

Determination of an Acidic Scale in Room Temperature Ionic Liquids

Cécile Thomazeau, Hélène Olivier-Bourbigou, Lionel Magna, Stéphane Luts, and Bernard Gilbert*

*Institut Français du Pétrole, 1 and 4 Avenue de Bois-Préau, 92852 Rueil-Malmaison, France, and
University of Liège, 4000 Liège, Belgium*

Received December 13, 2002; E-mail: lionel.magna@ifp.fr

Ionic liquids are attracting increasing attention as alternative solvents for a wide range of catalytic and organic reactions.¹ Previous works report that acidic chloroaluminates containing protons may be superacids, as evidenced by the determination of their Hammett functions (down to -18) and by their use for different acidic reactions.^{1,2} Nevertheless, chloroaluminates are very sensitive to hydrolysis. Traces of water can change the composition of the melt and the concentration of protons. As a result, it is difficult to accurately control the acidity of these ionic liquids. Non-chloroaluminate ionic liquids, air and moisture stable, have hence been developed and applied for acidic reactions.³ The miscibility of some ionic liquids with water has been proposed as a guide to the chemical behavior of Brønsted acids in ionic liquids.⁴ However, the determination of a Brønsted acidity scale in such solvents has not yet been considered.

In this paper, we would like to propose an acidity scale based on Brønsted acids in non-chloroaluminate ionic liquids. The goal of this acidity scale is ultimately to find a correlation between the catalytic activities measured in various acidic reactions.

The acidity of protons is mainly determined by their solvation. Indeed, weakly solvated protons possess a higher chemical activity.⁵ In solvents of low dielectric constant, dissociation of ion pairs involving protons should also be taken into account. Finally, the properties of protons depend on both the nature of the solvent and the nature and concentration of the acid.

In the present study, we report the behavior observed for different Brønsted acids soluble in ionic liquids. Strong acids such as HNTf₂ (NTf₂ = N(CF₃SO₂)₂) and HOTf (OTf = CF₃SO₃) were first evaluated. For comparison purposes, a weak acid such as AcH (AcH = CH₃CO₂H) was also investigated. The ionic liquids chosen for this application were [BMIM][NTf₂], [BMIM][BF₄], and [BMMIM][BF₄] ([BMIM] = 1-butyl-3-methylimidazolium, [BMMIM] = 1-butyl-2-methyl-3-methylimidazolium). These ionic liquids were synthesized according to published procedures.⁶ Subsequent washing of ionic liquids with a biphasic mixture H₂O:CH₂Cl₂ warranted the elimination of sodium and chloride impurities. Water was removed by vacuum drying.

The Brønsted acidity was evaluated from the determination of the Hammett acidity functions, using UV–visible spectroscopy. In the present case, this method consists of evaluating the protonation extent of uncharged indicator bases (named I) in a solution, in terms of the measurable ratio [I]/[IH⁺]. The chosen indicators belong to the same chemical family, mainly substituted dinitroanilines.

In a given solvent (s), assumed as being dissociating, the Hammett function (H_0) is defined as

$$H_0 = pK(I)_{aq} + \log\left(\frac{[I]_s}{[IH^+]_s}\right) \quad (1)$$

which can also be written as

$$H_0 = -\log a(H^+)_{aq} - \log \gamma(I)/\gamma(HI^+) - \log \Gamma(I)/\Gamma(HI^+) \quad (2)$$

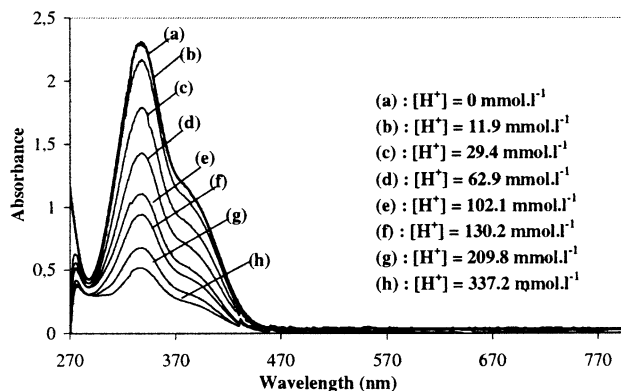


Figure 1. Absorption spectra of 2,4-dinitroaniline for various concentrations of HNTf₂ in [BMIM][NTf₂].

where $pK(I)_{aq}$ is the pK_a value of the indicator referred to an aqueous solution, $[IH^+]_s$ and $[I]_s$ are the molar concentrations of, respectively, the protonated and unprotonated forms of the indicator in the solvent s, the γ 's are the activity coefficients, and the Γ 's are the transfer activity coefficients from water to the solvent s. Equation 2 shows clearly that proposing H_0 as being equivalent to the pH is not strictly valid in a thermodynamical sense.⁷ It first assumes that the indicator solutions are diluted enough to consider the activity coefficients as unity. If the solvent s is water, the H_0 function then becomes identical to the pH, at infinite dilution. Second, it assumes that the ratio of the transfer activity coefficients of both I and HI^+ is unity and solvent independent. This simply means that the difference of solvation energy of the two I and HI^+ indicator forms does not depend on the solvent. In practice, the latter requirement is more difficult to meet. However, if one chooses indicator couples of very similar chemical structures, the ratios of the transfer activity coefficients, if not unity, can still be considered as constants, resulting in a slight but constant shift in the acidity function. This is why the Hammett function has proved very useful for semi-quantitative acidity comparison purposes.

In the first series of experiments, different concentrations of HNTf₂ in [BMIM][NTf₂] were prepared. Initial experiments have been made with 4-nitroaniline ($pK(I)_{aq} = 0.99$) and 2,5-dichloro-4-nitroaniline ($pK(I)_{aq} = -1.82$). These indicators were in their protonated form whatever the HNTf₂ concentration involved, which means that the acidity level is too high for such indicators. Hence, another indicator of lower $pK(I)_{aq}$ was chosen, where a full variation could be measured. For each acid concentration, the UV–visible spectrum of the 2,4-dinitroaniline indicator ($pK(I)_{aq} = -4.53$) was then recorded, as shown in Figure 1.

As the acid concentration increases, the absorbance of the unprotonated form of the indicator observed at 340 nm decreases. In the spectrum, the protonated form of the indicator cannot be seen due to its small molar absorptivity and its location, probably below 240 nm. By taking as the initial reference the total

Table 1. Calculation of the Hammett Function for Various Concentrations of HNTf₂ in [BMIM][NTf₂]^a

[H ⁺] mmol L ⁻¹	A _{max}	[I] (%)	[IH ⁺] (%)	H ₀ (±0.05)
0	2.3	100	0	
11.9	2.15	93.5	6.5	-3.35
29.4	1.76	76.5	23.5	-4.00
62.9	1.41	61.3	38.7	-4.35
102.1	1.09	47.4	52.6	-4.55
130.2	0.94	40.9	59.1	-4.70
209.8	0.67	29.1	70.9	-4.90
337.2	0.52	22.6	77.4	-5.05

^a Water content by Karl Fischer titration: 23 ppm.

Table 2. Comparison of Hammett Functions of Different Acids in [BMIM][NTf₂]^a

acid	[H ⁺] mmol L ⁻¹	H ₀ (±0.05)
HNTf ₂	175	-4.80
HOTf	175	-4.60
AcH	up to 1705	<i>b</i>

^a Indicator: 2,4-dinitroaniline (pK(I)_{aq} = -4.53). ^b No protonation of the indicator.

unprotonated form of the indicator (when no acid is added to the ionic liquid, spectrum a), we could determine the [I]/[IH⁺] ratio from the measured absorbances after each acid concentration (spectra b–h), and then the Hammett function is calculated (see Table 1).

In [BMIM][NTf₂], the Hammett function of HNTf₂ is included between -3.35 and -5.05, corresponding to concentrations ranging from 11.9 to 337.2 mmol L⁻¹. The linear H₀ correlation with the proton concentration has been verified. Considering the large errors for the extreme points, we found that the slope (1.06) is close to the expected unity value.

Addition of water to [BMIM][NTf₂] which already contains HNTf₂ (the molar ratio H₂O/HNTf₂ being equal to 1) induces an increase of the absorbance for the unprotonated form of the indicator. When this H₂O/HNTf₂ ratio is higher than 1, the absorbance of the unprotonated form of the indicator increases more. Hence, the addition of water decreases the acidity of the proton in the ionic liquid. Water behaves as a base, due to its more pronounced solvating character toward the proton than that of the solvent.

In the second series of experiments, we have studied the influence of added Brønsted acids in [BMIM][NTf₂] (Table 2).

In [BMIM][NTf₂] ionic liquid, triflic acid (HOTf) exhibits practically the same level of acidity as HNTf₂. For the same H⁺ concentration, the Hammett functions are, respectively, -4.80 and -4.60. In water, HNTf₂ and HOTf acids are known to be strong acids with almost the same strength. In anhydrous acetic acid, HOTf is more acidic (pK_a = 4.2) than HNTf₂ (pK_a = 7.0) due to the less dissociative character of this solvent as compared to that of water.⁸ As it is observed in an aqueous medium, the leveling effect of the ionic solvent limits the acidity level which can be reached with strong acids. Addition of AcH does not lead to a decrease of the absorption band of the unprotonated indicator. Acetic acid is then not acidic enough to protonate 2,4-dinitroaniline. As in an aqueous medium, AcH is a weaker acid than HOTf and HNTf₂ in [BMIM][NTf₂]. Furthermore, addition of an excess of AcH to a solution containing HNTf₂ results in an increase of the unprotonated indicator band, which indicates a basic behavior when the acidity level is very high.

Table 3. Comparison of Hammett Functions of HNTf₂ in Different Ionic Liquids

[H ⁺] mmol L ⁻¹	ionic liquid (ppm H ₂ O)	H ₀ (±0.05)
102.1	[BMIM][NTf ₂] (23)	-4.55 ^a
105	[BMIM][BF ₄] (141)	-7.00 ^b
105	[BMMIM][BF ₄] (16)	-7.05 ^b

^a Indicator: 2,4-dinitroaniline (pK(I)_{aq} = -4.53). ^b Indicator: 6-bromo-2,4-dinitroaniline (pK(I)_{aq} = -6.7).

The third series of experiments was devoted to the effect of the ionic liquid nature on the HNTf₂ acidity. The influence of the anion and cation nature of the ionic liquid is reported in Table 3.

In [BMIM][BF₄] and [BMMIM][BF₄], the Brønsted acidity of HNTf₂ is higher than that in [BMIM][NTf₂]. The Hammett functions of HNTf₂ in [BMIM][BF₄] and [BMMIM][BF₄] are, respectively, -7.00 and -7.05 for a [H⁺] concentration of 105 mmol L⁻¹. This suggests that the BF₄⁻ anion is less solvating toward H⁺ than is the NTf₂⁻ anion, leading to an increased acidity of the proton. Nevertheless, the cation ([BMIM] or [BMMIM]) has strictly no influence on the HNTf₂ acidity in these ionic liquids. The presence of a possible hydrogen bond between BF₄⁻ anion and the hydrogen in position 2 of the imidazolium does not seem to affect the acidic properties of these systems.

In conclusion, we have shown that in non-chloroaluminate ionic liquids based on the NTf₂⁻ and BF₄⁻ anions, to which an acid has been added, it is possible to reach acidity levels (measured as H₀) ranging from -3.35 to -7.00, depending on the ionic liquid and on the acid. These media are thus clearly less solvating than water. Concerning the behavior of water, we have evidenced its basic character in such ionic liquids. Complementary studies are in progress to complete the elaboration of acidic scales in room-temperature ionic liquids which could be further used as a predictive tool for studies of the acid-catalyzed reactions.

Supporting Information Available: Syntheses, characterization of ionic liquids, and UV-visible experiments (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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