# Electrochemical Determination of p$K_a$ of N-Bases in Ionic Liquid Media

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**ABSTRACT:** Two electrochemical techniques have been used to measure the p$K_a$ of N-bases in several ionic liquids (ILs). The first method corresponds to a potentiometric titration of a strong acid with the N-base using a platinized Pt indicator electrode immersed in the IL solution and maintained under dihydrogen atmosphere via gas bubbling. The second approach involves performing cyclic voltammetry at a platinized Pt electrode in a solution containing both strong acid and the conjugate weak acid of the N-base. Values of p$K_a$ obtained by one or the other approach are in good agreement with each other. The experimental data clearly demonstrated that acid/base chemistry in ILs is similar to that observed in molecular nonaqueous solvents; i.e., the relative strengths of the bases were in the right order and spaced ($\Delta$p$K_a$). It was also observed that the strength of N-bases is highly dependent on the anion of the ionic liquid; this observation indicates that pH-dependent reactions could be controlled by the appropriate choice of anion for bulk ILs or as an added co-ion to bulk IL.

Hydrogen Electrode pH Titration in [Bmim][NTf$_2$] Ionic Liquid
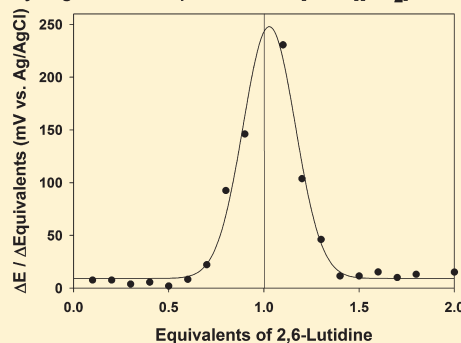
## 1. INTRODUCTION

The idea of Brønsted acidity and basicity [donation/accepting of protons (H$^+$)] in aqueous media is ubiquitously understood and is formally expressed as solution pH, which is related to the acidity ($K_a$) or basicity ($K_b$) constants of solutes through chemical equilibria with water. Essentially, water (the medium) acts to accept (i.e., solvates H$^+$ forming H$_3$O$^+$) or donate (forming OH$^-$) protons from/to dissolved solutes. The pH of aqueous solutions (pH = $-$log [H$_3$O$^+$]) can be calculated explicitly from known parameters or measured using a glass pH electrode which is calibrated against solutions of known pH (calculated from chemical equilibria principles).

The situation in nonaqueous media is more complicated and dependent on the media's strength as an acid or as a base (ability to donate or accept protons) and the media's dielectric constants. In nonaqueous media, the use of glass pH electrodes is often inappropriate and in numerous works spectroscopic techniques have been used to determine the acidity or basicity of solutes in molecular solvents. This approach relies on the spectroscopic determination of the extent of protonation (or deprotonation) of a pH-sensitive indicator (I) dissolved in the nonaqueous medium as the ratio [I]/[IH$^+$], followed by the application of the well-known Hammett relation.

In terms of developing a Brønsted acidity scale in pure ionic liquids (ILs), the spectroscopic approach has already been applied for strong Brønsted acids (e.g., HNTf$_2$ = bis(trifluoromethane)sulfonimide or HOTf = trifluoromethanesulfonic acid)[1,2] and weak carboxylic acids.[3] In addition, the basicity of some amines in ILs has also been investigated by spectroscopic methods via their reaction with 4-nitrophenol[4] and

trifluoroacetic acid.[5] The results obtained in these works allow comparison of the basicity strength of the investigated amines but does not really give p$K_a$ values per se since the titrant acids do not correspond to strong acids in the used ILs.[6]

Another approach to measurement of acidity or basicity constants ($K_a$ or $K_b$) of solutes in nonaqueous media is based on electrochemical techniques. Such measurements necessitate a strong acid (fully dissociated acid at unit H$^+$ activity or H$^+$ ion-paired with the IL anion) and H$_2$(g) in contact with a platinized platinum (P$-$Pt) potentiometric electrode in order to define an electrochemical origin-potential for the reference acidity scale. From this origin-potential reference, the p$K_a$ (or p$K_b$) of other dissolved acids (or conjugate bases) can be determined in two ways. First, the potential established at a P$-$Pt electrode in solutions containing the three species, weak acid, weak conjugate base, and H$_2$(g), is related to p$K_a$ (or p$K_b$) through the Nernst equation (vide infra). Alternatively, measurement (at P$-$Pt electrodes) of the dynamic reduction potentials of a strong acid (H$^+$) on the one hand and of protons of Brønsted weak acids on the other hand allows determination of $K_a$ (or $K_b$) in the nonaqueous environment, again through application of the Nernst equation (vide infra).

For the electrochemical approach to defining a Brønsted acidity scale, some recent relevant works have appeared. Bou Malhama et al.[7,8] have used the glass pH electrode in water/ionic liquid mixtures (from 0.0 to 77.4 v/v % of ionic liquid in water) to

assess the autoprotolysis constants of water/ionic liquids and to determine the dissociation constants for the corresponding conjugate acid/base pairs formed via autoprotolysis; strictly speaking, these are not ionic liquid measurements. Bautista-Martinez et al.[9] have recently reported a detailed description of the redox behavior of the $H^+/H_2(g)$ system at activated Pt in protic ionic liquids (PILs) media where, for each PIL, the oxidation potential of dihydrogen and the reduction potential of protons were indicative of Gurney-type energetics, thus demonstrating that "aqueous $pK_a$ data were generally appropriate in describing proton transfer energetics in PILs".

Significantly, in our previously published work on base-promoted catalytic oxidation of alcohols by the redox mediator TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) in ionic liquid media,[10] we showed that the rate of the alcohol oxidation reaction was a direct function of the aqueous $pK_a$ value of the chosen aromatic N-base. Then we decided to attempt to determine $pK_a$ values of N-bases in the used ILs media, since they were not known.

In this paper, we describe two electrochemical methods (which have been already used in nonaqueous molecular solvents) to determine the acidity of solutes in ionic liquid solutions. The first approach is potentiometric (equilibrium) where the potential of an "hydrogen P—Pt electrode" is measured in the presence of both conjugate acid—base species ($BH^+$ and B) and $H_2(g)$, while the second (dynamic method) involves performing cyclic voltammetry at a P—Pt electrode in solutions containing both strong and weak acids, without need of adding $H_2(g)$.

## 2. EXPERIMENTAL SECTION

**2.1. Ionic Liquid Media.** The used ILs were butylmethyimidazolium bis(trifluoromethane)sulfonimide [Bmim][NTf$_2$], butylpyrolidinium bis(trifluoromethane)sulfonimide [Bmpy][NTf$_2$], butylmethylimidazolium tetrafluoroborate [Bmim][BF$_4$], and ethylmethylimidazolium perfluoroethyltrifluoroborate [Emim]-[EtF$_5$BF$_3$]. [Bmim][NTf$_2$], [Bmpy][NTf$_2$], and [Bmim][BF$_4$] were prepared via ion metathesis in deionized water according a conventional procedure.[11,12] Samples of [Emim][EtF$_5$BF$_3$] were supplied kindly by Merck KGaA.

**2.2. Preparation of Pt Platinized (P—Pt) Working Electrodes.** The working electrode in potentiometric experiments (equilibrium method) was a platinum wire and in cyclic voltammetry experiments (dynamic method) was a platinum disk microelectrode. Both electrodes were covered with a fresh electrochemical coating of platinum, which allows obtaining an electrochemically quasireversible $H^+/H_2$ system. The electrodeposition of platinum on the electrode was obtained by electrolysis, at room temperature at constant current intensity [5 mA, 20 s for the disk microelectrode (area $\approx 2 \times 10^{-3}$ cm$^2$)[13] or 10 mA, 40 s for the wire electrode (diameter 0.5 mm, length $\approx$ 1 cm)], in a solution containing chloroplatinic acid (3 g) and lead acetate (0.02 g) dissolved in 100 cm$^3$ of distilled water. Pt wire acted as the anode during electrodepositing.

## 3. RESULTS AND DISCUSSION

The two electrochemical methods proposed above were applied in various ILs. Pyridine was used as a model base in order to compare the values of $pK_a$ obtained depending on both method and medium.

**3.1. Foreword.** Since ionic liquids are poorly dissociating media, strong electrolytes dissolved therein exist mainly as ion-pairs at ambient temperature. Given that acid—base couples always involve either a cationic acid form or an anionic basic form, this ion-pairing effect will influence the effective $pK$ value in the IL medium in the same way as it does in low dielectric constant organic solvent media. Also, at this point in time, no real information[14] is available describing the existence (or not) of a real strong acid in ILs. That is to say, no evidence has yet emerged indicating the existence of solvated protons in IL media (i.e., an "IL-$H^+$" species) as compared to the classical hydronium ion ($H_3O^+$) which exists in aqueous media. It is well-known that hydronium levels the acidity of all strong acids dissolved in aqueous and provides the origin of the aqueous pH scale. Notwithstanding, in ILs cation$^+$/anion$^-$ ion-pairs predominate; therefore, protons released from an ordinarily considered strong acid (i.e., low $pK_a$ in aqueous) dissolved therein will inevitably be associated with the anion part of the IL (denoted here as ILA$^-$). Consequently, no acid stronger than ILAH can exist in ILA$^-$-based ionic liquids. For example, in [Bmim][NTf$_2$], protons released from an ordinarily considered strong acid (e.g., HOTf, aqueous $pK_a \cong -13$) will interact with NTf$_2^-$ (HNTf$_2$ aqueous $pK_a \cong -4$) in a dynamic acid/base equilibrium to give $H^+$-NTf$_2^-$ ion pairs. It is this ion-pair that will be the strongest acid in the IL and thus provides the reference point for defining a pH scale in NTf$_2$ ILs.

Since many different anions (classified as acidic, neutral, or basic[14]) are used to create ILs, $pK_a$ data are not directly comparable between different ILs, or between ILs and molecular solvents, as they pertain to different reference states and therefore different acidity scales.

Also, in order to present here a simpler script of reactions and equations, ions (probably mainly ion-paired) are written as free dissociated species; in particular, $H^+_{solvated}$ will indicate the "strongest" acid which exists in the considered IL, and we will use, although not rigorously correct, the expression "strong acid" throughout.

**3.2. Potentiometric Determination of p$K_a$s in ILs.** *3.2.1. Potentiometric Measurement Procedure.* A glass electrochemical cell was equipped with the P—Pt wire electrode and an Ag/AgCl reference electrode which were connected to a high impedance voltmeter. Initially, the cell, thermostated at 298 K, was filled with 4 cm$^3$ of ionic liquid containing either HOTf or HNTf$_2$ (0.1 mol dm$^{-3}$), which, subject to the considerations above, can be considered as "strong acids" in ILs.[2,14,15] Dihydrogen (at 1 bar), which is poorly soluble in ILs,[16] was allowed to flow through the solution for at least 5 min in the otherwise airtight cell in order to obtain a stable initial potential value. Then the "strong acid" was titrated with a pure N-base by quantitative addition using a microliter syringe.

*3.2.2. Theory.* During the titration reaction of the "strong acid" with the base B, all species $H^+$, $BH^+$, B, and $H_2(g)$ are present in equilibrium in the solution and both redox systems shown in eqs 1 and 2 operate

$$H^+_{solvated} + e^- \leftrightarrows \frac{1}{2}H_2(g) \tag{1}$$

$$BH^+ + e^- \leftrightarrows \frac{1}{2}H_2(g) + B \tag{2}$$
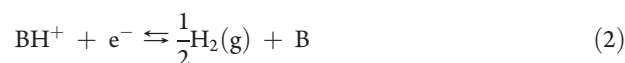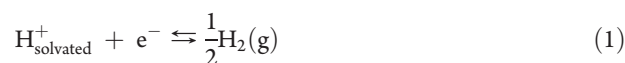
These redox processes allow the expression of the Nernst potential of the solution according to eq 3 (note that the "solvated" subscript on $H^+$ is not used in the equations for clarity

**Table 1. Reaction Balance for Addition of a Base B in a Solution of a Strong Acid**

| | $H^+$ | $+$ | $B$ | $\rightarrow$ | $BH^+$ |
|---|---|---|---|---|---|
| initial state | $C^0$ | | $0$ | | $0$ |
| first plateau: $x_{1(B)} < 1$ | $C^0(1 - x_{1(B)})$ | | $0$ | | $x_{1(B)}C^0$ |
| equivalence point: $x_{(B)} = 1$ | $0$ | | $0$ | | $C^0$ |
| second plateau: $x_{2(B)} > 1$ | $0$ | | $C^0(x_{2(B)} - 1)$ | | $C^0$ |
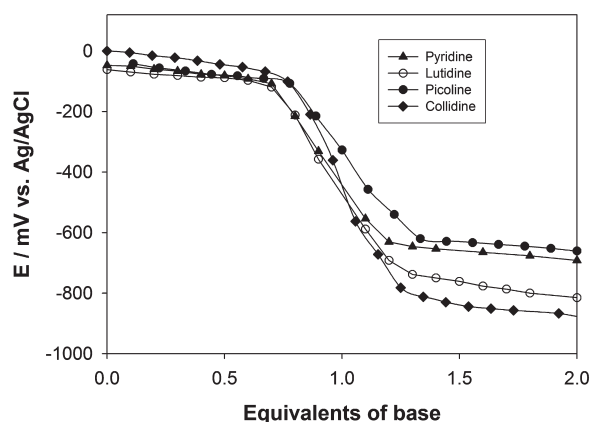


**Figure 1.** Potentiometric titration of $0.1$ mol dm$^{-3}$ HOTf by N-bases in [Bmim][NTf$_2$], 3-picoline, pyridine, 2,6-lutidine, and 2,4,6-collidine.

of presentation);

$$E = E_1 = E_2 = E_1^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{P_{H_2}^{1/2}} = E_2^0 + \frac{RT}{F} \ln \frac{a_{BH^+}}{a_B P_{H_2}^{1/2}} \tag{3}$$

where $E_1^0$ and $E_2^0$ are the respective standard reduction potentials (in the medium being examined) of the redox systems 1 and 2, $a_{H^+}$, $a_{BH^+}$, and $a_B$ are the respective activities of solutes, $P_{H_2}$ is the H$_2$ gas pressure, $R$ is the gas constant, $T$ is absolute temperature, and $F$ is Faraday's constant.

In the absence of information regarding activity of solutes in ionic liquid media, it is assumed here that activity will be equal to the molar concentration and eq 3 is then rewritten in the form of eq 4, which allows one to express the dissociation constant $K_a$ for the weak acid BH$^+$ as a function of the respective standard reduction potentials $E_1^0$ and $E_2^0$ through eq 5

$$E = E_1 = E_2 = E_1^0 + \frac{RT}{F} \ln \frac{[H^+]}{P_{H_2}^{1/2}} = E_2^0 + \frac{RT}{F} \ln \frac{[BH^+]}{[B]P_{H_2}^{1/2}} \tag{4}$$

$$E_2^0 - E_1^0 = \frac{RT}{F} \ln \frac{[H^+][B]}{[BH^+]} = \frac{2303RT}{F} \log_{10} K_a = -0.059 pK_a$$
$$(\text{at } T = 298 \text{ K}) \tag{5}$$

Under these conditions, when $[H^+_{\text{solvated}}] = 1$ mol dm$^{-3}$ and $P_{H_2} = 1$ bar (standard pressure), $E_1 = E_1^0$, which is the reference origin-potential for the acidity scale in the media. Here, HNTf$_2$ and HOTf were used to provide the solvated H$^+$ and it is assumed that they behave as "strong acids" within the media.

The potentiometric titration of H$^+_{\text{solvated}}$ by a base B shows a typical curve (cf. following figures) with plateaus on either side of a potential drop arising at the one-equivalence point of the neutralization reaction.

**Table 2. pK$_a$ Values of Some N-Bases in [Bmim][NTf$_2$], MeCN, and H$_2$O**

| solvent | pyridine | 3-picoline | 2,6-lutidine | 2,4,6-collidine |
|---|---|---|---|---|
| [Bmim][NTf$_2$] | $11.5 \pm 0.4$ | $11.2 \pm 0.4$ | $13.2 \pm 0.4$ | $15.2 \pm 0.4$ |
| acetonitrile | 12.5 | | 14.1 | 15 |
| water | 5.25 | 5.68 | 6.75 | 7.43 |
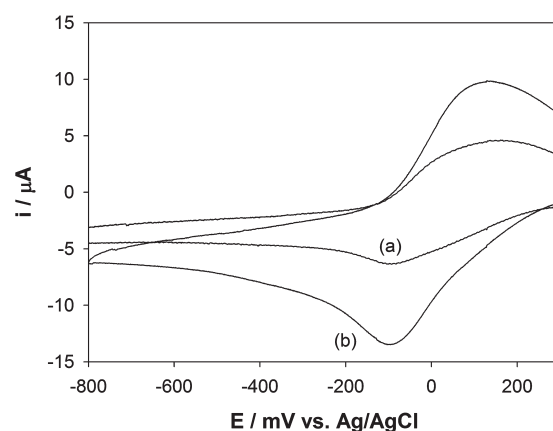


**Figure 2.** CV of "strong acids" in [Bmim][NTf$_2$] (scan rate 50 mV s$^{-1}$): (a) $5 \times 10^{-2}$ mol dm$^{-3}$ HOTf and (b) $5 \times 10^{-2}$ mol dm$^{-3}$ HOTf + $5 \times 10^{-2}$ mol dm$^{-3}$ HNTf$_2$.
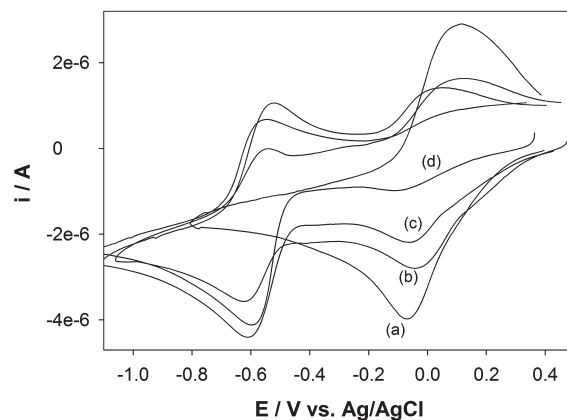


**Figure 3.** CV of HOTf + pyridine in [Bmim][NTf$_2$] (scan rate 50 mV s$^{-1}$): (a) $10^{-1}$ mol dm$^{-3}$ HOTf, (b) + 0.3 equiv pyridine, (c) + 0.5 equiv pyridine, (d) + 0.8 equiv pyridine.

The first plateau corresponds to an equivalent number $x_{1(B)}$ of added base lower than 1, while the second plateau is obtained when the base is in excess ($x_{2(B)} > 1$). From the initial concentration $C^0$ chosen for the "strong acid", the balance in substrates and products can be expressed easily (see Table 1).

At any point on the first plateau where H$^+_{\text{solvated}}$ is in excess ($0 < x_{1(B)} < 1$), applying of the Nernst equation (eq 4) yields eq 6

$$E = E_1 = E_1^0 + \frac{RT}{F} \ln \frac{C^0(1 - x_{1(B)})}{P_{H_2}^{1/2}} \tag{6}$$

Reciprocally, at any point on the last plateau where the base is in excess ($x_{2(B)} > 1$), applying of the Nernst equation (eq 4)
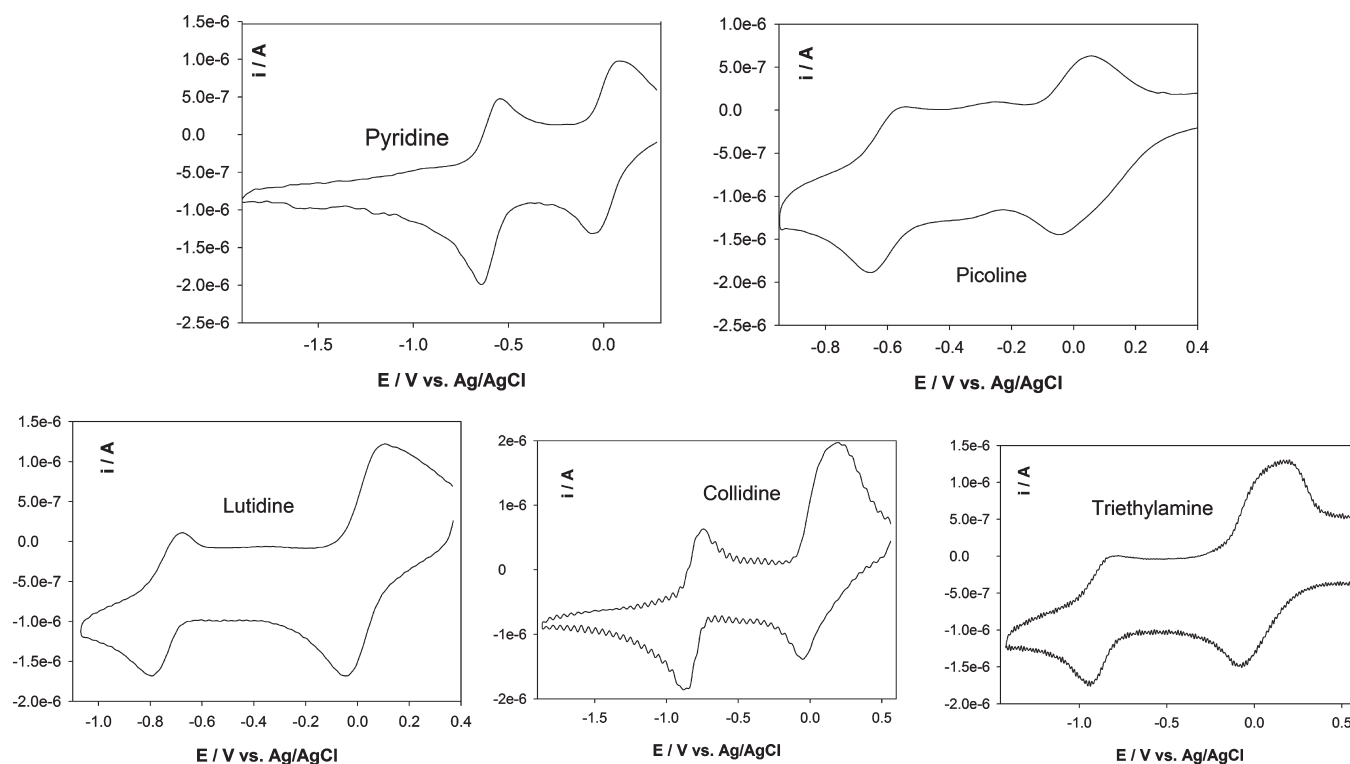
**Figure 4.** CVs in $[Bmpy][NTf_2]$ (scan rate 50 mV s$^{-1}$) of solutions of $8 \times 10^{-2}$ mol dm$^{-3}$ HOTf + various N-base ($4 \times 10^{-2}$ mol dm$^{-3}$).

yields eq 7

$$E = E_2 = E_2^0 + \frac{RT}{F} \ln \frac{C^0}{C^0(x_{2(B)} - 1) - P_{H_2}^{1/2}} \quad (7)$$

When considering a pair of points, one point on the first plateau ($E_1$, $x_{1(B)} < 1$) on the one hand and one point on the last plateau ($E_2$, $x_{2(B)} > 1$) on the other hand, subtraction of eq 7 from eq 6 and application of eq 5 leads to eq 8. Measurement of $E_1$ and $E_2$ therefore allows determination of acid dissociation constants $K_a$ in ionic liquid media.

$$pK_a = \frac{E_1 - E_2}{0.059} - \log_{10}[C^0(1 - x_{1(B)})(x_{2(B)} - 1)]$$
$$(\text{at } T = 298 \text{ K}) \quad (8)$$

*3.2.3. Potentiometric Determination of pK$_a$s of Aromatic N-Bases in [Bmim][NTf$_2$].* In order to verify the good working of the P–Pt electrode, trial experiments were first performed in an aqueous solution maintained under dihydrogen bubbling where acetic acid (AcOH) was titrated, at room temperature, with NaOH. Extraction of pK$_a$ values from this test-experiment results for AcOH in a pK$_a$ value of $4.7 \pm 0.4$, which agrees favorably with the literature value of 4.76.[17]

For experiments in IL medium, the initial starting conditions were solutions in $[Bmim][NTf_2]$ of the acid, typically 0.1 mol dm$^{-3}$ of HOTf, which was then titrated with pyridine or another pure N-base. Figure 1 shows titration curves obtained by addition of pyridine, 2,6-lutidine, 3-picoline, or 2,4,6-collidine. It is clear that the acid reacts with each base in the typical acid–base fashion, giving a single inflection maximum close to the one-equivalence point. According to theoretical part presented above, analysis of >10 data pairs of points per curve resulted in the pK$_a$

**Table 3. pK$_a$ Values of N-Bases Obtained by CV Method in $[Bmpy][NTf_2]$**

| pyridine | 3-picoline | 2,6-lutidine | 2,4,6-collidine | Et$_3$N |
|---|---|---|---|---|
| $10.4 \pm 1$ | $10.2 \pm 1$ | $12.9 \pm 1$ | $15.2 \pm 1$ | $15.3 \pm 1$ |

values as reported in Table 2 which are compared to pK$_a$ values in water[17] and a molecular organic solvent (MeCN).[18]

It is evident from Figure 1 and Table 2 that both pyridine and 3-picoline have very similar pK$_a$ values in the IL and are the weakest bases—behavior which is also observed in molecular solvents. It is also evident that 2,4,6-collidine is the strongest base (due to the inductive effects of three methyl groups) in the IL, again in keeping with behavior observed in molecular solvents.

**3.3. Dynamic Determination of pK$_a$s of Aromatic Bases in $[Bmpy][NTf_2]$.** Our second electrochemical approach to measure pK$_a$ values of N- bases in ILs is based on the use of cyclic voltammetry (CV), as was previously reported for the electrochemical measurement of pK$_a$ in molecular solvents.[19−21] Compared to the potentiometric titration approach, a major advantage of this method is the avoidance of the handling of hazardous gaseous dihydrogen, since H$_2$(g) is generated in situ at the working electrode by electroreduction of the protons of the acid solute(s) present in solution.

*3.3.1. Measurement Procedure.* CV measurements were performed using a VoltaLab 06 potentiostat in a three-electrode cell. The working microelectrode was a platinized Pt disk, while a Pt wire acted as the counter electrode and an Ag/AgCl system acted as the reference electrode. All measurements were performed at 298 K under an argon atmosphere. CVs were recorded in IL solutions containing both strong (subject to precedent considerations in theoretical part) and weak acids.

**Table 4. pK_a Value of Pyridine Obtained by CV Method in Various ILs**

| IL | $[Bmim][NTf_2]$ | $[Bmpy][NTf_2]$ | $[Bmim][BF_4]$ | $[Etmim][C_2F_5BF_3]$ |
|---|---|---|---|---|
| $pK_a$ of pyridine | $10.5 \pm 1$ | $10.4 \pm 1$ | $8.6 \pm 1$ | $8.4 \pm 1$ |

*3.3.2. Theory.* This dynamic method is also based on applying the Nernst equation (eq 4) which describes the two redox system shown in eqs 1 and 2. For these two reversible redox processes the difference between their voltammetric cathodic peak potentials ($\Delta E_{pc} = E_{pc_2} - E_{pc_1}$), anodic peaks potentials ($\Delta E_{pa} = E_{pa2} - E_{pa1}$), or half-wave potentials ($\Delta E_{1/2} = E_{P_{1/2(2)}} - E_{P_{1/2(1)}}$) is equal to the difference between their respective standard potentials ($E_2^0 - E_1^0$). Consequently, the $pK_a$ value of the $BH^+/B$ couple can be obtained easily according to eq 5.

*3.3.3. CV of "Strong Acid" in IL.* The application of the Nernst equation (eq 4) assumes that the "strong acid" used to establish the origin-potential is fully dissociated. Fortuitously, ionic liquids are frequently prepared from such "strong acids", e.g., $HNTf_2$ and $HOTf$; therefore, both these acids were investigated. Figure 2 shows voltammograms of these acids dissolved in $[Bmim][NTf_2]$.

It is evident from these CVs that protons derived from both acids are reduced in the ionic liquid medium at the same potential via a quasireversible electrochemical process and that either acid can be used as the "strong acid", as previously reported,[1,2,15] to establish an origin-potential. The reaction occurring during the redox process displayed in Figure 3 corresponds to the $H^+_{solvated}/H_2$ system (eq 1), where electrode potential $E$ and proton concentration are connected through the Nernst equation (eq 4). The cathodic peak currents ($i_{pc}$) are a linear function of the square-root of potential sweep-rate ($25-200$ mV s$^{-1}$), which is indicative of a diffusion-controlled process.

*3.3.4. CV of Mixed "Strong Acid" and Pyridine in BmimNTf_2.* Figure 2 above shows the quasireversible $H^+_{solvated}/H_2$ system in $[Bmim][NTf_2]$. Addition of pyridine to such solutions results in the appearance of a second quasireversible reduction process at more negative potentials, which is due to the redox reaction given in eq 2. This is clearly evidenced in Figure 3, which shows CVs obtained after successive additions of pyridine (Pyr) to HOTf solutions in $[Bmim][NTf_2]$. The reduction peak for $H^+_{solvated}$ decrease with the addition of Pyr, while the corresponding reduction peak for $PyrH^+$ increases. The cathodic peak currents ($i_{pc}$) (measured at the second peak), in a solution containing $H^+_{solvated}$ and $PyrH^+$, are also a linear function of $v^{1/2}$. ($25$ mV/s $\leq v \leq 200$ mV/s), which is indicative of a diffusion-controlled process.

Since the reduction potential of $PyrH^+$, relative to that for $H^+_{solvated}$ is connected to $K_a$ through eq 5, these measurements provide an alternative approach to determine $pK_a$ of the N-bases.

As presented above, the difference between cathodic peaks potentials ($\Delta E_{pc}$), anodic peaks potentials ($\Delta E_{pa}$), and half-wave potentials ($\Delta E_{1/2}$) have been applied to the curves shown in Figure 3 in order to calculate a mean value of the difference between the standard potential ($E_2^0 - E_1^0$) corresponding respectively to the reduction of pyridinium ion, $PyrH^+$, and the reduction of solvated $H^+$. Consequently, the $pK_a$ value of the $PyrH^+/Pyr$ couple can be calculated easily according to eq 5 and a mean value of $pK_{a(PyrH^+/Pyr)} = 10.5 \pm 1$ was obtained.

It should be noted that the uncertainties associated with CV-derived $pK_a$ values are higher than those observed with the potentiometric method. Actually, as noted in molecular solvents, electrochemical systems involving proton reduction/$H_2$ oxidation in ILs media are not rapid[5,21,22] even when using a

P−Pt electrode; therefore, the difference between the peak potential ($E_{pa} - E_{pc}$) is usually larger than the theoretical value of 59 mV. Consequently, values of $\Delta E_{pc}$ corresponding to proton reduction of each acid and $\Delta E_{pa}$ measured on the reverse scan may differ up to 0.1 V, which corresponds to 1.7 p$K$ units. Also, the ohmic drop in the IL medium (relatively low conductivity at ambient temperature[23]) may also be considered as a source of measurement uncertainty. Nevertheless, the $pK_a$ value of pyridine obtained from CV experiment ($10.5 \pm 1$) is consistent with the one from the potentiometric method ($11.5 \pm 0.4$).

*3.3.5. CV of Mixed "Strong Acid" and Various N-Bases in [Bmpy][NTf_2].* Determination of $pK_a$ of various N-bases by the CV method was achieved in $[Bmpy][NTf_2]$ as IL solvent. As can be seen in Figure 4, electrochemical behavior similar to the one observed with pyridine in $[Bmim][NTf_2]$ was obtained when adding various aromatic or aliphatic N-bases to HOTf solutions in $[Bmpy][NTf_2]$. The $pK_a$ values obtained from these experiments are reported in Table 3.

As observed by the potentiometric method in $[Bmim][NTf_2]$, and as previously reported in molecular solvents, the relative strength of the bases in $[Bmpy][NTf_2]$ is in the order pyridine $\approx$ 3-picoline < 2,6-lutidine < 2,4,6-collidine $\approx$ Et$_3$N.

In addition, $pK_a$ values of pyridine (which was chosen as reference) were measured by the CV method in various ILs, and the results are presented in Table 4. Although the direct comparison of these data is not thermodynamically rigorous, we can note the following observations. $pK_a$ values are very close in $[Bmpy][NTf_2]$ ($10.4 \pm 1$) and in $[Bmim][NTf_2]$ ($10.5 \pm 1$). This is not surprising, since the solvatation/ion-pairing of the cations $H^+$ and $BH^+$, and consequently their acidic strength, are probably much more dependent on the nature of the anion than on the nature of the cation of the IL. To test this assertion, additional CV measurements were made in solutions of a "strong acid" (HOTf or HNTf$_2$) + pyridine in $[Bmim][BF_4]$ and $[Emim][EtF_5BF_3]$ as the IL media.

Assuming that the basic strength of pyridine is not very dependent on the solvent, differences in $pK_a$ values of the $PyrH^+/Pyr$ acid−base couple in the four ILs used shows clearly an influence of the anion of the IL solvent. It is noteworthy that $pK_a$ values of pyridine are lower in $[Bmim][BF_4]$ and $[Etmim][C_2F_5BF_3]$ than in either $[Bmim][NTf_2]$ or $[Bmpy][NTf_2]$. To explain this behavior, it is supposed that in IL, $H^+$ is more strongly solvated/ion-paired with $BF_4^-$ or $C_2F_5BF_3^-$ than with $NTf_2^-$, i.e., that, as previously reported,[15] $HNTf_2$ is a much stronger acid than $HBF_4$ or $HC_2F_5BF_3$.

**3.4. Attempts to Measure $pK_a$ of Carboxylic Acids in ILs.** Applying the same electrochemical methods, attempts to determine the $pK_a$ of carboxylic acids in ILs were carried out where acetic acid was chosen as a model substrate. The potentiometric method was unsuccessful since no available acetate salt was sufficiently soluble in the ILs used. However, concerning the dynamic method, we achieved solutions of $HNTf_2 + AcOH$ in $[Bmpy][NTf_2]$. The corresponding CV curves show clearly the reversible signal assigned to the "strong acid", but a broad reduction peak for AcOH (which suggests a wide range of $pK_a$ values) gave unexpectedly high $pK_a$ values ($15-20$) when compared to those obtained for N-bases. Now, it was previously

reported that, in ILs, carboxylic acids are less dissociated than in water solution[3] and that H-bonds lead to oligomeric forms.[24] This behavior of carboxylic acids will probably yield to a large spectrum of p$K_a$ values, behavior which explains these observations. Obviously, further experiments are necessary to obtain more accurate information on this subject.

## 4. CONCLUSION

Both potentiometric and voltammetric measurement with platinized Pt electrodes have been shown to be capable of quantifying the acid/base properties of solutes dissolved in ionic liquids. Significantly, the more convenient voltammetric approach gave results in good agreement with the potentiometric measurements. The experimental data clearly demonstrated that acid/base chemistry in ILs is similar to that observed in molecular nonaqueous solvents, i.e., the relative strengths of the bases were in the right order and spaced ($\Delta$p$K_a$). These measurements support our previous observation that the rates of pH-dependent reactions (Tempo-catalyzed alcohol oxidations[10]) occur according to the relative p$K_a$ of N-base promoters dissolved in the IL medium. It is also significant that the strength of N-bases is highly dependent on the anion of the ionic liquid; this observation indicates that pH-dependent reactions could be controlled by appropriate choice of anion of bulk IL or as an added co-ion to bulk IL.

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