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Substituent Effects on Ferrocenes in Aluminum Chloride–Butylpyridinium Chloride Molten-Salt Mixtures

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The visible absorption spectra and reduction potentials of 11 ferrocenes containing electron-withdrawing substituents were determined in an *N*-*n*-butylpyridinium chloride–aluminum chloride molten salt. When the substituent(s) on the cyclopentadienyl ring(s) of ferrocene were varied, the reduction potential was caused to range over 1.25 V, and the wavelength for maximum absorption of visible light was varied by nearly 200 nm. These changes are greater than have been observed for similar ferrocenes in other nonaqueous solvents. Evidence is presented for specific interactions of particular ferrocenes with the molten salt.

Introduction

Mixtures of aluminum chloride and *N*-*n*-butylpyridinium chloride (BuPyCl) are liquid over a broad range of compositions below 30 °C and are intrinsically ionic conductors.[1] Their electrochemical voltage window of 4 V is limited by aluminum deposition (or BuPyCl reduction, depending on melt composition[2]) and chlorine evolution. They are thus excellent media in which to carry out electrochemical investigations of the coordination chemistry of inorganic ions in chloride media[3] and the interaction of organic molecules with aluminum chloride.[4]

In addition to their convenient electrochemical properties, chloroaluminate molten salts exhibit acid–base properties that enhance their versatility as solvents.[5] The concentrations of the major species in the melts are determined by the equilibria

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad (1)$$

$$2Al_2Cl_7^- \rightleftharpoons Al_3Cl_{10}^- + AlCl_4^- \qquad (2)$$

For the particular molten salt used in this work eq 1 and 2 fully describe the species in solution in the composition range between 66.6 mol % $AlCl_3$–33.3 mol % BuPyCl (the 2:1 melt) and 44 mol % $AlCl_3$–56 mol % BuPyCl (the 0.8:1 melt). For the purposes of this study, however, eq 1 is sufficient for analysis of the effects discerned.

This paper reports the results of electrochemical measurements in the molten-salt system of 11 ferrocenes substituted with strong electron-withdrawing groups. Correlations are made of the reduction potentials with the absorption spectra of the ferrocenes and with the Hammett constants σ°_m and σ°_p for the various substituent groups.

Considerable work has been carried out in nonaqueous media to determine appropriate linear free energy relationships among redox potentials of substituted ferrocenes,[6] determined as polarographic half-wave potentials or chronopotentiometric quarter-wave potentials, and the Taft[7] or Hammett[8,9] constants for the substituents. The Hammett σ_p function, which includes a resonance interaction contribution, appears to be the more applicable, although a blending of σ_m and σ_p functions has been used successfully.[10] Deviations from linearity of a plot of $E_{1/2}$ vs σ have been ascribed to specific interactions of the substituent with the central metal ion or to structural or conformational effects.[11] In general, the redox potential is shifted to more negative values by electron-donating substituents[12] and to more positive values by electron-withdrawing substituents.

Our interest in the redox behavior of substituted ferrocenes in low-temperature molten salts arose from their possible application as redox couples in a molten-salt photoelectrochemical cell.[13] The potential of the redox couple and the solubility of both redox species are important parameters in the design of photoelectrochemical cells. This study demonstrates that appropriate substitution of the ferrocene cyclopentadienyl ring provides an effective method for controlling the redox potential of the ferrocene system as well as its solubility in the molten salt.

Experimental Section

BuPyCl was prepared in 3-mol batches from pyridine and *n*-butyl chloride (Matheson Coleman and Bell) as has been described elsewhere.[5b,12]

The molten salts were prepared by mixing weighed amounts of BuPyCl and aluminum chloride (Fluka) in a Vacuum Atmospheres glovebox under an argon atmosphere in which the moisture content was typically less than 1 ppm. A pre-electrolysis step generally removed most of the pale yellow color of the melt. Current–voltage curves were obtained with use of a potentiostat (Princeton Applied Research, Model 173) equipped with a plug-in coulometer unit (Model 179). Working and indicator electrodes were either glassy-carbon (Tokai Electrode Manufacturing Co.) or tungsten rods (Materials Research Corp.). Reduction potentials were calculated by using the formula $E^\circ = {}^1/_2(E_{pa} + E_{pc})$.[14]

Some of the ferrocenes were ordered from supply houses. Compounds **2**, **7**, **9**, and **10** were ordered from Strem Chemicals, compound **11** was obtained from Sigma Chemical Co., and **12** was purchased from Aldrich. Compound **3** was prepared by simple esterification with ethanol of ferrocenecarboxylic acid ordered

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Table I. Reduction Potentials and Absorption Data for Substituted Ferrocenes in *N*-*n*-Butylpyridinium Chloride–Aluminum Chloride (2:1)

substituted ferrocene	reduction potential vs Al, V	abs max, nm	extinctn coeff (±5%)
N-phenylferrocenecarboxamide (1)	0.25	450	112
ferrocene (2)	0.28[a]	432	304
carbethoxyferrocene (3)	0.85	500	917
pivaloylferrocene (4)	0.975	562	1183
cyanoferrocene (5)	0.98	456	622
N,*N*-dimethylferrocenesulfonamide (6)	1.02	470	
acetylferrocene (7)	1.02	620	1445
ferrocenesulfonic acid ethyl ester (8)	1.05	440	304
formylferrocene (9)	1.13	530	560
1,1'-ferrocenedicarboxylic acid (10)	1.29	486	1022
1,1'-dibenzoylferrocene (11)	1.46	570	2935
1,1'-diacetylferrocene (12)	1.50	broad band	

[a] This study. Ferrocene has been determined by another group to be about 0.25 V vs Al in BuPyCl-$AlCl_3$.[25]

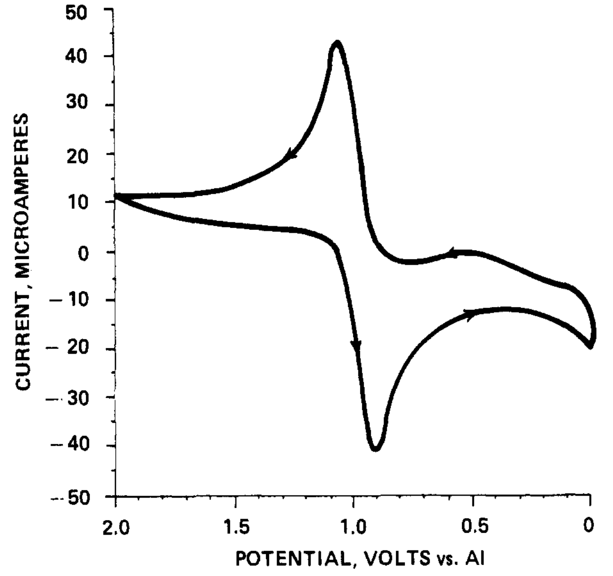

Figure 1. Cyclic voltammogram of a 0.014 *m* cyanoferrocene solution in a 2:1 $AlCl_3$–BuPyCl melt on tungsten electrode (area 0.07 cm^2), with scan rate 100 mV/s.

from Strem. Compound 8 was prepared by esterification of ferrocenesulfonyl chloride prepared as described in ref 16. Compound 4 was prepared by the Friedel–Crafts acylation of ferrocene with pivaloyl chloride. In addition, the following ferrocenes were prepared by procedures described in the literature: *N*-phenylferrocenecarboxamide (1),[15] *N*,*N*-dimethylferrocenesulfonamide (6),[16] and cyanoferrocene (5).[17]

Visible absorption spectra were measured in 1-cm cells with use of a visible–UV spectrophotometer (Cary-Varian Model 118CX); infrared spectra were recorded as KCl pellets (Beckman infrared spectrophotometer, Model IR 4260).

Results

Cyclic voltammograms were measured for the ferrocenes listed in Table I. The reduction potentials refer specifically to the molten salt with a mole ratio of aluminum chloride to butylpyridinium chloride of 2:1. The reference electrode was an aluminum wire immersed in the same electrolyte. In these systems the potential difference between anodic and cathodic current peaks was 150 mV at a 100 mV/s scan rate. While this is considerably larger than the 60-mV value associated with a reversible single-electron transfer, ohmic losses in the molten salt can account for only some of this apparent deviation from reversibility. Possibly these reactions are "quasi-reversible" or are complicated by a preceding or subsequent chemical reaction. All voltammograms were similarly distorted by this high-*iR* effect as illustrated in the voltammogram for cyanoferrocene (Figure 1).[18]

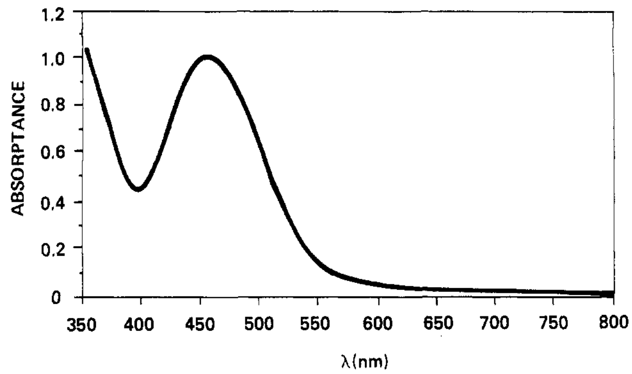

Figure 2. Absorbance of light vs wavelength for a 0.001 63 *m* cyanoferrocene solution in a 2:1 $AlCl_3$–BuPyCl melt.

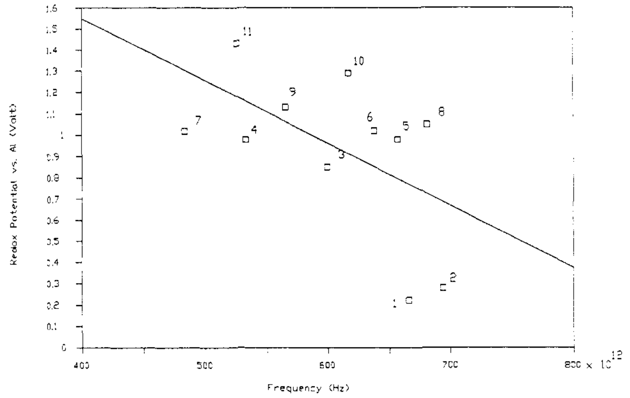

Figure 3. Redox potential as a function of frequency of light absorption for various substituted ferrocenes in a 2:1 $AlCl_3$–BuPyCl melt.

As has been found for ferrocenes in other nonaqueous solvents,[6,18] electron-donating substituents such as alkyl groups shift the reduction potential to values negative to that of ferrocene (0.28 V vs Al). Examples are the values for 1,1'-dimethylferrocene, 0.16 V, and decamethylferrocene, −0.40 V.[12] In general, electron-withdrawing groups such as the cyano group shift the potential to more anodic values compared to that of ferrocene (Table I). The reduction potential (0.25 V) determined for the carboxamide 1 is anomalous in that it is negative compared to the value of ferrocene itself.

Figure 2 shows the visible absorption spectrum of cyanoferrocene in the 2:1 molten-salt mixture. The cyanoferrocenium ion exhibits an absorption at 640 nm in this medium. These spectra are typical. Only a single absorption band was discernible for compounds 1–12 in most cases; the absorption maxima are listed in Table I. Also listed are the extinction coefficients calculated at λ_{max}. Substitution had a much larger effect on the spectra of the ferrocenes than on the corresponding ferrocenium ions. For the substituted ferrocenes the λ_{max} values varied from 440 to 620 nm; in contrast, the absorption maxima for the

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[18] Such deviations from reversibility are quite common for ferrocene systems; see: Blom, N. F.; Neuse, E. W.; Thomas, H. G. *Transition Met. Chem.* **1987**, *12*, 301.

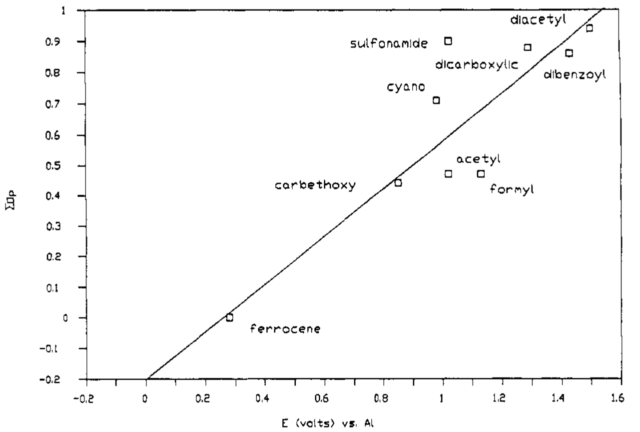

Figure 4. Hammett $\sum\sigma^\circ_p$ values plotted against E values for substituted ferrocenes. Substituent constant values were taken from: Isaacs, N. S. *Physical Organic Chemistry*; Longman: Essex, U.K., 1987; p 134.

various ferrocenium ions varied only between 620 and 640 nm.

Some substituents dramatically increased the probability of an electronic transition; in the case of 1,1′-diacetylferrocene the extinction coefficient was 1 order of magnitude higher than that of ferrocene. Higher extinction coefficients in substituted ferrocenes than in ferrocene having been ascribed to a lowering of the molecular symmetry of the system, resulting in an increased probability of the e_{2g}-to-a_{1g} symmetry-forbidden electronic transition.[19]

Figure 3 shows a test of the correlation between the frequency of the absorption maximum and the reduction potential in the 2:1 melt. Previous work[15] has shown that ferrocenes with more positive half-wave potentials tended to absorb light at lower frequencies, with good correlation between redox potential and frequency at the absorption maximum being rationalized[19] in terms of independent shifts of the energy of the e_{2g} molecular orbital to more negative values by the addition of electron-withdrawing substituents to the cyclopentadienyl ring. A similar tendency but with poor correlation ($r^2 \simeq 0.3$) was obtained in this study (Figure 3). This may reflect stronger substituent interactions with this medium than there are with the organic solvents utilized in previous studies.

The correlation between the reduction potentials and the Hammett constants for substituents is fair at best. The regression relationships determined for $\sum\sigma^\circ_{\mathrm{m\,or\,p}}$ vs E are

$$\sum\sigma^\circ_p = (0.75 \pm 0.16)E - (0.16 \pm 0.16) \qquad (3)$$

$$\sum\sigma^\circ_m = (0.6 \pm 0.12)E - (0.12 \pm 0.13) \qquad (4)$$

The plot for $\sum\sigma^\circ_p$ is shown in Figure 4. In our study of alkyl-substituted and quaternary-ammonium-substituted ferrocenes[12] the correlation for the $\sum\sigma^\circ_p$ plot ($r^2 > 0.99$) was noted to be significantly greater than that for $\sum\sigma^\circ_m$. For the current set of compounds there is virtually no difference in the correlation coefficients, with $r^2 = 0.76$ and 0.75 being calculated for eq 3 and 4, respectively. The constants of proportionality in both expressions are about half of that determined for similar ferrocenes in acetonitrile and about a third of that for the ferrocenes reported in our previous study.[12] This can be attributed to the much greater potential variation (1.25 V) of this set of ferrocenes in the molten salt. Such a large variation suggests specific interactions between the ferrocenes and the solvent medium.

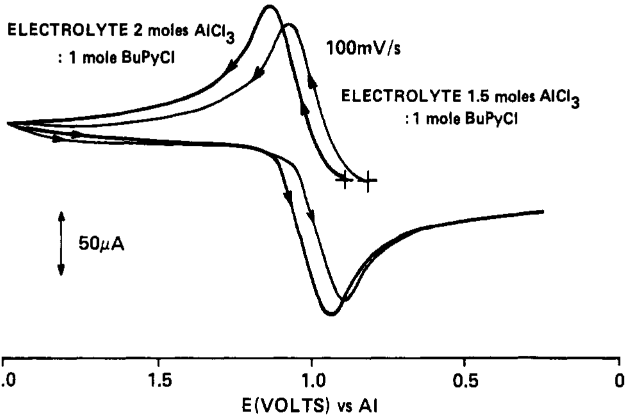

Figure 5. Cyclic voltammogram of acetylferrocene in a $AlCl_3$–BuPyCl melt on a tungsten electrode (0.07 cm²).

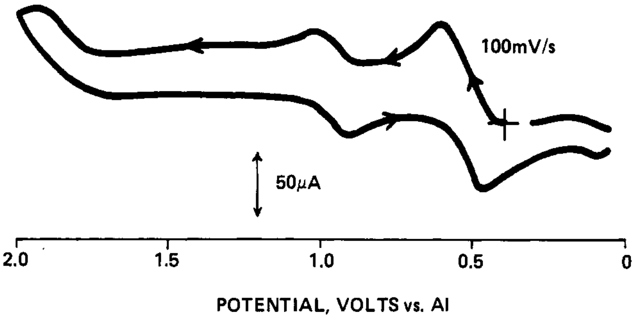

Figure 6. Cyclic voltammogram of acetylferrocene in neutral $AlCl_3$–BuPyCl molten salt.

To test for such an interaction, a detailed investigation of the electrochemical behavior of acetylferrocene was undertaken. The effect of changing the acidity of the molten salt on the cyclic voltammogram for acetylferrocene (7) on a tungsten microelectrode is shown in Figure 5. As the melt is made more basic by the addition of BuPyCl, it appears that the half-wave potential begins to shift to less positive values. However, further increase in basicity of the melt brought a more complicated behavior; at the 1:1 neutral composition a cyclic voltammogram was observed in which four redox reactions could be identified (Figure 6). The least anodic redox couple occurs at the potential associated with iron(II) chloride oxidation (0.1–0.2 V vs Al).[20] This species is present as an impurity in acetylferrocene but is not easily observed in the acid melt, since the oxidation is less reversible and occurs at potentials more positive than that of acetylferrocene oxidation.

The peak heights of the two redox reactions at 0.52 and 0.95 V (vs Al in the 2:1 melt) are both smaller than the observed peak height for acetylferrocene determined in the 2:1 melt when only one peak is observed. However, the sum of the two separate peak heights corresponds roughly to the value of the single peak height observed in the 2:1 melt (when correction is made for the dilution effect associated with the addition of salt required for the change in composition), suggesting that one species is converting into two. Increasing the proportion of BuPyCl in the molten salt resulted in an increase in the peak height of the less anodic oxidation wave at the expense of the more anodic one, until eventually only the less anodic process was observed at the scan rate of 100 mV/s. At the most basic composition studied, 0.8:1, the less anodic process

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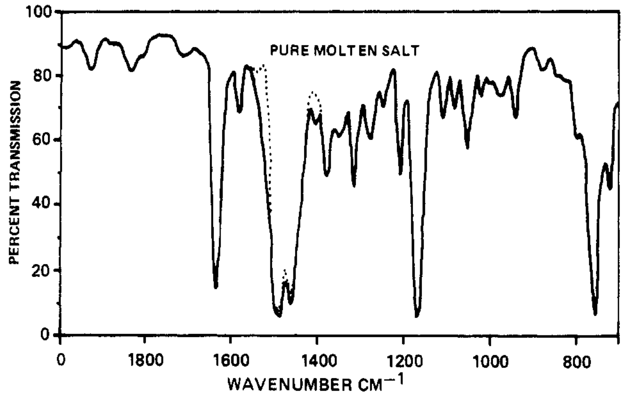


Figure 7. IR spectrum of acetylferrocene in 2:1 molten salt displaying a shoulder at 1510 cm^{-1}.

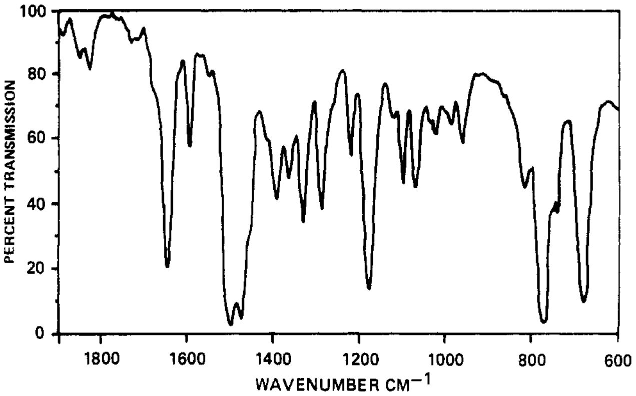
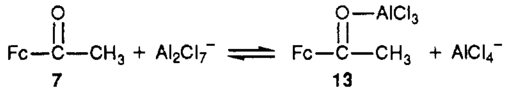


Figure 8. IR spectrum of acetylferrocene in 1:1 molten salt displaying a shoulder at 1680 cm^{-1}.

became irreversible in that no reduction peak was observed, and the anodic peak current was significantly lower than expected. This did not reflect the onset of decomposition of acetylferrocene, since the addition of aluminum chloride completely restored the oxidation and reduction peaks. Repetition of this procedure with ferrocene itself revealed neither a negative shift of the redox potential as the melt was made more basic nor appearance of an additional reversible wave at the 1:1 neutral composition.

The varying ratio of the two anodic peak heights as a function of solvent acidity, together with the near-constant value of the sum of the peak heights, indicates an equilibrium between two ferrocene species. The species with the more anodic redox potential is favored in the more acidic molten salt. Since a σ-complex of $AlCl_3$ and the aromatic system is ruled out by the fact that ferrocene itself does not exhibit this behavior (determined by a separate experiment), it appears most likely that this species results from direct addition of aluminum chloride to the carbonyl oxygen atom. There are precedents for such complexes in Friedel–Crafts reactions,[21] and recently an anthraquinone–aluminum chloride complex has been isolated from the aluminum chloride–butylpyridinium chloride molten salt.[22] It is evident that the equilibrium between the complexed and uncomplexed species must be relatively slow to allow for their simultaneous detection.

Since the concentration of free aluminum chloride in the acid melt is extremely low, the aluminum chloride adduct likely results from the reaction of acetylferrocene with the dialuminum heptachloride ion as shown by eq 5, where Fc presents the ferrocenyl group. In the basic molten salt



$$\underset{\mathbf{7}}{\mathrm{Fc{-}\overset{O}{\overset{\|}{C}}{-}CH_3}} + \mathrm{Al_2Cl_7^-} \rightleftharpoons \underset{\mathbf{13}}{\mathrm{Fc{-}\overset{O{-}AlCl_3}{\overset{\|}{C}}{-}CH_3}} + \mathrm{AlCl_4^-} \qquad (5)$$

the concentrations of $AlCl_4^-$ and Cl^- ions are high and the concentration of $Al_2Cl_7^-$ is low, whereas in the acidic melt the concentrations of $Al_2Cl_7^-$ and $AlCl_4^-$ are high and the concentration of Cl^- is low. Therefore, complex **13** should predominate in the acid molten salt; this is the form of the species undergoing reaction at redox couples of ca. 0.95 V (Figures 5 and 6).

Infrared absorption spectra obtained from acidic and basic solutions containing acetylferrocene support this scheme and correlate with the spectra obtained for anthraquinone[22] in the melt. In the 2:1 acid melt a shoulder was observed on the molten-salt absorption band at 1500 cm^{-1} (Figure 7). The band for the melt alone is shown by the dotted curve. The presence of this shoulder implies a change in the C=O bond strength indicative of complexation and is in agreement with the results of Giallonardo[23] and Cheek and Osteryoung.[22] The presence of uncomplexed acetylferrocene in the basic melt was indicated by the shoulder evident at 1680 cm^{-1} on the melt absorption band at 1650 cm^{-1} (Figure 8). This shoulder corresponds to the normal carbonyl stretch.

A coulometric experiment carried out at constant current in the 2:1 acid melt established that the oxidation involved one electron ($n = 0.95$). The redox potential was monitored on a carbon electrode at various stages of the conversion. A semilogarithmic plot of the potential against the quantity $Q/(Q_t - Q)$, where Q is the amount of charge passed at a given time and Q_t is the total charge passed, possesses a slope of 55 mV/decade. This is consistent with a one-electron oxidation of a monomer species.

The cyclic voltammetry experiments showed that the potential of the species **13** moved approximately 70 mV more cathodic when the composition changed from the 2:1 to the 1.2:1 molten salt. This indicates a dependence of the electrode reaction on the composition of the species in the molten salt, which was further investigated by a potentiometric experiment. An equimolar mixture of acetylferrocene–acetylferrocenium ion was prepared by constant-current oxidation of acetylferrocene in a 2:1 melt. The potential of a carbon rod was observed as the melt composition was adjusted to more basic values. A change in composition from the 2:1 to the 1.2:1 melt resulted in a 100-mV shift in the redox potential.

Discussion

The unusually large potential shift in the redox potential of substituted ferrocenes in the aluminum chloride–butylpyridinium chloride molten salt is attributed to a specific interaction of carbonyl oxygens with aluminum chloride. This interaction increases the electron-withdrawing power of the substituent so that the redox potential of the ferrocene/ferrocenium couple is shifted to more positive potentials than would be otherwise expected. In aqueous media cyano groups are similarly subjected to protonation,[24] and it is likely that such groups will also be complexed by aluminum chloride with similar effects on the redox potential. In the neutral molten salt, acetyl group substitution shifts the half-wave potential 0.26 V more positive (separate experiment). This compares with

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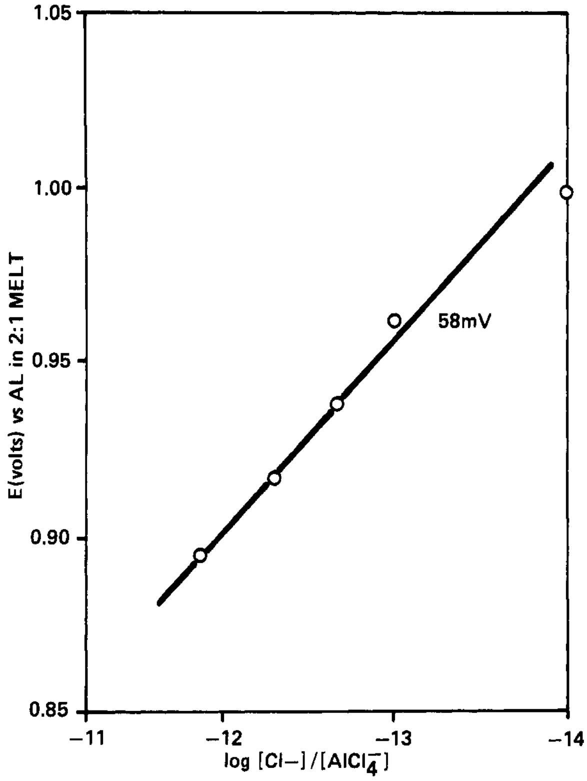
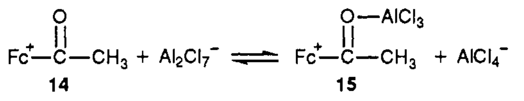


Figure 9. Plot of E vs log ([Cl$^-$]/[AlCl$_4^-$]) for a constant ratio of acetylferrocene to acetylferrocenium.

the 0.255-V shift observed in acetonitrile[11] and is additional evidence that the more negative redox couple corresponds to the uncomplexed acetylferrocene–acetylferrocenium ion couple.

At the neutral melt composition both complexed and uncomplexed species can be oxidized to their respective ferrocenium ions. This implies the existence of the equilibrium



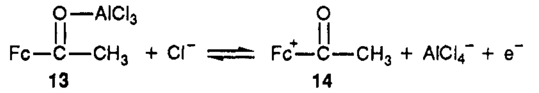
$$\underset{\textbf{14}}{\mathrm{Fc^{+}-\overset{\overset{O}{\|}}{C}-CH_3}} + \mathrm{Al_2Cl_7^-} \rightleftharpoons \underset{\textbf{15}}{\mathrm{Fc^{+}-\overset{\overset{O-AlCl_3}{\|}}{C}-CH_3}} + \mathrm{AlCl_4^-} \qquad (6)$$

A simple analysis of the dependence of the Nernst potential during the oxidation of acetylferrocene can be performed only if the concentrations of the oxidized and reduced species do not vary significantly as the acidity is changed. This appears to be the case in the acid melt, where no other species were detected by cyclic voltammetry and IR spectroscopy. The situation in the neutral melt has not been determined.

The Nernst equation for the oxidation of complexed acetylferrocene is

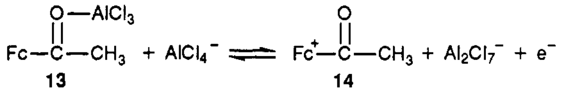
$$E = E° - (RT/nF) \ln ((\mathbf{13})/(\mathbf{15})) \qquad (7)$$

where (**13**) and (**15**) represent the activities of complexed acetylferrocene and complexed acetylferrocenium ion. If these are taken as constant, and the concentrations of the melt species are taken from the literature,[1a] then a slope of 58 mV/decade is obtained when the potential is plotted against the logarithm of the ratio of concentrations of chloride ion to tetrachloroaluminate ion (Figure 9). This implies an electrode reaction of



$$\underset{\textbf{13}}{\mathrm{Fc-\overset{\overset{O-AlCl_3}{\|}}{C}-CH_3}} + \mathrm{Cl^-} \rightleftharpoons \underset{\textbf{14}}{\mathrm{Fc^{+}-\overset{\overset{O}{\|}}{C}-CH_3}} + \mathrm{AlCl_4^-} + e^- \qquad (8)$$

or



$$\underset{\textbf{13}}{\mathrm{Fc-\overset{\overset{O-AlCl_3}{\|}}{C}-CH_3}} + \mathrm{AlCl_4^-} \rightleftharpoons \underset{\textbf{14}}{\mathrm{Fc^{+}-\overset{\overset{O}{\|}}{C}-CH_3}} + \mathrm{Al_2Cl_7^-} + e^- \qquad (9)$$

in the acid molten salt.

The loss of reversibility observed for uncomplexed acetylferrocene in the basic melt has not been fully investigated. However, at slightly basic composition, e.g., 0.9:1, the reduction of ferrocenium ion is observed at fast sweep rates and not at slow rates. This is consistent with the sensitivity of ferrocenium species to basic chloride solution.[25] This indicates that the product of acetylferrocene oxidation undergoes a chemical reaction with the melt which inhibits the reduction process.

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Registry No. **1**, 1272-47-5; **2**, 102-54-5; **3**, 1273-91-2; **4**, 32611-03-3; **5**, 1273-84-3; **6**, 63453-42-9; **7**, 1271-55-2; **8**, 63453-41-8; **9**, 12093-10-6; **10**, 1293-87-4; **11**, 12180-80-2; **12**, 1273-94-5; BuPyCl, 1124-64-7; W, 7440-33-7; C, 7440-44-0; AlCl$_3$, 7446-70-0.

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