting to note that the temperature dependence of $E_{\mathrm{T}}^{\mathrm{N}}$ in the range $0.1 \leq X_{[\mathrm{bmim}][\mathrm{BF}_4]} \leq 0.8$ is more than that observed in either the neat [bmim][BF$_4$] or the neat water. It is suggested that dipolarity/polarizability and/or HBD acidity of the IL−water mixture is very sensitive to the temperature change. It appears that the presence of HB interactions between C2−H of bmim$^+$ of IL and −O− of water and BF$_4^-$ of IL and −H of water render $E_{\mathrm{T}}^{\mathrm{N}}$ of the mixture extra sensitivity toward temperature change. The same may not be implied about the changes in π^* with temperature within aqueous [bmim][BF$_4$] mixtures (Figure 3B). The extent of decrease in π^* with temperature appears to be similar in the composition range $X_{[\mathrm{bmim}][\mathrm{BF}_4]} = \sim 0.3-1$, but it decreases dramatically in the water-rich region, i.e., $X_{[\mathrm{bmim}][\mathrm{BF}_4]} \leq 0.3$. This is conceivable as π^* is almost insensitive to temperature changes in water but it decreases with increasing temperature in IL [bmim][BF$_4$]. Similarly, the decrease in α with increasing temperature becomes more prominent as water is added to IL [bmim][BF$_4$] (Figure 3C), as α in water is more sensitive to temperature changes. The slope values appear to reach a plateau at $X_{[\mathrm{bmim}][\mathrm{BF}_4]} \sim 0.7$ and increase again when $X_{[\mathrm{bmim}][\mathrm{BF}_4]} \leq 0.3$. We infer that as water is added to [bmim][BF$_4$], an increase in temperature dependence of α combined with the temperature independence of π^* results in an overall increase in temperature dependence of the dipolarity/polarizability and/or HBD acidity manifested via the increase in temperature dependence of $E_{\mathrm{T}}^{\mathrm{N}}$. However, a subsequent decrease in temperature dependence of π^* as we move toward the water-rich region results in a decrease in temperature dependence of the dipolarity/polarizability and/or HBD acidity after reaching a maximum value. As indicated earlier, parameter β even in aqueous mixtures of [bmim][BF$_4$] is not affected significantly by the change in temperature; it is not possible to observe any trends in the extent of change in β with temperature (Figure 3D). Goodness of the fits to the linear expression between β and temperature at most compositions is also not acceptable (Table S2 and Figures S4 and S10, Supporting Information).

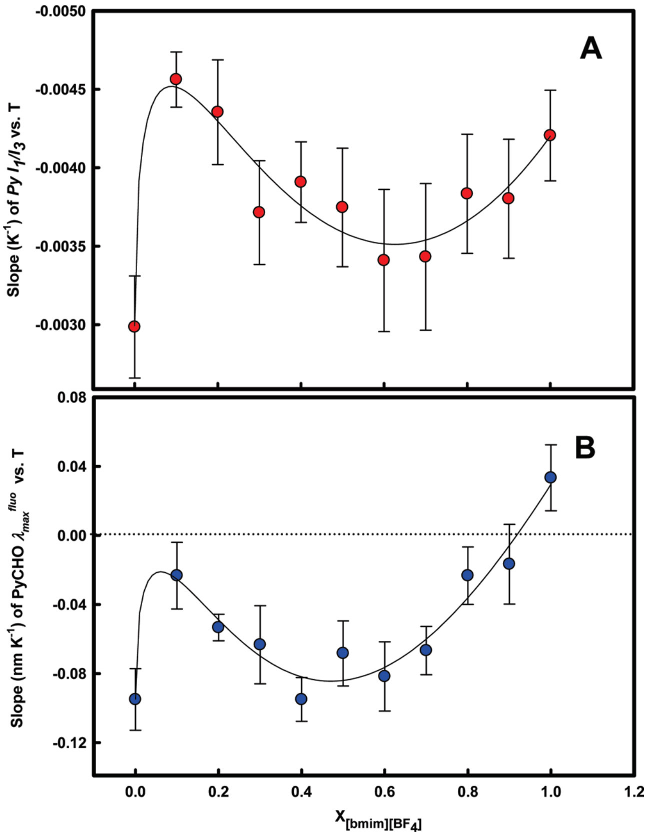

Figure 4. Slopes recovered from the linear regression analysis of pyrene I_1/I_3 (A) and pyrene-1-carboxaldehyde lowest energy fluorescence maxima $\lambda_{\max}^{\text{fluo}}$ (B), respectively, versus temperature as function of [bmim][BF$_4$] mole fraction ($X_{[\text{bmim}][\text{BF}_4]}$) within aqueous [bmim][BF$_4$].

Slopes of Py I_1/I_3 (panel A) and PyCHO $\lambda_{\max}^{\text{fluo}}$ (panel B), respectively, versus temperature at each composition for aqueous [bmim][BF$_4$] mixtures are presented in Figure 4. It appears from the data presented in Figure 4A that an aqueous mixture of IL [bmim][BF$_4$] having a small amount of IL (i.e., $X_{[\text{bmim}][\text{BF}_4]}$ *only* ~0.1) shows significant enhancement in the temperature dependence of Py I_1/I_3. This is attributed to our earlier observations that dilute aqueous solutions of ILs show significantly altered physicochemical properties as compared to those of neat water.[6c] For $X_{[\text{bmim}][\text{BF}_4]} \geq 0.1$, the extent of decrease in Py I_1/I_3 with increasing temperature, in general, appears to become smaller before increasing again to attain its value in IL [bmim][BF$_4$]. The latter behavior is in contrast with what is observed for $E_{\mathrm{T}}^{\mathrm{N}}$ (Figure 3A). Perhaps the effect of HBD acidity manifesting itself through the$E_{\mathrm{T}}^{\mathrm{N}}$ could be the reason for this observation (vide supra).[1k,19,24] Slopes of PyCHO $\lambda_{\max}^{\text{fluo}}$ versus temperature (Figure 4B) at different mixture compositions show a trend similar to that observed for probe pyrene (Figure 4A). However, too much emphasis may not be given to this trend as the slope values appear to be rather insignificant (e.g., a slope of 0.05 nm K^{-1} suggests that on changing temperature by 100 K, a mere change of 5 nm in PyCHO $\lambda_{\max}^{\text{fluo}}$ is observed). All-in-all, the insensitivity of PyCHO $\lambda_{\max}^{\text{fluo}}$ toward temperature change within our IL and aqueous IL systems is reasserted.

Conclusions

Temperature-dependent behavior of solvatochromic probes within [bmim][PF$_6$], [bmim][BF$_4$], and aqueous mixtures of [bmim][BF$_4$] is found to depend on the identity of the probe. Manifested through the behavior of betaine dye 33, the temperature dependence of the dipolarity/polarizability and/or HBD acidity within ILs [bmim][PF$_6$] and [bmim][BF$_4$], respectively, is observed to be less than that within water; in aqueous mixtures of [bmim][BF$_4$], this temperature dependence increased and was observed to be the most at $X_{[\text{bmim}][\text{BF}_4]} \sim 0.7$. Dipolarity/polarizability (π^*) obtained from the molecular absorbance of DENA show a trend similar to that by betaine dye 33 for ILs, but within water the behavior of this probe is nearly temperature independent. As [bmim][BF$_4$] is added to water, the temperature dependence of π^* increases. HBD acidity (α), obtained from the behavior of betaine dye 33 and DENA, of each of the ILs and water decreases with increasing temperature; the temperature dependence is less pronounced in ILs as compared to that in water. Subsequently, addition of [bmim][BF$_4$] to water decreases the temperature dependence of α. HBA basicity (β) obtained in concert with another absorbance probe NA appears to be independent of temperature within ILs as well as aqueous mixtures of IL [bmim][BF$_4$]. The fluorescence dipolarity probe pyrene behaves similarly to betaine dye 33 within two ILs and water as the temperature is changed; the behavior is different within the [bmim][BF$_4$] + water mixture. The lowest energy fluorescence wavelength maxima of pyrene-1-carboxaldehyde (a probe of static dielectric constant of the medium), though decreasing significantly with increasing temperature within water, is found to be insensitive to the temperature changes within the two ILs and the aqueous [bmim][BF$_4$] mixtures.

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Supporting Information Available: Scheme S1 (structures of the ionic liquids and probes), Tables S1 (slopes) and S2 (linear regression analysis results), and Figures S1−S12 (variations of results with mole fraction and temperature). This material is available free of charge via the Internet at http://pubs.acs.org.

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