Electrochemical Reduction of *N*-Methylphthalimide in the 1-Butyl-3-methylimidazolium Hexafluorophosphate Room-Temperature Ionic Liquid

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We report the results of the reduction of *N*-methylphthalimide in the air- and moisture-stable room temperature ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate [bmim][PF$_6$].[1] The electroreduction of phthalimide and its *N*-alkyl derivatives has been the focus of much investigation.[2-7] We demonstrate how the electrolyte employed and the source of protons are important factors in determining the mechanism of the reduction of *N*-methylphthalimide. We also discuss the relevance of these experiments to the broader topic of proton-donator strength in ionic liquids.

Two typical cyclic voltammograms for the reduction and oxidation of *N*-methylphthalimide in a 0.205 mol L^{-1} solution of the imide in [bmim][PF$_6$] at a glassy carbon disk electrode are shown in Figure 1. These scans were initiated from -1.0 V *vs.* Ag(I)/Ag toward more cathodic potentials. Potentials less than -2.4 V *vs.* Ag(I)/Ag were avoided to prevent reduction of the ionic liquid. When the scan is reversed at potentials greater than about -2.0 V *vs.* Ag(I)/Ag, the voltammogram exhibits a single reduction wave on the forward scan with a peak cathodic potential E_p^c = -1.79 V *vs.* Ag(I)/Ag and a single oxidation wave on the reverse scan with a peak anodic potential E_p^a = -1.71 V *vs.* Ag(I)/Ag. As the switching potential is made more cathodic, a second reduction wave with E_p^c = -2.10 V *vs.* Ag(I)/Ag becomes evident. There is no oxidation wave associated with this second reduction wave.

The addition of phenol markedly alters the redox behaviour of the imide, as demonstrated in Figure 2. Voltammogram A was recorded in a 0.6 mol L^{-1} solution of phenol in [bmim][PF$_6$]. This voltammogram shows that phenol is electrochemically inactive at potentials greater than -2.15 V *vs.* Ag(I)/Ag. Voltammogram B was recorded in a 0.063 mol L^{-1} solution of *N*-methylphthalimide in [bmim][PF$_6$], and is similar to those voltammograms in Figure 1 described above. The reduction wave for the loss of the first electron has E_p^c = -1.79 V *vs.* Ag(I)/Ag and I_p^c = 0.84 mA cm^{-2}. Voltammogram C was recorded in the same solution of *N*-methylphthalimide after the addition of approximately 10 molar equivalents of phenol. In marked contrast to the reduction of the imide by itself, there is a single reduction wave with E_p^c = -1.64 V *vs.* Ag(I)/Ag and I_p^c = 1.62 mA cm^{-2}; this peak current density is about twice that of process in Voltammogram B. The difference in the peak cathodic potentials of the first one-electron reduction in Voltammogram B and the two-electron reduction in Voltammogram C is 0.15 V. There is no oxidation wave on the return sweep, indicating that the product undergoes a chemical reaction following electrochemical reduction.

The comparison of the electrochemical reduction of *N*-methylphthalimide in conventional protic and aprotic solvents and [bmim][PF$_6$] is revealing. In aprotic solvents, both in the presence and absence of phenol, the reduction of *N*-methylphthalimide is characterised by two distinct single-electron electrochemical reduction steps followed by a chemical step. The electrochemical reduction of *N*-methylphthalimide in [bmim][PF$_6$] in the absence of phenol clearly follows the same mechanism. In acidic media, protonation of the imide occurs prior any electrochemical step: reduction occurs by a single two-electron step followed by the protonation of the anionic product. As the electrochemical reduction of *N*-methylphthalimide in the presence of phenol in [bmim][PF$_6$] has the same voltammetric characteristics as under low pH conditions this suggests it follows the same mechanism and that *N*-methylphthalimide is protonated prior to electrochemical reduction. Thus, it appears that the ability of phenol to protonate *N*-methylphthalimide has been enhanced by the ionic liquid medium.

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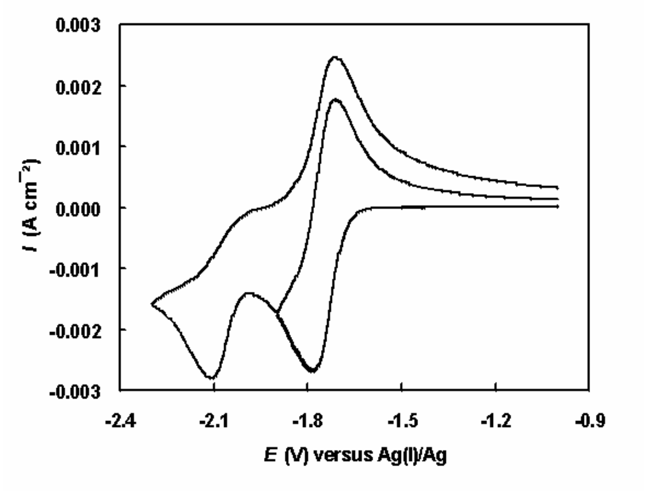

Figure 1. Cyclic voltammograms recorded at a glassy carbon disk electrode in a 0.205 mol L^{-1} solution of *N*-methylpthalimide in [bmim][PF$_6$] at 25 °C. The scans were initiated from -1.0 V toward more cathodic potentials at 0.040 V s^{-1}.

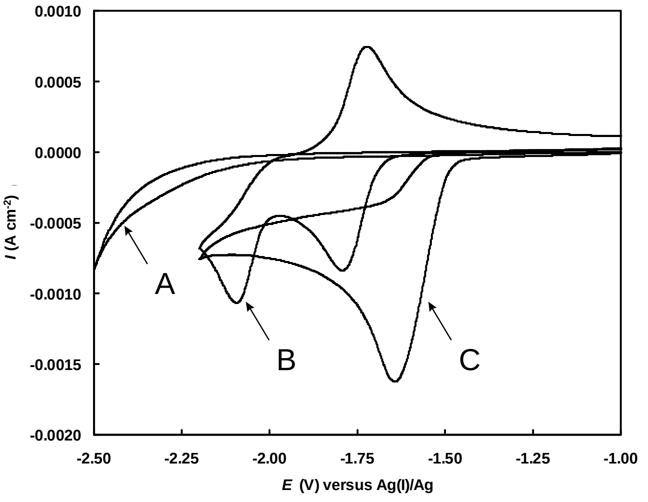

Figure 2. Cyclic voltammograms recorded at a glassy carbon disk electrode in solutions of [bmim][PF$_6$] at 25 °C containing: (A) 1.0 mol L^{-1} phenol; (B) 0.10 mol L^{-1} *N*-methylpthalimide; (C) 1.0 mol L^{-1} phenol and 0.10 mol L^{-1} *N*-methylpthalimide. The scans were initiated from -1.0 V at 0.040 V s^{-1}.