

On the characterization of some [bmim][X]/co-solvent binary mixtures: a multidisciplinary approach by using kinetic, spectrophotometric and conductometric investigations

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Abstract

In order to study the intrinsic characteristics and to evaluate the structural variations determined by the addition of a co-solvent to 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) we examined the behaviour of some probes in [bmim][BF₄]/co-solvent binary mixtures. The rate constants of the piperidino-catalyzed rearrangement of the *Z*-phenylhydrazone of the 3-benzoyl-5-phenyl-1,2,4-oxadiazole into the relevant 4-benzoylamino-2,5-diphenyl-1,2,3-triazole as well as the spectrometric properties of pyrene and Nile Red were evaluated. With the same purpose also ¹H NMR and conductivity measurements were carried out. By comparison the behaviour of 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonylimide)/1,4-dioxane mixtures has been analyzed. The whole of data confirms the presence of weak interactions that determine a partially preorganized structure for [bmim][X]. This is perturbed at some degrees by quantity and nature of guest molecules. For example conductivity measurements support the idea that different charged aggregates are present in the [bmim][X]/co-solvent binary mixtures.

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1. Introduction

Room temperature ionic liquids (RTILs) are defined as 'green' solvents because of their non-volatility and non-flammability.¹ To completely develop their laboratory and industrial use, a knowledge of their physico-chemical properties as well as of their effect on chemical reactivity appears necessary.² The latter has been explained on the grounds of a partially preorganized structure of RTILs.³ Alternatively the effect of medium has been attributed to a combination of their solvent properties such as hydrogen bond acidity (α) and basicity (β) as well as polarizability effects (π^*).⁴ Recently, a comparison between two models has been discussed.⁵

For practical reasons in several cases investigations are not carried out in pure RTILs. Thus, the reaction medium is a binary mixture more or less rich in RTIL and the co-solvent employed might be able to affect solvent parameters of RTILs as well as their organized structure. Thus, understanding of the structural and physico-chemical properties of the mixed systems appears desirable and recently it has been the main subject of some papers.⁶

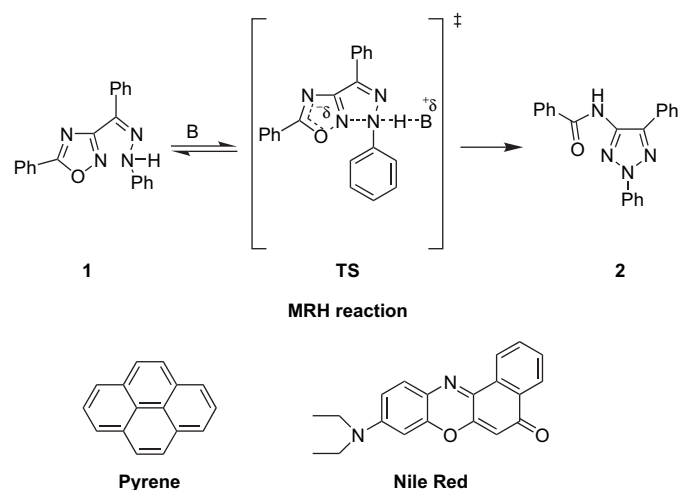
Within this line of research we have examined the properties of some binary mixtures constituted by the RTIL [bmim][BF₄] (bmim=1-butyl-3-methylimidazolium) with variable amounts of solvents largely used in RTIL studies, showing different properties such as polarity, hydrogen bond donor or acceptor ability, density and viscosity.⁷

The RTIL [bmim][NTf₂] [NTf₂=bis-(trifluoromethylsulfonylimide)] has been also tested to evaluate if, and how, the change of the anion counter-part could influence the behaviour of imidazolium RTILs.

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For this, we have now studied the effect of some binary mixtures on the kinetics of piperidino-catalyzed MRH (mononuclear rearrangement of heterocycles, see Scheme 1) of the Z-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (**1**) into the relevant 4-benzoylamino-2,5-diphenyl-1,2,3-triazole (**2**)⁸ and the spectroscopic (UV–vis and fluorescence, respectively) properties of Nile Red⁹ and pyrene¹⁰ (Scheme 1) in the presence of the same mixtures; with the same aim also some ¹H NMR and conductivity measurements in binary mixtures were carried out.



Scheme 1.

2. Results and discussion

2.1. Kinetic measurements

2.1.1. Kinetic study of the rearrangement of **1** into **2** in [bmim][BF₄]/co-solvent at constant volume of co-solvent and at constant molarity

The mononuclear rearrangement of heterocycles (MRH) is a peculiar intramolecular nucleophilic substitution (S_{Ni})

occurring via a bicyclic quasi-aromatic (10 π electrons) transition state.¹¹ It has been largely investigated in conventional organic solvents,^{8e} as well as in organized (micelles)¹² or in preorganized (cyclodextrins)¹³ systems and, recently, in RTILs.¹⁴

Kinetic study in different binary mixtures containing [bmim][BF₄] has been carried out at different piperidine (Pip) concentrations: according to previous reports,^{2p} this amine did not induce significant variations in organized RTIL structure in the range of concentrations used, unlike some other cyclic secondary amines tested.

In our previous investigations of the same reaction in RTILs,¹⁴ we have added the reagents dissolved in 75 μL of Diox to 500 μL of RTIL. In order to verify the influence of the nature of the co-solvent used, we have carried out new kinetic measurements both in pure RTIL ([bmim][BF₄]) or adding the same volume (75 μL) of different co-solvents. Moreover we have also carried out kinetic measurements in the presence of an equal number of moles ($\sim 8.80 \times 10^{-3}$ mol) of different co-solvents.

In all the cases considered, a linear dependence of the observed rate constant ($k_{A,R}$) on [Pip] was evidenced and a negative intercept was always calculated thus confirming some of our previous observations.^{14a}

In Table 1 the second-order rate constants (k_{II} calculated at 298 K) are reported as a function of the co-solvent used. Moreover the relative permittivity (ϵ)¹⁵ of co-solvents used, the E_{NR} ⁹ and $R_{I/III}$ ¹⁰ values measured by us (see below) are reported. Data in Table 1 indicate that the reaction rates are affected by the nature of the co-solvent used. For example, at constant volume of co-solvent, a reactivity ratio ~ 2.3 is calculated between the k_{II} in [bmim][BF₄]/H₂O and in [bmim][BF₄]/CH₂ClCH₂Cl.

The presence of the co-solvent seems capable of increasing the reaction rates: indeed the reaction always proceeds faster in the binary mixtures than in neat RTIL, the chlorinated solvents appearing the less efficient and the polar co-solvents the most efficient in accelerating the reaction.

Table 1

Second-order rate constants (k_{II}) for the MRH of **1** into **2** at 298 K in [bmim][BF₄]/co-solvent mixtures, polarity parameter (ϵ) of co-solvents and polarity parameters ($R_{I/III}$ and E_{NR}) of the binary mixtures

Entry	Co-solvent	ϵ	$k_{II}^{a, c}$ (M ⁻¹ s ⁻¹)	($k_{II}/k_{II,IL}$)	$E_{NR}^{b, c}$ (kJ/mol)	$R_{I/III}^{c, e}$	V^d (μL)	$k_{II}^{a, f}$ (M ⁻¹ s ⁻¹)	($k_{II}/k_{II,IL}$)	$E_{NR}^{b, f}$ (kJ/mol)	$R_{I/III}^{c, f}$
1			0.481 (0.041)	1	217.6	1.74		0.481 (0.041)	1	217.6	1.74
2	H ₂ O	80.10	1.23 (0.11)	2.6	211.6	0.78	15	1.27 (0.04)	2.6	216.1	0.99
3	MeCN	36.64	1.20 (0.03)	2.5	217.6	1.67	45	0.889 (0.044)	1.8	218.5	1.57
4	MeOH	33	1.20 (0.03)	2.5	216.1	1.70	35	1.63 (0.03)	3.4	216.5	1.63
5	CH ₂ ClCH ₂ Cl	10.42	0.525 (0.017)	1.1	217.9	1.48	70	0.538 (0.017)	1.1	217.6	1.54
6	CH ₂ Cl ₂	8.93	0.618 (0.027)	1.3	217.6	1.42	55	0.545 (0.022)	1.1	217.4	1.61
7	AcOEt	6.08	0.816 (0.030)	1.7	218.2	1.39	85	0.793 (0.042)	1.6	217.9	1.41
8	CHCl ₃	4.81	0.604 (0.023)	1.3	217.6	1.53	70	0.585 (0.025)	1.2	217.1	1.58
9	Diox	2.22	0.844 (0.028)	1.8	217.5	1.65	75	0.844 (0.028)	1.8	217.5	1.65

^a Standard deviations are given in parenthesis. The rate constants were reproducible within $\pm 3\%$.

^b The E_{NR} values were reproducible within 0.2 unities.

^c The $R_{I/III}$ values were reproducible within $\pm 3\%$.

^d Amount of co-solvent.

^e Data collected in [bmim][BF₄]/co-solvent (3:23, v/v) mixtures.

^f Data collected in [bmim][BF₄]/co-solvent ($X_{co-solvent} \sim 0.25$) mixtures.

Similar variations in the reaction rates, as a function of the co-solvent used, have been recently observed by Harper et al.,^{2k} in the base-catalyzed solvolysis of 3-chloro-3,7-dimethyloctane in [bmim][NTf₂], in the presence of methanol or benzyl alcohol.

In order to rationalize the observed trends, we tried to relate rate constants to polarity of the co-solvents used, but data in Table 1 show that no relationship can be evidenced between kinetic and polarity data. As a matter of fact, comparable rate constants were calculated in mixtures of co-solvents having significantly different polarity (see entries 2 and 4, column 4). In contrast, in mixtures with co-solvents having rather similar ϵ values, quite different reactivity data have been measured (see entries 7 and 8), thus indicating the occurrence of significantly different kinetic effects.

2.1.2. Kinetic study of the rearrangement of **1** into **2** in [bmim][BF₄]/co-solvent at variable mole fraction of RTIL

A comparison between data (columns 4 and 9) reported in Table 1 shows that the reactivity is affected also by the amount of co-solvent used. On the basis of the latter finding we have undertaken a kinetic study of the title reaction, as a function of RTIL mole fraction (different mole fraction ranges have been examined because of different relative solubilities). To carry out this investigation we have chosen only three solvents with different polarities and hydrogen bond abilities, namely Diox, AcOEt and MeOH.

In Figure 1, k_{II} values are reported as a function of RTIL mole fraction [data at 298 K for different binary mixtures are collected in Supplementary data (Table 3)]. In all the cases examined the plot of k_{II} versus the mole fraction of RTIL does not show a monotonic trend. Moreover, the MeOH co-solvent appears capable of inducing the largest increase in reactivity with respect to neat [bmim][BF₄]. Furthermore, the mole fraction corresponding to the highest reactivity depends on the very nature of the co-solvent used, going from $X_{MAX}=0.40$ (Diox) to ca. 0.80 (AcOEt and MeOH).

2.1.3. Kinetic measurements of the rearrangement of **1** into **2** in [bmim][NTf₂]/Diox mixtures

In order to ascertain the role played by the anion of RTIL in affecting the reaction rates in binary mixtures, we carried out further kinetic measurements for the [bmim][NTf₂]/Diox mixtures. In Figure 2, k_{II} values are reported as a function of RTIL mole fraction [data at 298 K for the studied binary mixtures are in Supplementary data (Table 4)].

They show a trend similar to that related to the [bmim][BF₄]/Diox mixtures with a different mole fraction corresponding to the highest reactivity ($X_{MAX} \sim 0.3$).

A comparison between the two binary systems [bmim][BF₄]/Diox and [bmim][NTf₂]/Diox shows that in the former case the presence of the co-solvent induces a higher reactivity variation with respect to neat RTIL ($\Delta k_{II} \sim 0.682$ for [bmim][BF₄] and $\Delta k_{II} \sim 0.260$ for [bmim][NTf₂]). On the other hand, the reactivity ratios ([bmim][BF₄]/[bmim][NTf₂]), going from neat RTILs to mixtures ($X_{RTIL}=0.3$), are ~ 4.6 and ~ 2.4 , respectively. Probably, the co-solvent has a greater

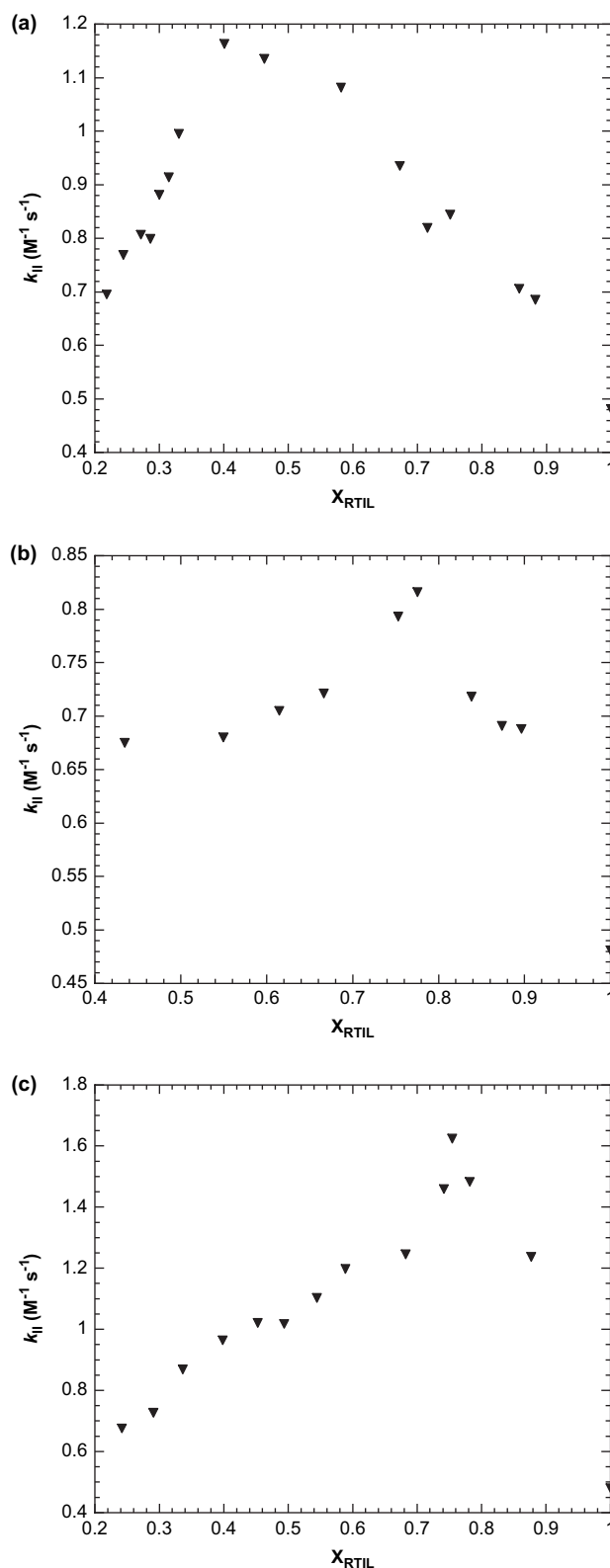


Figure 1. Plots of second-order rate constants (k_{II}) at 298 K versus RTIL mole fraction concerning the binary mixtures: (a) [bmim][BF₄]/Diox, (b) [bmim][BF₄]/AcOEt and (c) [bmim][BF₄]/MeOH.

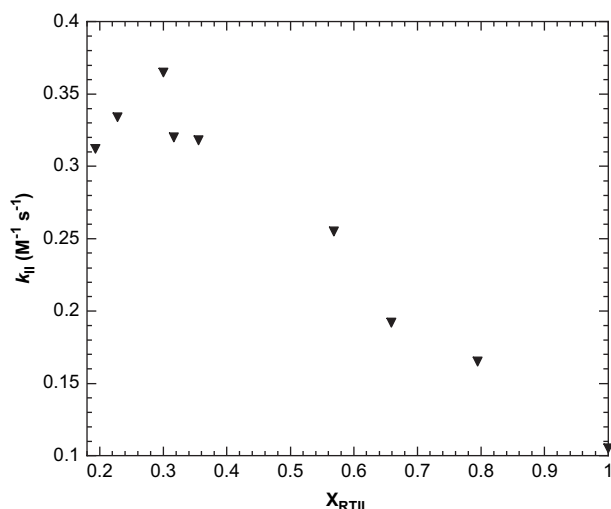


Figure 2. Plot of second-order rate constants (k_{II}) at 298 K versus RTIL mole fraction for [bmim][NTf₂]/Diox binary mixtures.

disorganizing effect on [bmim][BF₄], having a higher cross-linking degree than [bmim][NTf₂].

2.1.4. Activation parameters

Bearing in mind that RTILs containing aromatic moieties are capable of displaying self-organization, the presence of co-solvent could induce significant changes in their organized structure. Because even modest temperature variations can cause significant differences in the packing of RTILs, we thought it could be interesting to study the probe reaction, for different solvent mixtures, at different temperatures.

For kinetics carried out in RTILs, it has been reported that a sharp curvature in Arrhenius or Eyring plots could be observed, as a consequence of some significant structural changes in the RTIL.¹⁶ So, for a careful analysis of the temperature effect, the reaction was carried out at five temperatures going from 293 K up to 313 K.

In all the cases considered, an excellent linear correlation of $\log(k_{\text{A,R}}/T)$ versus $1/T$ was obtained, indicating that, in the analyzed range, the above upsetting effect is not operating and that the calculated activation parameters are only dependent on the nature of the MRH process. The activation parameters are reported in Table 2, kinetic data collected at different temperatures are available in the Supplementary data (Tables 5 and 6).

A narrow range of activation parameters was calculated. In particular, at constant volume of co-solvent, mean values of $\Delta H^\ddagger = 44 \pm 5$ kJ/mol and $\Delta S^\ddagger = -138 \pm 19$ J/K mol were calculated. The same values, $\Delta H^\ddagger = 43 \pm 5$ kJ/mol and $\Delta S^\ddagger = -138 \pm 16$ J/K mol, were calculated at constant number of moles of co-solvent. These values are not significantly different from those calculated for neat [bmim][BF₄]. Moreover similar results were also obtained for neat [bmim][NTf₂] and [bmim][NTf₂]/Diox binary mixtures.

Above data confirm^{14b} that weak interactions, scarcely sensitive to composition variation of binary mixtures, are operating in imidazolium-based ILs. Indeed, the studied reaction in

Table 2

Activation parameter^a values for the MRH of **1** in [bmim][X]/co-solvent binary mixtures

RTIL	Co-solvent	$\Delta H^\ddagger, \text{b}$ (kJ/mol)	$\Delta S^\ddagger, \text{b}$ (J/K mol)	$\Delta H^\ddagger, \text{c}$ (kJ/mol)	$\Delta S^\ddagger, \text{c}$ (J/K mol)
[bmim][BF ₄]		50	−122		
[bmim][NTf ₂]		45	−144		
[bmim][BF ₄]	H ₂ O	52	−105	40	−145
[bmim][BF ₄]	MeCN	38	−152	36	−161
[bmim][BF ₄]	MeOH	48	−118	49	−114
[bmim][BF ₄]	CH ₂ ClCH ₂ Cl	50	−121	50	−121
[bmim][BF ₄]	CH ₂ Cl ₂	34	−172	42	−145
[bmim][BF ₄]	AcOEt	46	−130	50	−116
[bmim][BF ₄]	CHCl ₃	43	−144	42	−145
[bmim][BF ₄]	Diox	38	−158	38	−158
[bmim][NTf ₂]	Diox	48	−135		

^a At 298 K the maximum errors are 3 kJ/mol and 8 J/K mol, respectively.

^b Data calculated in [bmim][BF₄]/co-solvent (3:23, v/v) mixtures.

^c Data calculated in [bmim][BF₄]/co-solvent ($X_{\text{co-solvent}} \sim 0.25$) mixtures.

Diox–water mixtures,^{8c} in the base-catalyzed pathways, shows higher values of enthalpic parameter ($\Delta H^\ddagger = 92 \pm 2$ kJ/mol) and more positive values for entropic contribute ($\Delta S^\ddagger$ ranges from -44.3 J/K mol to 2.1 J/K mol) according to the occurrence of strong substrate–solvent interactions.

In order to get deeper information about the organization degree and properties of the studied binary mixtures, we have used other probes, carrying out some other determinations.

2.2. Spectroscopic, ¹H NMR and conductivity measurements

2.2.1. Polarity measurements

Since the literature ϵ values (data in Table 1) refer to the pure co-solvent, it appeared more correct to have polarity parameters related to the binary mixtures. We choose pyrene and Nile Red, as solvatochromic probes: their planar and aromatic structures seemed suitable to intercalate between imidazolium layers, without excessively perturbing the RTIL structure.

In Table 1 the determined E_{NR} and $R_{\text{I/III}}$ values, collected for [bmim][BF₄]/co-solvent binary mixtures are reported.

It is worthwhile that the two solvatochromic probes seem to be scarcely affected by different micro-environments. In fact, narrow ranges of E_{NR} values (211.6–218.2 kJ/mol and 216.1–218.5 kJ/mol, see Table 1) were determined. Significantly larger variations (0.78–1.74 and 0.99–1.74, see Table 1) were calculated for $R_{\text{I/III}}$ values. Furthermore, it must be noticed that for both parameters, by excluding data concerning the [bmim][BF₄]/H₂O mixture, the above ranges become even narrower. The effect of H₂O on the RTIL structure has been extensively studied by Mele et al.,¹⁷ by means of NMR measurements, and it has been shown that the presence of water makes the imidazolium–imidazolium association looser, shifting the RTIL structure towards a different organization with a lower degree of ring stacking. Also in this case polarity parameters of binary mixtures were used for attempting to explain kinetic data. Once more they seem to be inadequate. For example, the E_{NR} parameter foresees no variation of polarity,

even if significant differences in reactivity were measured (see entries 3 and 6 of Table 1). The same conclusions can be pointed out considering the R_{III} polarity parameter.

In Figures 5–7 and in Tables 7–9 of Supplementary data the E_{NR} and R_{III} values, as a function of RTIL mole fraction, related to [bmim][BF₄]/co-solvent (Diox, AcOEt and MeOH) and [bmim][NTf₂]/Diox mixtures, are reported. In general R_{III} parameter, with the exception of [bmim][NTf₂]/Diox mixtures, has a non-monotonic trend, with maximum polarity values quite similar to those calculated from reactivity data. In contrast, E_{NR} 's give monotonic polarity trend decreasing in the presence of Diox and AcOEt and increasing in the presence of MeOH.

A comparison among polarity parameters concerning [bmim][BF₄] and [bmim][NTf₂] binary mixtures indicates that the different nature of RTIL anion is able to affect the answer of solvatochromic probe to solvent characteristics, giving rise to completely different polarity trend. On the other hand, it can be also supposed that the same probes affect in different ways, the structure of binary mixtures of the two RTILs, as a consequence of the different possible cation–anion interactions. Under this light, the different trends of E_{NR} and R_{III} values could be considered a result of different binary mixtures' organization around the solute molecules.

2.2.2. ¹H NMR measurements

The RTIL/co-solvent interactions were studied also by ¹H NMR spectrometry recording spectra of binary mixtures of [bmim][BF₄] with Diox, AcOEt and MeOH.

Firstly, we analyzed the effect of Diox addition to RTIL observing significant variations of NMR spectrum. For instance, the signal due to H-2 proton of imidazolium was split in a couple of signals of different intensities, the signal most shielded had the lowest intensity and was broad (see Fig. 9a of Supplementary data).

In general, for all of the binary mixtures examined, the co-solvent is capable of affecting both the chemical shift and the multiplicities of ¹H NMR signals. This fact has been previously ascribed to the existence of different ion pairs in solution.¹⁸ Furthermore, ¹H NMR measurements have underlined, in some cases, in the presence of co-solvents, the formation of nanostructures with polar and non-polar regions.^{19b} Among the co-solvents tested, AcOEt induces the highest signal broadening, whereas MeOH the lowest (see Fig. 8 of Supplementary data). This result could be related to different size, shape and structural flexibility of the three solvents used. We have extended the comparison to [bmim][NTf₂]/Diox mixtures, observing a smaller broadening of signals with respect to [bmim][BF₄]/Diox mixtures (see Fig. 9 of Supplementary data).

In general the co-solvent shifts imidazolium signals to downfield and, in all of the cases considered, variations of chemical shift are higher for H-2. Interestingly enough, variations in chemical shifts ($\Delta\delta = \delta_{\text{binary mixture}} - \delta_{\text{RTIL}}$), as a function of the RTIL mole fraction, shows a monotonic trend.

For the binary mixtures examined, the comparisons among $\Delta\delta$ values concerning H-2 proton of imidazolium cation, as a function of RTIL mole fraction, are reported in Figure 3

(see also Table 10 of Supplementary data). For [bmim][BF₄] mixtures (Fig. 3a), $\Delta\delta$ values are comparable and smaller in the presence of Diox ($\epsilon=2.22$) and MeOH ($\epsilon=33$), but higher in the presence of AcOEt ($\epsilon=6.08$): once more the variation in physico-chemical properties cannot be related only to the co-solvent polarity.

By comparing [bmim][BF₄]/Diox and [bmim][NTf₂]/Diox mixtures (Fig. 3b) a higher variation in H-2 chemical shift for the first binary mixture has been evidenced, in line with the higher [bmim][BF₄] organization.

2.2.3. Conductivity measurements

In Figure 4 conductivity values (Λ), collected at 298 K, for the same three above examined binary mixtures, as a function of RTIL mole fraction, are reported (see also Table 11 in Supplementary data).

In the presence of variable amounts of MeOH, the conductivity values give a smooth curve. A similar result was previously obtained by Han et al.,²⁰ on studying the [bmim][PF₆]/

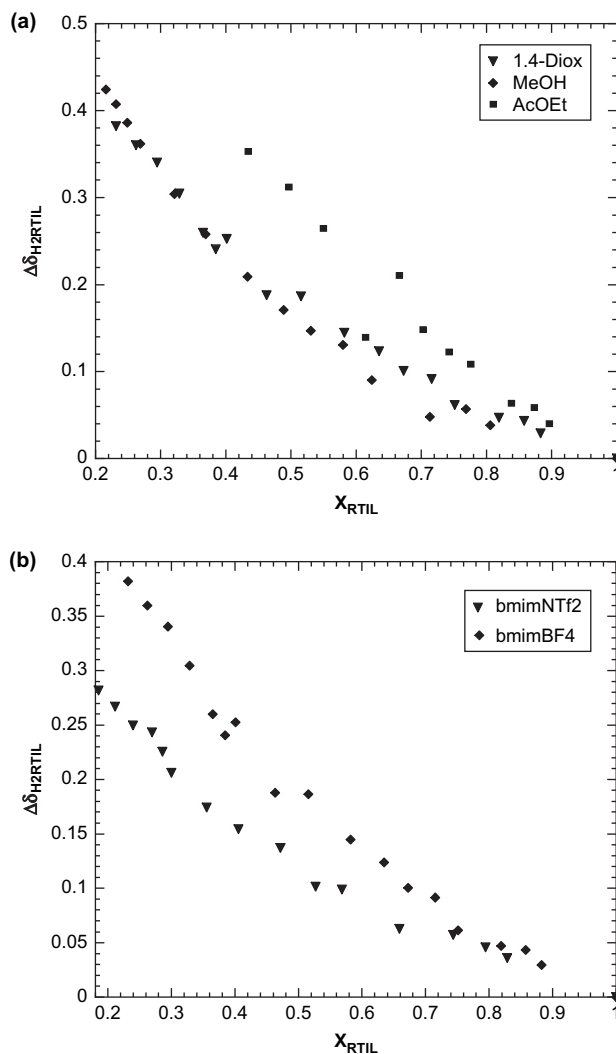


Figure 3. Variations of chemical shift ($\Delta\delta$) relative to H-2 proton of imidazolium ion, versus RTIL mole fraction, for: (a) [bmim][BF₄]/Diox, [bmim][BF₄]/AcOEt and [bmim][BF₄]/MeOH mixtures and (b) [bmim][BF₄]/Diox and [bmim][NTf₂]/Diox mixtures.

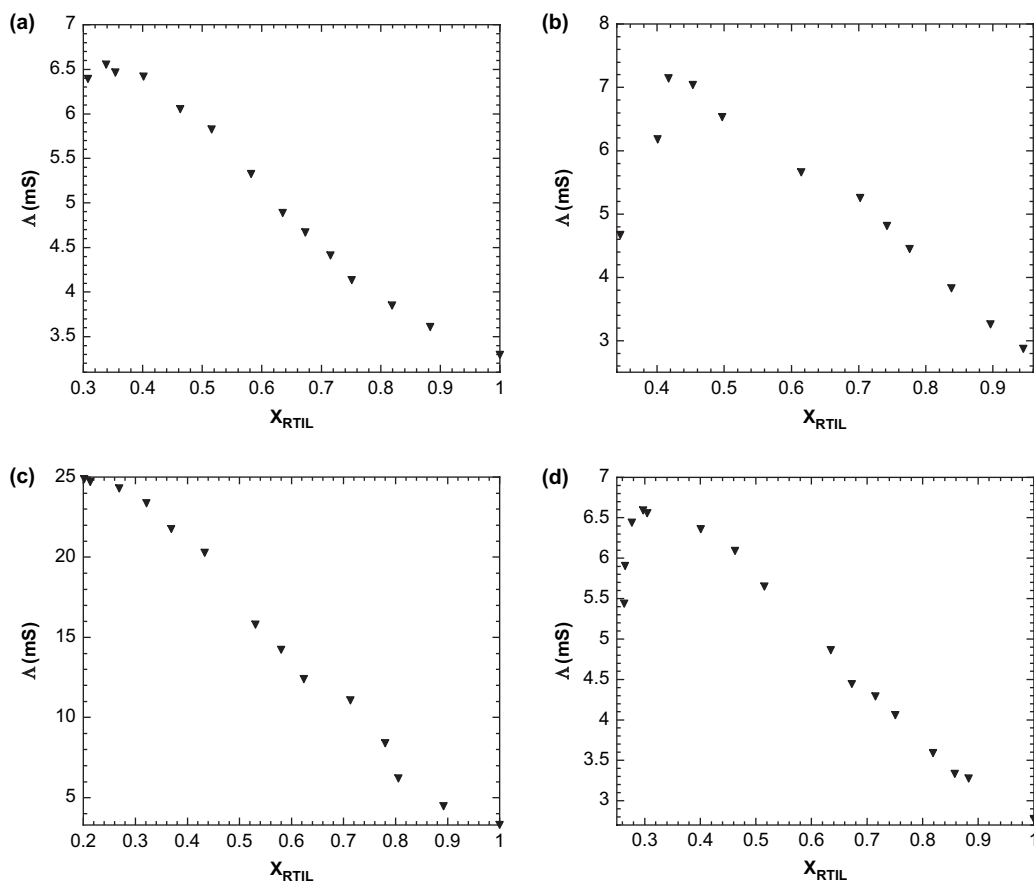


Figure 4. Plots of conductivity values (Δ) at 298 K, versus RTIL mole fraction, relative to: (a) [bmim][BF₄]/Diox, (b) [bmim][BF₄]/AcOEt, (c) [bmim][BF₄]/MeOH and (d) [bmim][NTf₂]/Diox binary mixtures.

MeCN binary mixtures. This was attributed to the miscibility on the molecular level of the two components, giving binary mixtures where the RTIL is present mainly as separate free ions. In our case this hypothesis seems further supported by the variation in conductivity values induced by the presence of co-solvent.

Among the solvents tested, MeOH induces the largest variation. As a matter of fact in the range of mole fraction considered (from 0.2 up to 1.0) conductivity values decrease from 25 mS up to 3.3 mS. In contrast, in the range examined for AcOEt and Diox (from 0.30 and 0.32 up to 1.0, respectively) the conductivity variations observed are, as expected on the grounds of the different physical characteristics of the three solvents examined, much smaller: the former inducing a slightly higher variation ($\Delta\Delta=3.85$ mS) than the latter ($\Delta\Delta=3.26$ mS).

On the other hand, a comparison between the two RTILs considered by us evidences that the variation in conductivity is slightly higher for [bmim][NTf₂] mixtures than for [bmim][BF₄] mixtures ($\Delta\Delta=3.26$ mS and 3.82 mS for [bmim][BF₄]/Diox and [bmim][NTf₂]/Diox, respectively), once more confirming a higher organization of [bmim][BF₄].

With the exception of [bmim][BF₄]/MeOH mixtures, in all of the other cases, conductivity values show a non-monotonic trend, quite similar to that concerning the k_{II} data. Both in [bmim][BF₄]/Diox mixtures and in [bmim][NTf₂]/Diox mixtures the maximum of conductivity is achieved at RTIL

mole fraction quite similar to that observed in kinetic measurements and, accordingly, the value increases going from [bmim][NTf₂] mixtures ($X_{MAX}\sim 0.3$) to [bmim][BF₄] mixtures ($X_{MAX}\sim 0.4$). In the presence of AcOEt, the RTIL mole fraction corresponding to the maximum value of conductivity is similar to that calculated in the presence of Diox ($X_{MAX}\sim 0.4$), but quite different from that calculated by kinetic data.

Non-monotonic experimental traces, such as the ones obtained by us, have been previously reported.²⁰ It is noteworthy that similar results were obtained also by FTIR²¹ and calorimetric measurements.¹⁹ In all the cases considered, these experimental trends were ascribed to the coexistence of different species in solution originated from RTIL, such as free ions, contact ion pairs and charged aggregates. The presence of a maximum has been considered as result of a balance between the contribution to conductivity of the different species present and solution viscosity.²¹ ESI-MS investigations have shown that each species has a different prevalence range.²²

The presence of co-solvent also affects the viscosity of the RTIL, indeed it can induce dramatic decreases in this parameter.²³ However, the viscosity and conductivity trends are not always in agreement between themselves. For dilute solutions in RTIL, low viscosity corresponds to low conductivity, as neutral ion pairs should be the predominant species. For concentrated solutions, a high conductivity, due to the presence of

charged aggregates, will be counterbalanced by a high and unfavourable viscosity.

In our case, starting from high RTIL mole fraction, the reaction rate increases up to a maximum. Probably, in this range, the decrease in viscosity favours the progress of the reaction, as a consequence of easier intramolecular and intermolecular motions. Furthermore, in the presence of Diox, at the same mole fraction, the variation in k_{II} values, respect to neat RTIL, is higher for the [bmim][BF₄] mixtures than for the [bmim][NTf₂] mixtures ($X_{Diox}=0.54$, $\Delta k_{II[bmim][BF_4]}=0.654\text{ M}^{-1}\text{ s}^{-1}$; $\Delta k_{II[bmim][NTf_2]}=0.158\text{ M}^{-1}\text{ s}^{-1}$). This result can be ascribed to a higher viscosity of [bmim][BF₄] ($\nu=233\text{ cP}$) with respect to [bmim][NTf₂] ($\nu=52\text{ cP}$).²⁴

As a consequence, the former RTIL should be more affected by addition of a second component having a lower viscosity. After the reaching of the maximum value, k_{II} values begin to decrease. As previously reported,¹⁴ for the probe reaction the reactivity increases in imidazolium RTILs. This accelerating effect with respect to conventional organic solvents, was not simply ascribed to a higher polarity of RTILs, but to their self-organized structure and to their organizing ability, which may allow the presence of feeble but cooperative interactions, such as $\pi-\pi$ interactions. These, occurring between the imidazolium rings and the bicyclic quasi-aromatic transition state, stabilize the latter and favour the progress of the reaction. It is expected that the charged aggregates are more efficient with respect to neutral ion pairs or free ions in carrying out this stabilizing effect.

On decreasing the RTIL mole fraction there will be a decrease in aggregate concentration. Thus, the favourable effect due to a lower viscosity will be largely counterbalanced by the minor stabilization of the transition state, so globally inducing a decrease in reaction rates. This hypothesis seems to be supported by conductivity trends. Therefore, the co-solvent seems to have an upsetting effect on the structure of the imidazolium RTILs.

Furthermore, disorganization process (with increase of the mole fraction of co-solvent added) seems to be affected by co-solvent nature. Considering the RTIL mole fraction, corresponding to the maximum k_{II} value, such as the transition point among two or more different species, this process is early in the presence of polar solvents, such as AcOEt and MeOH ($X_{MAX}\sim 0.8$), but rather late in the presence of apolar solvents, such as Diox ($X_{MAX}\sim 0.4$).

The effect of co-solvent changes with symmetry and coordination ability of the present RTIL anion. These determine a different degree of cross-linking for the two [bmim][X]²⁵ and consequently a different concentration of charged aggregates, capable of catalyzing the probe reaction, giving rise to slower reactions.

This hypothesis seems to be also supported by ΔA variation (see above). This parameter is slightly higher for [bmim][NTf₂] mixtures, which could indicate a higher concentration of free ions in its solutions. Furthermore, as it has a less ordered structure, it should be less affected by the presence of co-solvents. This could explain why the disorganization process of RTIL structure in the presence of [bmim][NTf₂] is delayed. This

hypothesis seems to be supported by both kinetic and ¹H NMR data, which give higher variations for [bmim][BF₄] binary mixtures.

3. Conclusions

Data collected here once more show that the imidazolium RTILs are very intriguing solvent media, acting as 'organized solvents'. As a consequence, any reaction carried out in these solvents could be strongly and differently affected by the RTILs' nature because of their peculiar structural characteristics. In some cases, they may act as 'entropic drivers'.^{3b} In imidazolium-based RTILs, different components are kept together by means of feeble but directional and cooperative forces. So, the resulting solvent media are differently sensitive, with respect to conventional organic solvents, to upsetting effects due to the presence of guest molecules, such as reactants or co-solvents. This agrees with the data previously reported by Armstrong et al. about the dependence of polarity measurements on the probe used.²⁶

As indicated by kinetic, conductivity and NMR data, the disorder degree, induced by co-solvents, depends on the nature of both RTIL components and co-solvent, resulting greater for the most cross-linked [bmim][BF₄] than for [bmim][NTf₂]. However, the effect that binary mixtures [bmim][X]/co-solvents can exert on a given reaction cannot be ascribable to simple polarity, viscosity or conductivity effects, but it is evident that a whole of parameters has to be considered in order to rationalize it.

Furthermore, by using kinetic data in the attempt of characterizing binary mixtures, one must remember that the extent of the co-solvent disorganizing effect depends on the nature of reaction probe used. Probably, the disorganizing effect increases when the reactions are characterized by highly ordered transition states.

4. Experimental section

4.1. Materials

Commercial H₂O, MeCN, MeOH, CH₂ClCH₂Cl, CH₂Cl₂, AcOEt, CHCl₃, Diox, pyrene and Nile Red were used without any further purification. Commercial [bmim][BF₄] was dried on a vacuum line at 60 °C for at least 2 h and stored in a dryer under argon and over calcium chloride. [bmim][NTf₂] was prepared according to a procedure previously reported.^{25b} Pip was freshly distilled before use. Compound **1** was prepared according to the method reported.²⁷

Binary mixtures were prepared by mixing suitable volumes, by using micro-syringes, of both co-solvent and RTIL. Different mole fraction ranges have been examined because of different relative solubilities.

4.2. Kinetic measurements and calculations

UV–vis spectra and kinetic measurements were carried out by using a spectrophotometer equipped with a Peltier

temperature controller, able to keep the temperature constant within 0.1 K. Kinetic runs were carried out over the temperature range 293–313 K. The sample for a typical kinetic run was prepared by mixing the proper RTIL, co-solvent and substrate solution into a quartz cuvette (optical path 0.2 cm). The solution obtained was thermostated, the proper volume of Pip solution (at six concentrations) added and the reaction rates measured by the disappearance of **1** at its λ_{MAX} . The concentration of substrate was constant and equal to 1.9×10^{-4} M; the amine concentration ranged from 2.2 M to 17×10^{-3} M. The course of the reactions was followed over at least three half-lives. Kinetic data were analyzed by means of the Kaleida-Graph 3.0.1 software. The apparent first-order rate constants obtained were reproducible within $\pm 3\%$.

4.3. Fluorescence spectra

Steady-state fluorescence spectra were acquired using a quartz cuvette (optical path 0.2 cm). The pyrene concentration was 2×10^{-7} M. Excitation and emission slits were set at 1.5 nm and the excitation wavelength was set to 337 nm. Spectra were recorded in the range 360–450 nm. Each spectrum was averaged over 50 scans.

4.4. UV–vis spectra

The Nile Red concentration, for UV–vis spectra, was equal to 5×10^{-5} M.

4.5. Conductivity measurements

Conductivity measurements were carried out by using a conductimeter equipped with a temperature controller. The commercial platinum electrode was calibrated at 298 K by using 1 mol/L aqueous KCl solution.

4.6. ^1H NMR measurements

NMR spectra were collected on a 250 MHz spectrometer. In NMR measurements suitable volumes of RTIL and co-solvent were mixed in a 5 mm NMR tube. A steam coaxial capillary tube loaded with DMSO- d_6 was used for the external lock of the NMR magnetic field/frequency and its signal was used as the ^1H NMR external reference at 2.56 ppm.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.11.033.

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