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Nonadditivity of Faradaic Currents and Modification of Capacitance Currents in the Voltammetry of Mixtures of Ferrocene and the Cobaltocenium Cation in Protic and Aprotic Ionic Liquids

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Abstract: Unexpected nonadditivity of currents encountered in the electrochemistry of mixtures of ferrocene (Fc) and cobaltocenium cation (Cc^+) as the PF_6^- salt has been investigated by direct current (dc) and Fourier-transformed alternating current (ac) cyclic voltammetry in two aprotic (1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate) and three protic (triethylammonium formate, bis(2-hydroxyethyl)ammonium acetate, and triethylammonium acetate) ionic liquids (ILs). The voltammetry of the individual $Fc^{0/+}$ and $Cc^{+/0}$ couples always exhibits near-Nernstian behavior at glassy carbon and gold electrodes. As expected for an ideal process, the reversible formal potentials and diffusion coefficients at 23 ± 1 °C in each IL determined from measurement on individual Fc and Cc^+ solutions were found to be independent of electrode material, concentration, and technique used for the measurement. However, when Fc and Cc^+ were simultaneously present, the dc and ac peak currents per unit concentration for the $Fc^{0/+}$ and $Cc^{+/0}$ processes were found to be significantly enhanced in both aprotic and protic ILs. Thus, the apparent diffusion coefficient values calculated for Fc and Cc^+ were respectively found to be about 25 and 35% larger than those determined individually in the aprotic ILs. A similar change in the $Fc^{0/+}$ mass transport characteristics was observed upon addition of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), and the double layer capacitance also varied in distinctly different ways when Fc and Cc^+ were present individually or in mixtures. Importantly, the nonadditivity of Faradaic current is not associated with a change in viscosity or from electron exchange as found when some solutes are added to ILs. The observation that the ^1H NMR T_1 relaxation times for the proton resonance in Cc^+ also are modified in mixed systems implies that specific interaction with aggregates of the constituent IL ionic species giving rise to subtle structural changes plays an important role in modifying the mass transport, double layer characteristics, and dynamics when solutes of interest in this study are added to ILs. Analogous voltammetric changes were not observed in studies in organic solvent media containing 0.1 M added supporting electrolyte. Implications of the nonadditivity of Faradaic and capacitance terms in ILs are considered.

1. Introduction

Traditionally, voltammetric studies have been undertaken in aqueous or organic solvent media containing about 0.1 M added supporting electrolyte. In these molecular solvent (electrolyte) media, it is assumed that the voltammetry of ferrocene ($[Fe(\eta^5\text{-}C_5H_5)_2]$ (Figure 1a), hereafter referred to as Fc) obtained from a pure solution of Fc, is not modified by addition of another solute such as the cobaltocenium cation ($[Co(\eta^5\text{-}C_5H_5)_2]^+$ (Figure 1b), hereafter referred to as Cc^+) as the PF_6^- salt. Thus, the voltammetry of the $Fc^{0/+}$ and $Cc^{+/0}$ processes are expected to be identical, irrespective of whether studies are derived from pure Fc or Cc^+ solutions or from mixtures of Fc or Cc^+. This will be true if addition of low concentrations of a solute do not modify the solvent (electrolyte) properties. This characteristic has allowed Fc and Cc^+ to be added to solutions containing other voltammetrically active species of interest and has allowed the use of the ideal $Fc^{0/+}$ and $Cc^{+/0}$ processes for reference scale calibration purposes in organic solvent (electrolyte) media.

Electrochemical studies in ionic liquids (ILs) are now very common.[1,2] In most cases, principles developed over many years for molecular solvent (electrolyte) media have been extended to the IL case. Thus, quasi-reference electrodes (QREs) in combination with in situ calibration with electrochemically

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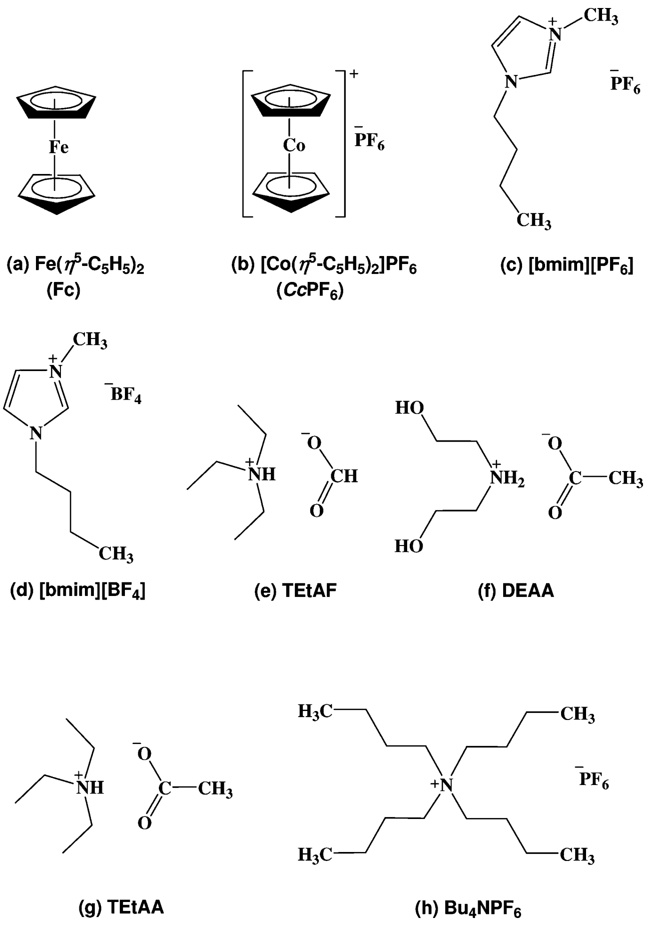

(a) $Fe(\eta^5\text{-}C_5H_5)_2$ (Fc)
(b) $[Co(\eta^5\text{-}C_5H_5)_2]PF_6$ (*Cc*PF_6)
(c) [bmim][PF_6]
(d) [bmim][BF_4]
(e) TEtAF
(f) DEAA
(g) TEtAA
(h) Bu_4NPF_6

Figure 1. Structures of the cationic and anionic components of the ionic liquids used in this study and the solutes under investigation.

reversible couples, such as Fc$^{0/+}$ or $Cc^{+/0}$ have also been seen to provide on attractive approach for the development of reference potential scales in ILs.[3−6] However, an ionic liquid plays the dual role of solvent and electrolyte and in this sense represents a different kind of medium for electrochemical studies, so care in extrapolation of concepts to the IL case is needed.

Initially, there was some concern that the Fc$^{0/+}$ process exhibited anomalous voltammetry in ILs. Thus, Brooks et al.[7a] reported nonlinear dc peak current versus Fc concentration plots in 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide. Additionally, Nagy et al.[7b] reported a concentration-dependent diffusion coefficient (*D*) for Fc in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) (Figure 1c) as did Eisele et al.[7c] in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) (Figure 1d). In view of the lack of complete agreement as to the ideality of the Fc$^{0/+}$ reference system, the $Cc^{+/0}$ process was recommended for potential calibration purposes in a range of ionic liquids.[6b] This system offers near-Nernstian behavior and exhibits a linear current versus Cc^+ concentration relationship over a wide concentration range. Subsequently, Compton and colleagues[6c] investigated in detail the voltammetry of the $Cc^{+/0}$ and Fc$^{0/+}$ processes over a wide range of concentrations and temperatures in eight ILs. They observed classical Stokes−Einstein dependence of diffusion on IL viscosity for both redox couples. Furthermore, the *D* values for the neutral and charged species were found to be independent of their concentration, indicating that both processes may be considered near-ideal for reference potential calibration processes.

Implicit in the in situ use of the Fc$^{0/+}$ and $Cc^{+/0}$ processes for potential calibration purposes is that addition of Cc^+ as the PF_6^- salt or Fc to ionic liquids does not modify the solvent (electrolyte) at a level where mass-transport processes or the double layer may be altered and hence modify the results relative to studies undertaken in their absence. However, as far as we are aware, this requirement has not yet been subjected to experimental confirmation. In this report, detailed studies on the oxidation of Fc and reduction of Cc^+ when both redox active species are simultaneously present have been undertaken in two aprotic ([bmim][BF_4] and [bmim][PF_6]) and three protic (triethylammonium formate (Figure 1e), bis(2-hydroxyethyl)-ammonium acetate (Figure 1f), and triethylammonium acetate (Figure 1g)) ionic liquids at glassy carbon (GC) and gold (Au) electrodes using both conventional dc and Fourier-transformed large-amplitude ac (FT-ac) techniques. Importantly, we show that complete additivity of Fc and Cc^+ Faradaic current applies in an organic solvent containing added supporting electrolyte, whereas this is not necessarily the case in IL media. Furthermore, we show that even addition of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (Figure 1h) modifies the voltammetry of Fc in an IL and that the double layer capacitance (C_{dl}) is not the same when both Fc and Cc^+ are simultaneously present as solutes as it is when they are individually present. The effect of the concentration on the apparent diffusion coefficients, double layer capacitance, reversible formal potential, and other aspects of the voltammetry in ILs is discussed when Fc, CcPF_6, and Bu_4NPF_6 are present in mixtures. The implications of nonadditivity of current are discussed in some detail. Finally, the NMR spectroscopic method has been applied

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to explore changes in the dynamics of the constituent IL cations and anions upon addition of Fc and $CcPF_6$ that may lead to nonadditivity of the Faradaic current and modification of the capacitance current.

2. Experimental Section

2.1. Reagents. Acetonitrile (Merck, HPLC grade, 99.9%), cobaltocenium hexafluorophosphate (Strem), ferrocene (BDH), and potassium chloride and $K_3[Fe(CN)_6]$ (Aldrich) were used as supplied by the manufacturer. High purity grade ($\geq$99.0%) 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate were purchased from Merck. Triethylammonium formate (TEtAF), bis(2-hydroxyethyl)ammonium acetate (DEAA), and triethylammonium acetate (TEtAA) were synthesized and purified according to procedures described elsewhere (also see Supporting Information).[3] All ILs were stored in a nitrogen-filled glovebox. Tetrabutylammonium hexafluorophosphate was purchased from GFS Chemicals and recrystallized twice from ethanol. Unless otherwise stated, all other reagents were of analytical grade purity, obtained from Sigma-Aldrich, and used without further purification.

2.2. Apparatus and Procedures. The glassy carbon (GC) and Au disk working electrodes were from Cypress (Cypress Systems, Lawrence, KS). Prior to each experiment, they were polished with 0.3 μm alumina (Buehler, Lake Bluff, IL) on a clean polishing cloth (Buehler), sequentially rinsed with distilled water and acetone, and then dried under nitrogen. All IL solutions were prepared inside a glovebox with stirring. Aprotic IL solutions containing mixtures of Fc and Cc^+ (as the PF_6^- salt) were prepared by adding an appropriate amount of $CcPF_6$ to Fc solutions with stirring or vice versa. Appropriate dilutions were carried out to give a range of concentrations. Other methods of preparation of these aprotic IL samples were also undertaken, but data were found to be independent of the method. Details of the preparation of Fc and Cc^+ solutions in viscous protic ILs are given in the Supporting Information.

dc cyclic voltammetric experiments were usually undertaken with a BAS100 electrochemical workstation (Bioanalytical System, West Lafayette, IN). Experiments in CH_3CN (0.1 M Bu_4NPF_6) employed a standard electrochemical cell containing a three-electrode arrangement with a Au disk working electrode, a Pt wire counter electrode, and a Ag/Ag^+ (CH_3CN, 10 mM $AgNO_3$) double junction reference electrode. Voltammetric measurements in ILs were undertaken inside a homemade nitrogen-filled glovebox, again employing a three-electrode configuration. In this case, Pt or Ag QREs were either placed directly into the IL or separated by a salt bridge filled with IL of interest. However, all potentials are reported versus the $Fc^{0/+}$ couple in order to minimize the problems associated with potential drift encountered with use of the QREs. GC (effective area = 0.0093 cm^2) or the Au (effective area = 0.0087 cm^2) disks were used as working electrodes. In studies in ILs, values of uncompensated resistance (R_u) were measured in a potential region where no Faradaic reaction occurs,[8a] using the RC time constant method available with the BAS instrument.

The working electrode effective areas were determined by measurement of the peak current obtained as a function of scan rate under linear sweep voltammetric conditions for the one-electron oxidation of Fc [1.0 mM in CH_3CN (0.1 M Bu_4NPF_6)] or reduction of $[Fe(CN)_6]^{3-}$ [1.0 mM in water (0.5 M KCl)] and use of the Randles–Sevcik equation (eq 1),[8b]

$$i_p = 0.4463nF(nF/RT)^{1/2}AD^{1/2}v^{1/2}C \qquad (1)$$

where i_p is the peak current (A), $n = 1$, A is the electrode area (cm^2), D is the diffusion coefficient of Fc (taken to be 2.3×10^{-5} cm^2 s^{-1}) or $[Fe(CN)_6]^{3-}$ (taken to be 7.6×10^{-5} cm^2 s^{-1}),[8b] C is the concentration (mol cm^{-3}), v is the scan rate (V s^{-1}), and other symbols have their usual meanings. The ionic liquid experiments were carried out in a small-volume homemade voltammetric cell which is designed to allow 100–300 μL of sample to be studied under a nitrogen environment. The water contents of all ILs were determined to lie within the range of 80–100 ppm as measured by the Karl Fisher titration method used with a model 831 Metrohm (Herisau, Switzerland) Karl Fischer coulometer. The dynamic viscosity of [bmim][BF_4] at 22 °C was measured with a Schott (Mainz, Germany) micro-Ubbelohde capillary viscometer.

A detailed description of the FT-ac cyclic voltammetric instrumentation is available elsewhere[9] and was used with the three electrode arrangements described above. Some conventional dc voltammetric experiments were carried out with the FT form of instrumentation by using a zero amplitude perturbation. The commercially available simulation software DigiSim,[10] and an in-house developed software package Monash Electrochemistry Simulator (MECSim)[11] were used to simulate the dc and ac cyclic voltammetric responses, respectively. Diffusion coefficient values were estimated by plotting the peak current obtained under linear sweep voltammetric conditions for the oxidation of Fc and reduction of Cc^+ as a function of square root of scan rate and use of the Randles–Sevcik relationship (eq 1). Four determinations of the peak current values were undertaken to obtain reported D values, which were then confirmed by comparison of simulated and experimental dc and FT-ac voltammograms. All voltammetric experiments were carried out at 23 ± 1 °C.

^{1}H NMR experiments were undertaken at 20 °C (magnetic field strength of 7.04 T) with a Varian Unity-Plus 300 MHz NMR Spectrometer. Chemical shifts were referenced to tetramethyl silane (TMS).

3. Results and Discussion

3.1. Aprotic Ionic Liquids.

3.1.1. dc Cyclic Voltammetry of Fc and Cc^+ Using Individually Prepared Aprotic IL Solutions. Initially, dc cyclic voltammograms for the oxidation of Fc and reduction of Cc^+ in [bmim][BF_4] and [bmim][PF_6] were obtained from individually prepared solutions at GC and Au electrodes. In these aprotic ILs, Fc exhibits a reversible one-electron oxidation process,[6,7]

$$\mathrm{Fc} \rightleftarrows \mathrm{Fc}^+ + e^- \qquad (2)$$

In contrast, Cc^+ exhibits two reversible one-electron reduction processes,[3,6]

$$Cc^+ + e^- \rightleftarrows Cc^0 \qquad (3)$$

$$Cc^0 + e^- \rightleftarrows Cc^- \qquad (4)$$

but only the first reduction process is considered in this study because the second reduction process has been reported to be solvent dependent.[6a] Panels a and b of Figure 2 show cyclic voltammograms obtained for the oxidation of Fc and reduction of Cc^+ in [bmim][BF_4] over a range of concentrations at the GC electrode. Well-defined $Fc^{0/+}$ and $Cc^{+/0}$ couples were

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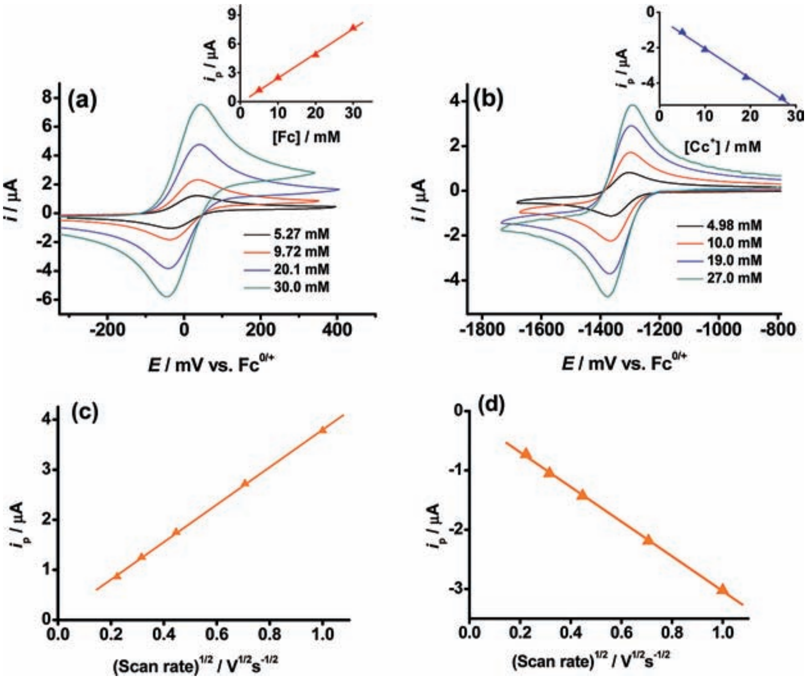

Figure 2. dc cyclic voltammograms obtained for the oxidation of Fc (a) and reduction of *Cc*$^+$ (b) at a GC electrode at 23 ± 1 °C in [bmim][BF$_4$] at a scan rate of 100 mV s^{-1} and the dependence of the peak currents for oxidation of 5.25 mM Fc (c) and reduction of 4.98 mM *Cc*$^+$ (d) on the square root of the scan rate. Insets in (a) and (b) represent the dependence of peak currents on the concentration of Fc and *Cc*$^+$, respectively.

observed, with midpoint potentials, E_m, of 0.000 and − 1346 ± 5 mV versus Fc$^{0/+}$, respectively. E_m was calculated from the average of the oxidation and reduction peak potentials and is approximately equal to the reversible formal potential $E^{\circ\prime}$. E_m values will differ from $E^{\circ\prime}$ if the *D* values of oxidized and reduced forms of Fc$^{+/0}$ and *Cc*$^{+/0}$ processes are not equal. According to Compton et al.[6c,12] *D* values for oxidized and reduced species in the *Cc*$^{+/0}$, Fc$^{+/0}$, and $O_2^{0/-}$ couples can be markedly different in ILs (up to a factor of 30 in the case of $O_2^{0/-}$), in contrast to the relatively small differences observed in aqueous or organic solvent media containing added supporting electrolyte. The insets in Figure 2a,b show the linear peak current versus concentration relationship for both Fc and *Cc*$^+$ over the concentration range of 5−30 mM in [bmim][BF$_4$]. Limitations in solubility made accurate values of higher concentrations of Fc difficult to obtain. However, *Cc*$^+$ is much more soluble, and the linear relationship for this process was maintained for *Cc*$^+$ concentrations up to 100 mM. The peak currents also are linearly proportional to the square root of the scan rate (Figure 2c,d), indicating that mass transport occurs by linear diffusion.[8b]

Quantitative details of dc cyclic voltammetric data obtained at GC and Au electrodes as a function of concentration and scan rate for both the Fc$^{0/+}$ and *Cc*$^{+/0}$ couples in [bmim][BF$_4$] are provided in Tables 1 and 2. The magnitudes of the ratio of oxidation to reduction peak current, i_p^{ox}/i_p^{red} for Fc (in Table 1), or reduction to oxidation peak current, i_p^{red}/i_p^{ox} values for *Cc*$^+$ (in Table 2), are close to unity at all electrode materials, concentrations, and scan rates examined, as expected for a chemically reversible process. The peak-to-peak separation between oxidation and reduction peak potentials, ΔE_p, obtained at low concentrations and slow scan rates for *Cc*$^+$ converges to the theoretical value of 57 mV predicted for an electrochemically reversible one-electron process at 23 °C. ΔE_p for the Fc$^{0/+}$ process converges less slowly to the ideal value of 57 mV because the current and hence iR_u drop per unit concentration for oxidation if Fc is larger than for reduction of *Cc*$^+$. Thus, the scan rate and concentration dependence of ΔE_p for both Fc$^{0/+}$ and *Cc*$^{+/0}$ processes are attributed to the presence of uncompensated resistance. The reversibility of the processes, after taking into account iR_u drop, is essentially in accordance with results provided by Sukardi et al.[6b] and Compton et al.[6c] in ILs, and confirmed by simulation that takes uncompensated resistance into account (see below).

3.1.2. Simulation of dc and ac Voltammograms When the Fc$^{0/+}$ and *Cc*$^{+/0}$ Couples Are Studied Individually in an Aprotic IL.

3.1.2.1. dc Cyclic Voltammetry. Panels a and b of Figure 3 provide a comparison of experimental and simulated dc cyclic voltammograms obtained at a Au electrode for the oxidation of Fc and reduction of *Cc*$^+$ in [bmim][BF$_4$], respectively, when either Fc or *Cc*$^+$ is present individually in the IL. Excellent agreement between experimental and simulated voltammograms was obtained over a wide range of concentrations for the Fc$^{0/+}$ and *Cc*$^{+/0}$ couples using *D* values of 8.6 × 10^{-8} and 6.1 × 10^{-8} cm^2 s^{-1}, $E^{\circ\prime}$ of 0.000 and −1351 mV, and the mechanisms described in eqs 2 and 3, respectively. As shown in Table 3, when *D* values are derived from eq 1, there is no significant variation in the *D* values of Fc and *Cc*$^+$ in the range of the concentrations examined, as also reported in refs 6c and 6b. The $E^{\circ\prime}$ values used in the simulation are similar to the E_m values of 0.000 and −1346 ± 5 mV for Fc$^{0/+}$ and *Cc*$^{+/}$, respectively. The smaller *D* values of Fc and *Cc*$^+$ obtained in [bmim][PF$_6$] relative to those in [bmim][BF$_4$] are attributed to the higher viscosity of [bmim][PF$_6$] (120 and 281 cP at 25 °C for [bmim][BF$_4$] and [bmim][PF$_6$], respectively[13]). The values of R_u needed to match simulated and experimental data were 2050 and 2150 Ω for [bmim][BF$_4$] and [bmim][PF$_6$], respectively, are in excellent agreement with the measured values of R_u obtained instrumentally of 1850 ± 200 and 2100 ± 200 Ω (see Experimental Section).

3.1.2.2. FT-ac Cyclic Voltammetry. The FT-ac cyclic voltammetric method was applied to studies of the Fc$^{0/+}$ and *Cc*$^{+/0}$

Table 1. Data Obtained by dc Cyclic Voltammetry for the Oxidation of Fc in [bmim][BF$_4$] at GC and Au Electrodes at 23 ± 1 °C

		GC electrode			Au electrode		
C_{Fc} (mM)^a	v (mV/s)^b	ΔE_p (mV)	i_p^{ox} (μA)	i_p^{ox}/i_p^{red}	ΔE_p (mV)	i_p^{ox} (μA)	i_p^{ox}/i_p^{red}
5.25	50	66	0.86	1.00	61	0.81	1.06
	100	68	1.25	1.03	66	1.17	1.06
	200	71	1.75	1.04	68	1.63	1.04
	500	78	2.72	1.03	79	2.54	1.05
	1000	87	3.78	1.05	87	3.55	1.08
9.70	50	68	1.67	1.06	64	1.59	1.02
	100	71	2.53	1.04	65	2.36	1.04
	200	78	3.28	1.05	70	3.15	1.05
	500	88	5.09	1.07	80	4.84	1.05
	1000	103	7.06	1.07	92	6.83	1.07
20.1	50	68	3.46	1.01	68	3.37	1.02
	100	79	4.85	1.02	79	4.65	1.02
	200	88	6.76	1.03	88	6.54	1.06
	500	110	10.6	1.04	100	9.88	1.05
	1000	123	14.6	1.06	110	14.1	1.06
30.0	50	78	5.50	1.04	78	5.38	1.02
	100	87	7.64	1.05	85	7.32	1.03
	200	96	10.8	1.06	95	10.2	1.03
	500	119	16.2	1.06	118	15.9	1.05
	1000	140	22.2	1.07	129	21.3	1.07

^{a} Concentration of Fc. ^{b} Scan rate.

Table 2. Data Obtained by dc Cyclic Voltammetry for the Reduction of Cc^+ in [bmim][BF$_4$] at GC and Au Electrodes at 23 ± 1 °C

		GC electrode			Au electrode		
C_{Cc^+} (mM)^a	v (mV/s)^b	ΔE_p (mV)	i_p^{red} (μA)	i_p^{red}/i_p^{ox}	ΔE_p (mV)	i_p^{red} (μA)	i_p^{red}/i_p^{ox}
4.98	50	57	−0.78	1.04	59	−0.75	1.08
	100	61	−1.11	1.03	62	−1.04	1.06
	200	60	−1.53	1.04	63	−1.45	1.07
	500	70	−2.28	1.03	65	−2.12	1.05
	1000	74	−3.21	1.01	69	−3.04	1.08
10.0	50	62	−1.54	1.03	60	−1.51	1.06
	100	66	−2.18	1.01	63	−2.11	1.04
	200	72	−3.02	1.00	70	−2.85	1.09
	500	81	−4.56	1.00	78	−4.27	1.10
	1000	92	−6.39	1.00	93	−6.05	1.12
19.0	50	66	−2.69	1.02	65	−2.65	1.07
	100	71	−3.76	1.04	70	−3.69	1.05
	200	77	−5.34	1.00	76	−5.19	1.06
	500	91	−8.35	1.01	91	−8.03	1.09
	1000	104	−11.8	1.00	102	−11.2	1.11
27.0	50	79	−3.08	1.00	73	−3.02	1.04
	100	83	−4.81	1.01	82	−4.75	1.08
	200	95	−6.84	1.00	94	−6.62	1.07
	500	116	−11.4	1.01	114	−10.9	1.05
	1000	141	−15.9	1.04	138	−15.2	1.09

^{a} Concentration of Cc^+. ^{b} Scan rate.

processes in ILs using a sine wave of frequency (*f*) 15 Hz and amplitude (ΔE) of 80 mV superimposed onto the dc waveform. Other parameters employed for these experiments are given in the figure captions. Parts c−f of Figure 3 provide well-defined fundamental and second harmonic components for the Fc$^{0/+}$ and $Cc^{+/0}$ processes in [bmim][BF$_4$] at a Au electrode. The third to sixth harmonics were also examined, but these are not displayed here. As shown in c and d of Figure 3, the background current contributes significantly to the fundamental harmonic ac component. In principle this is derived solely from the double layer capacitance. To quantify C_{dl}, this term was included in simulations available in the MECSim software package.[11] The C_{dl} value in [bmim][BF$_4$] calculated by comparing the experimental and simulated fundamental harmonic ac components at the Au electrode was 12.0 ± 0.3 μF cm^{-2} over the potential range of −360 to +340 mV when Fc is present and −760 to −1710 mV when Cc^+ is present, in the case when Fc and Cc^+ solutions were prepared individually in [bmim][BF$_4$] (other parameters are shown in the caption of Figure 3). This value of C_{dl} is an apparent one, as background current arising from surface functional groups or adventitious impurities and their Faradaic processes are neglected.[14] Thus, values of C_{dl} at a GC in particular, but also at Au electrodes, are dependent on the polishing format, the electrolyte, the potential, and the analyte.[15] Nevertheless, we obtain reproducible apparent C_{dl} values (±0.2%). In the case of the second- and higher harmonics, the background current is negligible in comparison to that arising from the Fc$^{0/+}$ and $Cc^{+/0}$ Faradaic processes (see e and f of Figure 3). This is as expected, because unlike the dc and fundamental harmonic terms, they are relatively insensitive to capacitance current.[15]

The $E^{\circ\prime}$ values again assuming equal D values for oxidized and reduced species, as calculated from the second harmonic data (e and f of Figure 3) for the Fc$^{0/+}$ and $Cc^{+/0}$ processes were 0.000 and −1345 mV, respectively, and in good agreement with those derived from dc voltammograms. The D values of 8.6×10^{-8} and 6.1×10^{-8} cm^2 s^{-1} for Fc and Cc^+ used in FT-ac simulation also agree with dc measured values of 8.6×10^{-8} and 6.2×10^{-8} cm^2 s^{-1}, respectively. The second harmonics also provide an estimate of R_u.[9b] The value used to simulate the Fc$^{0/+}$ and $Cc^{+/0}$ second harmonic processes was 2100 Ω. All these data suggest that when the Fc$^{0/+}$ and $Cc^{+/0}$ couples are studied from individually prepared solutions of Fc and Cc^+ in ILs, they behave as ideal one-electron charge-transfer

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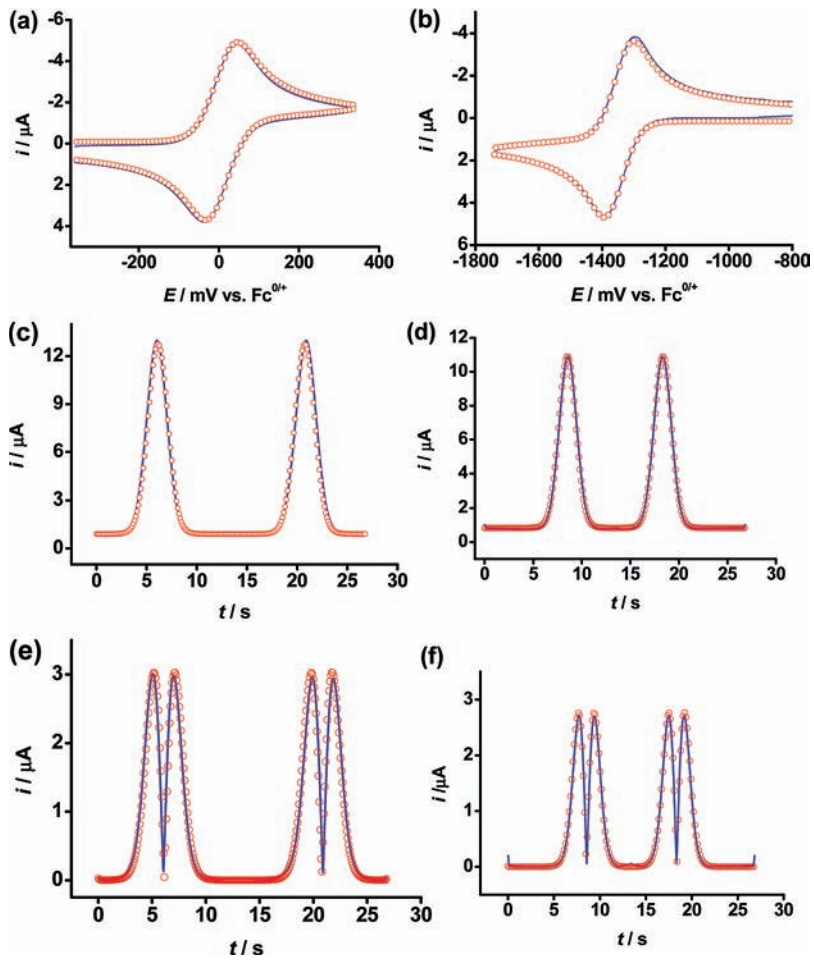

Figure 3. Comparison of experimental (—) and simulated (○) dc cyclic voltammograms obtained at 23 ± 1 °C with a Au electrode at a scan rate of 500 mV s^{-1} for the oxidation of 9.72 mM Fc (a) and reduction of 10 mM Cc^+ (b) when each process is studied individually in [bmim][BF$_4$]. The simulated dc cyclic voltammograms were calculated assuming a reversible one-electron-transfer process, and $D_{Fc} = D_{Fc^+} = 8.6 \times 10^{-8}$ cm^2 s^{-1}, $E°' = 0.000$ mV, $R_u = 2050\ \Omega$, $c = 9.72$ mM, and $v = 500$ mV s^{-1} for the Fc$^{0/+}$ and $D_{Cc^+} = D_{Cc} = 6.2 \times 10^{-8}$ cm^2 s^{-1}, $E°' = -1345$ mV, $R_u = 2050\ \Omega$, $c = 10$ mM, and $v = 500$ mV s^{-1} for the $Cc^{+/0}$ process. The simulated fundamental (c and d) and second harmonic (e and f) FT-ac cyclic voltammograms were obtained assuming the processes are reversible and using $v = 59.6$ (Fc$^{0/+}$) and 67 mV s^{-1} ($Cc^{+/0}$), $\Delta E = 80$ mV, $f = 15.01$ Hz, and $C_{dl} = 12.0\ \mu$F cm^{-2}.

Table 3. *D* Values Determined by dc Cyclic Voltammetry for the Oxidation of Fc and Reduction of Cc^+ in ILs at GC and Au Electrodes at 23 ± 1 °C

C (mM)[a]		10^8D (cm^2 s^{-1})			
		GC		Au	
Fc	Cc^+	[bmim][BF$_4$]	[bmim][PF$_6$]	[bmim][BF$_4$]	[bmim][PF$_6$]
5.25	0.00	8.60	5.62	8.68	5.75
9.70	0.00	8.54	5.59	8.61	5.64
20.1	0.00	8.72	5.68	8.59	5.60
30.1	0.00	8.67	5.72	8.67	5.65
0.00	4.98	6.12	2.68	6.15	2.64
0.00	10.0	6.07	2.57	6.12	2.47
0.00	19.0	5.88	2.38	5.95	2.29
0.00	27.0	5.93	2.32	5.96	2.44

[a] Concentration.

processes with all characteristics being close to those expected for Nernstian (reversible) processes.

3.1.3. Voltammetry of Mixtures of Fc and Cc^+ in Aprotic ILs.

3.1.3.1. dc Cyclic Voltammetry. Initially, studies were undertaken on mixtures in which concentration of both Fc and Cc^+ were ≥1 mM. Figure 4a illustrates cyclic voltammograms obtained at the GC electrode for the oxidation of 9.8 mM Fc and reduction of 10.1 mM Cc^+ in [bmim][BF$_4$]. For comparison, dc cyclic voltammograms obtained under similar conditions, but where oxidation of Fc and reduction of Cc^+ was studied individually in separate solutions, also are included in Figure 4a. Clearly, the Faradaic peak currents for both processes have increased in this particular mixed solution situation, compared with the values obtained from their individual solutions. Furthermore, the background current is significantly different for the two scenarios. Consequently, *D* values (hereafter referred to as D_{app}) derived from oxidation of Fc and reduction of Cc^+ in this mixed solution apparently have increased significantly. The estimated D_{app} values for Fc and Cc^+ using the Randles−Sevcik equation were now found to be 10.8×10^{-8} and 8.3×10^{-8} cm^2 s^{-1}, respectively in [bmim][BF$_4$]. Furthermore, (Figure 4b), excellent agreement between the experimental and simulated dc cyclic voltammograms is obtained with $D = 10.7 \times 10^{-8}$ cm^2 s^{-1} for Fc and $D = 8.2 \times 10^{-8}$ cm^2 s^{-1} for Cc^+.

If the dc cyclic voltammograms for the Fc$^{0/+}$ and $Cc^{+/0}$ couples are obtained simultaneously by scanning the potential from +440 to −1660 mV, but commencing the scan from −360 mV in the positive potential direction, the reduction of the $Cc^{+/0}$ couple is affected by the diffusion tail arising from the reduction component of the initially recorded Fc$^{0/+}$ process. To avoid this problem, cyclic voltammograms also were obtained with potentials confined to the range in which only significant dc

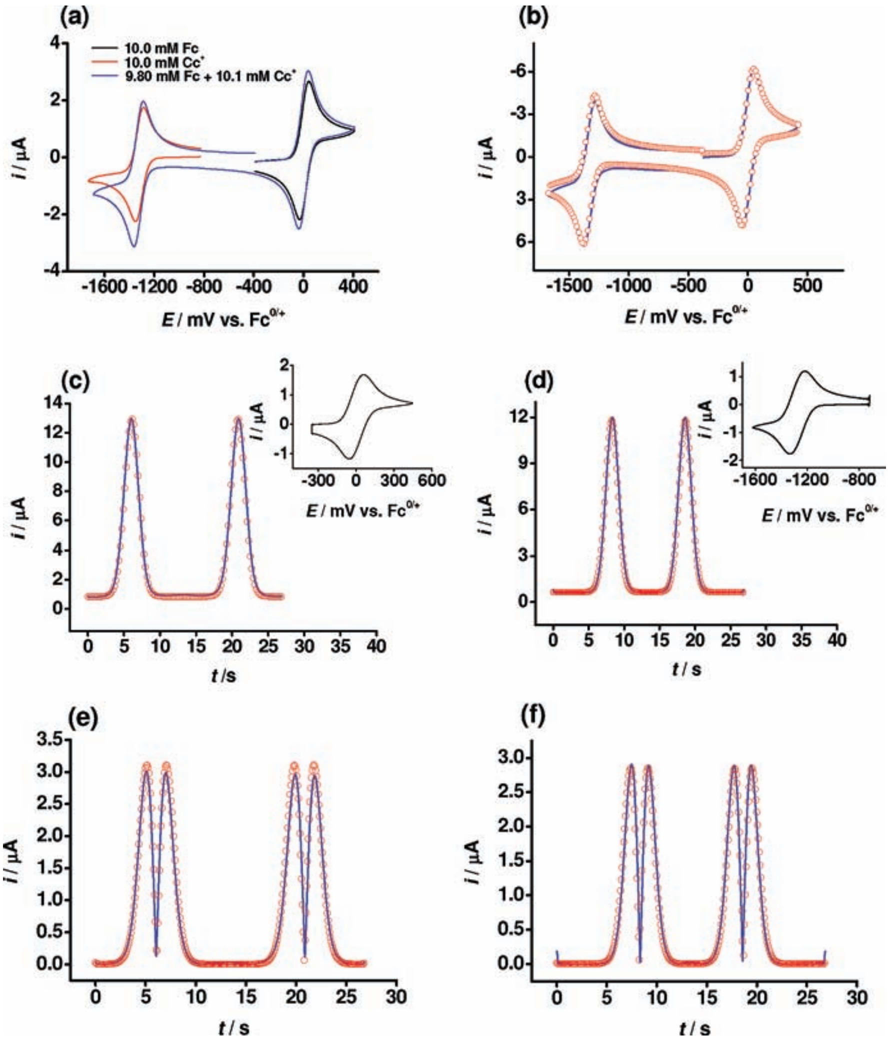

Figure 4. (a) dc cyclic voltammograms obtained at a GC electrode for the $\mathrm{Fc}^{0/+}$ and $Cc^{+/0}$ processes at 23 ± 1 °C when studied from individual (black and red, respectively) and mixed (blue) solutions in [bmim][$\mathrm{BF_4}$] (v, 100 mV s^{-1}). Comparison of experimental (−) and simulated (○) cyclic voltammograms for the oxidation of Fc and reduction of Cc^+ as a mixed solution in [bmim][$\mathrm{BF_4}$] (b−f). The simulated dc cyclic voltammograms (b) were calculated assuming reversible one-electron-transfer processes with $D_{\mathrm{Fc}} = D_{\mathrm{Fc}^+} = 10.7 \times 10^{-8}$ cm^2 s^{-1}, $E^{\circ\prime} = 0.000$ mV, $R_{\mathrm{u}} = 2050$ Ω, $c = 9.8$ mM, and $v = 500$ mV s^{-1} for the $\mathrm{Fc}^{0/+}$ and $D_{Cc^+} = D_{Cc} = 8.2 \times 10^{-8}$ cm^2 s^{-1}, $E^{\circ\prime} = -1345$ mV, $R_{\mathrm{u}} = 2050$ Ω, $c = 10.1$ mM, and $v = 500$ mV s^{-1} for the $Cc^{+/0}$ process. Fundamental (c, d) and second harmonics (e, f) FT-ac cyclic voltammograms were simulated using $D_{\mathrm{Fc}} = D_{\mathrm{Fc}^+} = 10.7 \times 10^{-8}$ cm^2 s^{-1}, and $C_{\mathrm{dl}} = 14.5$ μF cm^{-2} for $\mathrm{Fc}^{0/+}$ and $D_{Cc^+} = D_{Cc} = 8.2 \times 10^{-8}$ cm^2 s^{-1}, and $C_{\mathrm{dl}} = 14.5$ μF cm^{-2} for $Cc^{+/0}$ processes. Other parameters for simulating FT-ac cyclic voltammograms were the same as for Figure 3c and d. The aperiodic dc components for the oxidation of 9.8 mM Fc and reduction of 10.1 mM Cc^+ are shown as insets within (c) and (d), respectively.

Faradaic current is detected for the relevant process. Panels a and b of Figure 5 show dc cyclic voltammograms at the GC electrode in this format with a scan rate of 100 mV s^{-1} for the oxidation of Fc and reduction of Cc^+ when both are present at designated concentrations in [bmim][$\mathrm{BF_4}$]. Under these conditions, the peak currents for both Fc and Cc^+ increase linearly with concentration (see inset to Figures 5a, b, respectively). The data points displayed in the insets to a and b of Figure 5 represents the average of four determinations ($n = 4$), with a relative standard deviation of 3.7% (regression coefficient (r^2) = 0.9989) for 0−30 mM Fc and 4.1% ($r^2 = 0.9988$) for 0−50 mM Cc^+. Furthermore, peak currents for both $\mathrm{Fc}^{0/+}$ and $Cc^{+/0}$ processes retain their linear dependence on the square root of the scan rate as required for diffusion-controlled processes (see insets to c and d of Figure 5).

The cyclic voltammetric data obtained for $\mathrm{Fc}^{0/+}$ and $Cc^{+/0}$ processes at the GC electrode in the mixed-solution case are summarized in Table 4. Importantly, E_{m} ($\approx E^{\circ\prime}$) and the magnitudes of $i_{\mathrm{p}}^{\mathrm{ox}}/i_{\mathrm{p}}^{\mathrm{red}}$ (for $\mathrm{Fc}^{0/+}$) and $i_{\mathrm{p}}^{\mathrm{red}}/i_{\mathrm{p}}^{\mathrm{ox}}$ (for $Cc^{+/0}$) are found to be independent of the scan rate and concentration of the species examined, as expected for a reversible process. Again, ΔE_{p} data obtained at slower scan rates and lower concentrations converge toward the theoretical value of 57 mV predicted for a reversible one-electron process. Furthermore, deviations from the ideal behavior at scan rates greater than 100 mV s^{-1} and higher concentrations again can be attributed to uncompensated resistance. Thus, apart from the modified current values, in all other respects, the Faradaic processes behave analogously when mixtures of Fc and Cc^+ are studied under conditions where at least millimolar concentrations of both species are present.

3.1.3.2. Simulation of FT-ac Voltammetry Derived from Mixed Solutions of Fc and Cc^+ in Aprotic ILs. In order to quantify D_{app}, R_{u}, $E^{\circ\prime}$, and C_{dl} values when $\mathrm{Fc}^{0/+}$ and $Cc^{+/0}$ couples are studied in mixed solutions, fundamental and second harmonic FT-ac voltammograms were simulated and compared with experimental ones obtained at a GC electrode in [bmim][$\mathrm{BF_4}$] containing 9.8 mM Fc and 10.1 mM Cc^+ (Figure

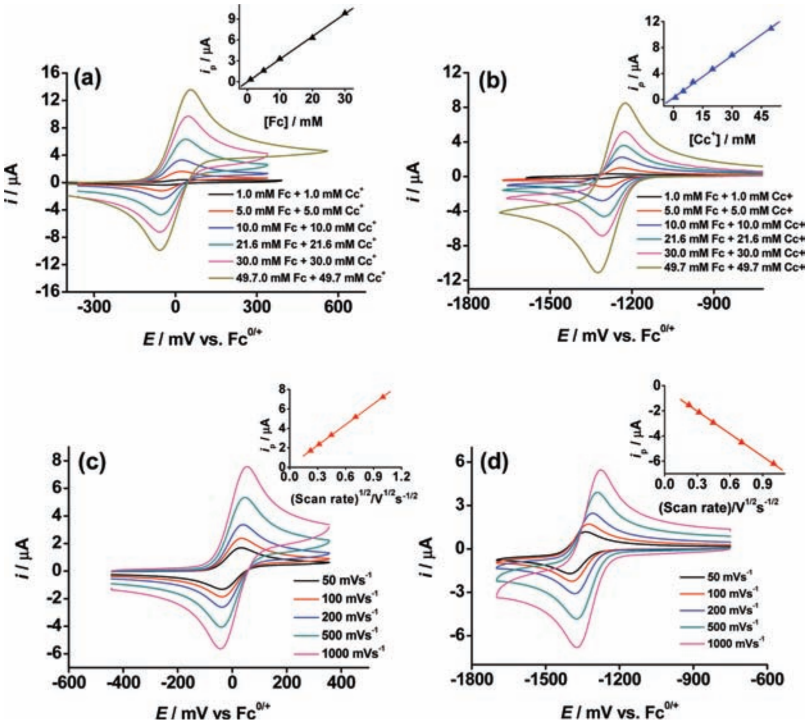

Figure 5. dc cyclic voltammograms obtained at a GC electrode at 23 ± 1 °C for the oxidation of Fc (a) and reduction of Cc^+ (b) when both are present in [bmim][BF$_4$] ($v = 100$ mV s^{-1}) and their dependence (c) and (d) on scan rate. Insets in (a) and (b) show the dependence of the peak currents on the concentration of Fc and Cc^+, respectively, while those in (c) and (d) show the dependence of the peak currents for 7.5 mM Fc and 7.5 mM Cc^+, respectively, on the square root of the scan rate.

Table 4. Data Obtained by dc Cyclic Voltammery Using a GC Electrode at 23 ± 1 °C for the Oxidation of Fc and Reduction of Cc^+ When Both Species are Simultaneously Present in [bmim][BF$_4$]

		Fc			Cc^+			
C (mM)[a]	v (mV s^{-1})[b]	ΔE_p (mV)	i_p^{ox} (μA)	i_p^{ox}/i_p^{red}	E_{m,Cc^+} (mV)[c]	ΔE_p (mV)	i_p^{red} (μA)	i_p^{red}/i_p^{ox}
1.00	50	58	0.15	1.01	−1339 ± 5	57	−0.13	1.01
	100	61	0.25	1.03	−1341 ± 5	61	−0.20	1.00
	200	60	0.37	1.00	−1351 ± 5	62	−0.30	1.03
	500	68	0.59	1.03	−1351 ± 5	66	−0.49	1.02
	1000	75	0.82	1.02	−1349 ± 5	71	−0.69	1.03
5.00	50	64	1.03	1.04	−1341 ± 5	57	−0.82	1.00
	100	66	1.36	1.03	−1345 ± 5	59	−1.21	1.01
	200	69	1.89	1.00	−1345 ± 5	60	−1.64	1.03
	500	77	2.96	1.03	−1349 ± 5	68	−2.57	1.00
	1000	88	4.14	1.05	−1350 ± 5	74	−3.61	1.04
10.0	50	62	2.03	1.03	−1342 ± 5	62	−1.68	1.01
	100	69	2.92	1.01	−1350 ± 5	66	−2.53	1.00
	200	76	3.93	1.00	−1348 ± 5	72	−3.34	1.04
	500	87	6.08	1.01	−1348 ± 5	81	−5.22	1.03
	1000	99	8.35	1.07	−1354 ± 5	92	−7.28	1.07
21.1	50	65	3.95	1.03	−1345 ± 5	66	−3.60	1.02
	100	77	5.38	1.01	−1350 ± 5	71	−4.83	1.03
	200	86	7.53	1.02	−1350 ± 5	77	−6.66	1.04
	500	108	12.0	1.05	−1353 ± 5	91	−10.7	1.05
	1000	117	17.1	1.06	−1356 ± 5	104	−15.4	1.08
30.0	50	74	5.85	1.04	−1345 ± 5	74	−5.43	1.02
	100	85	8.28	1.02	−1351 ± 5	83	−7.52	1.03
	200	94	11.3	1.07	−1351 ± 5	95	−10.3	1.04
	500	114	17.4	1.08	−1350 ± 5	113	−15.7	1.08
	1000	136	25.5	1.07	−1356 ± 5	137	−22.1	1.09
49.7	50	78	9.25	1.04	−1351 ± 5	75	−8.11	1.03
	100	87	13.2	1.03	−1355 ± 5	86	−11.9	1.04
	200	98	18.6	1.06	−1355 ± 5	97	−16.3	1.04
	500	119	28.9	1.09	−1358 ± 5	117	−25.5	1.07
	1000	144	40.3	1.08	−1358 ± 5	141	−35.8	1.07

[a] Concentration. [b] Scan rate. [c] Midpoint potential, where $E_m = E^{\circ\prime}$, assuming equal diffusion coefficients for oxidized and reduced species in the $Cc^{+/0}$ couple. All potentials were calibrated against that of the Fc$^{0/+}$ process, where midpoint potential of the Fc$^{0/+}$ couple ($E_{m,Fc}$) is zero under all conditions.

Table 5. $C_{dl}{}^{app}$ Values Determined at a Au Electrode at 23 ± 1 °C by FT-ac Voltametry (f = 15.0 Hz and ΔE = 80 mV) When Both Fc and Cc$^+$ are Simultaneously Present in [bmim][BF$_4$]

C (mM)[a]		$C_{dl}{}^{app}$ (μF cm^{-2})	
Fc	Cc^+	−360 to 340 (mV)[b]	−760 to −1710 (mV)[b]
1.00	1.00	10.4 ± 0.2	11.1 ± 0.1
5.00	5.00	12.2 ± 0.2	12.0 ± 0.1
10.0	10.0	14.5 ± 0.2	14.5 ± 0.2
21.6	21.9	18.1 ± 0.3	18.8 ± 0.4
30.0	30.0	21.7 ± 0.5	22.7 ± 0.4
49.7	49.7	25.1 ± 0.4	24.9 ± 0.5

[a] Concentration. [b] Against Fc$^{0/+}$.

Table 6. D_{app} Values of Fc and Cc^+ as Determined at a GC Electrode at 23 ± 1 °C in [bmim][BF$_4$] and [bmim][PF$_6$] When Both Species are Simultaneously Present in the Ionic Liquid

		$10^8 D$ (cm^2 s^{-1})			
C (mM)[a]		***Fc***		***Cc^+***	
Fc	Cc^+	[bmim][BF$_4$]	[bmim][PF$_6$]	[bmim][BF$_4$]	[bmim][PF$_6$]
1.00	1.00	10.8	7.04	8.21	3.22
5.00	5.00	10.6	7.13	8.09	3.47
10.0	10.0	10.7	7.18	8.13	3.28
21.6	21.9	10.6	7.24	8.10	3.29
30.0	30.0	10.4	7.06	8.20	3.31
49.7	49.7	9.88	6.31	7.98	3.40

[a] Concentration.

4 c−f). The dc cyclic aperiodic components, provided as insets in c and d of Figure 4, provide an estimate[9] of $E^{\circ\prime}$ based on the average of the dc peak potentials. Values calculated in this manner were 0.000 and 1345 ± 5 mV for Fc$^{0/+}$ and $Cc^{+/0}$, respectively. The separation of 1345 ± 5 mV in $E^{\circ\prime}$ values for the Fc$^{0/+}$ for $Cc^{+/0}$ process was independent of Fc and Cc^+ concentration, scan rate, and electrode material, and within experimental error, the same as previously reported in [bmim][PF$_6$].[6a] Uncompensated resistance of 2050 Ω provided the best fit between simulated and experimental data, and is in agreement with the measured value. However, a C_{dl} value of 14.5 ± 0.2 μF cm^{-2} was required to fit the background current of the fundamental harmonics (Figure 4). This outcome suggests that the Fc and Cc^+ in a mixed solution in IL increases the capacitance, since the value of C_{dl} obtained from solutions individually prepared in the IL was only 12.3 ± 0.2 μF cm^{-2} at a GC electrode.

Apparent C_{dl} values (hereafter referred to as $C_{dl}{}^{app}$) were estimated as a function of the concentration of Fc and Cc^+ in [bmim][BF$_4$] at a Au electrode. Values increase with increasing concentration of Fc and Cc^+ when both solutes are present in this IL (Table 5).

D_{app} values in [bmim][BF$_4$] and [bmim][PF$_6$] also were estimated by FT-ac voltammetry as a function of Fc and Cc^+ concentration in mixed solutions containing at least 1.0 mM of both species (Table 6). Under these conditions, D_{app} values of 10.7×10^{-8} and 8.2×10^{-8} cm^2 s^{-1} for Fc and Cc^+, respectively, were obtained in [bmim][BF$_4$] from both FT-ac voltammetry and use of MECSim simulations and dc cyclic voltammetric experiments employing DigiSim based simulations. Diffusion coefficients values for Fc and Cc^+ in these mixed solution were 7.1×10^{-8} and 3.3×10^{-8} cm^2 s^{-1}, respectively, in [bmim][PF$_6$]. Thus, D_{app} values are about 25 and 35% higher for Fc and Cc^+, respectively, than D_{app} values obtained when Fc and Cc^+ are studied individually in these ILs (Tables 6).

3.1.3.3. D$_{app}$ Values for Fc and *Cc*$^+$ as a Function of Low Concentrations of *Cc*$^+$ in Aprotic ILs. Figures 6a and 6b contain cyclic voltammograms at the GC electrode for the oxidation of 6.0 mM Fc and reduction of 0.13, 0.32, 0.75, 6.0, 12.0, 19.0, and 27.0 mM Cc^+ in [bmim] [BF$_4$]. Clearly, the presence of only a small concentration of Cc^+ has a significant effect on the peak current magnitude for the Fc$^{0/+}$ couple. Consequently, D_{app} values of Fc increase significantly within the concentration range of 0.13−1.0 mM (Table 7). At higher Cc^+ concentrations (1−100 mM), D_{app} values for Fc are almost independent of Cc^+ concentration (Figure 6c, Table 7). These data suggest that the presence of only low concentrations of Cc^+ (a cationic species) are needed to make a significant change in the D_{app} value of Fc in an IL.

3.1.3.4. *D*$_{app}$ Values for Fc and *Cc*$^+$ as a Function of Concentration of Fc in Aprotic ILs. Cyclic voltammograms at GC and Au electrodes of Fc and Cc^+ in a mixed condition were examined when the Cc^+ concentration was kept constant at 8.5 mM and Fc concentration varied from 0.50−20 mM. Under conditions relevant to Figure 6d, the reduction tail of the Fc$^{0/+}$ process has an effect on the reduction current of the $Cc^{+/0}$ process. When the cyclic voltammograms for each process were obtained separately, the separation of the reversible formal potentials of both processes and their calculated diffusion coefficients were independent of the concentrations of Fc within the above-mentioned range (Figure 6d), electrode material, and scan rate. D_{app}, E_m ($\approx E^{\circ\prime}$), and ΔE_m values obtained for the mixed solutions in [bmim][BF$_4$] are summarized in Table 7. The implication of all this data is that the presence of only a low concentration of Cc^+ is able to alter the mass-transport properties of the IL.

3.1.4. Voltammetry of Fc$^{0/+}$ in Aprotic ILs in the Presence of Bu$_4$NPF$_6$. Figure 7a provides examples of dc cyclic voltammograms for the oxidation of Fc in the presence of Bu$_4$NPF$_6$ instead of CcPF$_6$ in [bmim][BF$_4$] at a GC electrode. The Fc$^{0/+}$ process characteristics are changed in a similar manner as when CcPF$_6$ is added at both Au and GC electrodes. Thus, for a given Bu$_4$NPF$_6$ concentration, the Fc oxidation peak current increases linearly with concentration (Figure 7b) and the square root of the scan rate (50−1000 mV s^{-1}). However, when a 7.5 mM Fc solution was examined in the presence of the 0.32, 0.6, and 1.0 mM of Bu$_4$NPF$_6$ in [bmim][BF$_4$], the current for Fc$^{0/+}$ process increased with increasing concentration of Bu$_4$NPF$_6$ (Figure 7c). Consequently, D_{app} is a function of Bu$_4$NPF$_6$ in the low concentration range (Figure 7d, Table 8). These results are analogous to those found for Fc in the presence of low concentrations of CcPF$_6$ (0.13−1.0 mM), as described above.

3.1.5. Voltammetry of Fc$^{0/+}$ and *Cc*$^{+/0}$ in the Presence of Bu$_4$NPF$_6$ in Aprotic ILs. Figure 8a shows dc cyclic voltammograms obtained for the oxidation of 7.5 mM Fc in the presence of 16 mM of both CcPF$_6$ and Bu$_4$NPF$_6$ at a Au electrode. D_{app} values calculated for Fc and Cc^+ under these conditions are provided in Table 8. Simulated data with $E^{\circ\prime}$ of 0.000 (Fc$^{0/+}$) and −1345 mV ($Cc^{+/0}$), R_u of 2100 Ω, and D_{app} of 10.7×10^{-8} (Fc$^{0/+}$) and 8.2×10^{-8} cm^2 s^{-1} ($Cc^{+/0}$) and $C_{dl}{}^{app}$ of 13.5 and 15.5 μF cm^{-2} are also included in Figure 8. The D_{app}, $C_{dl}{}^{app}$, R_u, and E_m ($\approx E^{\circ\prime}$) values calculated via comparison of simulated and experimental voltammograms were identical within experimental error to those used when Fc$^{0/+}$ couple was studied in the presence of only 16 mM Cc^+ as the PF$_6{}^-$ salt. This study with Bu$_4$NPF$_6$ in combination with other results implies that the voltammetry of the Fc$^{0/+}$ and/or $Cc^{+/0}$ couples in an IL may

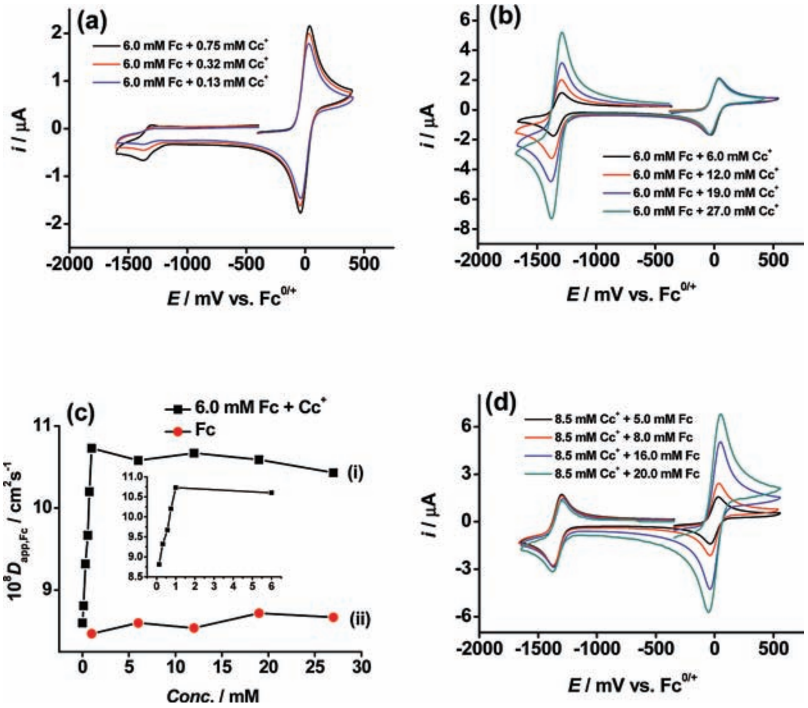

Figure 6. dc cyclic voltammograms obtained for the oxidation of Fc and reduction of Cc^+ at a GC electrode at 23 ± 1 °C in [bmim][BF$_4$] ($v = 100$ mV s^{-1}). (a, b) Fc concentration of 6.0 mM with designated concentrations of Cc^+. (c) Dependence of D_{app} (i) for Fc on the concentration of 6.0 mM of Fc as a function of concentration of Cc^+ and (ii) for 1.0−27 mM of Fc in the absence of Cc^+. Inset in (c) shows the dependence of D_{app} values on low concentrations of Cc^+ in the mixed solution. (d) 8.5 mM Cc^+ with designated concentrations of Fc.

Table 7. *D_{app} Values for Fc and Cc^+ and Other Parameters as Determined from dc Cyclic Voltammetry at a GC Electrode at 23 ± 1 °C in [bmim][BF$_4$] When Both Species are Simultaneously Present in the Ionic Liquid*

C_{Fc} (mM)[a]	C_{Cc^+} (mM)[b]	$E_{m,\,Cc^+}$ (mV)[c]	ΔE_m (mV)[d]	$10^8\ D_{app,Fc}$ (cm^2 s^{-1})	$10^8\ D_{app,Cc^+}$ (cm^2 s^{-1})
5.00	8.50	−1343 ± 5	1343 ± 5	10.7	8.21
8.00	8.50	−1346 ± 5	1346 ± 5	10.5	8.15
16.0	8.50	−1345 ± 5	1345 ± 5	10.6	8.10
20.0	8.50	−1347 ± 5	1347 ± 5	10.9	8.28
6.00	0.13	−1333 ± 5	1333 ± 5	8.81	8.24
6.00	0.32	−1345 ± 5	1345 ± 5	9.32	7.97
6.00	0.57	−1341 ± 5	1341 ± 5	9.67	8.22
6.00	0.75	−1334 ± 5	1334 ± 5	10.2	8.04
6.00	1.00	−1339 ± 5	1339 ± 5	10.7	8.17
6.00	6.00	−1333 ± 5	1333 ± 5	10.9	8.09
6.00	12.0	−1345 ± 5	1345 ± 5	10.8	8.31
6.00	19.0	−1341 ± 5	1341 ± 5	10.6	8.20
6.00	27.0	−1334 ± 5	1334 ± 5	10.4	8.27

[a] Concentration of Fc. [b] Concentration of Cc^+. [c] Midpoint potential of the $Cc^{+/0}$ couple, where $E_m = E°'$, assuming equal diffusion coefficients for oxidized and reduced species in the $Cc^{+/0}$ couple. All potentials were calibrated against that of the Fc$^{0/+}$ process, where midpoint potentials of the Fc$^{0/+}$ couple ($E_{m,\ Fc}$) is zero under all conditions. [d] Separation of the midpoint potentials of the $Cc^{+/0}$ and Fc$^{0/+}$ couples.

be modified by the presence of small concentrations of either electro-active or electro-inactive species.

3.1.6. Origin of Diffusion Coefficient Variation. In some cases, the variation of D values in ILs on addition of a solute can be attributed to changes in viscosity. This has been shown to be the case with addition of water (decrease in viscosity[16a]) or Li salt (increase in viscosity due to the strong coordination properties of lithium cations[16b]) to ILs. In contrast, in the work of Compton et al.,[6c,12] large difference in D for oxidized and reduced forms of redox couples (Fc$^{0/+}$, $Cc^{+/0}$, and O$_2^{\,0/-}$) have attributed to specific interactions with the ILs rather than to changes in viscosity.

3.1.6.1. Viscosity of Aprotic ILs Containing Fc and Cc^+. Viscosity is a key parameter that strongly influences a number of physicochemical properties and hence mass transport in voltammetry in IL.[3] The viscosity of the aprotic ILs was measured at 22 °C in [bmim][BF$_4$] and [bmim]PF$_6$] when Fc or Cc^+ was present over the range of 0−20 mM individually or simultaneously. No variation in the viscosity values attributed to addition of Fc or Cc^+ was detected within the experimental error of ±3%. Thus, for example, a dynamic viscosity value of 128.3 cP was found at 23 °C for neat [bmim][BF$_4$] (literature value = 120.0 cP at 25 °C[13]), 128.1 cP upon addition of 5 mM Fc, 128.6 cP on addition of 5 mM Cc^+, and 129.2 cP upon addition of 5 mM of both Fc and Cc^+ in a mixed solution. The value of 128.2 cP was found in the presence of 20 mM Fc, 130.4 cP in the presence of 20 mM Cc^+, and 130.9 cP for a mixed solution of 20 mM Fc and Cc^+. Thus, modification of D_{app} values in this study does not appear to be attributed to alteration in viscosity.

3.1.6.2. ^{1}H NMR Relaxation Data. The level and the nature of aggregation of pairs of ions (cation and anion) determines the physical and chemical properties of an IL and also solutes studied in an IL.[17] While, the addition of some solutes affects the degree and the nature of aggregation and hence modifies the IL viscosity and D_{app} (Stokes−Einstein relation-

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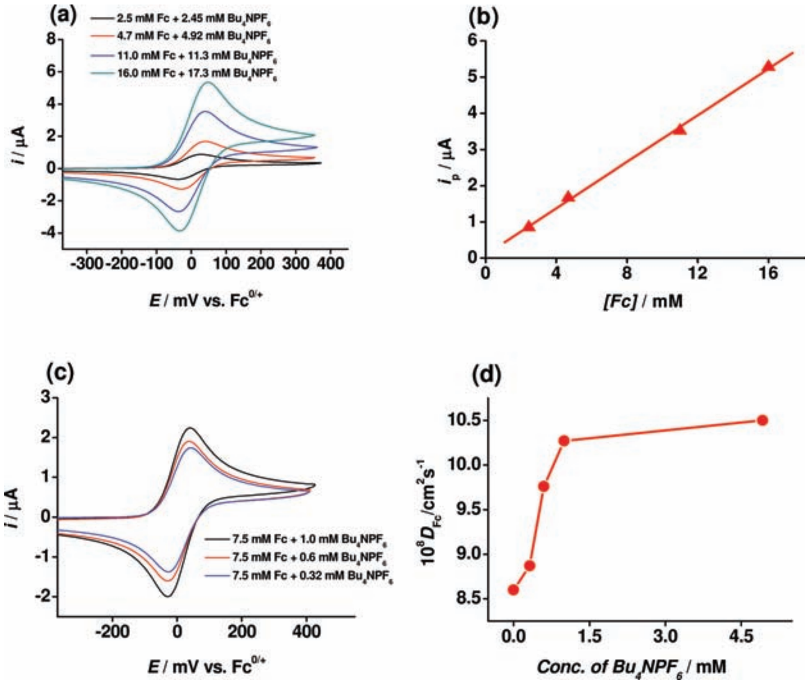

Figure 7. dc cyclic voltammograms ($\upsilon = 100$ mV s^{-1}) obtained for the oxidation of Fc at a GC electrode at 23 ± 1 °C in [bmim][BF$_4$] as a function of the concentration of Bu$_4$NPF$_6$ (a, c). Dependence of the oxidation peak current on the concentration of Fc (b), and D values for Fc on the concentration of Bu$_4$NPF$_6$ (d).

Table 8. D_{app} Values for Fc and Cc^+ Determined by dc Cyclic Voltammetry at a GC Electrode in [bmim][BF$_4$] at 23 ± 1 °C in the Presence of Bu$_4$NPF$_6$

C (mM)[a]			10^8 D (cm^2 s^{-1})	
Fc	Cc^+	Bu$_4$NPF$_6$	Fc	Cc^+
2.50	–	2.45	10.4	–
4.70	–	4.92	10.3	–
11.0	–	11.3	10.2	–
16.0	–	17.3	10.1	–
7.50	–	0.32	8.85	–
7.50	–	0.60	9.13	–
7.50	–	1.00	9.96	–
5.25	5.10	5.25	10.5	8.21
10.0	10.2	10.1	10.4	8.09
20.0	20.0	20.0	10.5	8.13
30.1	30.2	29.8	10.3	7.98

[a] Concentration.

ship),[18] this does not provide an explanation for the variation in D_{app} values found in this study. The effects of the addition of 10 mM Cc^+ and 10 mM Fc were investigated by NMR spectroscopy, where dynamic changes are expected to manifest themselves by variation in T_1 relaxation times.

^{1}H NMR resonance associated with the IL cations were collected and assigned as shown in Figure 9a for [bmim][BF$_4$]. On addition of Cc^+ and Fc, a new single resonance was detected for the Cc^+ ring protons. In view of the low concentration of Cc^+, relative to those of cations and anions in the ILs, its ^{1}H resonance was relatively weak but was still readily detected at the 10 mM concentration level. However, the expected resonance for Fc was not observed, presumably because of overlap with much stronger IL resonances.

Using a standard inversion recovery and spin echo method (CPMG), the T_1 relaxation times for all ^{1}H proton resonances observed in the NMR spectrum have been determined. Figure 9b summarizes the individual T_1 relaxation times for [bmim][BF$_4$] measured upon addition of either Fc or Cc^+ or both Fc and Cc^+. While the T_1 values associated with IL cation do not vary greatly as expected if the viscosity is not significantly altered, the T_1 values for ring protons detected from 10 mM Cc^+ species change significantly, and much greater than the experimental error of ±3%, upon addition of 10 mM Fc. The Cc^+ proton T_1 relaxation time is longer than that for the protons in ILs and becomes even longer when Fc is added, indicating that the level of Cc^+ interaction with other ions is weakened by the presence of Fc. Analogous NMR data were also found for T_1 values in [bmim][PF$_6$]. In this case, addition of Cc^+ as the PF$_6$ salt does not introduce a new anion, indicating exchange of BF$_4^-$ and PF$_6^-$ in the [bmim][PF$_6$] has not contributed significantly to ^{1}H resonance data.

Differences in the Cc^+ dynamics upon addition of Fc also can be followed by changes in the T_2 relaxation time of the Cc^+ proton resonance. The line width increases with increasing concentration of Fc in Cc^+ solution in [bmim][BF$_4$]. On the other hand, there is no effect of any significance on the T_2 relaxation time on the IL cations.

Physicochemical models of ionic liquids can be developed in an analogous manner to those proposed for ionic crystals. The anion and cation of the ILs form a stable pair with a strong dipole moment, which induces long-range order between pairs (aggregation). This aggregation is responsible for increased viscosity in comparison to that found for normal molecular solvents. Addition of a solute can affect the aggregation in two ways: to break down the aggregation, making ionic liquids more fluidlike and hence decreasing the viscosity or to condense the already existing aggregates to a larger aggregate (hydration of additional ions by aggregates), causing an increase in overall viscosity (slower dynamics). Addition of small concentration of CcPF$_6$, Fc, or Bu$_4$NPF$_6$, according to our findings, does not change the ionic liquids'

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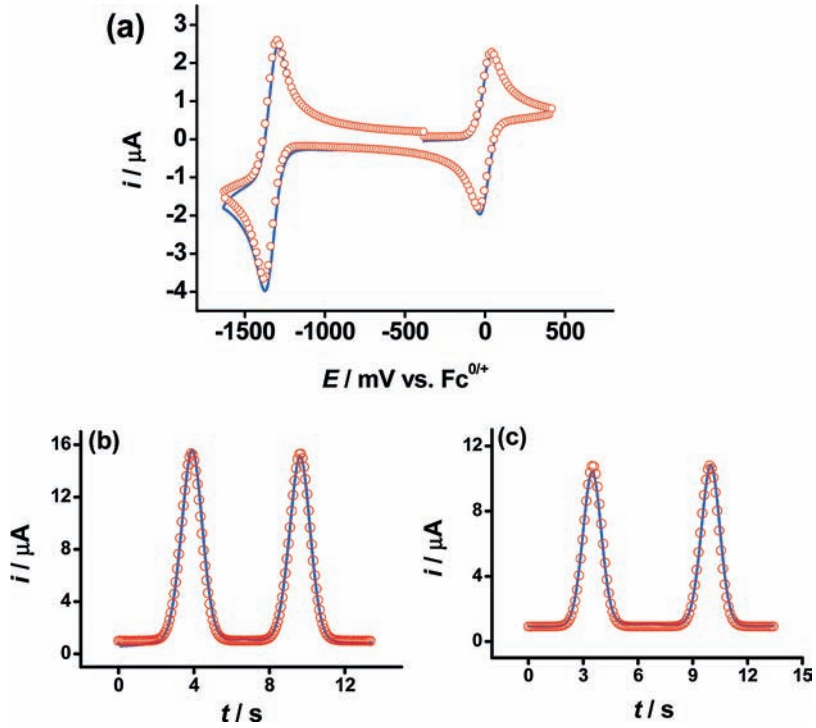

Figure 8. Comparison of experimental (−) and simulated (○) dc (a) and FT-ac (b, c) cyclic voltammograms obtained at a Au electrode at 23 ± 1 °C for the oxidation of 7.5 mM Fc and reduction of 16 mM Cc^+ (v = 500 mV s^{-1}) as mixed solutions in [bmim][BF_4] that also contain 16 mM Bu_4NPF_6. The simulated dc voltammogram was calculated assuming reversible one-electron-transfer processes and $D_{Fc} = D_{Fc^+} = 10.7 \times 10^{-8}$ cm^2 s^{-1}, $E^{\circ\prime} = 0.000$ mV, $R_u = 2060$ Ω, $c = 7.5$ mM, and $v = 500$ mV s^{-1} for the $Fc^{0/+}$ and $D_{Cc^+} = D_{Cc} = 8.2 \times 10^{-8}$ cm^2 s^{-1}, $E^{\circ\prime} = -1348$ mV, $R_u = 1980$ Ω, $c = 16$ mM, and $v = 500$ mV s^{-1} for the $Cc^{+/0}$processes. FT-ac cyclic voltammograms were calculated assuming reversible electron transfer and $D_{Fc} = D_{Fc^+} = 10.7 \times 10^{-8}$ cm^2 s^{-1}, and $C_{dl} = 13.5$ μF cm^{-2} for the $Fc^{0/+}$ and $D_{Cc^+} = D_{Cc} = 8.2 \times 10^{-8}$ cm^2 s^{-1} and $C_{dl} = 15.5$ μF cm^{-2} for the $Cc^{+/0}$ process. Other parameters used for simulating ac voltammograms are as for Figure 3c and d.

aggregation significantly (similar viscosity, see above) because these species interact only with the surfaces of the aggregates. However, there are many available spaces/surfaces that allow the dynamics to change when an individual species is added. When a combination of two (or more) species is present, additional interactions can take place. There are three possible scenarios when two solutes are added: (i) both species are equal in their interaction with the surfaces (not likely), (ii) one species preferentially aggregates at the surface and one next to it (likely, due to differences in size and/or charge), and (iii) the two species are attracted to each other more than to the ILs aggregate surfaces and are more mobile. A likely situation is that the additional ions reside on the fringes of the IL aggregates. Thus, via electromagnetic interactions with aggregates their mobility is varied, as measured by the electrochemical method for detecting D values. The larger D values and modified C_{dl}^{app} values therefore are assumed to be related to subtle changes in structure and ionic arrangement at the electrode−IL interface, respectively.

3.2. DC Voltammetry in Protic ILs. To establish whether the phenomena observed in aprotic ionic liquids are likely to be generic to the ionic liquid field, voltammetric studies were also undertaken with Fc, Cc^+, and mixtures of Fc and Cc^+ in TEtAF, DEAA, and TEtAA protic ionic liquids. When studied from individual solutions, the values of E_m ($\approx E^{\circ\prime}$) and D of Fc and Cc^+ were found to be independent of Fc and Cc^+ concentration and electrode material used for the measurements (Figures S1, S2, S3, and Table S1). Thus, the general characteristics of the individual $Fc^{0/+}$ and $Cc^{+/0}$ processes were indistinguishable from those found in [bmim][BF_4] and [bmim][PF_6]. E_m, D_{app}, and C_{dl}^{app} values were also determined and compared when the $Fc^{0/+}$ couple was studied in the presence of the $Cc^{+/0}$ couple. As observed with the aprotic ionic liquids, the Faradaic and capacitance currents for both the processes increased significantly in protic ionic liquids. For example, D_{app} values for Fc and Cc^+ were found to be 10.0×10^{-7} and 1.0×10^{-7} cm^2 s^{-1}, respectively, in TEtAA which were 23 and 29% higher than those obtained when both processes were studied individually in this ionic liquid (Table 9). Analogous results were also obtained in DEAA and TEtAF. The D_{app} values for Fc and Cc^+ were found to be 11.2×10^{-7} and 4.7×10^{-7} cm^2 s^{-1}, respectively, in TEtAF which were 28 and 34% higher than those obtained when both processes were studied individually in this ionic liquid (see Table S2). A significant increase in the C_{dl}^{app} value was found in the potential range of −400 to −200 mV vs $Fc^{0/+}$ when the $Fc^{0/+}$ process was studied in the presence of Cc^+ in TEtAF (Figure S4). A similar enhancement of C_{dl}^{app} values was also found when the process of $Cc^{+/0}$ was studied in the presence of the Fc in the potential range of −800 to −1000 mV vs $Fc^{0/+}$. dc cyclic voltammograms for the oxidation of designated concentrations of Fc in the presence of low concentration of Bu_4NPF_6 were also examined. The $Fc^{0/+}$ process characteristics are changed in a similar manner as observed above in aprotic ILs when Bu_4NFP_6 is added (an example is shown in Figure S5).

3.3. Voltammetry of Mixtures of Fc and Cc^+ in CH_3CN (0.1 M Bu_4NPF_6). To confirm that the $Fc^{0/+}$ and $Cc^{+/0}$ couples are additive in conventional molecular solvent (electrolyte) media, studies were undertaken with Fc, Cc^+, and mixtures of Fc and Cc^+ in CH_3CN with 0.1 M Bu_4NPF_6 as the supporting electrolyte. The peak currents for the oxidation of Fc and the

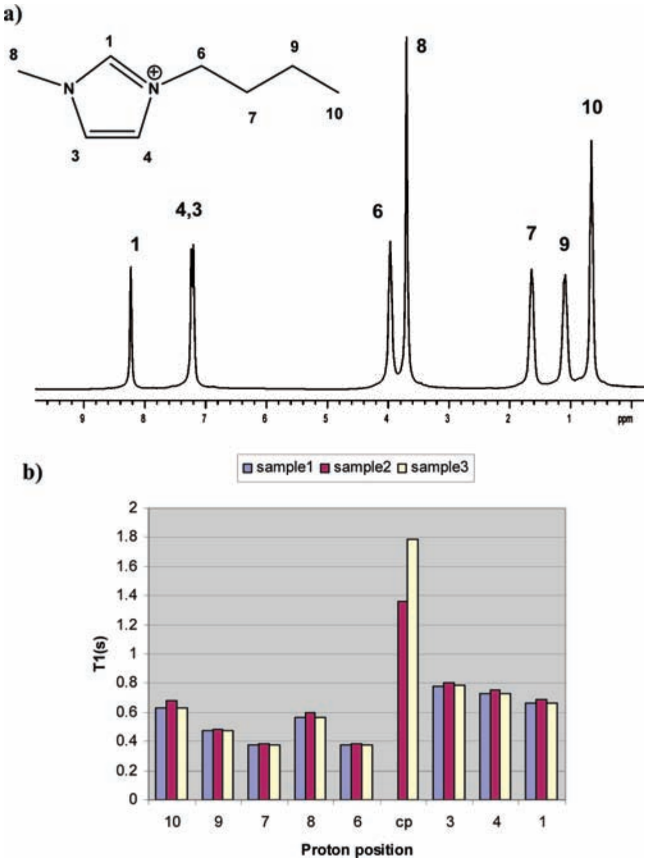

Figure 9. (a) ^{1}H NMR spectrum at 20 °C and assignment of resonances for neat [bmim][BF$_4$]. (b) ^{1}H NMR relaxation times when 10 mM Fc (sample 1), 10 mM *Cc*$^+$ (sample 2), and 10 mM Fc + 10 mM *Cc*$^+$ (sample 3) are dissolved in [bmim][BF$_4$].

Table 9. *D* Values Determined at a GC Electrode at 23 ± 1 °C by dc Cyclic Voltammetry for the Oxidation of Fc and Reduction of *Cc*$^+$ in DEAA and TEtAA

C (mM)^a		10^7 *D* (cm^2 s^{-1})			
		DEAA		TEtAA	
Fc	*Cc*$^+$	Fc	*Cc*$^+$	Fc	*Cc*$^+$
0.96	0.00	5.8×10^{-3}	–	–	–
0.00	0.96	–	1.1×10^{-3}	–	–
0.48	0.48	7.3×10^{-3}	1.3×10^{-3}	–	–
2.00	0.00	–	–	8.1	–
0.00	2.00	–	–	–	0.77
1.00	1.00	–	–	10	1.0

^{a} Concentration.

reduction of *Cc*$^+$ varied linearly with the square root of the scan rate (50−1000 mV s^{-1}) when the species were studied individually in CH$_3$CN (0.1 M Bu$_4$NPF$_6$). The magnitude of both i_p^{ox}/i_p^{red} (Fc$^{0/+}$) and i_p^{red}/i_p^{ox} (*Cc*$^{+/0}$) was close to unity at all electrode materials (GC and Au), concentrations (0.1−15 mM), and scan rates (50−1000 mV s^{-1}) examined, as expected for a chemically reversible process.[8b,19] The *D* values for Fc and *Cc*$^+$ in CH$_3$CN (0.1 M Bu$_4$NPF$_6$) were calculated to be 2.3 × 10^{-5} and 1.64 × 10^{-5} cm^2 s^{-1} using dc cyclic voltammetry and the Randles−Sevick equation, and excellent agreement between experimental and simulated data was observed under both dc and FT-ac conditions. The FT-ac data, assuming the processes are reversible, were simulated using the parameters $T = 296$ K, [Fc] = 1.02 mM, [*Cc*$^+$] = 1.03 mM, $E°'_{Fc} = 0.000$ mV and $E°'_{Cc^+} = -1338$ mV, D_{Fc} (= D_{Fc^+}) = 2.3 × 10^{-5} cm^2 s^{-1}, D_{Cc^+} (= D_{Cc}) = 1.64 × 10^{-5} cm^2 s^{-1}, $A = 0.0093$ cm^2, $R_u = 762\ \Omega$, and $C_{dl} = 6.8\ \mu$F cm^{-2} (for Au electrode). When Fc and *Cc*$^+$ were both present in CH$_3$CN (0.1 M Bu$_4$NPF$_6$), the characteristics of the Fc$^{0/+}$ and *Cc*$^{+/0}$ processes were indistinguishable from those found when studied individually. That is, no significant differences were found in R_u, C_{dl}, E_m (≈$E°'$), and *D* values over the concentration range of 0.1−10 mM. The separation of 1338 ± 5 mV in the $E°'$ values for Fc$^{0/+}$ and *Cc*$^{+/0}$ couples is consistent with values reported in many organic solvents.[19] These data enable the conclusion to be drawn that ionic liquids play a key role in the nonadditivity of the Fc$^{0/+}$ and *Cc*$^{+/0}$ processes.

4. Conclusions

The dc and FT-ac cyclic voltammetries of Fc$^{0/+}$ and *Cc*$^{+/0}$ have been studied as functions of Fc and *Cc*$^+$ concentrations in two aprotic and three protic ILs to determine whether the behavior in mixtures in these IL media is additive, relative to studies with individual Fc and *Cc*$^+$ solutions.

In the case of individually prepared solutions in [bmim][BF$_4$] and [bmim][PF$_6$] ILs, a linear dependence of the peak current on the Fc and *Cc*$^+$ concentrations was observed, as required for diffusion-controlled Fc$^{0/+}$ and *Cc*$^{+/0}$ processes. Excellent agreement between simulated and experimental voltammograms allowed the *D*, E_m (≈$E°'$), R_u, and C_{dl} values for both the Fc$^{0/+}$ and *Cc*$^{+/0}$ processes to be determined in these aprotic ILs. While the *D* and $E°'$ values for Fc and *Cc*$^+$ are independent of electrode material, scan rate, and concentration examined, the value of C_{dl} increases with increasing concentration of Fc and *Cc*$^+$.

The voltammetry of Fc in the presence of the *Cc*$^+$ and/or Bu$_4$N$^+$ also was studied in these aprotic ILs. Two nearly ideal Fc$^{0/+}$ and *Cc*$^{+/0}$ couples with reversible characteristics were found. However, in mixtures, the D_{app} values for Fc and *Cc*$^+$ increased significantly. C_{dl}^{app} values determined from individual and mixed Fc and *Cc*$^+$ conditions were also different. Thus, C_{dl}^{app} increased with the concentration of Fc and *Cc*$^+$, but had a larger magnitude when obtained from measurements made under conditions where both species are present. The differences in $\Delta E°'$ between the Fc$^{0/+}$ and *Cc*$^{+/0}$ processes was always 1345 ± 5 mV, irrespective of electrode material, scan rate, and concentration of Fc and *Cc*$^+$. The presence of only low concentrations of *Cc*$^+$ and/or Bu$_4$NPF$_6$ to the ILs significantly alters the voltammetric behavior of the Fc$^{0/+}$ couple in these aprotic ILs. The nonadditivity of Faradaic currents and double layer capacitance is attributed to variation in structures and hence mobilities of the IL constituent ionic species when Fc, *Cc*$^+$, and Bu$_4$N$^+$ are added as solutes to the ILs, as deduced from changes in NMR relaxation times detected in [bmim][BF$_4$] and [bmim][PF$_6$].

Analogous conclusions were reached from more limited studies in three protic ILs implying that nonadditivity of Faradiac and modification of background capacitance current represent generic features that should be considered in ionic liquid electrochemistry when multiple solutes are present. The present study showing nonadditivity of Fc and *Cc*$^+$ processes differs from the known sensitivity to the presence of adventitious water or halides in voltammetric studies of ionic liquids,[20] where changes in D_{app} arise from changes in bulk viscosity. The implications of data contained in this

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paper are significant in a fundamental sense, as specifically noted in this work, but also likely to be important in analytical applications where calibration curves prepared from an individual analyte may not necessarily be directly related to data derived from solutions containing mixtures of analytes. The independence of the voltammetry of multiple analytes present in real samples is an inherent underlying assumption in many analytical applications of voltmmetry in conventional solvent media containing naturally present or deliberately added supporting electrolyte. In another context, Compton et al. have noted[21] in studies of a range of ionic liquids that the oxidation of hydrogen decreased slightly upon addition of Cc^+, implying that a reaction occurred between hydrogen and Cc^+ or Cc. Thus, Cc^+ and Fc cannot be assumed to be innocent when added to an ionic liquid for in situ reference calibration purposes.

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Supporting Information Available: Synthesis of protic ILs, details of preparation of Fc and Cc^+ solutions in protic ILs, dc cyclic voltammograms and diffusion coefficients for the oxidation of Fc and reduction of Cc^+ in their individual and mixed solutions in TEtAF, DEAA, and TEtAA, dc cyclic voltammograms and diffusion coefficients for the oxidation of Fc in the presence of Bu_4NPF_6 in TEtAF. This material is available free of charge via the Internet at http://pubs.acs.org.

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