p-Nitrophenolate: A Probe for Determining Acid Strength in Ionic Liquids

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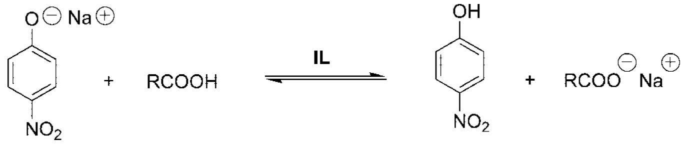

In order to obtain an acidity scale in room-temperature ionic liquid solutions, the protonation equilibrium of sodium *p*-nitrophenolate in [bm$_2$im][NTf$_2$] and in [bmpyrr][NTf$_2$], at 298 K, has been studied by means of spectrophotometric titration. Carboxylic acids differing in both structure and in water solution strength have been used. Data collected indicate that in the analyzed ionic liquid solutions carboxylic acids are less dissociated than in water solution. Furthermore, by virtue of a mutual interaction, the studied equilibrium seems to be affected by both the nature of the ionic liquids and the carboxylic acids.

Introduction

The thermodynamic properties of a solute, such as its acid or basic strength, are strongly affected by solvent properties. In the field of organic chemistry the quantitative determination of an acid or base strength may be useful in order to investigate the mechanism of a given reaction as a function of solvent nature. Furthermore, it is well-known that, among molecular descriptors, pK_a is one of the most important. These are the reasons why many papers have had, as their main subject, the determination of the acidity or the basicity for a given solute in organic solvents.[1] This topic may assume a significant importance if the considered solvent possesses peculiar features such as those shown by room-temperature ionic liquids (RTILs).[2] These organic salts, being formed only by ions, have low vapor pressure and flammability. Moreover, they furnish a completely different microenvironment than the one corresponding to conventional organic solvents. This, in turn, may allow us to understand the specific effects that they often exert on mechanism, rate, and selectivity of reactions carried out in such media. In ionic liquid (IL) solutions, the Coulomb's interactions are determinant, but for aromatic cations, also $\pi-\pi$-, cation$-\pi$-, or more generally ion$-$quadrupole-type interactions should play a significant role.[3] On the grounds of these different contributions, ILs have been described as polymeric supramolecular fluids[4] in which a solute, as a consequence of the strong solvent$-$solvent interactions, displays completely different solvation effects than those generally observed in conventional

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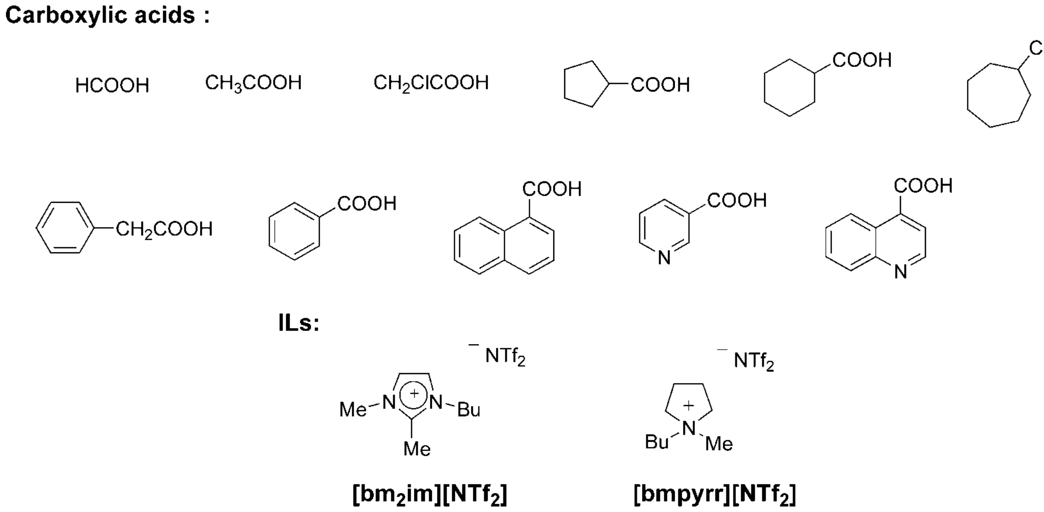
CHART 1. Structures of Used Carboxylic Acids and Ionic Liquids



solvents. In this respect, we have recently observed that ILs, performing scarce solvation effects, are media able to affect both nucleophilicity[5] and basicity of amines.[6] The acids, as well as bases, could be particularly sensitive to solvation effects. The carboxylic acids have been widely used in IL solutions both as substrates and catalysts.[7] Therefore, we wanted to get a quantitative estimation of their strength in these media. The need to have a measure of acid strength in IL solution has been recently claimed in the literature in order to control the acidity level of a given reaction medium.[8] On the other hand, as pointed out by Johnson et al., particular caution is needed in regard to possible mistakes deriving from the use, in IL solution, of pK_a values collected in aqueous solution.[9] Different methods have been used in order to obtain acidity scales in conventional organic solvents.[10] On the contrary, to the best of our knowledge, only spectrophotometric titration has been used to study the behavior of strong Brønsted acids in ILs solution.[11] In order to measure the strength of some carboxylic acids (Chart 1) we chose to follow, by means of UV−vis spectroscopy at 298 K, the protonation equilibrium of sodium *p*-nitrophenolate 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*-methylpyrrolidinium, NTf$_2$ = bis(trifluoromethylsulfonylimide)]. The chosen ILs differ in the cation's ability to give not only H-bond but also $\pi-\pi$ interactions. It is well-known that both these factors can be important in determining substrate behavior in IL solution. Furthermore, the [NTf$_2$] anion is a weakly basic anion, and its use can, in a way, provide the absence of any external interference in the acidity scale determination. On the other hand, the carboxylic acids chosen show different strength in water solution, but also significant changes in their structure (cyclic or not, aromatic or not) that can induce different interactions with the ions constituting ILs. The present experimental method, in our opinion, can be confidently applied to carboxylic acids having pK_a values ranging from 2.4 up to 5.

Results and Discussion

As a first step, we preliminary looked for the most suitable base and solvent system. We considered using *p*-nitroaniline as base, in [bmim][BF$_4$] solution. However, the addition of acetic acid did not induce changes in the UV−vis spectra. In addition, in the presence of sodium 2,4-dinitrophenolate, concentrated solutions (higher than 0.1 M) had to be added in order to obtain only small variations in the UV−vis spectra. Moreover, the low solubility of some carboxylic acids in methanol (the cosolvent used in this work, see the Experimental Section),[12] did not allow us to use this base. Thus, 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.[13] On the grounds of these results, we chose as solvent systems the less acidic [bm$_2$im][NTf$_2$] and [bmpyrr][NTf$_2$] and as base indicator the *p*-nitrophenolate. Regular variations were obtained in the UV−vis spectra as a function of acid concentration. In particular, in Figure 1 UV−vis spectra of sodium

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(12) The measurement samples have a mole fraction of IL of X ≅ 0.5. On the grounds of our previous reports (see: (a) D'Anna, F.; Frenna, V.; La Marca, S.; Noto, R.; Pace, V.; Spinelli, D. *Tetrahedron* **2008**, *64*, 672–680. (b) D'Anna, F.; Marullo, S.; Noto, R. *J. Org. Chem.* **2008**, *73*, 6224–6228), we are confident that data collected in the binary mixture can be referred to a partially organized solvent medium, such as neat IL.

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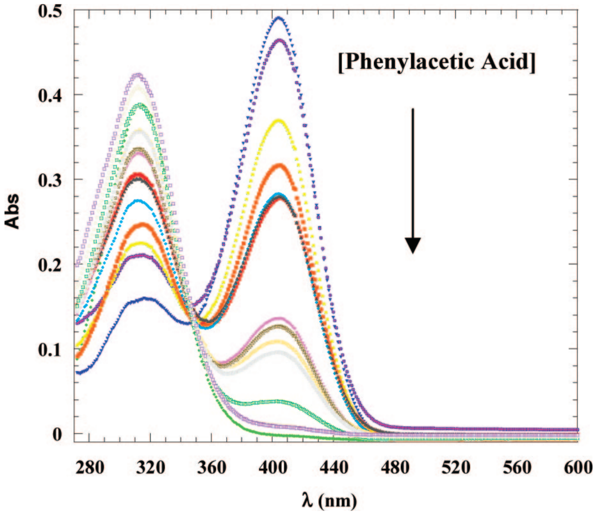

FIGURE 1. UV−vis spectra of sodium *p*-nitrophenolate (0.0002 M) in the presence of increasing concentrations of phenylacetic acid (0−0.006M) at 298 K in [bm$_2$im][NTf$_2$] solution.

p-nitrophenolate in the presence of increasing concentration of phenylacetic acid, in [bm$_2$im][NTf$_2$] solution at 298 K, show the absorbance decrease at $\lambda_{max} = 405$ nm and the corresponding increase at $\lambda_{max} = 310$ nm.

The presence of an isosbestic point at λ ~346 nm indicates that in IL solution a single equilibrium, such as the one depicted in eq 1, was operating:

$$\mathrm{ArO^-Na^+} + \mathrm{HA} \overset{K}{\rightleftharpoons} \mathrm{ArO}H + \mathrm{Na^+A^-} \tag{1}$$

The equilibrium constant can be defined as

$$K = \frac{[\mathrm{ArOH}][\mathrm{Na^+A^-}]}{[\mathrm{ArO^-Na^+}][\mathrm{HA}]} \tag{2}$$

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

$$\Delta A^2/A = (A_0 - A_i)^2/A_i = \Delta\varepsilon l K[\mathrm{HA}] \tag{3}$$

where A_i and A_0 are the absorbances, at a suitable wavelength, of *p*-nitrophenolate in the presence and in the absence of acid, respectively, $\Delta\epsilon$ is the variation in molar absorbitivity as a consequence of the protonation equilibrium, K is the equilibrium constant value, and l is the length of the optical path (for details of the calculation method see the Supporting Information). A typical fit of experimental data by means of eq 3 is depicted in Figure 2.

It is noteworthy that equilibrium constant values calculated by eq 2, in water solution, equal the ratio between the acid dissociation constant of carboxylic acid and that one corresponding to *p*-nitrophenol (pK_a = 7.15).[14] Thus, we calculated the K values reported in Table 1 by using literature pK_a data.[14] We are aware of the fact that K values could be affected, in IL solution, by stability constant values of two ion pairs (eq 1). However, at the beginning we could consider similar the stability of two ion pairs.

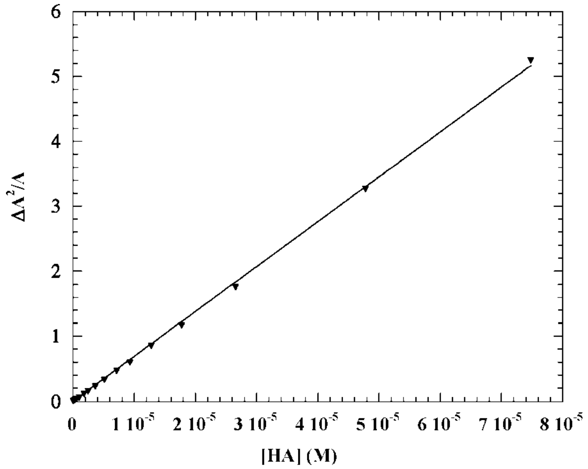

FIGURE 2. Plot of $\Delta A^2/A$ as a function of phenylacetic acid concentration in [bm$_2$im][NTf$_2$] solution at 298 K.

TABLE 1. Equilibrium Constant Values (*K*), at 298 K, Corresponding to Protonation of Sodium *p*-Nitrophenolate in Water, [bm$_2$im][NTf$_2$], and [bmpyrr][NTf$_2$] Solution

carboxylic acid	K_{H2O}[a]	$K_{[bm2im][NTf2]}$[b]	$K_{[bmpyrr][NTf2]}$[b]
formic	2500	8.3 (0.2)	0.67 (0.07)
acetic	254	6.6 (0.2)	0.92 (0.04)
chloroacetic	19900	154 (1)	1.79 (0.06)
cyclopentanoic	190	1.74 (0.01)	0.50 (0.01)
cyclohexanoic	176	1.56 (0.02)	0.55 (0.01)
cycloheptanoic		1.43 (0.04)	0.61 (0.01)
phenylacetic	742	9.70 (0.08)	0.92 (0.01)
benzoic	887	20.7 (0.1)	1.75 (0.06)
α-naphthoic	2810	48 (1)	1.4 (0.1)
nicotinic	2490	93 (1)	1.5 (0.1)
4-quinolinic	52500	740 (20)	1.220.04)

[a] See ref 14. [b] Standard deviations are given in parentheses.

In Table 1 are also reported the equilibrium constant values (K) determined in IL solution, as a function of carboxylic acids. For the sake of clarity, we will discuss our data as a function of the solvent and the carboxylic acid nature.

The data reported in Table 1 show that, in general, K values decrease along the series H_2O > [bm$_2$im][NTf$_2$] > [bmpyrr]-[NTf$_2$].

A first comparison between K values calculated in water solution and those collected in IL solution indicates the lower acidity of the studied carboxylic acids in the latter solvent system. The significant differences between K values are in line with that previously reported by MacFarlane et al. by comparison of the UV−vis spectra of *m*-cresol purple in water and in [BF$_4$]- or [PF$_6$]-based ILs, showing the lower proton transfer degree of the weak acid in these media.[15]

The position of the studied equilibrium (eq 1) is strongly favored by solvent ability to interact with the anionic species. Bearing in mind that, solvent medium being the same, the contribution due to solvation of phenolate remains constant, K values parallel the strengths of the acidic species. Thus, data obtained by us seem to indicate that, in general, the carboxylate anion is less solvated in ILs than in water solution. The scarce relevance of solvation effects in IL solution has been claimed on different occasions,[5] and in some cases, it has been ascribed

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to the thick network of solvent−solvent interactions.[16] These interactions make difficult a change in the solvent structure upon substrate insertion; in our case, in particular, they may hamper solvent reorganization around the carboxylate anion form that needs stabilization. In support of the fact that the properties of solvent systems containing ILs are heavily affected by the probe, a significant reorganization of the components of the solvent around the substrate has been recently pointed out in determining the activation parameters for the methanolysis of alkyl chlorides in IL solution.[17] However, it is well-known that acid−base equilibria become more complex on decreasing solvating power of the medium.[18] Indeed, poorly solvated anions may form both ion pairs and hydrogen-bond complexes. Thus, if the latter phenomenon operates extensively, K values reported in Table 1 account for the overall degree of proton transfer, which seems to be less significant in [bmpyrr][NTf_2].

The attempt to correlate K values collected in IL solution with those calculated in water solution gives a homogeneous trend only in the case of data in [bm_2im][NTf_2] solution. Indeed, a linear correlation was obtained plotting log $K_{[bm2im][NTf2]}$ versus log K_{H2O} ($i = -1.77 \pm 0.35$, slope $= 0.98 \pm 0.10$, $n = 9$, $r = 0.965$; see Figure 3 of the Supporting Information). The slope value of the regression analysis seems to indicate that the different structural effects, in determining the acidity, induce as a whole similar results in the two solvent systems. This is despite the fact that the two solvent systems have different polarity, structural order degree, and solvation ability.

The data collected in [bmpyrr][NTf_2] indicate that, with respect to water solution, this medium is able to induce some inversions of acidity. Indeed, in this IL acetic acid is stronger than formic acid, and for aromatic carboxylic acids, 6-π electron systems (benzoic and nicotinic) give stronger results than the corresponding 10-π electron systems (α-naphtoic and quinolinic). A similar behavior has been recently underlined also by Turmine et al. for pyridinium and acetic acid, determining acidity scales in some [bmim][BF_4]−water mixtures.[8] The comparison between data collected in the two ILs allows us to draw some interesting conclusions. As noted above, K values detected in [bm_2im][NTf_2] are higher than those detected in [bmpyrr][NTf_2]. Furthermore, in [bmpyrr][NTf_2] a narrower range of K values was detected, indicating a sort of leveling effect of this ionic solvent. A similar behavior in IL solution was detected by Gilbert et al. in determining the Hammett functions for TfOH and $HNTf_2$.[11] Furthermore, these results once more confirm the reports by MacFarlane et al.[15] regarding the peculiarity of each probe−IL system. On going from aromatic to aliphatic IL, the decrease in K values is more significant for aromatic carboxylic acids. Indeed, $K_{[bm2im][NTf2]}/K_{[bmpyrr][NTf2]}$ ranges from 2.3 up to 12.4 for aliphatic acids and from 11.0 up to 603 for the aromatic ones. This result cannot be explained on the grounds of a parameter such as E_T^N that should reflect medium polarity ($E_T^N = 0.541$ and 0.544 for [bm_2im][NTf_2] and [bmpyrr][NTf_2] respectively),[19] but in ILs it accounts for the solvent effect on well-described probe molecules. The result could be a consequence of ILs structural properties. Indeed, among used carboxylic acids, the aromatic ones are able to interact with bm_2im^+ cation also by means of $\pi-\pi$, cation−π, and π−quadrupole interactions.[3] Hence, the stabilizing effect due to these feeble but cooperative interactions should induce an increase in the proton transfer degree and consequently an increase in acidity. This is supported by data relevant to 6- and 10-π aromatic systems. The latter ones present higher acidity ratios, according to the presence of a more extended π system and conctact surface area.[20]

Further analysis of our data can be carried out by taking into account the structural properties of the carboxylic acids. In particular, a comparison between K values relevant to chloroacetic and acetic acids evidence a lower relevance of field effects in IL solution than in water solution ($K_{chloroacetic}/K_{acetic} = 85$ and 23 in H_2O and [bm_2im][NTf_2], respectively). This could be a further evidence accounting for the formation of a hydrogen-bonded complex, in which the intervention of the hydrogen bond donor/acceptor lowers the extent of electron density to be withdrawn by the chlorine atom and its overall electronic effect.

On the other hand, the comparison between K values relevant to formic and acetic acid, once more underlines the scarce relevance of solvation effect in IL solution. Indeed, unlike water solution, the steric hindrance increase does not induce significant acidity decrease in IL solution ($K_{formic}/K_{acetic} = 9.7$ and 1.3 for H_2O and [bm_2im][NTf_2], respectively). Bearing in mind that the higher acidity of formic acid in water is mainly due to a favorable entropic contribution,[21] data collected by us seem to indicate that in IL solution entropic factors are less significant, probably as a consequence of the less important solvation effects.

The last point to be analyzed, considering aliphatic carboxylic acids, is the increase in the ring flexibility on going from cyclopentanoic acid to cycloheptanoic acid. Data reported in Table 1 show that the increase in ring size does not induce significant variations in K values. Indeed, in both considered ILs, a narrow range of K values was obtained on going from cyclopentanoic to cycloheptanoic acid. This evidences the scarce influence that the ring flexibility exerts on acidity equilibrium. By contrast, this structural parameter negatively affected the rate of the amino induced dehydrobromination of some 1,1,1-tribromo-2,2-bis(phenylsubstituted)-ethanes ($k_{pyrrolidine}/k_{hexamethyleneimine} = 8.4$).[22] This result was ascribed to the disorganizing effect that the most flexible ring can exert on the organized structure of IL. The results could be ascribed to the different positions of functional group involved in the process, endocyclic for the amines and exocyclic for the carboxylic acid. Probably, the protonation of the endocyclic functional group induces higher conformational changes in the amine ring that, in turn, significantly affect the solvent structure.

Conclusions

In conclusion, the protonation equilibrium of sodium p-nitrophenolate has been proven a useful and promising probe reaction to determine the strength of carboxylic acids in IL solution. Data collected seem to indicate that, as a consequence of the less significant solvation effects, the strength of the acids is lower in IL than in water solution. Between two ILs used in

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this work, the [bm_2im][NTf_2] gives, on the whole, effects similar to water, whereas in [bmpyrr][NTf_2] solution the complexity of effects induces lower differences in the acids strength. This confirms that each cation−anion pair gives rise to a peculiar solvent system. As a consequence of this, solute properties such as acidity or basicity are a result of the cooperative action of its structure, the degree organization of ILs and the feeble interactions that come from it.

Experimental Section

Materials. [bm_2im][NTf_2],[23] [bmpyrr][NTf_2],[23] and sodium *p*-nitrophenolate[24] were prepared according to literature procedures. Methanol and carboxylic acids were used as purchased without further purification. 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 microsyringe. Sodium *p*-nitrophenolate and carboxylic acids were added as concentrated solution in methanol. The sodium *p*-nitrophenolate concentration was kept constant (0.0002 M). Each sample was thermostated at 298 K. The 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: Calculation details, Figure 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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