Tentative Determination of the Acidity Level in Room Temperature Ionic Liquids by Electrochemical Methods

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Abstract

In our attempt to evaluate the acidity levels reached by acidified ionic liquids (BMImBF\textsubscript{4}, BMImNTf\textsubscript{2} and BMImOTf + HOTf or HNTf\textsubscript{2}), the uncertainty on the pK\textsubscript{as} of the indicators needed for the Hammett spectrophotometric procedure was pointed out. As consequence another method is proposed, based on the H\textsuperscript{+}/H\textsubscript{2} couple potential measurement. In this purpose, if dynamic methods failed mainly for lack of sufficient reversibility, potentiometry with a hydrogen electrode gave meaningful results. The \( R_0(H^+) \) Strehlow function, could be calculated, using the Fe\textsuperscript{3+}-Fc couple as reference assumed as solvent independent. The obtained results show that i) the acidities are much higher than those in water; ii) the acidities measured by the hydrogen electrode are higher than those measured by the Hammett method; iii) the sequence of acidities for solutions of similar content of added acid is still BF\textsubscript{4}^- > NTf\textsubscript{2}^- > OTf^- as previously measured with the Hammett method.

Introduction

In recent years, ionic liquids (ILs) have been shown as promising solvents for a wide range of catalytic and organic reactions (1). Some of these solvents have even led to industrial applications (2).

Among various properties, the Brønsted acidity has been shown to play an important role for many reactions in such solvents (3). In this case, the acidity can be first generated from the ionic liquid itself either by the anion (4) or the cation (as containing an acidic proton on the nitrogen (5-6) or even a grafted acidic function (7)). When applied to catalytic reactions, these acidic ionic liquids are of great interest for their dual role as solvents and catalysts (3, 6-7). As second solution, the Bronsted acidity can be promoted by simply adding an acid to the ionic liquids which then play mainly the role of solvents (8). For instance, previous works report that acidic chloroaluminates containing protons behave as superacids, as evidenced by the determination of their Hammett functions (down to -18) and by their use for different reactions involving acids (3, 9). Non-chloroaluminate ionic liquids, supposedly air and moisture stable, have also been applied for acidic catalyzed reactions (7).
Considering the importance of the acidity, we already have proposed a simple method for the determination in such solvents of a Brønsted acidity scale based on the Hammett acidity functions $H_0$, obtained by using UV-Visible spectroscopy (10). The goal of this acidity scale is ultimately to find a correlation between the catalytic activities measured on a given acidic reaction and the solvent nature (11).

We have also shown however that the measurement of $H_0$, besides all the assumptions involved in the Hammett function concept, may actually not be strictly applicable to all ionic liquids because many of them seem to exhibit a low dissociating power and only an “apparent” $H_0$ is measured (12). Indeed, there is more and more question in the literature of “ions pairs” formation (13). If it is however somewhat difficult to conceptualize discrete individual ions pairs in a medium which is supposedly totally formed of ions, it can be easily understood that a given cation will be influenced by its anionic surrounding, i.e. essentially the solvent anions. That electrostatic interaction, eventually variable for different cations, is likely to lower the dissociation of the indicators used in the Hammett procedure, then their acidity constants will be affected and in turn the $H_0$ function. Consequently, the function must be considered only as an “apparent” function and the true acidity is probably higher than the one measured (thus corresponding to lower $H_0$ values). Nevertheless, on the basis of this “apparent” acidity function and assuming, in a first approximation, that all indicator cations undergo similar electrostatic interactions with the anions, we have proposed that the acidity depends mainly of the solvent anion following the classification $[PF_6^-] > [BF_4^-] > [NTf_2^-] > [OTf^-]$ (12).

In an effort to estimate the accessible level of acidity in acidified reference ionic liquids, namely BMImNTf$_2$, BMImOTf and BMImBF$_4$ (where BMIm = 1-butyl-3-methylimidazolium, NTf$_2$ = N(CF$_3$SO$_2$)$_2$ and OTf = CF$_3$SO$_3$), the objective of this report is twofold: first, starting from colorimetric indicators as we did in the past, to confirm that two different Hammett indicators in the same solvent do not necessary lead to identical $H_0$ function and to measure the magnitude of the difference; secondly, to evaluate another method, now based on electrochemical measurements, in order to avoid the uncertainty on the indicators acidity constants. The suggested method here consists in determining a potentiometric acidity function ($R_0$) based on the Strehlow assumption and the $H^+/H_2$ couple (14). This acidity function will then be compared with the Hammett function ($H_0$).

**Experimental**

**Reagents and Materials**

Anhydrous triflic acid (puriss. Fluka), bis-(trifluoromethylsulfonyl)imide (>95% Fluka), sodium tetrafluoroborate (98 % Aldrich) and lithium bistriflimide were stored in a glove box (with water and oxygen content below 1 ppm). All these compounds were used without further purification. $N$-methylimidazole (MIm) was distilled twice under reduced pressure with CaH$_2$. Acetonitrile, ethyl acetate, dichloromethane, 1-chlorobutane and 1-bromobutane were distilled twice with P$_2$O$_5$. Water was distilled three times in a quartz apparatus.
Syntheses

The ionic liquids used in this work were synthesized following published procedures (15) or purchased. All the syntheses were carried out under dry argon and all the products (even the commercial salts) were dried under vacuum ($10^{-2}$ mbar) over a week at 50 °C before storage in a glove box.

- **1-butyl-3-methylimidazolium chloride BMImCl:** Freshly distilled 1-chlorobutane was added into a classical reflux apparatus containing $N$-methylimidazole in acetonitrile. The solution was stirred for 4 days at 60 °C. Small portions of ethyl acetate were then added to the warm reaction mixture to reach the BMImCl solubility limit. The chloride salt was then crystallized from slowly cooling the solution down to 0°C. The crystals were filtered, washed repeatedly with cold ethyl acetate. BMImCl was finally obtained as a white hygroscopic solid after a second crystallization from an ethyl acetate/acetonitrile mixture.

- **1-butyl-3-methylimidazolium bromide BMImBr:** the procedure for BMImBr synthesis is the same as the one for BMImCl but, because the reaction is more exothermic, it is first initiated at room temperature for a day before being completed at 60°C for another day. It is to be mentioned that BMImBr is easier to prepare in a pure state than BMImCl since it crystallizes more easily and forms transparent needles.

- **1-butyl-3-methylimidazolium tetrafluoroborate BMImBF$_4$:** A solution of NaBF$_4$ and BMImCl was vigorously stirred at room temperature for 4 days in dichloromethane. The milky reaction mixture was filtered and concentrated in a Rotavapor. The obtained viscous liquid was dissolved in water and extracted by CH$_2$Cl$_2$ with a continuous distillation system. The CH$_2$Cl$_2$ was then evaporated and BMImBF$_4$ was obtained as a colorless viscous liquid.

- **1-butyl-3-methylimidazolium bistriflimide BMImNTf$_2$:** A solution of LiNTf$_2$ and BMImBr was vigorously stirred at room temperature for 2 days in dichloromethane. The obtained suspension was filtered and the residual bromide was extracted from the organic phase by small portions of tridistilled water. The CH$_2$Cl$_2$ was then evaporated and BMImNTf$_2$ was obtained as a colorless liquid.

- **1-butyl-3-methylimidazolium triflate BMImOTf:** This ionic liquid was purchased from Solvionic SA (Varilhes, France) and dried under vacuum for a week at 50 °C.

Characterization of reactants and solvent

Since the presence of impurities has a dramatic influence on the final acidities, great care has been taken to obtain as clean as possible solvents. However, despite the apparent ease of synthesis and purification, we found it almost impossible to prepare impurity-free liquids. The maximum residual water content determined by Karl Fischer coulometry is still about 100 ppm for the water miscible solvents, whereas it is below 30 ppm for the others.

The halide content is evaluated from the “AgNO$_3$ test” where, in presence of halides, a precipitate is observed. In the case of hydrophobic ionic liquids, the test is operated
during aqueous washing of the ionic liquid, on a sample of the aqueous layer. For hydrophilic ionic liquids, the test was made directly on a sample of the neat ionic liquid. This simple visual method allows the determination of halide amount as low as \(3 \times 10^{-3} \text{ mol.l}^{-1}\) (Cl\(^-\)) or \(10^{-3} \text{ mol.l}^{-1}\) (Br\(^-\)). These values were obtained from independent results based on quantitative voltammetric measurements on the halide oxidation wave.

The methylimidazole residual content was evaluated directly by an improved acid-base titration on the halide salt (BMImCl or BMImBr) used for the synthesis. The detection limit of the new method is of the order of 0.005 weight\% and the content was found below that limit for purified salts. Finally, the total content of basic impurities was determined by UV-Vis spectroscopy titration, by following the variation of the basic band of an adequate colored indicator. Both impurities titration methods will be published in detail elsewhere (16).

**Apparatus and procedures**

The UV-Vis spectra of colored indicator (CI) solutions were recorded with a Perkin-Elmer lambda 14 P spectrophotometer. All analyzed solutions were prepared in the glove box by diluting an acidic batch solution of appropriate CI into a neutral batch solution of the same CI of the same concentration (by using that procedure, the CI concentration is always maintained as constant). The acidic batch solution consisted in an aliquot of the neutral batch solution to which a strong acid (HNTf\(_2\) or HOTf) was added in such a manner that the CI was totally under its acidic form. For the recording, the ionic liquid solutions were kept under argon in 1mm path quartz UV cell, closed to prevent any contamination. None of the ILs, neither HOTf nor HNTf\(_2\) showed any absorption above 250 nm. For each solution, the reference was the same solution (same concentration in acid) but without colored indicator.

Cyclic voltametry, differential pulse voltametry and potentiometry were performed using a computer-controlled electrochemical system (Autolab PGSTAT 20) and all the measurements were performed in a five necks electrochemical cell held in the gloves box. These necks and all the electrodes are provided with Witeg glass joints with Teflon and Viton o’rings insuring vacuum tightness.

A three-electrode system was used for the cyclic voltammetry experiments: the counter electrode was a platinum foil and the reference electrode is made of a silver wire deeping into a AgOTf (10\(^{-2}\) M) | BMImOTf solution in a compartment separated by a glass frit (fig.1). The working electrode depends on the studied electroactive species: the hydrogen waves were recorded using a polished platinum disk (\(\varnothing = 1 \text{ mm}\)) whereas the location of the reversible Fc\(^+\)/Fc system was measured on a glassy carbon disk (\(\varnothing = 3 \text{ mm}\)).

Fig.1: Reference Electrode
The potential of the hydrogen electrode was measured at zero current in a two-electrode system by bubbling gaseous hydrogen in the solution. Although the cell was maintained inside the dry box for the whole experiment, the cell and tubing system was such that the hydrogen inlet and outlet were isolated from the argon atmosphere of the box. The outlet tubing was provided with a trap placed outside the box and filled with a hydrophobic IL in order to maintain the hydrogen pressure at 1 atm. while isolating the system from the external environment. The working electrode is a platinized platinum electrode (8 cm² area). For all potential measurements with the hydrogen electrode, the reference electrode is an aluminum wire deeping into a 57 mole % AlCl₃-BMImCl in a compartment separated from the solution by a glass frit. Indeed, we could not use the Ag⁺/Ag system as reference since, for equilibrating the pressures, the reference compartment is provided with a hole and the Ag⁺ would be reduced by hydrogen. After all potentiometric measurements, ferrocene is added to the final acidic solution and the location of the reversible Fc⁺/Fc system is measured by differential pulse voltammetry. In this purpose, a three-electrode system was employed using a platinum foil as the counter electrode, a glassy carbon disc (∅ = 3 mm) as working electrode (on which the hydrogen system is inactive) and the aluminum reference electrode.

Results and discussion

Confirmation of our previous results based on the Hammett acidity function

Previously, we have proposed to measure the Brønsted acidity of ionic liquids from the determination of the Hammett acidity functions (H₀), using UV-Visible spectroscopy (10-11). Let us first recall the main principles and limitations. The method consists of evaluating the protonation extent of uncharged indicator bases (named I) in the solution, in terms of the measurable ratio [I]/[IH⁺]. The chosen indicators (denoted below as CI) belong to the same chemical family, mainly substituted nitroanilines. In a given solvent (s), the Hammett function (H₀) is defined as in Equation 1 and 2:

\[
H₀ = pK_{aₐq} + \log \left( \frac{[I]_s}{[IH⁺]_s} \right)
\]

[1]

which can also be written as:

\[
H₀ = -\log a(H⁺ₐq) - \log \frac{\gamma(I)}{\gamma(IH⁺)} - \log \left( \frac{\Gamma(I)}{\Gamma(IH⁺)} \right)
\]

[2]

where pKₐₐq is the pKa value of the indicator referred to an aqueous solution, [IH⁺]ₙ and [I], are the molar concentrations of respectively the protonated and unprotonated forms of the indicator in the solvent s (measured from the UV-Visible spectrum), γ are the activity coefficients and Γ the transfer activity coefficients from water to the solvent s.

The method suffers however from a few limitations. At first, equation 2 shows clearly that H₀ is not strictly equivalent to the pH. This would be the case if one assumes that the concentrations are dilute enough (γ = 1) and that the ratio of the transfer activity coefficients of both I and HI⁺ is unity and solvent independent. This latter requirement is met however by choosing indicator couples of very similar chemical structures. In that case, the ratios of the transfer activity coefficients, if not unity, can still be considered as constant, resulting into a slight but constant shift in the acidity function.
Secondly, the solvent is assumed as being totally dissociating and consequently, the known pKa values of the indicators are also assumed as valid. As we have explained in our introduction, there are however indications in the literature that this is probably not the case and the pKas may be affected by cations-anions interactions (13). In our previous paper, we have also shown that two different indicators (2, 4-dinitroaniline, pKa = -4.53, et 2, 4-dichloro-6-nitroaniline, pKa = -3.32), in the same solvent (HNEt3NTf2) with the same acid (HNTf2) concentration, do not lead to the same H0 values. If two straight lines of unit slope for H0 versus log[H+] are obtained, the two lines do not coincide and a shift of 0.3 units was observed.

In order to confirm this surprising observation, new measurements were made, for instance with 4-nitrodiphenylalanine (pKa = -2.50) and 2, 4-dichloro-6-nitroaniline (pKa = -3.32), into BMImOTf to which HOTf has been added. The resulting spectra and correlation lines are shown in figures 2 and 3.

![Figure 2: Evolution in BMImOTf of -a- 4-nitrodiphenylalanine (pKa = -2.50) and -b- 2,4-dichloro-6-nitroaniline (pKa = -3.32) with the addition of HOTf.](image1)

![Figure 3: H0 versus –log[HOTf] for the two indicators 4-nitrodiphenylalanine (pKa = -2.50) and -b- 2,4-dichloro-6-nitroaniline (pKa = -3.32)](image2)
As it can be seen, despite the solvent and the added acid are the same, the acidity levels measured with both indicators are different and, this time, a shift of about 0.6 units is observed. Although the shift is small, it is beyond the measurement errors. Our interpretation is that the pKa values are affected by electrostatic interactions and the indicators are less dissociated than in sulfuric acid-water solutions (a fully dissociating solvent where the pKa measurements were made). The actual acidity level observed in our ionic liquids should consequently be higher than measured but the Hammett method is unable to tell us how much higher. Other ways of measuring the acidity are then needed.

Results from electrochemical measurements

Considering the difficulties we have encountered with the Hammett method, we have decided to try to evaluate the acidity from the direct measurement of the activity of the proton with electrochemical methods. This section presents our electrochemical results on the acidity of ionic liquids to which a given amount of acid (HOTf and HNTf₂) has been added.

At first, we have tested a membrane electrode (Solvotrode 6.0229.100 by Metrohm) reputed as responding to pH in aqueous as well as non-aqueous media. That electrode which includes its own reference compartment (an Ag/AgCl electrode deeping into ethanol + LiCl and a PCTFE frit) was initially calibrated in aqueous solutions of known pH values. If that electrode responds nicely in acidic aqueous dissociating media down to pH = 0, it deviates progressively from the measured H0 values in more acidic media (here H₂SO₄ + H₂O), leading to too low acidity levels (figure 4). Clearly, there are experimental problems with such electrode, one of them being the variation of the junction potential at the interface reference electrode-solution which is not corrected for.

![Figure 4: Plots of H0 (triangles) obtained from colored indicators and pH (squares) measured with the Solvotrode versus the molar percentage of H₂SO₄ in water.](image)

Another method is then needed. As emphasized by Tremillon (17) and considering the classical relationship presented in Equation 3, a pH acidity scale in a given solvent (s) corresponds to the chemical potential of the proton in that solvent, one unit of pH corresponding to one unit of $-\mu_\text{H}^\circ/RT$. 

\[ \mu_{H^+} = \mu_{H^+}^0 + RT \log a_{H^+}, \quad [3] \]

As in water, the ideal method is to measure the potential of the \( H^+/H_2 \) couple in a given solvent versus the conventional \( (a_{H^+} = 1)/H_2 \) reference electrode in the same solvent. A pH scale can then be built in that solvent. For non-aqueous systems, a difficulty arises when one wishes to compare various solvents on a common acidity scale, again because of the unknown variation of the junction potential between solvents for the reference electrode. This problem has been largely discussed in the literature and several solutions were proposed (17-18). One of them was suggested by Strehlow (14). The method consists in determining a potentiometric acidity function \( (R^0) \) based on the \( H^+/H_2 \) couple potential and the assumption that a carefully selected redox couple, chosen as common reference, would be solvent independent. In our case, we have used the Ferricinium/Ferrocene \( (Fe^+/Fc) \) couple for which the variation of solvation for the \( Fe^+ \) and \( Fc \), is assumed to be similar by changing solvents. The \( E^0 \) potential of such a system is then considered as constant and is used as common reference for comparison purposes. The measurement of the acidity referred to a common scale involves first the measurement of the \( H^+/H_2 \) potential versus a reference containing equal amounts of \( Fe^+ \) and \( Fc \) in the same solvent. A usual practice is to refer all values to the conventional pH scale in water; the potentials are then corrected for the \( E^0 \) differences of the \( Fe^+/Fc \) and \( H^+/H_2 \) couples in water. The potentiometric function \( R^0(H^+) \) is then obtained by applying Equation 4. As it is the case for \( H_0 \), more negative values correspond to higher acidities (then higher proton activities).

\[
R^0(H^+) = -\frac{3 \left( (E_{H^+/H_2,S}^0 - E_{Fc^+/Fc,S}^0) - (E_{H^+/H_2,O}^0 - E_{Fc^+/Fc,O}^0) \right)}{2.3RT} \quad [4]
\]

Since the \( H^+/H_2 \) couple is electro active on a platinum disk electrode, dynamic methods were first tested to evaluate the respective potentials. Examples of cyclic voltametry results are shown in figures 5 and 6 where protons are added as HOTf in BMImOTf. In both cases, the reference electrode is AgOTf/Ag into BMImOTf in a separated compartment.

**Fig. 5** Cyclic voltamograms on HOTf solutions into BMImOTf; WE = Pt disk \((0.8 \text{ mm}^2)\), scan rate = 50 mV sec\(^{-1}\), \( T=50^\circ \text{C} \).

**Fig. 6** Cyclic voltamogram of a Ferrocene solution into BMImOTf; WE = Vitreous carbon \((7 \text{ mm}^2)\), scan rate = 50 mV.sec\(^{-1}\), \( T=50^\circ \text{C} \).
As can be seen on figure 5, the protons are reduced and the produced hydrogen is oxidized back to protons on the platinum electrode but, although the intensity of the waves increases proportionally with the HOTf content, the shape of the waves indicates a quasi-reversible process, as already discussed in details by D. S. Silvester et al. (19). In addition, the irreversibility seems to increase with the HOTf concentration. Although the irreversibility will of course influence the location of the wave and the calculation of the \( E^0 \) is only approximate, a rough evaluation of \( R_0(H^+) \) can be made. For a HOTf concentration of 0.01 M, the \( H^+/H_2 \) half-wave potential is located at -0.61 V from our reference whereas the \( Fe^+/Fe \) falls at -0.249 V. Knowing that the \( Fe^+/Fe \ E^0 \) is +0.4 V vs the NHE (Normal Hydrogen Electrode), one can calculate a \( R_0(H^+) \) of about -2.9 (as defined by Strehlow, the function \( R_0^0 \) corresponds to a solution containing a [H+] = 1M).

In our previous publication, we found, by using the Hammett method for the same solvent, a \( H_0^0 \) of -4.3. Since the two functions should lead to similar values, the \( R_0^0(H^+) \) found here is probably too low. Three reasons could be at the origin of such difference: i) the reduction wave is not totally reversible and simple equations as we have used do not apply; ii) cyclic voltametry is a dynamic process and the reduction process consumes locally the protons; the diffusion layer is then depleted, resulting in a variation of the local acidity; iii) because these were initial test experiments, the \( H^+ \) concentration was not corrected for basic impurities.

In view of the previous results, only equilibrium measurements seem appropriate to measure the \( H^+/H_2 \) couple potential, i.e. potentiometry at zero current and the method we have used will be described below. Hydrogen gas is bubbled into a solution containing increasing known amounts of HOTf. The potential is then measured between a large area (8 cm\(^2\)) platinumized platinum electrode and our reference. For that reference, because of possible reduction by hydrogen gas, the \( Ag^+/Ag \) system was avoided and replaced by an aluminum electrode deeping into a 57-43 m% AlCl\(_3\)-BMImCl mixture. Such a reference electrode was found very stable but the junction potential is not known. This is why, after each set of experiments, ferrocene was added to the main solution and its \( E^0 \) was measured from differential pulse voltametry on a glassy carbon electrode. Indeed the \( H^+ \) is not reduced on glassy carbon and does not interfere with the \( Fe^+/Fc \ E^0 \) measurement. Knowing the \( Fe^+/Fc \ E^0 \) versus the reference, all the measured hydrogen electrode potentials can then be expressed versus the \( Fe^+/Fc \) couple and the \( R_0 \) or \( R_0^0 \) functions can be calculated.

Examples of experimental results are shown below. The solvent is BMImBF\(_4\) (10 ml) and the added acid is HNTf\(_2\). Figure 7 shows the hydrogen electrode potential variation as function of a few acid additions. The hydrogen gas bubbling is started at time = 0 and initially, about 20 minutes are needed for the solution to be saturated and the potential to stabilize. Once saturated, the potential stabilizes for each acid addition after 10 minutes. It is to be noticed that with our initial experimental setup and upon hydrogen bubbling, the potential was always drifting and never stabilized. The potential became stable only when we replaced all laboratory hoses used to carry the hydrogen gas to the dry box and the electrochemical cell by Teflon tubing.
Figure 7: Hydrogen electrode potential vs the Al$^{3+}$/Al reference electrode after addition of HOTf: a) 10.2 mmole, b) 20.3 mmole, c) 42.9 mmole.

Figure 8: Variation of the average potential measured after each acid addition and stabilization.

Several measurements were performed in BMImBF$_4$, BMImNTf$_2$ and BMImOTf at 25 °C. For all these solvents, the Fe$^+/$/Fc $E^0_0$, expressed versus our Al$^{3+}$/Al reference, was found very stable and almost solvent independent (0.450 ± 0.01 V). The added acids (HA) were HNTf$_2$ and HOTf, their concentrations being corrected for the initial basic impurities content as explained in the experimental part. Examples of calculated $R_0$ are presented in figures 9 and 10. The corresponding curves for HOTf in figure 9 and 10 are calculated from independent measurements. In figure 10, we have added the results obtained from the Hammett methods for comparison purposes.

Figure 9: Calculated $R_0$ for various acid concentrations (HA) in BMImBF$_4$ (T = 25°C) a) circles: HA = HOTf; b) triangles: HA = HNTf$_2$.

Figure 10: Comparison of a) squares: $H_0$ (Hammett function) and b) circles: $R_0$ (Strehlow function) for solutions of HOTf in BMImBF$_4$. 
As shown in figure 9, the calculated $R_0$ vary almost linearly with the logarithm of the acid concentration but the slopes (respectively -1.58 and -1.44) are not unity as expected. One possible reason for such a deviation is the actual concentration of protons which, especially in the low concentration range, is eventually still overestimated. Although we already applied a correction for the impurities, the precise evaluation of all initial impurities is still a difficult problem and involves large errors. Since the impurity content is subtracted from the total added acid concentration, the points corresponding to low acid concentrations are the most affected by this problem and as consequence, will modify significantly the slopes values.

Besides the slopes problem, one can deduce two important features from these figures: 1) in BMImBF$_4$, HOTf is a weaker acid than HNTf$_2$, in agreement with the findings of D. S. Silvester et al. (19 b). Since HOTf and HNTf$_2$ behave only as strong acids in usual solvents, their different behavior here confirms that the acidity level reached in BMImBF$_4$ is very high; 2) in the same solutions (same HOTf concentrations), the acidity levels measured from potentiometry with the hydrogen electrode are higher (lower $R_0$ values) than those measured from the Hammett method. For the three investigated solvents (BMImBF$_4$, BMImNTf$_2$ and BMImOTf) and the two acids (HOTf and HNTf$_2$), the observation is the same: the sequence of acidity we have proposed by the Hammett method is the same (BF$_4^-$ > NTf$_2^-$ > OTf$^-$) (12) but, as an average, the potentiometric method leads to acidity levels about one order of magnitude higher than those measured by spectrophotometry. This is in agreement with our proposition that the pKas used for the spectrophotometric indicators are not strictly applicable in the investigated ionic liquids.

Finally, an example of application is shown on figure 11 where a solution containing HOTf in BMImBF$_4$ is titrated by ethanol with the Pt-hydrogen electrode.

Figure 11: Potentiometric titration of a HOTf solution in BMImBF$_4$ by ethanol. $T= 25^\circ C$, [HOTf] = 0.454 M; WE = Pt-hydrogen electrode; REF = Al$^{3+}$/Al in 43-57 m% BMImCl-AlCl$_3$ in a separated compartment. All potentials were then referred to Fc$^+$/Fc in the same solvent and the $R_0$(H$^+$) were calculated according to the procedure explained in the text.
The titration ratio is the ratio \( \frac{N_{\text{Ethanol}}}{N_{\text{HOTf}}} \times 100 \) where \( N \) is the number of moles of the respective components. As the figure shows, ethanol behaves as a weak base of estimated \( pK_a = -4.9 \). In addition, the shape of the curve is indicative of the titration of a weak acid, in confirmation of our measurements of figure 9. Again, both observations, ethanol behaving as a base and the weak acidic character of HOTf, are indicative of a solution strongly acidic. More details will be given in a subsequent publication where we will show that, by potentiometric titration of an acidic solution with a strong base, the acidity can be varied in ionic liquids of about 17 orders of magnitude.

**Conclusion**

In our attempt to evaluate the acidity levels reached by acidified ionic liquids, we have first pointed out difficulties on using the Hammett spectrophotometric procedure, mainly because of the uncertainty on the \( pK_a \)s of the needed indicators. Other methods have then been tested, based on the \( \text{H}^+/\text{H}_2 \) couple potential measurement. If dynamic methods failed mainly for lack of sufficient reversibility, potentiometry at zero current, an equilibrium method, gave meaningful results. The \( R_0(\text{H}^+) \) Strehlow function, analogous to a \( \text{pH} \) function, could be calculated, using the \( \text{Fc}^- - \text{Fc} \) couple as reference assumed as solvent independent.

Two critical experimental problems were however encountered:

- as for the Hammett method, the residual impurities play a critical role on the final acidity level. Because of the high acidity level, most impurities act as bases and must be neutralized before reaching the actual acidity,

- the quality of the hydrogen gas influences strongly the stabilization of the hydrogen electrode potential.

Because of these experimental difficulties, the slopes of the measured potentials versus the log of the added acid amounts were not the expected ones. However, at this point, conclusions can still be made:

- provided all the impurities are neutralized, the hydrogen electrode potential increases with the amount of added acid indicating an increase in the acidity level as expected,

- the acidity levels are much higher than those in water (\( R_0(\text{H}^+) \) ranges between -3 and -9). In addition, the approximate calculated values of the \( R_0 \) Strehlow acidity function indicate a higher acidity level than that given by the Hammett \( H_0 \) function, for all investigated acid solutions. This is in agreement with our proposition that the Hammett function leads only to a minimal acidity level, since the \( pK_a \)s of the used indicators are probably affected by ionic association,

- besides the absolute value of the acidity, the sequence of acidities observed with the hydrogen electrode on solutions of similar content of added acid is still \( \text{BF}_4^- > \text{NTf}_2^- > \text{OTf}^- \) as we have measured with the Hammett method.
Finally, the acidity of proton (directly related to its chemical potential) is mainly determined by both its solvation state and its activity (concentration). All the presented results are in agreement with such proposition. Simple extrapolation from acids dissociations measured in aqueous solutions is useless since it overlooks the solvent contribution.

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References


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