716 *Inorg. Chem.* **1985**, *24*, 716-719

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Electrochemistry in Neutral Ambient-Temperature Ionic Liquids. 1. Studies of Iron(III), Neodymium(III), and Lithium(I)[†]

MAREK LIPSZTAJN[‡] and ROBERT A. OSTERYOUNG*

Received July 17, 1984

An ambient-temperature "neutral" ionic liquid composed of aluminum chloride and either *N*-1-butylpyridinium or 1-methyl-3-ethylimidazolium chloride, BuPyCl or ImCl, respectively, has been employed in studies that take advantage of their unusual properties. These include an extended electrochemical window, readily controlled additions of excess chloride (base) or aluminum chloride (acid), and the fact that the physical properties of the "neutral" melt do not change about the 1:1 mole ratio of $AlCl_3$ to RCl. Li^+ was found to be reducible in the "neutral" $AlCl_3$–ImCl melt, and its diffusion coefficient was found to be 8.6×10^{-7} $cm^2\ s^{-1}$. The stoichiometry of the complex formed between Nd(III) and Cl^- in the molten salt system was investigated by what is esstentially an amperometric titration and was found to be $NdCl_6^{3-}$. The structure of the Fe(III) chloro complex that exists in basic or acidic melts just slightly varying in composition from the neutral melt was also investigated; a constant value for the diffusion coefficient–viscosity product for the complex in both systems suggests no change in structure.

In the past several years low-temperature molten salt systems composed of aluminum chloride and either *N*-1-butylpyridinium chloride (BuPyCl) or 1-methyl-3-ethylimidazolium chloride (ImCl) have been found to be useful solvents for electrochemical and spectroscopic studies of both organic and inorganic species.[1-4]

Reactions that take place during the mixing of an organic chloride (RCl) and $AlCl_3$ may be written as

$$\begin{gathered} x\mathrm{RCl} + y\mathrm{AlCl_3} \rightarrow y\mathrm{RAlCl_4} + (x-y)\mathrm{RCl} \\ \mathrm{MC} = y/x < 1 \end{gathered} \qquad (1)$$

and

$$\begin{gathered} x\mathrm{RCl} + y\mathrm{AlCl_3} \rightarrow (2x-y)\mathrm{RAlCl_4} + (y-x)\mathrm{RAl_2Cl_7} \\ 1 < \mathrm{MC} < 2 \end{gathered} \qquad (2)$$

Reactions 1 and 2 correspond to the formation of "basic" (excess RCl) and "acidic" (excess $AlCl_3$) melts, respectively. A special case is where MC = 1.00, corresponding to the formation of the "neutral" melt,[5] i.e. pure, molten $R^+AlCl_4^-$.

The anionic components of these melts, $AlCl_4^-$, Cl^-, and $Al_2Cl_7^-$, are involved in an equilibrium reaction:

$$2\mathrm{AlCl_4^-} \rightleftarrows \mathrm{Cl^-} + \mathrm{Al_2Cl_7^-} \qquad (3)$$

with an equilibrium constant recently estimated as $K = [\mathrm{Cl^-}]\cdot[\mathrm{Al_2Cl_7^-}]/[\mathrm{AlCl_4^-}]^2 \approx 10^{-17}$.[3,6]

The purpose of this paper is to present studies in which a neutral melt is used for the investigation of chemical and electrochemical reactions.

Experimental Section

N-1-Butylpyridinium chloride and 1-methyl-3-ethylimidazolium chloride were prepared as previously described.[2,4] The approximately neutral $AlCl_3$–RCl melts were prepared by slow mixing of appropriately weighed amounts of the organic chlorides and carefully sublimed $AlCl_3$ (Fluka A.G., "Ironfree"); this roughly neutral melt was subsequently adjusted by addition of small amounts of either RCl or $AlCl_3$ to obtain the electrochemical window[5] indicative of a "true" neutral melt.

LiCl (Mallinckrodt, anhydrous, p.a.), $FeCl_3$ (Fisher Scientific Co., anhydrous, sublimed), and $NdCl_3$ (Alfa Products, anhydrous) were used without further purification.

The reference electrode was an Al wire (5N Alfa Inorganic) immersed in a 1.5:1 $AlCl_3$–RCl melt, and all potentials are given with respect to this electrode. The auxiliary electrode was also a coiled Al wire. The essential details of the experimental techniques, electrodes, and operations in the drybox (Vacuum Atmospheres) in which all experiments were carried out have been presented previously.[7]

Working electrodes were glassy carbon disk (area 0.196 and 0.071 cm^2), tungsten (0.078 cm^2), and platinum (0.049 and 0.12 cm^2). The electrode surface preparation procedure has been previously described.[8]

Results and Discussion

A neutral melt, a "neutral basic" melt (neutral + small excess of RCl), and a "neutral acidic" melt (neutral + small excess of $AlCl_3$) have several unique features that make them very useful. These include the following: (1) an increased electrochemical window, relative to a basic or acidic melt; (2) control of the concentrations of the main basic and acidic anionic components, Cl^- and $Al_2Cl_7^-$, in "neutral basic"[9] and "neutral acidic"[8] melts, respectively; (3) virtually the same physical properties (such as viscosity, density, and specific conductivity) accompanied, however, by huge differences in chemical properties.

The extension of the electrochemical window by ca. 1.5 V[5] enables us to investigate several redox systems inaccessible to study in basic or acidic melts. Some of these systems such as Cl_2/Cl^-[9] are of particular importance. We will show the application of this feature to the study of the Li^+/Li system.

Monitoring of Cl^- and $Al_2Cl_7^-$ concentration is possible by observing the diffusion-controlled chloride oxidation[9] and heptachloroaluminate reduction[8] current in "neutral basic" and "neutral acidic" melts, respectively. This feature can be used for direct determination of the stoichiometry of many chemical reactions occurring in these melts, particularly those involving the formation of metal ion chloro complexes. This is of particular utility in the case of nonelectroactive chloride-containing complexes such as those of the rare-earth elements. Since the Cl^- oxidation and $Al_2Cl_7^-$ reduction diffusion-limited current is proportional to concentration over a wide range of concentrations—up to at least 0.1 mol dm^{-3}—the complexation reactions can be studied under conditions of a large excess of the ligand over the metal ion. The method based on monitoring the Cl^- oxidation current was tested recently on Fe(III) chloride complexes.[9] From the decrease of chloride oxidation current occurring upon addition of $FeCl_3$ to a "neutral basic" melt containing small, known (excess) amounts of ImCl, the stoichiometry of the Fe(III)–Cl^- complex was determined as $FeCl_4^-$, which was in agreement with potentiometric studies of this system.[11,15] Figure 1 shows a voltammogram

---

[†] This paper was presented in part at the 165th Meeting of the Electrochemical Society, Cincinnati, OH, May 1984.

[‡] Department of Chemistry, University of Warsaw, 02 093 Warsaw, Poland.

(1) Chum, H. L.; Koch, V. R.; Miller, L. L.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 3264.
(2) Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.
(3) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603.
(4) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.
(5) Lipsztajn, M.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *130*, 1968.
(6) Karpinski, Z.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 1491.
(7) Robinson, J.; Osteryoung, R. A. *J. Electrochem. Soc.* **1978**, *125*, 1454.
(8) Robinson, J.; Osteryoung, R. A. *J. Electrochem. Soc.* **1980**, *127*, 122.
(9) Lipsztajn, M.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 1735.
(10) Fannin, A. A.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. *J. Phys. Chem.* **1984**, *88*, 2614.
(11) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 4079.
(12) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1983**, *22*, 1279.
(13) Habboush, D. A.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 1726.

0020-1669/85/1324-0716$01.50/0

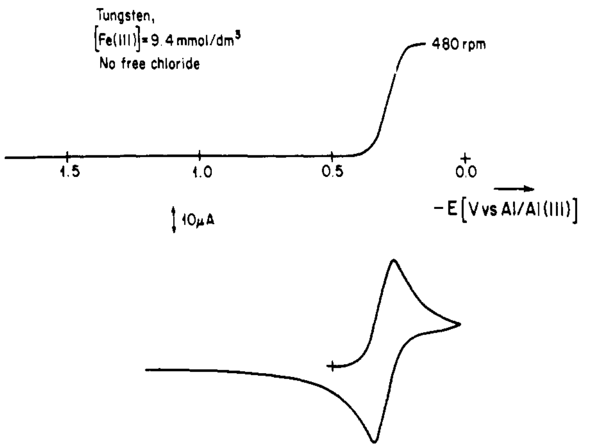

Figure 1. Cyclic voltammogram (at $v = 0.05$ V s^{-1}) (lower) and rotating-disk voltammogram (upper) (at 480 rpm) recorded for a 9.4 mmol dm^{-3} solution of Fe(III) in a neutral $AlCl_3$–ImCl melt; tungsten disk electrode (area 0.078 cm^2), $T = 305$ K.

obtained when the amount of $FeCl_3$ is *exactly* equivalent to the excess amount of chloride ions in a starting, "neutral basic" melt; no Cl^- oxidation current is detected after the addition of a *stoichiometric* amount of $FeCl_3$.

Another advantage of using a neutral melt involves the character of changes of physical and chemical properties of $AlCl_3$–RCl melts accompanying changes of melt composition near MC = 1.00. Viscosity, for instance, changes ~20-fold as the melt composition is changed from acidic (MC = 2.0) to very basic (MC = 0.45).[10] At the same time, huge changes in the concentration of Cl^-, $Al_2Cl_7^-$, and $AlCl_4^-$ occur; for example, Cl^- and $Al_2Cl_7^-$ concentrations change ca. 10^{25}-fold. Moreover, it is not possible to change one physical or chemical property and not change others at the same time. Thus, some particular system is usually studied over the entire range of melt composition, and the variations of chemical parameters of this system, such as equilibrium redox potentials, are interpreted in terms of only one variable. This variable is usually related to the acidity function defined as the negative of the logarithm of chloride ion concentration, pCl. This treatment is satisfactory only in some special cases, such as the complexation of metal ions with chloride ions when the interaction with other ligands, $AlCl_4^-$, and $Al_2Cl_7^-$ are, a priori, neglected.[11,12]

The analysis of electrochemical data on various systems in the $AlCl_3$–RCl molten salts indicates that diffusion coefficients are very sensitive to structural changes of the electroactive complexes. In the very spectacular case of Sb(III),[13] the Stokes–Einstein parameter, $D\eta/T$ (where D, η, and T denote diffusion coefficient, viscosity, and temperature, respectively), remains constant across the basic composition but differs by 300% from the value characteristic for Sb(III) in the acidic melts, which is also constant across the acidic melt composition. This characteristic of $D\eta/T$ values is typical for most systems and indicates that marked changes of structure occur in the proximity of a neutral melt. Using diffusion coefficients as a measure of structural changes, we will estimate if there are significant differences in the structure of Fe(III) complexes in basic and acidic melts.

(1) Li^+/Li System. LiCl is soluble in acidic melts;[14] however, no reduction of Li^+ was observed prior to the cathodic limit of these melts (i.e. the reduction of $Al_2Cl_7^-$). Since LiCl is not soluble in a neutral melt, we first prepared a "neutral acidic" $AlCl_3$–ImCl melt with a known excess of $AlCl_3$, and to this melt we added an equivalent amount of LiCl and thus obtained a $LiAlCl_4$ solution in a neutral melt.

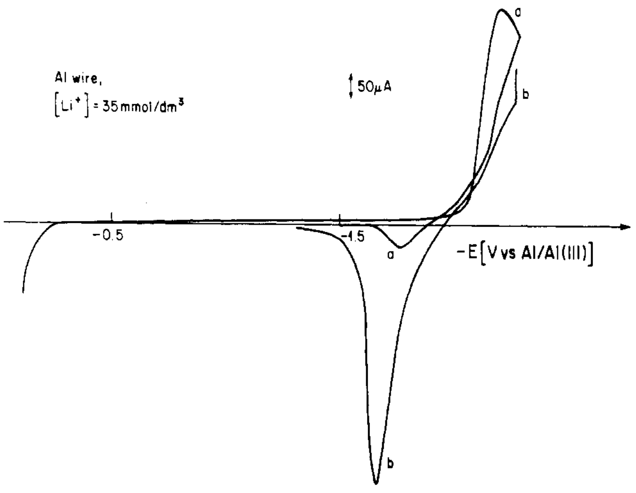

Figure 2. Cyclic voltammogram for Li^+ in a neutral $AlCl_3$–ImCl melt at an aluminum electrode (area 0.16 cm^2); $v = 0.05$ V s^{-1}, $T = 305$ K.

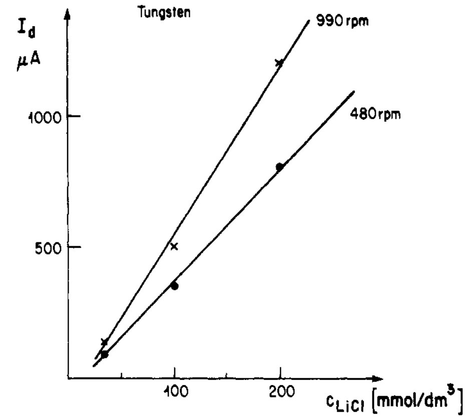

Figure 3. Concentration dependence of Li^+ reduction rotating-disk limiting current measured in a neutral $AlCl_3$–ImCl melt; tungsten disk electrode (area 0.078 cm^2), $T = 305$ K.

The reduction of lithium ion was observed on tungsten, glassy carbon, and aluminum electrodes. In Figure 2 the cyclic voltammogram of Li^+ in a neutral melt on an aluminum wire (area ~0.16 cm^2) is presented. The stripping peak of Li increased with the time of electrolysis (Figure 2b). The plating–stripping efficiency was always much less than unity but was best for the Al electrode. Open-circuit potentials measured after deposition of Li on Al wire were relatively unstable; the shift of E_{eq} was ca. 50 mV over 30 min.

In Figure 3 the concentration dependence of the Li^+ reduction current measured at a tungsten rotating disk electrode at two different rotation rates is presented. This dependence was studied in solutions of Li^+ of up to 200 mmol dm^{-3}; preparation of more concentrated solutions is possible. The limiting current adhered to the Levich equation dependence on $\omega^{1/2}$ up to 990 rpm. Since it was very difficult to renew the electrode after Li deposition, we avoided higher rotation rates. From the limiting rotating-disk current measured at tungsten and glassy carbon electrodes, the diffusion coefficient of Li^+ in a neutral $AlCl_3$–ImCl melt (T = 305 K, $\eta = 0.148$ P) was determined as $(8.6 \pm 0.3) \times 10^{-7}$ cm^2 s^{-1}. Further studies of the Li^+/Li system are in progress.

(2) Nd(III) Complexation. Nd(III) dissolves in the basic melt to form bluish, nonelectroactive chloride complexes. The stoichiometry of this reaction was studied as described above, and from the decrease of Cl^- oxidation limiting current that occurred upon addition of $NdCl_3$ to the "neutral basic" $AlCl_3$–ImCl melt, the stoichiometry of the complex formed was determined as $NdCl_6^{3-}$ (see Figure 4). In this experiment, which is equivalent to an amperometric titration, the decrease of the chloride oxidation current corresponds to a decrease of Cl^- concentration from 94.1 to 72.5 mmol dm^{-3}, upon making the solution 6.9 mmol dm^{-3} in $NdCl_3$, and subsequently to 32.4 mmol dm^{-3}, upon making it 13.2 mmol dm^{-3} in $NdCl_3$. The calculated number of additional Cl^-

---

(14) Piersma, B. J.; Wilkes, J. S. Frank J. Seiler Research Laboratory Technical Report FJSRF-82-0004; USAF Academy: Colorado Springs, CO, 1982.

(15) Nandjundiah, C.; Shimizu, D.; Osteryoung, R. A. *J. Electrochem. Soc.* **1982**, *129*, 2474.

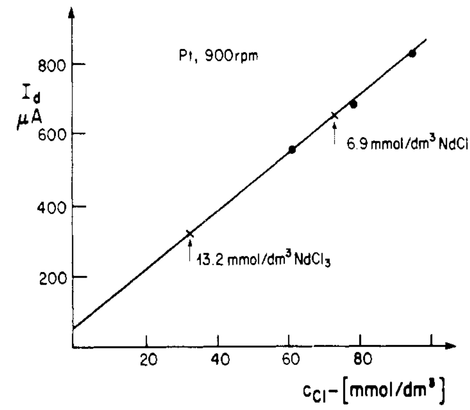

Figure 4. Decrease of chloride oxidation limiting current measured at a rotating disk platinum electrode (area 0.12 cm^2) in a "neutral basic" $AlCl_3$–ImCl melt upon addition of $NdCl_3$: ω = 900 rpm, T = 305 K.

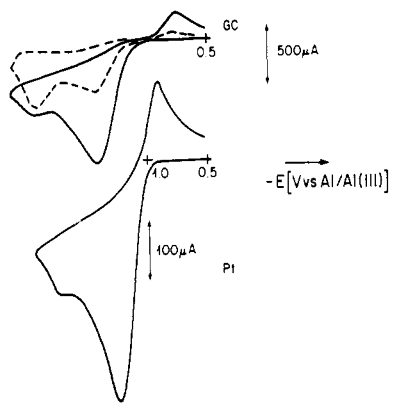

Figure 5. Cyclic voltammograms recorded at Pt (area 0.12 cm^2) and glassy carbon (area 0.196 cm^2) disk electrodes after the melt was made 6.9 mmol dm^{-3} in $NdCl_3$ (solid line) and 13.2 mmol dm^{-3} in $NdCl_3$ (dotted line) in the "neutral basic" $AlCl_3$–ImCl melt; [Cl$^-$] in the starting melt 94 mmol dm^{-3}, v = 0.05 V s^{-1}, T = 305 K.

ions bound to $NdCl_3$ was (94.1 − 72.5)/6.9 = 3.13 and (72.5 − 32.4)/13.2 = 3.04, respectively.

Cyclic voltammograms recorded after the addition of $NdCl_3$ (Figure 5) show a new anodic peak at potentials positive with respect to the free chloride oxidation peak; we believe this peak corresponds to the oxidation of chloride incorporated into the Nd(III) complex. Since neither of the electrodes used works well at very positive potentials (>2 V) in the presence of chloride ions (see e.g. ref 9), no detailed studies of this new peak were performed. Qualitatively, an increase of this new peak at the expense of the free chloride oxidation current was observed upon addition of subsequent portions of $NdCl_3$ (see Figure 5).

$NdCl_3$ was also studied in the "neutral acidic" $AlCl_3$–ImCl melt. In Figure 6 the decrease of the heptachloroaluminate limiting reduction current that occurs upon addition of $NdCl_3$ to the "neutral acidic" melt is presented. The decrease of the $Al_2Cl_7^-$ reduction current corresponded to a decrease of $Al_2Cl_7^-$ concentration from 35.9 to 25.5 mmol dm^{-3}, upon first making the melt 3.6 mmol dm^{-3} in $NdCl_3$, and subsequently to 11.8 mmol dm^{-3}, upon increasing it to 8.0 mmol dm^{-3} in $NdCl_3$ (a change of 4.4 mmol dm^{-3}. From this dependence, the stoichiometry of the reaction between $NdCl_3$ and $AlCl_3$ was established as 1:3 $NdCl_3$:$AlCl_3$ (the calculated values were (35.9 − 25.5)/(3.6 = 2.89 and (25.5 − 11.8)/4.4 = 3.11, respectively). That is, the $Al_2Cl_7^-$ is neutralized by $NdCl_3$ in a reaction:

$$3Al_2Cl_7^- + NdCl_3 \rightarrow Nd(III) + 6AlCl_4^- \qquad (4)$$

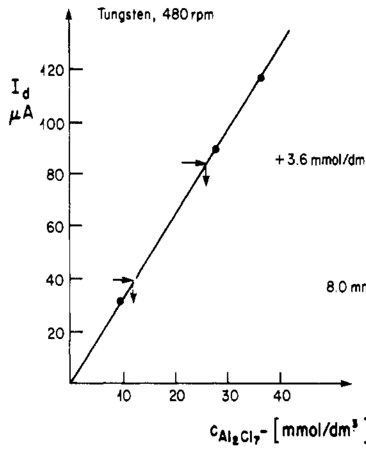

Figure 6. Decrease of heptachloroaluminate limiting reduction current measured at a rotating disk tungsten electrode (area 0.078 cm^2) in a "neutral acidic" $AlCl_3$–ImCl melt upon addition of $NdCl_3$; ω = 480 rpm, T = 305 K.

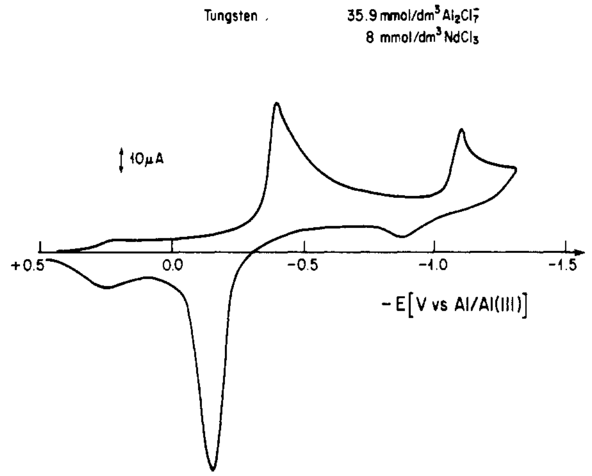

Figure 7. Cyclic voltammogram recorded at a tungsten disk electrode (area 0.078 cm^2) after addition of $NdCl_3$ to the "neutral acidic" $AlCl_3$–ImCl melt; v = 0.05 V s^{-1}, T = 305 K.

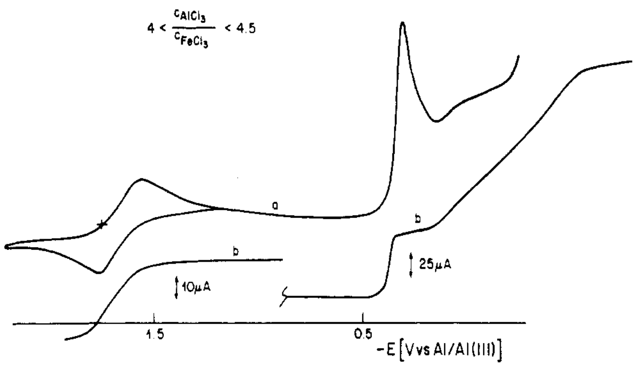

Figure 8. Cyclic voltammogram (a) and rotating-disk voltammogram (b) recorded at a tungsten electrode (area 0.078 cm^2) after addition of a fourfold excess of $AlCl_3$ to the 9.4 mmol dm^{-3} solution of Fe(III) in a neutral $AlCl_3$–ImCl melt (compare with Figure 1); v = 0.05 V s^{-1}, ω = 480 rpm, T = 305.

This indicates that no "free" chloride remains in the Nd(III) complex in acidic melts and suggests that Nd(III) is solvated by either $AlCl_4^-$ or $Al_2Cl_7^-$. Cyclic voltammograms recorded after addition of $NdCl_3$ (Figure 7) to the "neutral acidic" $AlCl_3$–ImCl melt show the presence of a new redox system at potentials more negative than the potential of heptachloroaluminate reduction. Dut to a very low solubility of Nd(III) complex in the "neutral acidic" melt, no further studies of this system have been performed at this time.

Comparison of Fe(III) Complexation in Basic and Acidic Melts. To determine the difference in the stoichiometry of the Fe(III) complexes in basic and acidic melts, solutions of $FeCl_4^-$ in a neutral melt (see Figure 1) were prepared. Small amounts of $AlCl_3$ were then incrementally added to this solution. A significant shift of

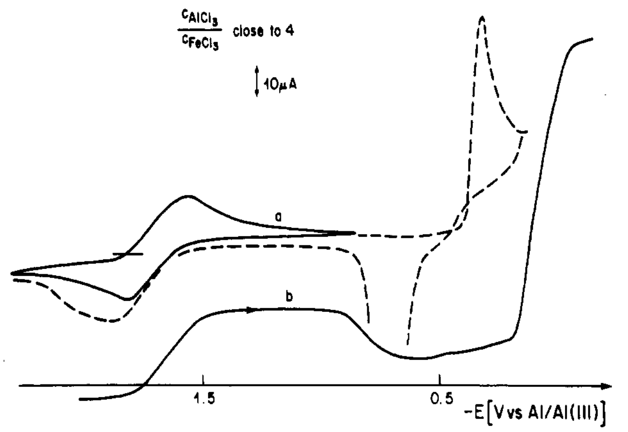

Figure 9. Cyclic voltammogram (a) and rotating-disk voltammogram (b) at a tungsten electrode (area 0.078 cm^2) after addition of less than fourfold excess of $AlCl_3$ to the 9.4 mmol dm^{-3} solution of Fe(III) in a neutral $AlCl_3$–ImCl melt (compare with Figures 1 and 8); v = 0.5 V s^{-1}, ω = 480 rpm, T = 305 K.

Table I. Diffusion Coefficients of Fe(III) at 305 K in $AlCl_3$-ImCl Melts

melt	10^7D, cm^2 s^{-1}	$10^{10}D\eta/T$, g cm s^{-2} K^{-1}
"neutral basic"	9.1	4.4
"neutral acidic"	9.0	4.3
acidic, MC = 1.23	9.3	4.3

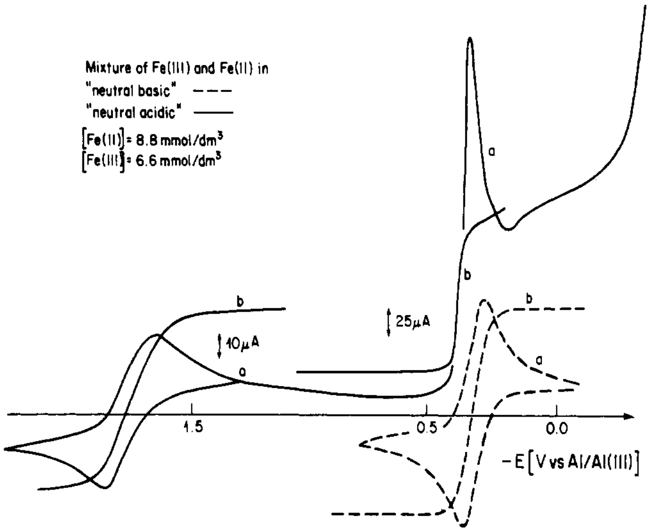

Figure 10. Comparison of cyclic voltammograms (a) and rotating-disk voltammograms (b) at a tungsten electrode (area 0.078 cm^2) for a mixture of Fe(III) and Fe(II) in a "neutral basic" (dotted line) and "neutral acidic" (solid line) $AlCl_3$–ImCl melt; v = 0.05 V s^{-1}, ω = 990 rpm, T = 305 K.

the Fe(III)/Fe(II) equilibrium potential in the anodic direction (ca. 1.5 V) was observed; this increased the oxidizing power of the Fe(III) and resulted in its being partially reduced to Fe(II), perhaps by hydroxyl-containing compounds (see below).

At more negative potentials (0.4 V) a reduction current due to Fe(0) deposition was observed. At mole ratio $n_{AlCl_3}/n_{FeCl_3} < 4$ an additional feature was observed; a drop of the Fe(III) reduction current at the rotating-disk electrode took place (see Figure 9). This effect was more pronounced at smaller n_{AlCl_3}/n_{FeCl_3} ratios and longer electrolysis time. It is related to the blockage of the electrode by an insoluble product ($FeCl_2$); this was also observed by Laher and Hussey.[11]

Further additions of $AlCl_3$ caused an anodic shift of the Fe(III)/Fe(II) equilibrium potential similar to those previously reported,[11,15] but this potential was not very stable due to the reduction of Fe(III) by impurities. However it was possible, using rotating-disk reduction currents for the reduction of both Fe(III) to Fe(II) as well as Fe(III) and Fe(II) to Fe(0), to monitor the transformation of Fe(III) into Fe(II) and to determine an accurate value of the diffusion coefficient of Fe(III) in the acidic melt. Due to the strong oxidizing properties properties of Fe(III) and the instability of Fe(III) in the acidic melts, no reliable value of $D_{Fe(III)}$ has been published.[15]

The measurement of $D_{Fe(III)}$ in an acidic melt was performed as follows. Small, known amounts of $FeCl_3$ were added to the mixture of Fe(III) and Fe(II). The increase of the Fe(III) → Fe(II) and the Fe(III) + Fe(II) → Fe(0) currents were measured and compared at the rotating disk electrode. When the transformation of Fe(III) into Fe(II) by impurities is negligible, the increase of the Fe(III) → Fe(II) reduction current should be exactly one-third of the increase of the reduction current to metallic iron for both the Fe(III) and Fe(II) reductions. Since the $Al_2Cl_7^-$ reduction potential shifts anodically even more than the Fe(III), Fe(II) → Fe(0) potential on going to more acidic melts, it was not possible to use the same procedure for melts more acidic than MC = 1.23. The comparison of the $D\eta/T$ values measured for Fe(III) in the basic acidic melts indicates no measurable difference (see Table I).

In another experiment, which is illustrated in Figure 10, a mixture of Fe(III) and Fe(II) in a "neutral basic" melt was prepared and to this solution was added sufficient excess of $AlCl_3$ to observe the electrochemical behavior of the Fe(III)/Fe(II) couple characteristic of the acidic melts (see above). A significant anodic shift of the equilibrium potential of the Fe(III)/Fe(II) couple was observed, but no significant change of the Fe(III) → Fe(II) reduction wave height was detected. Since the differences in viscosities of the starting, "neutral basic", and the final, "neutral acidic", melts are negligible, we feel this shows that the change of structure of an Fe(III) complex accompanying this change of melt composition is not significant.

This conclusion is in apparent disagreement with the potentiometric studies of this system reported by Laher and Hussey,[11] who postulated the formation of the $FeCl_2^+$ iron in very acidic (MC > 1.7) $AlCl_3$–BuPyCl melts in comparison with the formation of $FeCl_4^-$ in basic melts. It is possible however that this change of a structure occurs only in very acidic melts and could not be detected in the melts of moderate acidity (see above).

It is also worth mentioning that the number "4", describing the minimum excess of $AlCl_3$ over $FeCl_3$ necessary to transform the "basic behavior" of the Fe(III)/Fe(II) couple into "acidic behavior", seems to be meaningful and indicates that no "free" chlorides are incorporated into the Fe(II) complex existing in acidic melts. This conclusion is consistent with previous work.[11]

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research.

Registry No. $NdCl_6^{3-}$, 33613-62-6; $FeCl_4^-$, 14946-92-0; $Al_2Cl_7^-$, 27893-52-3; $AlCl_4^-$, 17611-22-2; $AlCl_3$, 7446-70-0; BuPyCl, 1124-64-7; ImCl, 65039-09-0; Fe, 7439-89-6; Nd, 7440-00-8; Li, 7439-93-2.