

# Solvent effects on chemical processes: new solvents designed on the basis of the molecular–microscopic properties of (molecular solvent + 1,3-dialkylimidazolium) binary mixtures

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The purpose of this work was to analyze the microscopic feature of binary solvent systems formed by a molecular solvent (acetonitrile or dimethylformamide or methanol) and an ionic liquid (IL) cosolvent [1-(1-butyl)-3-methylimidazolium tetrafluoroborate or 1-(1-butyl)-3-methylimidazolium hexafluorophosphate]. The empirical solvatochromic solvent parameters  $E_T(30)$ ,  $\pi^*$ ,  $\alpha$ , and  $\beta$  were determined from the solvatochromic shifts of adequate indicators. The behavior of the solvent systems was analyzed according to their deviation from ideality. The 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 solvent parameters corresponding to the selected binary mixtures with both ILs considered at similar mixed-solvent composition revealed that the difference is centered on the basic character of them. A kinetic study of a nucleophilic aromatic substitution reaction between 1-fluoro-2,4-dinitrobenzene (FDNB) and 1-butylamine (BU) developed in (acetonitrile or dimethylformamide + IL) solvent mixtures is presented in order to investigate and compare the solvent effects on a chemical process. For the explored reactive systems the solvation behavior is dominated by both the dipolarity/polarizability and the basicity of the media, contributing these solvent properties to accelerating the chemical process. Copyright © 2007 John Wiley & Sons, Ltd.

**Keywords:** molecular solvent; ionic liquid; binary mixtures; molecular–microscopic properties; solvatochromic parameters; aromatic nucleophilic substitution

## INTRODUCTION

Molecular solvents are the usual media where physical and chemical processes in solution take place.<sup>[1]</sup> In the last decade, the attention has been drawn to the use of room-temperature ionic liquids (ILs) as solvents for different applications, the interest being mainly based on their potential as solvents for clean technologies.<sup>[4–11]</sup> Because of the wide range of employable cations and anions, many new ionic solvents can be prepared. From the combination of pure solvents in binary mixtures, the availability and diversity of mediums increased considerably. Over the last few years, designing solvents with desired properties has become an important task for chemists in order to modulate processes in solution. The challenge consists in developing a 'desired solvent' with a particular use in mind.

To evaluate the behavior of a liquid as a solvent, the understanding of the solvation interactions at a molecular level is necessary. In this direction, it is of interest to quantify its most relevant molecular–microscopic solvent properties, which determine how it will interact with potential solutes. An appropriate method to study solute–solvent interactions is the use of solvatochromic indicators that reflect the specific and nonspecific solute–solvent interactions on the UV–Vis spectral band shifts. In this sense, 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<sup>[1]</sup> to measure solvent dipolarity/polarizability, though it is also sensitive to the solvent's hydrogen-bond donor (HBD) capacity. On the other hand, the  $\pi^*$ ,  $\beta$ , and  $\alpha$  (Kamlet, Abboud, and Taft)<sup>[12–14]</sup> multiparametric approach assigns different parameters to each particular solvent characteristics (dipolarity/polarizability, hydrogen-bond acceptor (HBA) basicity, and HBD acidity).

While the use of pure ILs as reaction media was investigated in a variety of chemical processes,<sup>[4–11]</sup> reactions carried out in their binary mixtures with molecular solvents have been less investigated. We have recently studied the kinetics of nucleophilic aromatic substitution ( $S_NAr$ ) reactions carried out in some

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molecular solvent/IL systems. The reaction between 1-fluoro-2,4-dinitrobenzene (FDNB) and 1-butylamine (BU) or piperidine performed in binary mixtures of the type (molecular solvent + alkylammonium salts) was particularly analyzed (Mancini, Fortunato, Adam, unpublished work).

At this point, the main purpose of this work is to investigate solvent systems resulting from the basis of binary mixtures formed by a molecular solvent (with different structures) and an IL cosolvent. With respect to the ionic cosolvent, we are particularly interested in ILs characterized by slighter HBD acidity than other ILs such as the alkylammonium type. In this direction, the selected liquids are based on 1,3-dialkylimidazolium cations. They exhibit a wide spectrum of physicochemical properties. It is demonstrated that their water content, density, viscosity, surface tension, melting point, and thermal stability are affected by the length of the alkyl chain and by the nature of the anion.<sup>[7,9]</sup>

The attention is given to the microenvironment of solutes in order to investigate the solvation capability of this type of binary mixtures. So far, the aims are: (i) to characterize the molecular–microscopic solvent properties measuring a set of empirical solvatochromic parameters for molecular solvent/IL systems; (ii) to analyze the response patterns *property versus solvent composition* focusing on the changes in the ability to develop the most relevant interactions (hydrogen-bond acidity, hydrogen-bond basicity, and polarity); (iii) to identify relevant mixtures paying particular attention to pronounced changes in the microscopic solvent feature in order to select ‘new solvents’; (iv) to carry out a kinetic study of a  $S_NAr$  reaction developed in those binary mixtures which present these relevant microscopic properties in order to investigate and compare the solvent effects on a chemical process with relation to the pure molecular solvent.

## RESULTS AND DISCUSSION

The selected ILs are composed of 1-(1-butyl)-3-methylimidazolium [bmim] as the cation and tetrafluoroborate and hexafluorophosphate as the anions: [bmim][BF<sub>4</sub>] ( $E_T^N = 0.67$ ,  $\pi^* = 1.05$ ,  $\alpha = 0.63$ ,  $\beta = 0.38$ ); [bmim][PF<sub>6</sub>] ( $E_T^N = 0.67$ ,  $\pi^* = 1.03$ ,  $\alpha = 0.63$ ,  $\beta = 0.21$ ).<sup>[5]</sup> The [bmim][BF<sub>4</sub>] and [bmim][PF<sub>6</sub>] were chosen taking into account that they are the most currently used ILs and they are nonprotic solvents. They comprise the same cation and a different anion. The anion mainly determines the water miscibility. With respect to their physical properties, [bmim][PF<sub>6</sub>], exhibits lower melting point, higher viscosity, higher density, and lower conductivity than [bmim][BF<sub>4</sub>]. While the latter one displays a complete miscibility with water at 25 °C, the first one shows a very low miscibility with this solvent.<sup>[7,8,9]</sup>

Taking into account their molecular–microscopic properties, while  $E_T^N$ ,  $\pi^*$ , and  $\alpha$  values are similar, the  $\beta$  value of [bmim][BF<sub>4</sub>] is near twofold the value corresponding to [bmim][PF<sub>6</sub>]. The  $E_T^N$  values lie in the range associated with polar HBD solvents such as short-chain alcohols.<sup>[11,16,17]</sup> The  $\pi^*$  values are high in comparison with nonaqueous molecular solvents and both the cation and the anion affect this parameter.<sup>[15]</sup> The  $\alpha$  values are largely determined by the nature of the cation; in this sense, it is known that 1-methyl-3-alkylimidazolium cations can act as weak HBDs because of the weak acidic C(2)—H hydrogen atom at the heterocyclic ring (which is the most acidic of all imidazolium H-atoms).<sup>[18–20]</sup> The  $\beta$  values are dominated by the nature of the anion. The hydrogen-bond acceptor basicity of the IL with [BF<sub>4</sub>] as

anion is parallel to the value of acetonitrile. The higher proton acceptor ability of [BF<sub>4</sub>] with respect to [PF<sub>6</sub>] has been confirmed employing other solutes as solvatochromic probes.<sup>[21]</sup>

The molecular solvents included in the analysis are acetonitrile (AN,  $E_T^N = 0.46$ ,  $\pi^* = 0.75$ ,  $\alpha = 0.19$ ,  $\beta = 0.40$ ), *N,N*-dimethylformamide (DMF,  $E_T^N = 0.40$ ,  $\pi^* = 0.89$ ,  $\alpha = 0$ ,  $\beta = 0.71$ ), and methanol (MeOH,  $E_T^N = 0.76$ ,  $\pi^* = 0.60$ ,  $\alpha = 0.98$ ,  $\beta = 0.66$ ).<sup>[1,22]</sup> The selection was done on the basis of their miscibility with the IL and their microscopic properties. AN is a polar HBA/HBD solvent, DMF is a polar aprotic HBA solvent, and MeOH is a protic solvent. It is important to remark that the microscopic solvent parameters for (MeOH + [bmim][BF<sub>4</sub>]) mixtures have been reported recently.<sup>[23]</sup>

### Characterization of binary solvent mixtures. Determination of the molecular–microscopic solvent parameters

The  $E_T^N$ ,  $\pi^*$ ,  $\alpha$ , and  $\beta$  solvatochromic parameters (which were determined UV–Vis spectroscopically by means of the adequate reference compounds) are listed in Table 1. Figure 1 shows the response patterns of the molecular–microscopic solvent properties on the overall IL mole fraction range. It can be observed that, in general, the binary mixtures with [bmim][PF<sub>6</sub>] exhibit similar dipolarity/polarizability, slightly higher acidity, and lower basicity (except at the lowest concentration of IL) than mixtures with [bmim][BF<sub>4</sub>]. The shape of the *property versus solvent composition* curves 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 $E_T^N$

On the one hand, as it has been mentioned above, the  $E_T^N$  values for the [bmim] ILs lie in the range corresponding to polar HBD solvents (such as short-chain alcohols).<sup>[1,24]</sup> On the other hand, it is known that the  $E_T^N$  scale is particularly sensitive to the HBD ability of the cation of ILs.<sup>[25]</sup> In connection with this, the experimental data reflect the expected results considering that both ILs contain the same cation: the parameter values and the shapes of the curves are similar for the mixtures with both ILs. The  $E_T^N$  values exhibit, in all cases, positive deviation from the ideal behavior. Moreover, whereas in the mixtures with AN, a slight synergetic effect takes place at high IL mole fractions, in the mixtures with MeOH this effect is clearly marked at all compositions. The prominence of the synergetic effect in mixtures with MeOH can be related to the fact that the  $E_T^N$  values of both pure solvents are nearly equal. Synergism on  $E_T^N$  values was reported for the [bmim][PF<sub>6</sub>] + ethanol solvent system.<sup>[26,27]</sup>

It is important to remark that the agreement between the  $E_T^N$  values for MeOH + [bmim][BF<sub>4</sub>] mixtures here determined and the recently reported values<sup>[23]</sup> is excellent ( $\Delta E_T^N \leq 0.02$ ).

#### Dipolarity/polarizability $\pi^*$

The plots presented in Fig. 1 show that  $\pi^*$  values exhibit positive deviations from the ideal behavior, which are more marked when the difference between the molecular–microscopic property of both pure solvents is larger. The  $\pi^*$  values of mixtures with both ILs are similar. For the mixtures with AN, the pattern shows an S type curve, whereas in mixtures with DMF the behavior is nearly ideal. Additionally, the results for MeOH + IL mixtures clearly reflect that the dipolarity/polarizability for these mixtures is

**Table 1.** Solvatochromic parameters  $E_T^N$ ,  $\pi^*$ ,  $\beta$ , and  $\alpha$  for binary mixtures of acetonitrile or dimethylformamide or methanol + [bmim][BF<sub>4</sub>] or [bmim][PF<sub>6</sub>], measured at 25 °C

Parameter	Ionic liquid mole fraction									
	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
AN + [bmim][BF <sub>4</sub> ]										
$E_T^N$	0.62	0.64	0.66	0.67	0.68	0.69	0.70	0.70	0.71	0.72
$\pi^*$	0.86	0.88	0.93	0.97	0.99	1.01	1.01	1.00	1.01	1.01
$\beta$	0.41	0.49	0.48	0.47	0.46	0.45	0.45	0.45	0.45	0.45
$\alpha$	0.58	0.61	0.61	0.61	0.62	0.62	0.63	0.64	0.65	0.66
DMF + [bmim][BF <sub>4</sub> ]										
$E_T^N$		0.56		0.63		0.65		0.67		0.67
$\pi^*$		0.95		0.98		1.00		1.00		1.02
$\beta$		0.68		0.56		0.48		0.42		0.38
$\alpha$		0.33		0.40		0.53		0.59		0.63
MeOH + [bmim][BF <sub>4</sub> ]										
$E_T^N$		0.84		0.83		0.80		0.78		0.77
$\pi^*$		0.95		1.00		1.03		1.04		1.04
$\beta$		0.46		0.47		0.46		0.43		0.41
$\alpha$		0.97		0.92		0.86		0.81		0.77
AN + [bmim][PF <sub>6</sub> ]										
$E_T^N$		0.62	0.64	0.65	0.66	0.67	0.68	0.68	0.69	0.69
$\pi^*$		0.87	0.89	0.91	0.93	0.94	0.96	0.97	0.98	0.98
$\beta$		0.40	0.35	0.30	0.27	0.24	0.22	0.20	0.19	0.17
$\alpha$		0.59	0.62	0.64	0.65	0.66	0.66	0.66	0.67	0.67
DMF + [bmim][PF <sub>6</sub> ]										
$E_T^N$		0.56	0.61	0.65	0.65	0.65	0.66	0.66	0.67	0.67
$\pi^*$		0.94	0.95	0.95	0.95	0.95	0.96	0.97	0.99	1.00
$\beta$		0.71	0.64	0.57	0.48	0.39	0.32	0.25	0.22	0.18
$\alpha$		0.34	0.40	0.46	0.53	0.59	0.60	0.61	0.62	0.63
MeOH + [bmim][PF <sub>6</sub> ]										
$E_T^N$		0.84		0.85		0.83		0.80		0.74
$\pi^*$		1.00		1.01		1.01		1.03		1.00
$\beta$	0.49	0.45		0.26		0.17		0.18		0.20
$\alpha$		0.93		0.98		0.96		0.87		0.77

dominated by the IL showing the largest preferential solvation. These results can be related to the ion indicator of nonspecific interactions which control the solvation pattern. It can be pointed out that the here determined  $\pi^*$  values of MeOH + [bmim][BF<sub>4</sub>] mixtures are, in all cases, higher than those reported previously ( $0.02 \leq \Delta\pi^* \leq 0.16$ ).<sup>[23]</sup>

#### Basicity $\beta$

The plots of  $\beta$  versus solvent composition presented in Fig. 1 reveal that in all cases the basicity values of the mixtures with [bmim][BF<sub>4</sub>] are higher than those of the mixtures with [bmim][PF<sub>6</sub>]. The general trend shows a negative deviation of  $\beta$  from the ideal behavior, excluding AN + [bmim][BF<sub>4</sub>] mixtures. This latter solvent system exhibits a synergetic effect for this property. In connection with this, it is important to notice that the basicity of [bmim][BF<sub>4</sub>] matches that of AN. The response patterns show that the influence of the IL is strong except at the lowest IL concentration, suggesting that the property values are dominated by the anion. These results can be related to the preferential solvation of the solutes by the ILs through the anions, with [BF<sub>4</sub>] being a better solvating species than [PF<sub>6</sub>]. On the other

hand, the calculated basicity of MeOH + [bmim][BF<sub>4</sub>] mixtures is lower than previously reported data ( $0.09 \leq \Delta\beta \leq 0.23$ ).<sup>[23]</sup>

#### Acidity $\alpha$

The plots presented in Fig. 1 show that  $\alpha$  values exhibit positive deviations from the ideal behavior. Two different response patterns can be observed, independently of the IL which takes part in the mixtures: (i) for AN and DMF the parameter values abruptly increase with small increases in cosolvent content, this effect being controlled by the IL; and (ii) the acidity decreases continuously when the IL is added to MeOH exhibiting a positive deviation from the ideal behavior. This last solvation pattern is controlled by the protic solvent. It can be noted that the calculated  $\alpha$  values of MeOH + [bmim][BF<sub>4</sub>] mixtures are lower than those previously reported ( $0.10 \leq \Delta\alpha \leq 0.18$ ).<sup>[23]</sup>

These results can be ascribed to two reasons: on the one hand, Reichardt's dye has a strongly hydrogen-bond accepting phenolate oxygen which interacts with the cation of the IL, and, on the other hand, the  $E_T(30)$  values are the key in the measurements of acidity  $\alpha$ .

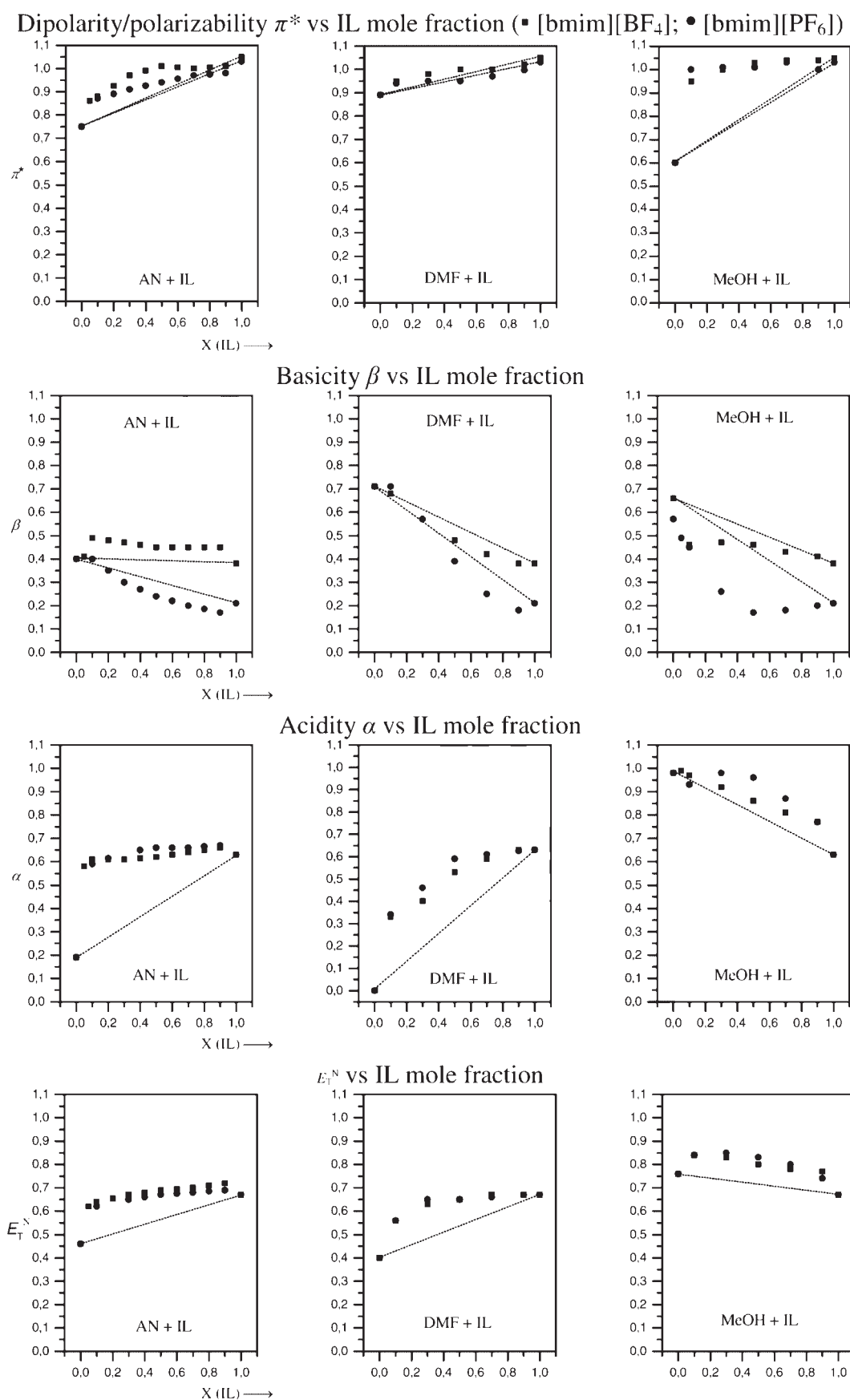


Figure 1. molecular–microscopic solvent properties versus mixed-solvent composition

**Table 2.** Selected binary solvent mixtures and their molecular–microscopic solvent properties

Solvent	Composition	$E_T^N$	$\pi^*$	$\beta$	$\alpha$
Liquid 1	$X_{AN} 0.9/X_{[bmim][BF_4]} 0.1$	0.64	0.88	0.49	0.61
Liquid 2	$X_{AN} 0.9/X_{[bmim][PF_6]} 0.1$	0.62	0.87	0.40	0.59
Liquid 3	$X_{AN} 0.5/X_{[bmim][BF_4]} 0.5$	0.69	1.01	0.45	0.62
Liquid 4	$X_{AN} 0.5/X_{[bmim][PF_6]} 0.5$	0.67	0.94	0.24	0.66
Liquid 5	$X_{DMF} 0.9/X_{[bmim][BF_4]} 0.1$	0.56	0.95	0.68	0.33
Liquid 6	$X_{DMF} 0.9/X_{[bmim][PF_6]} 0.1$	0.56	0.94	0.71	0.34
Liquid 7	$X_{MeOH} 0.5/X_{[bmim][BF_4]} 0.5$	0.80	1.03	0.46	0.86
Liquid 8	$X_{MeOH} 0.5/X_{[bmim][PF_6]} 0.5$	0.83	1.01	0.17	0.96

It is worth noticing that the MeOH + [bmim][PF<sub>6</sub>] mixtures exhibit a higher HBD ability than the MeOH + [bmim][BF<sub>4</sub>] mixtures. Considering that these solvents systems differ only in the nature of the anion, this behavior can be connected with an anion effect on the acidity: the HBD ability is controlled by the HBA ability of the anion. The more basic the anion, the greater the effect and this is particularly significant in a protic solvent such as MeOH.

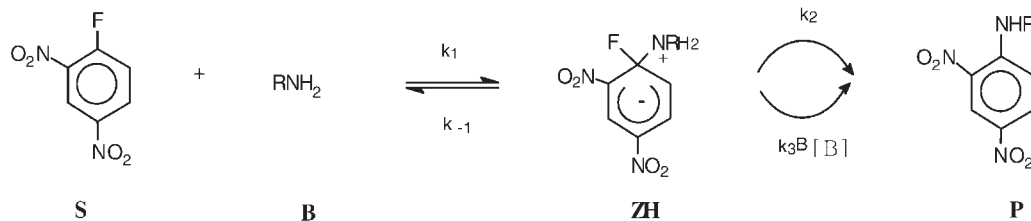
### Selection of 'new solvents'

As it is known, binary mixtures of solvents can be deliberately used to modify particular chemical characteristics of a 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 objective of providing 'new liquids' with particular solvating properties. It should be remarked that, in order to compare the behavior of [bmim][PF<sub>6</sub>] with respect to [bmim][BF<sub>4</sub>], the selected mixtures are of similar concentration for both ILs. The proposed 'new solvents' are presented in Table 2.

### General trends

Solvents 1 and 2 exhibit similar changes with respect to AN. On the one hand, the basicity remains constant or is slightly increased, the dipolarity/polarizability being moderately increased. On the other hand, the acidity is markedly increased. These new liquids are also comparable with respect to their HBD ability and dipolarity/polarizability but differ in the HBA ability which is slightly higher for liquid 1.

Solvent 3 exhibits a slightly higher dipolarity/polarizability than solvent 4, whereas this liquid is a slightly better HBD solvent. In spite of this, it is the basicity that clearly characterizes the solvation behavior of each liquid, solvent 3 being nearly two times more basic than solvent 4.

**Scheme 1.**

The changes observed in solvents 5 and 6 with respect to DMF are similar to those observed in solvents 1 and 2, the increases in  $\alpha$  values being smaller than those for AN. Both liquids have practically the same solvation pattern.

Solvents 7 and 8 show dipolarity/polarizability and basicity values comparable to those of the pure ILs, the acidity values being greatly increased with respect to the values of both ILs. From the comparison of their properties, it can be observed that the main divergence between them lies in the HBA ability which is higher for liquid 7.

### Solvent effects on chemical processes: Aromatic nucleophilic substitution reactions

In order to investigate this type of binary solvent systems as media to carry out chemical reactions, a kinetic study of the S<sub>N</sub>Ar reaction between FDNB and the primary amine BU was performed in some selected binary mixtures with AN and DMF, at 25 °C. Moreover, it is of interest to evaluate the behavior of the individual binary mixtures selected as 'new solvents'.

The reactions were carried out at pseudo-first-order conditions: they yielded the expected product [N-(2,4-dinitrophenyl)1-butylamine] in quantitative yield and proved to be first order in the corresponding substrate. The second-order rate constants  $k_A$  were calculated from the experimental pseudo-first-order rate constants  $k_\phi$  and the appropriate amine concentration. At this point it is important to remark that the reactions carried out in MeOH + IL mixtures do not generate N-(2,4-dinitrophenyl)1-butylamine in a quantitative way.

We assume that the reaction proceeds by the classical two-step mechanism shown in the Scheme 1. Application of the steady-state approximation for the concentration of ZH,  $d[ZH]/dt = 0$ , yields Eqn (1) for the second-order reaction rate constant  $k_A$ .

$$k_A = \frac{k_1 (k_2 + k_3^B [B])}{k_{-1} + k_2 k_3^B [B]} \quad (1)$$

**Table 3.** Second-order rate constants  $k_A$  ( $\text{l mol}^{-1} \text{s}^{-1}$ ) and pseudo-first-order rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) for the reaction between 1-fluoro-2,4-dinitrobenzene ( $4 \times 10^{-5} \text{ M}$ ) and 1-butylamine in (AN or DMF + IL) binary mixtures measured at  $25^\circ \text{C}$  (including the data in the pure molecular solvents)

Solvent	$X_{\text{IL}}$	[1-BU]/M				$k_A$
		0.002	0.004	0.006	0.008	
AN + [bmim][BF <sub>4</sub> ]	0 <sup>a</sup>	0.0150	0.0304	0.0454	0.0600	7.60
	0.1	0.0316	0.0623	0.0904	0.1185	14.4
	0.2	0.0344	0.0670	0.0950	0.1260	15.1
	0.3	0.0360	0.0660	0.1000	0.1342	16.4
	0.4	0.03650	0.0710	0.1040	0.1400	17.2
	0.5	0.0370	0.0740	0.1074	0.1440	17.7
	0.6	0.0359	0.0743	0.108	0.1420	17.6
	0.7	0.0398	0.073	0.1043	0.135	16.0
	0.8	0.0400	0.0733	0.100	0.121	13.4
AN + [bmim][PF <sub>6</sub> ]	0.1	0.0140	0.0297	0.0476	0.0681	7.60
	0.2	0.0161	0.0322	0.0500	0.0710	8.98
	0.3	0.0168	0.0320	0.0470	0.0625	9.01
	0.4	0.0163	0.0330	0.0526	0.0733	9.49
	0.5	0.0168	0.0329	0.0578	0.0761	10.1
DMF + [bmim][PF <sub>6</sub> ]	0 <sup>b</sup>	0.0714	0.1492	0.230	0.313	38.9
	0.1	0.0336	0.1180	0.2344	0.2144	32.9
	0.2	0.0400	0.1200	0.183	0.2080	28.4
	0.3	0.0545	0.1150	0.1560	0.2130	25.8
	0.4	0.0590	0.1270	0.1510	0.198	22.1

<sup>a</sup> Ref. 31.  
<sup>b</sup> Ref. 28.

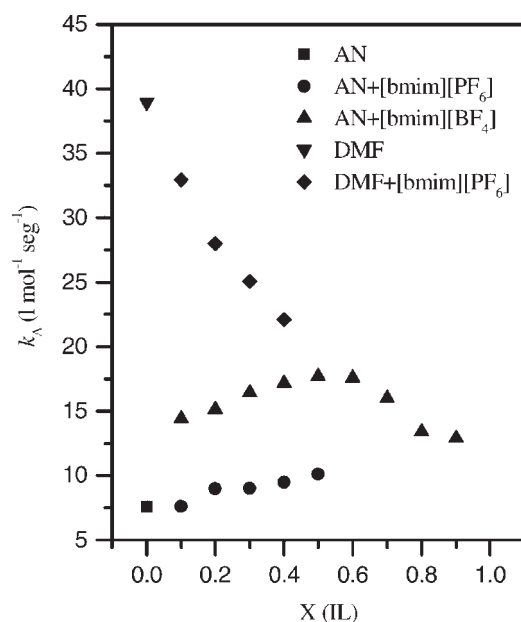
For the condition  $k_{-1} \ll k_2 + k_3^B[B]$  Eqn (1) is reduced to  $k_A = k_1$ , the formation of the intermediate is rate limiting, and the reaction is not base catalyzed. If the condition is not obeyed, the decomposition of the intermediate is rate limiting, and base catalysis is observed, the kinetic form of the catalysis depending on the relative magnitudes of  $k_{-1}$  and  $k_2 + k_3^B[B]$ .

Table 3 presents the experimental pseudo-first-order rate constants  $k_{\text{obs}}$  and the second-order rate constants  $k_A$  for reactions performed in AN + IL solvent systems. It can be pointed out that in mixtures with [bmim][BF<sub>4</sub>] the reaction was explored at the whole range of solvent composition, while in mixtures with [bmim][PF<sub>6</sub>] it was explored just from pure AN up to  $X_{\text{IL}} = 0.5$ . This can be related with the fact that at high IL concentrations the medium viscosity produces a disturbing trend in the results ( $\eta_{[\text{bmim}][\text{BF}_4]} = 154(20) \text{ cP}$ ;  $\eta_{[\text{bmim}][\text{PF}_6]} = 371(20) \text{ cP}$ ).<sup>[9]</sup> The kinetic data for the reaction carried out in DMF + [bmim][PF<sub>6</sub>] mixtures from pure DMF up to  $X_{\text{IL}} = 0.5$  are additionally presented. Moreover, with respect to the reactions carried out in both pure ILs, the formation of a colored 'complex' is evidenced as the substrate is dissolved. The kinetic results presented in Table 3 show that no acceleration in rate is produced for an increasing amount of amine, so the reactions do not exhibit base catalysis and the formation of the intermediate is rate determining. This trend is reasonable considering that base catalysis, in general, is

not operative in  $S_N\text{Ar}$  reactions with primary amines as nucleophiles.

In order to analyze the changes in the second-order rate constant when the IL is added to the molecular solvent, the plots  $k_A$  versus solvent composition are shown in Fig. 2. According to the kinetic response of the reactive systems, the following observations can be made:

- Undoubtedly, a synergetic effect on the reaction rate occurs in the case of AN + [bmim][BF<sub>4</sub>]: in some binary mixtures the  $k_A$  values are higher than those in pure AN and in the ( $X_{\text{AN}} 0.1/X_{\text{IL}} 0.9$ ) mixture. It can be observed that  $k_A$  values experiment a remarkable enhance when small amounts of IL are added to the molecular solvent. Focusing the attention on the proposed new solvents, the  $k_A$  values increase 90 and 133% (referred to the value in AN) at  $X_{\text{IL}} = 0.1$  (solvent 1) and at  $X_{\text{IL}} = 0.5$  (solvent 3), respectively. This special kinetic synergetic behavior was manifested in  $S_N\text{Ar}$  reactions between FDNB and secondary amines developed in some binary mixtures of molecular solvents, in which base catalysis is operative. In this case it is concluded that this effect is concerned with a complex combination of factors related to the variation of the influence of base catalysis (which changes with solvent composition) and to specific solvent



**Figure 2.** Plots of  $k_A$  versus  $X_{IL}$  for the reaction of 2,4-DNFB and 1-BU in (AN or DMF + [bmim][BF<sub>4</sub>] or [bmim][PF<sub>6</sub>]) binary mixtures (including the data in the pure molecular solvents)

effects, particularly hydrogen-bond interactions.<sup>[29]</sup> Here, it can be remarked that the synergism is manifested in non-catalyzed reactions.

- (ii) The  $k_A$  values experiment a slight enhancement in AN + [bmim][PF<sub>6</sub>] mixtures. As it is shown the reaction rate remains unchanged at  $X_{IL} = 0.1$  (solvent 2) while the second-order rate constant undergoes a percentage increase of 33% at  $X_{IL} = 0.5$  (solvent 4).
- (iii) If the kinetic data in mixtures with AN are compared between them the ratios corresponding to the new solvents (liquid 1/liquid 2 and liquid 3/liquid 4) are  $k_{A[bmim][BF_4]}/k_{A[bmim][PF_6]} = 1.9$  and 1.75 respectively, indicating that the system is near twofold more reactive in mixtures with [bmim][BF<sub>4</sub>] than in mixtures with [bmim][PF<sub>6</sub>].
- (iv) With respect to the reaction performed in DMF + [bmim][PF<sub>6</sub>] mixtures, the shape of the curve reveals that  $k_A$  values decrease continuously with the increase in the IL concentration.

At this point, it is of interest to relate the kinetic data with the molecular–microscopic solvent properties with the purpose to

aid in the interpretation of the solvent effects on the explored reaction.

#### Correlation analysis

The often linear correlation between empirical solvent parameters and other solvent-dependent properties (e.g., logarithms of rate, equilibrium constants) can be considered as manifestations of general free energy relationships (LFER). In order to interpret quantitatively the influence of the solvent effects on the explored reaction we have correlated the reported kinetic data and the quantified molecular–microscopic solvent properties by means of the multiparametric approach developed by Kamlet *et al.*<sup>[14]</sup> [Eqn (2)]:

$$\log k_A = Y + s\pi^* + a\alpha + b\beta \quad (2)$$

where  $s$ ,  $a$ , and  $b$  measure the relative susceptibilities of the reactive system with respect to the solvent properties (dipolarity/polarizability, HBD, and HBA ability). The results are presented in Table 4. As can be seen, the correlations are good. The signs and values of the  $s$ ,  $a$ , and  $b$  correlation coefficients reveal the following: (i) the incidences of the solvation effects ascribed to the dipolarity/polarizability and HBA character of the solvent are more important than that attributed to the HBD solvent ability; (ii) the dipolarity/polarizability and HBA solvent character manifest positive influence on  $k_A$  values whereas, in contrast, the incidence of solvation effects originated on the solvent HBD capability is negative. The data presented in Table 4 reveal that, in general, an accelerating effect on the reaction rate can be attributed to a combination of the dipolarity/polarizability and HBA ability of the solvent. Moreover, it can be pointed out that the observed kinetic synergetic effect on  $k_A$  values can be clearly related with the solvent basicity.

The results derived from the correlation analysis reveal that: (i) the reaction rate increases by the increasing solvent dipolarity/polarizability since the zwitterionic intermediate is more polar than the reactants and the activated complex leading to ZH is favored by increasing solvent dipolarity/polarizability; (ii) the reaction rate increases by the increasing solvent HBA ability for the reason that the zwitterionic intermediate and the corresponding transition state have HBD character owing to the extra hydrogen of the primary amine, and (iii) the reaction rate decreases with the increasing HBD ability of the solvent for the reason that the amine can be stabilized via hydrogen-bonding interactions.

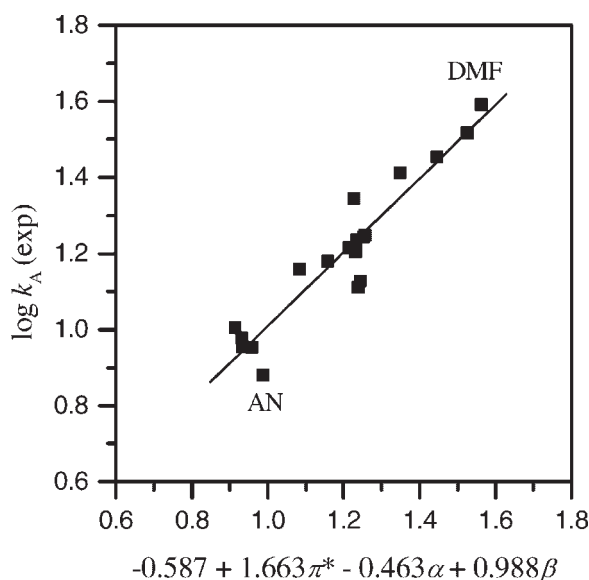
**Table 4.** Correlation coefficients ( $r$  and  $r^2$ ), standard deviation ( $SD$ ), intercept ( $Y$ ), and the parameters  $s$ ,  $a$ , and  $b$  (and their standard errors) and the number of data points ( $n$ ) corresponding to  $\log k_A = Y + s\pi^* + a\alpha + b\beta$  for the reaction between 2,4-DNFB and BU in binary mixtures (including the data in pure molecular solvents)

$r$ ( $r^2$ )	$SD$	$Y$ ( $s_Y$ )	$s$ ( $s_s$ )	$a$ ( $s_a$ )	$b$ ( $s_b$ )	$n$
0.947 (0.896)	0.0432	-3.249 (1.359)	2.661 (0.915)	-0.0059 (0.453)	6.076 (2.111)	10 <sup>a</sup>
0.904 (0.817)	0.065	-0.385 (0.259)	1.281 (0.427)	-0.103 (0.261)	0.821 (0.252)	15 <sup>b</sup>
0.946 (0.895)	0.073	-0.587 (0.274)	1.668 (0.418)	-0.463 (0.195)	0.988 (0.233)	20 <sup>c</sup>

<sup>a</sup> AN; AN + [bmim][BF<sub>4</sub>] mixtures ( $X_{AN} 0.1/X_{IL} 0.9$ ).

<sup>b</sup> AN; AN + [bmim][BF<sub>4</sub>] mixtures ( $X_{AN} 0.1/X_{IL} 0.9$ ), AN + [bmim][PF<sub>6</sub>] mixtures ( $X_{AN} 0.1/X_{IL} 0.5$ ).

<sup>c</sup> AN, DMF, AN + [bmim][BF<sub>4</sub>] mixtures ( $X_{AN} 0.1/X_{IL} 0.9$ ), AN + [bmim][PF<sub>6</sub>] mixtures ( $X_{AN} 0.1/X_{IL} 0.5$ ), DMF + [bmim][PF<sub>6</sub>] mixtures ( $X_{AN} 0.1/X_{IL} 0.4$ ).



**Figure 3.** Plot of the experimental  $\log k_A$  values for the reaction of 2,4-DNFB and 1-BU versus the predicted values calculated by the data of Table 4 for  $n = 20$

The correspondence between the experimental values of  $\log k_A$  and the corresponding values calculated by the data reported in Table 4 for  $n = 20$  was investigated. The results show that the linear correlation is good:  $\log k_A(\text{exp.}) = 0.039 + 0.970 \times \log k_A(\text{calc.})$ ;  $r = 0.945$ ;  $SD = 0.067$ . The corresponding plot is presented in Fig. 3. In connection with this and in order to illustrate the applicability of these results, the second-order rate constants at  $X_{[\text{bmim}][\text{PF}_6]} = 0.9$  were estimated:  $k_{A(\text{AN}+[\text{bmim}][\text{PF}_6])} = 7.43$  ( $\text{l mol}^{-1} \text{s}^{-1}$ );  $k_{A(\text{DMF}+[\text{bmim}][\text{PF}_6])} = 8.71$  ( $\text{l mol}^{-1} \text{s}^{-1}$ ).

## CONCLUSIONS

- The comparison of the molecular–microscopic solvent parameters corresponding to the explored binary mixtures with both ILs considered at similar mixed-solvent composition reveals that the difference between the explored mixtures is centered on the basic character.

For the proposed ‘new solvents’ 1, 2, 5, and 6, while it can be observed that the dipolarity/polarizability and basicity are similar to those of AN and DMF, the acidity is quite different being highly increased, particularly in the case of AN.

The most important difference between solvents 3 and 4 resides fundamentally in their basic character.

The individual selected solvent mixtures with MeOH (solvents 7 and 8) clearly differ in the  $\beta$  property.

The particular properties of these selected ‘new solvents’ converted them in an appropriate media for chemical processes.

- The multiparameter correlation treatment of the kinetic data with the molecular–microscopic solvent properties allowed us to determine the incidence of each type of solvent property on the kinetics of the reaction. For the explored reactive systems the solvation effects are dominated by both the dipolarity/polarizability and the basicity of the media, contributing these solvent properties to accelerating the chemical process.

The reactions carried out in solvents with AN +  $[\text{bmim}][\text{BF}_4]$  exhibited higher reaction rates than the ones performed in

mixtures with AN +  $[\text{bmim}][\text{PF}_6]$ . Considering that the reactions are noncatalyzed, these results can be related to a more efficient solvation of the transition state when the anion is  $[\text{BF}_4]$ . Moreover, the higher  $k_A$  values detected for the reaction performed in DMF +  $[\text{bmim}][\text{PF}_6]$  mixtures with respect to the mixtures with AN can also be related with the high HBA ability of the media.

The observed special kinetic synergetic effect in AN +  $[\text{bmim}][\text{BF}_4]$  mixtures can be principally attributed to the solvent basicity being an evidence that the mixed solvents behave as a ‘new solvents’ with particular solvating properties. Moreover it can be noted that this particular kinetic effect was not observed previously in noncatalyzed  $S_N\text{Ar}$  reactions developed in binary organic solvent systems.

## EXPERIMENTAL

### Reagents and solvents

2,4-DNFB and BU were purified as previously reported.<sup>[30,31]</sup>  $[\text{bmim}][\text{BF}_4]$  and  $[\text{bmim}][\text{PF}_6]$  were prepared according to literature procedure.<sup>[32,33]</sup> The crude ILs were purified through alumina and dried under vacuum. Solvatochromic indicators [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate; *N,N*-diethyl-4-nitroaniline; 4-nitroanisole; 4-nitroaniline; 4-nitrophenol], and molecular solvents were prepared and/or purified as previously reported.<sup>[30,31]</sup> The binary mixtures were prepared prior to use and stored under anhydrous conditions.

### Solvatochromic parameter measurements and calculations

The spectroscopic data were obtained with a Perkin-Elmer Lambda 40 UV/Vis spectrophotometer, equipped with a thermostatic cell holder. The indicator solutions were prepared just prior to use. The  $E_T(30)$  and  $E_N^N$  parameters were calculated according to the procedure reported elsewhere.<sup>[1]</sup> The microscopic properties  $\pi^*$ ,  $\beta$ , and  $\alpha$  were calculated according to general expressions collected by Marcus.<sup>[22]</sup>

### Kinetic procedures

The kinetics of the reactions was studied by UV–Vis spectrophotometry, essentially by the procedure previously described.<sup>[30,31]</sup> DNFB was dissolved in the pure solvents and the corresponding binary mixtures were prepared at the proper concentrations in order to yield the required IL mole fractions in the cell.

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