Electrochemical Proton Reduction and Equilibrium Acidity (p$K_a$) in Aprotic Ionic Liquids: Protonated Amines and Sulfonamide Acids

_Cameron L. Bentley,†‡ Alan M. Bond,†,* Anthony F. Hollenkamp,‡ Peter J. Mahon§ and Jie Zhang†,*_

†School of Chemistry, Monash University, Clayton, Vic 3800, Australia

‡CSIRO Energy, Box 312, Clayton South, Vic 3169, Australia

§Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn, Vic 3122, Australia
Abstract. Many organic compounds contain acidic and/or basic groups that dictate their physical, chemical and biological properties. For this reason, the acid dissociation constant, $K_a$, a quantitative measure of acid strength in solution, is a fundamentally important parameter in organic (synthetic) chemistry and related fields. In this study, the thermodynamics, kinetics and mechanisms of the proton reduction (hydrogen evolution) reaction at a platinum electrode have been investigated in the room temperature ionic liquid (IL) 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, using a range of nitrogen ($R_xNH$) acids as the proton source. The formal potential of the $H^{+}_{solvated}/H_2$ process (simulated by combining the classical Volmer and Tafel reactions) has been shown to be strongly dependent on the identity of the IL anion, making direct comparison of $pK_a$ data between ILs with different constituent anions impossible. Hydrogen evolution from weak nitrogen acids (protonated amines or sulfonamides) as the proton source is a diffusion controlled process which occurs in the potential region negative of the $H^{+}_{solvated}/H_2$ process. Simulations reveal that weak acid dissociation is limiting on the voltammetric timescale when $pK_a > 4$, meaning proton reduction via a $CE$ mechanism (where $C$ is the acid dissociation step) cannot account for the experimentally observed mass-transport limited currents. Under these conditions, proton reduction must proceed via an alternate pathway, where the weak acid undergoes direct reduction at the platinum electrode surface. Finally, the $pK_a$ values for ten weak nitrogen acids have been calculated ($5.2 \leq pK_a \leq 19.5$) from voltammetrically derived reversible half wave potentials ($E_{1/2}$) and diffusion coefficients ($D$), highlighting the utility of voltammetry as a convenient and relatively straightforward method for quantifying equilibrium acidity.

Keywords: hydrogen evolution reaction, voltammetry, acid dissociation constant, Brønsted acid/base
Introduction

Some of the most important reactions in biology and chemistry involve one or more proton (H+) transfer steps.\textsuperscript{1-5} The acid dissociation constant (\(K_a\)) of a Brønsted acid, HA, formally defined as follows, is a quantitative measure of acid strength:

\[
\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-
\]

\[
K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}
\]

(1)

Although the acid is taken to be a neutral species (HA) in Eq. 1, the following equation is equally valid for a cationic acid species, BH\(^+\) (\textit{i.e.}, a protonated neutral base, B):

\[
\text{BH}^+ \rightleftharpoons \text{H}^+ + \text{B}
\]

\[
K_a = \frac{[\text{H}^+][\text{B}]}{[\text{BH}^+]}
\]

(2)

The concept of Brønsted acidity/basicity is well established in aqueous media\textsuperscript{6}, where water, an amphoteric species, can act as a Brønsted base and accept a proton:

\[
\text{HA (or BH}^+) + \text{H}_2\text{O(base)} \rightleftharpoons \text{A}^-(\text{or B}) + \text{H}_3\text{O}^+
\]

(3)

or as a Brønsted acid and donate a proton:

\[
\text{A}^- (\text{or B}) + \text{H}_2\text{O(acid)} \rightleftharpoons \text{HA (or BH}^+) + \text{OH}^-
\]

(4)

From Eq. 3, it is clear that the hydronium ion (also known as a hydrated/solvated proton), H\(_3\)O\(^+\), which behaves as if it has a p\(K_a\) of \(-1.74\) (where p\(K_a = \text{-log}_{10}K_a\)), is the strongest acid that can exist in aqueous solution. The process shown in Eq. 3 effectively ‘levels’ the acidity of all strong acids \(pK_a < -1.74\) in aqueous media and is the origin of the aqueous p\(K_a\) scale.\textsuperscript{7,8}

Many organic compounds contain acidic and/or basic groups that dictate their physical, chemical and biological properties. Indeed, bond transformations in solution frequently involve the cleavage or formation of ‘R–H’ bonds. As described above, p\(K_a\) describes the Gibbs energy of ‘R–H’ bond heterolysis, making it a critically important thermodynamic parameter in...
The equilibrium acidity (pK$_a$) is a solvent dependent parameter, being influenced by the ability of the solvent to solvate each of the species outlined in Eqs. 1 (HA, H$^+$ and A$^-$) or 2 (BH$^+$, H$^+$ and B). It follows that solvent acidity/basicity, dielectric properties and ability to donate/accept hydrogen bonds can all influence the pK$_a$ of an acid in solution.$^{11,12}$ Although pK$_a$ data is most readily available in water$^{13,14}$, pK$_a$ scales have been established in a range of non-aqueous solvents, including acetonitrile$^{15}$, dimethylsulfoxide$^{11,16,17}$ and 1,2-dichloroethane$^{15}$. A variety of methods$^{18}$ have been employed to quantify equilibrium acidities in conventional media, including potentiometry$^{19}$, spectrophotometry$^{11,20}$ and voltammetry$^{12,16,17}$.

Air/water stable non-haloaluminate room temperature ionic liquids (ILs) have shown promise as replacements for volatile molecular solvents (such as those listed above) in a range of applications.$^{21}$ ILs are typically composed of a bulky organic cation and an inorganic anion with extensive charge delocalization. They are often referred to as ‘designer solvents’ because their physicochemical properties can be ‘tuned’ to an extent by changing their constituent cation and/or anion.$^{22,23}$ Relatively strong electrostatic (cohesive) forces operate within ILs, which means they often tend to be highly viscous and non-volatile.$^{24}$ Protons released from the dissociation of a Brønsted acid in an IL must associate with (or be ‘solvated’ by) the most basic component of the IL, most commonly the anion (A$^-_{IL}$):

$$\text{HA} + \text{A}^-_{IL} \rightleftharpoons \text{A}^- + \text{HA}_{IL} \quad (5)$$

where HA$_{IL}$ is the strongest acid that may exist in a given IL. HA$_{IL}$ effectively levels the acidity of strong acids in IL media, comparable to H$_3$O$^+$ in aqueous media. In other words, HA$_{IL}$ is origin of the pK$_a$ scale in IL media and for this reason pK$_a$ data are not directly comparable between ILs with different constituent anions.$^7,9,10$ From this point forward, ‘H$^+$’ refers to the
‘solvated’ proton species and is equivalent to HA_{IL} in the context of ILs. Unfortunately, absolute pK_{a} data for weak acids in ILs are scarcely available.\textsuperscript{7,9,10}

It can be shown\textsuperscript{7,12,25} that the difference in the formal potential (E^{0}') of the HA/H_{2} or BH^{+}/H_{2} couple and the H^{+}/H_{2} couple is proportional to the equilibrium acidity of HA or BH\textsuperscript{+} (\textit{i.e.}, \Delta E^{0}' \propto pK_{a}). Therefore, in this study, we will employ electrochemical methods such as cyclic voltammetry\textsuperscript{25} to probe the thermodynamics, kinetics and mechanisms of the H^{+}/H_{2} and HA/H_{2} (or BH\textsuperscript{+}/H_{2}) processes. The proton overall reduction reaction (or hydrogen evolution reaction, HER) is a conceptually simple process, involving the transfer of one electron per proton\textsuperscript{26-31}:

\begin{equation}
2H^{+} + 2e^{-} \rightleftharpoons H_{2}
\end{equation}

However, this reaction is subject to significant kinetic barriers, requiring an electrocatalyst to proceed at an economically viable rate.\textsuperscript{32} The HER has been most extensively studied in acidic aqueous media, where it is postulated to proceed via a combination of the following three elementary reactions\textsuperscript{27,29,32}:

\begin{align*}
\text{H}^{+} + \text{e}^{-} & \rightarrow \text{H}_{\text{ads}} & \quad (7) \\
2\text{H}_{\text{ads}} & \rightarrow \text{H}_{2} & \quad (8) \\
\text{H}_{\text{ads}} + \text{H}^{+} + \text{e}^{-} & \rightarrow \text{H}_{2} & \quad (9)
\end{align*}

where H_{ads} is a chemisorbed hydrogen atom and Eqs. 7, 8 and 9 are known as the Volmer, Tafel and Heyrovsky reactions, respectively.\textsuperscript{27} In a previous publication\textsuperscript{33}, we investigated the proton reduction reaction at a platinum electrode in a range of bis(trifluoromethanesulfonyl)imide ILs using H[NTf_{2}] as the proton source (\textit{i.e.}, the H\textsuperscript{+}/H_{2} process). Our results indicated that the Volmer reaction (Eq. 7) is the rate determining step for the HER in the IL media and that E^{0}'(H\textsuperscript{+}/H_{2}) is essentially insensitive to the identity of the IL cation.
Surprisingly, detailed studies available on the proton reduction process from weak acids in IL media are scarce. Doherty et al.\textsuperscript{7} have investigated the proton reduction process from five protonated amines (\textit{i.e.}, the BH\textsuperscript{+}/H\textsubscript{2} couple) at a platinum electrode in a range of ILs. The BH\textsuperscript{+}/H\textsubscript{2} process is quasi-reversible and occurs at potentials negative of the H\textsuperscript{+}/H\textsubscript{2} process. By assuming $\Delta E^0 \approx \Delta E_{1/2}$ (where $E_{1/2}$ is the reversible half-wave potential), an approximation which introduces considerable systematic error into the determination of $pK_a$ \textit{vide infra}, the authors estimated the $pK_a$ value directly from a transient cyclic voltammogram and found that the strength of a given acid depends strongly on the constituent anion of the IL.

In this paper, the thermodynamics, kinetics and mechanisms of the proton reduction (hydrogen evolution) reaction at a platinum electrode have been investigated in the room temperature ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide using ten nitrogen acids (protonated amines or sulfonamides, structures shown in Table 1) that cover a wide range of acidities as the proton source. The proton reduction process has been characterized predominantly using cyclic voltammetry with computational simulation. We also present a relatively straightforward method for calculating the $pK_a$ of weak acids in IL media, based on a combination of cyclic voltammetry and chronoamperometry. A companion study has also been undertaken using a range of oxyacids (phenols, carboxylic acids or sulfonic acids), which will be presented elsewhere.\textsuperscript{34}
Table 1. Names and structures of the protonated amines and sulfonamide acids (known collectively as nitrogen acids) investigated in this work.

<table>
<thead>
<tr>
<th>Name of the parent compound</th>
<th>Acid structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td><img src="image1.png" alt="Pyridine Structure" /></td>
<td>[Pyr‒H][NTf₂]</td>
</tr>
<tr>
<td>2-chloropyridine</td>
<td><img src="image2.png" alt="2-Chloropyridine Structure" /></td>
<td>[ClPyr‒H][NTf₂]</td>
</tr>
<tr>
<td>2,4-dichloropyridine</td>
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<td>[dClPyr‒H][NTf₂]</td>
</tr>
<tr>
<td>Aniline</td>
<td><img src="image4.png" alt="Aniline Structure" /></td>
<td>[An‒H][NTf₂]</td>
</tr>
<tr>
<td>N-methylimidazole</td>
<td><img src="image5.png" alt="N-Methylimidazole Structure" /></td>
<td>[MeIm‒H][NTf₂]</td>
</tr>
<tr>
<td>N-methylpyrrolidine</td>
<td><img src="image6.png" alt="N-Methylpyrrolidine Structure" /></td>
<td>[MePyrd‒H][NTf₂]</td>
</tr>
<tr>
<td>o-phenylenediamine</td>
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<td>[oPD‒H][NTf₂]</td>
</tr>
<tr>
<td>o-phenylenediamine</td>
<td><img src="image8.png" alt="O-Phenylenediamine Structure" /></td>
<td>[oPD‒H₂][NTf₂]₂</td>
</tr>
<tr>
<td>Saccharin</td>
<td><img src="image9.png" alt="Saccharin Structure" /></td>
<td>SACC</td>
</tr>
<tr>
<td>Di(benzenesulfonyl)amide</td>
<td><img src="image10.png" alt="Di(Benzenesulfonyl)amide Structure" /></td>
<td>DBSA</td>
</tr>
</tbody>
</table>
Experimental Section

Reagents. 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonylimide ([C$_2$ mim][NTf$_2$], Io-li-tec, $\eta = 33.7$ mPa s, $\rho = 1.52$ g cm$^{-3}$) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C$_2$mim][OTf], Merck, $\eta = 50.5$ mPa s, $\rho = 1.39$ g cm$^{-3}$) were dried under high vacuum ($\leq 10^{-2}$ mbar) at 45°C for 48 hours prior to use. The residual water content was less than 100 ppm as determined by Karl Fischer titration (Metrohm 831 KF Coulometer). Bis(trifluoromethanesulfonylimide (H[NTf$_2$], Sigma-Aldrich, 95%) was purified by sublimation under high vacuum. Ferrocene (Fc, Fluka, >98%) was recrystallized from n-pentane (Merck, EMSURE). N-methylimidazole (Sigma-Aldrich) was purified by vacuum distillation over lithium. Aniline (Sigma-Aldrich) was purified by vacuum distillation over potassium hydroxide (Merck). Trifluoromethanesulfonic (triflic) acid (H[OTf], Sigma-Aldrich, 98%), N-methylpyrroldidine (Sigma-Aldrich, 99%), pyridine (BDH, 99.8%), saccharin (Fluka, >99%), di(benzensulfonyl)amide (TCI, 97%), 2-chloropyridine (Sigma-Aldrich, 99%), 2,4-dichloropyridine (Combi-Blocks, 98%), $o$-phenylenediamine (Sigma-Aldrich, 99.5%), acetonitrile (Alfa-Aesar, anhydrous, 99.7%) and tetra-$n$-butylammonium hexafluorophosphate ([NBut$_4$][PF$_6$], Sigma-Aldrich) were used as supplied by the manufacturer. The protonated amine salts were prepared in methanol (Merck, >99.9%) by adding a stoichiometric amount of H[NTf$_2$] and stirring for several hours. Methanol was subsequently removed on a rotary evaporator and the remaining salt was dried under high vacuum at 45°C for at least 12 hours before use. All water-sensitive reagents were stored and handled under a dry argon atmosphere in a glovebox.

Electrochemical systems and procedures. All voltammetric experiments were carried out under benchtop conditions at ambient temperature (24 ± 1°C) with a Gamry Reference 600 Potentiostat/Galvanostat/ZRA (Gamry Instruments, USA). All solvents were degassed with N$_2$ prior to experimentation and a blanket of N$_2$ was maintained during the course of the
voltammetric experiments. A faraday cage was employed to minimize noise in all microelectrode experiments. Positive feedback $iR_u$ compensation ($R_u =$ uncompensated resistance) was employed in macroelectrode experiments ($R_u$ was estimated by electrochemical impedance spectroscopy). All voltammetric experiments were carried out using a standard 3-electrode arrangement with a working and reference electrode as described below and a Pt wire auxiliary electrode. An Ag wire which had been immersed in the IL under investigation (neat) and sealed in a fritted (Vycor glass frit) glass tube served as the pseudo reference electrode.

The pseudo reference electrode potential was calibrated against the formal potential of the IUPAC recommended Fc/Fc$^+$ process\textsuperscript{35} in the electrolyte of interest, taking into careful consideration the difference in the diffusion coefficients of Fc and Fc$^+$.\textsuperscript{27,36}

The Pt macrodisk with a nominal diameter of 1.6 mm was purchased from BASi (Bioanalytical Systems, USA) and the Pt microdisk with a nominal diameter of 20 µm was purchased from Metrohm (Switzerland). The Pt macrodisk electrode was activated by polishing with successively smaller (1 and 0.3 µm) aqueous alumina slurries (Kemet, UK) on a clean polishing cloth (Buehler, USA). Adherent alumina was removed by sonication in de-ionized water. The Pt microdisk electrode was activated by polishing with an aqueous slurry of 0.3 µm alumina and rinsed thoroughly with de-ionized water. The working electrode was preconditioned prior to sweeping by anodic polarization at 1.5 to 2.2 V vs. Fc/Fc$^+$ for ≤ 10 ms as has been previously reported.\textsuperscript{33} The active electrode area ($A$) of each of the electrodes was calibrated with convolution voltammetry\textsuperscript{37-39}, using the oxidation of a Fc solution of known concentration (2.0 mM in acetonitrile containing 0.10 M [NBu$_4$][PF$_6$]) and adopting a diffusion coefficient of $2.4 \times 10^{-5}$ cm$^2$ s$^{-1}$, as published under these conditions.\textsuperscript{25}

Viscosity was measured using the falling ball method with an Anton Paar Automated Microviscometer (AMVn). Density was measured with an Anton Paar DMA 4500M Density Meter.
Data treatment and processing. The algorithm used to calculate the convolved currents is the same as used previously. Derivative cyclic voltammograms (i.e., 1st order derivative of current or 2nd order derivative of charge) were constructed by differentiating experimental current data with respect to time using the differentiate function available in OriginPro 9.0 software. Savitzky-Golay data smoothing (polynomial order 2) was performed prior to estimating the derivative peak potentials. The diffusion coefficients \( D \) of \( \text{H}^+ \), \( \text{BH}^+ \) and \( \text{HA} \) were estimated from chronoamperometric \( (I-t) \) decay curves obtained at a microdisk electrode using the Shoup and Szabo\textsuperscript{40} method, as reported elsewhere.\textsuperscript{33, 36} The diffusion coefficient \( D \) of \( \text{H}_2 \) was estimated from the second (oxidative) step of a double-step chronoamperogram using numerical simulation as has been previously described.\textsuperscript{41} The sample time used in all chronoamperometric experiments was 0.01 s. Voltammetric simulations were undertaken using the DigiElch software package (v. 7F, Elchsoft, Germany). The \( pK_a \) of 2,4-dichloropyridine was estimated using the MarvinSketch software package (v. 14.12.15.0, Chemaxon).
Results and Discussion

Electroreduction of ‘solvated’ H⁺ in [C₂mim][NTf₂] and [C₂mim][OTf]. Initial investigations focused on establishing the proton reduction process from ‘solvated’ H⁺ in [C₂mim][NTf₂] and [C₂mim][OTf]. Prior to voltammetric cycling of the potential, the platinum electrode was preconditioned by ‘anodic polarization’ at oxidative potentials (typically > 1.5 V vs. Fc/Fc⁺), as was highlighted in a previous publication. Shown in Figure 1a is a cyclic voltammogram obtained from the reduction of H[NTf₂] at a platinum macrodisk electrode in [C₂mim][NTf₂]. This is a one electron per proton process, which occurs in the potential region just negative of the Fc/Fc⁺ process, producing molecular hydrogen (H₂) as per Eq. 6. The voltammetric peak-to-peak separation (ΔEₚ) increases with increasing scan rate, with values of 72.2, 82.2 and 92.3 mV at 100, 250 and 500 mV s⁻¹, respectively (see Figure S1), indicating that the H[NTf₂]/H₂ process is quasi-reversible (Rₘ is expected to negligible, see Experimental Section). In a previous publication, we demonstrated that H[NTf₂] is not dissociated when dissolved in ILs containing the [NTf₂]⁻ anion (i.e., the protons diffuse as H[NTf₂]). In other words, H[NTf₂] is the ‘solvated proton’ species in [C₂mim][NTf₂], comparable to H₃O⁺ in aqueous media. Since H[NTf₂] is the strongest acid that can exist in [C₂mim][NTf₂], the H[NTf₂]/H₂ process shown in Figure 1a will serve as the equilibrium acidity scale reference point in this medium.

Shown in Figure 1b is a cyclic voltammogram obtained from the reduction of H[OTf] in [C₂mim][OTf] at a platinum macrodisk electrode. Once again, ΔEₚ increases with increasing scan rate, albeit to a greater extent than in [C₂mim][NTf₂], with values of 105.4, 113.4 and 125.4 mV at 100, 250 and 500 mV s⁻¹, respectively (see Figure S2), indicating that the H[OTf]/H₂ process is quasi-reversible. Assuming that E⁰(Fc/Fc⁺) is solvent independent, the H[OTf]/H₂ process in [C₂mim][OTf] occurs at potentials approximately 300 mV more negative than the H[NTf₂]/H₂ process in [C₂mim][NTf₂]. Since H[OTf] is the ‘solvated proton’
species in [C₂mim][OTf] (comparable to H[NTf₂] in [C₂mim][NTf₂] or H₃O⁺ in H₂O), it is clear that the equilibrium acidity scale reference point is considerably different in [C₂mim][OTf] and [C₂mim][NTf₂], making direct comparison of pKₐ data between these media impossible.

Shown in Figure 1c is the proton reduction process obtained at a platinum macrodisk electrode when H[NTf₂] is dissolved in [C₂mim][OTf]. Again, ΔEₚ increases with increasing scan rate, with values of 107.4, 121.4 and 137.4 mV at 100, 250 and 500 mV s⁻¹, respectively (see Figure S3), indicating that this proton reduction process is quasi-reversible. The ‘H[NTf₂]/H₂ process’ appears to be very similar to the H[OTf]/H₂ process in [C₂mim][OTf], being a quasi-reversible, one electron per proton process, which occurs in the potential region approximately 350 mV negative of the Fc/Fc⁺ process. The close coincidence between the ‘H[NTf₂]/H₂’ and H[OTf]/H₂ processes indicates that the following equilibrium lies to the right in [C₂mim][OTf]:

\[
\text{H[NTf₂]} + [\text{OTf}^-] \rightleftharpoons [\text{NTf₂}]^- + \text{H[OTf]} \tag{10}
\]

In other words, H[NTf₂] behaves as a ‘strong acid’ in [C₂mim][OTf], undergoing complete dissociation to form H[OTf] and [NTf₂]⁻. Consequently, the H[OTf]/H₂ couple is responsible for the proton reduction process observed in Figure 1c. The higher proton affinity of [OTf]⁻ compared to [NTf₂]⁻ is thought to be due to the smaller size and more localized negative charge density of the former.⁹,¹⁰ Conversely, it would be expected that H[OTf] behaves as a ‘weak acid’ in [NTf₂]⁻ ILs, which was found to be the case in our companion study.³⁴
Figure 1. Comparison of the simulated (○) and experimental (—) concentration-normalized cyclic voltammograms showing the proton reduction process obtained from (a) 49.8 mM H[NTf₂] in [C₂mim][NTf₂], (b) 41.1 mM H[OTf] in [C₂mim][OTf] and, (c) 42.0 mM H[NTf₂] in [C₂mim][OTf] at a 1.6 mm dia. Pt macrodisk electrode with a scan rate of 250 mV s⁻¹. The arrows indicate zero current for each of the voltammograms. Simulation parameters are available in Table 2.
Simulation of the electroreduction of ‘solvated’ H⁺ in [C₂mim][NTf₂] and [C₂mim][OTf]. Also shown in Figure 1 are simulations of the cyclic voltammograms. A number of mechanisms were considered and the following was found to be consistent with the experimental data under a wide range of experimental conditions:

\[
\begin{align*}
H^+ + e^- & \rightleftharpoons H^+ \quad E^{0'}(H^+/H^+), k_{s{app}}, \alpha \quad (11) \\
H^+ + H^+ & \rightleftharpoons H_2 \quad K_{\text{dim}}, k_{\text{dim}} \quad (12)
\end{align*}
\]

where \(E^{0'}(H^+/H^+)\), \(k_{s{app}}\) and \(\alpha\) are the formal potential of the H⁺/H⁺ couple, apparent standard heterogeneous electron-transfer rate constant (\textit{vide infra}) and charge transfer coefficient respectively. Additionally, Eq. 12 has been treated as a homogeneous process with arbitrarily defined dimerization equilibrium constant \((K_{\text{dim}})\) and dimerization rate constant \((k_{\text{dim}})\) values.

Here, H⁺ denotes a ‘solvated’ proton, referring to the strongest acid which can exist in a given medium, which in the current context is equivalent to HA_{IL}. The reactions given in Eqs. 11 and 12 correspond to the Volmer and Tafel equations respectively (see Eqs. 7 and 8). Although in reality H⁺ is likely to be a surface confined species\(^{29,31}\), it has been treated as solution based (diffusing) species in the simulations, as justified in a previous publication.\(^{33}\) One consequence of treatment of the mechanism in this manner is that the process shown in Eq. 12 has no physical significance and the following parameters: \(k_{s{app}}, K_{\text{dim}}, k_{\text{dim}}\) and \(D_{H^+}\) are not quantitatively meaningful.\(^{16}\) For this reason, \(k_s\) has been given the superscript ‘app’ to signify that it is the ‘apparent’ heterogeneous rate constant used in the simulations.

In all simulations, it was taken that \(D_{H^+} = 10^{-10} \text{ cm}^2 \text{ s}^{-1}, K_{\text{dim}} = 10^4, k_{\text{dim}} = 10^{16} \text{ M}^{-1} \text{ s}^{-1}, \) uncompensated resistance \((R_u) = 0 \Omega\) and double layer capacitance \((C_{\text{dl}}) = 0 \text{ F}\). The \(E^{0'}\) value used in the simulations corresponds to the fictitious H⁺/H⁺ couple and is related to \(E^{0'}(H^+/H_2)\) as follows:
\[ E^0'(H^+/H^+) = E^0'(H^+/H_2) - \frac{RT}{2F} \ln(K_{\text{dim}}) = E^0'(H^+/H_2) - 0.118 \text{ V} \] (13)

where \( R \) is the gas constant, \( F \) is Faraday’s constant and \( T \) is temperature. The parameters derived by simulation of the experimental data are outlined in Table 2. The experiment-simulation comparison for the reduction of \( \text{H[NTf}_2\text{]} \) in \([\text{C}_2\text{mim}][\text{NTf}_2]\), \( \text{H[OTf]} \) in \([\text{C}_2\text{mim}][\text{OTf}]\) and \( \text{H[NTf}_2\text{]} \) in \([\text{C}_2\text{mim}][\text{OTf}]\) at multiple scan rates are provided in the Supporting Information (Figures S1 to S3). The mechanism shown in Eqs. 11 and 12 has been expanded upon below to simulate the reduction of protonated amines or sulfonamide acids in \([\text{C}_2\text{mim}][\text{NTf}_2]\).

As shown in Figures S1 to S3, excellent fits between the experimental and simulated voltammograms are achieved over a wide range of scan rates when using the simulation parameters outlined in Table 2. As was highlighted in a previous publication\(^{33}\), the main discrepancy between the experimental and simulated data is in the hydrogen underpotential deposition (UPD) region, prior to the main (solution based) reduction process.\(^9\) The formal potential of the \( \text{H}^+\slash\text{H}_2 \) process in \([\text{C}_2\text{mim}][\text{NTf}_2]\) is \(-0.026 \text{ V vs. Fc/Fc}^+\), compared to \(-0.342 \text{ V vs. Fc/Fc}^+\) in \([\text{C}_2\text{mim}][\text{OTf}]\). In addition, \( E^0'(\text{H}^+/\text{H}_2) \) obtained from \( \text{H[NTf}_2\text{]} \) in \([\text{C}_2\text{mim}][\text{OTf}]\), \(-0.340 \text{ V vs. Fc/Fc}^+\), is nearly identical to that obtained from \( \text{H[OTf]} \) in \([\text{C}_2\text{mim}][\text{OTf}]\), supporting our previous conclusion that \( \text{H[NTf}_2\text{]} \) acts as a strong acid in this media. Also highlighted in a previous publication\(^{33}\), the Volmer reaction (Eq. 11) is the rate determining step for the HER on Pt in the investigated ILs, where the second step (Eq. 12) is simply required to fulfill the stoichiometry requirements of the overall process (see Eq. 6).

Although the \( k_s^{\text{app}} \) values derived from the simulations are not quantitatively meaningful in an absolute sense, the relative magnitude of the values indicates that the hydrogen evolution reaction is more kinetically facile in \([\text{C}_2\text{mim}][\text{NTf}_2]\) \( (k_s^{\text{app}} \approx 0.02 \text{ cm s}^{-1}) \) than in \([\text{C}_2\text{mim}][\text{OTf}]\) \( (k_s^{\text{app}} \approx 0.004 \text{ cm s}^{-1}) \), in agreement with the previously noted \( \Delta E_p \) vs. scan rate trends. It is also
worth noting that degradation of the voltammetric response caused by slowing heterogeneous electron transfer kinetics with potential cycling\textsuperscript{33}, occurred more rapidly in [C\textsubscript{2}mim][OTf] than in [C\textsubscript{2}mim][NTf\textsubscript{2}] suggesting that that electrode ‘deactivation’ is intrinsically linked to the IL anion.

Table 2. Parameters extracted from the comparison of experimental cyclic voltammetric data for the electroreduction of ‘solvated’ H\textsuperscript{+} in [C\textsubscript{2}mim][NTf\textsubscript{2}] or [C\textsubscript{2}mim][OTf] and simulated data, based on the mechanism described by Eqs. 11 and 12.

<table>
<thead>
<tr>
<th>IL</th>
<th>Acid</th>
<th>(\nu^0(\text{H}^+\text{H}_2)) / V</th>
<th>(\alpha)</th>
<th>(k_{\text{app}}) / cm s(^{-1})</th>
<th>(D(\text{H}^+) / 10^{-7}) cm(^2) s(^{-1})</th>
<th>(D(\text{H}_2) / 10^{-5}) cm(^2) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C\textsubscript{2}mim][NTf\textsubscript{2}]</td>
<td>H[NTf\textsubscript{2}]</td>
<td>-0.026</td>
<td>0.50</td>
<td>0.022</td>
<td>3.1</td>
<td>2.2</td>
</tr>
<tr>
<td>[C\textsubscript{2}mim][OTf]</td>
<td>H[OTf]</td>
<td>-0.342</td>
<td>0.40</td>
<td>0.0043</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>[C\textsubscript{2}mim][OTf]</td>
<td>H[NTf\textsubscript{2}]</td>
<td>-0.340</td>
<td>0.40</td>
<td>0.0040</td>
<td>1.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Proton reduction from weak nitrogen acids in [C2mim][NTf2]. Further studies were focused on the proton reduction process from a range of weak nitrogen acids (*i.e.*, BH+/H2 or HA/H2 couple) in [C2mim][NTf2]. The name and structure of all of the nitrogen acids investigated were previously shown in Table 1. The electrode was activated prior to sweeping by oxidative pretreatment as discussed above. Representative cyclic voltammograms obtained from a typical monoprotonated amine, [Pyr–H][NTf2], are shown in Figure 2a. Proton reduction from [Pyr–H]+ gives rise to a one-electron per proton process at potentials approximately 700 mV negative of the H[NTf2]/H2 process (see Figure 1a). ΔEp increases with increasing scan rate, with values of 114, 120, 136 and 156 mV at 50, 100, 250 and 500 mV s⁻¹, respectively, indicating that proton reduction from this weak acid is a quasi-reversible process.

A diprotonated amine, [oPD–H2][NTf2]₂, was also investigated; representative cyclic voltammograms are shown in Figure 2b. Proton reduction from [oPD–H2][NTf2]₂ gives rise to two one-electron per proton processes in the potential regions approximately 200 mV and 550 mV negative of the H[NTf2]/H2 process (see Figure 1a), corresponding to the first and second deprotonation, respectively. Hydrogen UPD can be seen prior to the first proton reduction process at high scan rates; this was found to be the case with all of the acids investigated in this work. ΔEp for the process corresponding to the first deprotonation increases substantially with scan rate, with values of 142, 170 and 250 mV at 50, 100 and 250 mV s⁻¹, respectively. By contrast, ΔEp for the process corresponding to the second deprotonation increases to a lesser extent with scan rate, with values of 87.9, 93.8 and 108 mV at 50, 100 and 250 mV s⁻¹, respectively. These results qualitatively indicate that hydrogen evolution from monoprotonated [oPD–H]+ is more kinetically facile than from diprotonated [oPD–H2]²⁺ in this media, suggesting that the charge of the weak acid may influence the heterogeneous electron transfer kinetics of the proton reduction process.
Cyclic voltammograms obtained from two neutral sulfonamide acids, SACC and DBSA, are shown in Figure 3a and b, respectively. Proton reduction from SACC (see Figure 3a) occurs in the same potential region as [Pyr–H][NTf₂], approximately 700 mV negative of the H[NTf₂]/H₂ process. Hydrogen evolution from SACC is a quasi-reversible process, featuring large ΔEₚ values of 254, 284, 334 and 382 mV at 50, 100, 250 and 500 mV s⁻¹, respectively. Proton reduction from DBSA occurs in the same potential region as [oPD–H][NTf₂], approximately 550 mV negative of the H[NTf₂]/H₂ process. Once again, hydrogen evolution from DBSA is a quasi-reversible process, featuring large ΔEₚ values of 232, 278, 348 and 406 mV at 50, 100, 250 and 500 mV s⁻¹, respectively. The magnitude of these ΔEₚ values qualitatively indicate that hydrogen evolution from the sulfonamide acids is kinetically more sluggish than from monoprotonated amines of similar strength (i.e., [Pyr–H][NTf₂] or [oPD–H][NTf₂]). In the present case, it is unlikely this trend in heterogeneous kinetics (i.e., electrochemical reversibility) is solely attributable to the difference in the charge of the weak nitrogen acids, since amines and sulfonamides are structurally and chemically disparate species (explored in greater detail below). Cyclic voltammograms obtained from all of the weak acids outlined in Table 1 are included in the Supporting Information (Figures S4 to S13).
Figure 2. Cyclic voltammograms showing the proton reduction process obtained from (a) 50.2 mM [Pyr–H][NTf₂] and (b) 33.0 mM [oPD–H₂][NTf₂]₂ in [C₂mim][NTf₂] at a 1.6 mm dia. Pt macrodisk electrode with scan rates of 50, 100 and 250 mV s⁻¹.
Figure 3. Cyclic voltammograms showing the proton reduction process obtained from (a) 58.3 mM SACC and (b) 37.6 mM DBSA in [C2mim][NTf2] at a 1.6 mm dia. Pt macrodisk electrode with scan rates of 50, 100, 250 and 500 mV s⁻¹.
Simulation of the proton reduction process from weak nitrogen acids in [C₂mim][NTf₂]. The overall proton reduction process from a weak acid is:

\[ 2\text{BH}^+ + 2e^- \rightleftharpoons \text{H}_2 + 2\text{B} \quad (14) \]

\[ 2\text{HA} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{A}^- \quad (15) \]

where B/BH⁺ correspond to a neutral base/conjugate cation acid and HA/A⁻ correspond to a neutral acid/conjugate anion base. The two reactions described above are stoichiometrically equivalent and although the following discussion refers to the BH⁺/H₂ couple, it is equally applicable to the HA/H₂ couple. In order to simulate the BH⁺/H₂ process, a CE mechanism was considered, whereby proton reduction via the mechanism described by Eqs. 11 and 12 is preceded by dissociation of BH⁺:

\[ \text{BH}^+ \rightleftharpoons \text{H}^+ + \text{B} \quad K_a k_{\text{dissoc}}, k_{\text{assoc}} \quad (16) \]

where \( k_{\text{dissoc}} \) is the dissociation rate constant and \( k_{\text{assoc}} \) is the association rate constant. In all simulations, \( k_{\text{assoc}} \) was set to be \( 5 \times 10^8 \, \text{M}^{-1} \text{s}^{-1} \) which is thought to the approximate the diffusion controlled limit for a bimolecular reaction in this viscous electrolyte. Additionally, in all simulations it was assumed that \( D_B = D_{\text{BH}^+} \) and the parameters for Eqs. 11 and 12 were taken from Table 2. Simulations were carried out for [dClPyr‒H][NTf₂] using the diffusivity and p\( K_a \) values outlined in Table 3; the results are shown in Figure 4. Evidently, BH⁺ reduction solely via the CE pathway cannot support a mass-transport controlled current, even at 50 mV \text{s}^{-1}. This is because \( k_{\text{dissoc}} = K_a k_{\text{assoc}} \) and \( k_{\text{assoc}} \) cannot exceed the diffusion controlled limit, which, in the present case means \( k_{\text{dissoc}} \approx 300 \, \text{s}^{-1} \), making the reaction shown in Eq. 16 limiting on the voltammetric timescale.

Clearly, a parallel reaction pathway must be available to support the diffusion controlled currents observed experimentally. One possibility is that BH⁺ undergoes direct
reduction (DR mechanism) at the electrode surface without prior dissociation, giving rise to surface adsorbed H* as previously discussed:

\[ BH^+ + e^- \rightleftharpoons H^+ + B \]  

\[ E^0'(BH^+/H^+) \], \( k_{s}^{app}(DR) \), \( \alpha_{DR} \)  

(17)

This reaction is conceptually analogous to the direct reduction of water at platinum in neutral or basic aqueous solution.\(^\text{17}\) Simulations were carried out by combining Eqs. 11, 12, 16 and 17; the result is also shown in Figure 4. There is excellent agreement between the simulations and experimental data when the DR pathway (Eq. 17) also is considered. Simulation-experiment comparisons for all of the investigated weak acids are included in the Supporting Information (Figures S3 to S13). The parameters derived by simulation of the experimental data are outlined in Table 3.

**Table 3.** Parameters extracted from the comparison of experimental cyclic voltammetric data for the proton reduction process from ten weak nitrogen acids in [C\(_2\text{mim}\)][NTf\(_2\)] and simulated data, based on the mechanism described by Eqs. 11, 12, 16 and 17.

<table>
<thead>
<tr>
<th>Nitrogen Acid</th>
<th>( E^0'(BH^+/H_2) ) or (HA/H(_2)) / V</th>
<th>( \alpha_{DR} )</th>
<th>( k_{s}^{app}(DR) / \text{cm s}^{-1} )</th>
<th>( pK_a )</th>
<th>( D(\text{acid}) / 10^{-7} \text{ cm}^2 \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MePyrd–H][NTf(_2)]</td>
<td>-1.18</td>
<td>0.53</td>
<td>0.0080</td>
<td>19.5</td>
<td>4.0</td>
</tr>
<tr>
<td>[MeIm–H][NTf(_2)]</td>
<td>-0.977</td>
<td>0.50</td>
<td>0.018</td>
<td>16.1</td>
<td>3.2</td>
</tr>
<tr>
<td>[Pyr–H][NTf(_2)]</td>
<td>-0.810</td>
<td>0.50</td>
<td>0.045</td>
<td>13.2</td>
<td>3.5</td>
</tr>
<tr>
<td>[oPD–H][NTf(_2)]</td>
<td>-0.695</td>
<td>0.50</td>
<td>0.057</td>
<td>11.3</td>
<td>1.7</td>
</tr>
<tr>
<td>[An–H][NTf(_2)]</td>
<td>-0.664</td>
<td>0.50</td>
<td>0.053</td>
<td>10.8</td>
<td>2.0</td>
</tr>
<tr>
<td>[ClPyr–H][NTf(_2)]</td>
<td>-0.474</td>
<td>0.50</td>
<td>0.058</td>
<td>7.6</td>
<td>3.2</td>
</tr>
<tr>
<td>[dClPyr–H][NTf(_2)]</td>
<td>-0.395</td>
<td>0.50</td>
<td>0.055</td>
<td>6.2</td>
<td>2.4</td>
</tr>
<tr>
<td>[oPD–H(_2)][NTf(_2)]</td>
<td>-0.337</td>
<td>0.50</td>
<td>0.015</td>
<td>5.3</td>
<td>1.2</td>
</tr>
<tr>
<td>SACC</td>
<td>-0.797</td>
<td>0.42</td>
<td>0.0025</td>
<td>13.0</td>
<td>2.0</td>
</tr>
<tr>
<td>DBSA</td>
<td>-0.587</td>
<td>0.32</td>
<td>0.0014</td>
<td>9.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
As shown in Figures S3 to S13, excellent fits between the experimental and simulated voltammograms are achieved over a wide range of scan rates when using the simulation parameters outlined in Table 3. Once again, the main discrepancy between the experimental and simulated data is in the hydrogen UPD region. Fourteen orders of magnitude in acid strength ($K_a$) have been covered in this study, ranging from $pK_a = 5.3$ for [oPD–H$_2$][NTf$_2$]$_2$ to $pK_a = 19.5$ for [MePyrd–H][NTf$_2$]. The diffusion coefficients used in the simulations were initially estimated by double step chronoamperometry (see Experimental Section). $D_{BH^+}$ follows the expected trend, decreasing with increasing substituents size ($D_{[Pyr-H]^+} > D_{[ClPyr-H]^+} > D_{[dClPyr-H]^+}$), substituent number ($D_{[An-H]^+} > D_{[oPD-H]^+}$) and charge ($D_{[oPD-H]^+} > D_{[oPD-H$_2$]^2+}$).

As shown in Table 3, the $k_{\text{app}}$ among the monocationic protonated amine acids is comparable for [dClPyr–H]$^+$, [ClPyr–H]$^+$, [An–H]$^+$ and [oPD–H]$^+$ ($6.2 \leq pK_a \leq 11.3$) and then decreases with increasing $pK_a$ for [Pyr–H]$^+$ ($pK_a = 13.2$), [MeIm–H]$^+$ ($pK_a = 16.1$) and [MePyrd–H]$^+$ ($pK_a = 19.5$). This trend is not likely to be the result of a double layer effect, which would predict that the apparent $k_s$ increases at increasingly negative potentials for cationic species (assuming all of the processes are negative of the point of zero charge). Since Eq. 17 is the rate determining step, one possible explanation for this trend is that activation energy (overpotential) required to break the N–H bond is related to the heterolytic bond dissociation energy, which is larger for the weaker acids (proportional to $pK_a$). Also evident from the data in Table 3, the proton reduction process from monocationic nitrogen acids is more kinetically facile (electrochemically reversible) than from dicationic or neutral nitrogen acids of comparable strength. Since [oPD–H]$^+$ and [oPD–H$_2$]$^{2+}$ are structurally identical, the trend in $k_{\text{app}}$ is most likely related to the charge of the respective acids. A similar comparison cannot be made between the monocationic protonated amine acids and neutral sulfonamide.
acids, because structural variations in the vicinity of the acidic proton on the parent acid may affect the kinetics of the Volmer-type reaction shown in Eq. 17.

Further simulations carried using the CE (see Eqs. 11, 12 and 16), DR (see Eqs. 12 and 17) or CE + DR pathways are included in the Supporting Information (Figures S14 to S18). Setting $k_{\text{assoc}}$ to be the diffusion controlled value ($5 \times 10^8$ M$^{-1}$ s$^{-1}$) and using a ‘typical’ set of simulation parameters for proton reduction in [C$_2$ mim][NTf$_2$] (outlined in Table S1), it was found that proton reduction through the CE pathway could only attain a diffusion controlled current when $pK_a < 4$. It was also found that proton reduction through the DR pathway becomes insignificant when $pK_a < 2$. Although these are generalizations, as they strictly only apply under the conditions investigated ($r_0 = 0.0825$ cm, $v = 500$ mV s$^{-1}$), they do provide valuable insight into how the preferred proton reduction pathway relates to the strength of the weak acid. In line with the simulations, we have shown in our companion study$^{34}$ that H[OTf] has a $pK_a$ of approximately 2 in [C$_2$ mim][NTf$_2$], allowing proton reduction to proceed via the CE pathway. These simulations are in qualitative agreement with the studies by Evans et al.$^{16,17}$ on the reduction of weak acids in dimethylsulfoxide ($k_{\text{assoc}} \approx 1 \times 10^{10}$ M$^{-1}$ s$^{-1}$), where the authors postulated that there is a transition from the CE pathway to the DR pathway when $pK_a > 6$. 
Figure 4. Comparison of simulated and experimental (solid line) cyclic voltammograms showing the proton reduction process obtained from 38.7 mM [dClPyr–H][NTf$_2$] in [C$_2$ mim][NTf$_2$] at a 1.6 mm dia. Pt macrodisk electrode with a scan rate of 100 mV s$^{-1}$. The simulations were carried out using the CE mechanism only (dashed line, see Eqs. 11, 12 and 16) or the CE + DR mechanism (dotted line, see Eqs. 11, 12, 16 and 17). Simulation parameters are available in Table 2 (CE) or Table 3 (CE + DR).
Calculating the pK\textsubscript{a} of weak nitrogen acids in [C\textsubscript{2}mim][NTf\textsubscript{2}]. The hydrogen evolution reaction is given in Eq. 6, where H\textsuperscript{+} is the strongest acid which can exist in a given medium (i.e., a ‘solvated proton’), which in the current context is equivalent to H[NTf\textsubscript{2}]. If it is assumed that activities are equal to molar concentrations, as justified by Doherty and co-workers\textsuperscript{7}, the Nernst Equation for the H\textsuperscript{+}/H\textsubscript{2} couple is as follows:

\[ E = E^0'(\text{H}^+/\text{H}_2) + \frac{RT}{2F} \ln \frac{[\text{H}^+]^2}{[\text{H}_2]} \] (18)

Here, the concentration rather than pressure-based standard state of H\textsubscript{2} has been used. Proton reduction from a weak acid can be described by the process given in Eq. 14. Once again, if it is assumed that activities are equal to molar concentrations, the Nernst Equation for the BH\textsuperscript{+}/H\textsubscript{2} couple is as follows:

\[ E = E^0'(\text{BH}^+/\text{H}_2) + \frac{RT}{2F} \ln \frac{[\text{BH}^+]^2}{[\text{B}][\text{H}_2]} \] (19)

If Eq. 18 is subtracted from Eq. 19, we get:

\[ E^0'(\text{BH}^+/\text{H}_2) - E^0'(\text{H}^+/\text{H}_2) = \frac{RT}{F} \ln \frac{[\text{B}][\text{H}^+]}{[\text{BH}^+]} = -\frac{2.303RT}{F} \text{pK}_a \] (20)

so the pK\textsubscript{a} of an acid can be estimated if \( E^0'(\text{H}^+/\text{H}_2) \) and \( E^0'(\text{BH}^+/\text{H}_2) \) are known. Although \( E^0'(\text{H}^+/\text{H}_2) \) was previously estimated to be \(-0.026 \text{ V}\) using numerical simulation (see Table 2), it can be more conveniently calculated directly from a transient cyclic voltammogram (see Figure 1a) as follows. Under conditions where mass transport is governed solely by semi-infinite planar diffusion and H\textsuperscript{+} is the only species initially present in solution, the following relationship between \( E^0'(\text{H}^+/\text{H}_2) \) and the reversible half wave potential, \( E_{1/2} \), can be derived from Eq. 18 using the diffusion layer method\textsuperscript{17, 25, 30, 44}:  

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\[ E_0'(H^+/H_2) = E_{1/2}(H^+/H_2) - \frac{RT}{2F} \ln \left( \frac{\sqrt{D_{H_2}}}{\sqrt{D_{H^+}}} \right) - \frac{RT}{2F} \ln [H^+]_b \]  

(21)

where the subscript ‘b’ signifies ‘bulk concentration’. \( E_{1/2} \) can be estimated from a transient cyclic voltammogram as follows:

\[ E_{1/2} \cong \frac{E_{p,ox} + E_{p,red}}{2} = E_{mid} \]  

(22)

where \( E_{p,ox} \) and \( E_{p,red} \) are the oxidation and reduction peak potentials respectively. \( D_{H^+} \) and \( D_{H_2} \) can be estimated experimentally using double step chronoamperometry, as outlined in the Experimental Section. \( D_{H_2}/D_{H^+} \) is approximately equal to 100 (in a range of ILs\(^{33}\)) and \([H^+]_b\) is typically 0.02 to 0.05 M, meaning both of the logarithmic terms in Eq. 21 are significant.

The \( E_0'(H^+/H_2) \) values estimated using Eq. 21 are ‒0.027 V and ‒0.345 V in \([\text{C}_2\text{mim}][\text{NTf}_2]\) and \([\text{C}_2\text{mim}][\text{OTf}]\), respectively and are in excellent agreement with the values previously determined with numerical simulation (see Table 2). Likewise, \( E_0'(BH^+/H_2) \) can be estimated using numerical simulation (see Table 3) or directly from a transient cyclic voltammogram using the following equation, derived from Eq. 19 using the diffusion layer method\(^{17,25}\):

\[ E_0'(BH^+/H_2) = E_{1/2}(BH^+/H_2) - \frac{RT}{2F} \ln \left( \frac{4\sqrt{D_{H_2}D_B}}{D_{BH^+}^3} \right) + \frac{RT}{2F} \ln [BH^+]_b \]  

(23)

Once again, the derivation of Eq. 23 assumes mass transport to the electrode surface is governed solely by semi-infinite planar diffusion and BH\(^+\) is the only species initially present in solution. Although \( D_{BH^+} \) and \( D_{H_2} \) can be estimated using double step chronoamperometry, \( D_B \) cannot be readily estimated by electrochemical methods. If it is assumed that \( D_B = D_{BH^+} \), Eq. 23 reduces to:
\[ E^{0'}(\text{BH}^+/\text{H}_2) = E_{1/2}(\text{BH}^+/\text{H}_2) - \frac{RT}{2F} \ln \left( \frac{4\sqrt{D_{\text{H}_2}}}{\sqrt{D_{\text{BH}^+}}} \right) + \frac{RT}{2F} \ln [\text{BH}^+]_b \]  

(24)

Again, \( E_{1/2}(\text{BH}^+/\text{H}_2) \) can be estimated from a transient cyclic voltammogram using Eq. 22. The \( pK_a \) values calculated for all of the nitrogen acids are summarized in Table 4. In addition, experimental and simulated cyclic voltammograms obtained from the full spectrum of nitrogen acids investigated in the work are shown in Figure 5.

**Table 4.** \( pK_a \) (IL) values calculated in this work and \( pK_a \) (aq) values obtained from the literature for a range weak nitrogen acids.

<table>
<thead>
<tr>
<th>Acid</th>
<th>( pK_a ) (SIM)</th>
<th>( pK_a ) (CV)</th>
<th>( pK_a ) (DCV)</th>
<th>( pK_a ) (aq)(^{18})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pyr–H](^+)</td>
<td>13.2</td>
<td>13.3</td>
<td>13.4</td>
<td>5.21</td>
</tr>
<tr>
<td>[ClPyr–H](^+)</td>
<td>7.6</td>
<td>7.6</td>
<td>7.6</td>
<td>0.72</td>
</tr>
<tr>
<td>[dClPyr–H](^+)</td>
<td>6.2</td>
<td>6.2</td>
<td>6.2</td>
<td>0.11(^\dagger)</td>
</tr>
<tr>
<td>[An–H](^+)</td>
<td>10.8</td>
<td>10.8</td>
<td>10.9</td>
<td>4.60</td>
</tr>
<tr>
<td>[Melm–H](^+)</td>
<td>16.1</td>
<td>16.1</td>
<td>16.2</td>
<td>6.95</td>
</tr>
<tr>
<td>[MePyrd–H](^+)</td>
<td>19.5</td>
<td>19.5</td>
<td>19.8</td>
<td>10.46</td>
</tr>
<tr>
<td>[oPD–H](^+)</td>
<td>11.3</td>
<td>11.3</td>
<td>11.4</td>
<td>4.74</td>
</tr>
<tr>
<td>[oPD–H(_2)](^2+)</td>
<td>5.3</td>
<td>5.4</td>
<td>5.4</td>
<td>0.6</td>
</tr>
<tr>
<td>SACC</td>
<td>13.0</td>
<td>13.3</td>
<td>13.0</td>
<td>1.31</td>
</tr>
<tr>
<td>DBSA</td>
<td>9.5</td>
<td>9.8</td>
<td>9.6</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^\dagger\)Reliable literature data not available, \( pK_a \) (aq) was estimated using MarvinSketch software

The \( pK_a \) values estimated using numerical simulation are generally in excellent agreement with those determined directly from the cyclic voltammogram (CV) using Eqs. 21, and 24. The largest deviation between the two methods is approximately 0.3 \( pK_a \) units for the neutral sulfonamide acid, DBSA. This is not surprising, since \( E_{\text{mid}} \) most closely approximates \( E_{1/2} \) (see Eq. 22) when heterogeneous kinetics are reversible and the charge transfer coefficient (\( \alpha \)) is equal to 0.5; neither of these conditions are met in the case of DBSA (see Table 3). Also
included in the table are pKₐ values calculated using Eqs. 21 and 24 after estimating E₁/₂ from the derivative peak potentials of a derivative cyclic voltammogram (example shown in Figure S19). Although processing the data in this way (see Experimental Section) is unnecessary in the present case, it has been included here as a point of comparison because in our companion study on the reduction of oxyacids in [C₂mim][NTf₂], estimating E₁/₂ directly from the CV is complicated by the effects of homoassociation.³⁴ In that study, we found that the differential response of the derivative cyclic voltammetry (DCV) technique resolved fine details that are not readily discernable on the normal cyclic voltammogram⁴⁵,⁴⁶, allowing E₁/₂ to estimated with greater accuracy. As expected, the pKₐ values calculated using DCV method are in excellent agreement with those determined directly with CV or with CV plus numerical simulation.

Where available, aqueous pKₐ values have also been included in Table 4. In all cases the nitrogen acids dissociate less readily in [C₂mim][NTf₂] than in water. This is not surprising, since [C₂mim][NTf₂] is a weak hydrogen bond donating/accepting solvent compared to water⁴⁷ and the [NTf₂]⁻ anion is very weakly basic due to extensive charge delocalization.⁴⁷,⁴⁸ In addition, aprotic ILs are only considered to be ‘moderately polar’ solvents, with reported static dielectric constants being in the 10 to 20 range⁴⁹, compared to 80.1 for water⁵⁰. Nonetheless, there is a good correlation between the pKₐ (aq) and pKₐ (IL) data (see Figure S20) for the monocationic protonated amine acids, with pKₐ increasing in the order [dClPyr−H]⁺ < [CIpyr−H]⁺ < [An−H]⁺ < [oPD−H]⁺ < [Pyr−H]⁺ < [Melm−H]⁺ < [MePyrd−H]⁺ in both solvents. [oPD−H₂]²⁺ is a stronger acid than [dClPyr−H]⁺ in IL media, whereas the opposite is predicted in aqueous media. This is almost certainly a charge effect, reflecting the relative stability (or instability) of dications (BH²⁺) and monocations (BH⁺) in [C₂mim][NTf₂] compared to H₂O. The neutral sulfonamide acid, SACC, is the outlier in the pKₐ (aq) vs. pKₐ (IL) trend, having a considerably higher pKₐ (IL) value than expected relative to the cationic protonated amine
acids. A similar observation was made with neutral oxyacids and has been explored in further detail in our companion study.\textsuperscript{34}

Finally, by combining Eqs. 20, 21 and 24, the following relationship can be derived:

\[
\frac{-2.303RT}{F} \cdot \text{p}K_a = E_{1/2}(\text{BH}^+/\text{H}_2) - E_{1/2}(\text{H}^+/\text{H}_2) + \frac{RT}{2F} \ln \left( \frac{D_{\text{BH}^+}}{D_{\text{H}^+}} \right) + \frac{RT}{2F} \ln \left( \frac{[\text{BH}^+]_b[H^+]_b}{4} \right)
\]

In order to apply this equation in practice, a solution containing H[NTf\textsubscript{2}] and pyridine in a 2:1 ratio was prepared and characterized voltammetrically, as is shown in Figure 6. There are two reduction processes observable with cyclic voltammetry (see Figure 6a); the more positive process corresponds to the H\textsuperscript{+}/H\textsubscript{2} couple and the more negative process corresponds to the [Pyr‒H]\textsuperscript{+}/H\textsubscript{2} couple. \(E_{1/2}(\text{H}^+/\text{H}_2)\) and \(E_{1/2}(\text{BH}^+/	ext{H}_2)\) can be readily estimated from the peak potentials labeled in Figure 6a using Eq. 22. \(D_{\text{BH}^+}\) and \(D_{\text{H}^+}\) can be readily estimated by performing a potential step past each of the peaks (indicated in Figure 6a); chronoamperograms are shown in Figure 6b. The potential step to \(-0.323\ \text{V}\) vs. Fc/Fc\textsuperscript{+} corresponds to the mass-transport controlled reduction of H\textsuperscript{+} to H\textsubscript{2} (see Eq. 6), and from this chronoamperogram, \(D_{\text{H}^+}\) was estimated to be \(3.0 \times 10^{-7}\ \text{cm}^2\ \text{s}^{-1}\). The potential step to \(-1.023\ \text{V}\) vs. Fc/Fc\textsuperscript{+} corresponds to mass-transport controlled proton reduction from both H[NTf\textsubscript{2}] and [Pyr‒H][NTf\textsubscript{2}]; \(D_{\text{BH}^+}\) was estimated to be \(3.6 \times 10^{-7}\ \text{cm}^2\ \text{s}^{-1}\) from the chronoamperogram obtained by subtracting the \(I-t\) transient at \(-0.323\ \text{V}\) vs. Fc/Fc\textsuperscript{+} from the one at \(-1.023\ \text{V}\) vs. Fc/Fc\textsuperscript{+}.

Substituting the appropriate values into Eq. 25, the p\(K_a\) of pyridine was calculated to be 13.4, which is in excellent agreement with the previously determined values (see Table 4). This method has a number of advantages over the previously outlined methods, namely: (a) numerical simulation is not required; (b) only a single solution containing a 2:1 mixture of HA\textsubscript{IL} and B is required and; (c) preparation of [BH][A\textsubscript{IL}] is not required, the solution can be
prepared simply by adding B directly to a HA\textsubscript{IL}/IL mixture. It should be noted that a similar set of experiments have been previously reported by Doherty and co-workers\textsuperscript{7}, where they calculated the pK\textsubscript{a} value of [Pyr−H]+ to be 10.5 in [C\textsubscript{4}mim][NTf\textsubscript{2}]. Changing the alkyl chain length on the imidazolium cation is expected to have a minimal impact on pK\textsubscript{a}\textsuperscript{9,10}, so the large discrepancy between our value, 13.4, and their value, 10.5, is predominantly attributable to the method in which pK\textsubscript{a} was calculated from the voltammogram. In their work, the authors assumed \( \Delta E_{1/2} \approx \Delta E^0 \), neglecting the two additional logarithmic terms shown in Eq. 25. Although the first logarithmic term is somewhat negligible because \( D_{H^+} \approx D_{BH^+} \) (see Table 3), the second term is significant when working at millimolar concentrations, equaling −0.1 V or +1.7 pK\textsubscript{a} units when \([H^+]_b = [BH^+]_b = 40\, \text{mM}\). Furthermore, the authors assumed that H[OTf] behaves as a strong acid (\textit{i.e.}, undergoes 100\% ionization) in [C\textsubscript{4}mim][NTf\textsubscript{2}]; we have shown in our companion study\textsuperscript{34} that this is not likely to be the case.
Figure 5. Simulated (○) and experimental (—) concentration-normalized cyclic voltammograms showing the proton reduction process obtained from (top to bottom) 49.8 mM H[NTf₂], 33.0 mM [oPD–H₂][NTf₂]₂, 38.7 mM [dClPyr–H][NTf₂], 62.4 mM [ClPyr–H][NTf₂], 37.6 mM DBSA, 30.4 mM [An–H][NTf₂], 28.2 mM [oPD–H][NTf₂], 58.3 mM SACC, 50.2 mM [Pyr–H][NTf₂], 49.3 mM [Melm–H][NTf₂] and 29.4 mM [MePyrd–H][NTf₂] in [C₂mim][NTf₂] at a 1.6 mm dia. Pt macrodisk electrode with a scan rate of 100 mV s⁻¹. The arrows indicate zero current for each of the voltammograms. Simulation parameters are available in Table 3.
Figure 6. (a) A cyclic voltammogram obtained from the reduction of 33.1 mM H[NTf₂] and 24.3 mM [Pyr‒H][NTf₂] in [C₂mim][NTf₂] at a 1.6 mm dia. Pt macrodisk electrode with a scan rate of 100 mV s⁻¹. (b) Experimental (—) and Shoup-Szabo theoretical chronoamperograms (○) obtained from the solution outlined in (a) at a 20 µm dia. Pt microdisk electrode by (i) stepping the potential to −0.323 V vs. Fe/Fe⁺, (ii) stepping the potential to −1.023 V vs. Fe/Fe⁺, and (iii) subtracting curve (i) from curve (ii).
Conclusions

The thermodynamics, kinetics and mechanisms for the proton reduction (hydrogen evolution) reaction at a platinum electrode have been investigated in ionic liquid media using a range of nitrogen acids (protonated amines or sulfonamides) as the proton source. The formal potential of the H⁺/H₂ process (where H⁺ signifies a ‘solvated proton’ released from a strong acid) was found to be strongly dependent on the identity of the IL anion, making direct comparison of pKₐ data between ILs with different constituent anions impossible. Proton reduction from weak nitrogen acids \( i.e., HA/H₂ \) or \( BH⁺/H₂ \) was found to be a diffusion controlled process which occurs in the potential region negative of the H⁺/H₂ process (proportional to pKₐ). Numerical simulations, performed by combining the classical Volmer and Tafel reactions, revealed that weak acid dissociation is limiting on the voltammetric timescale when pKₐ > 4, meaning proton reduction \textit{via} a CE mechanism cannot account for the experimentally observed mass-transport limited currents. A parallel direct reduction (DR) pathway was considered in addition to the CE pathway and using this mechanism, the proton reduction response from ten weak nitrogen acids covering 14 orders of magnitude in acid strength (5.2 < pKₐ < 19.5) was successfully simulated. All of the investigated nitrogen acids dissociated to a much lesser extent in \([C₂mim][NTf₂]\) compared to water, indicating that the H⁺ solvating ability of the former solvent is considerably weaker than the latter. Finally, after estimating \( E_{1/2}(HA/H₂) − E_{1/2}(H⁺/H₂) \) or \( E_{1/2}(BH⁺/H₂) − E_{1/2}(H⁺/H₂) \) from a transient cyclic voltammogram and \( D_{HA}/D_{H⁺} \) or \( D_{BH⁺}/D_{H⁺} \) from a microdisk electrode chronoamperogram, the pKₐ values for each of the ten weak nitrogen acids were calculated using a straightforward formula, demonstrating the utility of voltammetry as a convenient method for calculating equilibrium acidities.
Associated Content

Supporting information. Simulation-experiment comparisons for the electroreduction of solvated H$^+$ in [C$_2$ mim][NTf$_2$] and [C$_2$ mim][OTf] (Figures S1 to S3), simulation-experiment comparisons for the proton reduction process from a range of weak nitrogen acids in [C$_2$ mim][NTf$_2$] (Figures S4 to S13), simulations showing the contributions of the CE and DR pathways to proton reduction from weak acids with $1 \leq pK_a \leq 5$ (Figures S14 to S18), derivative cyclic voltammogram for the proton reduction process obtained from [Pyr‒H]$^+$ in [C$_2$ mim][NTf$_2$] (Figure S19) and a plot of p$K_a$ (aq) vs. p$K_a$ (IL) (Figure S20). This material is available free of charge via the Internet at http://pubs.acs.org.

Author Information

Corresponding Authors

*E-mail: jie.zhang@monash.edu (J.Z) and alan.bond@monash.edu (A.M.B)

Notes

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References


\[ pK_a \propto E^0(\text{H}_2^{+} / \text{H}_2) - E^0(\text{HA} / \text{H}_2) \]

\[ \text{H}_2 + 2\text{A}^- \rightarrow 2\text{HA} + 2\text{e}^- \]

\[ 2\text{HA} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{A}^- \]

\[ 2\text{H}_2^{\text{solvated}} + 2\text{e}^- \rightarrow \text{H}_2 \]