The effect of some amines and alcohols on the organized structure of [bmim][BF_4] investigated by ^{1}H NMR spectroscopy

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Dedicated to Professor Nicolò Vivona on his 70th birthday

Abstract

The effect exerted by some amines and alcohols on the ^{1}H NMR spectra of 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] has been studied. This ionic liquid, which is one of the most widely used, is characterized by a high structural order degree, as a consequence of the symmetry and the coordination ability of the anion. In order to have information about the dependence of the detected effects on the alcohol or amine structure, some different primary, secondary and tertiary amines and alcohols have been considered. Furthermore, in the case of amines, their basicity has been also taken into account. Both amines and alcohols induce variation in chemical shifts values and signal multiplicity of imidazolium protons. Collected data show that, among imidazolium protons, the aromatic ones are the most affected by the presence of organic molecule. Cross-correlations among chemical shift values relevant to these protons allow us to explain how ^{1}H NMR spectrum variations depend on probe structural properties.

Keywords: Ionic liquids, binary mixtures, ordered structures

Introduction

During the last decade the search for new solvent systems has induced a growing interest in properties and applications of ionic liquids (ILs).[1] Initially, they have been claimed as new green solvents owing to their low vapour pressure and flammability, which favours their industrial applications.[2] However, the main advantages of their use are the higher yields, selectivities and reaction rates that can be detected with respect to conventional organic solvents.[3] Furthermore, the possibility of several different cation-anion combinations allows tailoring of the best IL for any chemical reaction. As a consequence each class of ILs (aliphatic or aromatic, hydrogenated or fluorinated) constitutes a separate class. For instance, both ILs formed by either aromatic or

aliphatic cations, owing to the occurrence of electrostatic interactions, are classified as ordered solvent media. However, in the former ones the ability to present also π–π or C-H---π interactions[4] has suggested to describe them rather as "polymeric supramolecular fluids".[5] Thus, the included reagent molecule, as a consequence of a mutual interaction in such systems, may affect the solvent order degree and change the overall properties of the solvent. Under this light, the shape and the structural organization of reagent molecules, together with their physical-chemical properties, can be important in determining the reactivity in ILs solutions. Some recent literature reports on this topic have underlined that the reactivity of amines in IL solution, both as nucleophiles[6] and bases,[7] is strongly affected by their structure. We have recently detected a disorganizing effect of the amine on the organized structure of IL, by means of ^{1}H NMR and UV-vis spectroscopy.[8] Furthermore, we have also pointed out that the presence of different organic solvents or water can affect the aggregates distribution in aromatic ILs and consequently their catalytic effect.

In general, NMR spectroscopy has been proved to be a powerful tool to investigate the structural organization of neat ILs, as well as their mixtures with solvents, substrates or non ionic surfactants.[9] The main advantage in using spectroscopic methods in order to understand the structurization of ILs, particularly in the presence of imidazolium cations, derives from their peculiar structural features. Indeed, differently from what detected in ordinary molecular solvents, in ILs the C-H bonds of imidazolium cations are extremely sensitive to chemical environment, which induces strong acidity, ion-pair formation and decomposition.[10]

On the grounds of these information, by using ^{1}H NMR spectroscopy we have studied the effect that some different amines (see Chart 1) can exert on the structure of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]). This is one of the most used ILs in organic synthesis. Furthermore, the extensive structural order degree, due to the high symmetry and coordination ability of its anion, makes it a good candidate for our investigation. Several primary, secondary and tertiary amines have been used, which have been chosen on the grounds of their different basicity, structure (open-chain or not) and steric hindrance. Moreover, the investigation has been also carried out in the presence of some aliphatic alcohols (primary, secondary or tertiary). Indeed, alcohols are frequently used in organic synthesis and, if used as co-solvents in IL solution, they may affect the reactivity in these solvent media, as previously mentioned. Finally, among chosen organic molecules, the comparison between cyclohexylamine and cyclohexylalcohol helped us to understand the importance of hydrogen bond donor/acceptor ability of guest molecule functional group in affecting IL properties, under the same alkyl group structure.

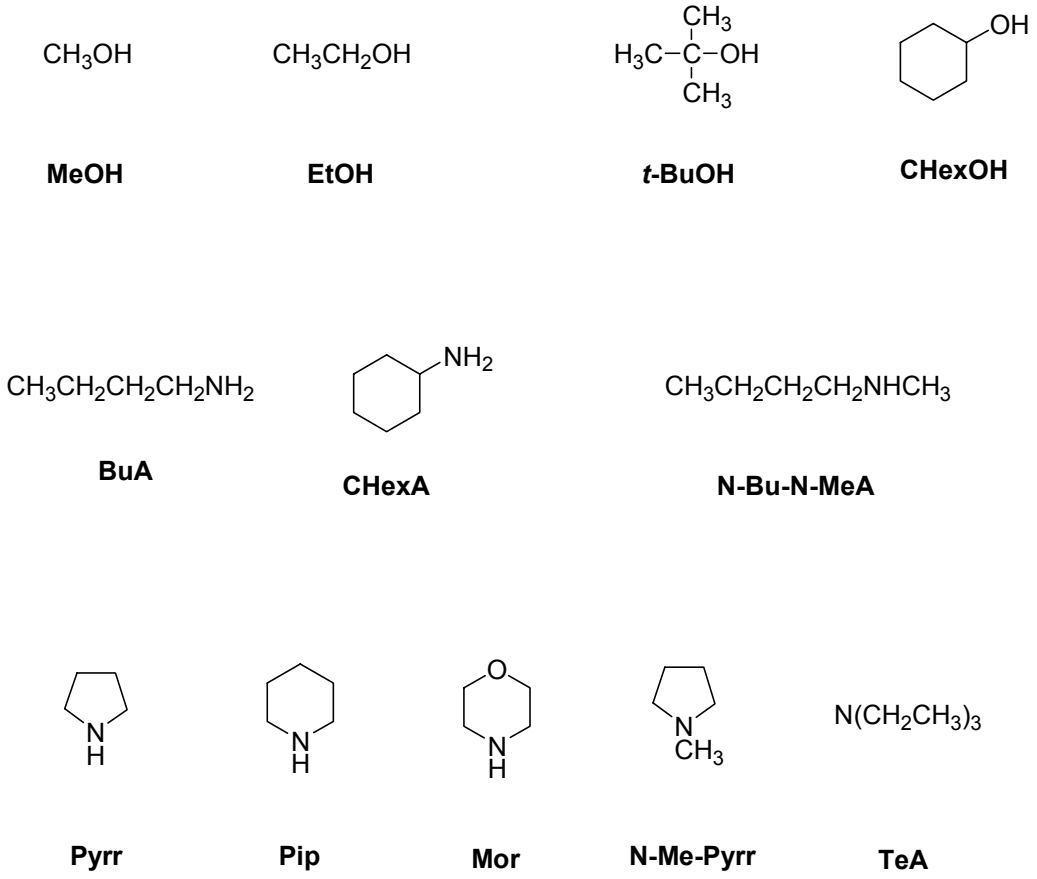


Chart 1. Structure of alcohols and amines used.

Results and Discussion

Measurement method

Suitable samples for NMR measurements were prepared in a 5 mm NMR tube, by mixing different volumes of IL and amine or alcohol, any other NMR solvent was not added. A steam capillary coaxial 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 ^{1}H NMR external reference at 2.56 ppm. In all cases samples were perfectly homogeneous. In Table 1 the ranges of amine or alcohol mole fractions investigated and literature pK_{BH}^+ values of amines used are reported.

Table 1. Investigated mole fraction ranges as a function of organic molecule and pK_{BH}^{+} of used amines

Substrate	$\Delta X_{substrate}$	pK_{BH}^{+}[a]
MeOH[b]	0 ÷ 0.80	
EtOH	0 ÷ 0.77	
t-BuOH	0 ÷ 0.57	
CHexOH	0 ÷ 0.32	
BuA	0 ÷ 0.65	10.68
CHexA	0 ÷ 0.62	10.66
Pyrr	0 ÷ 0.69	11.27
Pip	0 ÷ 0.50	11.12
Mor	0 ÷ 0.68	8.33
N-Me-Pyrr	0 ÷ 0.61	10.46

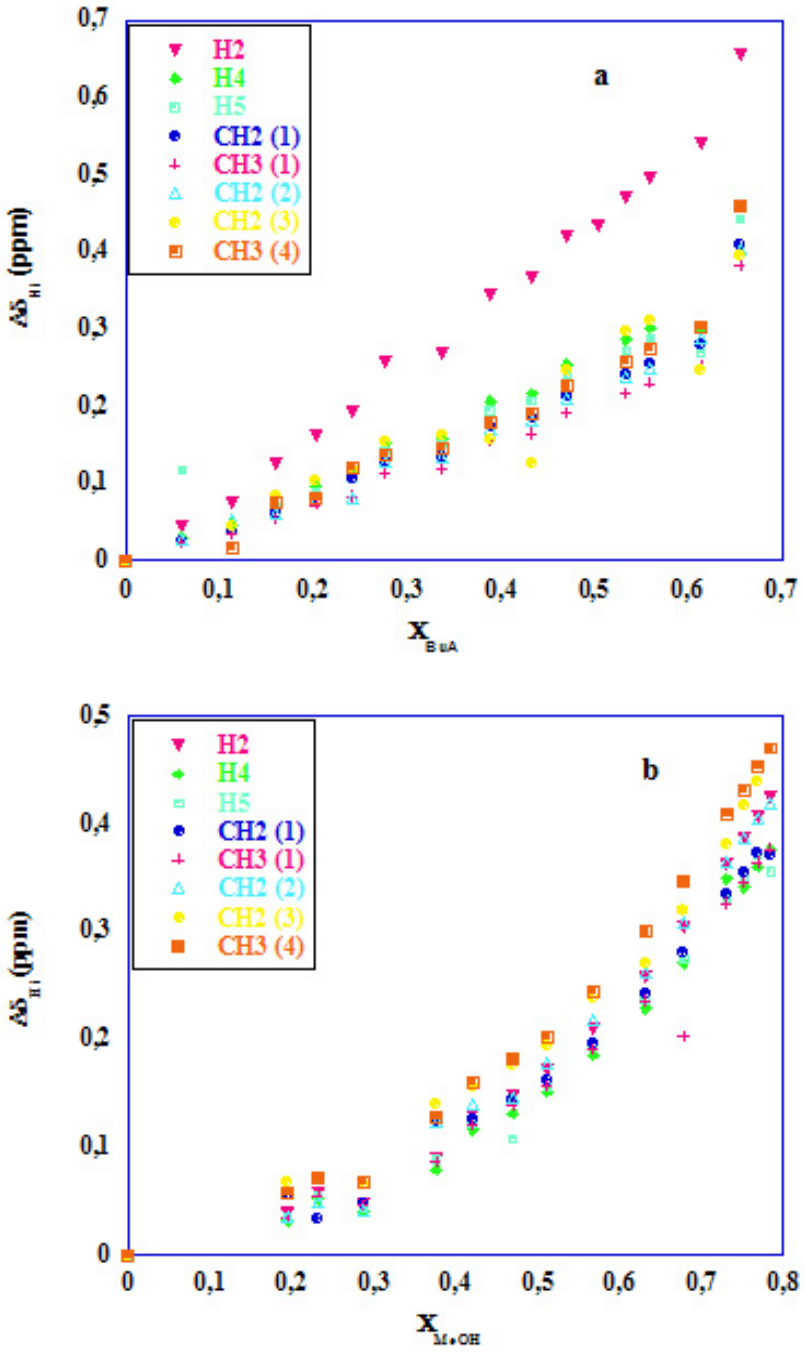
[a]See reference 11. [b]See reference 8.

In all the cases considered, the presence of an organic guest molecule induces significant variations for both the multiplicity of signals and the chemical shifts of imidazolium ion protons. In order to verify if these effects were instantaneous, all measurement solutions were analyzed in a time range of 48 h.

In general, the organic guest molecule causes a downfield shift for all protons of the imidazolium ion. These variations are a function of probe mole fraction, but not of time.

A different behavior was detected for the signals multiplicity. In general, all signals of imidazolium ion protons became broader on going from diluted to concentrated solution in IL. Furthermore, the signal shape changed as a function of time. As a matter of fact, a broadening of signals was detected on going from t = 24h to t = 48h, showing that the effect due to the presence of the guest molecule was a slow process, according to data previously reported by Dupont et al.[5b]

Since values of the observed chemical shifts ($\delta_{Hi,\ binary\ mixture}$) differ widely for different protons, we plotted our data as $\Delta\delta_{Hi}$ ($\Delta\delta_{Hi} = \delta_{Hi,\ binary\ mixture} - \delta_{Hi,\ IL}$). In Figure 1, as an illustrative case, chemical shift variations as a function of mole fraction for [bmim][BF_4]/BuA and [bmim][BF_4]/MeOH binary mixtures are reported.



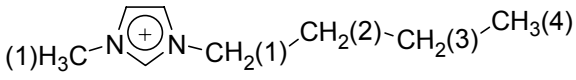


Figure 1. Chemical shift variations ($\Delta\delta_{Hi}$) as a function of organic molecule mole fraction relative to (a) [bmim][BF_4]/BuA and (b) [bmim][BF_4]/MeOH binary mixtures.

The amines effect

At first, we analysed the effect that some different amines could induce on the ^{1}H NMR spectra of [bmim][BF_4]. It is noteworthy that among amines only triethylamine and *N*-butyl-*N*-methylamine did not allow us to carry out the investigation. Indeed, in these cases, biphasic solutions were obtained also in the presence of a small volume (50 μL) of amine.

In order to have information about the effect of amines, we searched for correlations among collected values for different protons at increasing amine mole fraction. According to data previously reported, the slope of this linear correlation allows us to estimate the sensitivity of the interaction between the considered hydrogens and the amine.[12] In all cases a linear correlation was observed. In general, with the only exception of [bmim][BF_4]/N-Me-Pyrr binary mixture, the highest slope values were detected for correlations involving aromatic protons; whereas slope values near to unit were obtained for the aliphatic ones.

In Table 2 the fitting parameters relevant to the correlations involving aromatic protons for all [bmim][BF_4]/amine binary mixtures are reported. Data in Table 2 outline the largest influence on the H2 proton of imidazolium cation. This result perfectly agrees with data previously reported about different spectroscopic properties of C(2)-H bond, compared to C(4)-H and C(5)-H bonds, both in liquid and in gas phase.[13] Furthermore, a deep analysis of reactivity data previously reported outlines the crucial role played by H2 proton of imidazolium cation in determining the outcome of a given reaction in $bmim^+$ based ILs. Indeed, the high endo-selectivity and the rate enhancements of Diels-Alder reaction of cyclopentadiene with methyl acrilate has been ascribed to H-bond donor ability of the cation.[14] On the other hand, the kinetic study of nucleophilic aliphatic substitution of methyl *p*-nitrobenzenesulfonate in the presence of halides has shown that the relative nucleophilicities of these anions are a function of their interaction with H2 of imidazolium cation.[15] More recently, data collected by us about nucleophilic aromatic substitution of aryl halides in ionic liquids/[bmim][N_3] mixtures, to give corresponding aryl azides, have evidenced a negative H-bond donor solvent effect.[16]

For aromatic protons of imidazolium ion, the slope values significantly different from unit (Table 2) should indicate that these protons experience different solvent environments and this agrees with data previously reported by Headley et al.[12]

Table 2. Fitting parameters of correlation $\delta_{H2} = i + m\delta_{Hi}$ relative to imidazolium protons chemical shift in the binary mixture [bmim][BF_4]/amine

	H_i	$i \pm s_i$[a]	$m \pm s_m$[a]	R
		BuA		
H2	H4	(-3.42 ± 0.10)	(1.64 ± 0.01)	0.999
H2	H5	(-3.92 ± 0.10)	(1.73 ± 0.01)	0.999
		CHexA		
H2	H4	(-5.47 ± 0.16)	(1.93 ± 0.02)	0.999
H2	H5	(-6.23 ± 0.21)	(2.05 ± 0.03)	0.999
		Pyrr		
H2	H4	(-7.26 ± 0.24)	(2.16 ± 0.03)	0.998
H2	H5	(-5.78 ± 0.19)	(1.93 ± 0.03)	0.998
		Pip		
H2	H4	(-3.39 ± 0.29)	(1.62 ± 0.04)	0.997
H2	H5	(-2.78 ± 0.18)	(1.52 ± 0.02)	0.999
		Mor		
H2	H4	(-1.14 ± 0.09)	(1.31 ± 0.01)	0.999
H2	H5	(-1.17 ± 0.19)	(1.30 ± 0.02)	0.997
		N-Me-Pyrr		
H2	H4	(0.89 ± 0.22)	(1.04 ± 0.03)	0.992
H2	H5	(0.86 ± 0.18)	(1.03 ± 0.03)	0.995

[a] s_i, s_m = standard deviation

Previous reports have claimed a stronger acidity of H2 of imidazolium cation with respect to the other aromatic protons.[17] Under this light, the highest sensitivity to amine presence detected for this proton, could be ascribed to an acid-base interaction between imidazolium cation and amine. Amines pK_{BH^+} values show that the basicity increases along the series: Mor < N-Me-Pyrr < BuA ~ CHexA < Pip < Pyrr, whereas slope values relevant to δ_{H2} *vs* δ_{H4} or δ_{H2} *vs* δ_{H5} correlations change along the series: N-Me-Pyrr < Mor < Pip < BuA < CHexA < Pyrr. With the exception of Pyrr the slope values increase along the series: primary amine < secondary amine < tertiary amine. The trend of slope values is also different from that of amine basicity in IL recently measured by us through the stability of *p*-nitrophenol/amine ion-pair.[18] On the whole, these data seem to indicate that the amine basicity cannot be considered a parameter able to unequivocally explain the experimental results. They seem to be rather a function of the hydrogen bond donor ability of amino group, with the highest variations in chemical shift detected for primary amines having the largest number of acidic hydrogen atoms. Under this light, the effect of amine presence on the chemical shift values of $bmim^+$ protons could be rationalized considering its ability to interact, via H-bond, with the anion component of IL. This

should hamper the cation-anion interaction, inducing a decrease in the cross-linking and, consequently, a decrease in the structural order degree of IL. This hypothesis allows us to explain the largest sensitivity of H2 proton to amine presence. Indeed, according to previous reports,[19] among aromatic protons of imidazolium ion, the H2 proton is the one able to give the strongest interaction with the anion and, consequently, it is the most affected by amine presence. A similar amine structure effect was previously found by Welton et al.[20] and subsequently confirmed by us.[21] On the other hand, this interaction allows us to rationalize the lowest influence of the amine presence on the aliphatic protons of imidazolium ion, not interacting, with the IL anion.

The peculiar behavior of Pyrr needs a particular explanation. Indeed, unlike the secondary amines, Pyrr affects more significantly the H2 chemical shift of $bmim^+$ cation. This finding seems to indicate a particular disorganizing ability of this amine, probably as a consequence of its structure, and it is in line with the effect exerted on the structural organization of [bmim][BF_4] previously reported by us.[7a]

The disorganizing effect of amines are reflected also on signals multiplicity. As an illustrative case, in Figure 2 the aromatic regions of ^{1}H NMR spectra for [bmim][BF_4]/Pyrr, [bmim][BF_4]/Pip and [bmim][BF_4]/Mor binary mixtures, at $X_{amine} \sim 0.4$, are reported.

As it can be seen, according to linear correlations slopes, the highest disorganizing effect was detected in the presence of Pyrr. In general, the amine presence induces a broadening of the signal relevant to H2 proton and a loss of signals multiplicity for H4 and H5 protons. The latter ones become two signals having an apparent different intensity. These signal variations can be explained on the grounds of the presence of different ion-pairs in the mixtures and agree with literature data.[9i-h, 22] The analysis of spectra, as a function of time, shows a further broadening of signals, accounting for the occurrence of a slow process.

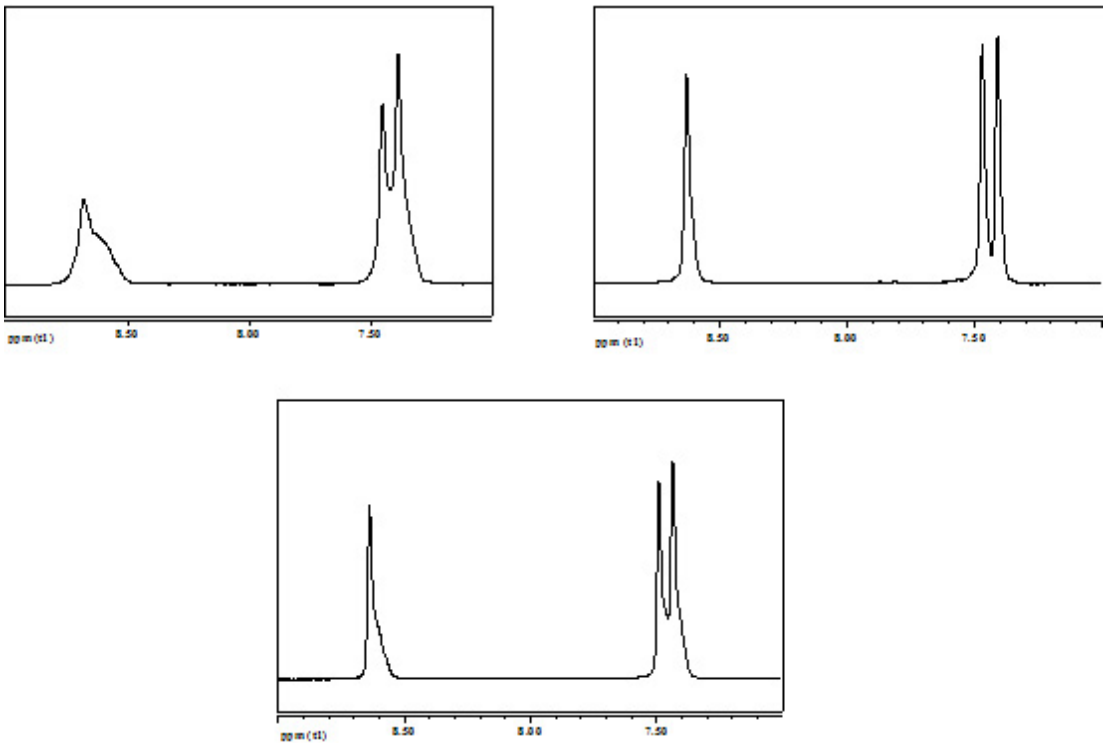


Figure 2. Aromatic regions of ^{1}H NMR spectra relative to (a) [bmim][BF_4]/Pyrr, (b) [bmim][BF_4]/Pip and (c) [bmim][BF_4]/Mor binary mixtures, at X_{amine} ~ 0.4.

The functional group effect

Bearing in mind all previous results, we analysed the effect of cyclohexylalcohol on the ^{1}H NMR spectrum of [bmim][BF_4]. In this case, under the same alkyl group structure, the effect of the functional group ability as H-bond donor/acceptor and, consequently its interaction with the anion of the IL should be evaluated. As well as the amines, the presence of alcohol molecule moved all signals of imidazolium protons to low fields, with the highest chemical shift variations detected for H2 of the imidazolium ring and the terminal group CH_3 of the butyl chain, showing that the guest molecule prevalently affects the more acidic (H2) and the more external protons (CH_3).

In Table 3 the fitting parameters relevant to correlations involving aromatic protons for [bmim][BF_4]/CHexOH binary mixtures are reported. For a useful comparison, data for [bmim][BF_4]/CHexA binary mixtures are also reported.

Table 3. Fitting parameters of correlation $\delta_{H2} = i + m\delta_{Hi}$ relevant to imidazolium protons chemical shift in the binary mixture [bmim][BF_4]/CHexA and [bmim][BF_4]/CHexOH

	H_i	$i \pm s_i$[a]	$m \pm s_m$[a]	R
		CHexA		
H2	H4	(-5.47 ± 0.16)	(1.93 ± 0.02)	0.999
H2	H5	(-6.23 ± 0.21)	(2.05 ± 0.03)	0.999
		CHexOH		
H2	H4	(-0.83 ± 0.17)	(1.27 ± 0.02)	0.999
H2	H5	(-1.48 ± 0.26)	(1.37 ± 0.04)	0.998

[a] s_i, s_m = standard deviation

Also in this case, among aromatic protons, H2 is the most affected by the alcohol presence. However, the comparison between slope values for [bmim][BF_4]/CHexA and [bmim][BF_4]/CHexOH mixtures shows that in the latter case, the guest molecule induces a weaker effect on the supramolecular structure of [bmim][BF_4]. This result could be ascribed to the weaker H-bond donor ability of the hydroxyl group with respect to the amino group, confirming that the main disorganizing effect is due to the interaction between the IL anion and probes acidic hydrogens.

A similar effect was detected considering the signals multiplicity. In Figure 3 the aromatic regions of ^{1}H NMR spectra relative to [bmim][BF_4]/CHexA and [bmim][BF_4]/CHexOH, at X_{guest} ~ 0.3 are reported. As it can be seen, signals relative to [bmim][BF_4]/CHexA binary mixture result broader, as a consequence of a more significant disorganizing effect.

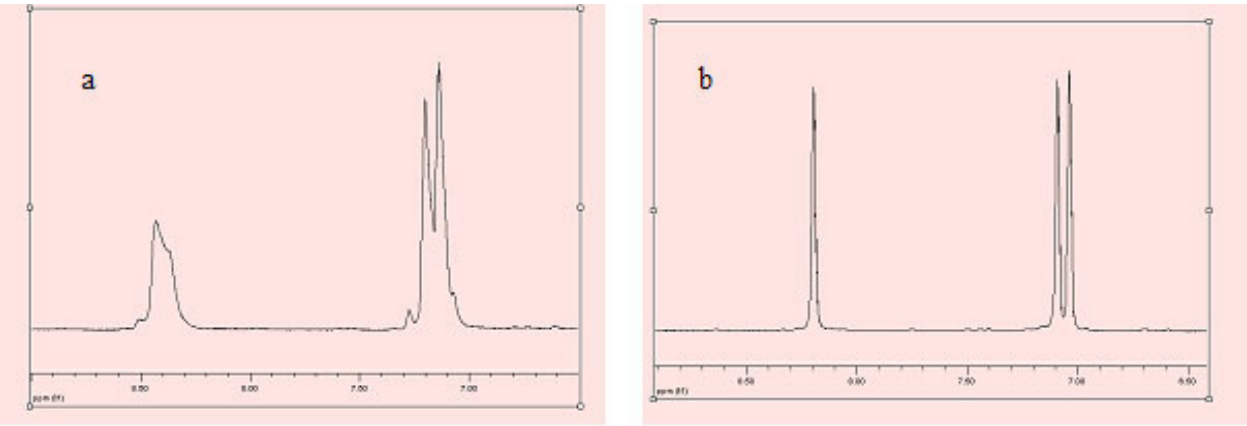


Figure 3. Aromatic regions of ^{1}H NMR spectra relative to (a) [bmim][BF_4]/CHexA, (b) [bmim][BF_4]/CHexOH at X_{amine} ~ 0.3.

The alcohols effect

In order to have information about the effect exerted by the alkyl group structure on the ^{1}H NMR spectrum of [bmim][BF_4], we studied binary mixtures formed in the presence of some aliphatic alcohols. The chosen alcohols showed different steric hindrances (MeOH, EtOH, *t*-BuOH) and structural order degree (acyclic alcohols and CHexOH). Also in this case, different mole fraction ranges were investigated as a function of the different solubility of alcohols in the used IL.

The chemical shift variations seem to be function of the nature of the alcohol. In Figure 3 $\Delta\delta_{H2}$ values, as a function of different alcohols mole fraction, are reported.

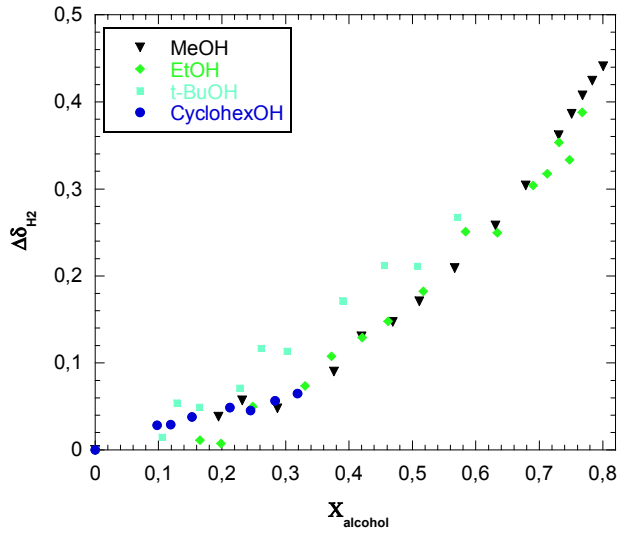


Figure 3. Chemical shift variations for imidazolium ion H2 in different [bmim][BF_4]/alcohol binary mixtures.

Among the alcohols considered, the largest chemical shift variations were detected in the presence of *t*-BuOH, whereas the lowest ones were detected in the presence of two primary alcohols. Also in this case we searched for correlations among collected values relevant to different protons, at increasing alcohol mole fraction. In Table 4 fitting parameters relative to correlations involving aromatic protons for all [bmim][BF_4]/alcohol binary mixtures are reported.

Data reported in Table 4 show that the slope values change along the series:

MeOH ~ EtOH < *t*-BuOH ~ CHexOH

In order to explain this trend, we have analysed collected data as a function of polarity and alkyl group steric hindrance of the alcohols used. Both these factors can affect the structural organization of the IL. In this case we have not considered the alcohol basicity as a parameter able to explain the experimental results. Indeed, as previously mentioned, this parameter is not able to explain data obtained in the presence of amines and, as it is well known, differences among basicities of amines are more significant than differences among basicities of alcohols.[23]

Data collected show that the observed trends for chemical shifts are opposite to alcohol polarities. Indeed, the E_T^N values for the alcohols used increase in the order:

t-BuOH < CHexOH < EtOH < MeOH

(E_T^N = 0.389, 0.500, 0.654, 0.762 for *t*-BuOH, CHexOH, EtOH and MeOH respectively).[24] Furthermore, *t*-BuOH and CHexOH having the lowest polarity, seemed to be the guest molecules able to induce a slightly larger shift.

Table 4. Fitting parameters of correlation $\delta_{H2} = i + m\delta_{Hi}$ relative to imidazolium protons chemical shift in the binary mixtures [bmim][BF_4]/alcohol

	H_i	$i \pm s_i$[a]	$m \pm s_m$[a]	R
		MeOH[b]		
H2	H4	(0.34 ± 0.11)	(1.11 ± 0.01)	0.999
H2	H5	(0.02 ± 0.22)	(1.15 ± 0.03)	0.996
		EtOH		
H2	H4	(0.06 ± 0.03)	(1.15 ± 0.01)	0.999
H2	H5	(-0.23 ± 0.07)	(1.20 ± 0.01)	0.999
		***t*-BuOH**		
H2	H4	(-0.52 ± 0.15)	(1.24 ± 0.02)	0.998
H2	H5	(-0.33 ± 0.19)	(1.20 ± 0.03)	0.997
		CHexOH		
H2	H4	(-0.83 ± 0.17)	(1.27 ± 0.02)	0.999
H2	H5	(-1.48 ± 0.26)	(1.37 ± 0.04)	0.998

[a]s_i, s_m = standard deviation. [b]See reference 8.

A more homogeneous trend can be found, taking into account the E_s parameter and then the structural requirements of alcohols used. Indeed, the steric requirements of alkyl group increases in the order: CH_3 < C_2H_5 < *t*-Bu < Cyclohexyl (E_s = -1.24, -1.31, -1.78, -2.03 for Me, Et, *t*-Bu and Cyclohexyl respectively).[25] This trend perfectly agrees with the increase in slope values reported in Table 4, suggesting that the effect due to alcohol presence could be mainly ascribed to alkyl group steric bulk that, in turn, may affect the structural organization of [bmim][BF_4].

The alcohol presence induces some significant variations also in signal multiplicities. In Figure 4 ^{1}H NMR spectra for [bmim][BF_4]/alcohol binary mixtures, at X_{ROH} = 0.37, are reported.

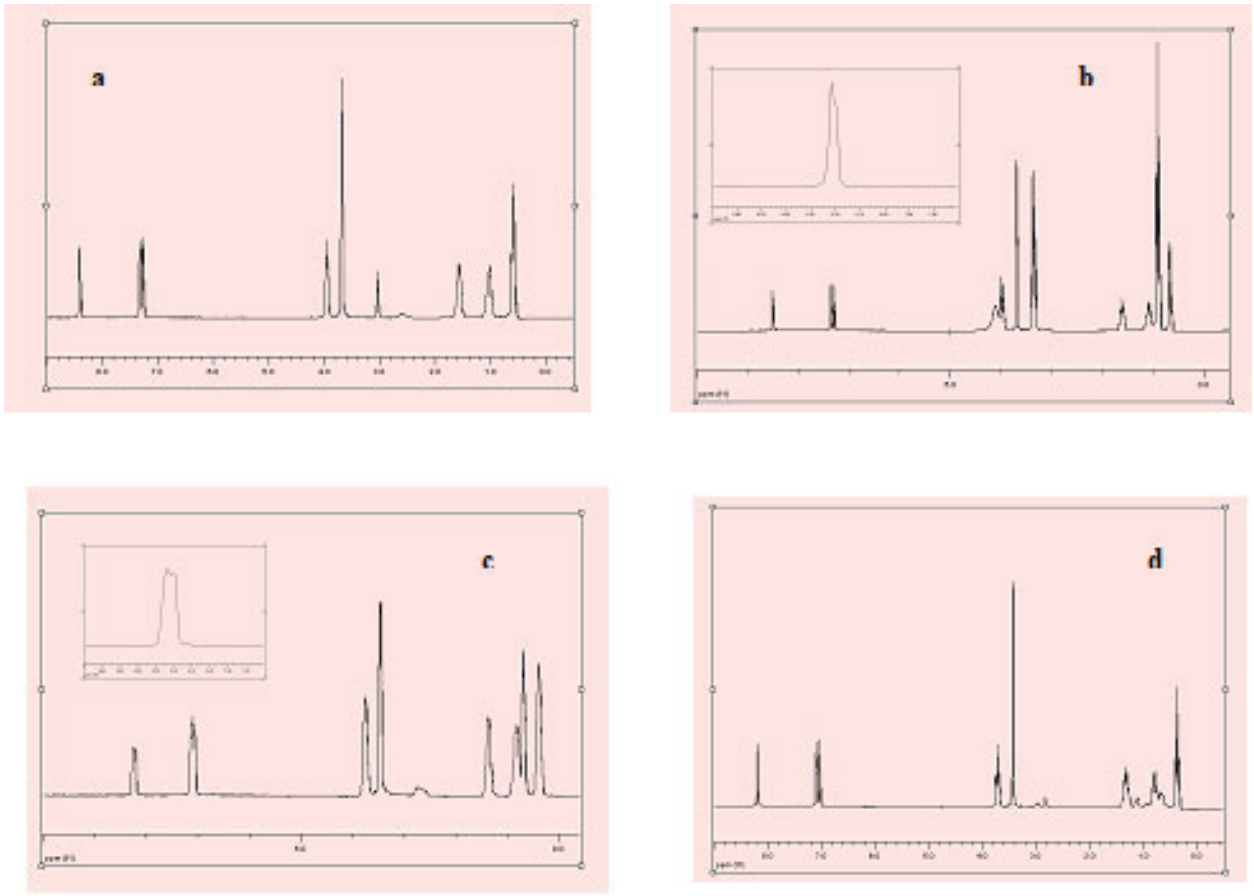


Figure 4. ^{1}H NMR spectra relevant to (a) [bmim][BF_4]/MeOH, (b) [bmim][BF_4]/EtOH, (c) [bmim][BF_4]/t-BuOH, (d) [bmim][BF_4]/CHexOH at X_{amine} ~ 0.37.

In particular, in the presence of EtOH and *t*-BuOH all signals undergo significant broadening (Figures 4b and 4c). Furthermore, a comparison between the signals relevant to H2 of imidazolium cation (see inset of Figure 4b and 4c), shows that the broadening is more significant in the presence of *t*-BuOH. This result seems to be further confirmed by a comparison between half height peak widths ($\Delta\nu_{1/2}$ = 0.052 and 0.092 in the presence of EtOH and *t*-BuOH respectively).

The influence on both cross correlations of chemical shift values and signals shape, detected in this work, perfectly agrees with data reported by Tubbs et al.[9i] and recently confirmed by us studying some IL/organic solvents binary mixtures.[8] These effects have been ascribed to the existence of an equilibrium between aggregates and isolated ions, that should exhibit different chemical shift values. According to our data,[8] in the absence of specific interactions, such as hydrogen bonding, this distribution is mainly affected by structural requirements of guest molecule, rather than by physical properties such as polarity.

Conclusions

Collected data show that the presence of an organic molecule is able to affect the ^{1}H NMR spectra of ionic liquids, such as [bmim][BF_4]. The variations detected both in chemical shifts and signals multiplicity can be ascribed to a disorganization of IL supramolecular structure. However, different factors must be taken into account as a function of the nature of the guest molecule. Indeed, in the presence of amines the driving force of the disorganizing effect is due to the ability of the guest molecule to interact, via hydrogen bond, with the IL anion. This induces a decrease in the cation-anion interaction and then in the cross-linking degree of [bmim][BF_4]. On the other hand, in the presence of alcohols, having a lower hydrogen bond donor ability, the supramolecular structure of [bmim][BF_4] is mainly affected by structural requirements of guest molecule, such as alkyl bulk. Above results are in line with evidences previously obtained by means of molecular dynamics simulations, carried out on mixtures of imidazolium based ILs and polar solutes such as MeOH and CH_3CN, showing a different location of the solute in the organized structure of ILs, as a function of its molecular properties.[26]

Experimental Section

Materials. [bmim][BF_4], was purchased and used without further purification. It was dried before use on a vacuum line at 70 °C for at least 2h, stored in a dryer under argon and over calcium chloride. Alcohols (fluorescence grade) were purchased and used without further purification. Amines were freshly distilled before use. NMR spectra were collected on a 300 MHz spectrometer.

Acknowledgements

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References

1. (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Wasserscheid, P.; Keim, M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3772. (c) Rogers, R. D.; Seddon, K. R. *Ionic Liquids as Green Solvents. Progress and Prospects*, ACS Symposium Series 856. American Chemical Society: Washington, DC, 2003. (d) Chiappe, C.; Pieraccini, D. *J. Phys. Org. Chem.* **2005**, *18,* 275. (e) Rogers, R. D.; Seddon, K. R. *Ionic Liquids III A: Fundamentals, Progress, Challenges and Opportunities,* ACS Symposium Series 901. American Chemical Society: Washington, DC, 2005. (f) Harper, J. B.; Kobrak, M. N. *Mini-Rev. in Org. Chem.* **2006**, *3*, 253. (g)

Malhotra, S. V. *Ionic Liquids in Organic Synthesis*. ACS Symposium Series 950. American Chemical Society: Washington, DC, 2005. (h) Chowdhury, S.; Mohan, R. S.; Scott, J. L. *Tetrahedron* **2007**, *63*, 2363. (i) *Ionic Liquids in Synthesis.* Wasserscheid, P.; Welton, T., Eds. Wiley–VCH: Weinheim, 2008.

2. (a) Rogers, R. D.; Seddon, K. R. *Ionic Liquids: Industrial Application to Green Chemistry*, ACS Symposium Series 818. American Chemical Society: Washington, DC, 2002. (b) Rogers, R. D.; Seddon, K. R.; Volkov, S. *Green Industrial Application of Ionic Liquids*, NATO Science Series II. Mathematics, Physics and Chemistry, Kluwer, Dordrecht, 2003, vol. 92. (c) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, *37*, 123.
3. (a) Chiappe, C.; Pieraccini, D. *Arkivoc* **2002**, (*xi*), 249. (b) Kaar, J. L.; Jesionowski, A. M.; Berberich, J. A.; Moulton, R.; Russell, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 4125. (c) Maruyama, T.; Yamamura, H.; Kotani, T.; Kamiya, N.; Goto, M. *Org. Biomol. Chem.* **2004**, *2*, 1239. (d) Sasaki, K.; Matsumara, S.; Toshima, K. *Tetrahedron Lett.* **2004**, *45*, 7043. (e) Mo, J.; Xu, L.; Xiao, J. *J. Am. Chem. Soc.* **2005**, *127*, 751. (f) Akiyama, T.; Suzuki, A.; Fuchibe, K. *Synlett* **2005**, 1024. (g) Ranu, B. C.; Jana, R. *J. Org. Chem.* **2005**, *70*, 8621. (h) Conte, V.; Floris, B.; Galloni, P., Mirruzzo, V.; Scarso, A.; Sordi, D.; Strukul, G. *Green Chem.* **2005**, *7*, 262. (i) Laali, K. K.; Sarca, V. D.; Okazaki, T.; Brock, A.; Der, P. *Org. Biomol. Chem*. **2005**, *3*, 1034. (j) Man, B. Y. W.; Hook, J. M.; Harper, J. B. *Tetrahedron Lett.* **2005**, *46*, 7641. (k) Lindén, A. A.; Johansson, M.; Hermanns, N.; Bäckvall, J. -E. *J. Org. Chem.* **2006**, *71*, 3849. (l) Chiappe, C.; Piccioli, P.; Pieraccini, D. *Green Chem.* **2006**, *8*, 277. (m) Yoshino, T.; Imori, S.; Togo, H. *Tetrahedron* **2006**, *62*, 1309. (n) Duan, Z.; Gu, Y.; Deng, Y. *J. Molecular Catalysis A: Chem.* **2006**, *246*, 70. (o) van Rantwiij, K. F.; Sheldon, R. A. *Chem. Rev.* **2007**, *107*, 2757. (p) Legeay, J. C.; Vanden Eynde, J. J.; Toupet, L.; Bazureau, J. *Arkivoc* **2007**, (*iii*), 13. (q) Ma, X.; Zhou, Y.; Zhang, J.; Zhu, A.; Jiang, T.; Han, B. *Green Chem.* **2008**, *10*, 59. (r) Yadav, J. S.; Reddy, B. V. S.; Sreedhar, P.; Kondaji, G.; Nagaiah, K. *Catalysis Comm.* **2008**, *9*, 590.
4. (a) Atwood, J. L. *Liquid Chlatrates, Inclusion Compounds*, Atwood, J. L.; Davies, J. E. D.; Mac Nicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1. (b) Su, B. –M.; Zhang, S.; Zhang, Z. C. *J. Phys. Chem. B* **2004**, *108*, 19510. (c) Iwata, K.; Kakita, M.; Hamaguchi, H. *J. Phys. Chem. B* **2007**, *111*, 4914. (d) Hanke, C. G.; Johansson, A.; Harper, J. B.; Lynden-Bell, R. M. *Chem. Phys. Lett.* **2003**, *374*, 85. (e) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. *Chem. Commun.* **2003**, 476. (f) Harper, J. B.; Lynden-Bell, R. M. *Mol. Phys.* **2004**, *102*, 85.
5. (a) Dupont, J. *J. Braz. Chem*. **2004**, *15*, 341. (b) Consorti, C. S.; Suarez, P. A.; de Souza, R. F.; Burrow, R. A.; Farrar, D. H.; Lough, A. J.; Loh, W.; da Silva, L. H. M.; Dupont, J. *J. Phys. Chem. B* **2005**, *109*, 4341. (c) Dupont, J.; Suarez, P. A. Z. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2441.
6. Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Navsaiah, A. V. *Tetrahedron Lett.* **2003**, *42*, 4364.

7. (a) D'Anna, F.; Frenna, V.; Pace, V.; Noto, R. *Tetrahedron* **2006**, *62*, 1690. (b) D'Anna, F.; La Marca, S.; Noto, R. *J. Org. Chem.* **2008**, *73*, 3397.
8. (a) D'Anna, F.; Frenna, V.; La Marca, S.; Noto, R.; Pace, V.; Spinelli, D. *Tetrahedron* **2008**, *64*, 672.
9. (a) Robinson, J.; Bugle, R. C. Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 3776. (b) Fannin, A. A. jr.; King, L. A.; Levisky, J. A.; Wilkes, J. S. *J. Phys. Chem.* **1984**, *88*, 2609. (c) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1994**, 3405. (d) Antony, J. H.; Mertens, D.; Dölle, A.; Wassercheid, P.; Carper, W. R. *Chem. Phys. Chem.* **2003**, *4*, 588. (e) Heimer, N. E.; Del Sesto, R. E.; Carper, W. R. *Magn. Res. Chem.* **2004**, *42*, 71. (f) Dupont, J.; Suarez, P. A. Z.; De Souza, R. F.; Burrow, R. A.; Kintzinger, J. –P. *Chem. Eur. J.* **2000**, 2377. (g) Mele, A.; Tran, C. D.; De Paoli Lacerda, S. H. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 4364. (h) Su, B. –M.; Zhang, S.; Zhang, Z. C. *J. Phys. Chem. B* **2004**, *108*, 19510. (i) Tubbs, J. D.; Hoffmann, M. M. *J. Sol. Chem.* **2004**, *33*, 381. (j) Wulf, A.; Fumino, K.; Michalik, D.; Ludwing, R. *Chem. Phys. Chem.* **2007**, *111*, 2506. (k) Li, N.; Cao, Q.; Gao, Y.; Zheng, L.; Bai, X.; Yu, L.; Zhao, X.; Zhang, J.; Zheng, L.; Bai, X.; Dong, B.; Li, Z.; Zhao, M.; Yu, L. *Chem. Phys. Chem.* **2007**, *8*, 2211. (l) Sing, T.; Kumar, A. *J. Phys. Chem. B* **2007**, *111*, 7843. (m) Bankmann, D.; Giernoth, R. *Prog. Nucl. Magn. Res. Spectr.* **2007**, *51*, 63. (n) Zhao, Y.; Gao, S.; Wang, J.; Tang, J. *J. Phys. Chem. B* **2008**, *112*, 2031.
10. (a) Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006**, *439*, 831. (b) Wassercheid, P. *Nature* **2006**, *439*, 797.
11. (a) Frenna, V.; Vivona, N.; Consiglio, G.; Spinelli, D. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1865. (b) Hall, H. R., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5441. (c) Lide, D. R. CRC *Handbook of Chemistry and Physics*, 80th ed.; CRC: London, 1999-2000.
12. (a) Headley, A. D.; Jackson, N. M. *J. Phys. Org. Chem.* **2002**, *15*, 52. (b) Headley, A. D.; Kotti, S. R. S. S.; Nam, J.; Li, K. *J. Phys. Org. Chem.* **2005**, *18*, 1018.
13. Wulf, A.; Fumino, K.; Michalik, D.; Ludwig, R. *Chem. Phys. Chem.* **2007**, *8*, 2265.
14. Aggarwal, A.; Lancaster, N. L.; Sethi, A. R.; Welton, T. *Green Chem.* **2002**, *4*, 517.
15. Lancaster, N. L.; Salter, P. A.; Welton, T.; Young, G. B. *J. Org. Chem.* **2002**, *67*, 8855.
16. D'Anna, F.; Marullo, S.; Noto, R. *J. Org. Chem.* **2008**, *73*, 6224.
17. Handy, S. T.; Okello, M. *J. Org. Chem.* **2005**, *70*, 1915.
18. D'Anna, F.; Noto, R. *Tetrahedron* **2007**, *63*, 11681.
19. (a) Köddermann, T.; Wertz, C.; Heintz, A.; Ludwig, R. *Chem. Phys. Chem.* **2006**, *7*, 1944. (b) Gozzo, F. C.; Santos, L. S.; Augusti, R.; Consorti, C. S.; Dupont, J.; Eberlin, M. N. *Chem. Eur. J.* **2004**, *10*, 6187. (c) Bini, R.; Bortolini, O.; Chiappe, C.; Pieraccini, D.; Siciliano, T. *J. Phys. Chem. B* **2007**, *111*, 598.
20. Crowhurst, L.; Lancaster, N. L.; Pérez-Arlandis, J. M.; Welton, T. *J. Am. Chem. Soc.* **2004**, *126*, 11549.
21. D'Anna, F.; Frenna, V.; Noto, R.; Pace, V.; Spinelli, D. *J. Org. Chem.* **2006**, *71*, 9637.

22. (a) Avent, A.; Chaloner, A. P.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1994**, 3405. (b) Bonhôte, P.; Dias, A. –P.; Papageorgiou, N.; Kalymnasundraram, K.; Gräzel, M. *Inorg. Chem.* **1996**, *35*, 1168.
23. Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.
24. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim 1988, 365.
25. Hansch, C.; Leo A. J. in *Substituent Constants for Correlation Analysis in Chemistry and Biology* 1979.
26. Canongia Lopes, J. N.; Costa Gomes, M. F.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 16816. (b) Padua, A. A. H.; Costa Gomes, M. F.; Canongia Lopes, J. N. A. *Acc. Chem. Res.* **2007**, *40*, 1087.