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Solvatochromic Parameters for Binary Mixtures of 1-(1-Butyl)-3-methylimidazolium Tetrafluoroborate with Some Protic Molecular Solvents

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The solvatochromic parameters (E_T^N , normalized polarity parameter; π^* , dipolarity/polarizability; β , hydrogen-bond acceptor basicity; α , hydrogen-bond donor acidity) were determined for binary solvent mixtures of 1-(1-butyl)-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) with water, methanol, and ethanol at 25 °C over the whole range of mole fractions. In nonaqueous solutions, the E_T^N value of the mixture increases with mole the fraction of [bmim]BF₄ and then decreases gradually to the value of pure [bmim]BF₄. Positive deviation from ideal behavior was observed for the solvent parameters E_T^N , π^* , and α , whereas the deviation of the β parameter is negative. The applicability of the combined nearly ideal binary solvent/Redlich–Kister equation for the correlation of various solvatochromic parameters with solvent composition was proved too for the first time. This equation provides a simple computational model to correlate and/or predict various solvatochromic parameters for many binary solvent systems. The correlation between the calculated and the experimental values of various parameters was in accordance with this model. Solute–solvent and solvent–solvent interactions have been applied for interpretation of the results.

Introduction

Room-temperature ionic liquids (RTILs) have recently gained increased interest as potential “green” replacements for volatile organic solvents due to their unique properties.^{1–6} These compounds are typically composed of organic cations with organic or inorganic anions and have negligible vapor pressure and a wide liquid range (i.e., over 300 K).⁷ An ideal solvent should have a very low volatility and should be chemically and physically stable, recyclable, reusable, and eventually easy to handle. Moreover, solvents that allow more selective and rapid chemical transformations will have a significant impact. Ionic liquids were recognized as a novel class of solvents.⁸ Initially developed by electrochemists, they are increasingly implied in many applications such as electrolytes for electrochemical devices and processes and solvents for organic and catalytic reactions as well as for separation–extraction processes and production of new materials.^{9–14}

To increase the efficiency of a process (e.g., separation, extraction, synthesis, etc.), one would like to “tune” a solvent or solvent mixture by addition of cosolvents. It is beneficial in many ways to understand how added cosolvents (or impurities) affect the physicochemical properties of RTILs. When an ionic liquid can be mixed with other green solvents such as water and alcohols, their physicochemical properties will be tunable, and one can prepare mixtures of solvents with suitable physicochemical properties and a lower fraction of RTILs.^{15–17} Ionic liquids based on the 1,3-dialkylimidazolium cation have generated a great deal of interest over the past few years as solvents in many different areas of chemistry.^{1,18–19} There are very few reports on how the cations and anions of these liquids interact

with solutes.^{20–27} The solubility of ethanol and water in 1-(1-butyl)-3-methylimidazolium hexafluorophosphate ([bmim]PF₆) is shown to be limited.²⁸ Therefore, solvatochromic parameters for binary mixtures of [bmim]PF₆ with water and ethanol have been determined up to mole fractions of $x = 0.4$ and 0.25 for ethanol and water, respectively.²⁹ However, 1-(1-butyl)-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) is totally miscible with water, methanol, and ethanol at room temperature.³⁰

The electronic transition energy of solvatochromic indicators of solvent polarity depends on the solvation sphere’s composition and properties, and therefore, the use of such indicators is a suitable method for studying solute–solvent interactions.³¹ Solvatochromic parameters have been demonstrated to be successful in correlating a wide range of chemical and physical properties, involving solute–solvent interactions as well as biological activities of compounds.^{32–36} For these reasons, the prediction of solvatochromic parameters solvent mixtures, based on a minimum number of experiments, provides a useful computational tool. To demonstrate the influence of the solvent composition on various solvatochromic parameters in binary solvent mixtures, the combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K)³⁷ equation has been applied to the experimental data for these parameters. This model has been applied to correlate accurately different physicochemical properties of solvent mixtures.^{38–43}

In this work, four solvatochromic parameters (i.e., E_T^N , normalized solvent polarity parameter; π^* , dipolarity/polarizability; β , hydrogen-bond acceptor basicity; α , hydrogen-bond donor acidity) have been determined for binary mixtures of ethanol, methanol, and water with [bmim]BF₄ at 25 °C over the whole range of mole fractions. The solvatochromic indicators used are Reichardt’s betaine dye for solvent polarity ($E_T(30)$ scale)⁴⁴ as well as 4-nitroanisole and 4-nitroaniline for measuring

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TABLE 1: Solvatochromic Parameters for Binary Mixtures of [bmim]BF₄ with Ethanol at 298.15 K

x_1^a	π^*	β	α	E_T^N
0	0.51	0.9	0.97	0.65
0.1	0.76	0.74	1.02	0.76
0.2	0.82	0.68	0.99	0.77
0.3	0.86	0.63	0.96	0.77
0.4	0.89	0.6	0.93	0.76
0.5	0.9	0.59	0.92	0.76
0.6	0.93	0.56	0.88	0.75
0.7	0.93	0.55	0.86	0.74
0.8	0.94	0.54	0.84	0.73
0.9	0.94	0.53	0.8	0.72
1	0.89	0.59	0.75	0.67

^a x_1 is mole fraction of [bmim]BF₄.

the Kamlet–Taft parameters.⁴⁵ The applicability of the CNIBS/R–K equation for the correlation of these solvatochromic parameters with solvent composition is also shown for three binary solvent mixtures.

Experimental Section

Materials. Spectroscopic grade high-purity methanol and ethanol were purchased from Merck (>99%). 4-Nitroanisole and 4-nitroaniline (Merck, 99%) were recrystallized from water/ethanol and water/acetone, respectively. Reichardt's betaine dye was obtained from Aldrich (>99%) and was used without further purification. Doubly distilled water was prepared as the solvent. 1-(1-Butyl)-3-methylimidazolium tetrafluoroborate (>98%), stored under argon, was purchased from Solvent-Innovation GmbH and was used as received. Karl Fischer titrations showed no detectable presence of water in freshly purchased [bmim]BF₄.

Methods. An ethanolic solution of the indicators were prepared and stored in a dark glass vial at ~4 °C. An appropriate aliquot of the solvatochromic probe primary solution was transferred into 1 cm quartz cuvettes, and its solution was evaporated by vacuum. The mixture of [bmim]BF₄ with molecular solvents (ethanol, methanol, or water) at different compositions was gravimetrically prepared (± 0.1 mg) for each binary solvent mixture separately and was transferred into the quartz cuvette. The solution was vigorously stirred with a magnetic stirrer, so that a steady-state solution was prepared. Final probe concentrations were $0.5\text{--}1 \times 10^{-4}$ mol dm⁻³. UV–vis absorption spectra of the solutions were recorded in the ranges $\lambda = 250\text{--}400$ nm (for 4-nitroanisole), $300\text{--}450$ nm (for 4-nitroaniline), and $420\text{--}600$ nm (for Reichardt's betaine dye), using a GBC UV–vis Cintra 40 spectrophotometer with a thermocell coupled to it. The temperature was maintained at 25 ± 0.1 °C, and all measurements were made in triplicate and averaged. The $E_T(30)$, π^* , β , and α parameters were calculated from the wavelength of maximum absorption according to the procedure reported in elsewhere.^{31,44} Because of the low solubility of Reichardt's dye in water, $E_T(30)$ or E_T^N could not be measured in pure water; for this reason, the literature value was used.³¹

Results and Discussion

The values of solvatochromic parameters (E_T^N , π^* , α , and β) have been determined in binary mixtures of ethanol, methanol, and water with [bmim]BF₄ from the wavenumbers of maximum absorption of the corresponding chemical probes at 25 °C over the whole range of mole fractions according to the procedure reported elsewhere (Tables 1–3).^{31,44} The plots for the solva-

TABLE 2: Solvatochromic Parameters for Binary Mixtures of [bmim]BF₄ with Methanol at 298.15 K

x_1	π^*	β	α	E_T^N
0	0.58	0.8	1.16	0.76
0.1	0.79	0.68	1.15	0.83
0.2	0.85	0.63	1.1	0.83
0.3	0.88	0.6	1.06	0.82
0.4	0.91	0.57	1.03	0.81
0.5	0.93	0.55	0.99	0.8
0.6	0.93	0.55	0.96	0.79
0.7	0.93	0.54	0.92	0.77
0.8	0.93	0.54	0.9	0.76
0.9	0.94	0.53	0.87	0.75
1	0.89	0.59	0.75	0.67

TABLE 3: Solvatochromic Parameters for Binary Mixtures of [bmim]BF₄ with Water at 298.15 K

x_1	π^*	β	α	E_T^N
0	1.1	0.46	1.3	1.00
0.1	1.03	0.6	1	0.84
0.2	0.99	0.62	0.95	0.81
0.3	0.99	0.6	0.91	0.78
0.4	0.96	0.59	0.89	0.76
0.5	0.96	0.57	0.86	0.75
0.6	0.96	0.56	0.85	0.75
0.7	0.96	0.54	0.81	0.73
0.8	0.95	0.54	0.82	0.73
0.9	0.94	0.53	0.81	0.72
1	0.89	0.59	0.75	0.67

tochromic parameters and their excess values versus cosolvent mole fractions are presented in Figures 1–6.

Ethanol/[bmim]BF₄ System. It is clear that by addition of [bmim]BF₄ to ethanol, the π^* value increases rapidly and finally decreases to its corresponding value in neat [bmim]BF₄ through a maximum at $x_{IL} = 0.9$ (Figure 1). The π^* parameter is derived from the change in the energy corresponding to the maximum absorption of the dye induced by the local electric field generated by the solvent. It is not surprising that π^* is greatly affected by the increasing dye-ion solute–solvent interactions when the mole fraction of the ionic liquid increases. A positive deviation from ideality is demonstrated by this parameter with a maximum at a mole fraction of around 0.2 for [bmim]BF₄ (Figure 2). Ideal mixtures have a linear relationship between the solvatochromic parameter and the solvent composition when the solvatochromic probe is equally solvated by the two constituents of the solvent mixture.^{31c} From Figures 1 and 2 it can be concluded that the probe is not equally solvated by the

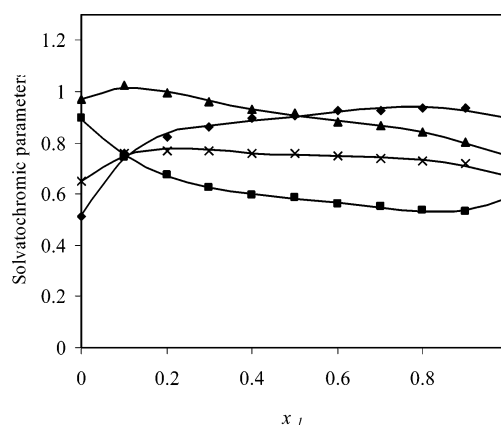


Figure 1. Solvatochromic parameters (E_T^N (x), π^* (◆), α (▲), and β (■)) for binary mixtures of [bmim]BF₄ with ethanol. (x_1 is the mole fraction of [bmim]BF₄.) The solid curves have been calculated from coefficients of eq 1 given in Table 4.

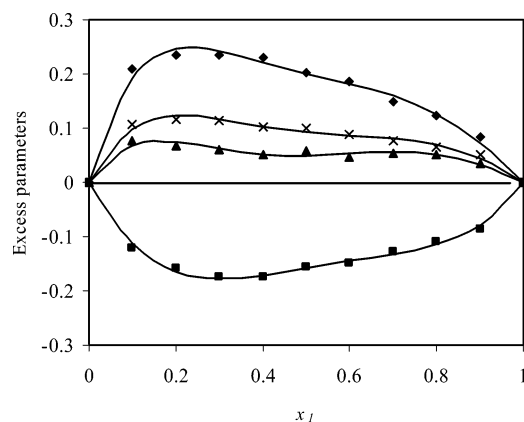


Figure 2. Excess parameters (ΔE_T^N (\times), $\Delta\pi^*$ (\blacklozenge), $\Delta\alpha$ (\blacktriangle), and $\Delta\beta$ (\blacksquare)) for binary mixtures of [bmim]BF₄ with ethanol. The solid curves have been calculated from coefficients of eq 1 given in Table 4.

two components of the binary solvent mixture, and therefore a “preferential solvation” of the probe is confirmed. Preferential solvation arises whenever the bulk mole fraction solvent composition differs from the solvation microsphere.³¹

The hydrogen-bond basicity of RTILs is mainly dominated by nature of the anion. The anion of [bmim]BF₄ is known to have a compact structure possessing much weaker basicity in comparison to ethanol. On addition of [bmim]BF₄ to ethanol, the basicity of the binary mixture decreases; the decrease is initially rapid but becomes more gradual at higher mole fractions of [bmim]BF₄. The β parameter produces a negative deviation from ideality (Figure 2).

The α parameter of the RTILs is largely affected by the nature of the cation, but there is also a smaller anion effect.²⁴ The α value for [bmim]BF₄ is moderately high but is lower than that for ethanol. It has been known that all three imidazolium ring hydrogen atoms are acidic and the acidity is decreased when the 2-position of the ring is substituted by a methyl group.⁴⁶ A careful examination of the α values clearly shows a moderate increase in hydrogen-bond donor (HBD) ability as very small amounts of [bmim]BF₄ are added, followed by a gradual decrease as more [bmim]BF₄ is added to ethanol (similar to the addition of [bmim]PF₆ to aqueous ethanol⁴⁷).

The normalized polarity parameter E_T^N of [bmim]BF₄ is higher than that of the ethanol ($E_T^N = 0.67$ and 0.65 , respectively). When small quantities of the ionic liquid are added, the E_T^N parameter increases sharply and then decreases smoothly to the value of pure RTIL. A synergism is observed for this parameter. This behavior is attributed to a hydrogen-bonding interaction between the RTIL and the ethanol to give a hydrogen-bonded complex in the media, which is more polar and a better HBD than the two constituents of the mixture.^{31a} The betaine dye has a highly dipolar ground state in comparison to the less dipolar excited state and, therefore, exhibits a significant permanent dipole moment, a large polarizable π -electron system, a substantial negative charge on the phenolate oxygen, and a positive charge on the pyridinium nitrogen. The negatively charged phenolate oxygen of the betaine dye in the electronic ground state can acquire an additional solvent stabilization by hydrogen-bonding interactions with the RTIL, which increases the E_T^N values.

Methanol/[bmim]BF₄ System. There is no distinct difference between the methanol/[bmim]BF₄ and ethanol/[bmim]BF₄ mixtures. Similar to ethanol/[bmim]BF₄, when [bmim]BF₄ is added to methanol, the π^* value increases rapidly and gradually reaches a maximum at $x_{IL} = 0.9$ and then decreases to its value

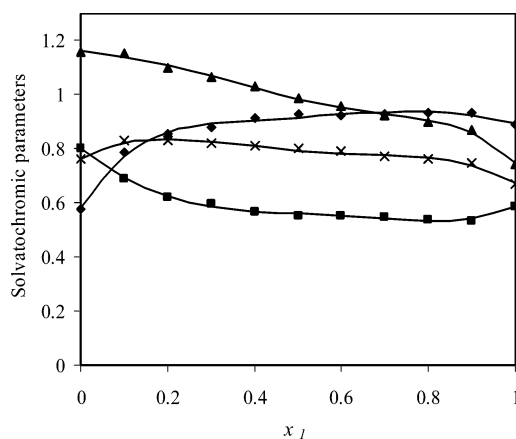


Figure 3. Solvatochromic parameters for binary mixtures of [bmim]BF₄ with methanol. Symbols and solid curves are similar to those in Figure 1.

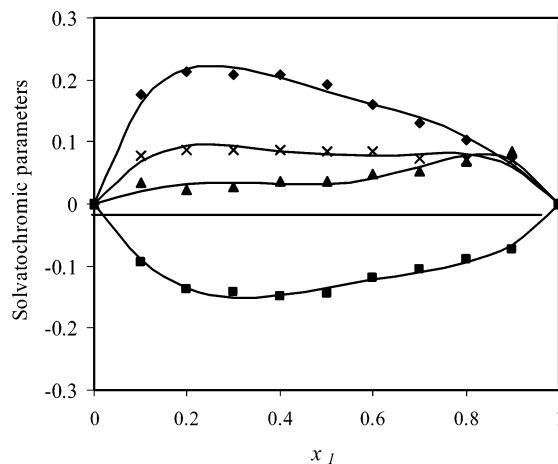


Figure 4. Excess parameters for binary mixtures of [bmim]BF₄ with methanol. Symbols and solid curves are similar to those in Figure 2.

in neat [bmim]BF₄ (Figure 3). This parameter induces a positive deviation from ideality because of preferential solvation, and again the probe is not equally solvated by the two components of the binary solvent mixture (Figure 4). During the addition of [bmim]BF₄ to methanol, the hydrogen-bond basicity of the mixture decreases; the decrease is initially rapid but becomes more gradual at higher [bmim]BF₄ mole fractions. The β parameter shows a negative deviation from ideality, and preferential solvation for the probe is expected (Figure 4). A decrease is observed for the α parameter with positive deviation from ideal behavior as the mole fraction of the RTIL increases. When small quantities of the ionic liquid are added, the E_T^N parameter increases to a maximum and then decreases to the value of the pure ionic liquid, which is similar to that of ethanol/[bmim]BF₄ system.

Water/[bmim]BF₄ System. The behavior of the solvatochromic probes dissolved in water/[bmim]BF₄ mixtures is different from the alcoholic mixtures. The normalized polarity parameter of water is higher than that of [bmim]BF₄ ($E_T^N = 1.00$ and 0.67 , respectively). The E_T^N parameter decreases rapidly with increasing mole fraction of [bmim]BF₄ and then gradually reaches its value in neat [bmim]BF₄ (Figure 5). It produces a negative deviation ($0 < x_{IL} < 0.8$) from ideality (Figure 6). The α and π^* parameters for water are also higher than those of [bmim]BF₄. It is clear that, as [bmim]BF₄ is added to water, the π^* and α parameters decrease to their values in neat [bmim]BF₄ with negative deviation ($0 < x_{IL} < 0.7$) from ideality. The hydrogen-bond basicity of [bmim]BF₄ is higher than that of

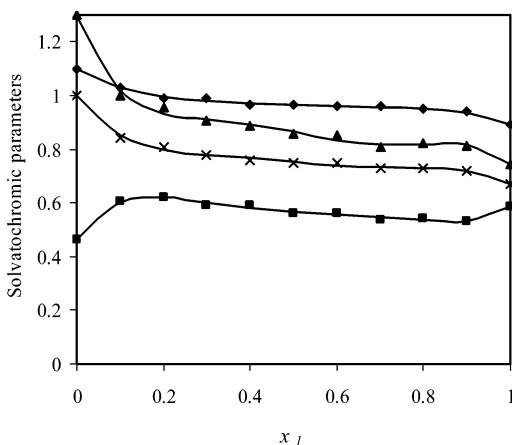


Figure 5. Solvatochromic parameters for binary mixtures of [bmim]-BF₄ with water. Symbols and solid curves are similar to those in Figure 1.

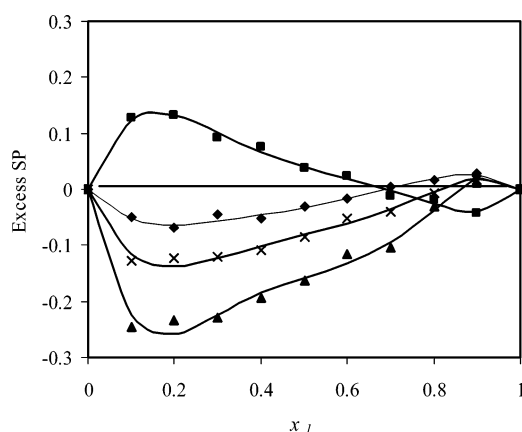


Figure 6. Excess parameters for binary mixtures of [bmim]BF₄ with water. Symbols and solid curves are similar to those in Figure 2.

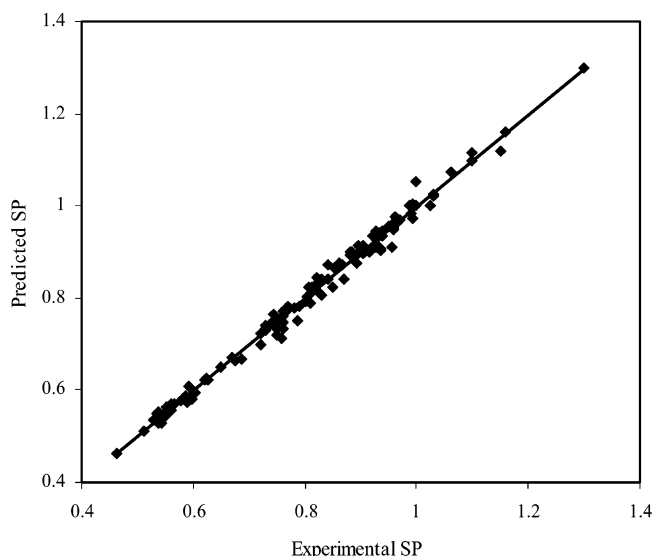


Figure 7. Predicted values of solvatochromic parameters from the correlation equations vs its experimental values for binary mixtures of [bmim]BF₄ with water, methanol, and ethanol.

water ($\beta = 0.59$ and 0.46 , respectively). This parameter initially produces a positive and then a negative deviation from ideality (Figure 6). Thus, the excess parameters for this binary solvent mixtures show an S-shaped profile with a negative minimum for π^* , α , and E_T^N and a positive maximum for β in the water-rich or alcohol-rich region.

Theoretical Calculations. The “excess solvatochromic parameters”, SP^E (SP is π^* , β , α , or E_T^N), can be calculated according to eq 1 in which the variation of any property is related to pure and mixed solvent properties

$$SP^E = SP_m - \sum_{i=1}^2 x_i SP_i \quad (1)$$

where SP_m and SP_i are the corresponding parameters for the solvent mixture and the pure solvents, respectively, and x_i is the mole fraction of one solvent.

The CNIBS/R-K model provides a simple method to correlate and/or predict the excess molar properties of a solute dissolved in a binary or ternary solvent mixture in terms of a weighted mole fraction average of solute properties in the pure solvents and contributions of solute-solvent and solvent-solvent interactions.^{38–43} The solvatochromic parameters (SP) in a binary solvent mixture at a constant temperature can be expressed as in eq 2

$$SP_m = x_1 SP_1^0 + x_2 SP_2^0 + x_1 x_2 \sum_{j=0}^k A_j (x_1 - x_2)^j \quad (2)$$

where SP_m , SP_1^0 , and SP_2^0 are solvatochromic parameters determined in mixed and pure solvents 1 and 2, respectively, and x_1 and x_2 are the mole fractions of the binary solvent mixture. A_j and j are the equation coefficients and the degree of the polynomial expansion. The numerical values of j can be varied between 0 and 3 to find an accurate mathematical representation of the experimental data. A partial least-squares regression (PLSR) method was used to fit the polynomials to the experimental data. A cross-validation method has been applied to predict any of the parameters. This method is a practical and reliable way to test the predictive significance when little data are available.⁴⁸ In Figure 7, the predicted values of SP (E_T^N , α , π^* , and β) obtained by the cross-validation method for various binary solvent mixtures from eqs 1 and 2 have been plotted versus the corresponding experimental values. Equation 3 is obtained for this correlation, and it is clear that the correlation is reasonable

$$SP_m^{\text{cal}} = 0.9988(\pm 0.0078) SP_m^{\text{exp}} - 0.0002(\pm 0.0063) \quad (3)$$

$$n = 132 \quad R^2 = 0.9922 \quad \sigma = 0.01467$$

Consequently, the average of coefficients has been reported in Table 4, in which the standard deviation, σ , was obtained from eq 4

$$\sigma = \left(\frac{\sum_{i=1}^n (SP_i^{\text{exp}} - SP_i^{\text{cal}})^2}{n} \right)^{1/2} \quad (4)$$

where n , SP_i^{exp} , and SP_i^{cal} are the number of the experimental data points, as well as the experimental and calculated solvatochromic parameter in the binary solvent mixtures, respectively.

Solvatochromic parameters and their excess values over the whole range of mole fractions have been calculated from the coefficients of eq 1 given in Table 4, and this has been demonstrated in Figures 1–6 by solid lines.

The model shows a strong correlation between predicted and experimentally measured values, and proportional and systematic errors were not observed. Therefore, the CNIBS/R-K model

TABLE 4: Average of Redlich–Kister Coefficients and Standard Deviation of the Excess Solvatochromic Parameters for Three Binary Mixtures

	A_0	A_1	A_2	A_3	σ
[bmim]BF ₄ /ethanol					
E_T^N	0.36120	-0.15199	0.62813	-0.36014	0.00520
π^*	0.78315	-0.38126	1.01172	-0.68944	0.00876
α	0.18750	0.03592	0.54535	-0.44953	0.00777
β	-0.62213	0.28879	-0.66751	-0.09231	0.00427
[bmim]BF ₄ /methanol					
E_T^N	0.30687	-0.07148	0.59849	-0.00031	0.00604
π^*	0.71313	-0.42135	0.80478	-0.42061	0.00781
α	0.11963	0.08751	0.57044	0.41470	0.00690
β	-0.53290	0.27785	-0.49078	-0.18120	0.00482
[bmim]BF ₄ /water					
E_T^N	-0.31922	0.37212	-0.32390	0.85937	0.00602
π^*	-0.12810	0.29892	-0.02248	0.36691	0.00510
α	-0.62013	0.46829	-0.79567	1.89002	0.01098
β	0.15825	-0.44159	0.46964	-1.08034	0.00521

is a reasonable one with high confidence for prediction of the solvatochromic parameters in binary solvent mixtures of [bmim]-BF₄ with ethanol, methanol, and water.

Conclusions

By comparing the solvatochromic parameters determined in binary solvent mixtures, one can conclude that all explored systems show basically similar E_T^N response patterns, except the aqueous solution. The E_T^N increases abruptly to a maximum with increasing [bmim]BF₄ mole fraction and decreases slowly to the value of pure [bmim]BF₄. The first region is attributed to an increasing dipolarity/polarizability of the media, and the second one is caused by a decreasing hydrogen-bond donor ability of the media. By addition of the RTIL to ethanol and methanol, the π^* value increases continuously along with increasing mole fraction of [bmim]BF₄. This parameter demonstrates a positive deviation from ideality. The hydrogen-bond acceptor ability of the binary mixture decreases on addition of [bmim]BF₄ to ethanol and methanol. This decrease is initially sharp but becomes more gradual at higher [bmim]BF₄ mole fractions and demonstrates a negative deviation from ideality. Addition of [bmim]BF₄ to all three solvents shows that the hydrogen-bond donor ability of the media has a decreasing trend, and a positive deviation from ideal behavior was observed for alcoholic solvent mixtures.

Finally, it was proved that the combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) equation can be used with confidence to achieve a correlation between the variation of the solvatochromic parameters with solvent composition, and this equation is able to predict the solvatochromic parameters at any compositions of [bmim]BF₄ with the three protic molecular solvents under study.

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Note Added after ASAP Publication. This article was released ASAP on March 11, 2006. The text between equations 2 and 3 has been revised. The correct version was posted on March 14, 2006.

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