The Formal Potentials and Electrode Kinetics of the Proton/Hydrogen Couple in Various Room Temperature Ionic Liquids

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1. Reagents and Instruments

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C₂mim][NTf₂]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C₄mim][NTf₂]) were prepared by standard literature procedures. 1-Butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]), 1-butyl-3-methylimidazolium trifluoromethylsulphonate ([C₄mim][OTf]), N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₄mpyr][NTf₂]) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, ([C₄dmim][NTf₂]) were kindly donated by Merck KGaA. [C₄mim][BF₄], [C₄mpyr][NTf₂] and [C₄dmim][NTf₂] were used as received. [C₄mim][OTf] was first diluted with CH₂Cl₂ and passed through a column consisting of alternating layers of neutral aluminium oxide and silica gel in order to remove residual acidic impurities. In all cases, no obvious and unexpected voltammetric behaviour was observed over the range of potential window studied using any particular RTIL. Bistrifluoromethanesulfonimide (H[NTf₂], Fluka, >95%) and silver trifluoromethanesulfonate (Ag[OTf], Aldrich, 99.95%) was used as received and kept under an argon atmosphere during and after use. Hydrogen gas (99.995% pure) was purchased from BOC gases, Manchester, UK.

All the electrochemical experiments were carried out using in a T-cell, Ag /Ag⁺ redox couple as reference and Pt coil as counter electrode, and measured by a computer controlled µ-Autolab potentiostat (Eco-Chemie, Netherlands). The electrode was polished on soft lapping pads with alumina slurries of size 1, 0.3 and 0.05 μm respectively, and a disposable micropipette tip was around the neck of the working electrode, into which RTILs and solute were placed. Then vacuum the T-cell about 120 minutes efficiently removed most of impurities from RTILs before the measurements. This system has been demonstrated to remove electrochemical features associated with water contamination of ionic liquids such as accelerated diffusion and decreased electrochemical windows, indicating negligible water content when treated in this manner.¹
Hydrogen gas was introduced through one arm of the T-cell, and evacuated from another arm into a fume cupboard. Temperature was controlled at 25°C (298K) throughout in a thermostated box which was used as a Faraday cage.

Fabrication of the micro-Ag/Ag⁺ Reference Electrode

The fabrication was reported previously. Electrode consisted of a disposable micropipette tip, into which [C₂mim][NTf₂] containing 10 mM silver triflate was placed. A 3 Å molecular sieve (the length, 2mm) was used to seal the end of the tip. Into the disposable micropipette tip was immersed an Ag wire. The reference electrode was tested vs. solutions of Ferrocene in [C₂mim][NTf₂], and the $E_f^0$ of Fc was found to be -0.273 ± 0.003 V at 25 °C. The reference electrode was checked in between every experiment, and if the E₁/₂ of ferrocene shifted more than 5 mV then the reference electrode was disposed of and a fresh electrode prepared (typically every 1 – 3 weeks, if stored in the dark).
2. Theory

**Chronoamperometry experiments**

The potential step technique was used to require diffusion coefficient and concentration. The fit between experimental and the semi-empirical equation for the time dependent current response proposed by Shoup and Szabo\(^3\) was optimized, in order to calculate the diffusion coefficient and concentration of reactant with the known electrode radius. The potential was stepped from a potential, corresponding to zero faradaic current, to a chosen potential, corresponding to transfer behaviour control, and the corresponding current was measured for 2s using a step time of 0.002s. The current is given by

\[
I = -4nFDcr_d f(\tau)
\]

where

\[
f(\tau) = 0.7854 + 0.8863\tau^{-\frac{1}{2}} + 0.2146\exp(-0.7823\tau^{-\frac{1}{2}})
\]

\(n\) is the number of electrons transfer, \(F\) is Faraday constant, \(D\) is the diffusion coefficient, \(c\) is the initial concentration of parent species, \(r_d\) is the radius of the disk electrode, and the dimensionless time parameter, \(\tau\) is given by.

\[
\tau = \frac{4Dt}{r_d^2}
\]

**Simulation of voltammetry**

We consider the hydrogen evolution reaction as a one electron transfer heterogeneous reaction.

\[\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2\]

The mass transport of the different species in the RTILs was solved in the cylindrical coordinate system by the equation below.
\[ \frac{\partial c}{\partial t} = D_X \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right) \]

where \( c \) is the concentration of hydrogen (H\(_2\)) or proton. \( X=H^+ \) or H\(_2\).

In cyclic voltammetry, when \( t > 0, z = 0 \) and \( r \leq r_e \), the boundary condition are the Butler-Volmer equation describing species \( A=H^+ \) and conservation of mass for species \( B=H_2 \):

\[
D_A \frac{\partial A}{\partial z} = k_c^0 c_{A,0} \exp \left[ -\alpha \frac{F(E - E_{f}^0)}{RT} \right] - k_a^0 c_{B,0} \exp \left[ \beta \frac{F(E - E_{f}^0)}{RT} \right]
\]

\[
D_A \frac{\partial A}{\partial z} = k'_c c_{A,0} \exp \left[ -\alpha \frac{F}{RT} \right] - k'_a c_{B,0} \exp \left[ \beta \frac{F}{RT} \right]
\]

\[
D_A \left( \frac{\partial A}{\partial z} \right)_0 = -2 \ D_B \left( \frac{\partial B}{\partial z} \right)_0
\]

Note that in the above, first order kinetics have been assumed for \( A \) or \( B \); this corresponds to the best fit of the experimental data as discussed later in this paper. Other kinetic/mechanistic possibilities were considered, notably those giving a rate law which was second order in \( A \).

The remaining boundary conditions are:

\[
t = 0, \text{ all } r, \text{ all } z \quad c_A = c_A^* \quad c_B = 0
\]

\[
t > 0, r > r_e, z = 0 \quad \frac{\partial c_A}{\partial z} = 0 \quad \frac{\partial c_B}{\partial z} = 0
\]

\[
t > 0, \text{ all } r, z \rightarrow \infty \quad \frac{\partial c_A}{\partial z} = 0 \quad \frac{\partial c_B}{\partial z} = 0
\]

\[
t > 0, r \rightarrow \infty, \text{ all } z \quad \frac{\partial c_A}{\partial r} = 0 \quad \frac{\partial c_B}{\partial r} = 0
\]

\[
t > 0, r = 0, \text{ all } z \quad \frac{\partial c_A}{\partial r} = 0 \quad \frac{\partial c_B}{\partial r} = 0
\]

In the cyclic voltammetry experiment, the applied potential, \( E \), varies as a function of time, \( t \), according to:

\[ E = | -vt + E_{\text{start}} - E_{\text{vertex}} | + E_{\text{vertex}} \]
where $E_{\text{start}}$ and $E_{\text{vertex}}$ are the starting and vertex potentials respectively.

The current at the electrode surface is calculated by

$$i = 2\pi f \int j_A r dr$$

where $j_A$ is current density. The problem is discretised using the Alternating Direct Implicit method (ADI)$^4, 5$ and solved numerically using the iterative Newton-Raphson scheme.$^6$ The discretised spatial mesh is analogous to that reported by Gavaghan$^7$ and converged to within 0.5%. All programs were written in C++ and compiled using a Borland compiler. The simulations were run on a desktop PC with a processor speed of $\approx 3$ GHz. Approximately 5 min of CPU time were required to simulate a single voltammetry.

3. Simulated voltammograms

The details of scan rate study of simulated datas (o) and experimental datas (-) for H[NTf$_2$] reduction, hydrogen oxidation and hydrogen evolution reaction over a range of RTILs at a Pt electrode vs Ag/Ag$^+$ reference redox couple

a. Scan rate study of HNTf$_2$ reduction on a range of RTILs

(1) [C$_4$mim][NTf$_2$] RTIL

(2) [C$_4$mpyr$_r$][NTf$_2$] RTIL
(3) [C$_4$dmim][NTf$_2$] RTIL

(4) [C$_4$mim][OTf] RTIL
Comment: The small deviation between theory and experiment likely arises from non-Faradaic effects.
b. Scan rate study of hydrogen oxidation on a range of RTILs

(1) [C$_{4}$mim][NTf$_2$] RTIL

\[ k' = 8 \times 10^{-3} \text{ cm s}^{-1} \]
\[ v = 100 \text{ mV s}^{-1} \]
\[ D_v = 2 \times 10^{-11} \text{ m}^2 \text{s}^{-1} \]
\[ D_C = 8.5 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \]
\[ C_C = 3 \text{ mM} \]
\[ C_i = 3 \text{ mM} \]
\[ \beta = 6.25 \times 10^{-6} \]
\[ \beta = 0.45 \]

(2) [C$_{4}$mpyr][NTf$_2$] RTIL

\[ k' = 6.5 \times 10^{-3} \text{ cm s}^{-1} \]
\[ v = 100 \text{ mV s}^{-1} \]
\[ D_v = 9.6 \times 10^{-12} \text{ m}^2 \text{s}^{-1} \]
\[ D_C = 3.8 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \]
\[ C_C = 5 \text{ mM} \]
\[ C_i = 5.25 \times 10^{-6} \]
\[ \beta = 0.55 \]
(3) $[\text{C}_4\text{mim}][\text{NTf}_2]$ RTIL

(4) $[\text{C}_4\text{mim}][\text{OTf}]$ RTIL
Comment: The small deviation between theory and experiment likely arises from non-Faradaic effects.
c. Hydrogen evolution reaction at a Pt electrode in RTILs, containing fixed concentration of HNTf₂ and various concentration of hydrogen, vs Ag / Ag⁺ redox couple under 25 °C (Experiment data (-) and optimization of theoretical curve (o)). A= HNTf₂, B= H₂

![Graph](image-url)

- [C₄mim][NTf₂]
  - CA=86mM, CB=3mM
  - CA=86mM, CB=2.25mM
  - CA=86mM, CB=0.95mM

- [C₄mpyr][NTf₂]
  - CA=110mM, CB=5.9mM
  - CA=110mM, CB=4.3mM
  - CA=110mM, CB=2.1mM