

Electrochemical Behaviour of Dissolved Proton Species in Room Temperature Ionic Liquids

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Understanding the nature of dissolved species in ionic liquids is important, particularly when using them as reaction media to replace volatile organic solvents. Electrochemical techniques such as cyclic voltammetry and potential-step chronoamperometry are very powerful tools used to study electrochemical reactions, elucidate mechanisms and quantify diffusion parameters. These techniques have been used in various studies on the behaviour of dissolved species in ionic liquids. Particularly, the behaviour of hydrogen or 'protic' species in ionic liquids can give some insight into the hydrogen bonding characteristics of the ionic liquids (individual cation/anion combination) and eventually the pH properties of the solvents. We have looked^{1,2} at the direct oxidation of hydrogen gas in ten ionic liquids with various cation/anion combinations. The mechanism involves the two-electron oxidation of hydrogen to the electrogenerated proton, which is thought to then combine with the anion (A^-) of the ionic liquid. The appearance and position of the reverse (reduction) peak on the voltammogram is thought to depend on three factors: (1) the stability of the solvated proton, HA, (2) the position of equilibrium of the protonation reaction $HA = H^+ + A^-$, and (3) any follow-up chemistry e.g. dissociation or reaction of the solvated proton, HA. This is discussed for all ten ionic liquids studied. Solubilities of hydrogen gas are found to be in the range ca. 3-10 mM and diffusion coefficients are calculated to be of the order $10^{-10} \text{ m}^2 \text{ s}^{-1}$, with no evidence that the Stokes-Einstein law applies for the diffusion of hydrogen gas in ionic liquids.

1). Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G. *J. Phys. Chem. B* 2007, **111**, 5000-5007

2). Silvester, D. S.; Ward, K.; Aldous, L.; Hardacre, C.; Compton, R. G. *J. Electroanal. Chem.* 2008, **618**, 53-60

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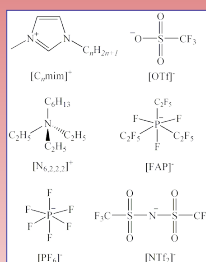
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Introduction

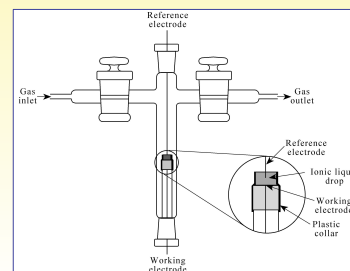
Room Temperature Ionic Liquids (RTILs) are liquids composed entirely of ions, with some common cations and anions shown on the right. In addition to other physical properties such as low volatility and high thermal stability, ionic liquids possess several favourable electrochemical properties, making them useful as solvents in electrochemical experiments.^{1,2} Their intrinsic conductivity means there is no need for supporting electrolyte, and their wide electrochemical windows allow the observation of voltammetric peaks which would otherwise have been curtailed by decomposition of the supporting electrolyte.⁴ They are typically 1-2 orders of magnitude more viscous than traditional solvents, and the diffusion coefficient of an electroactive species is accordingly lowered. Their low volatility and high thermal stability means they may find use as electrolytes in gas sensors,⁵ since here, in contrast to water based sensors, the RTIL electrolyte will not dry-out. It is of general interest to explore the oxidation of hydrogen (H₂) gas due to its major importance in fuel cells among other applications. The electrochemical oxidation of hydrogen has been extensively studied on Pt and Pd surfaces in protic solvents, but relatively little work has been done in aprotic solvents and RTILs. Concerning ionic liquids, conventional acid-base indicators have been used to physically probe the inherent acidity and basicity of RTILs; however, such probes are not calibrated towards ionic liquids and all observed colour changes can be the result of hydrogen-bonding interactions in addition to acid-base equilibria. In addition, the nature of the solvation of strong acids in ionic liquids (e.g. H₂S₆O₆²⁺) has still to be conclusively demonstrated, and little is understood about the nature and relative strength of acidity within these ionic systems, despite numerous previous applications of inherently Brønsted acidic ionic liquids. The work presented here may go towards understanding proton behaviour in RTILs and also may help to suggest if ionic liquids may be suitable solvent media for use in amperometric hydrogen gas sensors.

(1) M. C. Buzzeeo, R. G. Evans, R. G. Compton *ChemPhysChem* **2004**, *5*, 1106 (2) D. S. Silvester, R. G. Compton *Z. Phys. Chem.* **2006**, *220*, 1247 (3) J. H. Davis *J. Chem. Lett.* **2004**, *33*, 1072 (4) F. Endres *ChemPhysChem* **2002**, *3*, 144 (5) M. C. Buzzeeo, et al. *Anal. Chem.* **2004**, *76*, 4583



Experimental

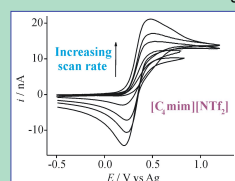
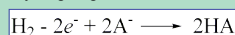
A conventional two-electrode arrangement is employed, with a 10µm diameter Pt (or Au) working electrode and Ag wire quasi-reference electrode. The electrodes are housed in a glass cell designed for investigating microsamples of ionic liquids under vacuum or with a controlled atmosphere. The microdisk is modified by addition of a section of a disposable micropipette tip to create a small cavity above the disk into which a drop (~20 µL) of ionic liquid is placed. The cell is then subjected to vacuum, which serves to remove impurities and trace atmospheric moisture present in the IL.



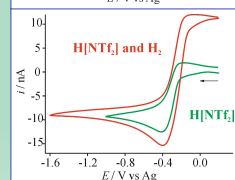
Gas inlet and outlet tubes are attached to the cell to allow the gas (H₂) to flow into the RTIL and be detected voltammetrically.

Results

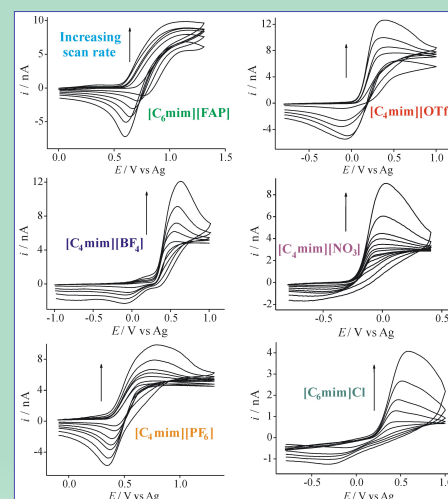
The electrochemical oxidation of hydrogen, H₂, has been studied in a series of room temperature ionic liquids (RTILs) on a platinum microdisk electrode (d=10µm) and a gold microdisk electrode (d=5µm). H₂ gas was allowed to diffuse through 20µL of the liquid for 30 mins to allow complete saturation. There were no noticeable oxidation peaks on the gold electrode, so we conclude that H₂ oxidation is voltammetrically inactive on gold. Sizeable, reproducible peaks, however, were seen on the Pt electrode. All of the results presented below focus on the voltammetry obtained on the 10µm diameter Pt electrode in a range of RTILs. The oxidation of hydrogen gas in RTILs is believed to follow the mechanism:



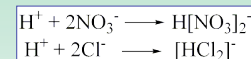
where A⁻ is the RTIL anion. The figure to the left (top) shows the oxidation of H₂ in [C₂mim][NTf₂] at scan rates of 100mVs⁻¹ to 4 Vs⁻¹. Activation of the Pt surface is required to obtain stable and reproducible voltammetry. There is also a reverse peak present, which corresponds to the reduction of the proton solvated by the anion of the ionic liquid i.e. H[NTf₂] (or H[NTf₂]_x⁺). In order to confirm this, the reduction of 130mM H[NTf₂] was studied in [C₂mim][NTf₂] in the absence and presence of H₂ gas (figure left bottom). The reduction peak for H[NTf₂] and corresponding oxidation peak occurs at the same potential as the H₂/HA redox couple, supporting the mechanism proposed above.



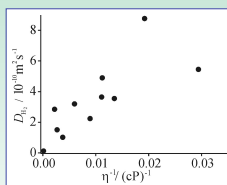
In order to study the effect of changing the nature of the anion, the oxidation of hydrogen was studied in RTILs with different anions (figure to the right). In [C₆mim][FAP], [C₄mim][OTf] and [C₄mim][PF₆], quasi-reversible voltammetry is observed, which indicates that the protons formed from the oxidation of H₂ combine with the anions of these RTILs, and the product, HA, is stable-enough to be detected voltammetrically. For [C₄mim][BF₄], [C₄mim][NO₃] and [C₆mim]Cl, the voltammetric behaviour is clearly different from the [NTf₂]⁻ based RTILs, as the reduction peak following the oxidation is much reduced in [C₄mim][BF₄], and is barely seen in [C₄mim][NO₃] and [C₆mim]Cl. Little work has been



reported concerning degradation of the [BF₄]⁻ anion, despite various papers reporting this for [PF₆]⁻. It is predicted that for [C₄mim][BF₄], the product H[BF₄] will dissociate to form BF₃ and toxic HF. The voltammograms shown in the figure seem to agree well with these findings, and this should be taken into account when handling [BF₄]⁻ based ionic liquids (particularly in the presence of proton sources) and applying them to green synthesis and indeed any application. For the chloride and nitrate ionic liquid, the absence of a back peak suggests that H[NO₃]₂⁺ and [HCl₂]⁺ are likely formed in a chemical step following the reaction, shown by the following equations:



| Ionic Liquid | η at 293 K /cP | D _{H2} /×10 ⁻¹⁰ m ² s ⁻¹ | c /mM | Dc /×10 ⁻¹³ m ² s ⁻¹ |
|---|----------------|--|-------|---|
| [C ₂ mim][NTf ₂] | 34 | 5.5 | 4.2 | 23.1 |
| [C ₄ mim][NTf ₂] | 52 | 8.8 | 3.3 | 29.0 |
| [C ₆ mim][FAP] | 74 | 3.6 | 6.6 | 23.8 |
| [C ₂ mim][OTf] | 90 | 3.6 | 4.3 | 15.5 |
| [C ₂ mim][BF ₄] | 112 | 2.2 | 5.2 | 11.4 |
| [N _{6,2,2}][NTf ₂] | 167 | 3.2 | 7.2 | 23.0 |
| [C ₄ mim][NO ₃] | 266 | 1.0 | 4.8 | 4.80 |
| [C ₄ mim][PF ₆] | 371 | 1.5 | 5.1 | 7.65 |
| [P _{14,6,6,6}][NTf ₂] | 450 | 2.9 | 7.9 | 22.9 |
| [C ₆ mim]Cl | 7453 | 0.13 | 9.7 | 1.26 |



$$D = \frac{k_B T}{6\pi\eta a}$$

Diffusion coefficients and solubilities were also calculated (see table). The diffusion coefficients are of the order 1×10⁻¹⁰ m²s⁻¹ (comparable to oxygen in RTILs) and the solubilities are ca. 3-10 mM. The ionic liquid with the highest Dc will give the highest current response (since steady-state current at a microdisk is proportional to Dc) and will therefore be the most suitable medium for sensing via the Clark-cell approach. All four [NTf₂]⁻ ionic liquids and [C₆mim][FAP] have Dc values greater than 20, suggesting that they are the most suitable media for hydrogen sensing, with [C₂mim][NTf₂] being the most sensitive. A plot of D vs. the inverse of viscosity should give a linear line through the origin according to the Stokes-Einstein equation (left). The plot for H₂ is shown to the left, and suggests that the Stokes-Einstein law does not apply strongly for hydrogen in ionic liquids.

Conclusions

The electrochemical oxidation of hydrogen gas has been studied in ten RTILs with a range of cations and anions. An oxidation peak is observed, corresponding to the two electron oxidation of molecular hydrogen to protons. The electrogenerated proton is believed to interact strongly with the anion of the RTIL. The appearance and position of the reverse (reduction) peak on the voltammogram is thought to depend on three factors: (1) the stability of the solvated proton, HA, (2) the position of equilibrium of the protonation reaction HA = H⁺ + A⁻, and (3) any follow-up chemistry e.g. dissociation or reaction of the solvated proton, HA. Solubilities of hydrogen gas are found to be in the range ca. 3-10 mM and diffusion coefficients are calculated to be of the order 10⁻¹⁰ m² s⁻¹, with no evidence that the Stokes-Einstein law applies for the diffusion of hydrogen gas in ionic liquids.

Acknowledgements

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[†]This poster has been adapted from two research articles: D. S. Silvester et al. *J. Phys. Chem. B* **2007**, *111*, 5000; and *J. Electroanal. Chem.* **2008**, *619*, 53