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Amine basicity: measurements of ion pair stability in ionic liquid media

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Dedicated to Professor Domenico Spinelli on the occasion of his 75th birthday

Abstract—The stability constants relevant to the formation of amine/*p*-nitrophenol ion pairs have been determined in [bmim][BF_4] solution, in the presence of butylamine, piperidine, and triethylamine, by using spectrophotometric measurements. In order to evaluate how the ion pair stability is affected by ionic liquid structure, piperidine has been chosen as model amine for studies in [bmim][PF_6], [bmim][NTf_2], [bm_2im][NTf_2] and in several [bmim][BF_4]/1,4-dioxane binary mixtures. Data obtained in ionic liquid solutions have been compared with those previously reported in conventional organic solvents.

1. Introduction

Commenting on our recent attempt[1] to correlate kinetic constant values relevant to the amino-catalyzed dehydrobromination of some 1,1,1-tribromo-2,2-bis(phenylsubstituted)ethanes in ionic liquid (IL) solution, a referee noted: "H_2O pK_a values are used as an indicator for basicity, despite ionic liquids being significantly different solvent environment for water. This is not a criticism of the authors, but rather illustrates the lack of such data in ionic liquids systems". We were aware of the fact that the amines basicity, measured in water, could not adequately describe their actual strength in ionic liquid systems. Indeed, the occurrence of peculiar IL–amine interactions or the scarce relevance of solvation effects should determine a different basicity in IL and in water. Under this light, different behaviors could be surely related to different IL–amine interactions. So, the observed reactivity trend, differing from the one expected on the basis of pK_{BH^+} values, could somehow reflect the amine basicity in ionic liquids.

For conventional solvents, kinetic data collected in a given solvent can be usually related to acidity data collected in a different medium. The application of Hammett's equation is a case. However, it is noteworthy that such an approach is justified by the fact that conventional solvents may be considered as a homogeneous class, constituted by a disordered or easily perturbable-ordered set of molecules. A similar condition is still valid on going from neat solvents to binary mixtures. A rather different situation is present in ionic liquids. These indeed, being formed only by ions, have been frequently considered as solvent media having 'peculiar' characteristics.[2] In particular, imidazolium ionic liquids have been recently described as 'polymeric hydrogen-bonded supramolecules that, mixed with other molecules, can be regarded as nanostructured materials'.[3] As a consequence, generally occurring solvation processes could be drastically reduced or absent in ionic liquid solution.

A careful analysis of recent literature reports shows that amines have been frequently used in IL solution both as nucleophiles and bases.[4] Therefore, we considered it interesting to evaluate base strength of amines in such solvent media. By analogy, with basicity measurements carried out in organic solvents, such as benzene,[5] 1,4-dioxane[6] or tetrahydrofuran,[7] we determined, by spectrophotometric measurements at 298 K, the stability constants of ion pairs formed by *p*-nitrophenol (ArOH) and three model amines, namely butylamine (BuA), piperidine (Pip), and triethylamine (TeA). These differ both in their steric requirements and structure. The present study was carried out using [bmim][BF_4] (bmim=1-butyl-3-methylimidazolium) as solvent. Furthermore, in order to evaluate the change in ion pair stability, induced by IL structure, we also determined the stability constant of Pip/ArOH ion pair in [bmim][PF_6], [bmim][NTf_2], and [bm_2im][NTf_2] [bm_2im=1-butyl-2,3-dimethylimidazolium; NTf_2=bis-(trifluoromethylsulfonylimide)]. These ion pairs differ in size, shape, coordination ability of anion or hydrogen bond donor ability of cation. Finally, because the addition of the reagents to the ionic

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liquid frequently requires the use of small amounts of co-solvent, we also determined the stability constant of Pip/ArOH ion pair in different [bmim][BF$_4$]/1,4-dioxane binary mixtures, X_{IL} ranging from 0.23 up to 0.75.

2. Results and discussion

2.1. Method

The first series of experiments was performed using 2,4-dinitrophenol. However, the UV–vis spectrum of this indicator in [bmim][BF$_4$] solution revealed that it was in its unprotonated form, which suggests that the acidity of this indicator is too high. Hence another indicator, having a lower acidity, namely the *p*-nitrophenol was chosen. In the absence of amine, this molecule, both in IL solution, as well as in dioxane, is in undissociated form ($\lambda_{\max}$=304 and 315 nm in dioxane and in IL, respectively). Nevertheless, the studied amines were able to induce phenol dissociation only in IL solution, as shown by UV–vis spectra (Fig. 1).

On increasing the base concentration, the absorbance of the unprotonated form of the indicator ($\lambda_{\max}$=415 nm) increases. Furthermore, the presence of an isosbestic point at λ=344 nm indicates that in IL solution a single equilibrium, such as the one depicted in Eq. 1, is operating:

$$\mathrm{ArOH} + \mathrm{Am} \overset{K}{\rightleftharpoons} \mathrm{ArO}^{\ominus}\ \mathrm{AmH}^{\oplus} \tag{1}$$

The equilibrium constant value can be defined as:

$$K = \frac{[\mathrm{ArO}^{\ominus}\ \mathrm{AmH}^{\oplus}]}{[\mathrm{ArOH}]\,[\mathrm{Am}]} \tag{2}$$

Considering the mass balances relevant to *p*-nitrophenol and Am, the absorbance variation can be expressed as (Eq. 3):

$$\Delta A = A_i - A_0 = \frac{S_{\mathrm{t}}\Delta\varepsilon K[\mathrm{Am}]}{1+K[\mathrm{Am}]} \tag{3}$$

where A_{i} and A_0 are the absorbances, at a suitable wavelength, of *p*-nitrophenol solutions in the presence and absence of amine, respectively, $\Delta\varepsilon$ is the variation in molar absorbitivity as a consequence of the ion pair formation, K is the equilibrium constant value and S_{t} is the analytical concentration of *p*-nitrophenol. In all the cases considered, the amine concentration, used to fit experimental data, was a bit smaller than the stoichiometric one. Also in this case we obtained experimental evidence relative to the cation–amine interaction according to the explanation previously reported.[8] Under these circumstances Eq. 3 can be rewritten as:

$$\Delta A = \frac{S_t\Delta\varepsilon K([\mathrm{Am}]-a)}{1+K([\mathrm{Am}]-a)} \tag{4}$$

where '*a*' is the amine concentration involved in the interaction with the IL cation. A typical fit of experimental data by means of Eq. 4, is depicted in Figure 2.

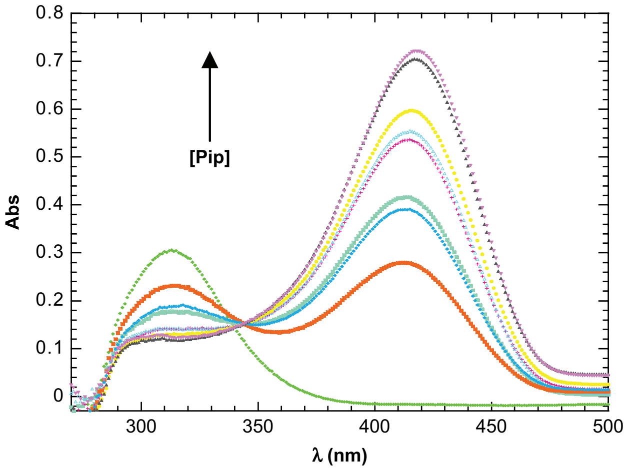

Figure 1. UV–vis spectra of *p*-nitrophenol in the presence of increasing concentrations of piperidine in [bmim][BF$_4$] solution at 298 K.

The equilibrium constant values (K), relevant to ion pair formation, in the presence of different amines, in [bmim][BF$_4$] solution, are reported in Table 1. For a useful comparison, some suitable literature K values are also reported. Data reported in Table 1 show that the basic strength of the amines is much higher in IL solution than in conventional organic solvents. In fact, a comparison with analogous data collected in benzene, using as probe the most acid 2,4-dinitrophenol (pK_{a} values 7.24[10a] for *p*-nitro- and 4.10[10b] for 2,4-dinitrophenol) shows that only small differences in K values are detected. In particular K ratios range from 0.26 for BuA to 4.0 for Pip and TeA.

The stability of the ion pair in IL solution increases along the series BuA<TeA<Pip. In this medium piperidine is the strongest base, while BuA is the weakest one. As far as base effects are concerned, for the rearrangement reaction in [bmim][BF$_4$], the same order has been observed.[8a] The same order was previously also determined in benzene

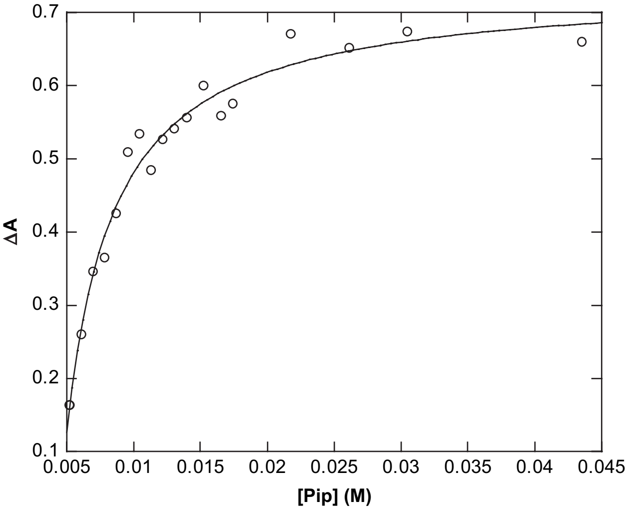

Figure 2. Plot of absorbance variation as a function of piperidine concentration in [bmim][BF$_4$] solution at 298 K.

Table 1. Equilibrium constant values (K) relative to ArOH/Am ion pair formation in [bmim][BF_4] solution at 298 K

Amine	K^{a} (M^{-1})	$K_{b/H2O}$^{b} (M^{-1})	$K_{benzene}$^{c} (M^{-1})
BuA	420	0.000562	110
Pip	1110	0.00132	4490
TeA	666	0.000478	2700

[a] K values are accurate to within ±5%.

[b] See Ref. 9.

[c] The acid indicator is the 2,4-dinitrophenol. See Ref. 5.

solution relative to the 2,4-dinitrophenol/Am ion pair.[5] By contrast, a different order can be observed in aqueous solution, namely TeA<BuA<Pip. It is noteworthy that the relative basicities of the three amines, in the three systems, are comparable. In fact, $K_{BuA}/K_{TeA}/K_{Pip}$=1:1.59:2.64 in IL solution, $K_{BuA}/K_{TeA}/K_{Pip}$=1:24.5:40.8 in benzene and $K_{bTeA}/K_{bBuA}/K_{bPip}$=1:1.12:2.80 in water. Actually, BuA in benzene seems to be significantly less basic than the other two amines.

Many different studies, carried out in IL solutions, have shown that their properties are largely affected by constituting ions; consequently the same is true for the reactivity of the substrates that they possibly dissolve. It is also important to bear in mind that a given reagent species can have different effects on ILs. Nevertheless, previous reports have shown that piperidine is not able to perturb the ordered structure of ILs.[1] Therefore, piperidine might be taken as model amine in order to determine the ion pair stability in different ILs. The stability constant values (K) relevant to ArOH/Pip, determined in different ionic liquids, are reported in Table 2.

Collected data show that the ion pair stability is significantly affected by the nature of both cation and anion. Indeed, for [bmim] ILs, the K value increases in the order: $K_{PF_6}<K_{NTf_2}<K_{BF_4}$ ($K_{PF_6}<K_{NTf_2}<K_{BF_4}=1:2.53:3.31$). For [$NTf_2$] ILs, it increases on going from [bm_2im][NTf_2] to [bmim][NTf_2] ($K_{bm_2im}/K_{bmim})=1:3.10$.

The stability of the ArOH/Pip ion pair was also determined in different [bmim][BF_4]/Diox binary mixtures. The stability constant values, as a function of IL mole fraction, are reported in Table 3. Reported data evidence that the stability of the ion pair and, in turn, the piperidine basicity linearly decreases with the IL mole fraction. Regression analysis of experimental data gives Eq. 5, K values 210 $M^{-1}$and 1440 M^{-1} for: X_{IL}=0 and 1, respectively, can be obtained.

$$K=(210\pm40)+(1230\pm90)\bullet X_{IL};\ r=0.990 \qquad (5)$$

Table 2. Equilibrium constant values (K) relative to ArOH/Pip ion pair formation in different ionic liquid solutions at 298 K

IL	K^{a} (M^{-1})
[bmim][BF_4]	1110
[bmim][PF_6]	335
[bmim][NTf_2]	848
[bm_2im][NTf_2]	274

[a] K values are accurate to within ±5%.

Table 3. Equilibrium constant values (K) relative to ArOH/Pip ion pair formation in [bmim][BF_4]/Diox binary mixtures at 298 K

IL	X_{IL}	K^{a} (M^{-1})
[bmim][BF_4]	0.75	1110
	0.62	1010
	0.51	840
	0.40	687
	0.31	625
	0.23	453

[a] K values are accurate to within ±5%.

Noticeably, a K value of 210 M^{-1} relative to pure dioxane solution can be extrapolated. This value could not be determined directly because we did not have any experimental evidence (i.e., significant variations in UV–vis spectrum) about the ion pair formation, even in the presence of high piperidine concentration (up to 4 M). It should be stressed that, as a consequence of the low solubility of [bmim][BF_4] in dioxane, we were not able to collect data for systems with less than X_{IL}=0.23. Therefore, the K value relevant to dioxane solution is the result of a very large extrapolation.

Overall, the collected data shows that ILs are solvent media able to increase amine basicity with respect to conventional solvents. This result may be ascribed to the peculiar characteristics of ILs and, in turn, to scarce relevance of solvation effects in these media. Furthermore, ion pair stabilization may also be important. It is known that the anionic part of IL is able to stabilize the ammonium ion, coordinating its acid protons.[4b] On the other hand, the cationic part of IL may stabilize the *p*-nitrophenate ion, by means of either hydrogen bond or π–π interactions.[11]

Taking into account the relative amine basicity, BuA is the most positively affected on going from benzene to IL, according to the presence of three acidic protons. The high reactivity of BuA as an amino-catalyst in the mononuclear heterocyclic rearrangement[8b] has been previously ascribed to the same structural characteristic. In addition, the different order of the amine basicity, on going from water to IL, could be a consequence of the more extensive solvation of ammonium ions in water solution. The latter effect, which reveals the crowded triethylammonium ion is less effective, induces a change in relative basicity order between TeA and BuA.

As far as the ArOH/Pip ion pair in different ILs is concerned, its relative stability seems to confirm the relevance of some anion–ammonium ion interaction. Indeed, the K value trend follows the ability of the anion to act as a hydrogen bond acceptor, as can be inferred by the β values of ILs (0.376 for [bmim][BF_4], 0.207 for [bmim][PF_6], and 0.243 for [bmim][NTf_2]).[12] However, the cationic part of IL also contributes to ion pair stabilization, as can be evidenced by the different K values collected in [bmim][NTf_2] and in [bm_2im][NTf_2], according to the α values of ILs (0.617 for [bmim][NTf_2] and 0.381 for [bm_2im][NTf_2]).[12] The latter result seems to indicate that π–π interactions are less important. Indeed, bm_2im^+ should be the most effective cation in the ion pair stabilization by means of π–π interaction, according to its highest r value (r=0 for [bmim][NTf_2]

and r=0.073 for [bm_2im][NTf_2]).[13] This may be attributed to electron repulsive effect exerted by the methyl group at the C2 position. By contrast, in our case, ion pair stability is higher in $bmim^+$ than in bm_2im^+. Two opposite effects could determine the observed order. The former effect, related to the extent of π–π interactions, favors the stability in bm_2im^+; the latter, related to a different order around the ion pair, favors the stabilization in $bmim^+$.

The relevance of the order around the ion pair also accounts for the decrease of ArOH/Pip ion pair stability on decreasing the IL mole fraction in [bmim][BF_4]/Diox binary mixtures. It is noteworthy that the addition of a co-solvent can partially destroy the polymeric structure of imidazolium ILs.[14] As a consequence, an increase of solvent separated IL ion pairs or free ion concentration, more apt to solvation processes, and a decrease in amine basicity should be detected. The linear trend K versus X_{IL}, seems be a sign that particular interactions between IL and co-solvent molecules are absent.

3. Conclusions

In conclusion, the data collected herein confirm the idea that ionic liquids represent an intriguing system having particular solvent properties linked, at least for imidazolium salts, to their organized structure. This allows the formation of stable ArOH/Am ion pairs. Determination of stability constants gives an idea of relative amine basic strengths. This work, to the best of our knowledge, has not been reported as yet.

4. Experimental

4.1. Materials

4.1.1. Compounds. [bmim][BF_4], [bmim][PF_6], 1,4-dioxane, and *p*-nitrophenol were used as purchased without further purification. [bmim][NTf_2] and [bm_2im][NTf_2] were prepared according to literature procedures.[15] ILs were dryed in vacuum at 60 °C for 2 h before use, then they were stored in a desiccator over calcium chloride. Butylamine, piperidine, and triethylamine were purified by distillation before use.

4.2. Mesurements and calculations

4.2.1. UV–vis spectra. The UV–vis spectra were recorded by using a spectrophotometer equipped with a temperature controller.

4.2.2. Spectrophotometric measurements. Samples for a typical spectrophotometric measurement were prepared injecting in a quartz cuvette (light path 0.2 cm) the appropriate volume of IL and 1,4-dioxane, by means of microsyringe. Amine and *p*-nitrophenol were added as concentrated solutions in 1,4-dioxane. The *p*-nitrophenol concentration was kept constant (0.0002 M). Each sample was thermostated at 298 K. The suitable wavelength was chosen by comparing the *p*-nitrophenol solution with the sample having the higher amine concentration. Experimental data were subjected to fitting regression analysis according to Eq. 4.

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