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Electrochemical Studies of Ferrocene and Ferrocenium Ion in Aluminum Chloride–*N*-1-Butylpyridinium Chloride Ionic Liquid

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Electrochemical studies of the ferrocene/ferrocenium ion system have been carried out in $AlCl_3$–*N*-1-butylpyridinium chloride ionic liquid at 40 °C as a function of melt composition. The ferrocene/ferrocenium electron-transfer process is reversible, and the formal potential of the ferrocene/ferrocenium cation couple varies only slightly with wide changes of solvent acidity. Ferrocene and ferrocenium ion are both stable in neutral butylpyridinium tetrachloroaluminate. In basic (excess BuPyCl) melts ferrocene is stable, while the ferrocenium cation is decomposed by Cl^- to $Fe(Cp)_2$ and $FeCl_4^-$. In acidic (excess $AlCl_3$) melts ferrocene is oxidized to ferrocenium ion by traces of oxygen and reacts with products of the reaction of water with the solvent. The ferrocenium cation is stable in the acid melts.

Introduction

Mixtures of aluminum chloride and alkylpyridinium halides[1-4] or other halides of large organic (R^+) cations[5] form ionic liquids at ambient temperatures. These systems have recently been used for a variety of electrochemical and spectroscopic studies[6,7] and exhibit interesting acid–base properties dependent upon the $AlCl_3$:RCl mole ratio. In precisely equimolar $AlCl_3$–RCl mixtures, the "neutral" solvent, organic cation tetrachloroaluminate, is formed. On addition of excess $AlCl_3$, acidic melts containing the Lewis acid, heptachloroaluminate, are formed. Basic solvent compositions (excess RCl) with high chloride ion activity can also be prepared.

To establish a potential scale in these molten salt systems that could be compared to studies in other solvents, the ferrocene/ferrocenium ion couple, widely used for this purpose in aqueous and nonaqueous solvents,[8,9] was employed initially in a 2:1 $AlCl_3$:ethylpyridinium chloride melt[2] and then in the aluminum chloride–*N*-1-butylpyridinium chloride ($AlCl_3$–BuPyCl) system.[3] These latter studies indicated that the ferrocene/ferrocenium ion couple is electrochemically reversible and stable on the time scale of cyclic voltammetric experiments. The ferrocene oxidation potential, measured vs. an Al electrode in a 2:1 $AlCl_3$:BuPyCl melt, was reported to be indepedent of melt acidity. The ferrocene/ferrocenium cation couple has thus been used as a reference couple against which redox potentials in the $AlCl_3$–BuPyCl system could be related to those in other solvents. However, recent studies of several metallocenes in $AlCl_3$–BuPyCl ionic liquid revealed complex chemistry dependent on melt acidity.[10-13] We have observed that ferrocene and ferrocenium ion undergo slow reactions in these melts. The problems inherent in the lack of stability and an effort to better understand the behavior of this "model" system prompted this study.

Experimental Section

Procedures used for purification of $AlCl_3$ (Fluka), synthesis and purification of *N*-1-butylpyridinium chloride, and preparation of the melts were similar to those described previously.[3] Ferrocene (Eastman Kodak) was sublimed on a water bath and dried in a vacuum desiccator. Ferrocenium tetrachloroferrate (Alfa Products) was used as received. Cyclopentadienyl anion was added as LiCp (Alfa Products), and anhydrous $FeCl_3$ (Fisher Scientific) was used as an Fe(III) source.

All experiments were carried out under a purified argon atmosphere in a Vacuum Atmospheres drybox with an HE 493 Dri Train. Constant temperature (40 ± 1 °C) was maintained with a Selectrol (Thermo Electric) temperature controller.

Equipment used in electrochemical experiments was the same as in previous work.[14] Tungsten (TE) and glassy-carbon (GCE) disk electrodes sealed in glass were used as working electrodes. The tungsten electrode had an area of 0.0784 cm^2, and the glassy-carbon disk had an area of 0.196 cm^2. Instead of the usual Al reference electrode, a Ag/Ag^+ (0.01 mol dm^{-3} Ag^+ in 1.5:1 $AlCl_3$:BuPyCl melt) reference electrode was employed and all potentials are referenced against this electrode. The potential of the Ag/Ag^+ (0.01 mol dm^{-3}) electrode was +0.590 V vs. an Al electrode in a 2:1 $AlCl_3$:BuPyCl melt. The Ag/Ag^+ reference electrode exhibited better potential reproducibility and stability. While deviations ±0.025 V for an Al electrode[15] have been reported, the maximum deviation between values of the ferrocene/ferrocenium ion formal potential in a given solution composition was ca. ±5 mV when the Ag/Ag^+ reference electrode was used.

As was shown in previous work,[14] the techniques of normal- and reverse-pulse voltammetry[16] can be successfully used for electrode processes at solid electrodes provided that initial conditions at the electrode surface are reestablished before each pulse application. This was accomplished by rotating the working electrode under computer control for the first 1 or 2 s of a 10-s delay time, during which the electrode was kept at a potential chosen so that no Faradaic process occurred.

Results and Discussion

Voltammetric Investigations. Results of preliminary voltammetric experiments agreed with the short-term electrochemical behavior of ferrocene reported previously.[3,10] Ferrocene dissolves readily in $AlCl_3$–BuPyCl mixtures, forming orange solutions. Cyclic voltammetric curves obtained for ferrocene at various solvent compositions are shown in Figure 1. In neutral and acidic melt compositions, a reversible couple at ca. −0.350 V vs. the Ag/Ag^+ reference electrode and a large irreversible peak at ca. +1.25 V were observed (Figure 1 (1 and 2)). In basic $AlCl_3$–BuPyCl mixtures, chloride oxidation sets the anodic limit of the solvent at less positive potentials

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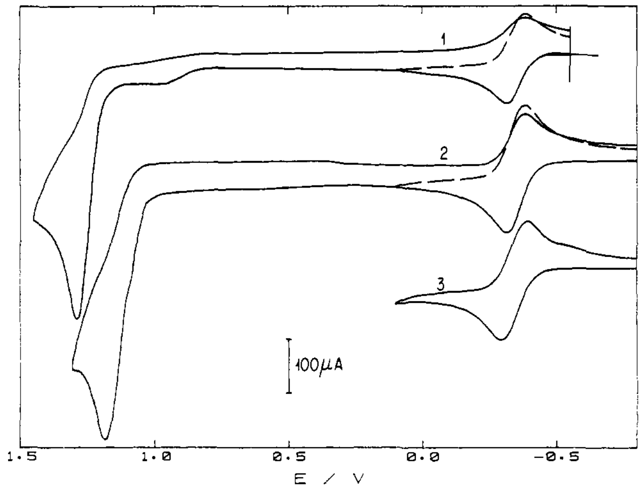

Figure 1. Cyclic voltammograms of ferrocene at different $AlCl_3$:BuPyCl mole ratios (v = 0.05 V/s; GCE): (1) 5.9 mM $Fe(Cp)_2$ in 1.7:1 melt; (2) 7 mM $Fe(Cp)_2$ in 1:1 melt; (3) 9.6 mM $Fe(Cp)_2$ in 0.75:1 melt.

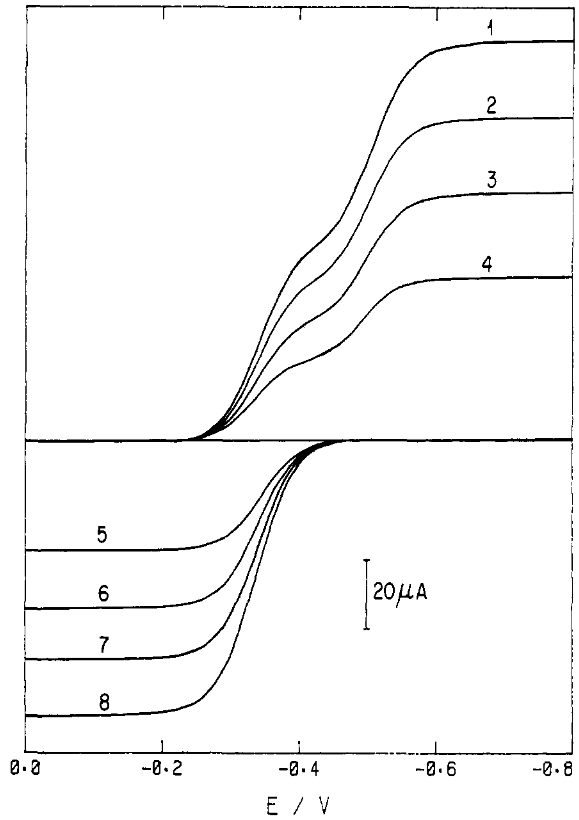

Figure 2. RDE voltammograms for 8 mM ferrocenium tetrachloroferrate (1–4) and 9 mM ferrocene (5–8) in neutral $AlCl_3$–BuPyCl melt. Rotation rate (rpm; TE): (1 and 8) 2500; (2 and 7) 1600; (3 and 6) 900; (4 and 5) 400.

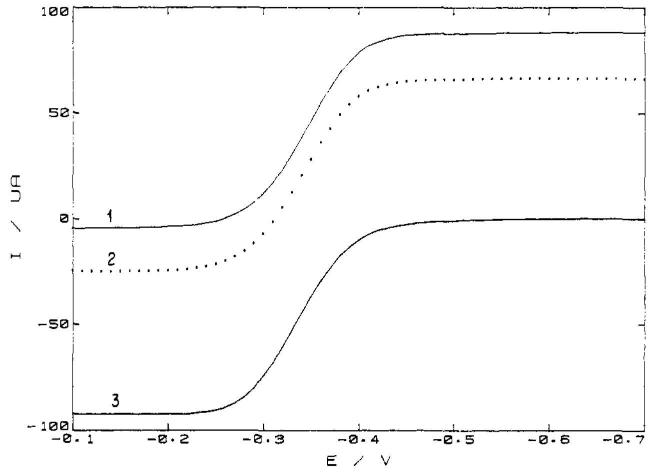

Figure 3. Normal- (3) and reverse-pulse (1 and 2) voltammograms for 7 mM ferrocene in neutral $AlCl_3$–BuPyCl melt (t_p = 0.1 s). τ (s): (1) 60.1; (2) 1.1. E_i (V; TE): (1 and 2) 0.0; (3) -0.8.

and the second anodic peak was not evident (Figure 1 (3)). Anodic processes occurring at potentials of the second voltammetric peak probably involved oxidation of the cyclopentadienyl ligand. The height of this wave observed at a rotating disk electrode (RDE) indicates that no less than four electrons per ferrocene molecule were exchanged. Apparently the second oxidation step leads to decomposition of the complex molecule; in cyclic voltammetry (CV) experiments the cathodic peak at ca. -0.4 V, reflecting ferrocenium cation reduction, was smaller then the corresponding anodic peak (Figure 1 (1 and 2)). However, when the scan direction was reversed at potentials less positive than the second anodic peak potential, the peak current ratio i_p^c/i_p^a was 1 and the difference in peak potentials was 0.065 V, indicating a reversible one-electron oxidation of ferrocene. These results confirmed the general voltammetric characteristic of the ferrocene/ferrocenium ion system in $AlCl_3$–BuPyCl mixtures[3,10] although even at a scan rate of 0.05 V s^{-1} a small cathodic peak at ~-0.55 V was evident in basic solutions (Figure 1 (3)), indicating more complex behavior of the $Fe(Cp)_2/Fe(Cp)_2^+$ couple in $AlCl_3$–BuPyCl ionic liquids.

More detailed electrochemical characterization of the ferrocene/ferrocenium ion system was obtained in a neutral butylpyridinium tetrachloraluminate ($AlCl_3$:BuPyCl = 1.0:1.0) since only at this solvent composition were both ferrocene and ferrocenium cation stable (vide infra). Figure 2 illustrates RDE voltammograms recorded at varying rotation rates in solutions of ferrocene and ferrocenium tetrachloroferrate in the neutral $AlCl_3$–BuPyCl ionic liquid. For the anodic wave, i vs. $\omega^{1/2}$ plots for currents at potentials on the rising portion of the wave and on the limiting current plateau were linear and passed through the origin. The log $[i/(i_l - i)]$ vs. E was linear and had a slope of 0.064 V (theoretical value for n = 1 at 40 °C is 0.062 V). Diffusion control of the ferrocene oxidation was also confirmed by normal-pulse voltammetric experiments. For pulse widths varied between 100 and 800 ms the time dependence of the limiting current agreed with the Cottrell equation (although at shorter times a small positive deviation of the current from the Cottrell relationship, similar to the one observed for iodine,[14] was evident). The log $[i/(i_l - i)]$ vs. E plots were linear with a slope of 0.063 V. Full electrochemical reversibility of the ferrocene/ferrocenium cation system was also observed in cyclic voltammetric and reverse-pulse voltammetric experiments. For CV, the anodic and cathodic peak potential difference was 0.065 V and i_p^c/i_p^a was 1. The reverse-pulse voltammetric wave had the same height and half-wave potential as the corresponding normal-pulse wave, for generation pulse width varied from 1 to 60 s (Figure 3), thus showing that the one-electron-oxidation product of ferrocene is stable and its reduction is diffusion controlled. The ferrocene oxidation product was unambiguously identified when RDE voltammetry for ferrocenium tetrachloroferrate solutions in neutral butylpyridinium tetrachloroaluminate produced two convective diffusion-controlled waves and the half-wave potentials for the first cathodic wave was within experimental error, the same as that for the ferrocene oxidation wave (Figure 2). Thus, in the anodic ferrocene oxidation, ferrocenium cation, stable in neutral $AlCl_3$–BuPyCl ionic liquid, is formed. Cyclic voltammetric results, obtained at different $AlCl_3$–BuPyCl mixture compositions, showed that, despite limited stability of ferrocene and

Table I. Diffusion Coefficients and Stokes–Einstein Products of Ferrocene and Ferrocenium Ion

$N_A:N_B$[a]	D, 10^{-7} $cm^2\ s^{-1}$	$D\eta/T$, 10^{-10} g cm s^{-2} K^{-1}	technique
	Ferrocene		
0.75:1	4.55	7.5	RDE
	3.9	6.4	NP
0.85:1	6.1	6.2	RDE
	5.9	6.0	NP
0.95:1	7.9	6.3	RDE
1.0:1.0	8.9	6.25	RDE
	9	6.3	NP
	Ferrocenium Cation		
1.0:1.0	6.8	4.8	RDE

[a] N_A = number of moles of $AlCl_3$. N_B = number of moles of BuPyCl.

ferrocenium ion in acidic and basic solutions, respectively (vide infra), the ferrocene/ferrocenium ion couple is electrochemically reversible throughtout the accessible range of the solvent compositions. From diffusion-controlled limiting currents in normal-pulse (NP) voltammetry and convective diffusion-limited currents in RDE voltammetry, a diffusion coefficient of ferrocene in neutral and basic $AlCl_3$–BuPyCl melts was calculated and the values obtained are collected in Table I, together with the Stokes–Einstein product ($D\eta/T$), which is approximately constant. Higher values of $D_{Fe(Cp)_2}$ in a 0.75:1 melt are obtained from RDE voltammetry than from NP voltammetry and are apparently caused by a follow-up reaction of ferrocenium cation decomposition (vide infra) that affected the RDE results. The diffusion coefficient of the ferrocenium cation could be measured only in the neutral butylpyridinium tetrachloroaluminate, and a value about 25% smaller than that for ferrocene was obtained (Table I). Since the iron–ligand distance in $Fe(Cp)_2^+$ is not much different from that in $Fe(Cp)_2$,[17] the larger apparent solvolytic radius of $Fe(Cp)_2^+$ may indicate ionic interactions of ferrocenium cation with the tetrachloroaluminate anion.

Stability of Ferrocene and Ferrocenium Cation as a Function of the $AlCl_3$–BuPyCl Ionic Liquid Composition. The stability of ferrocene and ferrocenium cation solutions in $AlCl_3$–BuPyCl mixtures was checked by repeatedly recording RDE voltammograms after solution preparation. Only in the neutral butylpyridinium tetrachloroaluminate did the height of the anodic wave of ferrocene, and of the cathodic wave of ferrocenium tetrachloroferrate, change by less than 5% over a 24-h period. However, in some experiments with neutral ferrocene solutions, a small cathodic wave due to ferrocenium reduction was observed; in some instances with neutral ferrocenium solutions a small ferrocene oxidation current appeared. These currents never amounted to more than 10% of the initial wave height. They probably resulted from inaccuracies in the melt composition and actually reflected the behavior of ferrocene/ferrocenium ion system in slightly acidic or basic solutions (vide infra).

The anodic wave observed at the RDE for ferrocene solutions in basic $AlCl_3$–BuPyCl mixtures remained intact over a period of a few days, showing stability of ferrocene in the ionic solvent. Cyclic voltammetry at scan rates higher than 0.1 V s^{-1} and reverse-pulse voltammetry at generation pulse widths less than 2 s showed reversible reduction of the ferrocenium cation formed during the anodic process; i_p^c/i_p^a and $(i_{DC} - i_{RP})/i_{NP}$ ratios equal to 1 showed stability of the ferrocenium ion on the time scale of these experiments (Figures 4 (1) and 5 (2)). However, results of similar experiments

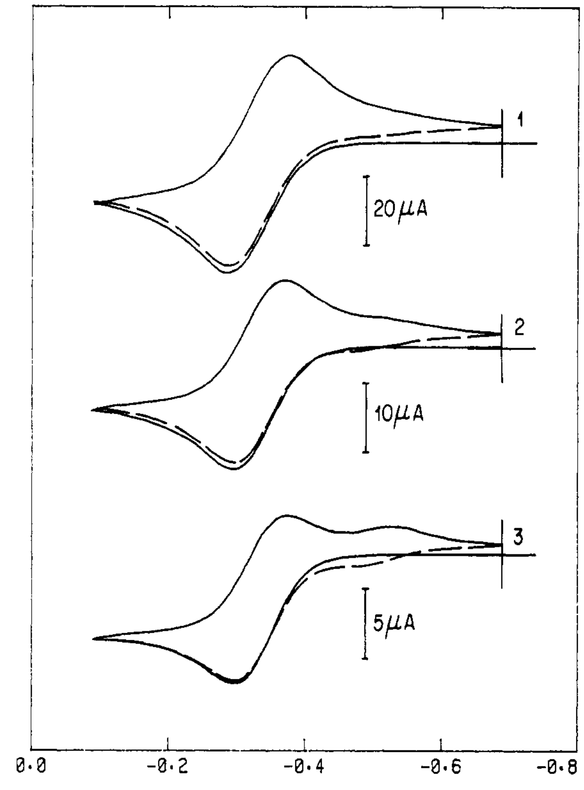

Figure 4. Cyclic voltammograms for 9.9 mM ferrocene in 0.75:1 $AlCl_3$:BuPyCl melt at different scan rates (v, V/s; TE): (1) 0.1; (2) 0.02; (3) 0.005.

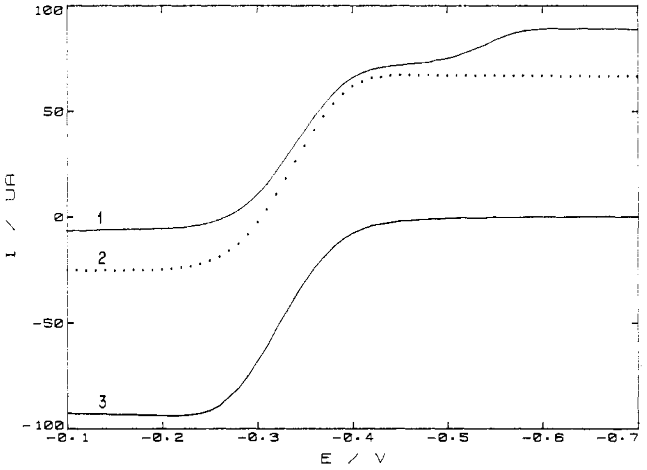

Figure 5. Normal- (3) and reverse-pulse (1 and 2) voltammograms for 9.9 mM ferrocene in 0.75:1 $AlCl_3$:BuPyCl melt (t_p = 0.1 s). τ (s): (1) 60.1; (2) 1.1. E_i (V; TE): (1 and 2) 0.0; (3) −0.8.

performed at lower scan rates in CV (below 0.05 V/s) and longer generation time in RP voltammetry (greater than 15 s) were found to be dependent upon melt composition in basic $AlCl_3$–BuPyCl melts. For solutions with $AlCl_3$:BuPyCl mole ratios greater than 0.85:1, the ferrocenium cation was stable over a period of time sufficient to complete the electrochemical experiment and the results were identical with those in the neutral solution, i.e., i_p^c/i_p^a and $i_{DC}i_{RP}/i_{NP}$ ratios were 1. For more basic $AlCl_3$–BuPyCl mixtures (at higher chloride concentrations), slow scan rate CV and RP voltammetry at long generation times revealed a follow-up chemical reaction of the ferrocenium cation formed in the anodic step (Figures 4 and 5). In CV a decrease in potential scan rate caused a gradual diminution of the i_p^c/i_p^a ratio and at the same time a second cathodic peak appeared (Figure 4). Upon reversal of the scan

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Table II. Concentrations of Compounds Formed after Addition of BuPyCl to a Solution of $Fe(Cp)_2FeCl_4$ in Neutral $AlCl_3$–BuPyCl Melt

time, h	C_{Cl^-}, mol dm^{-3}	$C_{Fe(Cp)_2^+}$, 10^{-3} mol dm^{-3}	$\Delta C_{Fe(Cp)_2^+}$, 10^{-3} mol dm^{-3}	$C_{Fe(Cp)_2}$, 10^{-3} mol dm^{-3}	$C_{FeCl_4^-}$, 10^{-3} mol dm^{-3}	$\Delta C_{FeCl_4^-}$, 10^{-3} mol dm^{-3}	$C_{FeCl_4^{2-}}$, 10^{-3} mol dm^{-3}
0	0.21	7.9		0	7.9		0
0.25	0.21	3.9	−4	2.8	9.1	1.2	0
0.5	0.21	1.8	−6.1	4.4	9.7	1.8	0
1	0.21	0	−7.9	5.9	10.4	2.5	0
2	0.21	0	−7.9	5.9	8.5	0.6	1.8
4	0.21	0	−7.9	6.0	7.0	−0.9	3.3
25	0.21	0	−7.9	5.9	5.1	−2.8	5.2
0	0.88	10.4		0	10.4		
0.25	0.88	0	−10.4	7.2	11.4	1	2.3
0.5	0.88	0	−10.4	7.1	10	−0.4	3.8
1	0.88	0	−10.4	7.2	7.3	−3.1	6.5
3	0.88	0	−10.4	7.1	2.5	−7.9	11.4
8	0.88	0	−10.4	7.1	0	−10.4	14.1

direction, a corresponding anodic peak was evident during the second anodic sweep. This new reversible redox couple could be identified as the $FeCl_4^-/FeCl_4^{2-}$ system; the peak potentials ($E_p^c = -0.545$ V vs. Ag/Ag$^+$ electrode, 0.045 V vs. Al electrode) were, within experimental error, identical with the values reported for the Fe(III)/Fe(II) couple in basic $AlCl_3$–BuPyCl ionic liquid.[18] Similar results were observed in RP voltammetric experiments. At large generation pulse widths the height of the first cathodic wave decreased and an $FeCl_4^-$ reduction wave appeared (Figure 5 (1)). These results show that in basic solutions ferrocenium cation formed in the anodic step undergoes a chemical reaction, leading to $FeCl_4^-$. The total height of the $Fe(Cp)_2^+$ and $FeCl_4^-$ reduction waves equaled the ferrocene oxidation wave, indicating that $Fe(Cp)_2^+$ and $FeCl_4^-$ were the only iron-containing products of ferrocene oxidation. In order to determine an overall stoichiometry of the ferrocenium cation decomposition reaction, butylpyridinium chloride was added to a solution of ferrocenium tetrachloroferrate in neutral butylpyridinium tetrachloroaluminate and changes in concentration of the different iron complexes were followed by RDE voltammetry (Figure 6). From known diffusion coefficients of the iron complexes (Table I[17]), the concentrations of $Fe(Cp)_2$, $Fe(Cp)_2^+$, $FeCl_4^-$, and $FeCl_4^{2-}$ were calculated and the results are shown in Table II. In the experiment in which a solution with an $AlCl_3$:BuPyCl mole ratio of 0.95:1 was prepared, a decrease of the $Fe(Cp)_2^+$ reduction and an appearance of an $Fe(Cp)_2$ oxidation wave was initially observed. The concentration of $FeCl_4^-$ increased at the same time. During the first hour after solution preparation, the number of moles of ferrocene and tetrachloroferrate ion formed in the ferrocenium cation decomposition reaction amounted to ca. 70 and 30% of the ferrocenium ion decomposed. The observed stoichiometry of the ferrocenium decomposition was, however, modified by a slow reduction of both iron(III) complexes, which was evident at times longer than 1 h, when there was no more ferrocenium left in solution. In more basic solutions ($AlCl_3$:BuPyCl = 0.8:1), the ferrocenium cation decomposition reaction was faster; after 15 min there was no ferrocenium cation in the solution (Table II). Also, the reduction of the $FeCl_4^-$ formed was faster in the more basic melt. In the 0.8:1 melt only $Fe(Cp)_2$ and $FeCl_4^{2-}$ were found after 8 h, while in a 0.95:1 $AlCl_3$:BuPyCl mixture a portion of the $FeCl_4^-$ remained unreduced after 25 h (Table II). In both basic solvent compositions, similar stoichiometry for the ferrocenium decomposition reaction was observed; somewhat less than one-third of the number of moles of ferrocenium cation that decomposed formed chloro complexes of Fe(III) and Fe(II) and somewhat more than two-thirds of the ferrocenium that decomposed was reduced to ferrocene. These results suggest the stoichiometric relationship

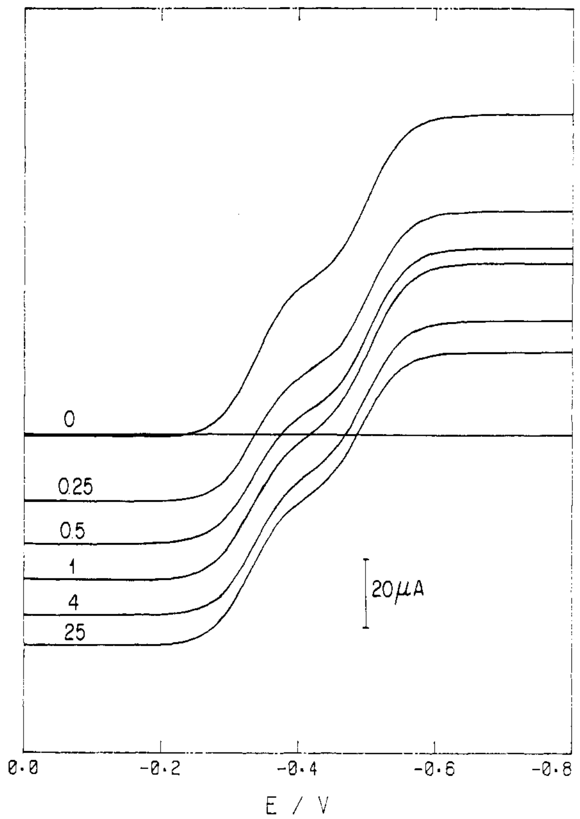

Figure 6. RDE voltammograms for ferrocenium tetrachloroferrate in 0.95:1 $AlCl_3$:BuPyCl melt as a function of time (time in hours indicated at the curves; initial concentration of $Fe(Cp)_2FeCl_4$ 7.9 mM; rotation rate 1600 rpm; TE).

$$3Fe(Cp)_2^+ + 4Cl^- = 2Fe(Cp)_2 + FeCl_4^- + 2Cp\cdot \quad (1)$$

Similar stoichiometry for reactions of ferrocenium cation with different nucleophilic reagents has been reported.[19] It implies that, in the primary step, a substitution of Cp$^-$ ligands by chloride ions occurs and then cyclopentadienyl ion generated in the first step reduces $Fe(Cp)_2^+$. The observed distinct dependence of this reaction rate on chloride ion concentration suggests that the first step involving an attack of chloride ion on ferrocenium cation determines the rate of the reaction. The pseudo-first-order rate constant estimated for the 0.95:1 melt from RDE voltammetric results (Table II) was ca. 8×10^{-4} s^{-1}. For a 0.75:1 melt this rate constant was estimated from

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results of double-step chronoamperometric experiments using the theoretical working curves calculated by Schwarz and Shain.[20] For generation pulse widths (τ) of 5 and 15 s, from currents measured during first and second steps at equal $t - \tau$ times, i_b/i_f ratios were calculated and then k_τ values found. The k_τ values obtained for $(t - \tau)/\tau$ equal to 0.04, 0.1, and 0.2 gave a pseudo-first-order rate constant of $(2 \pm 0.5) \times 10^{-2}$ s^{-1}. These rate constant values, estimated at chloride ion concentrations of 0.21 and 1.1 mol dm^{-3} for the 0.95:1 and 0.75:1 melts, respectively, give second-order rate constants of 1.8×10^{-2} and 1.7×10^{-2} s^{-1} mol^{-2} dm^6 and suggest a second-order dependence of the reaction rate on the chloride concentration. The proposed mechanism for the ferrocenium cation decomposition in basic $AlCl_3$–BuPyCl ionic liquid assumes that $Fe(Cp)_2^+$ is reduced by cyclopentadienyl ion. This was confirmed in experiments performed in LiCp solution in basic 0.75:1 $AlCl_3$:BuPyCl melt. Cyclic voltammetry of LiCp gave a totally irreversible anodic peak at ca. –0.38 V at a glassy-carbon electrode, indicating that the potential of Cp^- oxidation is more negative than the formal potential of the $Fe(Cp)_2^+/Fe(Cp)_2$ couple. When $FeCl_3$ was added to a LiCp-containing solution, an anodic RDE wave reflecting the presence of $FeCl_4^{2-}$ was immediately observed. Apparently, the Cp^- oxidation potential is more negative than the $FeCl_4^-/FeCl_4^{2-}$ formal potential, and thus cyclopentadienyl anion is able to reduce both $Fe(Cp)_2^+$ and $FeCl_4^-$. This, however, does not explain the slow reduction of $FeCl_4^-$ observed after the ferrocenium ion decomposition had been completed. Cyclopentadienyl ion released during the latter reaction rapidly reduces $Fe(Cp)_2^+$ ($FeCl_4^-$ cannot be reduced in the presence of $Fe(Cp)_2^+$ since the $FeCl_4^-$ redox potential is more negative); therefore, there are no Cp^- ions in the solution after all the $Fe(Cp)_2^+$ has decomposed or been reduced to ferrocene. The mechanism for the slow secondary reduction of $FeCl_4^-$ is not known. It is possible that the cyclopentadienyl radical formed by Cp^- oxidation reacts further to give another, slowly reacting reductant. This seems to be the most probable process since solutions of ferrocene (vide supra) and $FeCl_3$[18] in basic $AlCl_3$–BuPyCl ionic liquid are stable. A slow polyelectron oxidation of cyclopentadienyl ion by cerium(IV) sulfate has been observed.[21]

For solutions of ferrocene in acidic $AlCl_3$–BuPyCl mixtures RDE voltammetry revealed a composite anodic–cathodic wave, indicating the presence of both ferrocene and ferrocenium ion in the solution. Even for a freshly prepared solution of ferrocene in a 1.7:1 $AlCl_3$:BuPyCl melt, a small cathodic current was evident, and as Figure 7 shows, this solution was not stable; the ferrocene oxidation wave diminished and the ferrocenium reduction current increased with time. The changes observed in the RDE voltammograms indicated that the amount of ferrocenium cation formed was distinctly less than the decrease in the ferrocene concentration. When concentrations of $Fe(Cp)_2$ and $Fe(Cp)_2^+$ were calculated on the assumption of constant Stokes–Einstein products, $D\eta/T$, throughout the accessible range of $AlCl_3$–BuPyCl melts, the final concentration of ferrocenium cation was found to be over five times smaller than the initial ferrocene concentration. Additionally, neither the rate of ferrocene disappearance nor the yield of ferrocenium ion formed was reproducible, suggesting a contribution of trace impurities from the solvent and/or drybox atmosphere to the instability of ferrocene in acidic $AlCl_3$–BuPyCl mixtures. The formal potential of the ferrocene/ferrocenium couple is close to the negative limit of the solvent, i.e., to the potential of the Al(III)/Al couple. It is more negative than the formal potentials of iodide[14] as well as $Fe(bpy)_3^{2+}$, $Fe(phen)_3^{2+}$, and $Ru(bpy)_3^{2+}$,[22] which are all oxidized by molecular oxygen. This suggests that traces of oxygen from the drybox atmosphere could oxidize ferrocene. The latter reaction was indeed observed; ferrocene was immediately oxidized to ferrocenium ion when gaseous oxygen was bubbled through ferrocene solutions in acidic $AlCl_3$–BuPyCl melts. The redox potential of oxygen strongly depends on the acidity of $AlCl_3$–BuPyCl mixtures, and oxygen did not react with ferrocene in neutral butylpyridinium tetrachloroaluminate. RDE voltammograms recorded in ferrocene solutions before and after saturation of the solution with oxygen were the same; the ferrocene oxidation wave was observed (Figure 8 (2)). On the other hand, an immediate oxidation of ferrocene occurred upon addition of a small amount of $AlCl_3$ to the neutral melt; instead of the anodic wave a cathodic current, reflecting ferrocenium ion reduction, appeared (Figure 8 (1)). Additionally, a cathodic current at potentials more negative than –0.4 V was evident at a tungsten electrode in this slightly acidic solution (Figure 8 (1)). This current was not observed at a glassy-carbon electrode, and it increased significantly after water was added to the melt (vide infra). Thus, it was probably due to the hydrogen-evolution reaction.[23] The experiments with ferrocene oxidation by molecular oxygen showed that the reaction of ferrocene with traces of oxygen from the drybox atmosphere is one of the causes of the instability of ferrocene in acidic $AlCl_3$–BuPyCl mixtures. However, the amount of ferrocenium ion formed during these experiments was always distinctly less than the initial ferrocene concentration. In lengthy experiments without any deliberate oxygen introduction, the ferrocenium yield was below 20% (Figure 7). In experiments with oxygen bubbled into an acidic ferrocene solution, about 30% of the ferrocene was found as

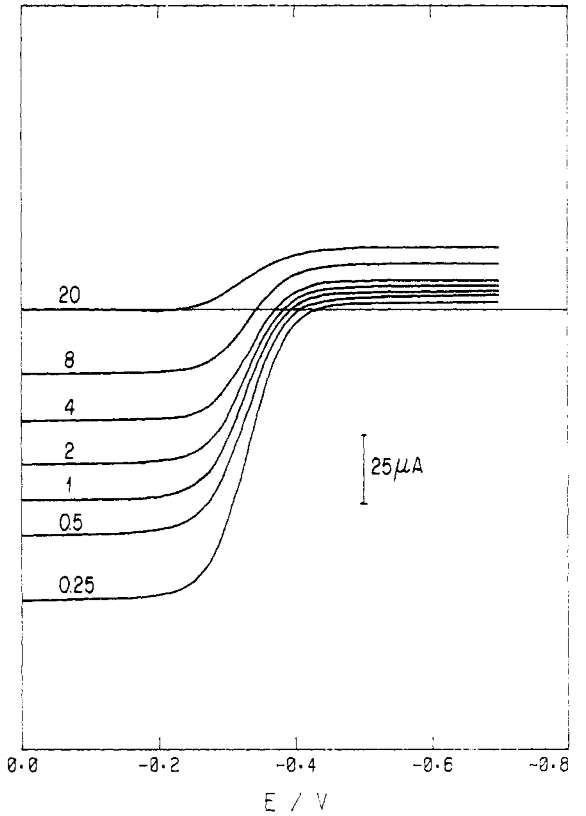

Figure 7. RDE voltammograms for ferrocene in 1.7:1 $AlCl_3$:BuPyCl melt as a function of time (time in hours indicated at the curves; initial concentration of $Fe(Cp)_2$ 5.9 mM; rotation rate 1600 rpm; GCE).

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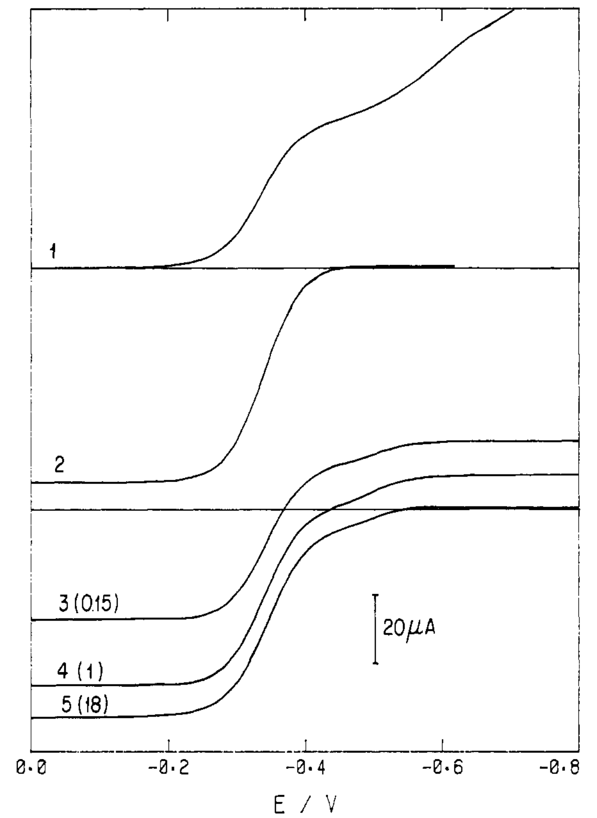

Figure 8. RDE voltammograms of 10 mM ferrocene in neutral $AlCl_3$–BuPyCl melt (2), with 20 mg of $AlCl_3$ added to this solution saturated with O_2 (1), and with composition of the latter solution adjusted to 0.95:1 by addition of BuPyCl (3, 4, 5) (time in hours after BuPyCl addition indicated at the curves; rotation rate 1600 rpm; TE).

ferrocenium ion, and in the experiment in slightly acidic melt the ferrocenium yield was ca. 70% (Figure 8). This indicates that there are parallel reactions of ferrocene in acidic solutions leading to the formation of different products. The formation of more than one iron-containing product of ferrocene reacting in acidic $AlCl_3$–BuPyCl mixtures was confirmed when, after the reaction with oxygen, the composition of the solution was adjusted to 0.95:1 $AlCl_3$:BuPyCl mole ratio by BuPyCl addition (Figure 8 (3, 4, 5)). Ferrocenium ion reacted with the basic melt, and the expected amount of $FeCl_4^-$, subsequently reduced to $FeCl_4^{2-}$, was formed. However, the ferrocene concentration found in the basic solution was greater than the ferrocenium concentration formed in the acidic melt (from ferrocene), and the total amount of $Fe(Cp)_2$ and $FeCl_4^{2-}$ in the final solution (Figure 8 (5)) was equal to the initial amount of $Fe(Cp)_2$ added to the neutral melt (Figure 8 (2)). This indicated that in acidic solution a portion of ferrocene was involved in a reversible reaction, and this ferrocene was recovered after the solution had been made basic. Such behavior was observed in all experiments with ferrocene in acidic melts; even when the yield of $Fe(Cp)_2^+$ was as low as 20%, more ferrocene was recovered by BuPyCl addition and the total amount of $Fe(Cp)_2$, $FeCl_4^-$, and $FeCl_4^{2-}$ was equal to the initial amount of ferrocene added to an acidic solution. Since the rate of this second ferrocene reaction was irreproducible and the reaction needed many hours for completion, the involvement of trace impurities from the drybox atmosphere was suspected. Besides traces of oxygen, traces of moisture are another reactive impurity in the argon-filled glovebox. Water reacts with $AlCl_3$–BuPyCl melts, giving off HCl.[23] Addition of water to acidic ferrocene solutions caused an immediate disappearance of the ferrocene oxidation wave at the RDE, but the ferrocenium cation was not formed, i.e., the cathodic wave was not observed. Water did not react with ferrocene in neutral butylpyridinium tetrachloroaluminate; the anodic wave remained intact (Figure 9 (2)). An addition of $AlCl_3$ was necessary to cause the reaction to occur. In a slightly acidic melt the reaction of ferrocene with "water" was rapid. An RDE voltammogram recorded immediately after $AlCl_3$ dissolution did not show a ferrocene oxidation wave; only a large cathodic current at potentials more negative than −0.4 V was evident (Figure 9 (1)). This current, apparently due to hydrogen evolution,[23] was not observed at a GCE and RDE voltammetry with a carbon electrode revealed a small ferrocenium cation reduction wave. However, only ca. 2% of the ferrocene initially present was oxidized to ferrocenium cation. As Figure 9 (3) shows, after an addition of BuPyCl two anodic waves, reflecting oxidation of 2 mM $FeCl_4^{2-}$ and 7.7 mM $Fe(Cp)_2$, were obtained. Thus, most of the ferrocene did not decompose in the reaction with "water" in acidic solution, but this result suggested a reversible formation of some stable ferrocene adduct that could not be electrochemically oxidized. This product of the ferrocene reaction with "water" in acidic $AlCl_3$–BuPyCl ionic liquid has not been identified. It is possible that ferrocenonium tetrachloroaluminate, which forms upon an introduction of HCl into a mixture of ferrocene and aluminium chloride in dichloromethane,[23] was formed in the acidic $AlCl_3$–BuPyCl melt in the presence of water.

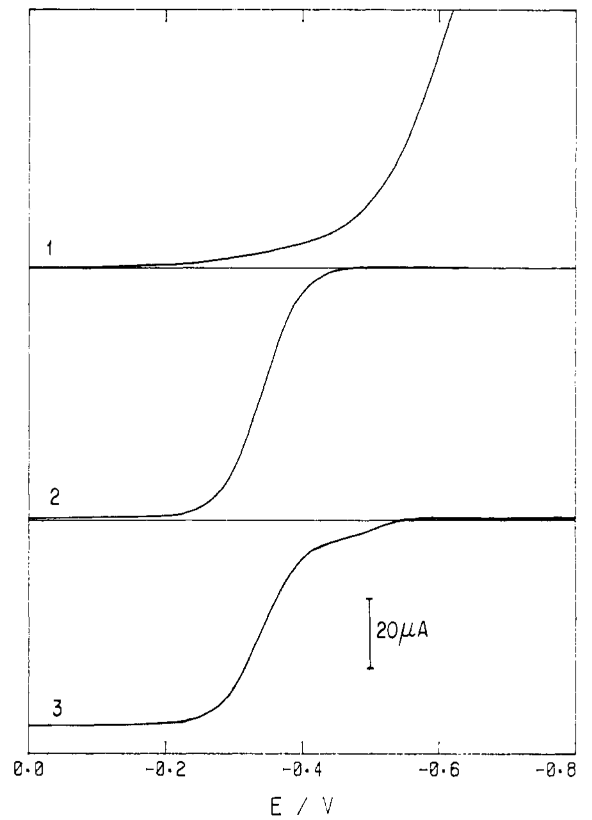

Figure 9. RDE voltammograms for 9.8 mM ferrocene in neutral $AlCl_3$–BuPyCl melt (2), with 4 μL of H_2O and 50 mg of $AlCl_3$ added (1), and with composition of the latter solution adjusted to 0.95:1 by addition of BuPyCl (3) (rotation rate 1600 rpm; TE).

These results show that the apparent instability of ferrocene in acidic $AlCl_3$–BuPyCl ionic liquid is due to reactions of ferrocene with traces of moisture and oxygen present in the drybox atmosphere or as impurities in the melt itself. Since these reactions were fast and appeared to proceed stoichiometrically, RDE voltammograms recorded in freshly prepared solution of ferrocene in acidic $AlCl_3$–BuPyCl mixture indicated the amounts of these impurities present in the melt. As Figure 7 shows, in the solution with a formal initial concentration of ferrocene of 5.9 mM, 4.3 mM $Fe(Cp)_2$ and 0.2 mM $Fe(Cp)_2^+$ were found after 15 min. Thus, the initial concentration of

Table III. Formal Potential of Ferrocene/Ferrocenium Ion Couple at Different $AlCl_3$:BuPyCl Mole Ratios

$N_A:N_B$[a]	$E^{\circ\prime}$,[a] V vs. Ag^+/Ag	$N_A:N_B$[a]	$E^{\circ\prime}$,[a] V vs. Ag^+/Ag
2:1	−0.318	1.1:1	−0.340
1.9:1	−0.322	1.0:1.0	−0.341
1.8:1	−0.323	0.95:1	−0.342
1.7:1	−0.327	0.85:1	−0.340
1.5:1	−0.330	0.8:1	−0.341
1.4:1	−0.333	0.75:1	−0.340
1.2:1	−0.340		

[a] N_A = number of moles of $AlCl_3$; N_B = number of moles of BuPyCl. [b] E or E' values vs. Al/Al(III) $AlCl_3$:BuPyCl, add +0.590 V.

the HCl was ca. 1.4 mM (a 1:1 stoichiometry of this reaction forming the nonelectroactive product was assumed), and the oxygen concentration in the solution was probably below 0.1 mM (reduction of oxygen to an aluminoxy species would require as many as four electrons per O_2 molecule). This indicates the relative purity of freshly prepared $AlCl_3$–BuPyCl melts; however, a melt in contact with the drybox atmosphere apparently absorbs traces of moisture and oxygen. It should be stressed, however, that water reacts with $AlCl_3$–BuPyCl ionic liquids.[23,25] Thus, these systems contain as impurities products of the reaction of water with the melt (probably HCl and an aluminohydroxy and aluminoxy species) but are virtually anhydrous.

Ferrocenium cation solutions in acidic $AlCl_3$–BuPyCl mixtures formed in the reaction of ferrocene with oxygen or prepared from ferrocenium tetrachloroferrate were stable for at least several days. Even a deliberate addition of water to the ferrocinium solution did not affect the ferrocenium cation reduction wave observed at the RDE. Thus, ferrocenium ion solutions could be used to determine a formal potential of the ferrocene/ferrocenium ion couple in acidic $AlCl_3$–BuPyCl ionic liquids. Unfortunately, however, an accurate concentration of ferrocenium cation in solutions prepared with $Fe(Cp)_2FeCl_4$ was not known; the height of the $Fe(Cp)_2^+$ reduction wave recorded in this solution immediately after its preparation was ca. 60% of the limiting current calculated from the Levich equation assuming a constant $D\eta/T$ product for $Fe(Cp)_2^+$, as the melt composition is changed. Moreover, RDE voltammetry did not reveal the expected presence of Fe(III) from the $FeCl_4^-$ counterion in this solution. The formal potential of the Fe(III)/Fe(II) couple in acidic $AlCl_3$–BuPyCl melts is very close to the positive limit of the solvent,[17] and Fe(III) is slowly reduced by the melt.[26] Since the Fe(III)/Fe(II) formal potential is more positive than the potential of the second ferrocene oxidation wave (Figure 1), it is possible that Fe(III) oxidizes the cyclopentadienyl ligand of the ferrocenium cation.

Formal Potential of the Ferrocene/Ferrocenium Ion System. Since the ferrocene/ferrocenium cation couple has been widely used as an internal reference couple for intersolvent standard potentials comparisons,[8,9] an accurate value of its formal potential in $AlCl_3$–BuPyCl ionic liquids was of interest. Table III shows the values of the ferrocene/ferrocenium ion formal potential across the entire range of solvent composition, which encompasses wide variation of system acidity. Data were obtained from cyclic voltammetric results in solutions of ferrocene in basic melt compositions and in ferrocenium tetrachloroferrate solution in acidic $AlCl_3$–BuPyCl mixtures. A value of the reversible half-wave potential for this electrochemically reversible system was calculated as average of CV peak potentials $(E_p^a - E_p^c)/2$. The half-wave potential values at given $AlCl_3$:BuPyCl mole ratios were reproducible with a maximum deviation less than ±5 mV. The $E_{1/2}$ values calculated from CV data did not differ by more than 10 mV from half-wave potentials obtained from RDE or NP voltammetry. The formal potential of the ferrocene/ferrocenium ion couple was then calculated from eq 2 with $E_{1/2}$ values obtained from

$$E^{\circ\prime} = E_{1/2} + (RT/2F)\ \ln\ (D_{ox}/D_{Red}) \qquad (2)$$

CV and a ratio of the Stokes–Einstein products for $Fe(Cp)_2^+$ and $Fe(Cp)_2$ (Table I). The values obtained were independent of solvent acidity throughout the basic, neutral, and slightly acidic regions (Table III). However, at $AlCl_3$:BuPyCl mole ratios greater than 1.2:1 a shift of the $Fe(Cp)_2^+/Fe(Cp)_2$ formal potential was evident, although the shift was only about 20 mV. This indicates a difference in interactions of ferrocene and ferrocenium cation with the solvent, probably a complexation of ferrocene by $AlCl_3$ that has been observed in nonpolar solvents[27] and/or ion-pair interactions between ferrocenium cation and tetrachloroaluminate anion. The total shift of the ferrocene/ferrocenium ion formal potential with wide variation of $AlCl_3$–BuPyCl ionic liquid acidity was very small, distinctly less than that recently reported for polypyridine complexes of Fe(III)/Fe(II) and Ru(III)/Ru(II).[22] Apparently the metal redox center is relatively unaffected by interactions with the ionic liquid.

Conclusions

(1) Very wide changes of $AlCl_3$–BuPyCl ionic liquid acidity cause a small shift of the ferrocene/ferrocenium ion formal potential at very acidic solvent compositions. The formal potential of this system is however constant throughout basic, neutral, and slightly acidic solvent composition range and equals −0.340 V vs. Ag^+/Ag reference electrode (0.250 V vs. Al electrode).

(2) Ferrocene and ferrocenium cation are stable in neutral butylpyridinium tetrachloroaluminate.

(3) In basic solutions ferrocene is stable, while ferrocenium ion is decomposed by chloride ions to ferrocene and tetrachloroferrate ion.

(4) Ferrocenium cation is stable in acidic melts. Acidic ferrocene solutions are unstable toward reactions with traces of moisture and oxygen.

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Registry No. $Fe(Cp)_2$, 102-54-5; $Fe(Cp)_2^+$, 12125-80-3; $Fe(Cp)_2FeCl_4$, 1287-09-8; $FeCl_4^-$, 14946-92-0; $AlCl_3$, 7446-70-0; BuPyCl, 1124-64-7; Cl^-, 16887-00-6; O_2, 7782-44-7; butylpyridinium tetrachloroaluminate, 67226-46-4.

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