Solvatochromic dipolarity micro-sensor behaviour in binary solvent systems of the (water + ionic liquid) type: application of preferential solvation model and linear solvation energy relationships

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The type of specific intermolecular and interionic interactions that are established when an ionic liquid is dissolved in water was here analysed. The study of the solvatochromic response of dipolarity micro-sensors based on Reichardt $E_T(30)$ and Kamlet–Abboud–Taft solvent scales and the application of the solvent exchange model confirmed the formation of different intersolvent complexes in binary mixtures of (water + [C$_4$mim] [BF$_4$]/[Br]) type. These complexes provide H-bond or electron pairs to the polar network, respectively. Moreover, for 4-methoxybenzenesulfonyl chloride hydrolysis reaction in the (water + [C$_4$mim] [BF$_4$]) system, a higher inhibition (13 times) on the k_{obs} values was observed. Multiple linear regression analysis that allows confirming the solvent effect upon the reactive system is due to the hydrogen-bond donor properties of intersolvent complex formed. Then, the correlation between two different solvent-dependent processes proved to be successful. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: binary solvent mixtures; empirical parameters; ionic liquid; linear solvation energy relationships; microscopic properties; solvatochromic probe

INTRODUCTION

Solvatochromic chemical probes have frequently been used for characterizing molecular solvents and their binary solvent mixtures.[1] Different single and multiparametric empirical scales of molecular-microscopic solvent properties have been developed from reference solutes that behave as probes reflecting changes in their solvation shell through variations in the ultraviolet (UV)-visible (Vis) absorption spectra. The E_T (30) scales of Dimroth and Reichardt and the Kamlet–Abboud–Taft (KAT's) scale, the latter constructed by the solvatochromic comparison method, are those mostly used in the uniparametric and multiparametric approaches, respectively.[2] These empirical solvent scales allow to obtain quantitative values of microscopic solvent properties and have been successfully applied to 'new environmentally friendly solvents' such as ionic liquids (ILs).[3]

The study of ILs and water (W) mixtures may provide some light on the equally unique properties of ILs. Polarity analysis has a great significance on the outcome of chemical reactions in solvent systems with different degree of aggregation. But because of the diverse behaviours exhibited by these liquids, in some cases, it becomes difficult to correlate their chemical structure with the microscopic parameters and/or with the reactivity. Consequently, contributions in this direction are of particular interest, especially in (W + ILs) systems. In binary mixtures of ILs with molecular solvents, in which preferential solvation is operative, the analysis of the multiple interactions arising from

each of the components must be thorough and rigorous. In this sense, it is our intention to clarify and to deepen the interpretation of some results. Some disagreements found in the literature not only about these property values but also in the interpretation and application of these scales lead us to consider whether the values emerging from the application of a particular scale are a consequence of an intrinsic property of the analysed system or alternatively a combination of factors involved in the process. At first, our attention has been focused on deducing the type of specific intermolecular and interionic interactions that are established between dipolarity micro-sensors and each component of the binary solvent mixture (W + ILs). Also, from this analysis, it could be possible to predict a more general behaviour of a solute within a reagent system. To this end, we chose a hydrolysis reaction in order to compare both solvent-dependent processes.

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The aims of this work are as follows: (a) determining a set of empirical solvatochromic parameters in order to obtain numerical values of the polarity for the binary (W + ILs) solvent systems under study; (b) analysing the variation of the solvatochromic parameters as a function of IL concentration; (c) understanding what type of force dominate in a particular property; (d) applying a preferential solvation model to the solvatochromic data[4] for the systems here studied; and (e) analysing how solvatochromic parameters influence the microscopic properties of these solvent systems on the chemical reactivity.

The ILs selected are composed of 1-butyl-3-methylimidazolium ([C$_4$mim]) as a cation and two different counterions: bromide [Br], representative of halide ions with localized charge and tetrafluoroborate [BF$_4$], representative of spherical inorganic anions, with an equally distributed negative charge on the four fluorine atoms. The incidence of IL anions in the solvation pattern of aqueous binary solvent mixtures will also be analysed.

RESULTS AND DISCUSSION

The $E_T(33)$ dye (**IA**) is chemically similar to Reichardt's dye. This probe with two chlorine atoms in its molecular structure is less hydrophobic and a better electron acceptor than that of the E_T(30) dye. In the present study, the $E_T(30)$ parameter was obtained from the experimental data of the indicator **IA** following equation $E_T(30) = 0.99(\pm0.03)E_T(33) - 8.1(\pm1.7)$ with $r = 0.9953$ and $n = 20$.[5]

The KAT multiparametric scale assigns different parameters to each particular solvent characteristic: polarizability/dipolarity (π^*), hydrogen-bond acceptor (HBA) capacity (β) and hydrogen-bond donor (HBD) ability (α).[2]c The microscopic properties were measured evaluating the solvatochromic behaviour of different molecular probes (Scheme 1).

SOLVATOCHROMIC RESPONSE

E_T^N polarity

The solvatochromism of probe **IA** was studied in binary mixtures of (W + ILs). The [C$_4$mim] [BF$_4$] is one of the most studied ILs, and the $E_T(33)$ values for that binary mixture in the whole range of compositions were previously reported by other researchers.[6] Some differences in the published values can be observed, especially for pure [C$_4$mim] [BF$_4$]. The $E_T(33)$ value obtained in this work is 61.60 kcal mol^{-1}. The values of all parameters determined in this work and the already published ones are presented in Table 1.
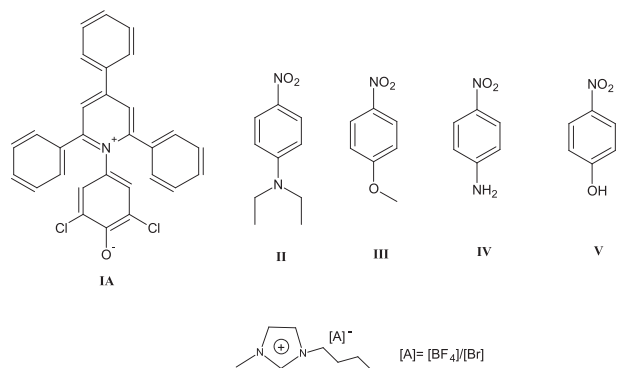
Scheme 1. Molecule structures of the solvatochromic dyes and ILs employed

Additionally, we have determined the $E_T(33)$ values when small amounts of both ILs are added to W so as to analyse how this addition can alter its molecular-microscopic properties. Thus, we can evaluate the link type that is established between the components of the ILs. In this sense, from the solvatochromic response analysis of this parameter, we can infer about what part of ILs interacts with W and with the solute (**IA**).

Figure 1 shows the variation of E_T^N values with the mole fraction of [C$_4$mim] [Br]/[BF$_4$] ILs in [W + IL] mixtures. In turn, the insert in Fig. 1 shows the response patterns of E_T^N values upon the addition of small amounts of IL. Note that the mole fraction corresponding to 2 M is almost 0.1.

In the same insert, it can be noticed that the microscopic properties of W are substantially modified by this small amount of IL (up to 0.2 M). The break of the hydrogen-bonding interactions of W produces a decrease in the polarity (the E_T^N values decrease). Both systems exhibit the same behaviour.

The break point observed in each of the patterns would indicate changes or a new arrangement in the solvation microsphere of the indicator. Some authors have related these changes with a change in the IL micro-aggregation process, associating them with a critical aggregation concentration (CAC). This tendency to self-aggregate was also observed in [C$_4$mim] [BF$_4$] aqueous solutions employing conductivity and surface tension measurements (CAC = 0.8 M).[7] In this work, we observed a break point in the E_T^N parameter, which can be related with polarity changes of the solvent mixture on the indicator solvation microsphere. These values are 0.75 and 1.32 M for [C$_4$mim] [BF$_4$]/[Br], respectively. The former is in excellent agreement with the reported one.[8] The differences between the CAC values would indicate that the cation–anion interaction could be greater for [C$_4$mim] [BF$_4$].

Finally, these values indicate that the equilibrium that leads to the formation of an intersolvent complex is more favoured when the anion is [BF$_4$], probably because of a greater IL tendency to interact with the W molecules. For this concentration range, the E_T^N polarity decrease (in percentage) for the mixtures with [C$_4$mim] [BF$_4$]/[Br] is 18% and 8%, respectively. This result would confirm the previous conclusion, that is, a higher interaction of W with the [BF$_4$] anion.

The composition of the binary mixtures, expressed as IL mole fraction (X_{IL} = 0.1–0.7/1.0) shows two somewhat different patterns, depending on the anion. The mixtures with [C$_4$mim] [BF$_4$] display an almost ideal behaviour while the ones with [Br] anion present a negative deviation of the parameter. Initially, this behaviour can be described in terms of the analysis of equilibrium intersolvent complex formation. Considering that the [C$_4$mim] [BF$_4$] establishes hydrogen bonding with W to a greater extent than [C$_4$mim] [Br], the constant of this equilibrium will be different for both ILs.[9] Thus, the prevalence of the ion-pair character in the IL will determine its interactions with the micro-sensor or W. Taking this into account, it is reasonable to think that the solvation microsphere of the probe will be preferentially solvated by [C$_4$mim] [Br].

In order to get a deeper insight on the solvation abilities of these ILs and compare the solvation behaviour between cations and anions, we applied a general preferential solvation model based on two solvent exchange processes.[4] This model allows to calculate the preferential solvation parameters (*f*) that measure the tendency of a probe to be solvated by the IL (S2) and the 'mixed solvent' or 'intersolvent complex' (S12), with reference to W (S1) in its solvation sphere. Thus, it is possible

Table 1. Solvatochromic parameters $E_T(33)$, E_T^N, π^*, β and α for (W + [C$_4$mim] [A]) systems at 25 °C, where [A] are the [BF$_4$] and [Br] counterions

Ionic liquid	[C$_4$mim] [A] (mol L^{-1})	[C$_4$mim] [A] mole fraction	$E_T(33)$ (kcal mol^{-1})	E_T^N	$\pi^*_{(II)}$	$\pi^*_{(III)}$	$\beta_{(IV)}$	$\beta_{(V)}$	$\alpha_{(II, IV)}$	$\alpha_{(III, V)}$	$\alpha_{(avg)}$
[C$_4$mim] [BF$_4$]											
	0		69.90[a]	1.00	1.34[b]	1.10[c]	0.17[b]	0.64	0.93	1.08	1.01
	0.20		69.56	0.94	1.34	1.06	0.26	0.61	0.90	1.10	1.00
	0.50		69.16	0.92	1.34	1.08	0.28	0.61	0.86	1.04	0.95
	0.70		68.73	0.91	1.34	1.10	0.30	0.62	0.83	1.00	0.92
	0.95		68.58	0.91	1.32	1.09	0.34	0.61	0.83	0.99	0.91
	1.00		68.48	0.90	1.31	1.09	0.35	0.62	0.83	0.99	0.91
	1.30		67.59	0.88	1.27	1.06	0.38	0.61	0.80	0.96	0.88
	1.40		67.43	0.87	1.24	1.06	0.42	0.61	0.82	0.95	0.89
	1.80		67.43	0.87	1.22	1.05	0.43	0.62	0.82	0.95	0.89
	2.0		67.12	0.87	1.20	1.05	0.44	0.61	0.83	0.93	0.88
		0.1	67.12[a]	0.86	1.22[b]	1.03[c]	0.35[b]	0.59	0.82	0.96	0.90
		0.2	66.05[a]	0.83	1.19[b]	0.99[c]	0.37[b]	0.58	0.77	0.92	0.85
		0.3	65.60[a]	0.82	1.15[b]	0.99[c]	0.39[b]	0.65	0.77	0.88	0.83
		0.4	64.61[a]	0.79	1.14[b]	0.96[c]	0.39[b]	0.63	0.72	0.84	0.78
		0.5	64.50[a]	0.78	1.11[b]	0.96[c]	0.38[b]	0.59	0.74	0.84	0.79
		0.6	63.87[a]	0.76	1.11[b]	0.96[c]	0.36[b]	0.58	0.70	0.80	0.75
		0.7	63.60[a]	0.76	1.08[b]	0.96[c]	0.38[b]	0.56	0.70	0.78	0.74
		0.8	62.90[a]	0.73	1.07[b]	0.95[c]	0.35[b]	0.53	0.66	0.75	0.71
		0.9	62.60[a]	0.73	1.06[b]	0.94[c]	0.35[b]	0.46	0.65	0.75	0.70
		1.0	61.42[a]	0.69	1.05[b]	0.89[c]	0.35[b]	0.49	0.58	0.71	0.64
[C$_4$mim] [Br]											
	0.20		69.56	0.94	1.36	1.10	0.24	0.62	0.88	1.06	0.97
	0.50		69.23	0.93	1.37	1.06	0.27	0.64	0.84	1.07	0.96
	0.70		68.89	0.92	1.37	1.03	0.30	0.63	0.82	1.07	0.95
	0.95		68.73	0.91	1.37	1.01	0.34	0.63	0.80	1.08	0.94
	1.00		68.53	0.91	1.37	1.01	0.35	0.63	0.79	1.07	0.93
	1.20		68.40	0.90	1.37	1.02	0.36	0.59	0.77	1.05	0.91
	1.40		68.01	0.89	1.37	1.00	0.39	0.57	0.73	1.04	0.89
	1.80		67.43	0.87	1.36	1.15	0.42	0.58	0.71	0.87	0.79
	2.00		67.35	0.87	1.35	1.20	0.41	0.60	0.70	0.81	0.76
		0.1	66.03	0.83	1.33	1.27	0.43	0.69	0.64	0.65	0.64
		0.2	63.61	0.76	1.29	1.27	0.55	0.72	0.49	0.48	0.48
		0.3	63.47	0.75	1.27	1.27	0.57	0.71	0.49	0.47	0.48
		0.4	63.05	0.74	1.26	1.27	0.59	0.69	0.47	0.45	0.46
		0.5	63.61	0.74	1.23	1.27	0.61	0.69	0.54	0.49	0.51
		0.6	63.05	0.74	1.20	1.27	0.63	0.69	0.52	0.45	0.48
		0.7	63.11	0.74	1.20	1.27	0.60	0.69	0.53	0.45	0.49

[a]Data from Ref.[6]
[b]Data from Ref.[5]
[c]Data from Ref.[10]

to describe quantitatively the composition of the solvation shell of the probe.

The values of the preferential solvation parameters ($f_{2/1}$, $f_{12/1}$ and $f_{12/2}$) obtained by applying the corresponding equation to experimental wavenumber values of indicators **IA**, **II**, **III**, **IV** and **V** in (W + [C$_4$mim] [Br]/[BF$_4$]) systems are presented in the Supporting information. Table 2 shows a summary of the results of this model application to small amounts of IL (mol L^{-1}) and to higher IL concentrations ($X > 0.1$).

The values of the $f_{2/1}$, $f_{12/1}$ and $f_{12/2}$ parameters suggest that the preferential solvation order for both ILs (up to 2 M) is mixed solvent > W > IL. It is interesting to observe that the $f_{2/1}$ values,

which measure the preferential solvation of the indicator **IA** by IL with reference to W, are less than unity in both systems, indicating that in this range of compositions, the probe–W interactions are significant.

For the mole fraction range, it is important to notice that (a) the preferential solvation orders in these systems are different from the ones obtained for the systems with small amounts of ILs and (b) the probe is sensitive to anion changes in the IL. In fact, the $f_{2/1}$, $f_{12/1}$ and $f_{12/2}$ values suggest that the preferential solvation order is mixed solvent > IL > W for the [BF$_4$] anion. On the other hand, for the systems with [C$_4$mim] [Br], that order is IL > W > mixed solvent. The higher probe solvation for IL when
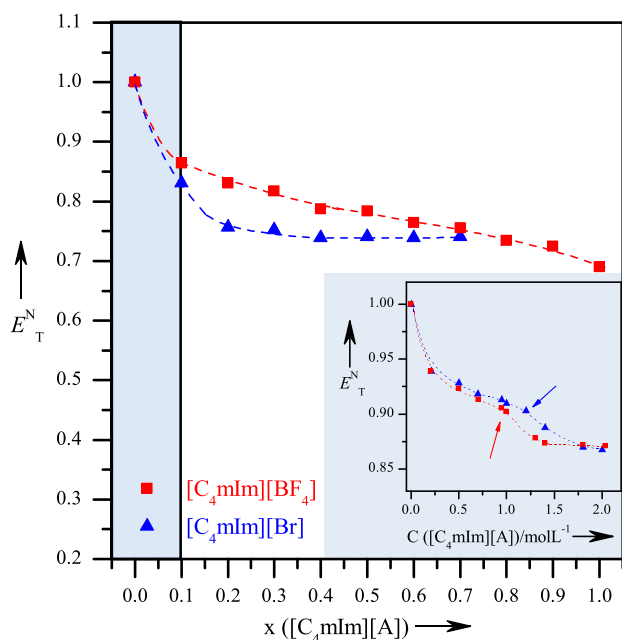
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Figure 1. Variation of E_T^N as a function of IL mole fraction for binary mixtures of [C$_4$mim] [Br]/[BF$_4$] with water. The insert shows the variation of E_T^N in aqueous solutions with small amounts of both ILs

the anion is [Br] is confirmed not only by the deviation from the ideal behaviour observed in this system but also by the preferential solvation order resulting from the application of the corresponding model.

π^*, β and α Parameters (solvent dipolarity/polarizability, basicity and acidity)

In the analysis of the solvatochromic response of the π^* values, it is important to note that the values obtained with micro-sensor **II** are, in general, higher than those calculated with **III** and depend on the anion nature (Table 1). Consequently, in most cases, the analysis from the π^* average values (π_{avg}^*) is not statistically consistent.

Figure 2 shows the response patterns of the molecular-microscopic solvent properties as a function of IL mole fraction or concentration (mol L^{-1}) for both solvent systems. Figure 2(a) presents the plots corresponding to the π_{II}^* trends for [C$_4$mim] [BF$_4$]/[Br]. The insert exhibits the patterns obtained as small amounts of IL are added to pure W.

The dipolarity/polarizability of both systems exhibits a similar behaviour. The mixtures display a continuous decrease with an increase of the IL concentration (mole fraction or mol L^{-1}), exhibiting a nearly linear tendency. The experimental values in the mixtures are very close to the average of the properties from the pure solvents thus indicating an additive behaviour. So, in these mixtures, the solute–solvent interactions do not affect the auto and mutual solvent–solvent interactions.

Considering the intersolvent complex formation and that the highest contribution to π^* value is the electrostatic force from IL, at small concentrations of IL, the micro-sensor measures the complex polarity, mainly the π–π interactions due to ring stacking. In this sense, the higher polarity observed for [C$_4$mim] [Br] in the mole fraction range ($X_{IL} = 0.1$–0.7) is due to a more effective interaction between aromatic rings.

A different behaviour is observed for dye **III** (Table 1),[10] because it remains almost invariable with IL concentration increase (mole fraction or mol L^{-1}). This behaviour is more marked when the counterion is [Br] (from $X_{IL} = 0.1$, the π_{III}^* values plunge into 1.27). At first glance, we could consider two possibilities: either the probe cannot detect small polarity changes or the polarity of the medium remains invariable. This last chance is not possible because dye **IA** was able to detect polarity changes in these systems. This result can be explained considering the structural difference in both indicators. Probe **III** has a lower electron-donor capacity, which determines its solvatochromic behaviour.

The application of the preferential solvation model to **II** dye suggests that at small concentrations of both ILs, the preferential solvation order is mixed solvent > W > IL. This trend was observed for the **IA** probe. It can also be seen that the probe–W interactions are significant in this range of compositions. On the other hand, for higher IL concentrations, the preferential solvation order is IL > mixed solvent > W.

Surprisingly, for dye **III**, the application of this model suggests that probe **III** is solvated indistinguishably by either the mixed solvent or IL or W. This observation holds for both ILs and for the whole range of compositions, which indicates that this probe is not able to sense the polarity variation between the different components of the mixture.

Parameter β was determined by the magnitudes of enhanced solvatochromic shifts for the homomorphic pairs (**II–IV**) and (**III–V**). For each individual indicator, the same behaviour and similar basicity values are observed for both ILs (Fig. 2b and 2c). In the mole fraction range, higher basicity values for [C$_4$mim] [Br] are detected.

In an earlier independent study, hydrogen-bond acceptor abilities of a variety of anions ([BF$_4$], [Cl] and [Br], among others) were reported using phenol and water as H-bond donors. The trend in H-bond acceptor ability found was [Cl] > [Br] >> [BF$_4$].[11] This tendency matches the one obtained in this work and in a previous work comprising (alcohol + IL) binary mixtures.[12]

Table 2. Summary of the preferential solvation order obtained by application of Eqs (1) and (2) to experimental wavenumbers, $10^4 \nu$ (cm^{-1}) of the indicators **IA**, **II**, **III**, **IV** and **V** in (W + [C$_4$mim] [Br]/ [BF$_4$]) systems at 25 °C

| Probe	[C$_4$mim] [BF$_4$] (mol L^{-1})	[C$_4$mim] [Br] (mol L^{-1})	[C$_4$mim] [BF$_4$] mole fraction	[C$_4$mim] [Br] mole fraction
IA	Complex > W > IL	Complex > W > IL	Complex > IL > W	IL > W > complex
II	Complex > W > IL	Complex > W > IL	IL > complex > W	IL > complex > W
III	Low sensitivity	Low sensitivity	Low sensitivity	Low sensitivity
IV	Complex > IL > W	Complex > IL > W	IL > W > complex	Complex > W > IL
V	Low sensitivity	Low sensitivity	Low sensitivity	Low sensitivity
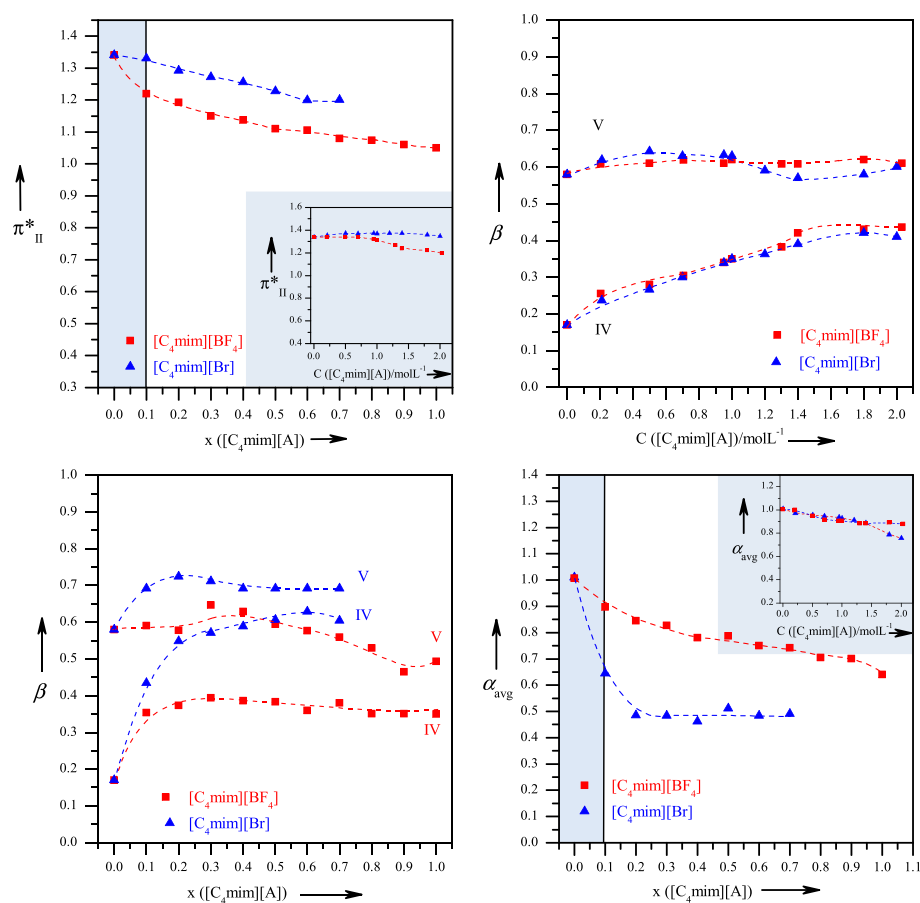
Figure 2. Variation of the π_{II}^*, β (**IV–V**) and α_{avg} parameters as a function of IL mole fraction or concentration (mol L^{-1}) for binary mixtures of [C$_4$mim] [Br]/[BF$_4$] with water. The insert shows the variation of π_{II}^* and α_{avg} parameters in aqueous solutions with small amounts of both ILs

To confirm this observation, we analysed the behaviour when both ILs are added to a molecular solvent that shows only HBA ability. Among the possible solvents, we chose DMSO because both ILs are soluble in it. When the IL is [C$_4$mim] [Br], Reichardt's dye does not show the characteristic long-wavelength absorption, which indicates a strong interaction between acidic protons at C$_2$ of imidazolium cation and the molecular solvent because the protonated species of dye is colourless. Figure 3 shows the Vis absorption spectra of Reichardt's dye dissolved in DMSO, after addition of increasing amounts of [C$_4$mim] [BF$_4$]. The insert exhibits the patterns obtained for [C$_4$mim] [Br].

Analysing the values from the homomorphic probes (**II–IV**) and (**III–V**) separately, the following can be noticed: (a) the difference of β parameter values from probes **IV**
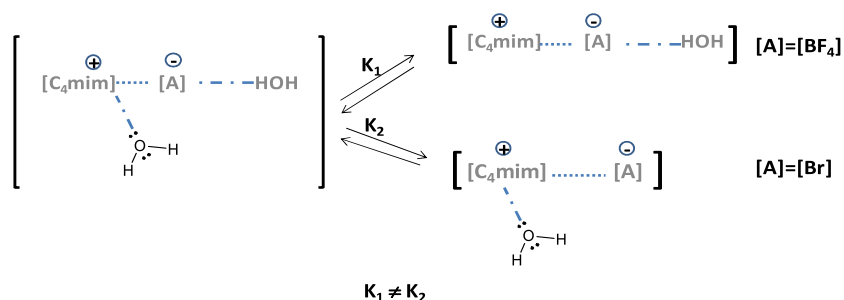
In the first instance, one could think this contradicts what was observed for probe **IA**, where we concluded that the [C$_4$mim] [BF$_4$] interacts more with water, shifting the equilibrium to the mixture complex formation. However, it must be remembered that probe **IA** measures the dipolarity/polarizability and HBD capacity of such complexes, whereas the **IV** measures the HBA characteristics of the solvent system. Because water weakens the cation–anion interactions, the weakest interactions being affected to a greater extent, in the equilibrium of complex formation it interacts with the ILs cation, leaving the [Br] anion freer to interact with the micro-sensor. In this case, the probe is recording the W action via its HBA character with the C$_2$–H of the imidazolic ring (Scheme 2).

This endorses what was observed with micro-sensor **IA** and ratifies that cation–anion interaction for [Br] is weaker than for [BF$_4$], which is in agreement with the findings of other authors where anions derived from strong acids interact weakly with the cation.[13] The previous findings can be represented as two competing equilibria. Scheme 3 shows the intersolvent complex formation equilibrium for both solvent systems. K$_1$ and K$_2$ constants are different in magnitude and dependent on the anion as a consequence of the participation of W through its HBA and HBD abilities. Also, equilibrium between micro-sensor and the intersolvent complex that competes with the intersolvent complex formation must be taken into account. In this sense, when the anion is [Br], a greater interaction between the dye **IA** and protons at C$_2$ of imidazolium cation should be expected.
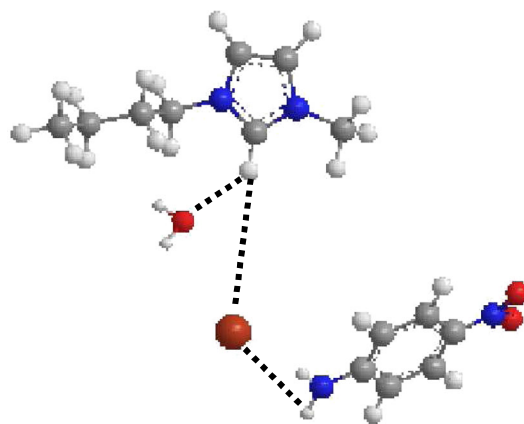
Scheme 2. Graphical representation of the interaction between probe IV and the (W+[C4mim] [Br]) intersolvent complex

and **V**, which reflects the different sensitivities of the probes, indicating different solute–solvent interactions that also depend on the solvent–solvent interactions (Table 1); (b) the β_V values are higher than the ones derived from dye **IV** (which is a weaker HBD probe), and they remain almost constant; and (c) The variation of parameter β_{IV} is higher than that corresponding to β_V for both systems.

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Scheme 3. Representation of the participation of water in the intersolvent complex formation

Figure 3. The UV/Vis absorption spectra of Reichardt's dye dissolved in DMSO, after addition of increasing amounts of [C$_4$mim] [BF$_4$]. The insert shows the same variation for [C$_4$mim] [Br]

This behaviour is not only related with the constancy of the π^*_{III} values but also with the less sensitivity of probe **V** to the basicity changes as compared with probe **IV**. This fact can arise from the different HBD ability and/or electron-donor capacity of the phenoxy/phenol groups in **III–V** probes with respect to the diethylamino/amino groups in **II–IV** indicators. This is confirmed by the application of the preferential solvation model, from which it can be concluded that probe **V** is solvated indistinguishably by either the mixed solvent or IL or W.

Figure 2(b) shows the β_{IV} values at small concentrations of the IL (up to 2 M). They present a continuous increase of the properties, exhibiting an almost linear behaviour. The $f_{2/1}$, $f_{12/1}$ and $f_{12/2}$ values suggest that the preferential solvation order is mixed solvent $>$ IL $>$ W, which is in agreement with the similar behaviour observed for both ILs.

From Fig. 2(c), at low IL mole fractions ($X_{IL} = 0.3$), the parameter manifests a positive deviation from the ideal behaviour in both IL systems, exhibiting a slight synergism with respect to the values in the pure solvents. Then, it remains almost constant. For the systems composed of [C$_4$mim] [BF$_4$], the $f_{2/1}$, $f_{12/1}$ and $f_{12/2}$ values

suggest that the preferential solvation order is IL $>$ W $>$ mixed solvent, while for the systems with [C$_4$mim] [Br], the order is mixed solvent $>$ W $>$ IL. This may be explained by a shift in the equilibrium of the intersolvent complex formation. In this case, the micro-sensor tends to interact more with the complex formed by [C$_4$mim] [Br]. It is interesting to note that a similar behaviour was observed with dye **IA** for the mole fraction range when the IL was [C$_4$mim] [BF$_4$].

The HBD ability of the solvent is described by parameter α. This value is deduced from the $E_T(30)$ value according to the conversion expression proposed by Marcus.[14] We determined the α values for each couple (**II–IV**), (**III–V**) and the corresponding averaged parameters. It is remarkable that parameter α is derived from the values corresponding to the other probes and that the effect of the estimated value of β on the accuracy of the resulting α values is much lower than for the other terms in Marcus equation. Consequently, for the discussion of its behaviour, only the α_{avg} values were considered.

The corresponding plots of parameter α variation versus IL composition (mol L^{-1} concentration or mole fraction) for both IL systems are shown in the Supporting information. Plots corresponding to the α_{avg} values (Fig. 2(d)) show that the acidity exhibits a progressive reduction as the [C$_4$mim] [BF$_4$] composition increases, following an almost linear behaviour. Regarding the mixtures composed of [C$_4$mim] [Br], the acidity experiences a huge decrease up to $X_{IL} = 0.2$ and then remains constant at higher IL compositions, exhibiting a negative deviation from the ideal behaviour. Taking into account that the selected solvent systems differ only in the nature of the anion and that the acidity α is mainly determined by the cation nature, the observed behaviour in α values is connected with an anion effect on the acidity. As it is expected, the pattern of α values is similar to the one corresponding to parameter E_T^N. Likewise, the acidity of the systems with a [BF$_4$] anion is higher than that corresponding to the systems with a [Br] anion. This result can be interpreted considering the behaviour observed for the homomorphic probes (**II–IV**). As small amounts of IL are incorporated to pure W, the systems with both ILs exhibit not only the same trend but also similar acidity values.

Finally, from the solvent parameters, it is possible to construct a chemical criterion that enables us to replace harmful molecular solvents. At the moment, the comparison of microscopic properties in this type of binary mixtures relies on the structural feature of the micro-sensors that determines their solvatochromic response.[15] Thus, zwitterionic probes interact strongly with the solvent part of the mixtures and emerge as suitable sensors that recognize the coulombic interactions present in the intersolvent complex.

Correlation between solvatochromic and reactivity process

If these solvent systems are designed to be used on a reactive process, then it is necessary to analyse the contribution of each microscopic property on a model chemical process that yields the same or similar effects. The linear solvation energy relationships allow us to interpret solvent effect upon a straightforward
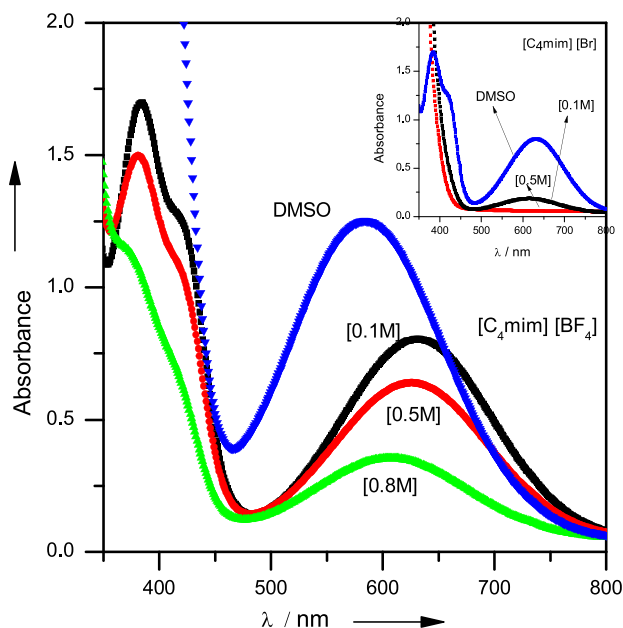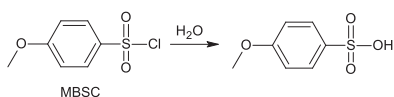
Scheme 4. Hydrolysis reaction of 4-methoxybenzenesulfonyl chloride

reactivity system. In this sense, we selected the hydrolysis reaction of 4-methoxybenzenesulfonyl chloride (MBSC) (Scheme 4).

Figure 4 presents the plots of k_{obs} versus ILs concentration. The shape of the curves clearly reflects similar kinetic response models although different in magnitude. The k_{obs} decreases 13 times with the addition of small amounts of [C_4mim] [BF_4] and only two times with [C_4mim] [Br]. This effect is concomitant with the solvatochromic response observed, but this indicates different susceptibilities between both solvent-dependent processes.

Multiple regression analysis gave the following correlations, where r is the correlation coefficient and n refers to the number of points (Eq (1, 2)).

$$logk_{obs}^{[C_4mim][BF_4]} = -12.86\ (\pm0.99) + 5.90\ (\pm0.82)\pi^*_{II}$$
$$+ 2.74\ (\pm0.63)\alpha_{avg} - 0.083\ (\pm0.55)\beta_{IV} \quad (1)$$
$$n = 10 \quad r = 0.994\ (\pm0.06)$$

$$logk_{obs}^{[C_4mim][Br]} = -0.12\ (\pm0.64) - 2.46\ (\pm0.45)\pi^*_{II}$$
$$+ 1.09\ (\pm0.07)\alpha_{avg} - 0.40\ (\pm0.01)\beta_{IV} \quad (2)$$
$$n = 10 \quad r = 0.995\ (\pm0.01)$$

These results show a very good correlation between both solvent-dependent processes. Then, solvatochromic dipolarity micro-sensors interpret the solvation effects produced by this kind of solvent mixtures on the model reaction. Thus, the coeffi-
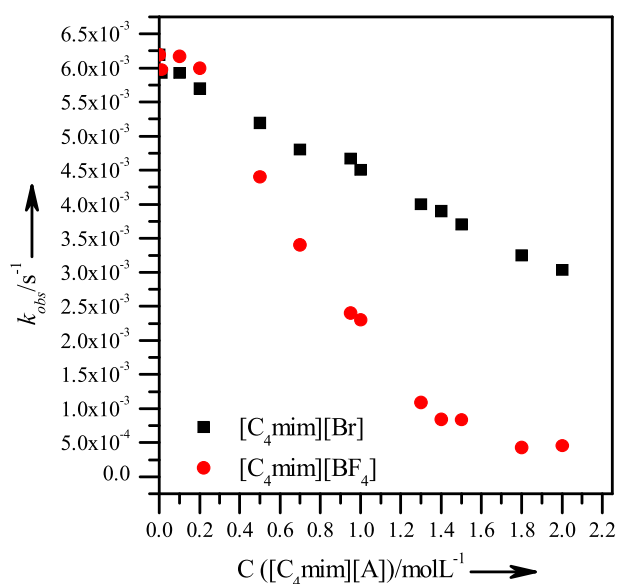
cients of the correlation reflect the properties of the solvent into which the solute is being transferred. Therefore, the magnitudes of the coefficients reveal the degree of interaction that a particular solvent property has upon the overall chemical process analysed. In this sense, dipolarity and HBD ability are more important for the (W + [C_4mim] [BF_4]) system, it being clear that the contribution of HBA ability to the correlation is minimal. Even more, the removal of this parameter did not modify the interpretation of results. On the other hand, for the (W + [C_4mim] [Br]) system, the dipolarity and HBA ability are responsible of the decrease in the k_{obs}.

The analysis of results can become less straightforward for [C_4mim] [Br] because the bromide anion could be competing as nucleophile. In this case, the results would be a combination of effects.[16] However, there is no certainty of the reason for this slowdown in the decrease of k_{obs} with respect to other solvent system, (W + [C_4mim] [BF_4]). At first, we would expect that an increase in the HBA ability of the complex could produce an increase in the W activity. Also, it is interesting to note that for the same IL concentration in (W + [C_4mim] [BF_4]) system, a large number of aggregates are present. This fact leads to a reagent solubility different from that of the (W + [C_4mim] [Br]) system.

CONCLUSIONS

The results presented in this work shed light on new features related to the behaviour of these ILs in aqueous solution against a reference solute. Thus, it is possible to understand their tendency to interact with potential solutes belonging to a reactive system. It was possible to confirm the type of link between the different components of IL, a higher cation–anion interaction when the anion is [BF_4] being proved. Water participates through its HBD ability with [BF_4] anion, whereas when the anion is [Br], the HBA ability with acidic H–atoms at the C_2 of the imidazolium cation predominates.

Whereas the binary mixtures of the type (W + [C_4mim] [Br]) promote the best rates of reaction, the analysis of multiple correlation allows us to confirm that the HBD property of the intersolvent complex formed when the IL is [C_4mim] [BF_4] is responsible for the high inhibition observed upon the reaction system selected. In the first instance, the provision of electron pairs by the intersolvent complex to the polar network could be responsible for the W activity increase. The differences observed in the microscopic properties of both complexes lend to a different solubility of the reagent in the aggregate. This fact would prevent the inhibition in the reaction.

Besides, the analysis of the solvatochromic dipolarity micro-sensors behaviour shows that the traditional KAT indicators (**III** and **V**) present low ability at discriminating the different components in the mixtures. Also, the divergence in the polarity and basicity values obtained from the micro-sensors **II–III** and **IV–V** revealed that the comparison of the microscopic solvent properties is closely related to the indicator identity; thus, KAT's 'dream' of obtaining a single property value by averaging those resulting from different probes, for these binary mixtures, is not yet operative. Therefore, the direct comparison of quantitative values should be carried out with caution. The constant revision of these values as well as the interpretation of behaviours and incorporation of useful tools for

Figure 4. Dependence of [C_4mim] [Br]/[BF_4] concentration on the pseudofirst-order constant (k_{obs}) for the hydrolysis reaction of MBSC at 25.0 °C

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analysing results such as solvation models or the application of the multiple correlations is of utmost interest.

EXPERIMENTAL

Reagents

2,6-Dichloro-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate (**IA**) for the determination of [E_T(33)] values as empirical solvent polarity parameter was prepared as a deeply blue material by the procedure reported in the literature.[6] The indicators *N,N*-diethyl-4-nitroaniline (**II**), 4-nitroanisole (**III**), 4-nitroaniline (**IV**) and 4-nitrophenol (**V**) were purchased from Aldrich (Buenos Aires, Argentina; purity 99 and 97%, respectively). ILs composed of [C$_4$mim] cations with [Br] and [BF$_4$] as counterions were prepared according to literature procedure.[17] To obtain spectroscopic grade ionic liquids, we start from high quality precursors that are purified prior to the synthesis of the ionic liquid. The crude [C$_4$mim] [BF$_4$] was dissolved in deionized water and extracted in the liquid–liquid extractor with dichloromethane for 48 h. The dichloromethane solution was filtered through a plug of silica, and the dichloromethane removed under vacuum. This process was repeated until the presence of bromide with silver nitrate proved negative. The IL was then heated under high vacuum for 48–72 h. For [C$_4$mim] [Br], the yellow solid obtained after the addition of the reagents was then washed with diethyl ether and dried under vacuum for 24 h. It was dissolved in water, and decolourizing charcoal was added. This solution was heated at 70 °C for 24 h, cooled and filtered. If necessary, the decolourizing charcoal step was repeated. The water was then removed using a lyophilizer. The resulting solid was then heated under high vacuum for 48–72 h at 60 °C. We checked each step of purification for UV–Vis and fluorescence spectroscopy, and we used these tools to determine the optical purity in the ILs. Also, because the pure ILs with imidazolium cation does not possess inherent fluorescence, we checked this aspect during the purification step.

Measurement of the solvatochromic parameters

The UV–Vis spectra were collected using a Shimadzu UV-1800 spectrophotometer, equipped with a thermostatic cell holder. The absorption spectra of the dyes (C = 10^{-5}–10^{-4} M) were collected at 25 ± 0.1 °C. The E_T(30) parameter was obtained from the experimental data of E_T(33) applying the corresponding linear correlation equation.[5] The E_T(30) and E_T^N parameters were calculated as reported elsewhere.[1] The parameter π^* was determined employing indicators **II** and **III**. The parameter β was determined by the magnitudes of enhanced solvatochromic shifts for dye (**IV**) relative to its homomorph (**II**) and for dye (**V**) relative to (**III**), according to the conversion expression proposed by Marcus.[14]

Analysis of the UV/Vis spectroscopic data

The model proposed by Bosch *et al.*[4] related the transition energy of a solvatochromic solute with the composition of a binary solvent mixture. In this work, we shall apply Eq (3). In the systems that present reinforcement of the structure of W in mixtures containing small amounts of a cosolvent, this model must be modified to consider this effect for the studied mixture. The ∆Y (Eq (4)) is a term of correction introduced to the original model. In it, S1 and S2 indicate the two pure solvents yielding the binary solvent mixture and S12 represents an intersolvent complex formed by hydrogen-bond interactions between S1 and S2. The solvation parameters ($f_{2/1}$ and $f_{12/1}$) that minimize the square residuals of the solvatochromic property values were computed by nonlinear regressions using the program written in MATLAB for Windows. The constant $f_{12/2}$ corresponding to the 12/2 exchange can be calculated from the relation $f_{12/1}/f_{2/1}$.

$$Y = \frac{Y_1(1-x_2)^2 + Y_2 f_{2/1}(x_2)^2 + Y_{12} f_{12/1}(1-x_2)x_2}{(1-x_2)^2 + f_{2/1}(x_2)^2 + f_{12/1}(1-x_2)x_2} + \Delta Y \quad (3)$$

$$\Delta Y = \frac{k f_{2/1}(x_2)^2 \left[(1-x_2)2 + f_{12/1}(1-x_2)x_2/2\right]}{\left[(1-x_2)^2 + f_{2/1}(x_2)^2 + f_{12/1}(1-x_2)x_2\right]2} \quad (4)$$

where *k* is a proportionality constant.

Kinetic procedures

Reaction kinetics was recorded by measuring the absorbance due to 4-methoxybenzenesulfonyl chloride (MBSC) at 270 nm in a Shimadzu UV-1800 spectrophotometer with a cell holder thermostated at 25.0 ± 0.1 °C. Stock solutions of MBSC were prepared in acetonitrile because of its low solubility in water. The final acetonitrile concentration in the reaction medium was <1% (v/v). The MBSC concentration was always approximately $1.2 \times 10 - 4$ M. The absorbance − time data of all kinetic experiments were fitted by first-order integrated equations, and the values of the pseudofirst-order rate constants, k_{obs}, were reproducible within 3%.

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