

New Solvents Designed on the Basis of the Molecular-Microscopic Properties of Binary Mixtures of the Type (Protic Molecular Solvent + 1-Butyl-3-methylimidazolium-Based Ionic Liquid)

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The main purpose of this work is to analyze the microscopic feature of solvent systems resulting from the basis of binary mixtures formed by a protic molecular solvent (methanol, ethanol, propan-1-ol, propan-2-ol, and 2-ethoxyethanol) and a 1-butyl-3-methylimidazolium (bmim)-based ionic liquid (IL) cosolvent composed of different anions (tetrafluoroborate, hexafluorophosphate, chloride, and bromide). At the same time, a complementary aim is to evaluate the incidence of anion type on the solvation pattern. The empirical solvatochromic parameters E_T^N , π^* , β , and α were determined from the UV–vis solvatochromic shifts of adequate probes. The behavior of the solvent systems was analyzed according to their deviation from ideality. E_T^N polarity and π^* dipolarity/polarizability exhibit positive deviation from ideal behavior in all binary mixtures at the explored compositions. Moreover, E_T^N and α parameters display synergetic effects in some binary mixtures composed of tetrafluoroborate and hexafluorophosphate anions. The influence of anion nature on the response patterns is clearly manifested in the basicity β and acidity α of the media. This is connected with the degree and type of interaction between the anions and the 1-butyl-3-methylimidazolium cation. The ion-pair character of the ionic liquids affects their interactions with a solute or a molecular solvent. The application of an appropriate preferential solvation model allowed us to obtain valuable information about solute–solvent and solvent–solvent interactions of the selected ionic liquid mixtures. It is possible to identify relevant mixtures paying particular attention to the most remarkable microscopic properties, the acidity and the basicity, in order to propose “new solvents”. Thus, the solvating feature can be tailored selecting the molecular and/or the ionic component at a particular composition. A simplified combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) equation is shown to satisfactorily predict the solvatochromic parameters within [protic molecular solvent + bmim-based IL].

Introduction

Molecular solvents are the usual media where physical and chemical processes take place.¹ In the past decade, the attention has been drawn to the use of room-temperature ionic liquids (RTILs) as solvents for different applications. The interest was mainly based on their potential as solvents for clean technologies.^{2,3} RTILs are organic salts composed of a wide range of cations and anions, which are in the liquid state under ambient conditions. As a result, many new ionic solvents can be prepared. Additionally, from the combination of pure solvents in binary mixtures, the availability and diversity of media increased considerably. In this direction, their physicochemical properties can be tailored not only changing the nature of the cation and/or the anion but also combining pure ionic liquids with molecular solvents in mixed-solvent systems. It should be noted that one advantage of these mixed solvents is that the salt need not to be liquid at room temperature but soluble in the selected molecular solvent. In this sense, the term ILs could include organic salts that are in the solid state at room temperature.

Over the past few years, designing solvents with desired properties has become an important task for chemists in order

to modulate processes in solution. The challenge consists of developing a “tailored solvent” for a variety of chemical applications. With this purpose in mind, it is necessary to understand the solvation interactions at a molecular level in order to evaluate the performance of a solvent. Consequently, it is of interest to quantify its most relevant molecular-microscopic properties, which determine how the solvent will interact with potential solutes. An appropriate method to study solute–solvent interactions is to employ solvatochromic indicators that reflect the specific and nonspecific solute–solvent interactions on the UV–vis spectral band shifts. A number of empirical solvatochromic parameters have been proposed to quantify the molecular-microscopic solvent properties. In most cases, only one indicator is used to build the respective scale. Among them, the $E_T(30)$ parameter was proposed by Dimroth and Reichardt to measure solvent dipolarity/polarizability, though it is also sensitive to the solvent’s hydrogen bond donor (HBD) capacity.¹ On the other hand, the π^* , β , and α (Kamlet, Abboud, and Taft)⁴ multiparametric approach assigns different parameters to each particular solvent characteristic: dipolarity/polarizability, hydrogen bond acceptor (HBA) basicity, and HBD acidity.

In a previous work, we have analyzed the microscopic feature of binary solvent systems formed by a molecular solvent (acetonitrile or dimethylformamide or methanol) and an ionic liquid cosolvent (1-butyl-3-methylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium hexafluorophosphate). The

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study focused on the identification of solvent mixtures with relevant solvating properties in order to select mixed solvents with particular characteristics. The comparison of the molecular-microscopic parameters corresponding to the selected binary mixtures of the molecular solvent with both ionic liquids, considered at similar mixed-solvent compositions, revealed that the differences were centered on the basic character of them.⁵

There is an important number of reports dealing with molecular-microscopic solvent properties of ILs based on 1,3-dialkylimidazolium cation.^{2f,3a,6} However, more comprehensive studies are required particularly lying on binary mixtures and varying systematically the structure of the ionic and/or molecular constituent. In this work, the main purpose is to investigate the microscopic characteristics of solvent systems resulting from binary mixtures formed by a protic molecular solvent (i.e., an alcohol) and an ionic liquid cosolvent. The attention is given to the microenvironment of solutes in order to acquire a deeper insight to the solute–solvent and/or solvent–solvent interactions within mixtures of ILs, in this case, with other *green solvents* such as simple alcohols. In reference to the ionic cosolvent, we have selected ionic liquids based on bmim cation but comprising different anions: tetrafluoroborate [BF₄], hexafluorophosphate [PF₆], chloride [Cl], and bromide [Br]. At the same time, we aspire to analyze the incidence of anion type on the solvation pattern. In connection with this, it has been verified that density, viscosity, surface tension, melting point, and thermal stability, among other physicochemical properties, are affected by the nature of the anion and by the length of the alkyl chain in the cation.

In order to evaluate the influence of anions and cations of ILs and to acquire a deeper understanding of solute–solvent and solvent–solvent interactions in the solvation pattern, we applied a preferential solvation model for binary mixtures.⁷ This model allows one to calculate the preferential solvation parameters that measure the tendency of a probe to be solvated by a cosolvent S2 and “mixed solvent” S12, with reference to solvent S1 in its solvation sphere.

As a final point, a simple mathematical model was applied in order to correlate the empirical solvatochromic parameters with solvent composition. For this purpose, the CNIBS/R–K equation was selected.⁸ This model has been previously used to correlate accurately different physicochemical properties in mixed solvent systems.⁹ It also provides a useful computational tool to predict solvent properties based on a minimum number of experiments.

In conclusion, the aims of this work are the following: (i) to characterize the molecular-microscopic solvent properties measuring a set of empirical solvatochromic parameters for (molecular solvent + IL) systems; (ii) to analyze for these solvent systems the response pattern property versus solvent composition focusing on the ability to develop the most relevant interactions (hydrogen bond acidity, hydrogen bond basicity, and dipolarity/polarizability); (iii) to evaluate the influence of anion–cation interactions on the solvation feature; (iv) to apply preferential solvation models; (v) to identify relevant mixtures paying particular attention to pronounced changes in the microscopic properties in order to propose “new solvents”; (vi) to predict solvatochromic parameters for the selected mixed solvents applying the CNIBS/R–K equation.

Experimental Methods

Reagents and Solvents. [bmim][BF₄], [bmim][PF₆], [bmim][Cl], and [bmim][Br] were prepared according to the literature procedure.¹⁰ The crude ILs were appropriately purified and dried

over a vacuum. Reichardt's betaine dye [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate] was purchased from Aldrich (>99%). *N,N*-Diethyl-4-nitroaniline (π^*) was prepared and purified as previously reported.¹¹ 4-Nitroaniline (β) was purchased from Aldrich (99%). High-purity molecular solvents were acquired from Merck (>99%).

Solvatochromic Parameter: Measurements and Calculations. The spectroscopic data were obtained with a SHIMADZU UV-1800 spectrophotometer, equipped with a thermostatic cell holder. The pure solvents were mixed in appropriate proportions by weight to give binary solvent mixtures at various compositions. The temperature was maintained at 25 ± 0.1 °C. The concentrations of the indicator solutions were 20 mM for the betaine and 0.05 mM for the other probes. The $E_T(30)$ and E_T^N parameters were calculated according to the procedure reported elsewhere.¹ The microscopic properties π^* , β , and α were determined according to general expressions collected by Marcus.¹²

Computational Methods. The parameters of solvation which minimize the square residuals of the solvatochromic property values were computed by no-linear regressions using the MATLAB 6.0 program.

The CNIBS/R–K coefficients were computed by fitting the experimental data by means of no intercept multiparameter least-squares analysis using STATGRAPHICS Plus 3.0.

Results and Discussion

As the salts selected comprise the same cation, their differences in the physicochemical behavior lie predominantly on the anion character. For instance, it mainly determines the melting point and the water miscibility. Thus, while [bmim][BF₄] and [bmim][PF₆] are liquids at room temperature, [bmim][Cl] and [bmim][Br] are solids. The [bmim][BF₄] displays a complete miscibility with water and [bmim][Cl] is miscible in almost the whole range of compositions.¹³ In contrast, [bmim][Br] and [bmim][PF₆] exhibit a very low miscibility in that solvent.^{2d–f,13,14} Furthermore, the thermal stability of ionic liquids depends on anion type, specifically on its coordinating ability, following the general stability order [halides] < [BF₄] \sim [PF₆] < [NTf₂]. Thus, ionic liquids containing weakly nucleophilic anions are the most stable.^{13,15}

Considering the molecular-microscopic properties of [bmim][BF₄] and [bmim][PF₆] ([bmim][BF₄]: $E_T^N = 0.67$, $\pi^* = 1.05$, $\alpha = 0.63$, $\beta = 0.38$); [bmim][PF₆]: $E_T^N = 0.67$, $\pi^* = 1.03$, $\alpha = 0.63$, $\beta = 0.21$),^{6c} while the E_T^N , π^* , and α values are similar, the β value of [bmim][BF₄] is nearly 2-fold the value corresponding to [bmim][PF₆]. In comparison with conventional molecular solvents, the polarity of 1,3-dialkylimidazolium-based ionic liquids corresponds to that of short-chain primary and secondary alcohols and secondary amides such as *N*-methylformamide.^{6h,16} The π^* values are high in comparison with molecular solvents because the effect of Coulombic interactions from the ions is incorporated as well as dipole and polarizability effects.^{3a,6c} The α values are largely determined by the nature of the cation. In this sense, 1-methyl-3-alkylimidazolium cations can act as weak hydrogen bond donors because of the weak acidic C(2)–H hydrogen atom at the heterocyclic ring (which is the most acidic of all imidazolium H-atoms).^{6c,17} The hydrogen bond basicity β is dominated by the anions, although the cations do appear to be playing a role.^{3a} Thus, considering the possible intermolecular solute–solvent interactions with 1,3-dialkylimidazolium-based ionic liquids as solvents, the imidazolium cation can act not only as a weak H-bond donor center suitable for bonding to HBA solutes but also as a Lewis acid suitable for

TABLE 1: Solvatochromic Parameters E_T^N , π^* , β , and α for Binary Mixtures of Ethanol, Propan-1-ol, Propan-2-ol, 2-Ethoxyethanol + [bmim][BF₄], Measured at 25 °C

parameter	ionic liquid mole fraction								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
EtOH + [bmim][BF ₄]									
E_T^N	0.782	0.798	0.795	0.793	0.782	0.773	0.759	0.722	0.692
π^*	0.870	0.945	0.994	1.020	1.018	1.030	1.026	1.040	1.027
β	0.611	0.533	0.468	0.448	0.440	0.429	0.423	0.393	0.379
α	0.930	0.907	0.87	0.839	0.77	0.744	0.72	0.700	0.660
POH + [bmim][BF ₄]									
E_T^N						0.776	0.777	0.767	0.776
π^*						0.999	1.011	1.019	1.023
β						0.463	0.475	0.441	0.462
α						0.807	0.797	0.773	0.786
2-POH + [bmim][BF ₄]									
E_T^N						0.749	0.762	0.757	0.759
π^*						1.000	0.988	1.019	1.016
β						0.487	0.501	0.466	0.419
α						0.741	0.761	0.745	0.760
2-EtOEtOH + [bmim][BF ₄]									
E_T^N	0.718	0.734	0.737	0.746	0.742	0.740	0.731	0.718	0.703
π^*	0.825	0.886	0.948	0.984	1.010	1.030	1.038	1.050	1.055
β	0.634	0.599	0.571	0.512	0.450	0.436	0.420	0.400	0.471
α	0.810	0.795	0.749	0.737	0.723	0.700	0.677	0.656	0.641

TABLE 2: Solvatochromic Parameters E_T^N , π^* , β , and α for Binary Mixtures of Ethanol, Propan-1-ol, Propan-2-ol, 2-Ethoxyethanol [bmim][PF₆], Measured at 25 °C

parameter	ionic liquid mole fraction								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
EtOH + [bmim][PF ₆]									
E_T^N						0.757	0.751	0.720	0.700
π^*						1.011	1.016	1.030	1.037
β						0.320	0.341	0.290	0.260
α						0.774	0.754	0.700	0.650
POH + [bmim][PF ₆]									
E_T^N							0.741	0.730	0.716
π^*							1.020	1.020	1.020
β							0.324	0.274	0.288
α							0.730	0.725	0.682
2-POH + [bmim][PF ₆]									
E_T^N							0.715	0.715	0.706
π^*							1.017	1.006	1.016
β							0.336	0.349	0.271
α							0.671	0.667	0.661
2-EtOEtOH + [bmim][PF ₆]									
E_T^N	0.721	0.730	0.737	0.750	0.746	0.742	0.733	0.728	0.709
π^*	0.852	0.906	0.963	1.006	1.039	1.035	1.048	1.040	1.022
β	0.572	0.484	0.401	0.396	0.315	0.268	0.226	0.211	0.308
α	0.801	0.793	0.761	0.742	0.725	0.715	0.700	0.673	0.659

bonding to electron-bond donor (EPD) solutes. It also constitutes a polarizable six π -electron system able to interact with polarizable solutes. The anion acts as a HBA center or as a Lewis base, suitable for bonding to HBD and electron-bond acceptor (EPA) solutes, respectively.

On the other hand, the protic molecular solvents selected for this work are ethanol (EtOH) ($E_T^N = 0.65$, $\pi^* = 0.54$, $\beta = 0.75$, $\alpha = 0.86$), propan-1-ol (PrOH) ($E_T^N = 0.62$, $\pi^* = 0.52$, $\beta = 0.90$, $\alpha = 0.84$), propan-2-ol (2-PrOH) ($E_T^N = 0.57$, $\pi^* = 0.48$, $\beta = 0.84$, $\alpha = 0.76$), and 2-ethoxyethanol (EtOEtOH) ($E_T^N = 0.62$, $\pi^* = 0.66$, $\beta = 0.73$, $\alpha = 0.71$).¹² The present work also includes methanol ($E_T^N = 0.76$, $\pi^* = 0.60$, $\beta = 0.66$, $\alpha = 0.98$)¹² as molecular solvent for the binary solvent mixtures with [bmim][Cl] and [bmim][Br]. The selection of these molecular solvents was done mainly on the basis of their

hydrogen bond donor capacity, allowing them to establish strong solvent–solvent interactions with ILs. On one hand, the alkanols are very useful solvents. On the other hand, it is well-known that 2-ethoxyethanol has the useful property of dissolving chemically diverse compounds and, additionally, it is widely used in commercial and industrial applications.

Compositions of the Binary Solvent Mixtures. The compositions of the solvent mixtures were dependent on the mutual miscibility between the molecular solvents and the selected ionic liquids. The [bmim][BF₄] displays a complete miscibility with ethanol and 2-ethoxyethanol, but it is partially soluble in propan-1-ol and propan-2-ol, so the range of the binary mixture compositions used in this case was from X_{IL} (ionic liquid mole fraction) = 0.6 to pure ionic solvent. Alternatively, [bmim][PF₆] is wholly soluble only in 2-ethoxyethanol, exhibiting a low

TABLE 3: Solvatochromic Parameters E_T^N , π^* , β , and α for Binary Mixtures of Methanol, Ethanol, Propan-1-ol, Propan-2-ol, 2-Ethoxyethanol + [bmim][Cl], Measured at 25 °C

parameter	ionic liquid mole fraction								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
MeOH + [bmim][Cl]									
E_T^N	0.769	0.739	0.708	0.686	0.669	0.630	0.625	0.611	0.606
π^*	0.993	0.970	0.997	1.070	1.125	1.130	1.173	1.140	1.111
β	0.740	0.810	0.879	0.917	0.946	0.920	0.908	0.897	0.888
α	0.840	0.724	0.596	0.493	0.381	0.325	0.248	0.266	0.261
EtOH + [bmim][Cl]									
E_T^N	0.726	0.717	0.696	0.679	0.663	0.651	0.613	0.616	0.610
π^*	0.900	0.945	0.954	1.020	1.018	1.070	1.094	1.085	1.073
β	0.810	0.843	0.846	0.928	0.987	1.000	0.975	1.010	1.033
α	0.743	0.689	0.613	0.548	0.460	0.374	0.280	0.273	0.285
POH + [bmim][Cl]									
E_T^N	0.706	0.718	0.698	0.682	0.663	0.649	0.623		
π^*	0.816	0.894	0.941	0.980	1.001	1.030	1.042		
β	0.834	0.845	0.850	0.885	0.915	0.918	0.924		
α	0.760	0.706	0.627	0.569	0.484	0.429	0.357		
2-POH + [bmim][Cl]									
E_T^N	0.668	0.675	0.669	0.654	0.642	0.630	0.608		
π^*	0.791	0.880	0.919	0.980	1.004	1.030	1.033		
β	0.875	0.886	0.886	0.883	0.887	0.916	0.980		
α	0.692	0.637	0.576	0.512	0.439	0.396	0.324		
2-EtOEtOH + [bmim][Cl]									
E_T^N	0.688	0.681	0.673	0.656	0.637	0.625	0.617	0.608	0.595
π^*	0.794	0.873	0.921	0.951	0.992	1.040	1.024	1.080	1.097
β	0.819	0.841	0.823	0.875	0.908	0.923	0.921	0.920	0.912
α	0.743	0.681	0.593	0.512	0.442	0.392	0.345	0.299	0.248

TABLE 4: Solvatochromic Parameters E_T^N , π^* , β , and α for Binary Mixtures of Methanol, Ethanol, Propan-1-ol, Propan-2-ol, 2-Ethoxyethanol + [bmim][Br], Measured at 25 °C

parameter	ionic liquid mole fraction						
	0.1	0.2	0.3	0.4	0.5	0.6	0.7
MeOH + [bmim][Br]							
E_T^N	0.786	0.774	0.740	0.712	0.689		
π^*	0.948	1.001	1.027	1.060	1.073		
β	0.571	0.588	0.607	0.670	0.723		
α	0.860	0.771	0.680	0.608	0.507		
EtOH + [bmim][Br]							
E_T^N	0.746	0.741	0.719	0.722	0.711		
π^*	0.888	0.964	1.027	1.030	1.028		
β	0.639	0.586	0.524	0.546	0.556		
α	0.814	0.752	0.658	0.640	0.621		
POH + [bmim][Br]							
E_T^N	0.711	0.718	0.714	0.701	0.690		
π^*	0.819	0.901	0.913	0.984	1.032		
β	0.734	0.744	0.735	0.758	0.766		
α	0.784	0.752	0.704	0.631	0.541		
2-POH + [bmim][Br]							
E_T^N	0.686	0.670	0.692	0.680	0.683		
π^*	0.826	0.890	0.925	0.967	1.033		
β	0.783	0.810	0.800	0.740	0.649		
α	0.714	0.673	0.626	0.592	0.542		
2-EtOEtOH + [bmim][Br]							
E_T^N	0.696	0.700	0.696	0.687	0.681	0.667	0.657
π^*	0.798	0.886	0.952	0.980	1.025	1.036	1.073
β	0.790	0.796	0.776	0.777	0.777	0.780	0.771
α	0.761	0.700	0.633	0.603	0.524	0.490	0.428

solubility in the other solvents. In these last cases, the compositions of the binary mixtures with ethanol vary from $X_{IL} = 0.6$ up to the pure ionic liquid and for the binary mixtures with propan-1-ol and propan-2-ol, respectively, from $X_{IL} = 0.7$ up to the pure ionic liquid.

Taking into account that [bmim][Cl] and [bmim][Br] are in the solid state at room temperature, the compositions of their binary mixtures were selected in order to achieve a homogeneous solution. Therefore, the compositions of (methanol/ethanol/2-ethoxyethanol + [bmim][Cl]) solvent systems envelop

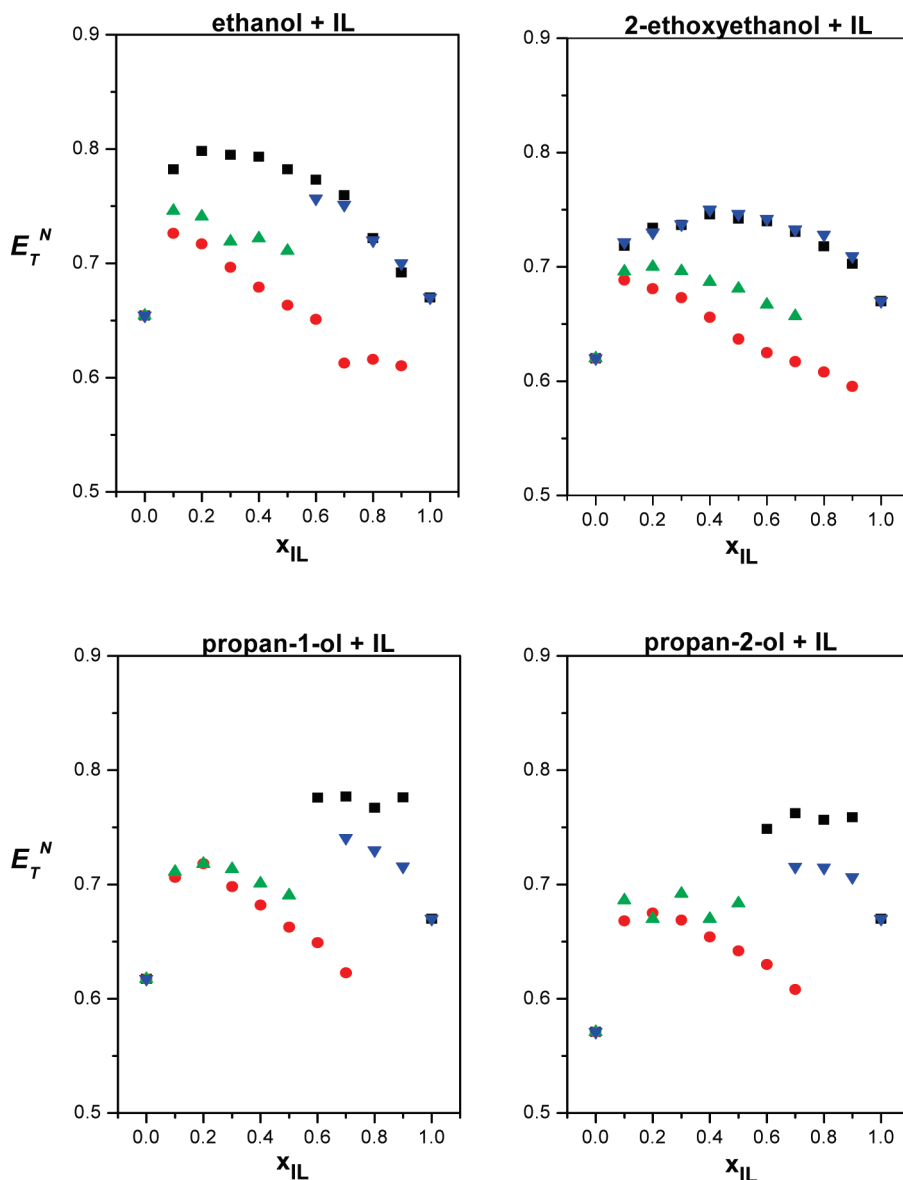


Figure 1. Variation of E_T^N with X_{IL} in (protic molecular solvent + IL) mixtures. (■, [bmim][BF₄]; ▼, [bmim][PF₆]; ●, [bmim][Cl]; ▲, [bmim][Br]).

from no ionic liquid to $X_{IL} = 0.9$. For binary mixtures with propan-1-ol and propan-2-ol, the compositions cover up to $X_{IL} = 0.7$. Finally, the [bmim][Br] salt shows the lowest miscibility in the studied molecular solvents. The compositions for its mixtures with methanol, ethanol, propan-1-ol, and propan-2-ol range up to $X_{IL} = 0.5$ and up to $X_{IL} = 0.7$ for its mixture with 2-ethoxyethanol, respectively. These results are clearly related to the anion influence.

Molecular-Microscopic Solvent Parameters. The E_T^N , π^* , α , and β solvatochromic parameters corresponding to the binary mixtures with [bmim][BF₄]/[PF₆] and [bmim][Cl]/[Br], respectively, are listed in Tables 1–4.

Figures 1–5 show the response patterns of the molecular-microscopic solvent properties as a function of IL mole fraction for all mixed solvents. The shape of the curves *property vs solvent composition* reflects the experimental behavior patterns of the explored mixtures to the chemical properties of the reference probes, being analyzed according to their deviation from ideality.

Polarity E_T^N . From the analysis of the data (Tables 1–4, Figures 1 and 5), it is observed that E_T^N values for all mixtures

vary from 0.57 to 0.80 (including the pure solvents), indicating that the parameter values do not spread so much. In general, the systems explored exhibit positive deviation from the ideal behavior. As it was previously reported for the mixtures of [bmim][BF₄]/[PF₆] with MeOH,⁵ the parameter exhibits a slight synergism in the binary systems composed of these ILs and the selected alcohols and this synergetic effect are clearly manifest in the whole range of ionic liquid compositions for (ethanol + [bmim][BF₄]) and (2-ethoxyethanol + [bmim][BF₄]/[PF₆]) solvent systems. The maximum positive deviation values (in percentage) calculated for these systems with respect to the additive behavior are 22% for the (ethanol + [bmim][BF₄], $X_{IL} = 0.2$) system and 17% for the last two mixtures ($X_{IL} = 0.4$).

For the mixtures comprised of [bmim][Cl]/[Br], the E_T^N values increase with respect to the values in pure alcohols, being more pronounced at low IL mole fractions. The synergism on E_T^N values was also reported for similar binary solvent systems.^{18,6i}

The solvation effect of betaine dye is more important for HBD and EPA solvents than EPD solvents.^{1a,19} Therefore, the E_T^N scale is particularly sensitive to the HBD ability of the cation

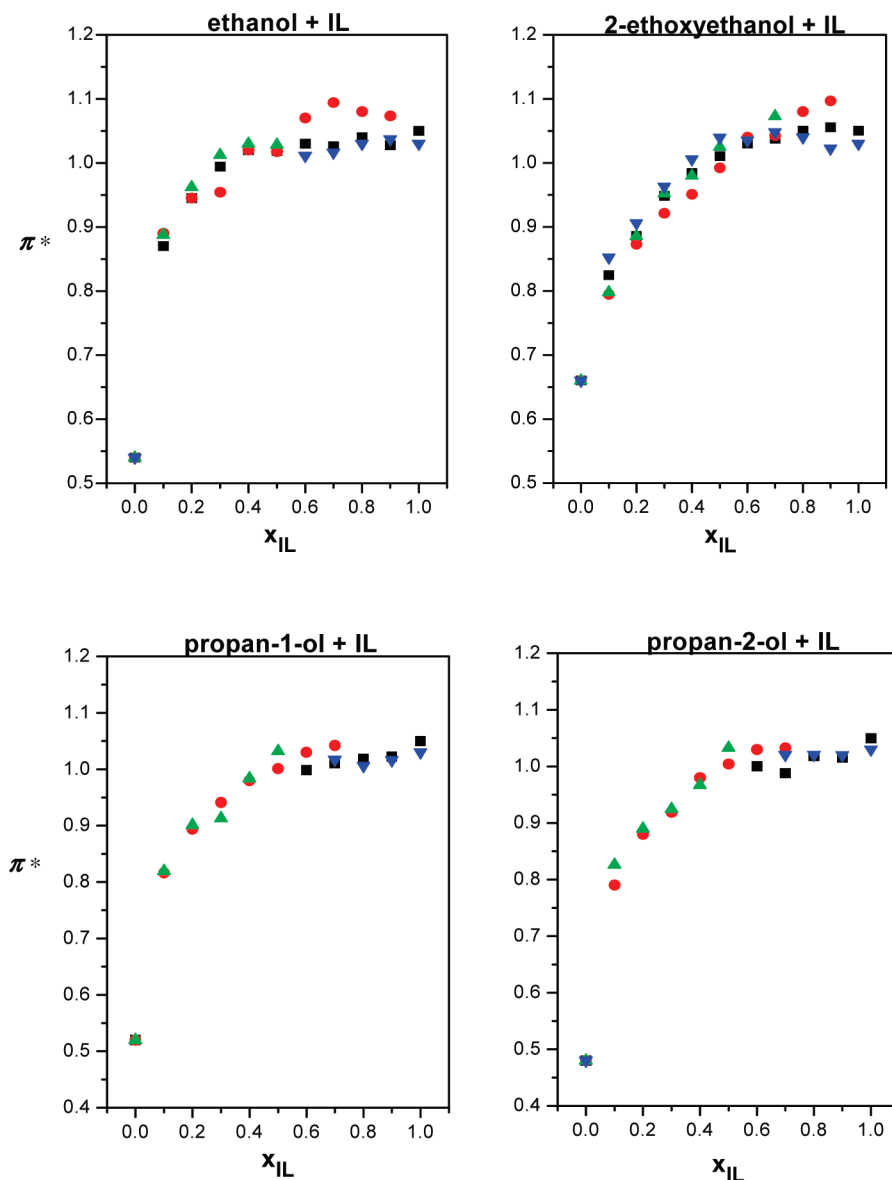


Figure 2. Variation of π^* with X_{IL} in (protic molecular solvent + IL) mixtures. Symbols are equivalent to those in Figure 1.

part of the ionic liquids.^{6c,h} In this work, all ILs contain the same cation, so it is reasonable that the parameter values and the shapes of the curves would be similar. In spite of this, the betaine dye can take part in hydrogen bond formation with alcohols via its phenoxide oxygen and the hydroxylic proton, forming 1:1 intermolecular complexes.²⁰ On the other hand, 1,3-dialkylimidazolium-based ionic liquids can act as acceptors to establish hydrogen bonding with alcohols, competing with the betaine for the hydroxylic hydrogen, and, at the same time, can act as donors to interact with the dye through hydrogen bonding. These interactions have a singular effect on the parameter values.

Dipolarity/Polarizability π^* . The plots presented in Figures 2 and 5 show that π^* values experience a marked increase by adding small amounts of the IL. Moreover, they exhibit positive deviations from the ideal behavior in all systems. For instance, the (ethanol + [bmim][BF₄]) mixture at $X_{IL} = 0.1$ exhibits a maximum deviation of 47% with respect to the ideal additive behavior. It can be observed (Tables 1–4) that π^* magnitudes are comparable despite the molecular alcohol involved. The patterns between [bmim][BF₄]/[PF₆] and [bmim][Cl]/[Br] are complementary, particularly in mixtures with propan-1-ol and propan-2-ol.

Basicity β . The plots of β vs *solvent composition* presented in Figures 3 and 5 reveal that the basicity values of the mixtures with [bmim][Cl] are the highest ones, whereas the mixtures with [bmim][PF₆] display the smallest magnitudes of the property. For all binary mixtures, the basicity β follows the order [bmim][Cl] > [bmim][Br] > [bmim][BF₄] > [bmim][PF₆].

The systems (ethanol/2-ethoxyethanol + [bmim][BF₄]) and (2-ethoxyethanol + [bmim][PF₆]) manifest a negative deviation from the ideal behavior (maximum deviation of 27% at $X_{IL} = 0.3$, 19% at $X_{IL} = 0.5$, and 38% at $X_{IL} = 0.7$, respectively), as it was observed in MeOH previously.⁵ For the mixtures of [bmim][BF₄]/[PF₆] with the other alcohols, it can be observed that while the ionic liquid composition increases the parameter value decreases.

With regard to the systems with [bmim][Cl], the general trend shows that the basicity increases as the ionic component is also increased, reaching the highest magnitude for the system with ethanol. Its mixture with methanol exhibits a maximum positive deviation of 22% considering $X_{IL} = 0.9$ as the pure solvent. The mixtures with [bmim][Br] do not follow a clear trend. For the systems with 2-ethoxyethanol, a clear opposite tendency is manifest between [bmim][Cl]/[Br] and [bmim][BF₄]/[PF₆].

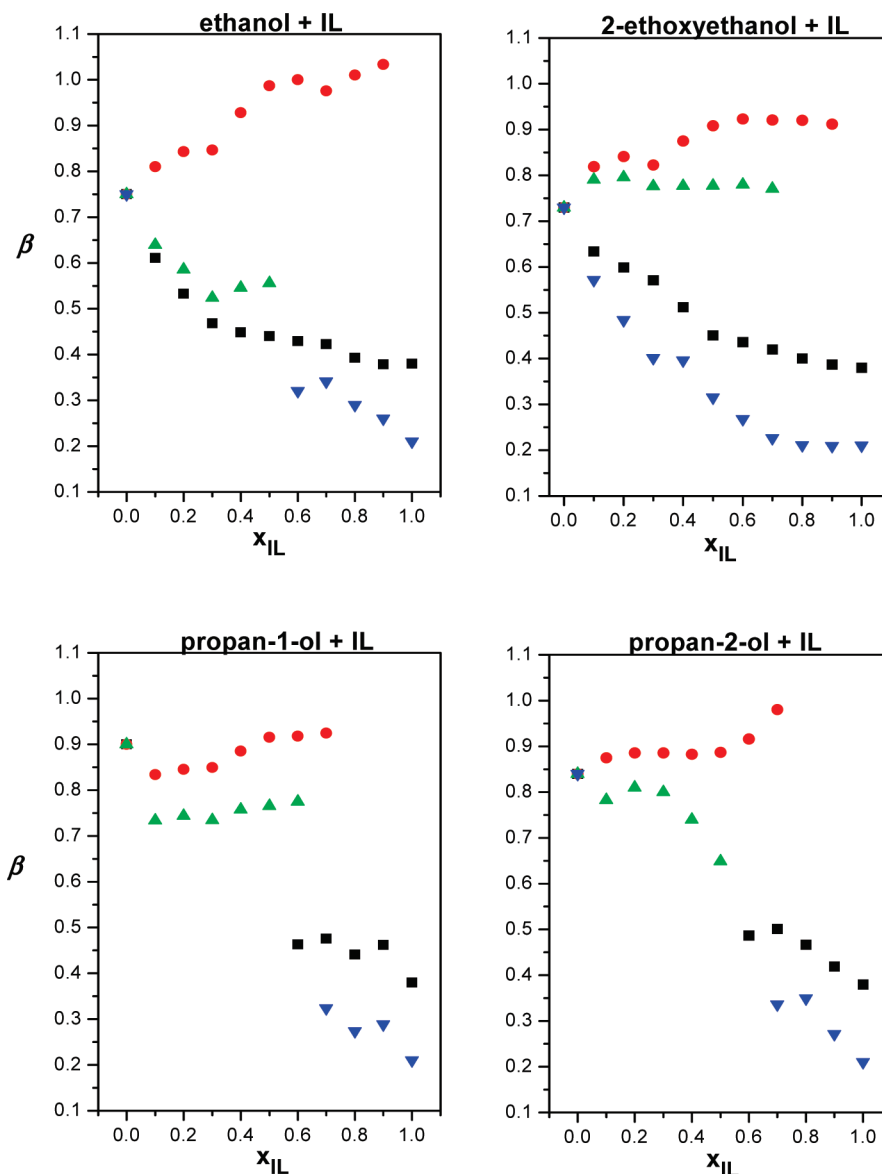


Figure 3. Variation of β with x_{IL} in (protic molecular solvent + IL) mixtures. Symbols are equivalent to those in Figure 1.

Acidity α . The plots presented in Figures 4 and 5 show that α values exhibit a progressive reduction as the IL composition increases. The mixtures with [bmim][BF₄] in ethanol and in 2-ethoxyethanol manifest a positive deviation from the ideal behavior at low compositions of the IL (maximum deviation of 11% at $x_{IL} = 0.1$ and 15% at $x_{IL} = 0.1$, respectively), exhibiting a gradual linear decrease at higher compositions. The mixture [2-ethoxyethanol + [bmim][PF₆]] exhibits the same pattern, with a maximum deviation of 15% at $x_{IL} = 0.1$. Additionally, a slight synergetic effect takes part in these systems at low ionic liquid compositions. For the systems with [bmim][Cl] or [bmim][Br], the hydrogen bond donor ability experiments a marked decrease, following approximately an additive behavior. The mixtures of [bmim][Cl] with ethanol and methanol exhibit negative deviations at high compositions of IL. Considering $x_{IL} = 0.9$ as the pure solvent, the maximum deviations are 38% at $x_{IL} = 0.7$ and 48% at $x_{IL} = 0.5$, respectively. As a general tendency, the property follows the order [bmim][PF₆] \sim [bmim][BF₄] > [bmim][Br] > [bmim][Cl]. This trend is roughly opposite to the one observed for the basicity β .

α , β Parameters: Influence of the Anion and Cation Interactions. At first glance, the hydrogen bond basicity β is controlled by the anions, with basicity increasing as the strength

of the conjugate acid of the anion decreases. In our case, the pK_a trend of the conjugate acids follows the order HPF₆ \sim HBr < HCl < HBF₄. If it would be the only factor, the expected IL basicity would follow the opposite tendency. However, this is a general trend because the hydrogen bond acceptor ability of the ionic liquid also depends on the cations. The overall ability of the ionic liquid to form a hydrogen bond with a solute molecule comes from an antagonist relationship between its constituent ions.^{3a} This fact may be described in terms of two competing equilibria. If we consider the equilibrium between the anion and a solute, first the anion can hydrogen bond to the cation. As more preferential this last equilibrium is the interaction anion-solute is less favored. Thus, the prevalence of the ion-pair character in the ionic liquid will determine its interactions with other species, such as a probe or a molecular solvent.

The interactions between cations and anions in ILs are too complex; they involve not only Coulombic interactions but also van der Waals and other dipole-dipole derived interactions. For example, the aromatic p_π interactions above and below the ring plane of imidazolium cations can interact with the anion electron cloud, giving rise to significant dispersion forces. All the possible interactions would be different if the ions are charge dense or charge diffuse or polarizable species. The selected ionic

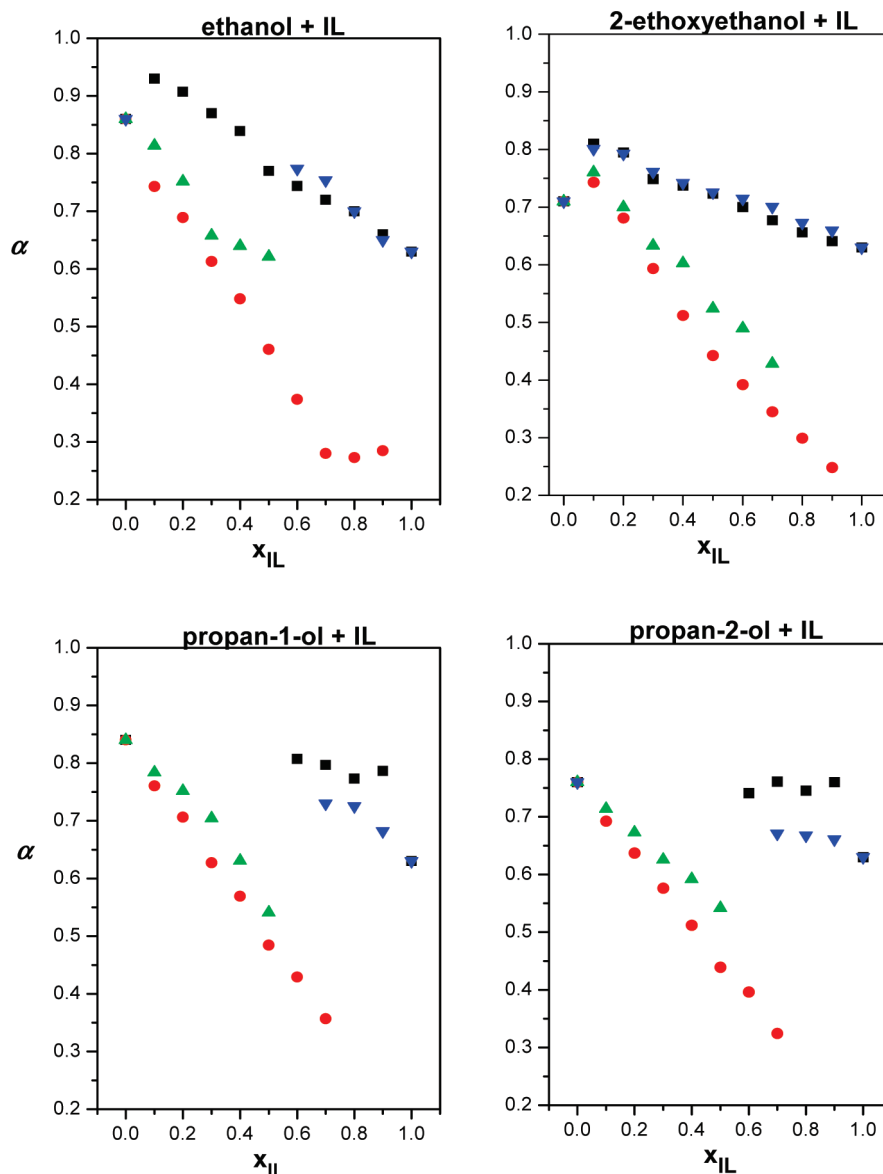


Figure 4. Variation of α with x_{IL} in (protic molecular solvent + IL) mixtures. Symbols are equivalent to those in Figure 1.

liquids in this work comprise the charge delocalized 1-butyl-3-methylimidazolium cation, the [Cl]/[Br] anions with a high degree of charge localization, and [BF₄] and [PF₆] as charge delocalized anions. In this direction, the ion pairs arising from [bmim][Cl] and [bmim][Br] would be more loosely bound than those from ILs with the fluorinated anions. In line with this, [bmim][Cl] and [bmim][Br] would exhibit more basicity than [bmim][BF₄] and [bmim][PF₆], because their anions are more available to interact with the probe. The basicity β trend observed experimentally is in agreement with this interpretation. Additionally, the higher proton acceptor ability of [BF₄] with respect to [PF₆] employing other solutes as solvatochromic probes was reported.²¹ In an earlier independent study, proton acceptor abilities of a variety of anions ([BF₄], [Cl], and [Br], among others) were reported using phenol and water as proton donors. The trend in proton acceptor ability was [Cl] > [Br] \gg [BF₄].²²

Taking into account the IL–alcohol interactions, it is known that water and small alcohols modify the ordered three-dimensional networks of cations and anions of ionic liquids. For example, in water at infinite dilution, ionic liquid components break away from their pure environment and settle in the

water environment, probably as separated ions. As the concentration of the IL increases, its anions and cations begin to interact with each other, directly or mediated by water. At higher concentrations, ionic liquid ions cluster together with a very similar arrangement to that in the pure state.²³ Water and small alcohols are hydrogen bonded strongly with the anion rather than the cation. The degree and type of interaction will depend on both the IL and the alcohol.

In the solvent systems with [bmim][BF₄] and [bmim][PF₆], the basicity β decreases as the IL concentration increases. This tendency is the consequence of a favored interaction between anion and cation and/or between the IL and the corresponding alcohol. This last strong association can be connected with the negative deviation from ideality exhibited in some mixtures, in which a singular complex formed by the IL and the alcohol (a “mixed solvent”) surrounds the probe, solvating it preferentially.

On the other hand, the basicity increases with higher concentrations of the IL for the systems comprised of [bmim][Cl] or [bmim][Br] (although the trend is more clear for the anion [Cl]). Considering that the ion pairs in these ILs are looser, allowing a better interaction with the probe, the tendency can be ascribed to a preferential solvation by the ionic liquid and

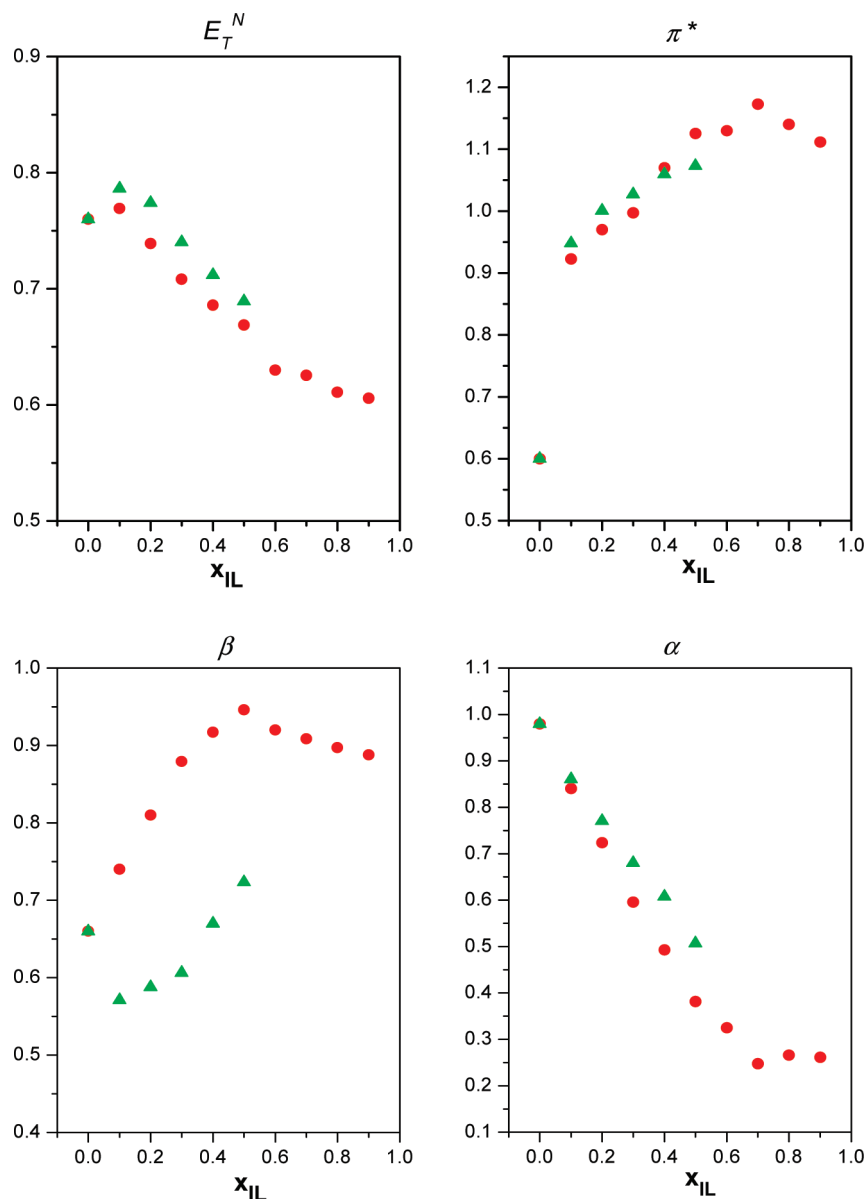


Figure 5. Variation of E_T^N , π^* , β , and α parameters with X_{IL} in (MeOH + [bmim][Cl]/[Br]) systems. Symbols are equivalent to those in Figure 1.

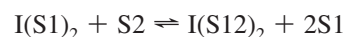
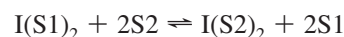
as a consequence to a lesser preponderance of the “mixed solvent” in the solvation process.

The acidity α trend is consistent with the previous analysis. Taking into account that these solvent systems differ only in the nature of the anion and that α values are mainly determined by the nature of the cation, the behavior can be connected with an anion effect on the acidity. The solvent system with the highest basicity is the one with the highest acidity. The positive deviation manifest in some solvents with [bmim][BF₄] and [bmim][PF₆] and the slight synergetic effect can be explained by the strong intersolvent interactions mentioned above. The almost linear decrease of the property in several mixtures comprised of [bmim][Cl] and [bmim][Br] also demonstrated that the “mixed solvent” is less favored, although slight negative deviation in some solvents with [bmim][Cl] can be noticed.

It is worth noticing that the $E_T(30)$ values are the key in the measurements of acidity α and that Reichardt’s dye has a strongly hydrogen bond accepting phenolate oxygen which interacts with the cation of the ionic liquid.

Preferential Solvation Model. The application of preferential solvation models in mixed solvents is a useful tool to describe

the behavior of solvatochromic indicators and the structure of binary mixtures, providing valuable solute–solvent and solvent–solvent structural information. Thus, in order to evaluate the solvation pattern experimentally observed and to obtain a deeper insight about the influence of anion and cation type on the solvation behavior, we applied the Buhvestov^{7a,b} and Skwierczynski^{7c} models, which are based on a simple exchange of two solvents according to the following scheme:



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. The equations in the above scheme reflect the total exchange of solvent 1 by solvent 2 in the solvation sphere of the indicator and the

TABLE 5: Preferential Solvation Parameters Obtained by Application of eqs 1 and 2 to Experimental Wavenumbers, 10⁴ν (cm⁻¹), of Indicators I (*N,N*-Diethyl-4-nitroaniline), II (4-Nitroaniline), and III (Reichardt's Dye) in the Selected Binary Mixtures at 25 °C

probe	solvent	Y_1^a	Y_2^a	Y_{12}^a	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	k	ssr ^b
I	MeOH + [bmim][BF ₄] ^c	25.39 (0.67)	24.19 (1.05)	24.66 (0.90)	6.592	13.84	2.099	-1.46	2.4e-004
	MeOH + [bmim][PF ₆] ^c	25.59 (0.60)	24.24 (1.03)	24.56 (0.93)	2.310	28.92	12.52	-1.65	0.0015
	MeOH + [bmim][Cl] ^c	25.64 (0.59)	23.91 (1.13)	23.85 (1.15)	9.054	1.298	0.143	-0.97	0.0074
	EtOH + [bmim][BF ₄]	25.80 (0.54)	24.20 (1.04)	24.29 (1.01)	16.15	32.88	2.036	-1.18	0.0003
	EtOH + [bmim][Cl]	25.77 (0.55)	24.12 (1.07)	23.98 (1.12)	3.242	0.515	0.159	-0.90	0.0023
	2-EtOEtOH + [bmim][BF ₄]	25.42 (0.66)	24.18 (1.05)	24.11 (1.07)	0.188	5.423	28.77	-0.74	1.1e-004
	2-EtOEtOH + [bmim][PF ₆]	25.42 (0.66)	24.26 (1.02)	24.04 (1.09)	2.450	5.856	2.389	-0.70	0.0012
	2-EtOEtOH + [bmim][Cl]	25.42 (0.66)	23.99 (1.11)	24.98 (0.80)	31.49	16.33	0.519	-0.72	0.0007
	MeOH + [bmim][BF ₄] ^c	27.25 (0.66)	26.74 (0.38)	26.57 (0.61)	0.595	1.878	3.160	-0.85	0.0014
	MeOH + [bmim][PF ₆] ^c	27.45 (0.66)	27.37 (0.21)	27.68 (0.21)	0.693	4.249	6.123	-0.74	7.2e-007
II	MeOH + [bmim][Cl]	27.50 (0.66)	25.18 (0.88)	25.09 (0.89)	4.821	0.210	0.043	-1.4	0.0007
	EtOH + [bmim][BF ₄]	27.41 (0.75)	26.87 (0.38)	26.90 (0.40)	1.390	6.508	4.680	-0.77	7.4e-004
	EtOH + [bmim][Cl]	27.38 (0.75)	24.98 (1.02)	24.89 (1.00)	2.304	1.336	0.580	-1.0	0.0033
	2-EtOEtOH + [bmim][BF ₄]	27.09 (0.73)	26.83 (0.38)	26.76 (0.38)	0.642	2.367	3.685	-0.80	0.0017
	2-EtOEtOH + [bmim][PF ₆]	27.09 (0.73)	27.40 (0.21)	27.18 (0.21)	0.660	3.182	4.821	-0.60	7.2e-007
	2-EtOEtOH + [bmim][Cl]	27.09 (0.73)	25.14 (0.92)	26.20 (0.89)	6.105	5.571	0.912	-0.93	0.0033
	MeOH + [bmim][BF ₄] ^c	19.40 (0.76)	18.32 (0.67)	20.20 (0.83)	1.530	8.686	8.249	1.52	0.0014
	MeOH + [bmim][PF ₆] ^c	19.34 (0.76)	18.35 (0.67)	19.42 (0.77)	5.831	21.37	3.666	1.55	1.5e-007
	MeOH + [bmim][Cl]	19.35 (0.76)	17.58 (0.60)	18.62 (0.69)	8.154	1.543	0.189	0.37	0.0004
	EtOH + [bmim][BF ₄]	18.27 (0.66)	18.27 (0.66)	18.33 (0.67)	9.948	22.04	2.215	1.26	3.4e-007
III	EtOH + [bmim][Cl]	18.10 (0.65)	17.57 (0.60)	18.16 (0.65)	27.95	5.852	0.209	0.22	0.0005
	2-EtOEtOH + [bmim][BF ₄]	17.76 (0.62)	18.32 (0.67)	18.36 (0.67)	4.067	18.98	4.667	0.98	9.8e-008
	2-EtOEtOH + [bmim][PF ₆]	17.76 (0.62)	18.33 (0.67)	18.36 (0.67)	2.893	20.28	7.011	1.04	1.5e-007
	2-EtOEtOH + [bmim][Cl]	17.76 (0.62)	17.49 (0.60)	18.16 (0.65)	42.95	19.73	0.459	0.17	0.0001

^a Y (calculated solvatochromic property, π^* , β , and E_T^N). ^b ssr (regression sum of squares). ^c Data from ref 5.

exchange by the mixed solvents, respectively. The constants in these processes are defined by the preferential solvation parameters ($f_{2/1}$ and $f_{12/1}$) that relate the ratio of the mole fractions of solvents S1 and S2 and the mixed solvent S12 (structure attributed to the formation of intersolvent complexes or associates by hydrogen bond interactions) solvating the probe (x_1^s , x_2^s , and x_{12}^s) to the ratio of the mole fractions of the two solvents in the bulk mixed solvent (x_1 and x_2 , respectively). The constants $f_{2/1}$ and $f_{12/1}$ measure the tendency of the probe to be solvated with cosolvent S2 and "mixed solvent" S12, with reference to solvent S1. The constant $f_{12/2}$ corresponding to the 12/2 exchange can be calculated from the relation $f_{12/1}/f_{2/1}$. Thus, the solvatochromic mixture property Y can be evaluated as an average of the properties in pure solvents S1, S2, and S12 (Y_1 , Y_2 , and Y_{12} , respectively), according to eq 1:

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

The correction term ΔY (eq 2) was introduced originally^{7a,b} to take into account the enhancement of water structure caused by the alcohol molecules in alcohol–water mixtures at low mole fraction of alcohol:

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

where k is a proportionality constant.

As it was discussed previously in this work, the solvation patterns are characterized by exhibiting a significant change as low amounts of IL are added to the molecular alcohols, particularly for the dipolarity/polarizability and basicity proper-

ties. In order to take into account this ionic liquid effect on the solvatochromic property Y of the mixtures, the wavenumbers of maximum absorptions of the solvatochromic indicators (*N,N*-diethyl-4-nitroaniline, 4-nitroaniline, and Reichardt's betaine dye) at different compositions of S1 (alcohol) and S2 (IL) were fitted to eqs 1 and 2. The results are presented in Table 5. The experimental data⁵ corresponding to MeOH + [bmim][BF₄]/[bmim][PF₆] mixtures were also included in the analysis.

N,N-Diethyl-4-nitroaniline (I) is sensitive to the dipolarity/polarizability of the solvent. Since it shows positive solvatochromism, a decrease in the property increases the wavenumber of maximum absorption. Table 5 shows that the wavenumbers of maximum absorptions of pure solvents (Y_1 and Y_2) increase in the order [bmim][Cl], [bmim][BF₄], [bmim][PF₆], MeOH, EtOEtOH, and EtOH. The wavenumbers of maximum absorptions of the mixed solvent S12 (Y_{12}) are close to Y_2 values, and in some mixtures, they are lower than Y_1 and Y_2 values. Mixed (MeOH/EtOH + [bmim][Cl]) display the strongest dipolarity/polarizability, exhibiting a minimum in the Y_{12} values. In general, the order of the preferential solvation parameters $f_{2/1}$, $f_{12/1}$, and $f_{12/2}$ suggests that, while in the mixtures with [bmim][BF₄] and [bmim][PF₆], the probe is preferentially solvated by the mixed solvent and, while in the mixtures with [bmim][Cl], it is solvated preferentially by the IL. Particularly in MeOH and EtOH solvent systems, the dipolarity/polarizability property exhibits a huge increment as a low concentration of the ionic liquid is present in the mixture; this effect is manifest as a decrease in the wavenumbers of maximum absorptions and as negative values in k constants.

4-Nitroaniline is also a positive indicator and is sensitive to both solvent dipolarity/polarizability and to solvent hydrogen bond basicity. The combination of these solvent properties determines the order of the wavenumbers of the maximum absorption of this indicator (Y_1 , Y_2 , and Y_{12}). The wavenumbers of maximum absorptions of the pure solvents (Y_1 and Y_2) increase in the order [bmim][PF₆], [bmim][BF₄], MeOH, EtO-

TABLE 6: Selected Binary Solvent Mixtures and Their Molecular-Microscopic Solvent Properties

solvent	composition	E_T^N	π^*	β	α
liquid 1	$X_{\text{EtOH}} 0.9/X_{[\text{bmim}][\text{BF}_4]} 0.1$	0.782	0.870	0.611	0.930
liquid 2	$X_{\text{EtOH}} 0.7/X_{[\text{bmim}][\text{BF}_4]} 0.3$	0.795	0.994	0.468	0.870
liquid 3	$X_{\text{EtOH}} 0.7/X_{[\text{bmim}][\text{Cl}]} 0.3$	0.696	0.954	0.846	0.613
liquid 4	$X_{\text{EtOH}} 0.7/X_{[\text{bmim}][\text{Br}]} 0.3$	0.719	1.027	0.524	0.658
liquid 5	$X_{\text{EtOH}} 0.1/X_{[\text{bmim}][\text{Cl}]} 0.9$	0.610	1.073	1.033	0.285
liquid 6	$X_{\text{EtOH}} 0.4/X_{[\text{bmim}][\text{PF}_6]} 0.6$	0.757	1.011	0.320	0.774
liquid 7	$X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{BF}_4]} 0.1$	0.718	0.825	0.634	0.810
liquid 8	$X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{PF}_6]} 0.1$	0.721	0.852	0.572	0.801
liquid 9	$X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{Cl}]} 0.1$	0.688	0.794	0.819	0.743
liquid 10	$X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{Br}]} 0.1$	0.696	0.798	0.790	0.761
liquid 11	$X_{\text{EtOEtOH}} 0.3/X_{[\text{bmim}][\text{PF}_6]} 0.7$	0.733	1.048	0.226	0.754
liquid 12	$X_{\text{EtOEtOH}} 0.3/X_{[\text{bmim}][\text{Cl}]} 0.7$	0.617	1.024	0.921	0.345
liquid 13	$X_{\text{POH}} 0.1/X_{[\text{bmim}][\text{BF}_4]} 0.9$	0.776	1.023	0.462	0.786
liquid 14	$X_{\text{POH}} 0.1/X_{[\text{bmim}][\text{PF}_6]} 0.9$	0.716	1.020	0.288	0.682
liquid 15	$X_{\text{POH}} 0.9/X_{[\text{bmim}][\text{Cl}]} 0.1$	0.706	0.816	0.834	0.760
liquid 16	$X_{\text{POH}} 0.9/X_{[\text{bmim}][\text{Br}]} 0.1$	0.711	0.819	0.734	0.784
liquid 17	$X_{\text{POH}} 0.3/X_{[\text{bmim}][\text{Cl}]} 0.7$	0.623	1.042	0.924	0.357
liquid 18	$X_{2\text{POH}} 0.3/X_{[\text{bmim}][\text{Cl}]} 0.7$	0.608	1.033	0.980	0.324
liquid 19	$X_{\text{MeOH}} 0.5/X_{[\text{bmim}][\text{Cl}]} 0.5$	0.669	1.125	0.946	0.381
liquid 20	$X_{\text{MeOH}} 0.5/X_{[\text{bmim}][\text{Br}]} 0.5$	0.689	1.073	0.723	0.507

EtOH, EtOH, and [bmim][Cl]. The wavenumbers of maximum absorptions of the mixed solvent S12 (Y_{12}) are close to Y_2 values in most mixtures. The solvents with [bmim][PF₆] exhibit the highest values of Y_{12} . For mixed (MeOH + [bmim][PF₆]), Y_{12} is higher than the Y_1 and Y_2 values, manifesting a minimum in

the β basicity. The k constants are less negative than in the previous probe, as the increase in the wavenumbers is partially compensated by the variation in dipolarity/polarizability. On the other hand, mixed (MeOH + [bmim][Cl]) displays the lowest Y_{12} value, indicating a maximum in the HBA property.

In the solvent systems with [bmim][PF₆] and [bmim][BF₄], the $f_{2/1}$ parameters are lower than unity, indicating that the indicator is preferentially solvated by the alcohol; $f_{12/1}$ and $f_{12/2}$ are higher than unity, suggesting that the mixed solvent is solvating preferentially. Thus, the preferential solvation order is mixed solvent > IL > alcohol. For the solvent systems comprised of [bmim][Cl], the $f_{2/1}$, $f_{12/1}$, and $f_{12/2}$ values suggest that the preferential solvation order is IL > mixed solvent > alcohol.

Reichardt's betaine dye exhibits negative solvatochromism and is sensitive to dipolarity/polarizability and hydrogen bond donor ability. The wavenumbers of maximum absorptions of the pure solvents (Y_1 and Y_2) increase in the order [bmim][Cl], EtOEtOH, EtOH, [bmim][PF₆] \approx [bmim][BF₄], MeOH. The wavenumbers of maximum absorptions of the corresponding alcohol-IL S12 solvents (Y_{12}) increase approximately in the same order. In the mixtures exhibiting a slight synergism on the E_T^N parameter (and in α parameters, although to a minor extent), the Y_{12} values are somewhat higher than the Y_1 and Y_2 values, especially in (MeOH + [bmim][BF₄]/[PF₆]) solvent systems. The k constants are positive as expected and, in general, similar in absolute values to the positive indicators. The $f_{2/1}$ values,

TABLE 7: Redlich-Kister Coefficients, Standard Errors of the Estimate (se), and Correlation Coefficients (R^2) for E_T^N Values Corresponding to (Protic Molecular Solvent + IL) Binary Mixtures

A_0 (s_0)	A_1 (s_1)	A_2 (s_2)	A_3 (s_3)	se	R^2
0.3204(± 0.0197)		MeOH + [bmim][BF ₄] 0.8633(± 0.0908)		0.0086	0.9909
0.4552(± 0.0088)	-0.0768(± 0.0348)	MeOH + [bmim][PF ₆] 0.5156(± 0.0409)	-0.1754(± 0.0905)	0.0039	0.9989
-0.0958(± 0.0156)	-0.1955(± 0.0312)	MeOH + [bmim][Cl] 0.1628(± 0.0719)		0.0068	0.9216
-0.1404(± 0.0061)	-0.13850(± 0.0445)	MeOH + [bmim][Br] 0.6270(± 0.0648)		0.0016	0.9979
0.4784(± 0.0106)	-0.1313(± 0.0415)	EtOH + [bmim][BF ₄] 0.4589(± 0.0487)	-0.8883(± 0.1082)	0.0046	0.9987
0.1028(± 0.0210)	-0.2687(± 0.0826)	EtOH + [bmim][Cl] 0.3212(± 0.0969)	-0.4494(± 0.2152)	0.0092	0.9711
0.1383(± 0.0144)		EtOH + [bmim][Br] -1.5707(± 0.1081)		0.0056	0.9932
0.1785(± 0.0049)	-0.3162(± 0.0183)	POH + [bmim][Cl] 0.1147(± 0.0471)	-0.9425(± 0.0847)	0.0017	0.9996
0.1493(± 0.0123)	-0.3308(± 0.0610)	POH + [bmim][Br] -1.0095(± 0.1219)		0.0033	0.9987
0.2203(± 0.0053)	-0.2643(± 0.0269)	2-POH + [bmim][Cl] -1.1350(± 0.0824)		0.0028	0.9989
0.2473(± 0.0324)		2-POH + [bmim][Br] -1.5760(± 0.2431)		0.0125	0.9807
0.3775(± 0.0128)	-0.0999(± 0.0502)	EtOEtOH + [bmim][BF ₄] 0.4329(± 0.0589)	-0.4188(± 0.1307)	0.0056	0.9969
0.3861(± 0.0184)		EtOEtOH + [bmim][PF ₆] 0.4697(± 0.0847)	-0.5506(± 0.0956)	0.0080	0.9930
0.1196(± 0.0102)	-0.1939(± 0.0402)	EtOEtOH + [bmim][Cl] 0.3560(± 0.0471)	-0.4217(± 0.1046)	0.0045	0.9928
0.1685(± 0.0065)	-0.1911(± 0.0326)	EtOEtOH + [bmim][Br] -0.8816(± 0.0996)		0.0034	0.9971

TABLE 8: Redlich–Kister Coefficients, Standard Errors of the Estimate (se), and Correlation Coefficients (R^2) for the π^* Values Corresponding to (Protic Molecular Solvent + IL) Binary Mixtures

A_0 (s_0)	A_1 (s_1)	A_2 (s_2)	A_3 (s_3)	se	R^2
0.7845(± 0.0440)	$-0.5517(\pm 0.1727)$	MeOH + [bmim][BF ₄] 1.3591(± 0.2026)	$-1.9144(\pm 0.4497)$	0.0191	0.9938
0.7494(± 0.0627)		MeOH + [bmim][PF ₆] 1.5513(± 0.2888)	$-3.6676(\pm 0.3260)$	0.0273	0.9863
0.9575(± 0.0829)		MeOH + [bmim][Cl] 1.2877(± 0.3819)	$-2.6519(\pm 0.4312)$	0.0361	0.9820
0.9437(± 0.0178)	$-1.6177(\pm 0.2599)$	MeOH + [bmim][Br] $-4.8362(\pm 0.9257)$	$-8.1606(\pm 0.8379)$	0.0045	0.9999
0.8858(± 0.0305)	$-0.7591(\pm 0.1197)$	EtOH + [bmim][BF ₄] 1.0949(± 0.1403)	$-1.3437(\pm 0.3115)$	0.0133	0.9972
0.8673(± 0.0483)		EtOH + [bmim][Cl] 1.4470(± 0.2223)	$-2.7087(\pm 0.2510)$	0.0210	0.9932
0.9926(± 0.0621)	$-0.9958(\pm 0.3069)$	EtOH + [bmim][Br] $-2.7176(\pm 0.6133)$		0.0166	0.9982
0.8961(± 0.0272)	$-0.3298(\pm 0.1021)$	POH + [bmim][Cl] 0.6170(± 0.2632)	$-2.0536(\pm 0.4739)$	0.0098	0.9990
1.0121(± 0.0269)		POH + [bmim][Br] $-3.3237(\pm 0.2025)$		0.0104	0.9987
1.0280(± 0.0211)	$-0.2500(\pm 0.1064)$	2-POH + [bmim][Cl] $-3.0168(\pm 0.3252)$		0.0110	0.9986
1.1084(± 0.0188)		2-POH + [bmim][Br] $-0.8623(\pm 0.3702)$	$-5.1516(\pm 0.5080)$	0.0056	0.9998
0.6080(± 0.0165)	$-0.2996(\pm 0.0647)$	EtOEtOH + [bmim][BF ₄] 0.3887(± 0.0759)	$-0.3479(\pm 0.1685)$	0.0072	0.9977
0.6925(± 0.0240)	$-0.2741(\pm 0.0942)$	EtOEtOH + [bmim][PF ₆] 0.2178(± 0.1105)	$-0.9618(\pm 0.2453)$	0.0104	0.9961
0.4433(± 0.0297)	$-0.3074(\pm 0.0594)$	EtOEtOH + [bmim][Cl] 0.4139(± 0.1369)		0.0129	0.9872
0.6027(± 0.0162)	$-0.2515(\pm 0.0455)$	EtOEtOH + [bmim][Br] 0.4366(± 0.1097)		0.0067	0.9984

which measure the preferential solvation of the indicator by IL with reference to the alcohol, are higher than unity in all solvents. The [bmim][Cl] ionic liquid displays the highest values of this parameter. For the mixtures with [bmim][BF₄] and [bmim][PF₆], the high $f_{12/1}$ and $f_{12/2}$ values demonstrated that the indicator is preferentially solvated by the mixed solvent S12. On the other hand, for the solvent systems comprised of [bmim][Cl], the $f_{2/1}$, $f_{12/1}$, and $f_{12/2}$ values suggest that the preferential solvation order is IL > mixed solvent > alcohol.

Selection of “New Solvents”. As it is known, binary mixtures of solvents can be deliberately used to modify particular chemical characteristics of reaction media. In connection with this, we have focused our attention on those binary mixtures as part of the solvent systems explored in this work, with particular molecular-microscopic solvent properties. In this sense, we selected individual solvent mixtures with the purpose of providing “new solvents” with particular solvating properties (Table 6).

General Trends. Liquids Comprise Ethanol. In liquid 1 ($X_{\text{EtOH}} 0.9/X_{[\text{bmim}][\text{BF}_4]} 0.1$), the acidity is synergic with respect to the pure solvents, exhibiting the highest value of the property corresponding to the whole IL mixtures with ethanol. Simultaneously, this liquid manifests the maximum positive deviation from the ideal behavior on π^* property.

Liquids 2 ($X_{\text{EtOH}} 0.7/X_{[\text{bmim}][\text{BF}_4]} 0.3$), 3 ($X_{\text{EtOH}} 0.7/X_{[\text{bmim}][\text{Cl}]} 0.3$), and 4 ($X_{\text{EtOH}} 0.7/X_{[\text{bmim}][\text{Br}]} 0.3$) are comparable with respect to their dipolarity/polarizability, exhibiting a huge increase in reference to pure ethanol. Liquid 2 is characterized by its HBD

ability (which is parallel to pure ethanol). Liquid 3 displays the highest HBA ability, while in liquid 4 both properties are similar.

Liquid 5 ($X_{\text{EtOH}} 0.4/X_{[\text{bmim}][\text{PF}_6]} 0.6$) exhibits almost analogous dipolarity/polarizability with respect to previous solvents and is characterized by a HBD acidity similarly to liquid 1 but at a higher concentration of the ionic component. For liquid 6 ($X_{\text{EtOH}} 0.1/X_{[\text{bmim}][\text{Cl}]} 0.9$), its HBA ability can be remarked.

Liquids Comprise 2-Ethoxyethanol. Liquids 7 ($X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{BF}_4]} 0.1$), 8 ($X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{PF}_6]} 0.1$), 9 ($X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{Cl}]} 0.1$), and 10 ($X_{\text{EtOEtOH}} 0.9/X_{[\text{bmim}][\text{Br}]} 0.1$) are characterized by a HBD acidity higher than the pure alcohol. They exhibit similar dipolarity/polarizability and a significant HBA ability. Moreover, liquids 9 and 10 are more hydrogen bond acceptor than 2-ethoxyethanol. Liquids 11 ($X_{\text{EtOEtOH}} 0.3/X_{[\text{bmim}][\text{PF}_6]} 0.7$) and 12 ($X_{\text{EtOEtOH}} 0.3/X_{[\text{bmim}][\text{Cl}]} 0.7$) are HBD and HBA solvents, respectively. Liquid 11 exhibits the maximum negative deviation on basicity observed in the all of the solvent systems.

Liquids Comprise Propan-1-ol and Propan-2-ol. Liquids 13–17 contain propan-1-ol as molecular solvent. Liquids 13 and 14 have higher HBD than HBA ability, and their solvation behavior is comparable to solvents 2, 6, and 11. On the other hand, liquids 15 and 16 display significant HBA and HBD capability, likewise to liquids 9 and 10. Liquid 17 has the basicity markedly increased and higher than pure propan-1-ol. With regard to the mixtures comprising propan-2-ol at the same compositions corresponding to the liquids with propan-1-ol, the

TABLE 9: Redlich–Kister Coefficients, Standard Errors of the Estimate (se), and Correlation Coefficients (R^2) for the β Values Corresponding to (Protic Molecular Solvent + IL) Binary Mixtures

A_0 (s_0)	A_1 (s_1)	A_2 (s_2)	A_3 (s_3)	se	R^2
−0.2019(±0.0221)	0.1865(±0.0869)	MeOH + [bmim][BF ₄] −0.9661(±0.1019)	1.5190(±0.2262)	0.0096	0.9912
−1.0062(±0.0240)	0.5768(±0.0480)	MeOH + [bmim][PF ₆] −0.2781(±0.1106)		0.0104	0.9977
0.6376(±0.0161)	−0.4116(±0.0633)	MeOH + [bmim][Cl] −0.3645(±0.0742)	0.3202(±0.1648)	0.0070	0.9975
0.1550(±0.0410)	1.2482(±0.1182)	MeOH + [bmim][Br]		0.0122	0.9738
−0.5055(±0.0110)	0.6077(±0.0432)	EtOH + [bmim][BF ₄] −0.3977(±0.0507)	−0.3248(±0.1125)	0.0048	0.9986
−0.3943(±0.0404)	0.7857(±0.1165)	EtOH + [bmim][Br]		0.0120	0.9926
	0.3311(±0.0425)	POH + [bmim][Cl] −0.6677(±0.0811)		0.0064	0.9798
−0.3283(±0.0382)		POH + [bmim][Br]	2.5935(±0.2873)	0.0148	0.9871
−0.0942(±0.0074)	0.0730(±0.0278)	2-POH + [bmim][Cl] 1.2674(±0.0716)	0.8795(±0.1290)	0.0027	0.9914
−0.3873(±0.0118)	−1.5854(±0.0583)	2-POH + [bmim][Br]	2.4864(±0.1166)	0.0032	0.9974
−0.3762(±0.0300)	−0.3513(±0.1527)	EtOEtOH + [bmim][BF ₄] 0.3591(±0.1791)	1.5884(±0.3975)	0.0169	0.9548
−0.6460(±0.0448)		EtOEtOH + [bmim][PF ₆]	1.2485(±0.3090)	0.0259	0.9614
−0.3230(±0.0239)	0.2406(±0.1246)	EtOEtOH + [bmim][Cl]	−0.9829(±0.3245)	0.0138	0.9650
0.1138(±0.0052)		EtOEtOH + [bmim][Br]	−1.0223(±0.0472)	0.0027	0.9955

solvation properties are analogous. However, liquid 18 stands out among them, exhibiting an enhanced basicity, similar to liquid 5.

Liquids Comprise Methanol. Liquids 19 and 20 are HBA solvents, particularly the first one. This liquid manifests the maximum positive deviation on basicity and the maximum negative deviation on acidity considering all solvent systems. In contrast, the liquids selected in a previous work⁵ comprising [bmim][BF₄] and [bmim][PF₆], at the same compositions, are clearly HBD solvents.

Redlich–Kister Equation to Correlate Solvatochromic Parameters. Solvatochromic parameters have been demonstrated to be successful in correlating a wide range of chemical and physical properties involving solute–solvent interactions. Because of their empirical origins, their ability to make a priori predictions has been somewhat limited. For these reasons, the prediction of solvatochromic parameters in mixed solvents based on a minimum number of experiments provides a useful computational tool.

In order to mathematically represent the effects of composition on various solvatochromic parameters in binary solvent systems, the combined nearly ideal binary solvent/Redlich–Kister equation has been applied for the experimental data of these parameters.^{6i,24} Thus, the aim of this work is to evaluate the applicability of the CNIBS/R–K model for calculating various solvatochromic parameters (E_T^N , π^* , α , and β) in (protic molecular solvent + 1,3-dialkylimidazolium-based ionic liquid) binary mixtures at 25 °C.

According to this model, the empirical solvatochromic parameters (SP) in a binary solvent mixture at constant temperature can be expressed as

$$SP_m = X_1 SP_1^0 + X_2 SP_2^0 + X_1 X_2 \sum_{j=0}^k A_j (X_2 - X_1)^j \quad (3)$$

where SP_m , SP_1^0 , and SP_2^0 are solvatochromic parameters determined in mixtures and neat solvents 1 and 2, respectively. X_1 and X_2 are the mole fractions of the components in the mixtures. In this work, X_1 and X_2 are the mole fractions corresponding to the protic solvent and to the ionic liquid, respectively. A_j and j are the equation coefficients and the degree of the polynomial expansion, respectively. The numerical values of j can be varied to find an accurate mathematical representation of the experimental data. The numerical values of A_j can be computed by fitting the experimental values of $SP_m - (X_1 SP_1^0 + X_2 SP_2^0)$ against $X_1 X_2 (X_2 - X_1)$, $X_1 X_2 (X_2 - X_1)^2$, and $X_1 X_2 (X_2 - X_1)^3$ by using no intercept multiparameter least-squares analysis. Regression analysis was performed to fit the polynomials to our experimental data. In Tables S1–S4 (Supporting Information) are shown the number of experimental data points in each set (n), the solvatochromic parameters SP, and statistics of correlation equations including the standard deviation (σ) and the mean percentage deviation (MPD), which were calculated according to eqs 4 and 5, respectively:

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

TABLE 10: Redlich–Kister Coefficients, Standard Errors of the Estimate (se), and Correlation Coefficients (R^2) for the α Values Corresponding to (Protic Molecular Solvent + IL) Binary Mixtures

A_0 (s_0)	A_1 (s_1)	A_2 (s_2)	A_3 (s_3)	se	R^2
0.1932(± 0.0208)		MeOH + [bmim][BF ₄] 0.6132(± 0.0960)	0.8964(± 0.1084)	0.0091	0.9816
0.5704(± 0.0150)		MeOH + [bmim][PF ₆] 1.2046(± 0.1037)		0.0087	0.9943
−0.9325(± 0.0263)	−0.3814(± 0.1034)	MeOH + [bmim][Cl] 0.2794(± 0.1212)	0.5767(± 0.2691)	0.0115	0.9971
−0.9372(± 0.0225)	−0.9353(± 0.1635)	MeOH + [bmim][Br] −0.9799(± 0.2382)		0.0058	0.9992
0.1404(± 0.0215)	−0.4217(± 0.0430)	EtOH + [bmim][BF ₄] 0.6413(± 0.0992)		0.0094	0.9771
−0.4749(± 0.0247)	−0.7736(± 0.0971)	EtOH + [bmim][Cl] −0.3386(± 0.1139)	1.1839(± 0.2528)	0.0108	0.9932
−0.4248(± 0.0178)	−0.4758(± 0.0498)	POH + [bmim][Cl] −0.3945(± 0.1201)		0.0073	0.9956
−0.5978(± 0.0011)	−1.2318(± 0.0164)	POH + [bmim][Br] −0.3713(± 0.0585)	0.8565(± 0.0529)	0.0003	0.9999
−0.3773(± 0.0171)	−0.4260(± 0.0478)	2-POH + [bmim][Cl] −0.3267(± 0.1154)		0.0071	0.9948
−0.4161(± 0.0168)	−0.2386(± 0.0485)	2-POH + [bmim][Br] 0.0050		0.0050	0.9961
0.1694(± 0.0222)		EtOEtOH + [bmim][BF ₄] 0.5447(± 0.1024)	−1.2216(± 0.1156)	0.0097	0.9781
0.2092(± 0.0136)		EtOEtOH + [bmim][PF ₆] 0.5994(± 0.0625)	−0.9266(± 0.0706)	0.0059	0.9927
−0.1366(± 0.0065)	−0.2132(± 0.0257)	EtOEtOH + [bmim][Cl] 0.5390(± 0.0302)	−0.9920(± 0.0670)	0.0028	0.9975
−0.1468(± 0.0241)	−0.3790(± 0.1213)	EtOEtOH + [bmim][Br] −1.2422(± 0.3708)		0.0126	0.9609

$$\text{MPD} = \frac{100}{n} \sum_{i=1}^n \left| \frac{\text{SP}_i^{\text{exp}} - \text{SP}_i^{\text{cal}}}{\text{SP}_i^{\text{exp}}} \right| \quad (5)$$

where SP_i^{exp} and SP_i^{cal} are experimental and calculated values of SP. The Redlich–Kister coefficients (A_i) along with their standard errors (s) and the standard error of the estimate (se), obtained from the correlation equations for each parameter in the binary mixtures, are shown in Tables 7–10. The molecular-microscopic properties along with solvent systems included in all the tables are the ones that adjusted accurately to the

mathematical model. Experimental data published previously⁵ corresponding to (MeOH + [bmim][BF₄]/[bmim][PF₆]) were also fitted to eq 3. As can be seen from the statistics of the proposed equations [R^2 (correlation coefficient), se (standard error of the estimate), σ , and MPD], the model is statistically valuable. Some systems display so little data points to fit the model and other systems adjust to a linear [β , (EtOH + [bmim][Cl])] or to a polynomial regression [α , (EtOH + [bmim][Br])] when the parameter is plotted vs X_2 .

In Figure 6, the predicted values of SP (E_T^N , π^* , α , and β), calculated using the coefficients (A_i) obtained from eq 3 corresponding to the whole solvent mixtures included in the correlation analysis have been plotted versus the corresponding experimental values. Equation 6 was obtained showing an excellent linear correlation:

$$\text{SP}^{\text{cal}} = 0.9993(\pm 0.0024)\text{SP}^{\text{exp}} - 0.0007(\pm 0.0019) \quad (6)$$

$$n = 516 \quad R = 0.9985 \quad \sigma = 0.0011$$

An overall value of $\sigma = 0.0011$ confirms reasonable good agreement between the experimental solvatochromic parameters and the ones calculated according to the CNIBS/R–K model. These results allow us to conclude that this model is suitable to predict solvatochromic parameters of binary solvent systems composed by 1,3-dialkylimidazolium-based ionic liquids with different anions and various alcohols.

Conclusions

The compositions of the solvent mixtures are dependent on both the nature of the protic solvent and on the anion type of

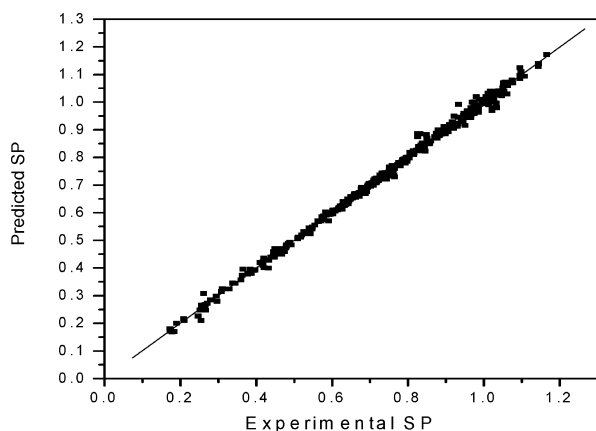


Figure 6. Predicted values of solvatochromic parameters from correlation equations vs experimental values for all the binary mixtures included in the correlation analysis (results of the fit are provided in eq 6).

the ionic liquid. With ethanol and 2-ethoxyethanol as molecular solvents, the IL part of this work displays large solubility, particularly when the anions are [BF₄] or [Cl]. The ionic liquids [bmim][PF₆] and [bmim][Br] exhibit the lowest solubility, so their mixtures were explored at the smallest range of compositions.

In general, E_T^N displays a similar response pattern in all solvent systems exhibiting positive deviation from ideal behavior characterized in some mixtures by a synergetic effect. The mixtures composed of [bmim][BF₄] and [bmim][PF₆] exhibited higher E_T^N polarity. The feature of π^* dipolarity/polarizability also shows similar solvation patterns in spite of the involved alcohol. Moreover, the values of the property matched for all ILs as they are compared at the same range of compositions.

The influence of anion nature is clearly manifest through specific solute–solvent and solvent–solvent interactions (β basicity and α acidity). The systems comprised of [Cl]/[Br] anions display the highest values of basicity, while the systems composed of [BF₄]/[PF₆] exhibit the maximum values of acidity. This trend is connected with the degree and type of interaction between the anions and the 1-butyl-3-methylimidazolium cation. Thus, in [bmim][BF₄] and [bmim][PF₆], the ion-pair character is enhanced with respect to [bmim][Cl] and [bmim][Br], affecting their interactions with a solute or a molecular solvent.

The α parameter, the same as the E_T^N polarity, also shows a synergetic behavior in the systems (ethanol/2-ethoxyethanol + [bmim][BF₄]), but the effect is less prominent.

Most of the solvent systems exhibit a nonideal additive behavior (see the Results and Discussion). This result can be ascribed to the preferential solvation of the cybotactic region by any of the solvents present in the mixture, to the occurrence of strong solvent–solvent interactions that can generate complex intersolvent structures affecting solute–solvent interactions, or to a combination of the two phenomena.

The preferential solvation model applied allowed relating the positive and negative deviations and the synergetic effect exhibited for the solvatochromic properties with the predominance of a species in the solvation sphere of the indicators. In the solvent system comprised of [BF₄]/[PF₆] anions, the probes are preferentially solvated by the mixed solvent, while in the systems with [Cl]/[Br] anions the IL controls the solvation behavior. These results are in connection with the incidence of the ion-pair character of the IL involved.

It is possible to select binary mixtures with particular solvating properties varying not only the solvent compositions but also changing the nature of the ionic or the molecular component of the system. Thus, while liquids 6, 11, and 14 have a prominent HBD ability and a relatively low basicity, liquids 5, 12, 17, 18, and 19 are HBA solvents. On the other hand, liquids 9, 10, 15, and 16 are HBD/HBA solvents. Therefore, we have proposed 20 “tailored solvents” that can promote specific solute–solvent and solvent–solvent interactions. These results show how important the employment of these types of binary solvent systems can be, for instance, as reaction media.

The experimental data of E_T^N , π^* , β , and α parameters of 15 binary mixtures of the type [protic molecular solvent + IL] at various compositions have been fitted to the CNIBS/R–K model. The model proved to be statistically valuable, showing a strong correlation between predicted and experimentally measured values.

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Supporting Information Available: Tables showing the number of experimental data points in each set (n), the solvatochromic parameters SP, and statistics of correlation equations including the standard deviation (σ) and the mean percentage deviation (MPD). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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