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Preferential Solvation and Behavior of Solvatochromic Indicators in Mixtures of an Ionic Liquid with Some Molecular Solvents

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Structural and intermolecular interactions of solvatochromic probes 4-nitroaniline, 4-nitroanisole, and Reichardt's dye were investigated in the binary mixtures of 2-hydroxy ethylammonium formate as an ionic liquid with *N,N*-dimethyl formamide, dimethyl amine, and dimethyl sulfoxide. Solvatochromic parameters (E_T^N, normalized polarity parameter; π^*, dipolarity/polarizability; β, hydrogen-bond acceptor basicity; α, hydrogen-bond donor acidity) were determined in ionic liquid mixtures at 25 °C using UV−vis spectroscopy. E_T^N parameters obtained from absorbance of Reichardt's dye within various mixtures of ionic liquid were observed to be higher than predicted values from ideal additive behavior. Synergistic solvation behavior for some mixtures was observed. The combined nearly ideal binary solvent/Redlich−Kister (CNIBS/R-K) equation was used for various parameters correlation to predict solvatochromic parameters. Preferential solvation model was applied for the first time in the ionic liquid mixtures to study solvent mixtures effects on solvation of indicators, and from these information solute−solvent and solvent−solvent interactions were interpreted. Preferential solvation (specific solute−solvent interactions) or the solvent−solvent interaction is the reason for deviation from ideal behavior of probes.

Introduction

Ionic liquids are recognized as a class of new solvents with applied properties. Ionic liquids are ideal solvents with attractive applications in separation, synthesis, extraction, and electrochemical processes. When an ionic liquid (IL) is mixed with other solvents, physical and chemical properties will be tunable. Hence ILs can be used as cosolvents in binary or ternary solvents mixtures to increase the efficiency of the processes and change physicochemical properties of the solvents.[1−3] Various interactions in mixed solvents are much more complex than in neat solvents when the solute is surrounded preferentially by the mixture components or the complex which formed by the interaction of both components. In this situation, strong negative Gibbs energy of solvation is leaded.[4,5] To interpret the behavior of solvents in chemical processes, an understanding of the solution interactions with solute is necessary. Solvatochromism is a way to study solute−solvent interactions that show specific and non specific solute−solvent interactions. Solvatochromism is solvent dependence of the electronic spectrum of solutes. Intensity, position, and shape of absorption bands of dissolved chromophores is influenced by the change in solvents, according to their electronic and molecular structure, due to the different stabilization of their electronic ground and excited states.[6]

2-Hydroxy ethylammonium formate is a simple IL with easy preparation and a good miscibility with most of solvents.[7] In countining our studies,[7−10] in order to obtain information on structural and physicochemical properties of IL/solvents, we have monitored the behavior of selected solvatochromic absorbance probes within these mixtures. On the basis of these probes' responses, four solvatochromic parameters (i.e., E_T^N, normalized solvent polarity parameter; π^*, dipolarity/polarizability; β, hydrogen-bond acceptor (HBA) basicity; α, hydrogen-bond donor (HBD) acidity) were determined in binary mixtures of 2-Hydroxy ethylammonium formate with with *N,N*-dimethyl formamide (DMF), dimethyl amine (DMA), and dimethyl sulfoxide (DMSO). The CNIBS/R-K equation for correlation of these parameters and preferential solvation model for analyze solvents interactions were applied for three binary solvents mixtures.

Experimental Section

Materials. 2,6-Diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Reichardt's dye 30) was purchased from Aldrich (>99%) and was used without further purification. 4-Nitroaniline and 4-nitroanisole (Merck, 99%) were recrystallized multiple times with water/ethanol and water/aceton befor use. DMF, DMA, and DMSO were purchased from Merck. Ethanol amine and formic acid (Reidel de Hean) were purified according to the literature.[11]

Methods. 2-Hydroxy ethylammonium formate was prepared by adding excess amount of formic acid to 2-amino ethanol dropwise in a two-necked flask under nitrogen atmosphere with vigorous stirring. The flask was mounted in an ice bath. Stirring was continued for 20 h at room temperature. Excess formic acid was evaporated under high vacuum at 50 °C. The IL was characterized as described in the literature.[12]

All indicator stock solutions were prepared in ethanol and stored in dark glass vials at ∼4 °C. An appropriate amount of the indicator solution from the stock was transferred to the quartz cuvette, and its solution was evaporated by vacuum. The mixture

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TABLE 1: Solvatochromic Parameters for Binary Mixtures of IL with DMF

X(IL)	E_T^N	π^*	β	α
0	0.41	0.88	0.76	0.18
0.1	0.77	0.91	0.79	0.94
0.15	0.78	0.94	0.76	0.93
0.2	0.79	0.97	0.74	0.93
0.25	0.79	0.98	0.74	0.93
0.3	0.80	1.00	0.72	0.92
0.35	0.81	1.04	0.68	0.92
0.4	0.83	1.08	0.64	0.93
0.45	0.83	1.11	0.61	0.92
0.5	0.84	1.14	0.58	0.90
0.55	0.84	1.18	0.54	0.88
0.6	0.85	1.21	0.50	0.87
0.65	0.86	1.25	0.46	0.87
0.7	0.87	1.29	0.42	0.86
0.75	0.87	1.34	0.36	0.83
0.8	0.88	1.39	0.30	0.81
0.85	0.88	1.44	0.25	0.78
0.9	0.88	1.46	0.23	0.76
0.95	0.89	1.40	0.30	0.83
1	0.89	1.15	0.59	1.01

of IL with molecular solvents (DMF, DMA, and DMSO) at different composition was prepared gravimetrically (±0.1 mg) and was transferred into the quartz cuvette. The solution was stirred vigorously with a magnetic stirrer. Concentration of probes were 1×10^{-4} mol dm^{-3}. UV−vis spectral curves were recorded using a GBC UV−vis Cintra 40 spectrophotometers, and the temperature of the 1 cm quartz cell was controlled.

Results and Discussion

2-Hydroxy ethylammonium formate is an organic salt composed of 2-hydroxy ethylammonium as cation and formate as anion. 2-Hydroxy ethylammonium cation can act as strong hydrogen bond donor due to the presence of strong acidic O−H and N−H groups. Also, the positive charge on nitrogen atom increases the capability of this IL for hydrogen bond donating. Hydroxide group in cation structure can be participate as hydrogen bond acceptor. The UV−vis absorption spectra of the probes recorded in solvents mixtures. Four solvatochromic parameters (SP) have been determined at 25 °C over the whole range of solvents compositions according to the procedure reported elsewhere.[13−18] Equations 1−4 show the relationship between solvatochromic parameters and experimental values.

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{32.4}$$
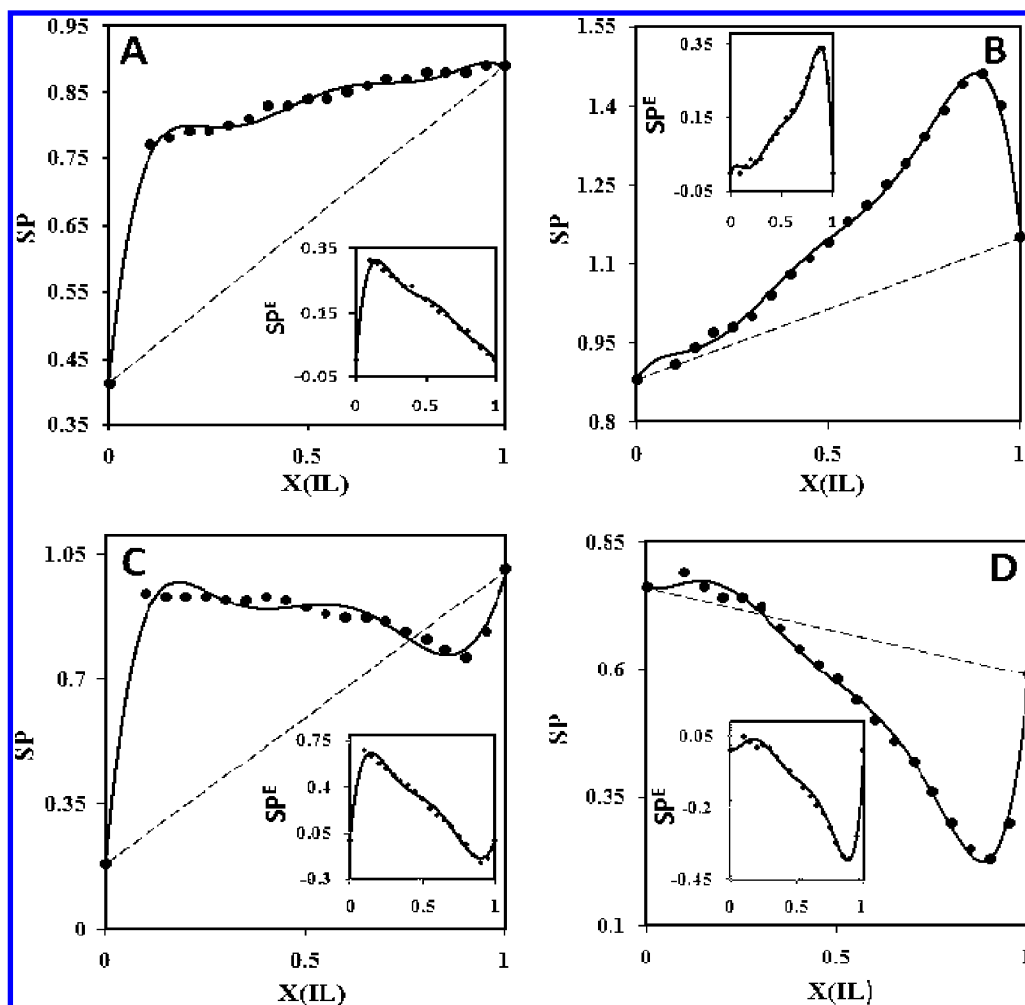
(1)

Figure 1. Solvatochromic parameters (SP) and excess solvatochromic parameters (SP^E) versus X(IL) for IL/DMF system. (A) E_T^N, (B) π^*, (C) α, and (D) β. X(IL) is the mole fraction of the ionic liquid.

$$\pi^* = \frac{34.12 - \nu_{ANS}}{2.343} = 0.427(34.12 - \nu_B) \quad (2)$$

$$\beta = \frac{31.10 - 3.14\,\pi^* - \nu_{ANI}}{2.79} \quad (3)$$

$$\alpha = 0.186(10.91 - \nu_B) - 0.72\,\pi^* \quad (4)$$

In which ν_B, ν_{ANI}, and ν_{ANS} are the maximum wavenumbers of Betaine dye, 4-nitroaniline, and 4-nitroanisole respectively in kK.

Reichardt's dye (30) exhibits an unusually high solvatochromic absorbance band shift, from $\lambda_{max} \sim 810$ nm for diphenyl ether to $\lambda_{max} \sim 453$ nm for water.[13,19,20] Considerable charge transfer from the phenolate to the pyridinium part of the zwitterionic molecule is occurred. Due to the zwitterionic nature of this probe, behavior of Reichardt's dye is strongly affected by HBD acidity of solvent; donating of hydrogen bond stabilize the ground state more than the excited state.[21]

IL/DMF Mixtures. The E_T^N parameter for 2-hydroxy ethylammonium formate is significantly higher than this parameter in imidazolium-based ionic liquids with BF_4 and PF_6 anions.[7,22] It is clear that E_T^N paremeter for IL is higher than that in neat DMF (Table 1) indicating higher dipolarity/polarizability and/

or hydrogen bond donating acidity of 2-hydroxy ethylammonium formate relative to that of DMF. Upon addition of 0.1 mol fraction of IL to DMF, the E_T^N increases dramatically (Figure 1,A) due to the solvation of Reichardt's dye preferentially by IL resulting in HBD capability or as a result of strong solvent−solvent interactions between IL and DMF forming a more dipolar species in the solution resulting in enhanced dipolarity of region around the probe. Preferential solvation arises whenever the bulk mole fraction solvent composition differs from the solvation microsphere.[7] A positive deviation from ideality is shown by this parameter with a maximum at a mole fraction of around 0.2 for IL.

The π^* parameter is derived from the change in solvents maximum absorption energy of the dye induced by the local electric field.[7] By addition of IL to DMF, π^* parameter increases rapidly and finally decreases to its corresponding value in pure IL through a maximum at $X_{IL} = 0.8$ (Figure 1,B). This parameter is affected by the increasing dye-ion solute−solvent interactions when the mole fraction of IL increases. A positive deviation from ideality is observed. In IL/DMF system, the π^* values confirm high solvent−solvent interactions in this media and synergetic effect in this media can be related to hydrogen bonding interaction between IL and DMF to give a complex structure which is more polar than the two constituents of mixture.
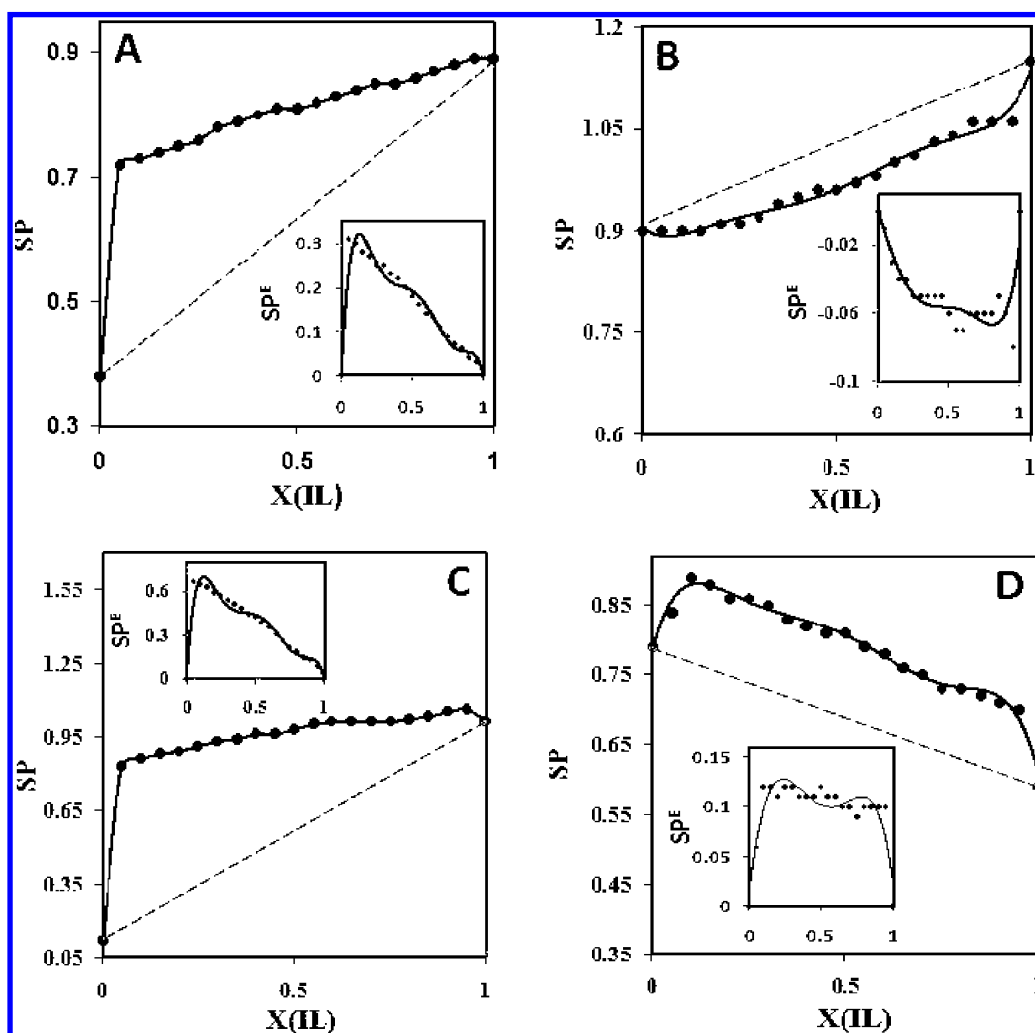

Figure 2. Solvatochromic parameters (SP) and excess solvatochromic parameters (SP^E) versus X(IL) for IL/DMA system. (A) E_T^N, (B) π^*, (C) α, and (D) β.

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TABLE 2: Solvatochromic Parameters for Binary Mixtures of IL with DMA

X(IL)	E_T^N	π^*	β	α
0	0.38	0.90	0.79	0.12
0.05	0.72	0.90	0.84	0.83
0.1	0.73	0.90	0.89	0.86
0.15	0.74	0.90	0.88	0.88
0.2	0.75	0.91	0.86	0.89
0.25	0.76	0.91	0.86	0.91
0.3	0.78	0.92	0.85	0.93
0.35	0.79	0.94	0.83	0.94
0.4	0.80	0.95	0.82	0.96
0.45	0.81	0.96	0.81	0.96
0.5	0.81	0.96	0.81	0.98
0.55	0.82	0.97	0.79	1.00
0.6	0.83	0.98	0.78	1.01
0.65	0.84	1.00	0.76	1.01
0.7	0.85	1.01	0.75	1.01
0.75	0.85	1.03	0.73	1.01
0.8	0.86	1.04	0.73	1.02
0.85	0.87	1.06	0.72	1.03
0.9	0.88	1.06	0.71	1.05
0.95	0.89	1.06	0.70	1.06
1	0.89	1.15	0.59	1.01

The α parameter increases drastically with increasing mole fraction of IL, and after a gradual decrease until $X_{IL} = 0.9$, reaches its value in neat IL. It produces a positive deviation (0 $< X_{IL} < 0.8$) from ideality. It can be concluded that cation of IL with the $-NH_3^+$ group enjoys from more acidity than DMF, therefor most of IL mixtures have great HBD acidity. The hydrogen-bond acceptor basicity of IL is lower than that of DMF. The HBA sites on DMF ($-NH_2$, $=O$) are stronger than these sites on IL ($-OH$, CO_2^-), hence with increasing of mole fraction of IL, β parameter decreases smoothly and sever synergetic effects for this parameter is observed. This parameter initially produces a positive and then a negative deviation from ideality. The excess parameters for this mixture similar to the α parameters demonstrate an S-shape profile.

IL/DMA mixtures. Figure 2 shows the solvatochromic parameters change in IL/DMA system. Behavior of Reichardt's dye in IL/DMA mixture is similar to the IL/DMF. A sharp increasing in E_T^N parameter that continued with gradual increase to pure IL. During the addition of IL to DMA, an increase in dipolarity/polarizability with negative deviation from ideal behavior is observed. When small quantities of the ionic liquid are added, the β parameter increases to a maximum and then decreases to the value of the pure ionic liquid. The β values (Table 2) confirm high solvent−solvent interactions in this media. The E_T^N parameter is a blend of dipolarity/polarizability and HBD acidity of the media. Thus the behavior of the plots is also related and the plot of E_T^N is combination of the plots of α and π^*. The trend of α has stark resemblance to that of E_T^N
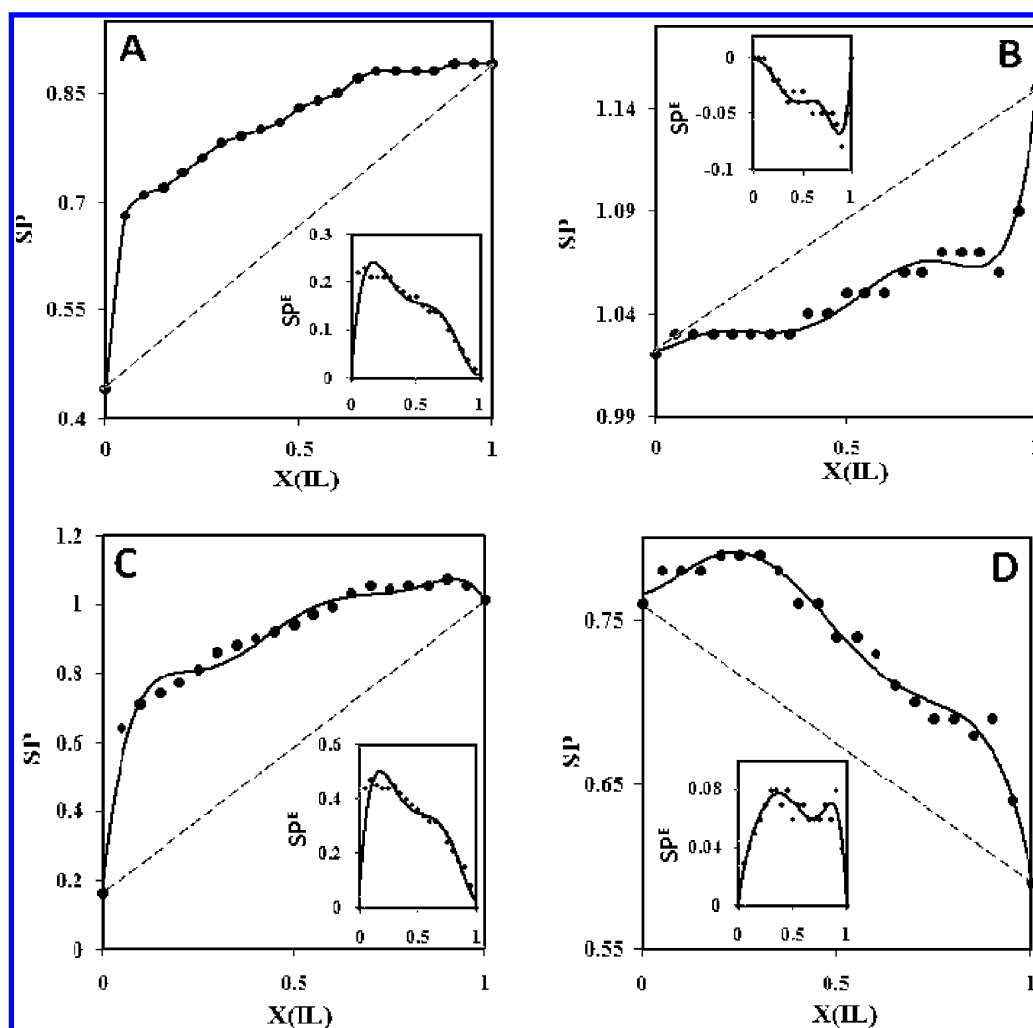

Figure 3. Solvatochromic parameters (SP) and excess solvatochromic parameters (SP^E) versus X(IL) for IL/DMSO system. (A) E_T^N, (B) π^*, (C) α, and (D) β.

TABLE 3: Solvatochromic Parameters for Binary Mixtures of IL with DMSO

X(IL)	E_T^N	π^*	β	α
0	0.44	1.02	0.76	0.16
0.05	0.68	1.03	0.78	0.64
0.1	0.71	1.03	0.78	0.71
0.15	0.72	1.03	0.78	0.74
0.2	0.74	1.03	0.79	0.77
0.25	0.76	1.03	0.79	0.81
0.3	0.78	1.03	0.79	0.86
0.35	0.79	1.03	0.78	0.88
0.4	0.80	1.04	0.76	0.90
0.45	0.81	1.04	0.76	0.92
0.5	0.83	1.05	0.74	0.94
0.55	0.84	1.05	0.74	0.97
0.6	0.85	1.05	0.73	0.99
0.65	0.87	1.06	0.71	1.03
0.7	0.88	1.06	0.70	1.05
0.75	0.88	1.07	0.69	1.04
0.8	0.88	1.07	0.69	1.05
0.85	0.88	1.07	0.68	1.05
0.9	0.89	1.06	0.69	1.07
0.95	0.89	1.09	0.64	1.05
1	0.89	1.15	0.59	1.01

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	A_4	σ
			IL/DMF			
E_T^N	0.659	−0.460	1.344	−1.830		0.017
π^*	0.361	0.546	7.665	2.666		0.023
α	1.126	−1.410	1.712	−5.917		0.036
β	−0.226	−0.772	−1.787	−3.252		0.026
			IL/DMA			
E_T^N	0.727	−0.373	−0.540	−2.256	3.782	0.026
π^*	−0.240	0.003	0.179	−0.378	−0.938	0.011
α	1.688	−0.637	−1.252	−4.956	8.626	0.050
β	0.459	−0.148	−0.115	0.201	1.960	0.009
			IL/DMSO			
E_T^N	0.533	−0.118	0.908	−1.861		0.022
π^*	−0.125	0.024	−0.270	−0.718		0.007
α	1.191	−0.289	2.116	−3.149		0.046
β	0.252	−0.168	0.388	0.530		0.076

parameter, concluded α has major allocation in E_T^N parameter. Smooth behavior of π^* parameter confirmed this claim.

IL/DMSO Mixtures. Figure 3 depicts the variation in solvatochromic parameters in this mixture and corresponding values reported in table 3. The plots in Figure 3 show that there is no distinct difference between the IL/DMA and IL/DMSO mixtures. E_T^N and α parameters show increasing behavior with positive deviation from ideal behavior. Similar hydrogen bonding acceptor sites (one pair of electron and an electronegative atom) and analogy in structure with two methyl groups in each molecule can lead to similar interactions in IL/DMSO and IL/DMA mixtures.

Solvatochromic Parameters and Redlich−Kister Model. Prediction of solvatochromic parameters of various mixtures, using a minima number of data, need a careful computational model. The combined nearly ideal binary solvent/Redlich−Kister (CNIBS/R-K) equation provides a model to predict the excess molar properties of a solute dissolved in a binary or ternary solvent mixtures in term of a weighted mole fraction of solute and corresponding solute−solvent and solvent−solvent interactions.[23−29] The "excess solvatochromic parameters", SP[E] (SP is E_T^N, π^*, α and β) can be calculated according to eq 5

$$SP^E = SP_m - \sum_{i=1}^{2} x_i SP_i^o \qquad (5)$$

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. According to the CNIBS/R-K model, the empirical solvatochromic parameters in a binary solvent mixture at a constant temperature can be expressed as in eq 6

$$SP_m = x_1 SP_1^o + x_2 SP_2^o + x_1 x_2 \sum_{j=0}^{k} A_j (x_1 - x_2)^j \qquad (6)$$

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 4 to find an accurate mathematical representation of the experimental data.[7] Regression analysis was done to fit the polynomial to experimental data, and the results of the fit are reported in Table 4 where the standard deviation (δ) is calculated according to eq 7

$$\sigma = \left(\frac{\sum_{i=1}^{n} (SP_i^{exp} - SP_i^{cal})^2}{n} \right)^{1/2} \qquad (7)$$

In which 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. The model shows reasonably good agreement between the experimental and calculated parameters. In Figure 4, the predicted values of solvatochromic parameters from the correlation equations versus the corresponding experimental values have been plotted and eq 8 is obtained for this correlation.
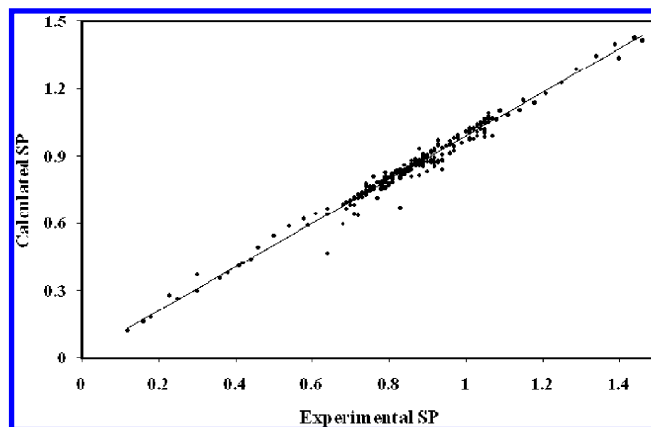

Figure 4. Predicted values of solvatochromic parameters from the correlation equations vs their experimental values for binary mixtures of IL with DMF, DMA, and DMSO.

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$$SP_m^{cal} = 0.9733(\pm 0.00889)\, SP_m^{exp} + 0.01337(\pm 0.00789)$$

$$n = 248 \quad R^2 = 0.979 \quad \sigma = 0.02811 \quad (8)$$

No proportional and systematic errors were observed and the model demonstrates good correlation between predicted and experimentally measured values at ambient conditions. Therefore, the CNIBS/R-K equation is a reasonable model with high confidence for prediction of SP in binary solvents mixtures of IL with DMF, DMA and DMSO.

Preferential Solvation Model. Interest on preferential solvation in mixed solvents has increased noticeably in recent years.[13−18] The interpretation of the main features requires simple models that may describe the behavior of solvatochromic indicators and the structure of binary solvents; these models may provide valuable solute−solvent and solvent−solvent structural information.[30] For the first time preferential solvation in an ionic liquid was analyzed in this work with the Buhvestov[16] and Skwierczynsi[31] models, which are based on a simple exchange of two solvents according to eqs 9 and 10

$$I(S1)_2 + 2S2 \leftrightarrow I(S2)_2 + 2S1 \quad (9)$$

$$I(S1)_2 + S2 \leftrightarrow I(S12)_2 + S1 \quad (10)$$
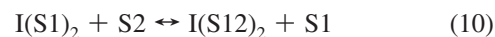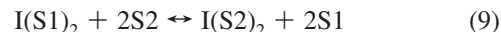
where I stands for the corresponding indicator, S1 and S2 for the pure solvents, and S12 for the mixed solvent. I(S1) represents the indicator solvated by the S1 component, I(S2) by the S2 component, and I(S12) by the S12 mixed solvent. Equation 9 reflects the total exchange of solvent 1 by solvent 2 in the solvation sphere of the indicator, and eq 10 corresponds to the exchange by the mixed solvent. The constants $f_{2/1}$, corresponding to the process described by eq 9, and $f_{12/1}$, corresponding to that by eq 10, can be evaluated using eqs 11−13

$$f_{2/1} = \frac{x_2^S/x_1^S}{(x_2^o/x_1^o)^2} \quad (11)$$

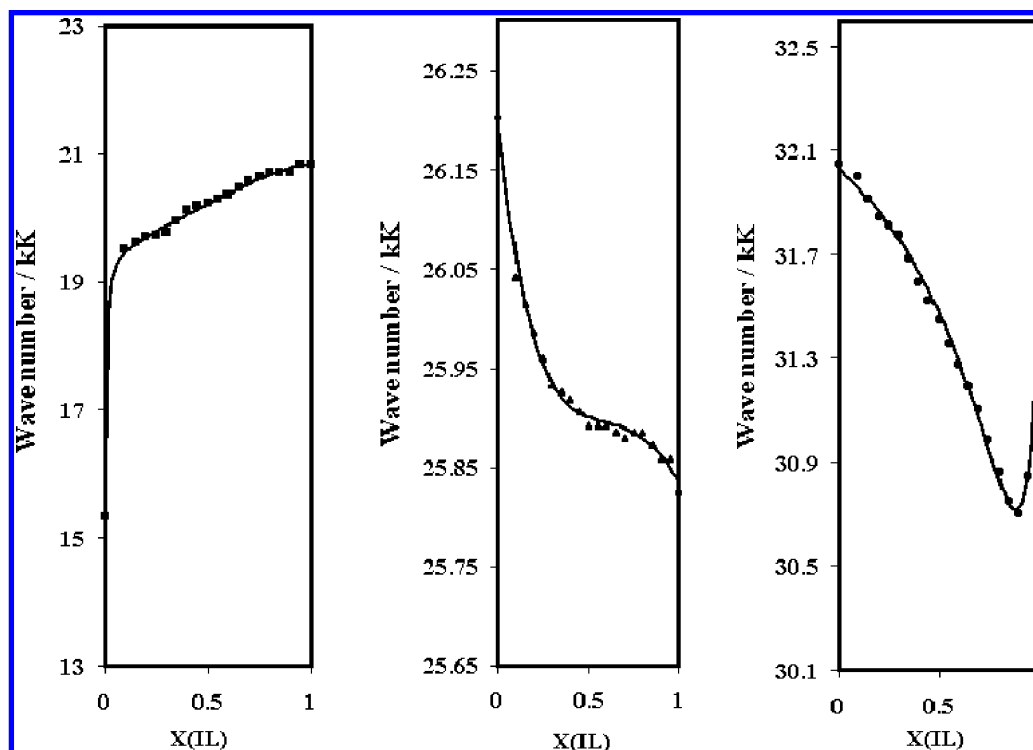$$f_{12/1} = \frac{x_{12}^S/x_1^S}{x_2^o/x_1^o} \quad (12)$$

Figure 5. Maximum wave number of indicators' absorbance in IL/DMF system. Betaine dye (■), 4-nitroaniline (▲), and 4-nitroanisole (●). Continuous lines calculated using eq 11 from the SP in these mixtures.

TABLE 5: Parameters and Standard Deviation Obtained by Application of the Preferential Solvation Model

indicator	solvent	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	N	R^2	K	σ
4-nitro anisole	IL/DMF	32.03	31.40	28.41	0.023	0.192	8.34	20	0.99	1.82	0.00103
	IL/DMA	32.02	31.50	32.00	1.84	4.79	2.60	21	0.96	−0.25	0.0012
	IL/DMSO	31.73	31.43	31.68	0.55	8.26	15.01	21	0.93	0.06	0.0004
4-nitro aniline	IL/DMF	26.19	25.83	25.55	1.73	2.6	1.50	20	0.99	0.98	0.00008
	IL/DMA	26.06	25.79	24.84	10.12	4.10	0.40	21	0.88	2.09	0.0006
	IL/DMSO	25.76	25.84	25.36	1.93	2.96	1.53	21	0.97	1.02	0.00015
betaine dye	IL/DMF	15.33	20.82	19.50	90.51	190.37	2.10	20	0.99	2.72	0.0025
	IL/DMA	15.07	20.80	19.30	31.12	110.53	3.55	21	0.99	3.5	0.0056
	IL/DMSO	15.78	20.80	18.76	37.85	71.30	1.88	21	0.99	5.62	0.005

$$f_{12/2} = \frac{f_{12/1}}{f_{2/1}} \quad (13)$$

$$\Delta Y = \frac{kf_{2/1}(x_2^o)^2[(1-x_2^o)^2 + f_{12/1}(1-x_2^o)x_2^o/2]}{[(1-x_2^o)^2 + f_{2/1}(x_2^o)^2 + f_{12/1}(1-x_2^o)x_2^o]^2} \quad (14)$$

where x_i^S is the mole fraction of the solvent i in the solvation sphere of the indicator, and x_i^o represents the bulk mole fraction.

Thus the solvatochromic mixture property Y_{12} can be evaluated from those of pure solvents, Y_1 and Y_2, according to eqs 15. The model for the modification of the solvatochromic property shoud be corrected with ΔY term (eq 14), where k is a proportionality constant.

$$Y = \frac{Y_1(1-x_2^o)^2 + Y_2 f_{2/1}(x_2^o)^2 + Y_{12} f_{12/1}(1-x_2^o)x_2^o}{(1-x_2^o)^2 + f_{2/1}(x_2^o)^2 + f_{12/1}(1-x_2^o)x_2^o} + \Delta Y \quad (15)$$

Eventually general eq 15 is tested for the mixtures studied in this work. The wave numbers have been fitted to the proposed
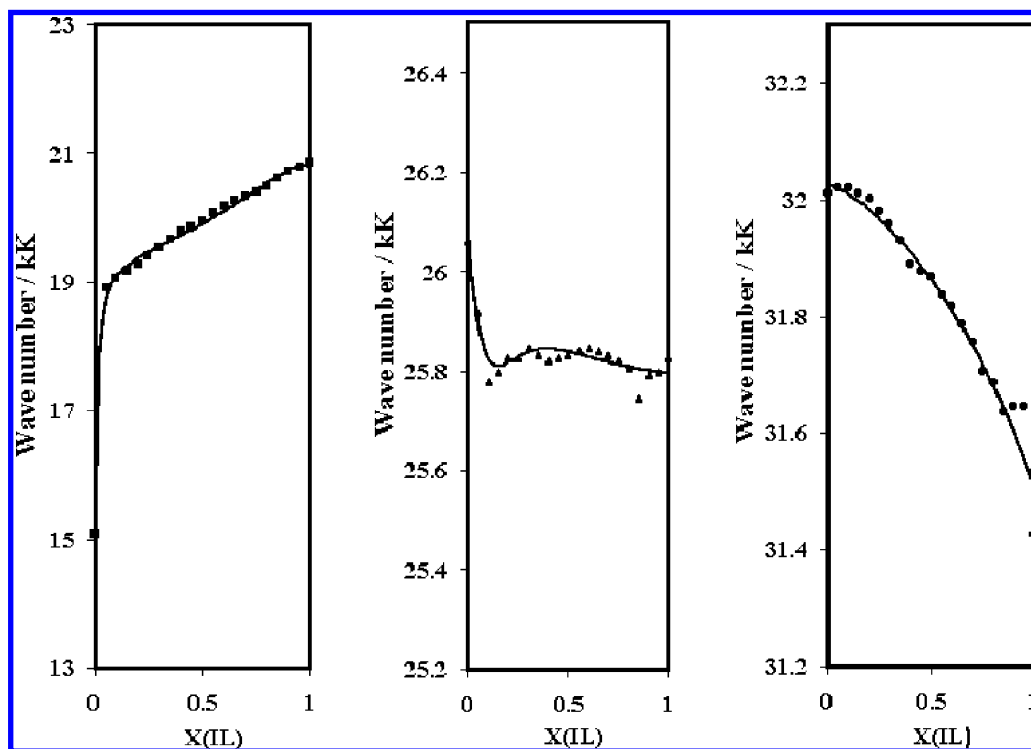

Figure 6. Maximum wave number of indicators' absorbance in IL/DMA system. Betaine dye (■), 4-nitroaniline (▲), and 4-nitroanisole (●).
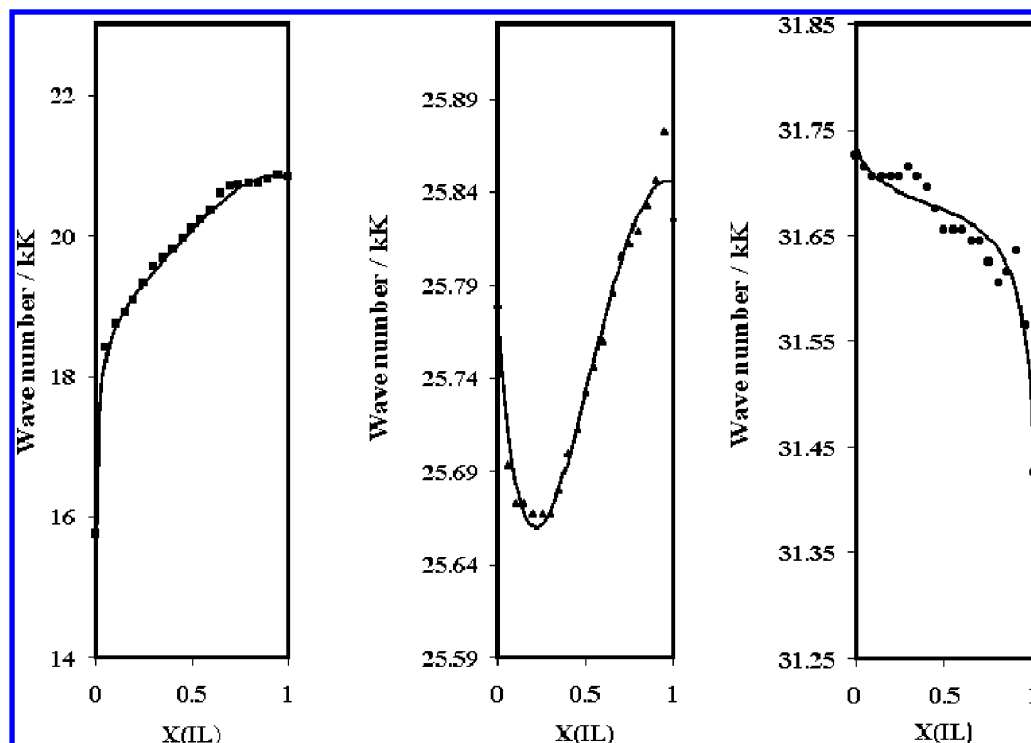

Figure 7. Maximum wave number of indicators' absorbance in IL/DMSO system. Betaine dye (■), 4-nitroaniline (▲), and 4-nitroanisole (●).

eq 15 and the parameters obtained are given in Table 5. Three binary systems exhibit a complex behavior for all three indicators. 4-Nitroanisole shows a pronounced minimum in IL/DMF mixture and rapid decreasing in IL/DMA and IL/DMSO mixtures (Figures 5−7). The observed in the absorption maxima of the pure solvents according to the preferential solvation model is in order DMSO < DMA ≈ DMF, and for mixed solvents in the order IL/DMF < IL/DMSO < IL/DMA; therefore pure DMA and DMF show similar polarity/dipolarizability effects. The IL/DMF mixtures display strong polarity/dipolarizability compared to IL/DMSO, as inferred from the Y_{12} values. The IL/DMA mixtures, with higher Y_{12} solvatochromic property, display somewhat lower polarizability. The Y_{12} value of mixed IL/DMF is lower than Y_1 and Y_2 values, hence the polarity/dipolarizability for this mixture is stronger compared to neat DMF and IL. The lower $f_{2/1}$ parameters of 4-nitroanisole indicate that solvation is not preferential in mixtures. Likewise, the $f_{12/1}$ and $f_{12/2}$ parameters reveal that this indicator is preferentially solvated by the mixed solvents. The synergism effect that was observed for π^* values in IL/DMF mixtures can be related to these strong solvent−solvent interactions (Figure 1). 4-Nitroaniline is sensitive to both HBA basicity and polarity/dipolarizability of solvents. It displays a minimum for IL/DMA and IL/DMSO in the molecular solvent-rich region (Figures 6 and 7), whereas for IL/DMF only a decreasing profile appears. The preferential solvation parameters indicate that this indicator is preferentially solvated by IL in IL/DMA mixtures. The $f_{2/1}$ parameter is low and one can concluded that 4-nitroaniline is solvated preferentially by molecular solvents in IL/DMF and IL/DMSO mixtures. For all systems, the low $f_{12/1}$ and $f_{12/2}$ values demonstrate that the indicator is not solvated preferentially by the mixed solvents compared to the pure components. Betaine dye is particulary sensitive to HBD acidity of solvents and dipolarity/dipolarizability effect, and shows strongly positive solvatochromism (Figures 5−7). An analysis of the preferential solvation parameters indicates that this probe is preferentially solvated by the IL and mixed solvents, as inferred from the very high $f_{2/1}$ and $f_{12/1}$ values. The sharp increasing of E_T^N in all mixtures can be explained by these preferential solvation effects.

Conclusions

In binary mixtures, solvatochromic indicators allow us to quantify the different solute−solvent and solvent−solvent interactions. Solvatochromic probes absorbance behavior of 2-hydroxy ethylammonium formate as an ionic liquid with DMF, DMA, and DMSO have been considered and four solvatochromic parameters determined in these mixtures. All studied systems show similar E_T^N response patterns. E_T^N parameters are observed to be higher than those expected from ideal behavior, suggesting enhanced HBD acidity as well as dipolarity/dipolarizability of the mixtures. It is demonstrated that Redlich−Kister mathematical formulation model can adequately predict solvatochromic parameters with appropriate accuracy. Prefer-

ential solvation in these solvents mixtures confirms the solute−solvent and especially intense solvent−solvent interactions between IL and molecular solvents.

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