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Delineating Solute–Solvent Interactions in Binary Mixtures of Ionic Liquids in Molecular Solvents and Preferential Solvation Approach

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The effect of solute–solvent and solvent–solvent interactions on the preferential solvation of solvatochromic indicators in binary mixtures of ionic liquids with molecular solvents has been investigated. The binary mixtures of the pyridinium-based ionic liquids 1-butylpyridinium tetrafluoroborate ([BP][BF₄]), 1-butyl-3-methylpyridinium tetrafluoroborate ([3-MBP][BF₄]), and 1-butyl-4-methylpyridinium tetrafluoroborate ([4-MBP][BF₄]) with molecular solvents like water, methanol, and dichloromethane have been selected for this investigation. The effect of addition of ionic liquids to molecular solvents on the polarity parameters E_T^N , Kamlet–Taft parameters, hydrogen bond donor ability (HBD) (α), hydrogen bond acceptor ability (HBA) (β), and polarizability (π^*) was obtained. The polarity parameters of the mixture display nonideality on addition of ionic liquids to water and dichloromethane. On the other hand, strong synergetic effects were seen in the ionic liquid–methanol binary mixtures. The preferential solvation models have been employed to analyze the collected data in order to achieve information on solute–solvent interactions in these binary mixtures.

Introduction

In the past few decades, there has been growing concern about the environmental effects of the toxic releases from chemical industries. This has led to the search for “greener” alternatives for volatile organic compounds. Ionic liquids are one of the more popular alternatives, mainly due to their insignificant vapor pressure, thermal and chemical stabilities, and excellent recyclability.¹ The infinite number of possible combinations of cations and anions available at our disposal has led to them being tagged as “designer solvents”. Ionic liquids have wide applications such as in organic synthesis,^{1,2} catalysis,³ electrochemistry, and solvent extraction of a variety of compounds.⁴ However, the wide variety of cations and anions available makes a systematic study very difficult. Unless the optimal choice of cation and/or anion is made on the basis of well-established physicochemical data, the use of ionic liquids can even affect the process in an adverse manner. Recently, we have demonstrated that cycloaddition reactions are inhibited in ionic liquids possessing high viscosities.^{5,6} The high viscosity of ionic liquids is also a constraint in obtaining the optimum performance in many electrochemical devices employing these compounds as electrolytes. The effect is further complicated by the high sensitivity of viscosity not only to the choice of constituent ions but also to the presence of impurities and cosolvents. In particular, the addition of cosolvents like water, methanol, etc. can strongly affect the physical and chemical properties of ionic liquids such as viscosity, electrical conductivity, and reactivity as well as solvation and solubility properties.⁷ Previous results from our group have shown that addition of small amounts of cosolvents to ionic liquids lowers the viscosity of ionic liquids drastically.⁸ The lowering effect in viscosity of ionic liquids can be greatly enhanced by selecting a polar solvent.

Successful and effective application of ionic liquids as solvent media in organic transformations, extraction, electrochemical, and microbiological processes require a precise knowledge of polarity of these compounds. The polarity of solvents and ionic

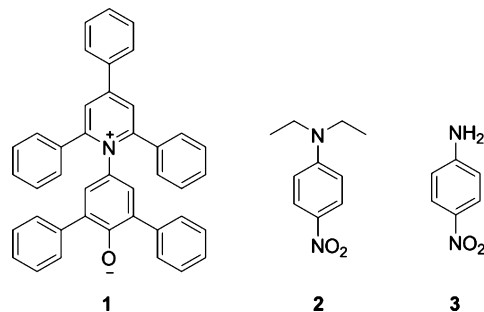


Figure 1. Reichardt's dye (1), *N,N*-diethyl-4-nitroaniline (2), and 4-nitroaniline (3) used as probe molecules for polarity determination.

liquids is a crucial property that has been correlated to kinetic profile of organic reactions. The polarities of many ionic liquids have been studied in terms of $E_T(30)$ (electronic transition energy in kcal/mol) and the Kamlet–Taft polarity parameters,⁹ α , the hydrogen bond donor ability (HBD) (acidity), β , the hydrogen bond acceptor ability (HBA) (basicity), and π^* , polarizability, and were determined using three indicator dyes: Reichardt's dye (1), *N,N*-diethyl-4-nitroaniline (2), and 4-nitroaniline (3) (Figure 1).

Several recent publications have demonstrated that the commonly used ionic liquids are reasonably polar solvents, having polarity greater than those of solvents like acetone, dimethyl sulfoxide, etc. but less than those of water and short-chain alcohols.¹⁰ A comprehensive account of the polarity of ionic liquids has been recently presented by Reichardt.¹¹ An interesting aspect of polarity of ionic liquids is thermosolvatochromism, i.e., the temperature-dependent variation in the polarity of ionic liquids. There are very few reports available on thermosolvatochromism in ionic liquids.¹² Recently, we have studied that thermosolvatochromism in pyridinium-, pyrrolidinium-, and phosphonium-based ionic liquids was explained on the basis of change of cation, substitution of alkyl chain on cation, and anion effect.¹³ For the pyridinium- and pyrrolidinium-based ionic liquids, polarity decreases with temperature

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while it increases with temperature in the case of phosphonium-based ionic liquids.

Solute–solvent and solvent–solvent interactions using solvatochromic probes or dyes can vary with the amount and nature of cosolvents, even as trace impurities. The interaction of a dye in a binary solvent system depends on the composition of solvation sphere since solute–solvent interaction is much more complex in mixed solvent systems than in pure solvents. The solute can interact to a greater extent with one of the solvents present in the mixture, and in turn, the solvent–solvent interactions can also strongly affect solute–solvent interactions. In a pure solvent, the composition of the sphere of solvation of the indicator is the same as in the bulk solvent. However, in a mixed solvent, the solvatochromic indicator interacts to a different extent with the solvents of the mixture and hence the composition of the solvation sphere is different from the composition of the bulk solvent. This phenomenon is known as *selective* or *preferential solvation*. There are many reports available on the solute–solvent and solvent–solvent interaction in binary mixtures of conventional organic solvent binary mixtures. The data have been fitted to models, which gives information about the preferential solvation of dye by either of solvent or mixed solvents. Preferential solvation model was used by Roses et al.,¹⁴ for example, to explain the polarity of binary mixtures of formamides with hydroxylic solvents having similar $E_T(30)$ values.

On the other hand, the significant lowering of viscosity of ionic liquids upon addition of cosolvents is a result of changes in ionic interactions of ionic liquids and cosolvents. This situation from the point of view of polarity in the ionic liquids + cosolvents has been investigated to a lesser extent. The solute–solvent interactions and behavior of a solvation probe or dye in binary mixture of ionic liquids with molecular solvents has recently been investigated.¹⁵ It has been shown that Reichardt's dye is more preferentially solvated by ionic liquids and mixed solvents with respect to cosolvent added. The hyperpolarity within the [BMIM][PF₆] and tetraethylene glycol mixture has also been studied. The polarities as well as Kamlet–Taft parameters for mixtures have higher values as compared to those of pure solvents.¹⁶ This behavior is also known as the synergetic effect, wherein the measured property shows deviations in magnitude greater than the values in the pure components themselves. Such a behavior is easily observable in the form of a pronounced maxima or minima when plotted as a function of the mole fraction of either of the solvents. In view of the scarcity of experimental data on the polarity of the ionic liquids solutions, it is difficult to interpret the phenomenon.

In continuation of our ongoing work on ionic liquids,¹⁷ we now present the polarity variations in the binary mixtures of the pyridinium-based ionic liquids with three solvents—water, methanol, and dichloromethane—in order to investigate the extent of the preferential solvation. The cosolvents were chosen with a wide range of polarity values in order to understand the effect of cosolvent polarity on the solvation in the binary mixtures of ionic liquids. We have measured the polarity parameters for three ionic liquids: 1-butylpyridinium tetrafluoroborate ([BP][BF₄]), 3-methyl-1-butylpyridinium tetrafluoroborate ([3-MBP][BF₄]), and 4-methyl-1-butylpyridinium tetrafluoroborate ([4-MBP][BF₄]). The cosolvents used were water, methanol, and dichloromethane.

Experimental Section

Materials. The spectroscopic indicator dyes **1** and **3** were used as obtained. The dye **2** was purchased from Frinton laboratories (99% purity). Pyridine, 3-picoline, 4-picoline, and 1-bromobutane were distilled prior to their use. Sodium tetrafluoroborate (NaBF₄) was used as purchased without further purification. Deionized water having conductivity 18.2 Ω was used in the investigation. Spectroscopic grade methanol and dichloromethane were used for all the polarity measurements.

Synthesis of Ionic Liquids. The ionic liquids studied in this work were synthesized and characterized according to the previously reported literature procedure.¹⁸ All the ionic liquid samples were thoroughly dried under vacuum for several hours prior to their use. Also, the water content of the ionic liquids was measured before making solution by Karl Fischer coulometer and did not exceed 50 ppm for any sample.

Polarity Measurements. The measurements were carried out according to our earlier report.¹³ Different concentrations of ionic liquids [BP][BF₄], [3-MBP][BF₄], and [4-MBP][BF₄] in water, methanol, and dichloromethane were prepared. The freshly prepared solution of dye in dichloromethane was added dropwise to a precisely measured volume of pure ionic liquids and the dichloromethane was removed under high vacuum. The solvents water, methanol, and dichloromethane were added in appropriate amounts to the ionic liquids in order to prepare the required solutions. The solution of dye was added to the cuvette for measurement of wavelength at maximum absorption.¹² The temperature of the cuvette was stabilized at 298.15 K using a Peltier setup with an accuracy of ±0.01 K. The calculations of polarity parameters were done as given below. All the polarity parameters are reproducible to ±0.4%. Throughout this paper, x_2 refers to the mole fraction of the ionic liquids, remembering that $x_1 + x_2 = 1$, where x_1 is the mole fraction of the solvent.

Solvatochromic Polarity Analysis. The polarity parameters were determined as follows. The $E_T(30)$ electronic transition energy parameter is obtained from the spectroscopic shift of Reichardt's dye 30 (probe 1), as defined by eq 1

$$E_T(30) = h\nu_{\max} N_A = 2.8591\nu(1)_{\max} \quad (1)$$

The dimensionless normalized E_T^N scale was introduced, using water ($E_T^N = 1.00$) and tetramethylsilane (TMS) ($E_T^N = 0.00$) as reference solvents to fix the scale, in accordance with eq 2

$$\begin{aligned} E_T^N &= [E_T(\text{solvent}) - E_T(\text{TMS})] / [E_T(\text{water}) - E_T(\text{TMS})] \\ &= [E_T(\text{solvent}) - 30.7] / 32.4 \end{aligned} \quad (2)$$

The polarizability π^* parameter is determined from the spectroscopic shift of *N,N*-diethyl-4-nitroaniline (probe 2, Figure 1), as follows:

$$\nu(2)_{\max} = 27.52 - 3.182\pi^* \quad (3)$$

The HBA or β parameter is determined using the spectroscopic shift of 4-nitroaniline (probe 3) with respect to *N,N*-diethyl-4-nitroaniline (probe 2, Figure 1) and eq 4:

$$\nu(3)_{\max} = 1.035\nu(2)_{\max} - 2.8\beta + 2.64 \quad (4)$$

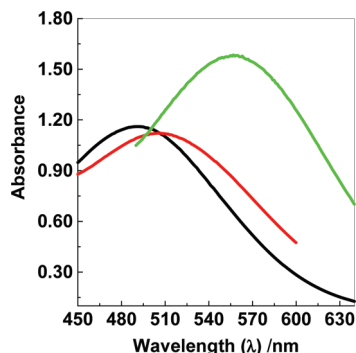


Figure 2. Typical UV–visible spectra for Reichardt's dye 30 in pure [BP][BF₄] (green line), for $x_2 = 0.024$ (black line), for $x_2 = 0.284$ of [BP][BF₄] (red line) in water.

TABLE 1: Polarity Parameters of Ionic Liquids and Solvents

no.	solvents	E_T^N	α	β	π^*
1	[BP][BF ₄]	0.637 ^a	0.520	0.450	1.082
2	[3-MBP][BF ₄]	0.651	0.560	0.423	1.071
3	[4-MP][BF ₄]	0.636	0.530	0.533	1.066
4	water	1.000	1.120	0.178	1.325
5	methanol	0.762	1.030	0.578	0.771
6	dichloromethane	0.309	0.040	0.059	0.733

^a References 11 and 13.

The HBD or α parameter can then be calculated using $E_T(30)$ with respect to π^* by

$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \quad (5)$$

Results and Discussion

The microscopic properties of the solvents are always reflected through bulk or macroscopic properties like dielectric permittivity, dipole moment, refractive index, and polarity. The microscopic properties are a measure of the structure and dynamics of the solvation sphere of dye through macroscopic parameters, E_T^N , and Kamlet–Taft parameters of dipolarity/polarizability (π^*), hydrogen-bond acceptor basicity (β), and hydrogen-bond donor acidity (α). The microscopic parameters were determined from solvatochromic measurements, which measure the properties in the solvation sphere of the solvatochromic indicator. The pure solvents do not give rise to preferential solvation, since the compositions of the solvation sphere and bulk solvent are identical. Typical UV–visible spectra of pure [BP][BF₄] and its aqueous solutions are demonstrated in Figure 2.

In binary mixtures, preferential solvation is a fairly common phenomenon, which leads to many interesting consequences. In the case of ionic liquids, such preferential interactions may be manipulated to give the desired outcome of any chemical process. The polarity parameters for pure ionic liquids and solvents at 298.15 K are shown in Table 1. As expected, the polarity of ionic liquids is lower than that of water and methanol but higher than that of solvents like dichloromethane. The polarity values of the pure liquids conform to the values reported in the literature.^{10–12}

After ascertaining the purity of our samples and observing the good agreement between the literature values and experimentally measured values, we focused our attention on binary mixtures of ionic liquids. We were interested in understanding if the hyperpolarity trends observed in the literature were

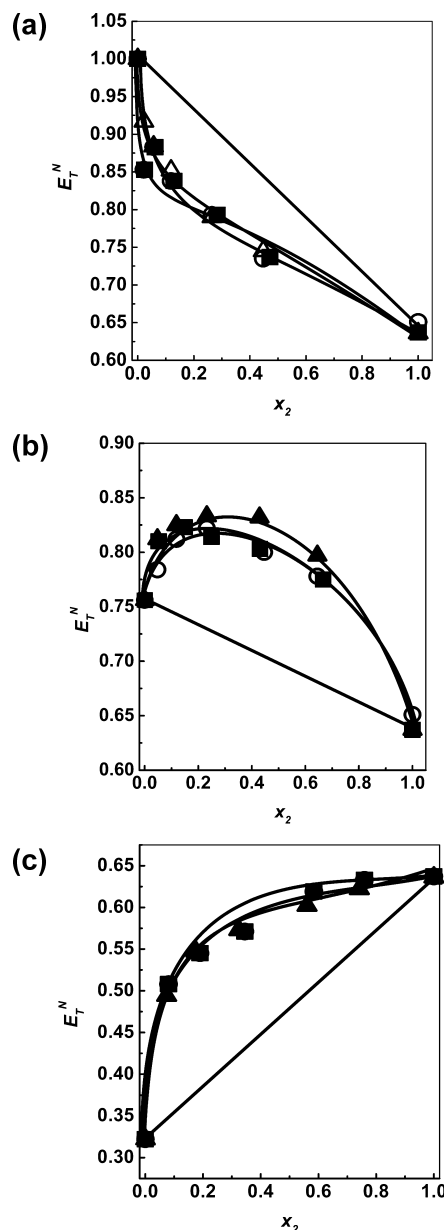


Figure 3. (a) Plots of E_T^N – x_2 for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (△) in water. (b) Plots of E_T^N – x_2 for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (△) in methanol. (c) Plots of E_T^N – x_2 for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (●), and [4-MBP][BF₄] (▲) in dichloromethane.

restricted to the particular combination of ionic liquid + molecular solvents or were a more general phenomenon in nature.

Figure 3, a, b, and c, shows the plots of E_T^N with x_2 of binary mixtures of the pyridinium-based ionic liquids in water, methanol, and dichloromethane, respectively. The polarity observed above shows a strongly nonideal behavior in all binary mixtures studied. There are some interesting variations related to the cosolvent used. For the binary mixtures of the pyridinium ionic liquids in water, it is observed that the polarity of mixtures decreases with increase in concentration of all the ionic liquids. All the three ionic liquids show this peculiar nonideal behavior on the addition of ionic liquids to water, indicating a similar strong solvent-specific interaction between the water and ionic liquids. In the case of binary mixture of ionic liquids in methanol, the variations in the polarity parameters are different

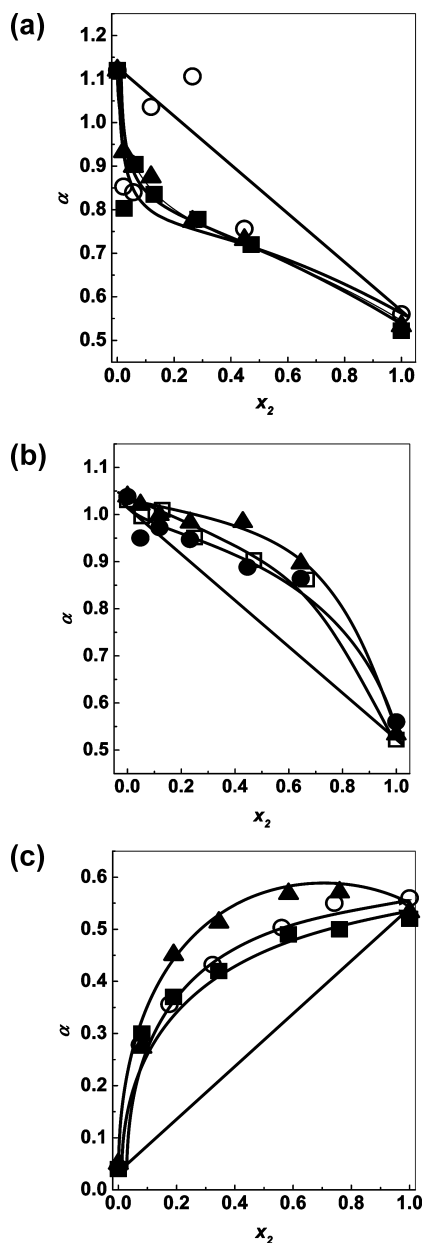


Figure 4. (a) Plots of α against x_2 for the binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in water. (b) Plots of α against x_2 for the binary mixtures of [BP][BF₄] (□), [3-MBP][BF₄] (●), and [4-MBP][BF₄] (▲) in methanol. (c) Plots of α against x_2 for the binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in dichloromethane.

in nature, as shown in Figure 3b. For the binary mixtures in methanol, E_T^N shows a positive deviation, in fact suggesting a strong synergistic effect, in which the polarity of the mixture is higher than that of either of the pure solvents. This is apparently opposite to the trend observed in the aqueous mixtures. The fact that methanol differs from water by the presence of only a methyl group makes such a difference more relevant. In dichloromethane, the nonideality observed is greater than that seen in aqueous binary mixtures, but no synergistic attenuation of polarity is observed.

The HBD parameter α shows analogous behavior as E_T^N with respect to the composition of the binary mixtures (Figure 4a–c). This is expected since both parameters reflect the hydrogen bond donor ability of the solvents. The E_T^N parameter is a scale with multiple contributions, but the hydrogen bond donor ability is the more dominant one of all, along with the polarizability

interactions. In other words, the ability of the solvents to stabilize the ground state and excited state of Reichardt's dye determines the observed values to a very large extent. Accordingly, in the present work, the α parameter was determined indirectly, from the measurements of E_T^N and polarizability of the binary mixtures. Hence, it is expected that the variations with composition are reflected in both the systems. But, nonetheless, some subtle differences can provide useful insights into the nature of probe-dependent solute–solvent interactions. For example, the α parameter does not show the synergistic effect in the ionic liquid + methanol binary mixtures as seen for Reichardt's dye.

On the contrary, a marginal synergistic effect is seen for the binary mixtures with dichloromethane (especially for the [4-MBP][BF₄] + dichloromethane system), although it was not observed for the E_T^N measurements for these systems. The presence and position of alkyl substituents do not affect the variations to a very great extent in binary mixtures with water or methanol, but considerable difference is seen when dichloromethane is employed as a cosolvent (Figure 4, parts a and b as compared to part c).

The difference between the synergy of the E_T^N and α parameters in the ionic liquid + methanol binary systems needs to be analyzed in greater detail. It has been proposed earlier that synergistic effects are not entirely characteristic of the mixtures studied but are also determined by the systems employed to study the mixtures.¹⁹ The choice of the systems—the polarity probe, for example—can be decisive in determining the nature of the molecular interactions and the extent of synergy observed.

This approach also explains the stark difference of the hydrogen bond acceptor capacity as measured by the β parameter in comparison to the parameters discussed earlier. (Figure 5a–c) The β parameter increases with the increasing concentration of an ionic liquid in aqueous systems, since an ionic liquid possesses higher β value than that of water. While the binary mixtures in water and dichloromethane show a strong degree of nonideality, it is the ionic liquid + methanol systems that are remarkable for their highly synergistic hydrogen bond acceptor property.

The polarizability parameter π^* shows a decrease with an increase in the concentration of ionic liquids (see Figure 6a–c). However, no strongly synergistic trends in this variation are witnessed for the binary mixtures in all the three cosolvents. This makes the synergy observed for the E_T^N parameter of the ionic liquid mixtures in methanol more interesting—since both the dominant contributing parameters do not reflect the synergy, its origin must be some interesting molecular interactions. At this stage, it would be difficult to speculate about the nature of such interactions. But the emergence of such variation in synergy among the same binary mixtures emphasizes the need for more extensive studies in the near future.

The parameters E_T^N , α , β , and π^* exhibit nonideal behavior. However, for the binary mixtures of ionic liquids in methanol, the E_T^N , α , and π^* parameters show positive deviations while β shows negative deviation. This is opposite to the trend observed in aqueous mixtures. The fact that methanol differs from water in the presence of only a methyl group makes this difference more relevant due to a decrease in extent of strong hydrogen bonding in methanol. For ionic liquid–methanol mixtures, the E_T^N parameter shows an interesting synergetic effect, in which the polarity of mixtures is higher than that of either of the pure solvents.

The synergetic effect is observed when HBD acidity α of the solvent (ionic liquids in this case) is complemented by a

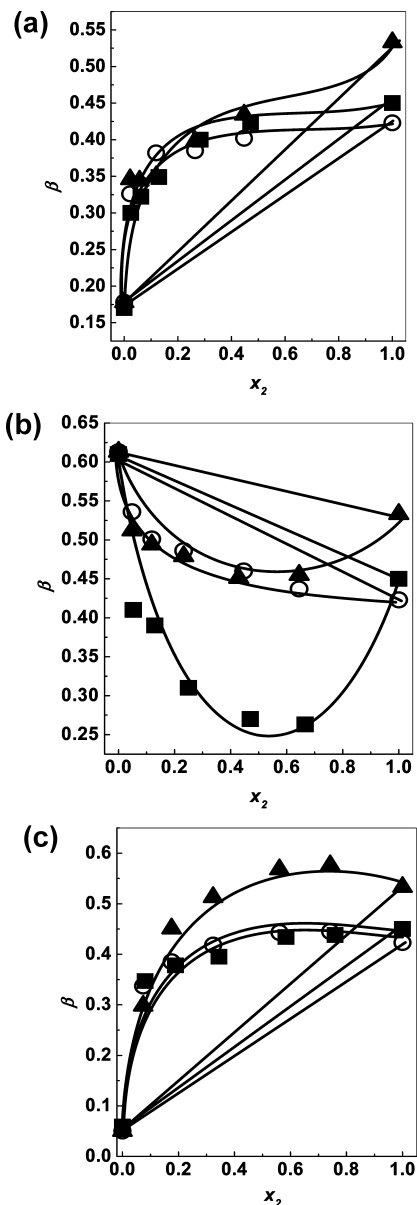


Figure 5. (a) Plots of β against x_2 for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in water. (b) Plots of β against x_2 for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in methanol. (c) Plots of β against x_2 for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in dichloromethane.

strong HBA basicity β of the solvent, methanol, having similar polarity in terms of E_T^N values. Such complementary interactions lead to the formation of hydrogen-bonding complexes with interesting deviations from the ideal behavior. There is a formation of hydrogen bond complex between the two solvents, which is more polar than pure methanol and ionic liquids.

The binary mixtures of ionic liquids with dichloromethane show a more pronounced nonideal behavior as compared to binary mixtures ionic liquids with water and methanol. The polarity difference between ionic liquids and dichloromethane is large, so that for an ionic solute the preferential solvation of the dye or probe is greater by ionic liquids rather than dichloromethane. The nonideality is thus observed for ionic liquid mixtures with highly polar cosolvents like water and methanol as well as nonpolar solvents like dichloromethane. A detailed analysis of these synergetic effects and nonideal behavior would lead to a greater understanding of the

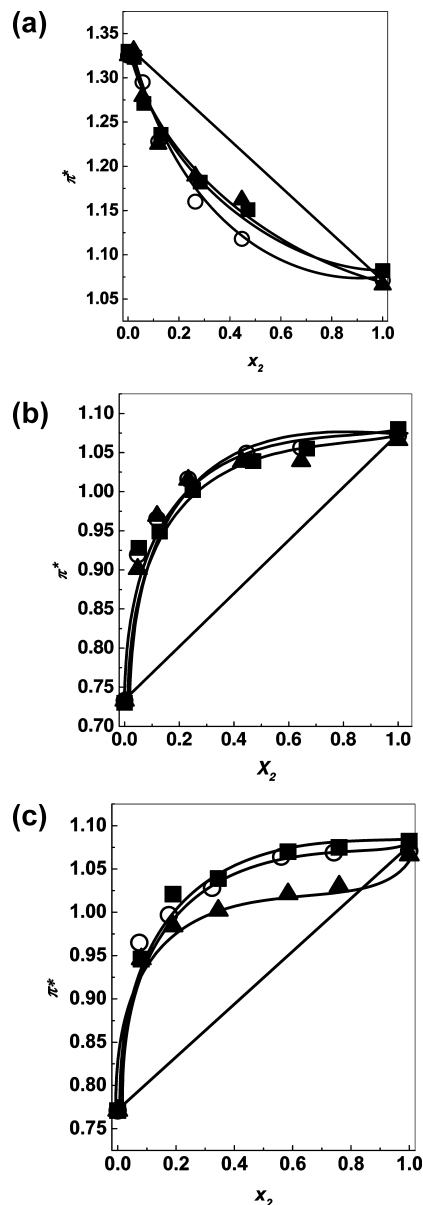


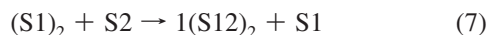
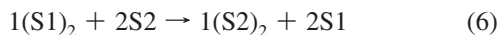
Figure 6. (a) Plots of π^*x_2 for the binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in water. (b) Plots of π^*x_2 for the binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in methanol. (c) Plots of π^*x_2 for the binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in dichloromethane.

solute–solvent interactions. Below, we attempt to correlate the obtained data with the help of two models and compare the results in order to understand which one of them explains the observations more satisfactorily.

Preferential Solvation Model. It has been proposed that preferential solvation is a measure of the deviation of $E_T(30)$ values from linearity with the addition of cosolvents in the binary mixtures.²⁰ The preferential solvation equations were derived on the basis of the same solvent exchange theory and used for the description of the $E_T(30)$ values of binary mixtures of ionic liquids with molecular solvents.²¹ The synergism is observed for the HBA and HBD solvents by forming hydrogen bond complex which is more polar than either of two pure solvents. Hence these models allow us to understand the both synergetic as well as nonsynergetic effect in binary mixtures of solvents from the correlation parameters. The transition energy of a solvatochromic indicator is an average of the

transition energies of solvent in solvation microsphere of the indicator and changes with mole fraction of solvents added.

Model 1. The preferential solvation model is based on the two-step solvent-exchange model first proposed by Skwierczynski and Connors²¹



where S1 and S2 indicate the two pure solvents and S12 represents a solvent formed by the interaction of solvents 1 and 2. $1(S1)_2$, $1(S2)_2$, and $1(S12)_2$ indicate Reichardt's dye solvated by solvents S1, S2, and S12, respectively. The two solvent-exchange processes can be defined by two preferential solvation parameters, $f_{2/1}$ and $f_{12/1}$, which measure the tendency of the indicator to be solvated by solvents S2 and S12 with reference to solvent S1 solvation.

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \quad (8)$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{(x_2^0/x_1^0)^2} \quad (9)$$

In eqs 8 and 9, x_1^s , x_2^s , and x_{12}^s are the mole fractions of solvents S1, S2, and S12, respectively, in the sphere of solvation of indicator and x_1^0 and x_2^0 are the mole fractions of the two solvents in the bulk mixed solvent.

The E_T^N polarity of the mixed solvent is calculated as an average of the E_T^N values of solvents S1, S2, and S12 in the sphere of solvation of the indicator.

$$E_T^N = x_1^s E_{T1}^N + x_2^s E_{T2}^N + x_{12}^s E_{T12}^N \quad (10)$$

From eqs 8–10, a general equation that relates the E_T^N polarity of a binary mixture to the E_T^N polarities of the two pure solvents, the preferential solvation parameters, and the solvent composition can be derived according to

$$E_T^N = \frac{E_{T1}^N(1 - x_2^0)^2 + E_{T2}^N f_{2/1} (x_2^0)^2 + E_{T12/1}^N f_{12/1} (1 - x_2^0) x_2^0}{(1 - x_2^0)^2 + f_{2/1} (x_2^0)^2 + f_{12/1} (1 - x_2^0) x_1^0} \quad (11)$$

$$E_{T12}^N = \frac{E_{T1}^N + E_{T2}^N}{2} \quad (12)$$

Equation 11 is an operative expression to correlate the polarities in the solution of ionic liquids. But this model cannot explain for synergetic mixtures. In the case of synergetic mixtures, we explained the preferential solvation using model 2 as shown below.

Model 2. Model 1 is a more generalized model and defined by the solvent-exchange process. But it cannot explain the synergetic behavior observed in methanol–ionic liquids binary mixture. In order to explain the synergetic effect, model 2 has been introduced and it describes the hydrogen bond complex

TABLE 2: Fitting Parameters Obtained from Model 1

no.	solvents	ionic liquids	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	σ
1	water	[BP][BF ₄]	1	0.637	0.819	45.66	67.05	0.001
2		[3-MBP][BF ₄]	1	0.651	0.826	80.79	86.08	0.001
3		[4-MBP][BF ₄]	1	0.636	0.818	23.56	26.73	0.001
4	DCM	[BP][BF ₄]	0.322	0.637	0.480	556.0	161.5	0.001
5		[3-MBP][BF ₄]	0.322	0.651	0.487	118.3	39.52	0.001
6		[4-MBP][BF ₄]	0.322	0.636	0.480	366.4	105.3	0.004

formation in methanol and ionic liquids. We also attempted to fit this model 2 for water–ionic liquids and dichloromethane–ionic liquids binary mixtures but the estimated parameters were showing high errors.

$$E_T^N = E_{T1}^N + \frac{a(x_2^0)^2 + c(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_1^0} \quad (13)$$

where a and c are the fitting parameters.

Results of Correlations. The experimental data were subjected to the above models using eqs 11 and 13 using only one parameter, E_T^N . Model 1 is used for water and dichloromethane and model 2 is for methanol. The regression parameters are shown in Table 2.

1. Ionic Liquids–Water Binary Mixtures. From model 1, two parameters $f_{2/1}$ and $f_{12/1}$ were determined. The parameter $f_{2/1}$ is the tendency of solvent 2 (ionic liquid) to solvate the dye with reference to solvent 1 while $f_{12/1}$ measured the tendency of the indicator to be solvated by mixture with reference to solvent 1. The $f_{2/1}$ and $f_{12/1}$ for the ionic liquids [BP][BF₄]-water system are 45.66 and 67.05, respectively. In Figure 7 are shown the ΔE_T^N values as a function of x_2 for [BP][BF₄] in water. ΔE_T^N is defined as the difference between E_{Texp}^N and E_{Tcorr}^N . E_{Texp}^N is the value of E_T^N obtained from our experimental work while E_{Tcorr}^N is the value of E_T^N from the use of the model. The values of $f_{2/1} \gg 1$ designate that the dye is more solvated by [BP][BF₄], even if water is more polar than [BP][BF₄]. The solvation sphere is enriched with ionic liquid rather than with water. This may partially arise due to the hydrophobicity of the probe molecule. Also, the $f_{12/1} > f_{2/1}$ shows that mixture forms a complex which has greater affinity toward the dye as compared to the pure [BP][BF₄]. Similarly, for the system [3-MBP][BF₄]-H₂O, the parameters $f_{12/1}$ and $f_{2/1}$ are 80.79 and 86.08, respectively, and for the [4-MBP][BF₄]-H₂O, system $f_{12/1}$, $f_{2/1}$ are 23.56 and 26.73. It is obvious that the composition of the solvation sphere is affected more by methyl substitution on the pyridinium cation. Additionally, the values of $f_{12/1}$ and $f_{2/1}$ for [3-MBP][BF₄]-H₂O are higher than for the two other systems. It may be due to the asymmetric nature of cation of [3-MBP][BF₄] which leads to stronger solute–solvent interactions as compared to the sym-

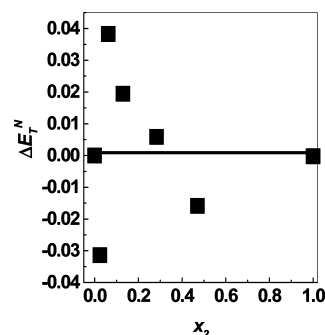


Figure 7. Plot of ΔE_T^N vs x_2 for the [BP][BF₄]-water system.

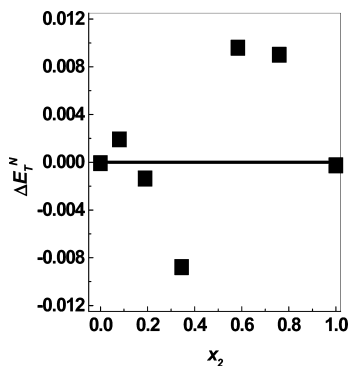


Figure 8. Plot of ΔE_T^N vs x_2 for the [BP][BF₄]-dichloromethane system.

TABLE 3: Fitting Parameters Obtained from Model 2

no.	solvents	ionic liquids	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{12/1}$	$f_{2/1}$	σ
1	methanol	[BP][BF ₄]	0.756	0.637	0.833	11.15	51.89	0.001
		[3-MBP][BF ₄]	0.756	0.636	0.859	3.50	9.45	0.003
		[4-MBP][BF ₄]	0.756	0.651	0.859	4.321	22.06	0.002

metric cations [BP]⁺ and [4-MBP]⁺. The dye is more preferentially solvated by the mixture and by [3-MBP][BF₄] at the same rate. For the [4-MBP][BF₄]-H₂O system, parameters $f_{12/1}$ and $f_{2/1}$ are 23.56 and 26.73, respectively, and indicate that the dye is preferentially solvated by [4-MBP][BF₄] as compared to water. The difference in the values of $f_{12/1}$ and $f_{2/1}$ for all the system shows that methyl group substitution plays an important role in the preferential solvation study.

2. Ionic Liquids–Dichloromethane Mixtures. The preferential solvation of ionic liquids–dichloromethane is investigated through model 1, and the estimated parameters are shown in Table 2. In the case of binary mixture of [BP][BF₄]-dichloromethane, the parameters $f_{12/1}$ and $f_{2/1} \gg 1$ indicate that the indicator dye is strongly preferentially solvated by ionic liquids and mixture only. The values $f_{12/1}$ and $f_{2/1}$ are 156 and 161.54, respectively, which demonstrate that solvation is more pronounced by ionic liquids compared to mixture with reference to dichloromethane. The observed trend for preferential solvation for all the system is as [BP][BF₄]-dichloromethane > [4-MBP][BF₄]-dichloromethane > [3-MBP][BF₄]-dichloromethane. The results of the application of model 1 are shown for the system in Figure 8 in which the ΔE_T^N values are plotted as a function of x_2 .

3. Ionic Liquid–Methanol Mixtures. Model 2 is used for studying preferential solvation in the ionic liquids–methanol binary mixtures for which the three parameters $f_{12/1}$, $f_{2/1}$, and E_{T12}^N were determined. The E_T^N values of both [BP][BF₄] and methanol are close to each other and hence synergism is observed. The synergism effect observed in [BP][BF₄]-methanol, [3-MBP][BF₄]-methanol, and [4-MBP][BF₄]-methanol are shown in Figure 3b. It can be observed that E_{T12}^N obtained from model 2 is higher than those for the pure solvents, which is observed from the plots. The parameters $f_{12/1}$, $f_{2/1}$, and E_{T12}^N obtained from model 2 are shown in Table 3. The values of $f_{12/1}$ and $f_{2/1}$ for the [BP][BF₄]-methanol system are 11.15 and 51.89 and show that the preferential solvation by the mixture and of [BP][BF₄] and methanol more than pure [BP][BF₄] with reference to methanol due to synergism. The same is observed for the methanolic solution of [3-MBP][BF₄] and [4-MBP][BF₄]. The dye is preferentially solvated by the hydrogen bond complex as [BP][BF₄]-methanol > [4-MBP][BF₄]-methanol > [3-MBP][BF₄]-methanol.

An examination of Figures 7–9 shows that the E_T^N parameter for all three types of mixtures of ionic liquids can be successfully

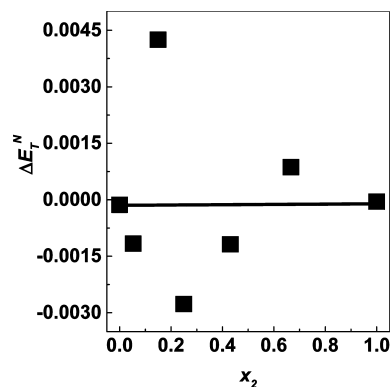


Figure 9. Plot of ΔE_T^N vs x_2 for the [BP][BF₄]-methanol system.

represented by the use of models 1 and 2. The ΔE_T^N values are within the experimental errors.

Conclusions

In summary, we have demonstrated that the electronic transition energies of a binary mixture of an ionic liquid is not the linear function of the compositions of the mixtures. Both positive and negative deviations from the ideal mixing are witnessed. This behavior is also shown by other polarity parameters. The behavior explained using preferential solvation models. Solute–solvent and solvent–solvent interactions are delineated with the help of estimated parameters. The parameters obtained explain the strong synergism observed for some of the mixtures which form the strong hydrogen bond complexes between methanol and ionic liquids.

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