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Voltammetric Characterization of the Ferrocene|Ferrocenium and Cobaltocenium|Cobaltocene Redox Couples in RTILs

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Received: October 18, 2007; In Final Form: November 21, 2007

Ferrocene, Fc, and cobaltocenium hexafluorophosphate, CcPF₆, have been recommended for use as internal reference redox couples in room-temperature ionic liquids (RTILs), as well as in more conventional aprotic solvents. In this study, the electrochemical behavior of Fc and CcPF₆ is reported in eight commonly used RTILs; [C₂mim][NTf₂], [C₄mim][NTf₂], [C₄mim][BF₄], [C₄mim][PF₆], [C₄mim][OTf], [C₄mim][NO₃], [C₄mpyr][NTf₂], and [P_{14,6,6,6}][FAP], where [C_{*n*}mim]⁺ = 1-butyl-3-methylimidazolium, [NTf₂][−] = bis-(trifluoromethylsulfonyl)imide, [BF₄][−] = tetrafluoroborate, [PF₆][−] = hexafluorophosphate, [OTf][−] = trifluoromethylsulfonate, [NO₃][−] = nitrate, [C₄mpyr]⁺ = *N*-butyl-*N*-methylpyrrolidinium, [P_{14,6,6,6}]⁺ = tris-(*n*-hexyl)-tetradecylphosphonium and [FAP][−] = trifluorotris(pentafluoroethyl)phosphate, over a range of concentrations and temperatures. Solubilities and diffusion coefficients, *D*, of both the charged and neutral species were determined using double potential-step chronoamperometry, and CcPF₆ (36.5–450.0 mM) was found to be much more soluble than Fc (27.5–101.8 mM). It was observed that classical Stokes–Einstein diffusional behavior applies for Fc and CcPF₆ in all eight RTILs. Diffusion coefficients of Fc and CcPF₆ were calculated at a range of temperatures, and activation energies calculated. It was also determined that *D* for Fc and CcPF₆ does not change significantly with concentration. This supports the use of both Fc and CcPF₆ to provide a well-characterized and model redox couple for use as a voltammetric internal potential reference in RTILs contrary to previous literature reports in the former case.

1. Introduction

Room-temperature ionic liquids (RTILs) are salts that exist in the liquid phase at and around 298 K^{1,2} and are comprised of a bulky, asymmetric organic cation and usually an inorganic but sometimes an organic anion. RTILs have been described as “designer solvents”³ as varying the combination of the cations and anions allows variation in melting point, viscosity, and solubility, leading to ionic liquids with properties suitable for the task at hand. Intrinsic electrical conductivity, low vapor pressure (low-volatility), high chemical and thermal stability, and low combustibility are a few of the properties possessed by ionic liquids, as well as favorable solvating properties.^{1,2,4,5} Due to the near-zero volatility of these solvents, they are considered “greener” for the environment as they do not evaporate like volatile organic compounds (VOCs).^{2,3} Diffusion coefficients of electroactive species are lower in RTILs, compared with, e.g., water and acetonitrile, as RTILs are typically 1–2 orders of magnitude more viscous than the more conventional solvents.^{1,2} They have been employed as electrolytes in a wide range of electrochemical applications^{1,2,4,6} as they offer wider potential windows than conventional solvents allowing, e.g., electrodeposition of metals and semiconductors that are normally out of the range of conventional solvents.⁷ Their intrinsic conductivity means that addition of supporting

electrolyte is not necessary, and as a result, the experimental setup can be simplified.^{1,2,4,5}

Reference electrodes are required in electrochemistry to measure or control electrode potentials and allow comparisons to be made between voltammetric data and between data in other solvents. The search for suitable reference electrodes for use in RTILs is currently active⁸ and is described in a recent chapter.⁹ Many authors use a quasi-reference electrode in combination with an electrochemically reversible couple, for example, IUPAC recommend the use of the ferrocene | ferrocenium (Fc|Fc⁺) or cobaltocenium | cobaltocene (Cc⁺|Cc) redox couple in aprotic solvents, and Bond et al. have used Fc and CcPF₆ in RTILs in this context.^{5,10,11}

Both systems are considered likely “ideal” potential standards although it has been reported by Brooks et al.,¹² Eisele et al.,¹³ and Nagy et al.¹⁴ that ferrocene is less than a “model” redox probe in some respects. All three reports^{12–14} show that the diffusion coefficient of ferrocene increases linearly with *c* at low concentrations of ferrocene. However, the behavior at higher concentrations was very different; Brooks and Doherty¹² showed an “exponential” dependence of *D* on *c* above ca. 33 mM Fc in [C₄mim][NTf₂], Nagy et al.¹⁴ reported a plateau of *D* of Fc in [C₄mim][PF₆] at concentrations above 2.5 mM, and Eisele et al.¹³ observed a more rapid, but not exponential, increase of *D* with *c* at concentrations above 15 mM Fc in [C₄mim][BF₄]. These reports suggest that Fc|Fc⁺ is less well understood in RTIL media than in conventional aqueous media. In response to this, Bond et al.¹⁵ discussed the behavior of the CcPF₆ in RTILs and the effect of concentration on the diffusion coef-

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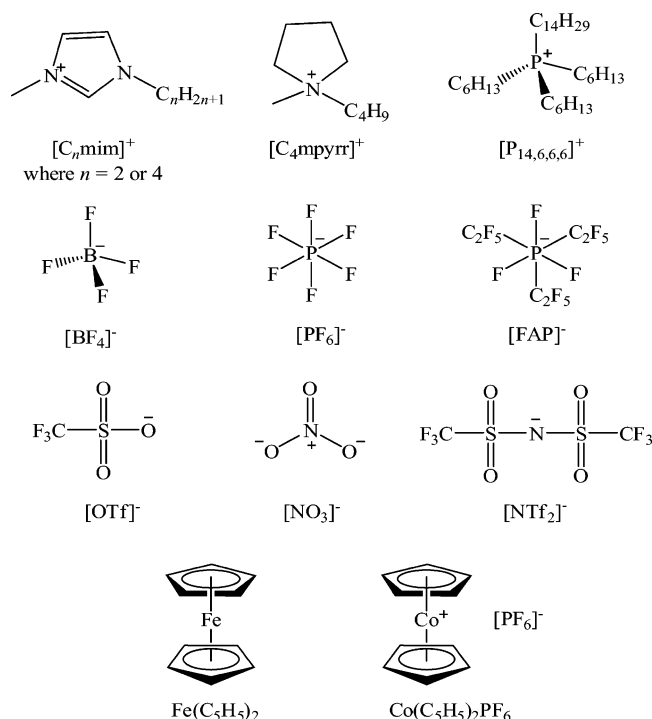


Figure 1. Structures of all the anions and cations employed in this study and the species under investigation.

ficients of the species. It was observed that the Cc^{+10} redox system exhibits ideal reversible, one-electron electrochemistry, with diffusion that is independent of concentration of species over a wide range, which lead to the conclusion that the Cc^{+10} system provides a superior potential reference redox system. However, corresponding experiments were not undertaken on the $\text{Fc}^{0/+}$ redox system.

The current paper reports the voltammetry of ferrocene (Cp_2Fe , where $\text{Cp} = (\text{C}_5\text{H}_5)$, hereafter referred to as Fc) and cobaltocenium hexafluorophosphate, (Cp_2CoPF_6 , hereafter referred to as CcPF_6 , where $\text{Cc}^+ = \text{Cp}_2\text{Co}^+$) in eight different RTILs; $[C_2\text{mim}][\text{NTf}_2]$, $[C_4\text{mim}][\text{NTf}_2]$, $[C_4\text{mim}][\text{BF}_4]$, $[C_4\text{mim}][\text{PF}_6]$, $[C_4\text{mim}][\text{OTf}]$, $[C_4\text{mim}][\text{NO}_3]$, $[C_4\text{mpyr}][\text{NTf}_2]$, and $[P_{14,6,6,6}][\text{FAP}]$ (see Figure 1 for structures of cations and anions of RTILs used). Solubilities for both Fc and CcPF_6 and diffusion coefficients for Fc , Fc^+ , Cc^+ , and Cc are reported, and the effect of concentration on diffusion of each species is also discussed. In addition, temperature studies were undertaken, allowing calculation of activation energies in the eight RTILs.

2. Experimental Section

2.1. Chemical Reagents. Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$, Aldrich, 98%), cobaltocenium hexafluorophosphate ($\text{Co}(\text{C}_5\text{H}_5)_2\text{PF}_6$, Acros Organics, 98%), acetonitrile (MeCN , Fischer Scientific, dried and distilled, 99%), and tetra-*n*-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, 99%) were used as received without further purification. 1-Ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide, $[C_2\text{mim}][\text{NTf}_2]$, 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide, $[C_4\text{mim}][\text{NTf}_2]$, and *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)imide, $[C_4\text{mpyr}][\text{NTf}_2]$ were prepared by standard literature procedures.^{16,17} 1-Butyl-3-methylimidazolium tetrafluoroborate, $[C_4\text{mim}][\text{BF}_4]$, (high purity), 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4\text{mim}][\text{PF}_6]$, (high purity), 1-butyl-3-methylimidazolium trifluoromethylsulfonate, $[C_4\text{mim}][\text{OTf}]$, (high purity) and tris(*n*-hexyl)tetradecylphosphonium trifluorotris(pentafluoroethyl)phosphate, $[P_{14,6,6,6}][\text{FAP}]$ were kindly donated by Merck KGaA. $[C_4\text{mim}][\text{BF}_4]$,

$[C_4\text{mim}][\text{PF}_6]$ and $[P_{14,6,6,6}][\text{FAP}]$ were used as received. $[C_4\text{mim}][\text{OTf}]$ was first diluted with CH_2Cl_2 and passed through a column consisting of alternating layers of neutral aluminum oxide and silica gel in order to remove residual acidic impurities. The synthesis of 1-butyl-3-methylimidazolium nitrate, $[C_4\text{mim}][\text{NO}_3]$ was adapted from a previously published procedure.¹⁸ AgNO_3 (5.36 g, 0.032 M) and $[C_4\text{mim}]\text{Cl}$ (5.00 g, 0.029 M) were dissolved separately in minimum amounts of ultrapure water. The $[C_4\text{mim}]\text{Cl}$ solution was then slowly added to the stirred AgNO_3 solution. After stirring overnight the solution was filtered to remove the AgCl precipitate, the water was removed and the IL dried under high vacuum at 70 °C overnight. The IL was then dissolved in 400 mL dry methanol, small amounts of activated charcoal and acidic alumina were added as seeds for the remaining AgCl , and the solution left overnight in a freezer. This solution was then filtered and the process repeated. The methanol was removed, and the ionic liquid was dried under high vacuum conditions.

2.2. Instrumental. All electrochemical experiments were performed using a computer-controlled μ -Autolab potentiostat (Eco-Chemie, Netherlands). The voltammetry of all Fc and CcPF_6 solutions were studied using a conventional two-electrode arrangement, consisting of a 10 μm diameter platinum working electrode and a 0.5 mm diameter silver wire quasi-reference electrode. The microelectrode was modified with a small section of disposable pipet tip to form a cavity on the electrode surface into which microlitre quantities of RTIL is added. The electrodes were housed in a T-cell (reported previously)¹⁹ which is specifically designed to allow samples to be studied under a controlled atmosphere. The liquid was purged under vacuum prior to, and during, experimental analysis.

Saturated solutions of Fc and CcPF_6 were made up directly in 60 μL of ionic liquid and stirred for ca. 12 h. 20 μL of this solution was then placed in the T-cell and electrochemical analysis was undertaken. Saturated solutions were then diluted by ca. 50% by adding 20 μL of blank RTIL to the T-cell and temperature studies were performed in a thermostated box (previously described by Evans et al.²⁰ which also functioned as a Faraday cage). The temperature was accurate to ± 1.0 K. To carry out further concentration studies, solutions were prepared by dissolving Fc and CcPF_6 in 60 μL RTIL in vials, which were then diluted by various amounts of RTIL to give a range of concentrations. The microdisk working electrode was polished prior to each experiment, using 1.0 and 0.3 μm alumina-water slurry, respectively, on soft lapping pads (Buehler, Illinois). The electrode was calibrated by analyzing the steady-state voltammetry of a 2 mM solution of Fc in acetonitrile containing 0.1 M TBAP, to give the electrode diameter, adopting a value of D of ferrocene in MeCN of $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.²¹

2.3. Double Potential Step Chronoamperometric Experiments. Double potential step chronoamperometric transients were achieved using a sample time of 0.01 s. The solution was pretreated by holding potential at a point of zero current for 20 s, after which the potential was stepped to a position after the peak (oxidative for Fc and reductive for CcPF_6), and the current was measured for 5 s. The potential was then stepped back to a point of zero current, and the current response measured for a further 5 s. In order to extract diffusion coefficients and solubility data from these transients, the first potential step was fitted using the a nonlinear curve fitting function in the software package Origin 7.0 (Microcal Software Inc.) following eqs 1–3, as proposed by Shoup and Szabo²² for the time-dependent current response at microdisk electrodes. The equations used in this approximation are sufficient to describe the current response to within an accuracy of 0.6%.

$$I = -4nFDcr_d f(\tau) \quad (1)$$

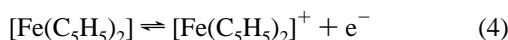
$$f(\tau) = 0.7854 + 0.8863\tau^{-1/2} + 0.2146 \exp(-0.7823\tau^{-1/2}) \quad (2)$$

$$\tau = \frac{4Dt}{r_d^2} \quad (3)$$

where n is the number of electrons transferred, F is the 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 t is the time. The value for the radius (previously calibrated) was fixed, and 100 iterations were performed by the software to give a value for the diffusion coefficient and the product of the number of electrons multiplied by concentration after optimization of the experimental data. To model the second potential step, a computer simulation program (described by Klymenko et al.)²³ was employed. Values of D and nc obtained from Shoup and Szabo²² analysis of experimental data were input into simulation software and values of D for the reverse step were varied until the best fit between theoretical and experimental data was achieved.

3. Results and Discussion

3.1. Cyclic Voltammetry for Oxidation of Ferrocene and Reduction of Cobaltocenium Hexafluorophosphate in Various RTILs. **3.1.1. Electrochemical Oxidation of Fc.** Figure 2a shows typical cyclic voltammetry for the oxidation of a saturated (ca. 77 mM determined from potential step chronoamperometry) solution of ferrocene in [C₄mim][NTf₂] on a 10 μ m diameter platinum electrode at scan rates from 10 to 1000 mV s⁻¹. The voltammetry is reported against a 0.5 mm diameter silver wire quasi-reference. Ferrocene is oxidized by one-electron to Fc⁺ at a peak potential of +0.43 V vs Ag (at 1000 mV s⁻¹), and reduced back to Fc at a potential of +0.34 V vs Ag (at 1000 mV s⁻¹), corresponding to eq 4.



The peak separation, ΔE_{pp} , decreases with increasing scan rate, (opposite to that expected for an electrochemically reversible process at macroelectrodes),²⁴ as there is a transition from steady state behavior at slower scan rates to transient behavior at faster scan rates. According to the inequality given in eq 5, true steady state behavior can only be achieved at scan rates much less than 31 mV s⁻¹, for Fc in [C₄mim][NTf₂].

$$v \ll \frac{RTD}{nFr_d^2} \quad (5)$$

where v is the scan rate, R is the universal gas constant and T is the absolute temperature, assuming $D = 3.77 \times 10^{-11}$ m² s⁻¹ (from electrochemical oxidation of saturated Fc, see later), and $r_d = 5.6 \mu\text{m}$. In all RTILs studied, the peak current increases systematically with scan rate but plots of peak current vs square root of scan rate do not typically pass through the origin; the latter is behavior characteristic only of voltammetry at macro electrodes.²⁴ Due to the magnitude of D (ca. 1×10^{-11} m² s⁻¹) and considering the inequality given in eq 5, the voltammetry observed is intermediate of micro/macro electrode behavior. A subsequent publication may address the issue of extracting kinetic parameters from voltammetry in this intermediate region.

Double potential step chronoamperometry was then performed in order to calculate diffusion coefficients of Fc and its oxidized

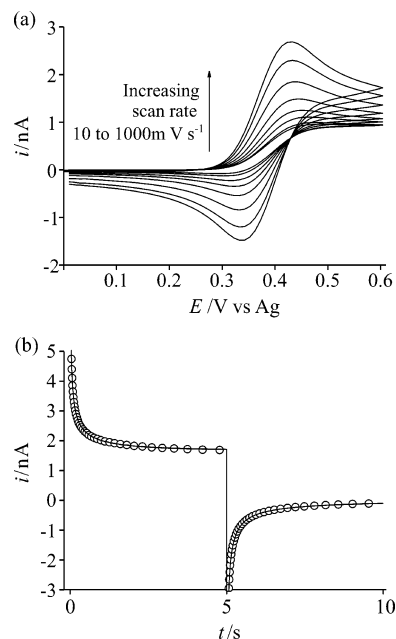


Figure 2. (a) Cyclic voltammetry for the oxidation of saturated ferrocene in [C₄mim][NTf₂] on a platinum microelectrode (diameter 10 μ m) at varying scan rates (10, 20, 40, 70, 100, 200, 400, 700, and 1000 mV s⁻¹). (b) Experimental (—) and fitted theoretical (○) double potential step chronoamperometric transients measured on the same system across the redox couple Fc^{0/+}. The potential was stepped from +0.10 to +0.60 and back to +0.10 V.

species, Fc⁺. The potential was stepped from +0.10 to +0.60 V (oxidation of Fc to Fc⁺), and then stepped back to +0.10 V (reduction of Fc⁺ to Fc) and the transient obtained is shown as the solid line in Figure 2b. The diffusion coefficient, D and solubility, c of neutral Fc was determined from analysis of the experimental data for the first potential step using Shoup and Szabo²² approximations. A computer simulation program²³ was then employed to model the second potential step to give D_{Fc^+} . Figure 2b shows the best theoretical fit (○) to the experimental double potential step chronoamperograms (—) for the redox couple Fc^{0/+} in [C₄mim][NTf₂]. This process was repeated for the remaining RTILs in order to find concentrations (solubilities) and diffusion coefficients of Fc and Fc⁺ in each ionic liquid. Table 1 shows the results from chronoamperometric fitting in eight RTILs. As can be seen, Fc is moderately soluble in all ionic liquids (28–102 mM), corresponding well to that observed in the literature.^{5,10}

When simulating double potential-step chronoamperometric transients, it was determined that the ratio $D_{\text{Fc}}/D_{\text{Fc}^+} \neq 1$, suggesting that the neutral Fc species diffuses more quickly than the charged Fc⁺ species through the ionic liquid media. This is consistent with that reported by Lagunas et al.²⁵ for D_{Fc} and D_{Fc^+} in the RTILs [C₄mim][OTf], [C₄mim][NTf₂] and [C₄mim][PF₆]. For all RTILs, the value of the ratio falls in the range 1–2, with the exception of the [P_{14,6,6,6}][FAP] ionic liquid, which gives a ratio of 7.80 for $D_{\text{Fc}}/D_{\text{Fc}^+}$. This unusually high ratio is confirmed by the increased asymmetrical behavior between the forward and reverse peaks shown by the cyclic voltammetry in this RTIL (not included here). A similar qualitative effect has also been observed for *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) in [P_{14,6,6,6}][FAP] and [P_{14,6,6,6}][NTf₂].^{20,26} The relationship between D and η for all eight ionic liquids will be discussed in Section 3.2.

3.1.2. Electrochemical Reduction of CcPF₆. Analogous experiments to the previous section were then repeated for cobaltocenium hexafluorophosphate. Typical cyclic voltammetry

TABLE 1: Diffusion Coefficients and Solubilities of Fc in Various RTILs^a

ionic liquid	viscosity ^b / cP	$D_{\text{Fc}}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	$D_{\text{Fc}^+}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	$D_{\text{Fc}}/D_{\text{Fc}^+}$	solubility/ mM
[C ₂ mim][NTf ₂]	34 ¹⁶	5.34 ± 0.05	3.90	1.37	62.3 ± 1.2
[C ₄ mim][NTf ₂]	52 ¹⁶	3.77 ± 0.04	2.65	1.43	77.4 ± 0.5
[C ₄ mpyr][NTf ₂]	89 ³³	2.31 ± 0.04	1.55	1.50	91.2 ± 0.2
[C ₄ mim][OTf]	90 ¹⁶	2.36 ± 0.04	1.80	1.31	58.3 ± 0.1
[C ₄ mim][BF ₄]	112 ¹⁶	1.83 ± 0.02	1.30	1.85	27.5 ± 0.2
[C ₄ mim][NO ₃]	266 ³⁴	0.83 ± 0.05	0.63	1.32	51.4 ± 2.2
[C ₄ mim][PF ₆]	371 ³⁴	0.59 ± 0.05	0.31	1.91	38.2 ± 1.5
[P _{14,6,6,6}][FAP]	464 ³⁵	0.86 ± 0.02	0.11	7.80	101.8 ± 2.0

^a D_{Fc} values were determined using Shoup and Szabo²² fitting function for chronoamperometric data. D_{Fc^+} were achieved by simulation of experimental chronoamperometric transients.²³ Temperature 299 ± 1 K. Error bars calculated from the standard deviation of the best theoretical fits from several repeat potential step chronoamperograms. ^b Viscosity values at 293 K.

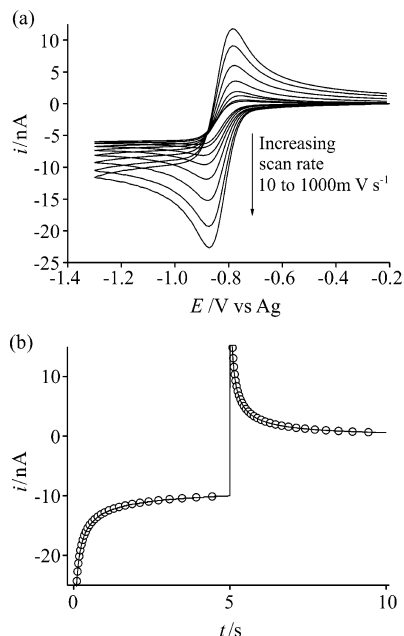
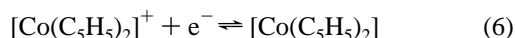


Figure 3. (a) Cyclic voltammetry for the reduction of saturated cobaltocenium in [C₄mim][NTf₂] on a platinum microelectrode (diameter 10 μm) at varying scan rates (10, 20, 40, 70, 100, 200, 400, 700, and 1000 mV s⁻¹). (b) Experimental (—) and fitted theoretical (○) double potential step chronoamperometric transients measured on the same system across the redox couple Cc^{+/0}. The potential was stepped from -0.40 to -1.30 and back to -0.40 V.

for the reduction of saturated (ca. 383 mM determined from potential step chronoamperometry) CcPF₆ in [C₄mim][NTf₂] on a 10 μm diameter platinum electrode (vs a 0.5 mm diameter silver wire), at scan rates from 10 to 1000 mV s⁻¹ is shown in Figure 3a. The voltammetry gives rise to a reduction peak at -0.88 V vs Ag (at 1000 mV s⁻¹), corresponding to the reduction of cobaltocenium (Cc⁺) to cobaltocene (Cc), and an oxidation peak at -0.80 V vs Ag (at 1000 mV s⁻¹) corresponding to the reoxidation of Cc to Cc⁺, in a reversible, one-electron transfer, following eq 6.



As with ferrocene, a transition from steady state to transient behavior results in the peak separations, ΔE_{pp} , decreasing with increasing scan rate, opposite to the behavior expected on a macroelectrode.²⁴ According to the inequality given in eq 5, true steady state behavior can only be achieved at scan rates much less than 18 mV s⁻¹ for CcPF₆ in [C₄mim][NTf₂], assuming $D = 2.22 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (from electrochemical reduction of saturated Cc⁺). Again, for all RTILs, a systematic increase of peak current with scan rate is observed, although,

the behavior observed is not characteristic of voltammetry at macroelectrodes as a plot of peak current vs square root of scan rate does not pass through the origin.²⁴ The magnitude of D achieved (ca. $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) is consistent with behavior intermediate to that observed at micro/macro electrodes.

Double potential step chronoamperometry was also performed on the system to calculate diffusion coefficients of Cc⁺ and Cc. The potential was stepped from -0.40 V to a position after the reduction peak (-1.30 V) and then stepped back to the original value of -0.40 V. Figure 3b shows the best theoretical fit (○) achieved from simulation of the experimental (—) chronoamperometric transient. The first potential step was analyzed using a nonlinear curve fitting function, based on Shoup and Szabo²² approximation to determine a value for D_{Cc^+} , and then the double potential step simulation program²³ was used to model the second step. This was repeated for all ionic liquids and Table 2 shows the solubility of CcPF₆ and D values for both the charged and the neutral species. The solubilities of CcPF₆ in the ionic liquids are much higher (36.5–450 mM) than those of the neutral Fc, which is not unexpected since Cc⁺ is a charged species and may likely interact more favorably with the RTIL anions. As was observed with Fc|Fc⁺ (see section 3.1.1), the charged Cc⁺ species diffuses more slowly through the RTIL leading to a ratio $D_{\text{Cc}^+}/D_{\text{Cc}} \neq 1$. The $D_{\text{Cc}^+}/D_{\text{Cc}}$ ratios all fall within the range 1–2, with the exception of the tetraalkylphosphonium liquid, which has a slightly higher ratio of 3.08. The solubility of CcPF₆ in [P_{14,6,6,6}][FAP] is also much lower than in the other seven RTILs, possibly due to the more “organic” nature of the RTIL. Although we have no knowledge of the solubility of neutral cobaltocene it is likely to be much less soluble than charged cobaltocenium species. Therefore it is possible that cobaltocene may precipitate on to the electrode surface; this possibility should be considered if the Cc⁺|Cc redox couple is employed as an internal potential reference.

3.2. Stokes–Einstein Behavior. The Stokes–Einstein relation²⁴ (shown in eq 7) predicts that a linear relationship between diffusion coefficient and the reciprocal of viscosity is observed for a simple diffusing species.

$$D = \frac{k_{\text{B}}T}{6\pi\eta\alpha} \quad (7)$$

where D is the diffusion coefficient, k_{B} is the Boltzmann constant, T is the temperature, and α is the hydrodynamic radius of the diffusing species (assuming the molecule is spherical). In order to show if the Stokes–Einstein relationship applies for both Fc and CcPF₆ in RTILs, a plot of D vs $1/\text{viscosity}$ for all 8 RTILs was made, and is shown in Figure 4a for Fc and Figure 4b for CcPF₆. It has previously been shown that this relationship is followed for *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in several RTILs²⁷ and is commonly observed in conventional solvents,²⁴ however, it has been shown that for

TABLE 2: Diffusion Coefficients and Solubilities of CcPF₆ in Various RTILs^a

ionic liquid	viscosity ^b /cP	$D_{Cc+}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	$D_{Cc}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	D_{Cc+}/D_{Cc}	solubility/mM
[C ₂ mim][NTf ₂]	34 ¹⁶	3.16 ± 0.03	4.10	1.29	382.7 ± 3.8
[C ₄ mim][NTf ₂]	52 ¹⁶	2.22 ± 0.04	3.10	1.42	349.9 ± 4.0
[C ₄ mpyrr][NTf ₂]	89 ³³	1.45 ± 0.02	2.10	1.45	254.2 ± 0.2
[C ₄ mim][OTf]	90 ¹⁶	1.31 ± 0.02	1.80	1.38	405.8 ± 0.3
[C ₄ mim][BF ₄]	112 ¹⁶	1.11 ± 0.02	1.50	1.35	327.1 ± 0.5
[C ₄ mim][NO ₃]	266 ³⁴	0.58 ± 0.02	0.76	1.32	450.0 ± 0.6
[C ₄ mim][PF ₆]	371 ³⁴	0.47 ± 0.02	0.77	1.65	113.4 ± 0.2
[P _{14,6,6,6}][FAP]	464 ³⁵	0.33 ± 0.02	1.00	3.09	36.5 ± 1.8

^a D_{Cc+} values were determined using Shoup and Szabo²² fitting function for chronoamperometric data. D_{Cc} were achieved by simulation of experimental chronoamperometric transients.²³ Temperature 299 ± 1 K. Error bars calculated from the standard deviation of the best theoretical fits from several repeat potential step chronoamperograms. ^b Viscosity values at 293 K.

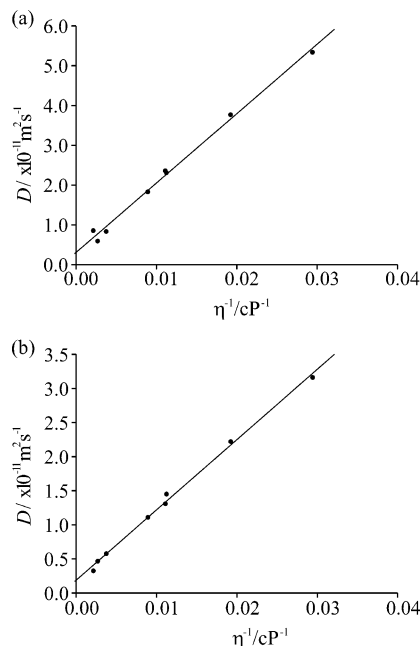


Figure 4. Stokes–Einstein plots of diffusion coefficient (D) vs $1/\text{viscosity}$ (η^{-1}) for (a) ferrocene and (b) cobaltocenium hexafluorophosphate. D values were obtained from chronoamperometric analysis of both species, and are included in Tables 1 and 2.

very small molecules, e.g., H_2 ,²⁸ SO_2 ,²⁹ and O_2 ³⁰ that this relation does not apply. This work will investigate this behavior to see if it applies for Fc and CcPF₆. As seen in Figure 4 there is excellent linearity for both Fc and CcPF₆ in the eight different ionic liquids, which suggests, at least in the sense that $D \propto 1/\eta$, that Stokes–Einstein’s relationship holds well for these species in RTILs, and that the $\text{Fc}^{0/+}$ and Cc^{+0} redox couples may to that extent be considered “model” systems.

3.3. Concentration Dependence of Diffusion Coefficient Study. It has been suggested in the literature that the diffusion coefficient of ferrocene varies with concentration of species in RTIL.^{12–14} To investigate this, we have looked at the diffusion coefficient of ferrocene and cobaltocenium hexafluorophosphate at a range of concentrations in two commonly used ionic liquids: [C₄mim][NTf₂] and [C₄mpyrr][NTf₂]. Figure 5a shows typical cyclic voltammetry for the reduction of CcPF₆ at concentrations of 29.6, 73.3, 108.3, and 160.2 mM (as determined from potential step chronoamperometry), in [C₄mim][NTf₂] on a 10 μm diameter platinum electrode (vs silver quasi-reference), at 100 mV s^{-1} . As can be seen, the peak current for the reduction peak increases with concentration. Double potential step chronoamperometry was undertaken at a range of concentrations to determine diffusion coefficients for Cc^{+} and Cc . Figure 5b shows typical experimental double potential-step chronoamperograms (—), along with the best

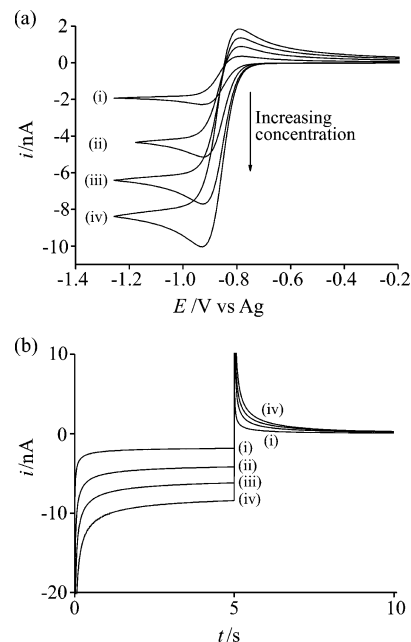


Figure 5. (a) Cyclic voltammetry for the reduction of cobaltocenium hexafluorophosphate on a platinum microelectrode (diameter 10 μm) in the RTIL [C₄mim][NTf₂] at varying concentrations of (i) 29.6 mM, (ii) 73.3 mM, (iii) 108.3 mM, and (iv) 160.2 mM, at 100 mV s^{-1} . (b) Double potential step chronoamperograms measured on the same system across the redox couple Cc^{+0} at concentrations of 29.6, 73.3, 108.3, and 160.2 mM. The potential was stepped from -0.40 to -1.30 V, and back to -0.40 V.

TABLE 3: Concentration Study of Fc and CcPF₆ in [C₄mim][NTf₂]^a

conc. Fc/ mM	$D_{Fc}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	conc. CcPF ₆ / mM	$D_{Cc+}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$
77.4	3.77 ± 0.03	350.0	2.22 ± 0.04
43.7	3.61 ± 0.04	160.2	2.14 ± 0.05
20.5	3.89 ± 0.05	108.3	2.20 ± 0.02
16.7	3.89 ± 0.05	73.3	2.21 ± 0.03
8.4	3.91 ± 0.05	29.6	2.22 ± 0.03
2.8	3.99 ± 0.10	8.1	2.18 ± 0.05

^a Values shown were determined from potential step chronoamperometric analysis using the Shoup and Szabo²² approximation. Error bars calculated from the standard deviation of the best theoretical fits from several repeat potential step chronoamperograms. Temperature 299 ± 1 K.

theoretical fit (O), following the fitting procedure reported in the experimental section. The same process was repeated for CcPF₆ in [C₄mpyrr][NTf₂], and for Fc in both [C₄mim][NTf₂] and [C₄mpyrr][NTf₂]. The data obtained at various concentrations are shown in Table 3 for Fc and CcPF₆ in [C₄mim][NTf₂], and Table 4 for Fc and CcPF₆ in [C₄mpyrr][NTf₂]. These results

TABLE 4: Concentration Study of Fc and CcPF₆ in [C₄mppyrr][NTf₂]^a

conc. Fc/ mM	$D_{Fc}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	conc. CcPF ₆ / mM	$D_{Cc+}/$ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$
91.2	2.31 ± 0.04	254.2	1.45 ± 0.02
78.9	2.60 ± 0.11	115.8	1.43 ± 0.03
41.3	2.55 ± 0.04	78.5	1.41 ± 0.03
30.8	2.72 ± 0.04	57.2	1.39 ± 0.02
30.2	2.58 ± 0.03	25.1	1.43 ± 0.03
10.4	2.55 ± 0.05	7.8	1.38 ± 0.05

^a Values shown were determined from potential step chronoamperometric analysis using the Shoup and Szabo²² approximation. Error bars calculated from the standard deviation of the best theoretical fits from several repeat potential step chronoamperograms. Temperature 299 ± 1 K.

indicate that there is no significant variation in the apparent diffusion coefficient of either Fc and CcPF₆ in both ionic liquids.³¹ In addition, the ratio of the diffusion coefficients of the neutral and charged species remained constant over the whole concentration range, leading us to question the nonidealities previously reported^{12–14} for ferrocene. In the latter context we note the difficulties of quantitatively dissolving some materials in RTILs, and especially in the case of the more viscous liquids, the problems associated with the dilution of “stock” solutions. All D and c values quoted in this paper are accurately determined from potential step chronoamperometry following the Shoup and Szabo²² expression. This method is well-established; the reliability of this method in RTILs and aprotic solvents has been demonstrated previously,³² and allows for the accurate, simultaneous determination of D 's and c 's. The concentrations thus inferred in our studies were always close to those made up giving particular confidence in the data presented.

3.4. Temperature Study and Calculation of Activation Energies. Cyclic voltammetry was next undertaken on solutions of Fc and CcPF₆ in the eight RTILs under investigation at a range of temperatures (299, 303, 313, 323, and 333 K). Figure 6a shows the cyclic voltammogram observed for the oxidation of ca. 37 mM Fc in [C₂mim][NTf₂] on a 10 μm diameter platinum electrode at 100 mV s⁻¹, at increasing temperature. The peak currents increase systematically with temperature, suggesting that the diffusion coefficients are increasing, as expected from the decrease in viscosity with temperature. A small shift in potential is also observed, probably due to the shift in the Ag quasi-reference with increased temperature.

Double potential step chronoamperometry was undertaken on both species at the range of temperatures in order to calculate the diffusion coefficients of Fc and Fc⁺, and Cc⁺ and Cc. Figure 6b shows the experimental double potential step chronoamperograms for the Fc/Fc⁺ couple at temperatures of 303, 313, 323, and 333 K under the same conditions as Figure 6a. The limiting currents of the first step increase systematically, and the decay of the second step becomes less steep when the temperature is increased. The experimental data was theoretically fitted (via the Shoup and Szabo expression²² and the double potential step simulation program²³) to calculate D_{Fc} and D_{Fc^+} . It was found that the ratio of the diffusion coefficients of the neutral and charged species was approximately constant over the temperature range 299–333 K for both Fc and CcPF₆. The diffusion coefficients were analysed in terms of Arrhenius-type behavior following eq 8²⁴

$$D = D_0 \exp\left(\frac{-E_{a,D}}{RT}\right) \quad (8)$$

where D is the diffusion coefficient of the electroactive species,

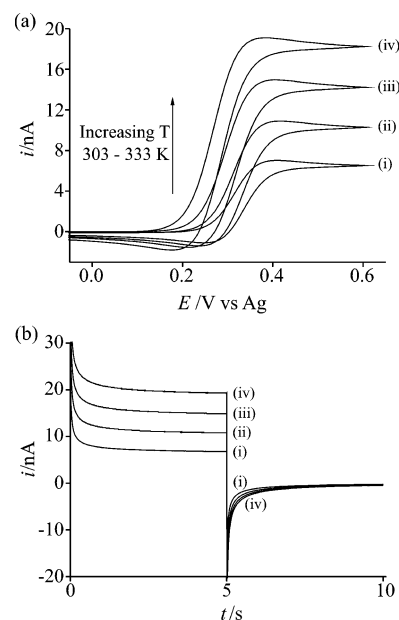


Figure 6. (a) Cyclic voltammetry for the oxidation of ferrocene on a platinum microelectrode (diameter 10 μm) in the RTIL [C₂mim][NTf₂] at varying temperatures of (i) 303 K, (ii) 313 K, (iii) 323 K, and (iv) 333 K, at 100 mV s⁻¹. (b) Double potential step chronoamperograms measured on the same system across the redox couple Fc^{0/+} at temperatures of 303, 313, 323, and 333 K. The potential was stepped from 0.0 to +0.60 V, and then back to 0.0 V.

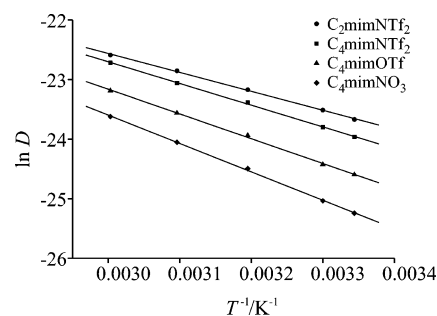


Figure 7. Arrhenius plots of $\ln D$ vs T^{-1} over the range 298–333 K for the diffusion coefficients of ferrocene in 4 RTILs. Diffusion coefficients were obtained from chronoamperometric analysis following the Shoup and Szabo²² expression.

D_0 is a constant corresponding to the hypothetical diffusion coefficient at infinite temperature, R is the universal gas constant, and $E_{a,D}$ is the diffusional activation energy of the electroactive species.

Figure 7 shows a plot of $\ln D$ vs $1/T$ for Fc in four representative RTILs, and Figure 8 shows the same plot for CcPF₆. The remaining plots for Fc and CcPF₆ in the other four RTILs investigated is shown in the Supporting Information. In all cases, a high degree of linearity is observed (least-squares correlation coefficient >0.95 for Fc and >0.97 for CcPF₆). Table 5 summarizes the temperature-dependent diffusion coefficients for each system in terms of activation energy of diffusion, $E_{a,D}$. As can be seen, the activation energies for both Fc and CcPF₆ are very similar. These can be compared to activation energies for viscosity, $E_{a,\eta}$, for each of the RTILs, which have been calculated from viscosity/temperature measurements reported in the literature, and are included in Table 5. The $E_{a,\eta}$ values are similar to the experimentally determined $E_{a,D}$ values. It is also observed that the more viscous ionic liquids have correspondingly larger activation energies.

A slight deviation of $E_{a,D}$ from $E_{a,\eta}$ is observed for CcPF₆ in [C₄mim][BF₄], and particularly in [C₄mim][PF₆]. One explanation

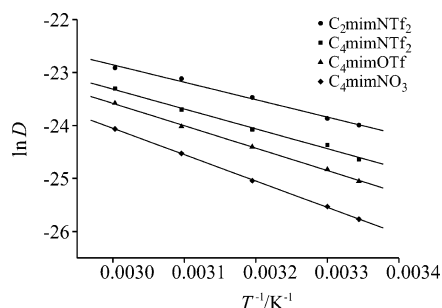


Figure 8. Arrhenius plots of $\ln D$ vs T^{-1} over the range 298–333 K for the diffusion coefficients of cobaltocenium hexafluorophosphate in 4 RTILs. Diffusion coefficients were obtained from chronoamperometric analysis following fitting to the Shoup and Szabo²² expression.

TABLE 5: Activation Energies of Diffusion, ($E_{a,D}$) of Fc and CcPF₆ Obtained from Plots of $\ln D$ vs T^{-1} for Eight RTILs Investigated in the Temperature Range 299, 303, 313, 323, and 333 K

RTIL	$E_{a,D}(\text{Fc})/\text{kJ mol}^{-1}$	$E_{a,D}(\text{CcPF}_6)/\text{kJ mol}^{-1}$	literature $E_{a,\eta}/\text{kJ mol}^{-1}$
[C ₂ mim][NTf ₂]	26.4	27.3	24.9 ³⁶
[C ₄ mim][NTf ₂]	30.2	31.1	28.8 ³⁶
[C ₄ mpyr][NTf ₂]	34.6	35.3	30.4 ³³
[C ₄ mim][OTf]	34.5	35.1	28.7 ³⁴
[C ₄ mim][BF ₄]	35.8	39.0	33.4 ³⁴
[C ₄ mim][NO ₃]	43.9	41.3	38.3 ³⁴
[C ₄ mim][PF ₆]	42.9	52.7	38.3 ³⁴
[P _{14,6,6,6}][FAP]	43.9	42.3	40.5 ²⁶

tion for this observation is the possibility that Cc⁺ is paired with the [PF₆][−] anion. Cc⁺ has a strong affinity for [PF₆][−] in [C₄mim][PF₆] which may be why there is such a difference in activation energies for CcPF₆ in this liquid. Fc is a neutral species and does not have the same affinity for the [PF₆][−] RTIL anion, (or in fact, any of the anions used in this study), which also explains why the $E_{a,D}$ values for Fc are uniformly closer to the $E_{a,\eta}$ values quoted in the table.

4. Conclusions

The voltammetry of both Fc and CcPF₆ was investigated over a range of concentration and temperature in eight room-temperature ionic liquids. Solubilities and diffusion coefficients were successfully determined by analysis and simulation of double potential step chronoamperograms. It was also shown that the diffusion coefficients of the neutral and charged species were measurably different. This difference in diffusion coefficients of the neutral and charged species has to be taken into account when attempting to model voltammetry for these redox couples. The diffusion coefficient of both Fc and CcPF₆ was not found to vary significantly with concentration. Furthermore, both Fc and CcPF₆ were observed to conform to classical Stokes–Einstein behavior in terms of their viscosity dependence, suggesting that both redox couples may be considered as almost-“ideal” reference electrode materials.

Acknowledgment. E.I.R. thanks the EPSRC; D.S.S. thanks Schlumberger Cambridge Research; and L.A. thanks the Department of Education and Learning in Northern Ireland and Merck GmbH for financial support.

Supporting Information Available: Figures showing the Arrhenius plots for Fc and CcPF₆ in the four ionic liquids not

presented in the main text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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