Voltammetric Studies on Decaphenylferrocene, Substituted Decaphenylferrocenes, and Their Oxidized Forms in Dichloromethane and Ionic Liquids

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Cyclic voltammetric studies have been undertaken on highly insoluble decaphenylferrocene (DPFc), on substituted forms of the compound [methyl (Me_2DPFc, Me_6DPFc, and Me_{10}DPFc), bromide (Br_2DPFc), and ethynyl ($Ethin_2$DPFc)], and on their more soluble one-electron-oxidized $DPFc^+$ forms. Studies with $DPFc^+$ and its derivatives dissolved in dichloromethane (DCM) enable the reversible potentials ($E^{0\prime}$) of one-electron reduction processes, $DPFc^+$(DCM) + $e^- \leftrightarrows$ DPFc(DCM), to be established. $E^{0\prime}$ values obtained from these measurements exhibit the expected substituent dependence. Voltammetric studies with arrays of insoluble DPFc microparticles adhered to an electrode surface in contact with DCM (0.1 M Bu_4NPF_6) or ionic liquids are connected to the oxidized solid or dissolved forms of $DPFc^+$ via a range of pathways that are determined by the kinetics and thermodynamics of dissolution and reprecipitation processes. Comparative data obtained with more soluble ferrocene, ferricinium, and decamethylferrocene microparticles support the hypothesis that dissolution processes play an important role in determining the nature of the voltammetric response of adhered microparticles.

Introduction

Electrochemical studies on ferrocene (Fc) compounds are very widespread.[1] Typically, a well-defined reversible Fc $\rightleftharpoons$ Fc^+ + e^- process is detected when both Fc and Fc^+ are soluble in the media of interest. In the case of decaphenylferrocene (DPFc), the preparation and characterization of the symmetrical form of the highly insoluble ferrocene derivative proved to be highly challenging.[2−4] Furthermore, lack of solubility in many media has meant electrochemical studies in organic solvents have been restricted[2,3] to reduction of the more soluble $DPFc^+$ to DPFc in dichloromethane (DCM) or acetonitrile,[2,5] although the complex oxidation of DPFc and $DPFc^+$ adhered to an electrode surface in contact with aqueous (or water/aceotonitrile (70:30) mixed solvent) electrolyte solutions has been described.[6,7]

No electrochemical data are available on substituted forms of DPFc. The challenge to be met in order to obtain such data and hence establish the substituent effect is to find media that eliminate or take into account the presence of dissolution or precipitation processes[8,9] that almost certainly will accompany a $DPFc^+$ + $e^- \leftrightarrows$ DPFc type electron transfer process. Ionic liquids[10] that have been used as an alternative to organic solvents with electrolyte in electrochemical studies on Fc and other compounds[11−13] may provide an opportunity to achieve this goal with respect to the DPFc system.

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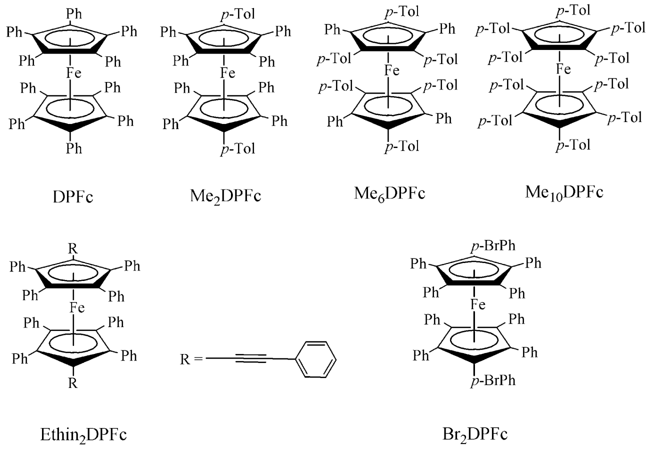
Table 1. Physical Properties of Ionic Liquids

ionic liquid	viscosity/cP	density	melting point/°C	conductivity/ms cm^{-1}	potential window/V	solubility in water/mass%	saturated water contain/mass%
BMIM·PF_6[a]	312[b]	1.37[b]	10	6.56[c]	4.5[d]	2.297[e]	2.116[e]
emim·tfsa[f]	35	1.520	−3	9.6	4.5	1.8	1.4
P14·tfsa[g]	85[h]	1.41[i]	−18	2.2[h]	5.5		

[a] Data are from ref 10a. [b] Measured at 30 °C. [c] Measured at 60 °C. [d] Data are from ref 10b. [e] Data are from ref 22. [f] Data are from ref 14 and were measured at 20 °C except that the value of density was obtained at 22 °C. [g] Data are from ref 15. [h] Measured at 20 °C. [i] Measured at 25 °C.

Chart 1. Structures of DPFc and Its Derivatives


DPFc

Me_2DPFc

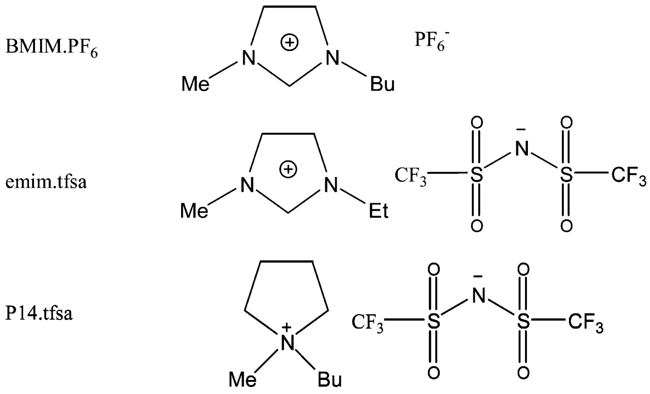
Me_6DPFc

$Me_{10}DPFc$

$Ethin_2DPFc$

Br_2DPFc

Chart 2. Structures of Ionic Liquids Used in the Present Studies


BMIM.PF_6

emim.tfsa

P14.tfsa

In this study, we report the voltammetry of DPFc and its substituents adhered to electrode in contact with DCM (0.1 M Bu_4NPF_6) or ionic liquids and on $DPFc^+$ derivatives dissolved in DCM (0.1 M Bu_4NPF_6). The combination of approaches allows the role of dissolution/reprecipitation processes to be elucidated and also to establish conditions that minimize their influence.

Experimental Section

Chemicals. Cobalticinium hexafluorophosphate ($[Co(Cp)_2][PF_6]$, 98%, Strem Chemicals), ferricinium hexafluorophosphate ($[Fc][PF_6]$, Sigma-Aldrich), ferrocene (Fc, >98%, Merck), decamethylferrocene (DMFc, 97%, Sigma-Aldrich), KPF_6 (98%, Sigma-Aldrich), and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM·PF_6, >97%, Sigma-Aldrich) were used as received from the manufacturer. The other ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl) amide (emim·tfsa) and *N*-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) amide (P14·tfsa), were synthesized according to literature procedures.[14,15] The structures of the ionic liquids and their physical properties are summarized in Chart 2 and Table 1, respectively. Decaphenylferrocene (DPFc), $[DPFc^+][BF_4^-]$, and its derivatives (see Chart 1) were synthesized, purified, and characterized as described in the literature.[2] To study the voltammetry of $DPFc^+$ derivatives, suspensions of these compounds were oxidized with a slight molar excess of $NOPF_6$ (Strem Chemicals) in dichloromethane (DCM, HPLC grade, BDH) containing 0.1 M Bu_4NPF_6 (GFS, recrystallized twice before use) as the electrolyte.

Instrumentation and Procedures. Voltammetric measurements were undertaken with a BAS 100B (Bioanalytical Systems, Indiana) electrochemical workstation. A conventional three-electrode cell was employed, with 1 mm diameter glassy carbon (GC) working and Pt wire counter electrodes. In experiments involving adhered $[Fc][PF_6]$ microparticles, a 50 μm diameter Pt microdisk electrode was used as the working electrode. An Ag wire dipped in a tube containing BMIM·PF_6, P14·tfsa, or emim·tfsa, and which was separated from the test solution by a glass frit, was used as a quasi-reference electrode in studies employing bulk ionic liquids. The potential of this quasi-reference electrode was then calibrated against that of the IUPAC recommended $[Co(Cp)_2]^{+/0}$ process using a 1 mM $[Co(Cp)_2][PF_6]$ solution ($Co(Cp)_2$ = cobaltocene) as an internal reference.[16] For voltammetric measurements in thin layer ionic liquids in contact with aqueous electrolyte solution, Ag/AgCl (3 M NaCl) was used as the reference electrode.

Similar to the case with other neural organometallic compounds,[11a−d] the dissolution kinetic of DMFc in BMIM·PF_6 is extremely slow. To prepare a 2 mM BMIM·PF_6 solutions of DMFc, the solvent containing solid DMFc was left in an ultrasonic cleaner for ca. 3 h at 40 °C.

To prepare a microparticle modified electrode, a few milligrams of solid compounds was placed on weighing paper. The GC electrode was then pressed onto the paper substrate and rubbed over the solid so that some of the microcrystalline solid adhered to the electrode surface. Typically, on a 1 mm diameter electrode, the equivalent of a solid layer containing microgram quantities of sample was achieved by this method.

After preparation as described above, the chemically modified electrode was placed directly in contact with ionic liquid solution. Alternatively, it was coated with a layer of ionic liquid[11b] (ca. 1 μL for a thick layer and much less than 1 μL for a thin layer) prior to being placed in contact with the conventional 1−2 mL volume of aqueous electrolyte solutions. The basic principles relevant to the latter technique that involves formation of electrode/adhered material/ionic liquid/aqueous electrolyte interfaces have been described in detail elsewhere[11b] and resemble those used in studies of electron transfer reactions across immiscible organic solvent/aqueous electrolyte interfaces as pioneered by Anson and co-workers.[17] The schematic diagram shown in Figure 1 provides a representation of the working electrode configuration and interfaces present in three different configurations. Prior to the attachment of solid, the GC working electrode was polished with a

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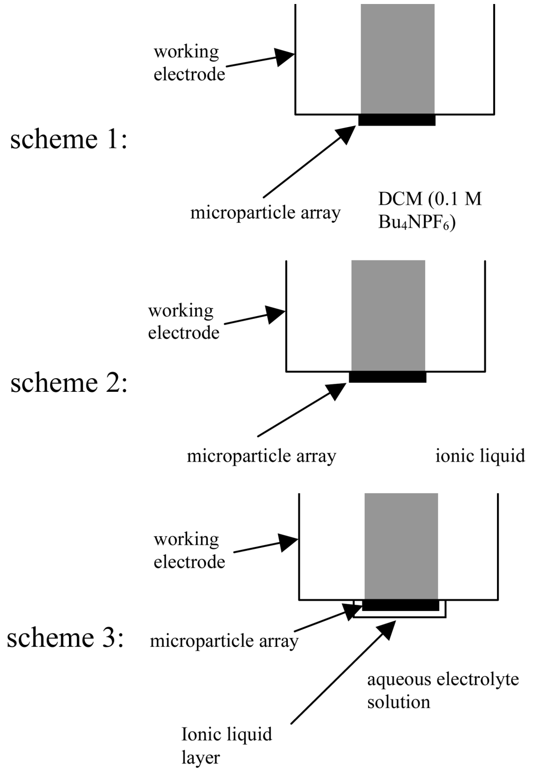

Figure 1. Schematic illustration of the different forms of chemically modified GC electrode/solution interfaces used in this study. Scheme 1: microparticle array in contact with dichloromethane (electrolyte) media. Scheme 2: microparticle in contact with ionic liquid. Scheme 3: microparticle/ionic liquid/aqueous electrolyte configuration.

0.3 μm Al_2O_3 (Buehler) slurry, washed successively with water and acetone, and finally dried with tissue paper.

All experiments were conducted at a temperature of 20 ± 1 °C, and solutions were degassed with high-purity nitrogen for at least 5 min prior to undertaking voltammetric measurements.

Results and Discussion

Voltammetry of Dissolved Oxidized DPFc$^+$ and Its Derivatives in Dichloromethane. Direct measurements of the reversible DPFc(dissolved) $\leftrightarrows$ DPFc$^+$(dissolved) + e$^-$ oxidation process are not possible because of the insolubility of DPFc and its derivatives in most media. However, the oxidized DMFc$^+$ forms of the compounds are soluble in nonpolar organic solvents such as dichloromethane (DCM). Consequently, initial voltammetric data in this paper are reported on the reduction DPFc$^+$(dissolved) using solutions prepared quantitatively by the reaction

$$\text{DPFc(solid)} + \text{NO}^+ \rightarrow \text{DPFc}^+\text{(dissolved)} + \text{NO}\uparrow \quad (1)$$

in DCM (0.1 M Bu_4NPF_6).

In principle, the electrochemical reduction of DMFc$^+$ and derivatives in DCM would be expected to follow the

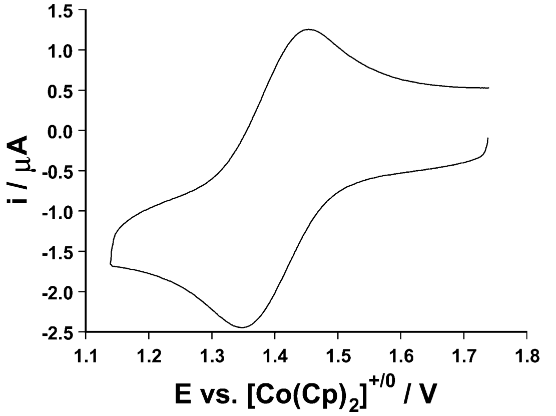

Figure 2. Cyclic voltammogram of 0.5 mM Br_2DPFc^+ dissolved in DCM (0.1 M Bu_4NPF_6) at a 1.5 mm diameter GC electrode (v = 0.2 V s^{-1}).

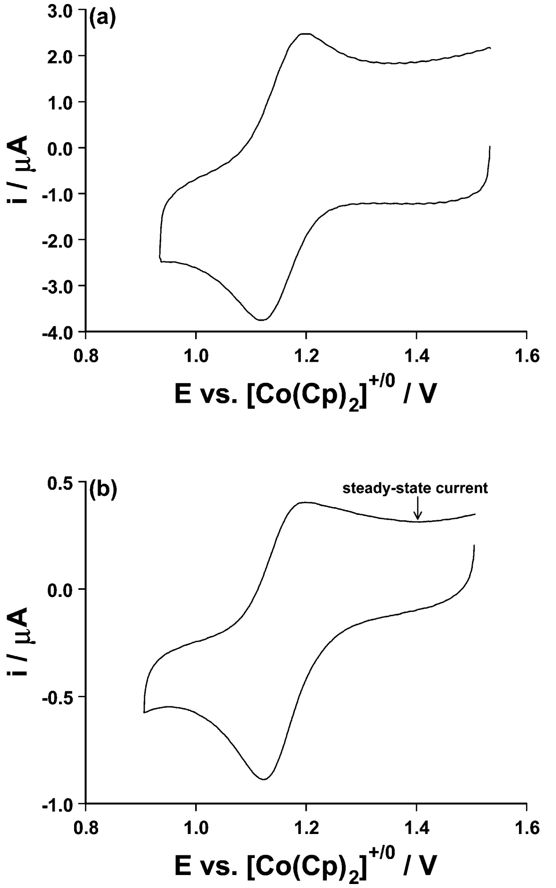

Figure 3. Cyclic voltammograms of 0.25 mM $Me_{10}DPFc^+$ dissolved in DCM (0.1 M Bu_4NPF_6) at a 1.5 mm diameter GC electrode (v = 1 (a) and 0.1 (b) V s^{-1}).

reaction scheme

$$\begin{tikzcd} \text{DPFc}^+\text{(dissolved)} + \text{e}^- \arrow[r, shift left, harpoon] & \text{DPFc(dissolved)} \arrow[l, shift left, harpoon] \arrow[d] \\ & \text{DPFc(solid)} \end{tikzcd} \quad (2)$$

However, if the rate of the DPFc(dissolved) → DPFc(solid) process is slow on the voltammetric time scale, then the simpler

$$\text{DPFc}^+\text{(dissolved)} + \text{e}^- \leftrightarrows \text{DPFc(dissolved)} \quad (3)$$

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Table 2. $E^{0'}$ Values Obtained by Cyclic Voltammetry for the One-Electron Reduction of $DPFc^+$ and Derivatives Dissolved in DCM (0.1 M Bu_4NPF_6) at a Glassy Carbon Electrode

	$DPFc^+$	$Me_{10}DPFc^+$	Me_6DPFc^+	Me_2DPFc^+	$Ethin_2DPFc^+$	Br_2DPFc^+
$E^{0'}$/V vs $[Co(Cp)_2]^{+/0}$	1.310	1.160	1.200	1.270	1.340	1.400
$E^{0'}$/V vs $Fc^{0/+}$	−0.040	−0.190	−0.150	−0.080	−0.010	0.050

process would be detected. Under these circumstances, the reversible potential ($E^{0'}$) for the reaction in eq 3 can be readily obtained.

Figure 2 shows a cyclic voltammogram for the $Br_2DPFc(DCM)^{+/0}$ process obtained via reduction of $Br_2DPFc(DCM)^+$ dissolved in DCM (0.1 M Bu_4NPF_6). This voltammogram exhibits all the characteristics expected for a solution phase electrochemically reversible process. Thus, the peak current for the reduction component of the process I_p^{red} depends linearly on the square root of the scan rate ($v = 0.05$ to 1 V s^{-1}) and the magnitude of the ratio of peak current for the reduction and oxidation (I_p^{ox}), I_p^{red}/I_p^{ox}, is unity. A midpoint potential, E_m, of 1.400 ± 0.005 V vs $[Co(Cp)_2]^{+/0}$ was obtained from the average of the reduction E_p^{red} and oxidation E_p^{ox} peak potentials $[(E_p^{red} + E_p^{ox})/2]$. As expected for a reversible process, E_m is independent of scan rate (0.05 to 1 V s^{-1}) and hence provides an excellent approximation of $E^{0'}$. The peak-to-peak separation, ΔE_p, value of 90 mV at a scan rate of 0.2 V s^{-1} is larger than the theoretically expected value of 56 mV at 20 °C.[18] However, the known reversible process for oxidation of ferrocene exhibits a similar ΔE_p value under the same conditions. Consequently, ΔE_p broadening is attributed to the presence of an uncompensated resistance in the high-resistance DCM media. Thus, reduction of Br_2DPFc^+ under voltammetric conditions is consistent with the simple reaction Br_2DPFc^+(dissolved) + $e^- \leftrightarrows$ Br_2DPFc(dissolved) for which $E^{0'} = 1.400 \pm 0.005$ V vs $[Co(Cp)_2]^{+/0}$ or 0.050 ± 0.005 V vs $Fc^{0/+}$.

Other derivatives of $DPFc^+$ exhibit reversible reductive voltammetry analogous to that for $[Br_2DPFc]^+$, with the notable exception of $Me_{10}DPFc$. In the case of a 0.25 mM solution of $[Me_{10}DPFc]^+$, only at scan rates of greater than 1 V s^{-1} (Figure 3a) is a simple reversible $Me_{10}DPFc^+$(dissolved) + $e^- \leftrightarrows$ $Me_{10}DPFc$(dissolved) process detected. The $E^{0'}$ value of 1.160 ± 0.005 V vs $[Co(Cp)_2]^{+/0}$ obtained under these conditions means that $[Me_{10}DPFc]^+$ is easier to reduce than $[Br_2DPFc]^+$ by 240 mV so that a significant substituent effect is evident. At slower scan rates and for a concentration of 0.25 mM, the voltammetry is more complex. Thus, at a scan rate of 0.1 V s^{-1}, an almost potential-independent current is observed at potentials more positive than E_p^{ox} (see Figure 3b) in the reverse or oxidative potential sweep direction. Furthermore, the shape of the oxidation component is no longer that expected for a (planar) diffusion-controlled process. This close to potential-independent component also is detected upon repetitive cycling of the potential at a scan rates of 0.2 V s^{-1} but is less evident when the concentration of $Me_{10}DPFc^+$ is decreased to 0.1 mM. It would seem that under slow scan rate conditions, reduction of $Me_{10}DPFc^+$(dissolved) occurs as in eq 3 to give insoluble $Me_{10}DPFc$, which partially blocks the electrode surface, thereby giving rise to an array of pinholes. Voltammetry at partially blocked surfaces or pinholes gives rise to radial diffusion and hence a steady-state (potential-independent) component.[19]

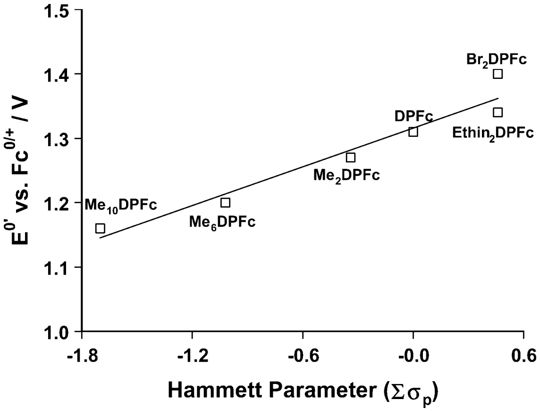

Figure 4. Linear relationship between $E^{0'}$ and the Hammett substituent parameter for decaphenylferrocene and designated derivatives.

$$\begin{tikzcd} \mathrm{Me_{10}DPFc^+(DCM)} + e^- \arrow[r, shift left] & \mathrm{Me_{10}DPFc(DCM)} \arrow[l, shift left] \arrow[d, "\text{precipitation/adsorption and formation of partially blocked surface}"] \\ & \mathrm{Me_{10}DPFc(surf)} \end{tikzcd} \qquad (3)$$

$E^{0'}$ values found for the $DPFc^+$(dissolved) + $e^- \leftrightarrows$ DPFc(dissolved) process are summarized in Table 2. Using the $E^{0'}$ value for the unsubstituted DPFc of 1.310 V vs $[Co(Cp)_2]^{+/0}$ as a reference point reveals that progressive substituation of a Me group onto the phenyl ring makes the cations easier to reduce (Me_xDPFc harder to oxidize). Conversely, substitution by Br makes reduction of the cation more difficult (oxidation of Br_2DPFc easier). These substituent effects are as expected on the basis of the electron-withdrawing effect of Br and electron-donating influence of the Me group. The substituent effect found in the case of $Ethin_2DPFc$ is relatively small. Hammett (σ_p) substituent parameters are calculated from literature data[20] (for $Fe(C_5H_n$-$(C6H4R)_{5-n})_2$: R = H, $\sigma_p = 0.0$; R = Br, $\sigma_p = 0.23$; R = Me, $\sigma_p = -0.34$; R = ethyne, $\sigma_p = 0.23$). The expected linear relationship between $E^{0'}$ and $\sum\sigma_p$ ($\sum\sigma_p$ is calculated as $(5 - n)\sigma_p$ in the present case) is obtained, as shown in Figure 4.

Voltammetric Oxidation of Adhered Microparticles of DPFc and Derivatives in Contact with DCM. Since DPFc and its derivatives are insoluble in DCM, it is possible to study the voltammetry of microparticles of these compounds adhered to a GC electrode surface in contact with DCM (0.1 M Bu_4NPF_6). Voltammograms obtained with microparticles of adhered DPFc, Me_2DPFc, Me_6DPFc, or $Ethin_2DPFc$ all exhibit

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the following characteristics. In the initial cycle of the potential, a large oxidation peak current is detected at potentials that are considerably more positive than $E^{0'}$. In contrast, the significantly smaller reduction component has a peak potential that occurs at the value expected for dissolved DPFc^+. The reduction component also exhibits many other characteristics expected for a solution phase, diffusion-controlled, one-electron-transfer process. In the second and subsequent cycles of the potential, the large oxidation peak current is replaced by a much smaller limiting current. In contrast, the reduction process remains at the same potential. However, the peak current for reduction and the oxidative limiting current both progressively decrease in magnitude with cycling of the potential.

Figure 5a illustrates the particular case for voltammetric oxidation of adhered microparticles of $\mathrm{Me_2DPFc}$. A close relationship with cyclic voltammograms obtained for reduction of $\mathrm{Me_{10}DPFc^+(DCM)}$ (Figure 3) is detected when both experiments are examined under conditions of repetitive cycling. This analogous behavior suggests that oxidation of DPFc(surf) to $\mathrm{DPFc^+(surf)}$ is followed by dissolution to give $\mathrm{DPFc^+(DCM)}$. In turn, reduction of $\mathrm{DPFc^+(DCM)}$ to DPFc(DCM) is followed by its reprecipitation, giving rise to an electrode surface containing solid DPFc, in a film format that allows the process $\mathrm{DPFc^+(dissolved)} + e^- \leftrightarrows \mathrm{DPFc(dissolved)}$ to occur in second and subsequent potentials at pinholes of a bare GC electrode. A reaction scheme consistent with the voltammetric oxidation of an array of microparticles of DPFc is summarized in eq 4.

$$\begin{tikzcd}
\mathrm{DPFc(surf)} + \mathrm{PF_6^-(DCM)} \arrow[r, shift left] & \mathrm{[DPFc][PF_6](surf)} + e^- \arrow[l, shift left] \arrow[d, "\text{dissolution}"] \\
\mathrm{DPFc(DCM)} \arrow[u, "\text{reprecipitation in the form of a film containing pinholes}"] \arrow[r, shift left] & \mathrm{DPFc^+(DCM)} + e^- + \mathrm{PF_6^-(DCM)} \arrow[l, shift left]
\end{tikzcd} \tag{4}$$

In the case of oxidation of microparticles of $\mathrm{Br_2DPFc}$, cyclic voltammograms (Figure 5b) exhibit many of the characteristics of a solution phase, diffusion-controlled, one-electron-transfer process even in the first cycle of the potential. However, a rapid peak current decay accompanies cycling of the potential. In this case, oxidation of $\mathrm{Br_2DPFc(solid)}$ rapidly leads to formation of $\mathrm{Br_2DPFc^+(DCM)}$, which is then reduced to $\mathrm{Br_2DPFc(DCM)}$, which remains soluble (at least in the region of the electrode surface rather than reprecipitating on the electrode surface) on the voltammetric time scale. Equation 5 describes the oxidation of microparticles of $\mathrm{Br_2DPFc(DCM)}$.

$$\begin{tikzcd}
\mathrm{Br_2DPFc(surf)} + \mathrm{PF_6^-(DCM)} \arrow[r, shift left] & \mathrm{[Br_2DPFc][PF_6](surf)} + e^- \arrow[l, shift left] \arrow[d, "\text{dissolution}"] \\
\mathrm{Br_2DPFc(DCM)} \arrow[r, shift left] & \mathrm{Br_2DPFc^+(DCM)} + e^- + \mathrm{PF_6^-(DCM)} \arrow[l, shift left]
\end{tikzcd} \tag{5}$$

For oxidation of $\mathrm{Me_{10}DPFc}$, two well-resolved processes (labeled 1 and 2 in Figure 5c) are exhibited in all cycles of the potential with E_m values of 1.150 and 1.295 V vs $[\mathrm{Co(Cp)_2}]^{+/0}$. The E_m value for process 1 is very close to the $E^{0'}$ value of 1.160 V established for the $\mathrm{Me_{10}DPFc^{+/0}(DCM)}$ reaction, as are many of the other voltammetric characteristics associated with this solution phase process. Consequently, process 1 is assigned to the reaction scheme in eq 6. The second process is then logically assigned to a fully solid-state process (eq 7), the implication being that the very high local concentration of the dissolved $\mathrm{Me_{10}DPFc^+}$ prevents complete dissolution of $[\mathrm{Me_{10}DPFc}][\mathrm{PF_6}]$, at least on the voltammetric time scale.[9b]

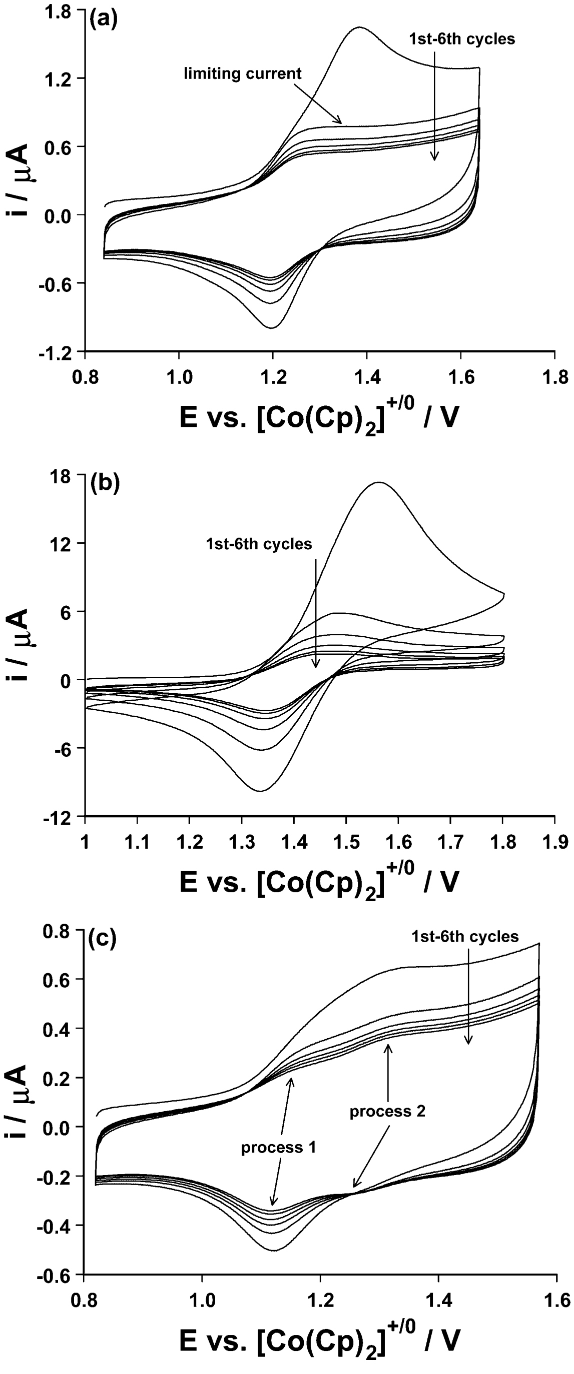

Figure 5. Cyclic voltammograms obtained at a scan rate of 0.2 V s^{-1} when microparticles of (a) $\mathrm{Me_2DPFc}$, (b) $\mathrm{Br_2DPFc}$, and (c) $\mathrm{Me_{10}DPFc}$ adhered to a 1.5 mm diameter GC electrode are in contact with DCM (0.1 M $\mathrm{Bu_4NPF_6}$).

E_m values for the first oxidation process are summarized in Table 3 and in all cases are close to the $E^{0'}$ values established for the $\mathrm{DPFc^{+/0}(DCM)}$ process.

Voltammetric Studies with Ionic Liquids. The equivalence of data obtained from adhered organome-

$$\begin{tikzcd}
\mathrm{Me_{10}DPFc(surf)} + \mathrm{PF_6^-(DCM)} \arrow[r, shift left] \arrow[r, shift right, leftarrow] & {[\mathrm{Me_{10}DPFc}][\mathrm{PF_6}]\mathrm{(surf)}} + e^- \arrow[d, "\text{dissolution}"] \\
\mathrm{Me_{10}DPFc(DCM)} \arrow[r, shift left] \arrow[r, shift right, leftarrow] & \mathrm{Me_{10}DPFc^+(DCM)} + e^- \\
 & + \\
 & \mathrm{PF_6^-(DCM)}
\end{tikzcd} \qquad (6)$$

$$\mathrm{Me_{10}DPFc(surf)} + \mathrm{PF_6^-(DCM)} \rightleftharpoons [\mathrm{Me_{10}DPFc}][\mathrm{PF_6}]\mathrm{(surf)} + e^- \qquad (7)$$

tallic microparticles and dissolved compound has been reported in the studies involving ionic liquids when the product is thermodynamically soluble and dissolves rapidly.[11] However, in this case, DPFc and derivatives are very insoluble in the ionic liquids and the oxidized forms are only sparingly soluble. The latter feature was ascertained by oxidation of DPFc and derivatives by a slight molar excess of $\mathrm{NOPF_6}$. Consequently, only the voltammetry of adhered solid could be obtained in ionic liquid studies.

Voltammetry of DPFc and $[\mathrm{DPFc^+}][\mathrm{BF_4^-}]$ Microparticles Adhered to an Electrode in Contact with BMIM·$\mathrm{PF_6}$. Voltammetric oxidation of DPFc and reduction of $[\mathrm{DPFc^+}][\mathrm{BF_4^-}]$ microparticles adhered to a GC electrode surface have been studied using the electrode/solid/BMIM·$\mathrm{PF_6}$ configuration shown in Figure 1. Voltammograms obtained in the first cycle of potential exhibit only small currents. In contrast, voltammograms obtained for second and subsequent cycles are well-defined and essentially constant for at least 20 cycles of the potential. Figures 6a and 7a show the second cycle of the potential when microparticles of DPFc or $[\mathrm{DPFc^+}][\mathrm{BF_4^-}]$, respectively (adhered to a GC electrode), are in contact with bulk BMIM·$\mathrm{PF_6}$. Similar voltammetric profiles are obtained when the solids are adhered to Pt or Au electrodes. Furthermore, voltammograms (Figures 6b and 7b) obtained with a modified GC electrode coated with a thin or thick layer of ionic liquid interfaced to an aqueous (0.1 M $\mathrm{KPF_6}$) electrolyte (Figure 1) are essentially indistinguishable from those obtained when the electrode is in contact with bulk BMIM·$\mathrm{PF_6}$.

Scan rate (0.02 to 1 V $\mathrm{s^{-1}}$)-independent ΔE_p and peak widths at half-height, $W_{1/2}$, values detected in cyclic voltammograms (Figures 6 and 7) are significantly larger than expected for either fully dissolved or fully surface-confined processes. The peak current dependence on the scan rate is intermediate between linear and square root and hence does not fully comply with theoretical predictions for either of the fully dissolved or surface-confined cases. These voltammetric features resemble those encountered for the DCM situation with adhered particles of $\mathrm{Me_{10}DPFc}$, which implies that two unresolved processes are present (eqs 8 and 9). Cyclic voltammograms for the reduction of TCNQ (TCNQ = 7,7,8,8-tetracyanodimethylquinone) also exhibit two well-resolved analogous processes, in addition to a dissolved $\mathrm{TCNQ^{0/-}}$(ionic liquid) process.[9b] In the present case, the dissolved DPFc(ionic liquid)$^{0/+}$ process is not detected, presumably because of the low solubility of both DPFc and $\mathrm{DPFc^+}$ in BMIM·$\mathrm{PF_6}$.

$$\begin{tikzcd}
\mathrm{DPFc(surf)} + \mathrm{PF_6^-(ionic\ liquid)} \arrow[r, shift left, "\text{3 phase junction}"] \arrow[r, shift right, leftarrow] & {[\mathrm{DPFc}][\mathrm{PF_6}]\mathrm{(surf)}} + e^- \arrow[d, "\text{dissolution}"] \\
\mathrm{DPFc(ionic\ liquid)} - e^- \arrow[u] \arrow[r, shift left] \arrow[r, shift right, leftarrow] & \mathrm{DPFc^+(ionic\ liquid)} \\
 & + \\
 & \mathrm{PF_6^-(\ ionic\ liquid)}
\end{tikzcd} \qquad (8)$$

$$\begin{tikzcd}
\mathrm{DPFc(surf)} + \mathrm{PF_6^-(\ ionic\ liquid)} \arrow[r, shift left, "\text{3 phase junction}"] \arrow[r, shift right, leftarrow] & {[\mathrm{DPFc}][\mathrm{PF_6}]\mathrm{(surf)}} + e^- \arrow[d, shift left, leftarrow] \arrow[d, shift right] \\
 & {[\mathrm{DPFc}][\mathrm{PF_6}]\mathrm{(bulk\ adhered\ solid)}}
\end{tikzcd} \qquad (9)$$

Voltammetry of DPFc and Derivatives in Contact with Ionic Liquids. The shapes of cyclic voltammograms obtained with adhered microparticles of DPFc and derivatives in contact with BMIM·$\mathrm{PF_6}$, emim·tfsa, and P14·tfsa are compound and ionic liquid de-

Table 3. Comparison of E_m (vs $[\mathrm{Co(Cp)_2}]^{+/0}$) Values Obtained from Voltammograms When Microparticles of DPFc and Its Derivatives Are Adhered onto a GC Electrode Surface That Is Then Placed in Contact with DCM (0.1 M $\mathrm{Bu_4NPF_6}$) and $E^{0\prime}$ (vs $[\mathrm{Co(Cp)_2}]^{+/0}$) Values for $[\mathrm{DPFc}]^{+/0}$(DCM) Processes

	DPFc	$\mathrm{Me_{10}DPFc}$	$\mathrm{Me_6DPFc}$	$\mathrm{Me_2DPFc}$	$\mathrm{Ethin_2DPFc}$	$\mathrm{Br_2DPFc}$
E_m/V	1.320	1.150	1.210	1.290	1.350	1.420
$E^{0\prime}$/V	1.310	1.160	1.200	1.270	1.340	1.400

Table 4. Peak and Midpoint Potential Values (vs $[\mathrm{Co(Cp)_2}]^{+/0}$) Obtained in Cyclic Voltammetric Studies When Microparticles of DPFc and Its Derivatives Are Adhered to a 1 mm Diameter GC Electrode in Contact with an Ionic Liquid (v = 0.1 V $\mathrm{s^{-1}}$)

	ionic liquid											
	BMIM·$\mathrm{PF_6}$				emim·tfsa				P14·tfsa			
	E_p/mV				E_p/mV				E_p/mV			
compound	ox.	red.	E_m/mV	ΔE_p/mV	ox.	red.	E_m/mV	ΔE_p/mV	ox.	red.	E_m/mV	ΔE_p/mV
DPFc	1527	1410	1469	117	1423	1410	1417	13	1500	1360	1430	140
[DPFc][$\mathrm{BF_4}$]	1527	1410	1469	117	1426	1410	1418	16	1510	1360	1435	150
$\mathrm{Me_{10}DPFc}$	1218	1211	1215	107	1425	1389	1407	36	1288	1170	1229	118
	1544[a]	1330[a]	1437	214								
$\mathrm{Me_6DPFc}$	1490	1292	1391	198	1263	1244	1254	19	1413	1363	1388	50
					1433[a]	1395[a]	1414	38	1550[a]	1534[a]	1542	16
$\mathrm{Me_2DPFc}$	1415	1366	1391	49	1450	1293	1372	157	1420	1320	1370	100
									1622[a]			
$\mathrm{Ethin_2DPFc}$	1408	1319	1364	89	1440	1360	1400	80	1567	1494	1531	73
$\mathrm{Br_2DPFc}$	1509	1429	1469	80	1553	1425	1489	128	1730	1537	1634	193

[a] Two resolved processes detected.

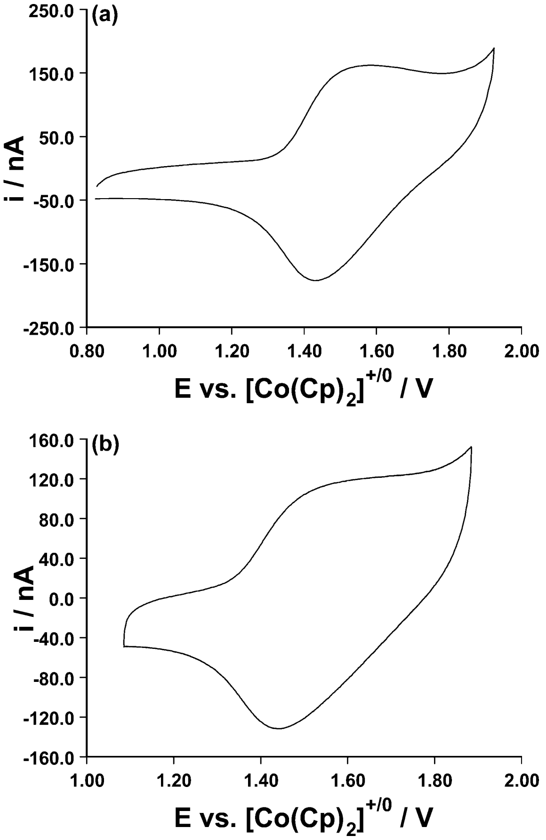

Figure 6. Cyclic voltammograms of (a) DPFc microparticles adhered to a 1 mm diameter GC electrode ($v = 0.1$ V s^{-1}) in contact with bulk BMIM·PF_6 (scheme 2, Figure 1) and (b) as for (a) but with the microparticles being coated with a thin layer of BMIM·PF_6 prior to being placed in contact with aqueous (0.1 M KPF_6) electrolyte solution (scheme 3, Figure 1).

pendent. For example, when DPFc derivatives are adhered to a GC electrode surface in contact with P14·tfsa (Figure 8, second cycle of potential), clear evidence for partially resolved processes is obtained in the cases of oxidation of Me_6DPFc and Me_2DPFc, unresolved overlapping processes are evident in the case of Me_{10}DPFc, and a single essentially reversible process is found in the cases of $Ethin_2$DPFc and Br_2DPFc.

Peak potential data obtained at a scan rate of 0.1 V s^{-1} for oxidation of DPFc and derivatives in contact with the three ionic liquids of interest in these studies are summarized in Table 4. All data are essentially independent of scan rate, over the range 0.02 to 1 V s^{-1}, and in all cases the peak height dependence on the scan rate is intermediate between linear and square root. Examples involving observation of two well-resolved peaks (e.g., data as in Figures 8b and 8c) are highlighted in Table 4. These cases, as well as those where broad peaks are detected, are attributed to the coexistence of two reaction schemes of the kind summarized in eqs 8 and 9. Also noteworthy is the fact that ΔE_p is significantly less than the theoretically predicted value of 56 mV for a solution phase one-electron reversible process at 20 °C[18] for some compound-ionic liquid combinations. Ideal thin film, fully surface-confined, reversible voltammetry would exhibit a ΔE_p value of zero, so that “thin layer” type behavior probably contributes to some voltammetric responses.

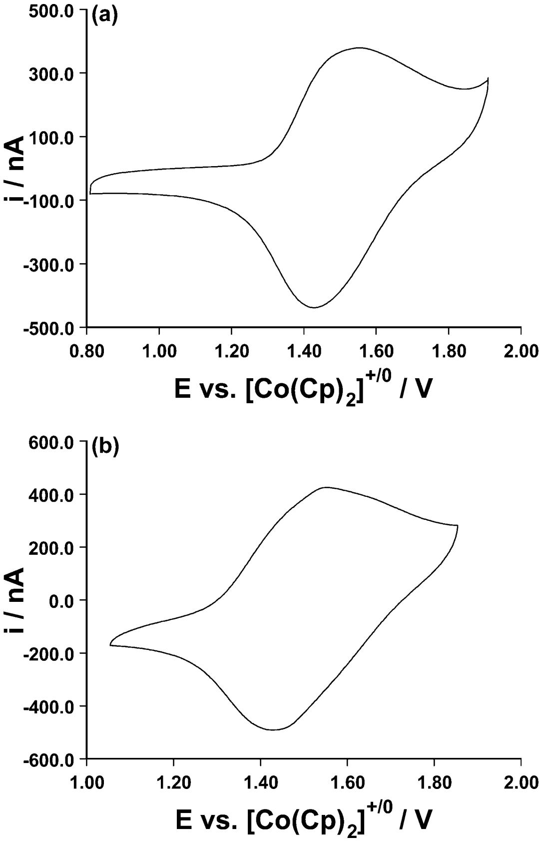

Figure 7. Cyclic voltammograms of (a) $[DPFc^+][PF_6^-]$ microparticles adhered to a 1 mm diameter GC electrode ($v = 0.1$ V s^{-1}) in contact with bulk BMIM·PF_6 (scheme 2, Figure 1) and (b) as for (a) but with the microparticles being coated with a thin layer of BMIM·PF_6 prior to being placed in contact with aqueous (0.1 M KPF_6) electrolyte solution (scheme 3, Figure 1).

E_m values, where converted to the $[Co(Cp)_2]^{+/0}$ scale, are not highly ionic liquid dependent (Table 4), but are generally more positive (less than 200 mV) than $E^{0'}$ values obtained in dichloromethane (Table 2) or when microparticle-modified electrodes are placed in contact with DCM (Table 3). It also may be noted that cyclic voltammograms of adhered DPFc (or $DPFc^+BF_4^-$) covered by a thin layer of either emim·tfsa or P14·tfsa in contact with 0.1 M KPF_6 aqueous solution (saturated with appropriate ionic liquid) are indistinguishable from those obtained when the microparticle array is directly in contact with the bulk ionic liquid. This result implies that the thin layer method (Figure 1, scheme 3) can be generally applied to obtain the voltammetric characteristics of an adhered solid in contact with ionic liquid, as supported by data available in a previous study.[11b]

Voltammetry of Adhered Fc, $[Fc^+][PF_6^-]$, and DMFc Microparticles. The voltammetry of Fc in BMIM·PF_6 has been reported.[11d] In contrast to the situation prevailing with DPFc or [DPFc][BF_4] (Figures 6 and 7), voltammetric characteristics when Fc- or $[Fc^+]$-$[PF_6^-]$-modified electrodes are placed in contact with BMIM·PF_6 may be indistinguishable from those obtained for a reversible diffusion-controlled system with an $E^{0'}$ value of 1334 ± 5 mV vs $[Co(Cp)_2]^{+/0}$ (Figures 9a and 9b) because of the rapid dissolution of Fc^+ and absence of reprecipitation of Fc[11d] (Fc and [Fc][PF_6] are moderately soluble in BMIM·PF_6). Importantly, the peak currents in experiments shown in Figure 9 at a

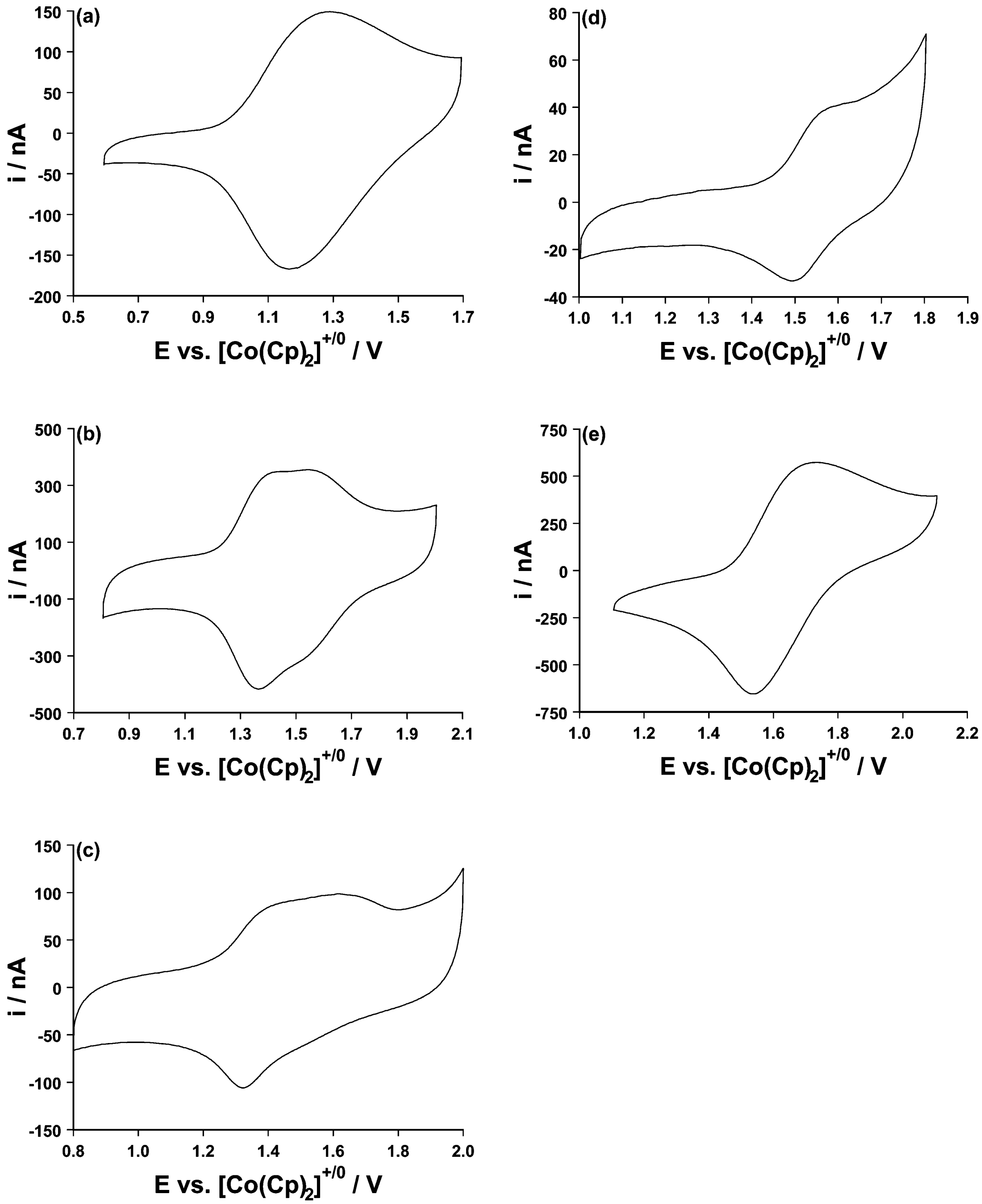

Figure 8. Cyclic voltammograms obtained when microparticles of DPFc derivatives ($v = 0.1$ V s^{-1}) are adhered to a GC electrode in contact with P14·tfsa (scheme 2, Figure 1) for (a) Me$_{10}$DPFc, (b) Me$_6$DPFc, (c) Me$_2$DPFc, (d) Ethin$_2$DPFc, and (e) Br$_2$DPFc.

50 μm diameter Pt microelectrode are of comparable magnitude to those found for DPFc and DPFc$^+$ (Figures 6 and 7) at a much larger 1 mm diameter electrode, implying that the high solubility of Fc relative to DPFc is a significant factor.

Studies were also undertaken with DMFc, which has an intermediate level of solubility in BMIM·PF$_6$. When DMFc is dissolved in BMIM·PF$_6$, a reversible, DMFc(ionic liquid) $\rightleftharpoons$ DMFc$^+$(ionic liquid) + e$^-$ process is detected with an $E^{0'}$ value of 0.856 V vs [Co(Cp)$_2$]$^{0/+}$ or −0.478 V vs Fc$^{0/+}$ (Figure 10a). This potential may be slightly less negative than found in DCM (−0.544 V vs Fc$^{0/+}$) or acetonitrile (−0.504 V vs Fc$^{0/+}$).[21] However, voltammograms for oxidation of DMFc (dissolution in BMIM·PF$_6$ is kinetically slow) microparticles adhered to a 1 mm GC electrode surface in contact with BMIM·PF$_6$ exhibit many of the characteristics reported for oxidation of microparticles of DPFc. Thus, the initial oxidation process (labeled process a in Figure 10b) occurs at a more positive potential than $E^{0'}$. Additionally, the peak current decreases on cycling of the potential, as expected if dissolution of DMFc$^+$(solid) is rapid. In contrast with the voltammogram obtained from microparticles of DPFc, a new oxidation process (process b in Figure 10b) is detected in second and subsequent cycles of potential at a potential around 0.87 vs [Co(Cp)$_2$]$^{0/+}$ and is assigned to the oxidation of dissolved DMFc (DMFc$^+$ is more soluble than DPFc$^+$ in BMIM·PF$_6$). The key processes in the voltammetric

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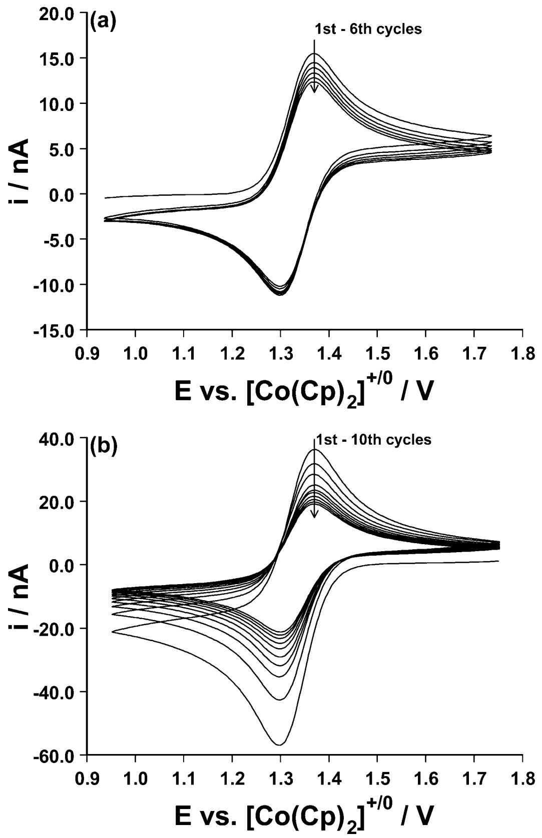
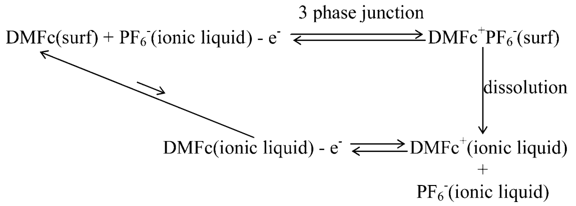


Figure 9. Voltammograms obtained on repetitive cycling of the potential at a scan rate of 0.1 V s^{-1} when an array of solid Fc (a) or [Fc][PF_6] (b) microparticles are adhered to a 50 μm diameter Pt disk electrode that is placed in contact with BMIM·PF_6.

oxidation of microparticles of DMFc therefore can be represented by eq 10.



(10)

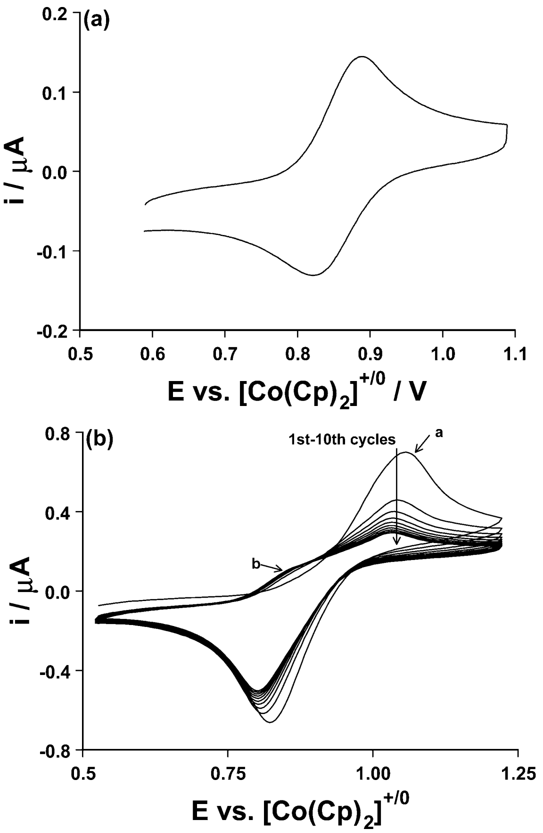


Figure 10. Cyclic voltammogram at a 1 mm diameter GC electrode ($v = 0.1$ V s^{-1}) for (a) DMFc (2 mM) dissolved in BMIM·PF_6 and (b) DMFc adhered to the electrode surface and placed in contact with BMIM·PF_6.

Conclusions

Cyclic voltammetric experiments with $DPFc^+$ and its derivatives enable $E^{0'}$ values for the solution phase $DPFc^+ + e^- \leftrightarrows DPFc$ process to be detected in DCM because the rate of precipitation of DPFc is slow on the voltammetric time scale. The expected substituent effect is observed. On the other hand, studies with solid DPFc, derivatives of DPFc, DMFc, and Fc, and their one-electron-oxidized forms adhered to an electrode surface in contact with DCM (0.1 M Bu_4NPF_6) or an ionic liquid reveal that the nature of the cyclic voltammetric response detected under these conditions is critically dependent on the solubility and the kinetics of dissolution and reprecipitation of the adhered solid in both the oxidized and reduced forms. In particular, dissolution processes may give rise to the detection of multiple reaction pathways. For example, if the dissolution of oxidized solid is both thermodynamically and kinetically favorable, $E_m = E^{0'}$. If the dissolution of the oxidized species is less favorable, but still a major pathway, E_m values obtained upon repetitive cycling of the potential may still equal the $E^{0'}$ value for the solution phase process. In contrast, for situations where both oxidized and reduced forms of the ferrocene are sparingly soluble, E_m reflects contributions from multiple reaction schemes that may involve dissolution and reprecipitation steps and conversion from thick film to thin film behavior. In these cases, the kinetics of dissolution and precipitation play an important role in determining the number of processes detected and the difference between E_m and $E^{0'}$ values.

Data obtained in this study confirm that the use of a microchemical technique in which the solid particle array on an electrode surface is covered by a thin layer of water immiscible ionic liquid in contact with aqueous electrolyte solution provide an efficient method of establishing the electrochemical behavior of adhered solids or dissolved species in ionic liquids, but via a more cost-effective approach than use of bulk ionic liquid, because only microliter volumes of expensive ionic liquids are required.

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