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Electronic and Steric Effects: How Do They Work in Ionic Liquids? The Case of Benzoic Acid Dissociation

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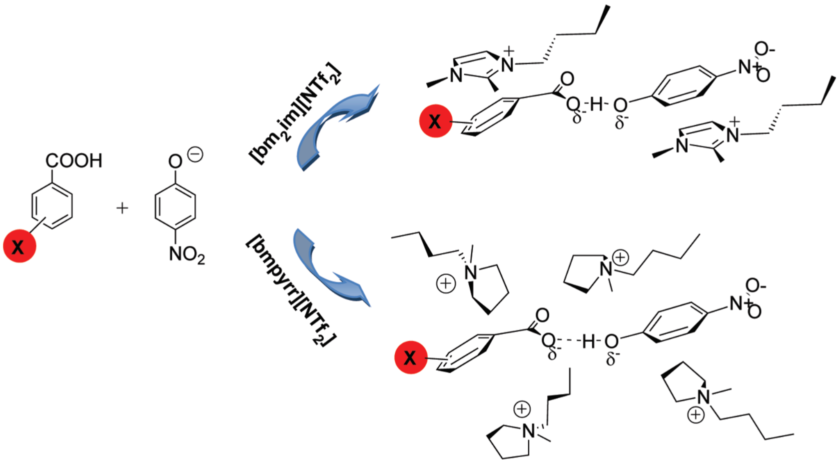

The need to have a measure of the strength of some substituted benzoic acids in ionic liquid solution led us to use the protonation equilibrium of sodium *p*-nitrophenolate as a probe reaction, which was studied by means of spectrophotometric titration at 298 K. In order to evaluate the importance of electronic effect of the substituents present on the aromatic ring, both electron-withdrawing and -donor substituents were taken into account. Furthermore, to have a measure of the importance of the steric effect of the substituents both para- and ortho-substituted benzoic acids were analyzed. The probe reaction was studied in two ionic liquids differing for the ability of the cation to give hydrogen bond and $\pi-\pi$ interactions, namely [$\mathrm{bm_2im}$][$\mathrm{NTf_2}$] and [bmpyrr][$\mathrm{NTf_2}$]. Data collected show that benzoic acids are less dissociated in ionic liquid than in water solution. Furthermore, the equilibrium constant values seem to be significantly affected by both the nature of ionic liquid cation and the structure of the acid. In particular, the ortho-steric effect seems to operate differently in water and in the aromatic ionic liquid, determining in this solvent medium a particular behavior for ortho-substituted benzoic acids.

Introduction

The pK_a determination of an organic acid or base plays a significant role in different fields of chemical research. During the years, a plethora of papers on the topic have underlined the importance of pK_a knowledge in rationalizing pharmacological effect of organic compounds,[1] reaction mechanisms,[2] properties of new organic materials,[3] and so on. However, in all cases, different authors agree in outlining an important point: acid or base properties of a solute are heavily affected by the microenvironment in which they are determined. Consequently, different reports in the literature have had, as the main subject, the pK_a determination in nonaqueous solvents and the comparison of the results obtained with values previously collected in water solution.[4] In particular, as far as benzoic acids are concerned, the study of the effects due to a different nature and position of the substituent on the aromatic ring, together with

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the effects deriving from solvation phenomena, have played a significant role in the field of physical organic chemistry.[5]

Generally, two different viewpoints have been argued about the essence of solvation phenomena. The first one considers the extent of solute−solvent interactions as a result of physical parameters of solvent (such as electrical permittivity and refraction index) and molecular characteristics of solute. The second one hypothesizes that solvation phenomena are determined by specific interactions between solvent and solute. During the years, this distinction between "universal" and "specific" solvation has been subjected to criticism, although it is largely used for practical applications.

Such a kind of analysis may become more complex when solvent media show peculiar features such as those characterizing ionic liquids (ILs). These new generation solvents have been frequently highlighted for their environmentally friendly properties (low vapor pressure and flammability).[6] As well as for conventional solvents, ILs have been considered under different points of views. Indeed, they have been frequently assimilated to conventional solvents, and their solvation phenomena have been rationalized on the grounds of classical solvent parameters, such as α, β, π^*, and so on.[7] On the other hand, a different picture of these solvent media describes them as polymeric supramolecular fluids in which a solute is not solvated but included in their tridimensional structure.[8] Furthermore, they have been also depicted as molten salts and their different effects rationalized on the grounds of electrostatic interactions.[9] Of course, irrespective of the viewpoint considered, the acid−base equilibria and the relevant $\mathrm{p}K_a$ values, determined in these solvent media, will be heavily affected by the properties of IL used.

Taking into account this information, and in the framework of our studies on ILs properties,[10] we thought it could be interesting to determine the acid strength of some substituted benzoic acids in IL solution. The need to have a measure of the acid strength in IL solution has been claimed in order to control the acidity level in these media[11] and to avoid the

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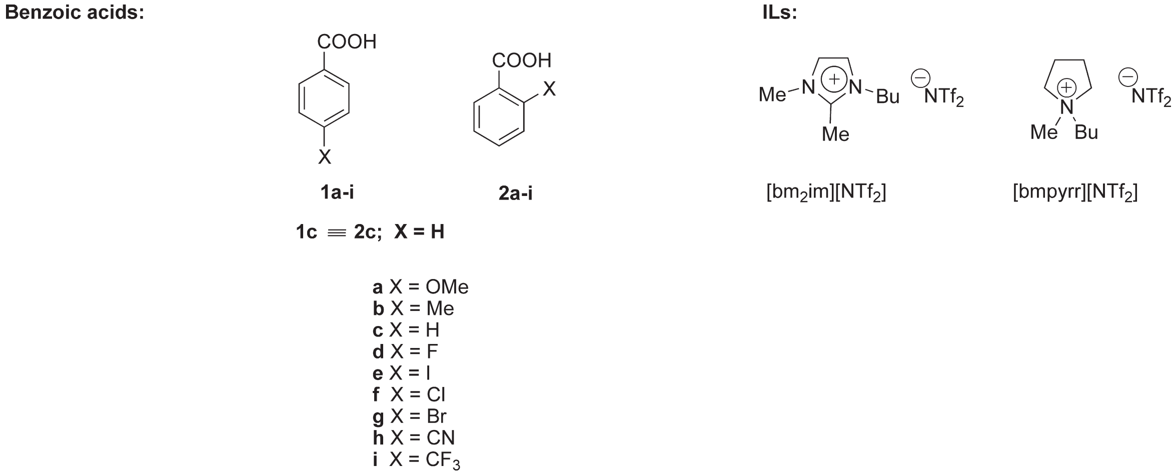
CHART 1. Structure of Benzoic Acids and ILs Used



1a-i **2a-i**

[bm2im][NTf2] [bmpyrr][NTf2]

1c ≡ **2c**; X = H

a X = OMe
b X = Me
c X = H
d X = F
e X = I
f X = Cl
g X = Br
h X = CN
i X = CF3

possible mistakes deriving from the use, in IL solution, of pK_a values collected in aqueous solution.[12]

We used the protonation equilibrium of sodium *p*-nitrophenolate as probe reaction, which recently allowed us to have a measure of the acidity of some aliphatic and aromatic carboxylic acids.[13] The reaction was followed by means of UV−vis spectroscopy at 298 K.

We turned out our attention to some para- and ortho-substituted benzoic acids (see Chart 1). In particular, the different nature of the substituents present on the aromatic ring could allow to evaluate the importance of the electronic effect in determining the acid strength in IL solution. Furthermore, it would be possible to verify if the acid strength may be affected not only by classical electronic effects, but also by peculiar solute−solvent interactions. On the other hand, the different position of the substituent on the aromatic ring (ortho and para position) could allow for estimation of the importance of its steric effect. We were not able to study the target reaction for nitro-substituted benzoic acids because the strong absorption band superimposed on the one of the *p*-nitrophenolate anions did not allow for a reliable measurement of the equilibrium constant.

The probe reaction was studied in [bm$_2$im][NTf$_2$] and in [bmpyrr][NTf$_2$] solution [where bm$_2$im = 1-butyl-2,3-dimethylimidazolium, bmpyrr = *N*-butyl-*N*-methylpyrrolidimium, NTf$_2$ = bis(trifluoromethansulfonyl)imide]. The chosen ILs differ in the cation's ability to give H-bond and $\pi-\pi$ interactions as well. It is well-known that both these factors can be important in determining the behavior of a solute in IL solution. Furthermore, the [NTf$_2^-$] anion is a weakly basic anion, and its use does not probably affect the acidity scale determination. In our opinion, the present experimental method can be confidently applied to carboxylic acids having pK_a values ranging from 2.4 to 5.

Results and Discussion

It has been previously reported[13] that in IL solution the sodium *p*-nitrophenolate, unlike from *p*-nitroaniline or 2,4-dinitrophenolate, is a base able to undergo changes in the UV−vis spectra that can be correlated to the strength of the used benzoic acids. We analyzed the behavior of sodium *p*-nitrophenolate in [bmim][BF$_4$] and in [bmim][NTf$_2$] solution. However, in both cases, the indicator is found in protonated form also in the absence of an acid. Probably, the acidity of H2 of the bmim$^+$ ion was sufficiently high to protonate the base indicator. On the grounds of this results, we chose as solvent systems the less acidic [bm$_2$im][NTf$_2$] and [bmpyrr][NTf$_2$].

Regular variations in the UV−vis spectra are obtained as a function of acid concentration. As an illustrative example, UV−vis spectra of sodium *p*-nitrophenolate in the presence of increasing concentration of *p*-chlorobenzoic acid, in [bm$_2$im][NTf$_2$] solution at 298 K, are reported in Figure 1. Spectra show the absorbance decrease at λ_{max} = 402 nm and the corresponding increase at λ_{max} = 310 nm. Moreover, the presence of a neat isosbestic point at $\lambda \sim 344$ nm indicates that in IL solution a single equilibrium, such as the one depicted in eq 1, is operating:

$$\mathrm{ArO^-\,Na^+ + HA} \overset{K}{\rightleftharpoons} \mathrm{ArOH + Na^+A^-} \quad (1)$$

The equilibrium constant can be defined as

$$K = \frac{[\mathrm{ArOH}][\mathrm{Na^+A^-}]}{[\mathrm{ArO^-\,Na^+}][\mathrm{HA}]} \quad (2)$$

Considering the mass balances relevant to *p*-nitrophenolate and carboxylic acid, the absorbance variation can be expressed as

$$(\Delta\mathrm{Abs})^2/\mathrm{Abs_i} = (\mathrm{Abs_0} - \mathrm{Abs_i})^2/\mathrm{Abs_i} = \Delta\varepsilon d K[\mathrm{HA}] \quad (3)$$

where Abs$_i$ and Abs$_0$ are the absorbances, at a suitable wavelength, of *p*-nitrophenolate in the presence and in the absence of acid, respectively, $\Delta\varepsilon$ is the variation in molar absorbitivity as a consequence of the protonation equilibrium, K is the equilibrium constant value, and d is the length of the optical path (for details of the calculation method see ref 13).

It is noteworthy that in water solution equilibrium constant values, calculated by eq 2, equal the ratio between the

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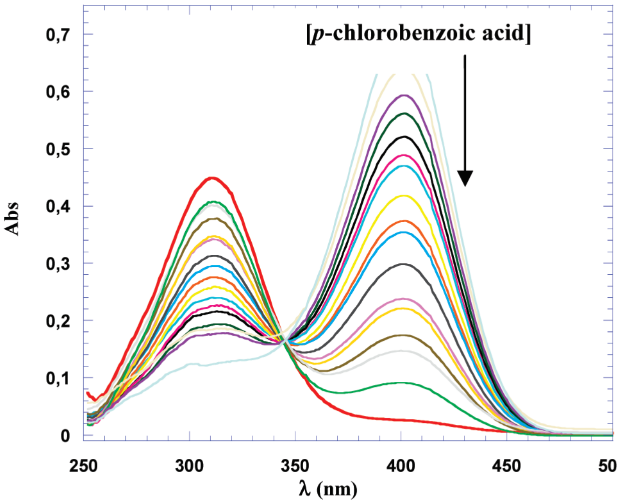

FIGURE 1. UV–vis spectra of sodium *p*-nitrophenolate (0.0002 M) in the presence of increasing concentrations of *p*-chlorobenzoic acid (0–0.006 M) at 298 K in [bm_2im][NTf_2] solution.

TABLE 1. Equilibrium Constant Values (*K*), at 298 K, Corresponding to Protonation of Sodium *p*-Nitrophenolate in Water, [bm_2im][NTf_2], and [bmpyrr][NTf_2] Solution

benzoic acid	K_{H2O}[a]	$K_{[bm2im][NTf2]}$[b]	$K_{[bmpyrr][NTf2]}$[b]
1a (*p*-OMe)	620	12.5	1.22
1b (*p*-Me)	790	31.1	2.71
1c = **2c** (H)	910	20.7	1.75
1d (*p*-F)	1020	51.6	5.30
1e (*p*-I)	1480	39.1	2.01
1c (*p*-Cl)	1480	74.6	1.83
1g (*p*-Br)	1510	98.8	3.14
1h (*p*-CN)	3980	28.6	3.21
1i (*p*-CF_3)		204	29.8
2a (*o*-OMe)	1150	15.9	3.16
2b (*o*-Me)	1740	18.7	3.00
2d (*o*-F)	7580	179	25.4
2e (*o*-I)	20000	55.7	10.0
2f (*o*-Cl)	17000	152	10.7
2g(*o*-Br)	20400	33.8	6.25
2h (*o*-CN)	11800	21.3	6.90
2i (*o*-CF_3)		117	23.2

[a] See ref 14. [b] *K* values are the average between two independent measurements and are reproducible within ±5%.

acid dissociation constant of carboxylic acid and that one corresponding to *p*-nitrophenol ($pK_a = 7.15$).[14] Thus, we calculated the *K* values for water solution reported in Table 1 by using literature pK_a data.[14]

In Table 1, the equilibrium constant values (*K*) determined in IL solution by eq 3, as a function of benzoic acids, are also reported. We are aware of the fact that *K* values in IL solution could be affected by stability constant values of two ion pairs (eq 1). However, at a first approximation level we may assume that the two ion pairs have similar stabilities.

For the sake of clarity, we will discuss our data as a function of the solvent and the substituent.

Influence of the Solvent. Analysis of data reported in Table 1 shows that *K* values decrease along the series $K_{H2O} > K_{[bm2im][NTf2]} > K_{[bmpyrr][NTf2]}$. The higher acidity of benzoic acids in water solution than in IL solution perfectly agrees with the observation reported by MacFarlane et al.,[15] comparing the UV–vis spectra of *m*-cresol purple and bromocresol purple in water, in [BF_4^-] and [PF_6^-] based ILs, showing the lower proton transfer degree of the weak acids in the latter solvent media. This trend recalls the one we recently detected for carboxylic acids.[13] *K* values can be considered as a measure of the proton transfer degree. Obviously, on the basis that the electronic effect, as accounted for σ values, is not dependent on the solvent nature, the proton transfer degree is strongly favored by the solvent ability to stabilize the benzoate anion. Thus, our results seem to indicate that the benzoate anion is less stabilized in IL solution than in water solution. The less relevance of solvation effects in IL solution has been claimed on different occasions,[10] and in some cases, it allowed to rationalize the higher reactivity of organic species in these media.[10a,c,f] Furthermore, it is noteworthy that the solute–solvent interactions in IL solution could be completely different from those detected in conventional solvents. Indeed, as recently underlined by Lynden-Bell,[16] ILs cannot be assimilated to continuous media. Rather, they are characterized by dynamic heterogeneous environments[17] in which, as a consequence of thick network of solvent–solvent interactions, the reorganization around a solute molecule is slower and energetically less easy than in ordinary molecular solvents.[18] In our case, the feeble but cooperative interactions determining the supramolecular structure of ILs could cause an opposition to the solvent reorganization around the benzoate anion, disfavoring the target reaction.

The different solvent behavior of ILs used in this work with respect water is also testified by the fact that the attempt to correlate *K* values calculated in water solution to *K* values collected in IL solution gave bad results in both cases (see Figures 2–6 of the Supporting Information). Furthermore, no correlation exists between *K* values collected in [bm_2im][NTf_2] and in [bmpyrr][NTf_2] (see Figure 7 of the Supporting Information). Once again, this latter result confirms the reports by MacFarlane et al.[15] about the peculiarity of each IL–probe system.

As far as data collected in IL solutions are concerned, *K* values decrease on going from the aromatic to the aliphatic IL, evidencing a lower proton transfer degree in [bmpyrr][NTf_2] than in [bm_2im][NTf_2]. In general, the $K_{[bm2im][NTf2]}/K_{[bmpyrr][NTf2]}$ ratio ranges from 6.8 up to 40.8 for para-substituted benzoic acids and from 3.1 up to 14.2 for *o*-substituted isomers. This trend cannot be explained on the grounds of a different polarity of two ILs. Indeed, the apparent polarity parameters for [bm_2im][NTf_2] and [bmpyrr][NTf_2] are quite similar (E_T^N = 0.541 and 0.544, E_{NR} = 218.20 and 218.70 kcal/mol, π^* = 0.984 and 0.971 for [bm_2im][NTf_2] and [bmpyrr][NTf_2], respectively).[10j,19] On the other hand, also the H-bond acceptor basicity of solvent, frequently

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considered as one of the main factors determining the strength of benzoic acids in molecular solvents,[20] does not account for the differences in K values collected in IL solution (β = 0.239 and 0.252 for [bm$_2$im][NTf$_2$] and [bmpyrr]-[NTf$_2$], respectively).[19]

It is well-known that the acid−base equilibria become more complexes on decreasing the solvating power of the medium, and poorly solvated anions may form both ion pairs and hydrogen bond complexes.[21] In IL solution, as a consequence of a less relevance of solvation effects, the species formed at equilibrium could be more conveniently depicted as a bimolecular species in which the proton is shared by the acid and the base. This species, having a more extended π contact surface area, should be able to interact with the aromatic cation of [bm$_2$im][NTf$_2$] also by means of $\pi-\pi$, cation$-\pi$, and $\pi-$quadrupole interactions.[22] Hence, on the grounds of these feeble interactions, a larger stabilization and consequently an increase in the acid strength should be detected.

A comparison among the data collected in the two ILs used in this work shows that, particularly for para isomers, K values collected in [bmpyrr][NTf$_2$] span in a narrower range, evidencing for this IL a tendency to exert a sort of leveling effect. A similar behavior was previously detected by us[13] and also by Gilbert et al.[23] on determining the Hammett functions for TfOH and HNTf$_2$.

In our opinion, in order to get a better understanding of the different behavior of the two ILs used in this work, the nature of solvent−solvent interactions in each solvent medium must be taken into account. Both ILs are obviously characterized and stabilized by electrostatic cation−anion interactions. However, as mentioned, the tridimensional structure of [bm$_2$im][NTf$_2$] is further stabilized by additional cation−cation interactions, such as $\pi-\pi$ interactions. This further stabilization could induce an increase in the energy request needed to adapt the solvent cage to the solute molecule. As a consequence, a faster and easier solvent reorganization around a solute molecule could be detected in [bmpyrr][NTf$_2$] than in [bm$_2$im][NTf$_2$]. This induces a range of different solute−solvent interactions that accounts for the span of K values in [bmpyrr][NTf$_2$] solution.

Effect of the Substituent. First, in order to identify the nature of the relationship between the acid strength and the electronic effect of the substituent, we tried to correlate K values collected in IL solution with Hammett σ values. However, in all cases considered only poor correlations were obtained (see Figures 8 and 9 of the Supporting Information). Bad results were also obtained by taking into account the E_s parameter (see Figures 10−13 of the Supporting Information) or attempting a biparametric correlation. In this light, we hypothesized that steric and electronic parameters collected in water solution are unable to describe quantitatively the substituent effect in IL solution. The lack of correlation among data in ILs and in water should be a consequence of fact that enthalpy−entropy compensation effect is not operating. This is not surprising and seems to confirm the peculiar solute−solvent and solvent−solvent interactions present in IL solutions. A similar result was previously obtained by Chiappe et al. on studying the addition of trihalides to unsaturated compounds.[24]

In general, according to data calculated in water solution, in IL solution the halo-, cyano-, and trifluoromethyl-substituted benzoic acids show K values higher than those of unsubstituted benzoic acid. As far as para isomers are concerned, in both IL solutions the trifluoromethylbenzoic acid was the strongest acid, despite the fact that the trifluoromethyl group is a less able electron-withdrawing substituent than the cyano group ($\sigma_{p\text{-CF3}}$ = 0.54, $\sigma_{p\text{-CN}}$ = 0.66).

In [bm$_2$im][NTf$_2$] solution, the para-substituted benzoic acids considered above show a further peculiar behavior. Indeed, in this IL K values strongly depend on the nature of each substituent as testified for example by the acidity increase induced by the halogen with respect to benzoic acid (K_X/K_H = 1.1, 1.6, 1.7, and 1.6 for F, Cl, Br, and I in water solution, whereas K_X/K_H = 1.9, 2.5, 3.6, and 4.8 for I, F, Cl, and Br in [bm$_2$im][NTf$_2$] solution). This result confirms the importance of the specific solute−solvent interactions in IL solution. In [bmpyrr][NTf$_2$] solution, as a consequence of the above-mentioned easier reorganization of solvent around the solute molecule, the substituent discrimination is less marked.

As far as electron-donating substituents are concerned, according to data collected in water solution, the *p*-methoxy substituent induces a decrease of benzoic acid strength. Differently, the *p*-methyl-substituted benzoic acid in both IL solutions results a bit stronger species than the unsubstituted one.

In the case of ortho-substituted benzoic acids, for each IL, we first tried to correlate K values with those corresponding to para isomers (see Figures 14 and 15 of the Supporting Information). In both cases, no correlation exists, as was unsurprising taking into account the behavior of para- and ortho-substituted benzoic acids in water. However, the K value trend (as following discussed) seems to indicate that solute−solvent interactions for ortho derivatives are different from those present for para isomers. In general, the behavior of ortho isomers, as far as the electronic effect is concerned, seems to recall the one just discussed for para isomers. In this case, the analysis of K values cannot be carried out only on the grounds of the electronic effect. Indeed, it is well-known that the steric or proximity effect of the substituent heavily affects the dissociation equilibrium of benzoic acids in conventional solvents, and as will be discussed later, this effect differently operates also in IL solution.

Among ortho isomers, **2d** in both IL solutions was the strongest acid, notwithstanding the fluorine atom is the smallest substituent. In [bmpyrr][NTf$_2$] solution, more significant acidity increases were induced by the presence of electron-withdrawing substituents with respect to those ones detected for para isomers in the same solvent medium.

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Analysis of data collected as a function of the acid structure shows once more that the substituent position on the aromatic ring differently affects the acid strength in aqueous and in IL solution. Indeed, in aqueous solution, the *K* values corresponding to ortho-substituted benzoic acids are higher than the ones corresponding to para isomers. The higher acidity of ortho-substituted benzoic acids with respect to the corresponding para isomers has been deeply investigated in aqueous solution in conventional organic solvents and in their binary mixtures.[4a,5c] This behavior has been frequently ascribed to the proximity between the carboxyl group and the substituent, which induces an increase in the angle between the benzene ring and the plane of carboxyl group. This effect, on the whole, causes a decrease in the conjugation of carboxyl group with the aromatic nucleus. As a consequence, the −M effect of carboxyl group, responsible for the relative weakness of benzoic acids, is hampered. Generally, in water solution the acid strength of the ortho-substituted benzoic acids increases on increasing the size of the ortho substituent. Data collected in conventional solvents show that the extent of this effect is heavily affected by the solvent nature; in particular, solvent polarity seems to play an important role.

By analogy with that previously detected in water solution, a deeper analysis of data collected in [bmpyrr][NTf$_2$] shows that, with the exception of *o*-trifluoromethylbenzoic acid, all ortho isomers are stronger acids than the corresponding para isomers. Conversely, in [bm$_2$im][NTf$_2$] solution a more complex behavior was observed. Indeed, *o*-F, *o*-Cl, *o*-I, and *o*-OMe benzoic acids were stronger than the corresponding para isomers. An opposite trend was detected for Br, CN, CF$_3$, and Me derivatives. Once more, these differences in the behavior of two ILs cannot be explained on the grounds of a different apparent solvent polarity or substituent steric hindrance. Probably, above results are a consequence of the different ability of two ILs to reorganize around solute molecules. This factor might affect the twisting of the carboxyl group respect to the plane of the aromatic ring. On the whole, these data seem to indicate a lower relevance of the ortho steric effect in [bm$_2$im][NTf$_2$] solution. These results perfectly agree with those previously collected by us about a lower significance of steric effects in determining the reactivity of 1,1,1-tribromo-2,2-bis(2,5-dimethoxyphenyl)-ethanes in [bmim][BF$_4$].[25] It is worth noting that the coplanarity between the carboxyl group and the ortho substituent could possibly favor, provided it is possible, the formation of an intramolecular hydrogen bond, which consequently should account for a lower tendency of the acid group to share the proton with the *p*-nitrophenolate anion.

As far as *K* values relevant to halo-substituted benzoic acids are concerned, a partial twisting of the carboxyl group seems to be operating in the presence of smaller substituents (F and Cl; r_v = 1.47, 1.75, 1.85, and 1.98 Å for F, Cl, Br, and I, respectively),[26] as testified by K_o/K_p ratios (K_o/K_p = 3.5, 2.0, 0.3, and 1.4 for F, Cl, Br, and I, respectively). These results are probably a consequence of a higher electron density on F and Cl.

It is noteworthy that the observed trend in IL solution is completely different from the one detected in water solution. Indeed, in the latter case, the highest acidity increases were detected in the presence of the largest substituents, Br and I, as a consequence of the largest phenyl−carboxyl interplanar angle in crystalline 2-substituted benzoic acids (η = 1.3, 13.7, 18.3, and 28 for *o*-F, *o*-Cl, *o*-Br, and *o*-I, respectively).[5c]

As noted above, in [bmpyrr][NTf$_2$] solution, with the only exception of the trifluoromethyl derivative, the ortho isomers show *K* values higher than those of the para isomers. In this case, the weaker solvent−solvent interactions and the less organized tridimensional structure, in which only electrostatic interactions are operative as a consequence of the aliphatic nature of the cation, probably allow the carboxyl group twisting, thus determining the strength of acids.

Conclusions

The use of the protonation equilibrium of the *p*-nitrophenolate anion has allowed us to determine the acid strength of some substituted benzoic acids in IL solution. In particular, data collected show that, as a consequence of the peculiar IL−solute interactions, benzoic acids show a lower proton transfer degree in IL than in water solution. Furthermore, the different solvent−solvent interactions operating in the two ILs give rise to their different ability to discriminate the benzoic acids on the grounds of the nature and substituent position. As a matter of fact, for ortho-substituted benzoic acids, our data evidence the importance of the specific and peculiar interactions operating on this substrates series.

Once again, data collected confirm that ILs constitute a class of solvents for which it is hard to operate a solvent behavior generalization similar to the one normally made for conventional solvents. As a matter of fact, bearing in mind that differences in acid strength are often determined by changes in entropy values, our data seem to indicate that the proton transfer degree in IL solution is strongly affected by variations in this thermodynamic parameter. This should explain the lack of correlation between *K* and σ values, normally found when enthalpy−entropy compensation is operating. Furthermore, it supports the idea that the solvent shows a significant structural order degree. Consequently, the picture of ILs as "polymeric supramolecular fluids" is, in our opinion, the one that better describes their behavior.

Experimental Section

Materials. [bm$_2$im][NTf$_2$],[27] [bmpyrr][NTf$_2$],[27] and sodium *p*-nitrophenolate[28] were prepared according to literature procedure. Methanol and benzoic acids were used as purchased without further purification. ILs were dissolved before use in CH$_2$Cl$_2$ and stirred overnight, at room temperature, in the presence of active charcoal (1% w/w). The solution was filtered over a neutral aluminum oxide pad. Colorless ILs were dried in vacuum at 60 °C for 2 h before use, and then they were stored in a desiccator over calcium choride.

Measurements and Calculations. UV−vis Spectra. The UV−vis spectra were recorded by using a spectrophotometer equipped with a temperature controller.

Spectrophotometric Measurements. Samples for a typical spectrophotometric measurement were prepared by injecting in a quartz cuvette (light path 0.2 cm) the proper volume of IL (500 μL), sodium *p*-nitrophenolate solution (50 μL), and carboxylic acid solution (25 μL) by means of a microsyringe.

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Sodium *p*-nitrophenolate and carboxylic acids were added as concentrated solution in methanol.[29] The sodium *p*-nitrophenolate concentration was kept constant (0.0002 M). Each sample was thermostated at 298 K. A suitable wavelength was chosen by comparing the sodium *p*-nitrophenolate solution with the sample having the highest acid concentration. Each measurement was repeated twice, and K values were reproducible within 5%. Experimental data were subjected to fitting regression analysis according to eq 3.

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Supporting Information Available: Plots of log K_{IL} vs log K_{H2O}, log K_{IL} vs σ values, and log $K_{IL,p}$ vs log $K_{IL,o}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[29] All UV−vis measurements were carried out by using methanol as cosolvent (ca. 13% by volume, see the Experimental Section). However, on the grounds of our previous results,[10e] we are confident that these binary mixtures could be compared to neat IL.