ABSTRACT

The electrochemical properties of 1-butyl-3-methylimidazolium hexafluorophosphate solutions of lithium, sodium and potassium hexafluorophosphate and of ferrocene were investigated. Formal reduction potentials of \(-2.96 \pm 0.01\) V and \(-3.35 \pm 0.01\) V vs. the ferrocene/ferrocenium couple were obtained for sodium and potassium using normal pulse voltammetry. The presence of adsorption maxima in the lithium normal pulse voltammograms necessitated the use of chronopotentiometry to determine a lithium formal potential of \(-2.45 \pm 0.02\) V. An apparent anomaly in the rotating disk voltammograms for ferrocene oxidation in this ionic liquid was found to be due to the high value of the Schmidt number, \(3.5 \times 10^7\). Analysis of the current transient resulting from application of a voltage step to the rotating disk can be used to determine the associated Schmidt number without prior knowledge of the viscosity and density of the solvent, or diffusion coefficient of the reacting species.

INTRODUCTION

Ionic liquids have recently become of considerable interest as solvents for a variety of potential chemical processes (1). We have been investigating the electrochemical properties of alkali metals in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF\(_6\)) for possible battery applications. In addition to a wide potential window (ca. 4.5 V) and good chemical stability, bmimPF\(_6\) is also hydrophobic (2), which should impart additional long-term stability to a battery system.

While it is possible to deposit lithium and sodium metal at a platinum electrode from bmimPF\(_6\) solutions of the ions, determination of the formal potential is complicated by the onset of solvent reduction. Utilizing a hanging mercury drop electrode (HMDE) as the working electrode circumvents this problem, since the favorable free energy of formation of the alkali metal amalgams (\(\Delta G_f\) (kJ/mol) = Li: \(-82\), Na: \(-73\), K: \(-92\)) (3) shifts the reduction potential of the alkali metal ions to more positive values. An additional advantage to using an HMDE is that the electrochemical properties of potassium can also be examined even though the reduction of K\(^+\) normally occurs past the cathodic limit for bmimPF\(_6\) (See Figure 1). The formal potentials and diffusion coefficients of lithium, sodium and potassium were obtained from bmimPF\(_6\) solutions of...
the hexafluorophosphate salts of these metals using an HMDE and two silver wires as pseudo-reference and counter electrodes.

Another area of interest related to the development of high-energy density batteries is the in situ formation of conductive polymers. While it is possible to use chemical oxidants to prepare conductive polymers, electrochemical polymerization would seemingly promote the formation of a more intimate contact between the electrode material and polymer. In our initial efforts into this area using a Pt/Pt rotating disk and ring-disk electrode, RDE and RRDE, in bmimPF₆, we obtained disk voltammograms for the oxidation of ferrocene as shown in Figure 2A. These voltammograms were taken at 200, 400, and 800 rpm and scan rates, employing a staircase waveform, of 10 mV/s - a 20 mV step and a 2 s delay in current measurement following application of the step. Initiating the scan on the plateau of the disk voltammogram resulted in the curves shown in Figure 2B. While we have previously utilized rotating disk electrodes in studies with haloaluminate ionic liquids (4, 5, 6), there does not appear to have been any RDE studies using the non-haloaluminate ionic liquids. Since there is at least an order of magnitude difference between the viscosity of the haloaluminate melts that we have previously studied and that of bmimPF₆, we show below that the unexpected voltammetric behavior noted above results from the large viscosity of the bmimPF₆.

EXPERIMENTAL

The 1-butyl-3-methylimidazolium chloride (bmimCl) was prepared as previously reported (7) and recrystallized from acetonitrile/ethyl acetate. The bmimPF₆ was prepared by stirring an aqueous solution of bmimCl with a 10% molar excess of HPF₆ (60% aqueous solution, Aldrich) for the alkali metal studies, and KPF₆ for the RRDE studies. After washing the light yellow, water immiscible phase with five portions of water, the remaining impurities were removed by stirring a 50% by volume bmimPF₆/acetonitrile solution overnight with decolorizing carbon and Brockmann activity I neutral alumina (Aldrich). Following removal of the carbon and alumina by filtration, the clear solution was then placed under vacuum and held at 110°C for four hours to remove all remaining acetonitrile and residual water. Lithium (99.99%), sodium (98%) and potassium (98%) hexafluorophosphate (Aldrich) were used as received. Ferrocene (Kodak) was sublimed before use.

All electrochemical experiments were performed in a dinitrogen filled Vacuum Atmospheres dry box equipped with an MO40-2 Dri-Train. Normal pulse (NP) voltammetry, chronoamperometry, and chronopotentiometry (CP) were performed using an EG&G (model 283) PAR potentiostat and in-house computer control programs. Formal potentials and diffusion coefficients were determined using a Kemula (8) hanging mercury drop working electrode (area = 0.0177 cm²). A Pine Instrument Co. Pt/Pt ring-disk electrode (disk diameter: 4.57 mm; ring inner diameter: 4.93 mm; ring outer diameter: 5.38 mm; collection efficiency: 22%) and MSR speed controller were used for the RRDE studies. Bipotentiostatic control was provided by an EG&G (model 400) LC detector. A silver wire pseudo-reference electrode, and a silver wire counter electrode were used for all experiments. The ferrocene/ferrocenium couple (Fc/Fc⁺) was used as an internal reference standard for all potential measurements.
RESULTS AND DISCUSSION

Formal Potentials of Alkali Metals in bmimPF$_6$

The chronoamperometric data from five solutions with concentrations ranging from 10 mM to 50 mM of the hexafluorophosphate salt of each alkali metal were used to determine the diffusion coefficients of the corresponding alkali metal in bmimPF$_6$ (see Table 1). Each solution was run in triplicate, and the average current from these runs was plotted vs. $t^{1/2}$ in order to determine the linear portion of each curve. Since linear behavior was observed from around 2 s to 10 s, the Cottrell equation (9) could be used to extract the diffusion coefficient of the alkali metal cation in the melt, $D_{melt}$, from the slope of the line. At times greater than 10 s, a deviation from linearity was observed that was presumably due to convection.

Normal pulse voltammetry was used to determine the half-wave potentials of the bmimPF$_6$ solutions of the alkali metal couples. Non-linear regression analysis of the sodium and potassium NP voltammograms was used to determine half-wave potentials of $-2.02 \pm 0.01$ V and $-2.24 \pm 0.01$ V vs. Fe/Fc$^+$ for sodium and potassium, respectively. Unfortunately, it was not possible to perform a similar analysis on LiPF$_6$/bmimPF$_6$ solutions due to the presence of adsorption maxima (10) in the NP voltammograms (see Figure 3). Since chronopotentiometry (CP) is relatively insensitive to adsorption induced potential shifts, this technique was used to determine the Li/Li$^+$ redox potential.

In CP, the potential required to maintain a constant current at the working electrode is recorded. Upon initiating the experiment, the potential at the working electrode for a reversible system rapidly changes from its rest potential to a value consistent with the Nernst equation. The transition time, $\tau$, is the time at which the concentration of the electroactive species at the electrode surface has been depleted. If the diffusion coefficients of the reduced and oxidized species are identical, then the half-wave potential is the electrode potential at $\tau/4$, $E_{\nu/4}$. The half-wave potential of lithium in the melt listed in Table 1 is the average value obtained by CP at an HMDE from four different solutions with concentrations ranging from 47 to 58 mM.

Using the treatment of Scordilis-Kelley et al. (11), it is possible to calculate the formal potential of the alkali metals dissolved in bmimPF$_6$ using Eq. 1 where $a_M$(aq) is the activity coefficient of the metal ion (calculated using the Debye-Hückel equation for the electrolyte solutions used to measure the corresponding $E_{1/2}$(aq) values (12)), and $D_{melt}$ and $D_{aq}$ are the diffusion coefficients of the alkali metal ion in the melt and aqueous solution, respectively.

$$E^{\infty}(\text{melt}) = E_{1/2}(\text{melt}) + E^\circ(aq) - E_{1/2}(aq) + \frac{RT}{nF} \ln \left[ a_M(aq) \left( \frac{D_{melt}}{D_{aq}} \right)^{1/2} \right]$$ [1]

Three different pulse widths were used to determine the reduction potential of sodium and potassium, and the appropriate values (12, 13) were substituted into Eq. 1 to produce the formal potentials shown in the last column of Table 1. Of the three alkali
metals examined in this study, only lithium has a sufficiently positive formal potential to avoid reduction of the solvent, which occurs at approximately -2.5 V vs. Fe/Fe⁺.

### Table I. Formal reduction potentials for alkali metals in bmimPF₆

| M  | tₚ (ms) | E₁/₂ (melt) (V)ᵃ | Dₘelt x 10⁸ (cm²/s) | E₁/₂ (aq) (V)ᵇ,c | E₀ (aq) (V)ᵇ,c | E₀⁺ (melt) (V)ᵃ |
|----|--------|-----------------|--------------------|------------------|----------------|----------------|
| Li | ------ | -1.348 (0.025)  | 1.9 (0.5)          | 1.04             | -2.024         | -3.040         |
| Na | 400    | -2.012          | 1.4 (0.1)          | 1.35             | -1.864         | -2.713         | -2.953 |
|    | 800    | -2.017          |                    |                  |                |                | -2.958 |
|    | 1600   | -2.024          |                    |                  |                |                | -2.965 |
| K  | 400    | -2.229          | 4.5 (0.2)          | 1.98             | -1.884         | -2.924         | -3.351 |
|    | 800    | -2.235          |                    |                  |                |                | -3.356 |
|    | 1600   | -2.235          |                    |                  |                |                | -3.356 |

a) vs. Fe/Fe⁺ b) vs. NHE c) Ref. 12 d) Ref. 13

### Rotating Ring-Disk Voltammetry

Bruckenstein and Prager developed an equation to estimate the time for the transient current following application of a potential step to an RDE to achieve a steady-state value (14). The pertinent equation is:

\[
\tau = \frac{\omega r (D/\eta)^{1/3} (0.51)^{2/3}}{1.3} \geq 1.3
\]

where \(\omega_r\) is the rotation rate in radians/s, \(\tau\) is the time in seconds to attain a value to within one percent of the disk steady-state value after application of a potential step, \(D\) is the diffusion coefficient in cm²/s, \(\eta\) is the kinematic viscosity, which is the solvent viscosity, \(\rho\), divided by the density, \(\rho\). At ambient temperature, 22°C, the viscosity of the bmimPF₆ is 3.26 poise, and the density is 1.37 g/cc (15). The value of \(D\) for ferrocene obtained from Levich plots at the RDE was 7.3 x 10⁻⁸ cm²/s. This gives a Schmidt number, \(S_c\), the kinematic viscosity of the solvent divided by the diffusion coefficient of the reactant, of ~3.3 x 10⁷ compared to values of ~1,000 in aqueous solutions (9). Insertion of these values into Equation 2 gives rise to a value of \(\tau\) of ~10⁶/\(f\) s, where \(f\) is the rotation rate in revolutions/s. The value of 10⁶ corresponds to the number of revolutions required to come to within 1% of the steady-state value regardless of rotation rate. At 200 rpm, this requires 32 s, while it takes 8 s at 800 rpm. In contrast, it only requires ~3 rotations to attain steady-state conditions in water, or ~ 0.22 s at 800 rpm. In Figure 2, what is termed the delay time, 2 s, is the time after application of the 20 mV potential step in the staircase to the electrode at which the current is measured. In the
forward scan, the reacting ferrocene concentration does not go to zero at the electrode surface until well past the peak. In the reverse scan, not all of the ferrocenium is swept away from the disk surface and the current at the disk becomes cathodic, much as it would in the reverse scan of a cyclic voltammogram. Note that the ring, set at zero volts, still experiences ferrocenium reduction even as the disk passes cathodic current.

Using sufficiently long values of the delay time to decrease the scan rate – a value of $\tau$ at a 20 mV step height, for instance, which corresponds to a scan rate of ~ 0.6 mV/s at 200 rpm – gives rise to voltammograms in both the forward and reverse direction that show reversible behavior. This is demonstrated in Figure 4, where the reverse scan voltammograms for delay times of $\tau$ are fit to reversible behavior with the COOL algorithm – see below. Table II shows the collection efficiencies and diffusion coefficients for ferrocene calculated for slow scan rates where reversible behavior, such as in Figure 4, is found. The collection efficiency is seen to be in accord with that predicted from the ring-disc geometry. It can be pointed out that using ultramicroelectrodes in such viscous media would also require very slow scan rates to avoid hysteresis in the steady-state forward/reverse linear scan voltammograms.

Table II. Collection efficiencies and diffusion coefficients for ferrocene calculated for slow scan rates at RDE

| Rotation Rate (rpm) | $E_{1/2}$ (V) | Disk $i_{ss}$ (µA) | Ring $i_{ss}$ (µA) | $D \times 10^8$ (cm$^2$/s) | Collection Efficiency (%) |
|---------------------|---------------|--------------------|--------------------|----------------------------|---------------------------|
| 200                 | 0.308         | -3.957             | 0.826              | 7.3                        | 20.9                      |
| 400                 | 0.311         | -5.394             | 1.148              | 6.9                        | 21.3                      |
| 600                 | 0.313         | -6.690             | 1.419              | 7.1                        | 21.2                      |
| 800                 | 0.315         | -7.874             | 1.656              | 7.3                        | 21.0                      |
| 1000                | 0.317         | -8.900             | 1.850              | 7.4                        | 20.8                      |

| Rotation Rate (rpm) | $E_{1/2}$ (V) | Disk $i_{ss}$ (µA) | Ring $i_{ss}$ (µA) | $D \times 10^8$ (cm$^2$/s) | Collection Efficiency (%) |
|---------------------|---------------|--------------------|--------------------|----------------------------|---------------------------|
| 200                 | 0.321         | -3.759             | 0.795              | 6.8                        | 21.2                      |
| 400                 | 0.320         | -5.061             | 1.093              | 6.3                        | 21.6                      |
| 600                 | 0.322         | -6.347             | 1.367              | 6.5                        | 21.5                      |
| 800                 | 0.323         | -7.512             | 1.598              | 6.8                        | 21.3                      |
| 1000                | 0.323         | -8.406             | 1.772              | 6.8                        | 21.1                      |

In prior work by Meyers et al., Equation 3 was developed to evaluate normal pulse currents at rotating disk electrodes (16).
\[
\frac{Dt}{\delta_w^2} = \frac{1}{6} \left\{ \frac{1}{2} \ln \frac{1 - R^3}{(1 - R)^3} - \sqrt{3} \arctan \left( \frac{\sqrt{3}R}{R + 2} \right) \right\}
\]

where \( R = \frac{i_{ss}}{i_{inst}} \), \( \delta_w = 1.8049D^{1/3} \nu^{1/6} \omega^{-1/2} \), \( i_{ss} \) is the steady-state current at the disk, and \( i_{inst} \) is the instantaneous current at time \( t \). Substitution of the definition of \( \delta_w \) into this equation yields an implicit solution for \( R \).

\[
\omega t = 0.54294 \left( \frac{\nu}{D} \right)^{1/3} \left\{ \frac{1}{2} \ln \frac{1 - R^3}{(1 - R)^3} - \sqrt{3} \arctan \left( \frac{\sqrt{3}R}{R + 2} \right) \right\}
\]

However, for the purposes of comparison with experimental data, the ratio, \( \frac{i_{inst}}{i_{ss}} = R^{-1} \), is sought as a function of \( t \). Substitution of \( 1/R^1 \) for \( R \), \( S_c \) for \( \nu/D \), and further rearrangement gives

\[
0.54294S_c^{1/3} \left\{ \frac{1}{2} \ln \frac{1 - R}{R^{-1}} - \sqrt{3} \arctan \left( \frac{\sqrt{3}}{1 + 2R^{-1}} \right) \right\} - \omega t = 0
\]

This relationship can be expressed as \( f(R^{-1}) = 0 \) where \( f(R^{-1}) \) is the left-hand-side of Equation 5. The root of this equation is located by the method of false position (regula falsa) (17), which has the specific advantage that evaluation of the function outside of bracketed limits is never attempted. Since the root is always larger than unity, the lower limit is set at unity. The upper limit of the bracket is specified as about 250 due to considerations of the dynamic range of the current transient.

The root of Equation 5 is a function of two parameters, \( \alpha \), which is known from experimental conditions and \( S_c \). The root, \( R^{-1} \), is a function of an as yet unspecified value of \( S_c \), which can be estimated from current transients by non-linear least squares analysis. The dimensionless current function, \( R^{-1} \), is related to the transient, \( i(t) \), by:

\[
i(t) = aR^{-1}(S_c, \omega t) + b
\]

where \( a \) and \( b \) are a scaling factor and a bias current, respectively. The value of \( \alpha \) is known for each current measurement from experimental conditions. The remaining nonlinear parameter, \( S_c \), is varied using the COOL algorithm (18, 19) until the correlation of \( i(t) \) vs. \( R^{-1} \) is maximized. This estimates \( S_c \) assuming that the model utilized in Equation 3 is complete and correct.

A plot of the transients' fit to the model with the COOL algorithm is shown in Figure 5. The data are fit using the data to 8 s for each rotation rate, though only the data to 8 s is shown. The best fit value for the log10 (\( S_c \)) is 7.83 ± 0.06 for 200 rpm, 7.72 ± 0.10 for 400 rpm, and 7.56 ± 0.08 for 800 rpm, compared to the value of 7.51 calculated from the kinematic viscosity and the experimentally determined D. Thus, the transient...
behavior, even for the viscous ionic liquids, appears to be well characterized by these theoretical calculations and can be used to evaluate Schmidt numbers.

Thus, what we originally perceived as an anomaly in the rotating disk electrode behavior in bmimPF$_6$ is shown to be a consequence of the very high viscosity, which results in a very large value of the Schmidt number and drastically affects the transient response. This should be of concern to those carrying out electrochemical experiments in such liquids as it can modify the anticipated behavior.

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Figure 1. Current density vs. potential for a 25 mM KPF₆ solution in [bmim]PF₆, 500 mV/s at a) Pt and (b) hanging mercury drop electrode.
Figure 2. Forward (A) and reverse (B) scan RRDE voltammograms with rotation rates of (a) 200, (b) 400 and (c) 800 rpm. Delay time of 2s, 20 mV potential steps, and a ring potential of 0 V vs. silver wire reference electrode.
Figure 3. Normal pulse voltammograms (400 ms pulse width) for (a) 48 mM LiPF$_6$ (b) 30 mM NaPF$_6$ and (c) 19 mM KPF$_6$ dissolved in bmimPF$_6$.

Figure 4. Reverse scan RRDE voltammograms of 6 mM ferrocene/bmimPF$_6$ solution at 200 (□), 400 (△) and 800 (O) rpm with delay times equal to 1 τ. Solid lines calculated using COOL algorithm for a 1-electron reversible oxidation.
Figure 5. Current transients collected at rotation speeds of 200 ( ○ ), 400 ( * ), and 800 ( ● ) rpm. Solid lines correspond to non-linear least squares fit of the data from 0.1 to \( t = \tau \) s assuming that Equation 2 is followed.