ELECTROCHEMICAL STUDIES OF TRANSITION METALS IN MOLTEN ALUMINUM CHLORIDE–N-METHYL PYRIDINIUM CHLORIDE

C.L. Hussey and L.A. King

Frank J. Seiler Research Laboratory (AFSC)
United States Air Force Academy, Colorado 80840
Abstract

Copper(II) dissolved readily in aluminum chloride-N-methylpyridinium chloride (67-33 mol %) melt and underwent two reduction steps. The first reduction step, Cu(II) + e⁻ → Cu(I) (E° = 1.85V vs Al) was reversible at both glassy carbon and tungsten electrodes. The diffusion coefficient for the Cu(II) species was 2.9 x 10⁻⁷ cm²/sec. The second reduction step, Cu(I) + e⁻ → Cu (E° = 0.78V vs Al), was controlled by rate of nucleation in the initial phase of deposit formation on platinum, tungsten, and glassy carbon electrodes. Potentiostatic current-time transients for copper deposition on the latter two electrodes were found to obey the criteria for instantaneous three dimensional nucleation followed by hemispherical growth of the nuclei. The equilibrium constant for the reaction Cu(II) + Cu → Cu(I) was appreciably larger than observed for this reaction in acidic, inorganic chloroaluminate melts.

Iron(III) chloride also was soluble in the melt, but FeCl₃ - melt solutions slowly decomposed. The proximity of the Fe(III)/Fe(II) standard potential (E° = 2.05V vs Al) to the anodic limit of the melt at ca. 2.2V suggested that the instability of the solutions resulted from slow oxidation of the melt by Fe(III). The Fe(III) + e⁻ → Fe(II) electrode reaction was found to be quasireversible at glassy carbon and tungsten electrodes. The standard heterogeneous rate constant, kₘ, and cathodic transfer coefficient, α, for this electrode reaction were determined with a glassy carbon rotating disc electrode (GC-RDE). The diffusion coefficient for the Fe(III) species was found to be 3.5 x 10⁻⁷ cm²/sec. It was not possible to study deposition of iron onto glassy carbon or tungsten electrodes since overpotentials cathodic of aluminum deposition (0.0V vs Al) were required to initiate nucleation.

INTRODUCTION

Recently, investigations of the ionic conductivity and physical properties of aluminum chloride-N-alkylpyridinium halide molten salts were completed in this laboratory (1). This study has generated interest in the use of these liquids, particularly the 67-33 mol % compositions which are liquid at room temperature, as electrolytes for secondary batteries, solvents for metallurgical separations, and media...
for electrodepositing various metals. Practical application of these unique molten salts for these purposes depends upon knowledge of the electrochemical behavior of metal solutes in them.

The distribution of chloroaluminate species with melt composition in aluminum chloride-N-alkylpyridinium chloride melts appears to differ considerably from that of inorganic chloroaluminate melts. Raman spectral studies of aluminum chloride-N-(n-butyl)pyridinium chloride revealed that the 67-33 mol% composition of this melt may consist almost entirely of Al$_2$Cl$_7^-$ (2). This is in contrast to high temperature inorganic chloroaluminate melts, e.g., AlCl$_3$-KCl (67-33 mol %), which have been shown to contain AlCl$_4^-$, Al$_2$Cl$_7^-$, and Al$_2$Cl$_6$ (3).

The Cu(II)/Cu(I) and Cu(I)/Cu couples have been studied previously in the ternary AlCl$_3$-NaCl-KCl (66-20-14 mol%) melt at 135°C (4) and in the equimolar region of the AlCl$_3$-NaCl melt at 175°C (5). The electrochemistry of the Fe(III)/Fe(II) couple has also been studied in the latter melt system (5). However, voltammetric data for these couples in acidic (AlCl$_3$ rich) regions of these melts were not reported. In this paper the electrochemical behavior of the Cu(II)/Cu(I), Cu(I)/Cu, and Fe(III)/Fe(II) electrode processes in the aluminum chloride-N-methylpyridinium chloride (67-33 mol %) melt are reported and compared, when possible to results previously obtained in inorganic chloroaluminate melts. Techniques used for this investigation were stationary and rotating disc electrode voltammetry, chronoamperometry, controlled potential coulometry, and potentiometry.

**EXPERIMENTAL**

**Apparatus** - The cells used for voltammetry, chronoamperometry, and controlled potential coulometry, the electrochemical instrumentation, and the dry atmosphere system were described in a previous publication (6). A glassy carbon working electrode, geometrical area = 0.22 cm$^2$, was constructed according to the procedure given by Phillips et al. (7). A tungsten disc working electrode was prepared by sealing a 3.2 mm tungsten rod (Alfa-Ventron Corp., m5N5; t4N) in a 4mm i.d. canary glass tube, slicing off the end, and polishing the exposed surface successively with 600 grit silicon carbide paper, 320 mesh Carbordinum powder (Fisher Scientific Co.), and finally with Type B alumina (Fisher Scientific Co.). The geometrical area of the tungsten electrode was 0.080 cm$^2$. Working electrodes for copper deposition studies consisted of either the tungsten disc, the glassy carbon disc, or a platinum wire (Englehard Industries, Inc.) of 0.4 cm$^2$ geometrical area. Potentials reported in this study were measured with reference to an aluminum electrode in pure melt. Resistance compensation was applied during cyclic voltammetric measurements according to instructions given in the instrument manual supplied by the manufacturer. Only 1% of the total signal was fed back. This represented a resistance drop of approximately 80 Ω between the working and reference electrodes.
Reagents - Synthesis of N-methylpyridinium chloride as well as preparation, purification, and physical properties of the 67-33 mol % aluminum chloride-N-methylpyridinium chloride melt appear in another publication (1). Copper(II) chloride (Great Western Inorganics, 99.999%) was obtained and used without further purification. Copper(I) chloride (Baker "Analyzed Reagent", J. T. Baker Chemical Co.) was obtained and found to contain substantial amounts of Cu(II). Coulometric analysis revealed 33.9% by weight copper(II) chloride in the Cu(I) stock. This material was not subjected to pretreatment; however, when it was used appropriate corrections for the presence of Cu(II) were made. Copper foil, 0.13 mm thick, (99.9%, J. T. Baker Chemical Co.) was immersed briefly in aqueous HNO₃, rinsed thoroughly with triply distilled water, and dried with absolute ethanol prior to use. Iron(III) chloride (Matheson, Coleman, and Bell, anhydrous reagent, sublimed) and iron(II) chloride (Ventron Corp., anhydrous) were used as received.

Neutron Activation Analysis Samples - Samples of copper were deposited onto tungsten sheets by controlled potential electrolysis from melt containing Cu(II). The deposit covered sheets were removed from the drybox and washed free of melt with distilled water. The deposits were scraped from the sheets with a spatula, washed repeatedly by suspension in distilled water followed by centrifugation, dried and weighed, and dissolved in concentrated nitric acid (Baker "Analyzed Reagent") prior to activation.

RESULTS AND DISCUSSION

Copper(II) - Introduction of copper(II) chloride into the (67-33 mol %) aluminum chloride-N-methylpyridinium chloride melt resulted in a bright yellow solution. This is in contrast to the green color of Cu(II) solutions in the ternary AlCl₃-NaCl-KCl (66-20-14 mol %) melt at 135°C which Anders and Plambeck (4) observed and attributed to Cu(II) solvated by chloride. Based on the presence of Al₂Cl₇⁻ as the sole solvating species in the melt used for the present study, this color difference must reflect participation of Al₂Cl₇⁻ ions in the solvation of Cu(II) rather than chloride. In agreement with the results of Boxall et al. (5) in AlCl₃ rich AlCl₃-NaCl melt no solubility problems were encountered in the present melt and solutions 50mM in Cu(II) were prepared readily. Solutions of Cu(II) were stored in the drybox for several months with no visual or electrochemical evidence for decomposition.

Polarograms constructed from current-time transients which illustrate the reduction of Cu(II) at glassy carbon and tungsten electrodes are shown in Figs. 1 and 2 respectively. The first reduction wave in these polarograms was well defined with both electrodes and gave linear log [(i_d - i)/i] vs E plots. A value of n = 1.0 was calculated from the slopes of both plots, indicating that the waves were due to the reversible reduction of Cu(II) to Cu(I). Controlled potential coulometric reduction of Cu(II) to Cu(I) at 1.5 V gave n = 0.98 confirming
this. The dependence of the polarographic diffusion current for this wave on the Cu(II) concentration is shown in Fig. 3. A slight positive deviation of the diffusion current at low Cu(II) concentrations was evident and was attributed to a weak adsorption of the reactant. Similar positive deviation in the diffusion current at low Cu(II) concentrations was observed with a tungsten electrode. However, voltammetric behavior indicative of weak adsorption (8) was not obtained at scan rates of up to 5V/sec. The exact cause of the increased diffusion currents at low Cu(II) concentration could not be determined. The second wave in the polarograms (Figs. 1 and 2) was attributed to reduction of Cu(I) to the metal since a tungsten electrode polarized to 0.4 V became coated with a deposit of finely divided copper metal. The Cu(I) reduction process will be discussed in more detail in the next section.

Cyclic voltammograms of the melt background at a glassy carbon electrode and of Cu(II) at glassy carbon and tungsten electrodes are shown in Fig. 4. The reduction peak at 1.83V and oxidation peak at 1.89V in the latter two voltammograms illustrate the solution red-ox behavior of the Cu(II)/Cu(I) couple. Cyclic voltammetric data obtained for this reaction at a glassy carbon electrode in a 7.36mM Cu(II) solution at 30°C are presented in Table I. Examination of this table reveals that at low scan rates $E_{p^a-E_p^c}$ and $E_{p^c-E_p^b}$ approach theoretical values of 0.060V and -0.029V expected for a one electron reversible process at 30°C. At faster scan rates these values increased suggesting that the Cu(II)/Cu(I) electrode reaction might be quasi-reversible. However, values of $i_{pa}/i_{pc}$ obtained with a glassy carbon rotating disc electrode were constant with rotation rate at potentials corresponding to the ascending portion of the polarographic wave for Cu(II) reduction (Fig. 1) over a range of rotation rates of from 105 to 419 rad/sec. The voltammetric current function, $i_{pa}/v^2$ was constant and $i_{pa}/i_{pc}$ was 1.0 indicating that the Cu(II)/Cu(I) couple was not complicated by homogeneous kinetic processes in the range of scan rates employed.

The results obtained in this study for the Cu(II)/Cu(I) electrode process differ from those reported by Boxall et al. (5) in chloride rich AlCl₃-NaCl at 175°C. These workers found the electrode process to be dependent on Cu(I) concentration in their melt which they attributed to the low solubility of CuCl₂ (ca. 5mM). In addition, they report the Cu(II)/Cu(I) couple to be reversible at CuCl concentrations less than 5mM (although $E_{p^a-E_p^c}$ was 20% larger than theoretical) but obscured by Cl₂ evolution at CuCl concentrations below 2mM. In contrast, Cu(II)/Cu(I) electrochemistry is relatively straightforward and independent of concentration in the low temperature melt employed in the present study. The lack of excess chloride ion also permits greater anodic voltammetric excursion, particularly at glassy carbon electrodes.

Potentiostatic rotating disc electrode experiments were used to obtain diffusion coefficients for Cu(II) as a function of temperature. Figure 5 shows plots of $i_L$ vs. $v^1/2$ constructed from rotating disc data
at 1.6 V which span a temperature range of 30 to 70°C and a rotation rate of 105 to 419 rad/sec. Diffusion coefficients for Cu(II) calculated from these plots using the Levich equation obeyed the expression

$$\log D = -\frac{1242}{T} - 2.375$$  \[1\]

The diffusion coefficient for Cu(II) calculated from Eq. [1] at 25°C was 2.9 x 10^{-7} cm²/sec and compared well with published values of the diffusion coefficients of iron diimine complexes in aluminum chloride-N-ethylpyridinium bromide (67-33 mol %) at 25°C (10). The activation energy for the diffusion of Cu(II) was estimated from Eq. [1] to be 5.7 kcal/mol. This value is very close to that measured for Nb(V) in chloride rich AlCl₃-NaCl (11).

Table I. Voltammetric Data for the Reduction of Cu(II)

| V (V/sec) | E_p⁰ (V) | E_p⁰ | E_p⁰ - E_p⁰ | i_p / i_p⁰ | i_p / i_p⁰ |
|----------|----------|-------|-------------|-------------|-------------|
| 0.010    | 1.823    | 0.067 | -0.030      | 2.3         | 1.00        |
| 0.020    | 1.825    | 0.065 | -0.031      | 2.3         | 1.01        |
| 0.050    | 1.822    | 0.069 | -0.029      | 2.3         | 1.03        |
| 0.100    | 1.819    | 0.074 | -0.029      | 2.3         | 1.04        |
| 0.200    | 1.817    | 0.078 | -0.029      | 2.3         | 1.05        |
| 0.500    | 1.825    | 0.097 | -0.043      | 2.3         | 1.07        |
| 1.000    | 0.820    | 0.104 | -0.036      | 2.2         | 1.10        |

*Calculated using Nicholson's empirical procedure (9).

Copper(I) - Cu(I) was added to the melt most conveniently by polarizing a copper foil electrode. Polarization of the foil 0.50 V anodically from its rest potential gave an initial current of 0.3 mA/cm². Solutions of Cu(I) in the melt produced in this fashion were colorless and stable indefinitely, provided precautions were taken to avoid exposing the melt to oxygen. After prolonged exposure to a dry atmosphere containing oxygen, Cu(I) solutions became faintly yellow, suggesting the formation of Cu(II). As a precaution only freshly yellow, colorless Cu(I) solutions were used in this work. Cu(I) solutions obtained by exhaustive coulometric reduction of Cu(II) at 1.0 V were also colorless.
Voltammetric waves for the Cu(I)/Cu couple are also evident in Fig. 4. At the tungsten electrode the voltammogram was of the form expected for deposition and stripping of an insoluble substance. The behavior observed at the glassy carbon electrode was different than at the tungsten electrode in that current hysteresis was observed anodic of the deposition peak at 0.16V and the stripping peak was broad and poorly defined. This hysteresis persisted during the scan until a potential sufficient to reoxidize the deposit was reached. As the scan rate was increased the broad stripping peak began to exhibit shoulders, suggesting that it was a composite of several stripping peaks. In addition, deposition peaks at both tungsten and glassy carbon shifted cathodically with scan speed. The shifts were 0.10V and 0.18V per order of magnitude increase in scan speed, respectively.

Further indication that the reduction of Cu(I) was markedly dependent on the nature of the electrode material is shown by comparison of the second wave in Figs. 1 and 2. Current-time transients for data points on the ascending portion of the second waves in these figures exhibited maxima both for glassy carbon and tungsten electrodes. However, a diffusion current was obtained with the tungsten electrode at potentials cathodic of 0.57V. No diffusion current, as would be evidenced by constant values of \( i t^2 \) with decreasing potential, was obtained at a glassy carbon electrode prior to the increase in background current at about 0.2V. When the polarogram in Fig. 1 was constructed from current-time data at longer times, a wave with a diffusion limited plateau was observed just anodic of the increase in background current at 0.2V. This wave shifted anodically with an increase in the time at which the data were taken from the current-time curves. This shift was about 0.015V per second increase in time. The wave for Cu(I) reduction at a tungsten electrode (Fig. 2) was not shifted appreciably when constructed from current-time data at longer times.

The maxima observed in current-time curves and the rapid cathodic shift of the reduction peak potential with increasing voltammetric scan rate were reported in a number of previous studies of metal deposition from molten salts (6, 12, 13). These observations indicate that the initial phase of deposit formation is controlled by rate of nucleation.

To study further the influence of different electrode materials on the rate of nucleation during copper metal deposition, current-time transients were measured at glassy carbon, tungsten, and platinum electrodes in a 9.14mM Cu(I) solution (Figs. 6, 7, and 8). Examination of Fig. 6 shows that considerable overpotential was required to induce nucleation and growth on glassy carbon. Both the slope of the ascending portions of the current-time curve and the time delay of the current maxima were dependent on the applied potential. Values of the current and time taken from the rising portion of the current-time transients were fit best by a plot of \( i vs t^2 \) (Fig. 9) while the descending portions of the transients exhibited the usual \( 1/t^2 \) decay. Similar results were obtained with the tungsten electrode (Fig. 7), but
a smaller overpotential was required to initiate copper metal deposition. The ascending portions of the current-time transients were again proportional to $t^{1/2}$ (Fig. 10). An increase in Cu(I) concentration resulted in a decrease in the overpotential required to induce nucleation at both glassy carbon and tungsten electrodes. This was most evident during cyclic voltammetric scans. For example, at the tungsten electrode at a scan rate of 0.020V/sec in a 9.14mM Cu(I) solution the copper deposition peak occurred at 0.448V while at the same scan rate in a 24.6mM Cu(I) solution this peak was observed at 0.575V. Nucleation of copper metal on platinum (Fig. 8) was much faster than observed on the other two electrodes. In fact, the narrow potential range in which nucleation phenomena could be observed at this electrode precluded detailed analysis of the ascending portion of current-time curves with equipment available for this study. Deposition of copper metal onto platinum proceeded readily at 0.5V and a smooth adherent deposit was produced. The absence of prolonged nucleation and the relative ease with which copper was plated onto platinum may be due in part to the fact that both copper and platinum metal have similar crystal structures. The platinum electrode was thus a less foreign substrate for deposition than were glassy carbon or tungsten.

The copper deposition process on both glassy carbon and tungsten obeyed the criteria of Hills et al. (12) for instantaneous three dimensional nucleation followed by hemispherical growth of the nuclei. Similar results were reported by Rolland and Mamantov (13) for deposition of aluminum on glassy carbon from slightly acidic AlCl$_3$-NaCl melts at 175°C. Boxal et al. (5) reported a small nucleation peak on chronopotentiograms obtained during Cu(I) reduction at a tungsten electrode in the equimolar AlCl$_3$-NaCl melt, but gave no further details.

Codeposition of Aluminum with Copper - The increase in current beginning around 0.2V (which can be seen in Fig. 2) indicated that another component of the melt was undergoing reduction. This merited investigation since the wave at 0.2V was absent from melts which did not contain Cu(II) or Cu(I). The background current for both polarograms was 2 x 10$^{-6}$ A or less in this region. To gain insight into the process occurring during this reduction, copper metal was deposited from a Cu(I) solution onto separate tungsten sheets at 0.4V and 0.1V until the sheets were uniformly coated with thick deposits. The sheet polarized at 0.4V was covered with a finely divided deposit of reddish metallic copper which appeared to be of high quality, while the sheet polarized at 0.1V was covered with a dark brown deposit. Identical deposits were obtained on glassy carbon electrodes at these potentials, although the deposition process was initiated more slowly. Neutron activation analysis of the dark brown deposit indicated that the deposit contained about 25 mol % aluminum. (The deposit did not contain detectable quantities of chlorine.) The deposit obtained at 0.4V did not contain detectable quantities of either aluminum or chlorine. Thus, it was concluded that the reduction wave occurring at potentials cathodic of 0.2V was due to codeposition of aluminum with copper.
Standard Potentials - Data for construction of a Cu(II)/Cu(I) Nernst plot were obtained by pipetting together solutions of Cu(II) and Cu(I) prepared by dissolving CuCl₂ and CuCl individually in two otherwise identical melts. A Nernst plot for the Cu(II)/Cu(I) couple constructed from this data and corrected for Cu(II) contamination of the Cu(I) solution is shown in Fig. 11. The standard potential for the Cu(II)/Cu(I) couple was determined from least squares treatment of the data shown in Fig. 11 and is given in Table II. The standard potential value for the Cu(II)/Cu(I) couple is in good agreement with values of $E_y (\sim 1.86 \text{V})$ estimated polarographically (Figs. 1 and 2) and corrected for the cell resistance.

Table II. Standard Potential Data at 30.0 ± 0.1°C

| Reaction          | $E^\circ$ (V) | Molar          | Slope of Nernst Plot |
|-------------------|---------------|----------------|---------------------|
| Cu(II) + e $\rightarrow$ Cu(I) | 1.851 ± 0.000 | 1.851 ± 0.000 | 0.0597 ± 0.0003     |
| Cu(I) + e $\rightarrow$ Cu | 0.777 ± 0.001 | 0.787 ± 0.001 | 0.0600 ± 0.0005     |
| Fe(III) + e $\rightarrow$ Fe(II) | 2.045 ± 0.000 | 2.045 ± 0.000 | 0.0647 ± 0.0008     |

A Cu(I)/Cu Nernst plot on a molar basis (Fig. 12) was constructed using data obtained by coulometric generation of Cu(I) at a copper foil electrode. The Cu(I)/Cu standard potential determined from least squares treatment of the data shown in Fig. 12 appears in Table II, as does a value of the molal standard potential for this couple. Data in Table II were used to calculate the value of $5.0 \times 10^{17}$ for the Cu(II) $\rightarrow$ Cu $\rightarrow$ equilibrium constant on a molal basis. This value is about three orders of magnitude larger than the value reported for this reaction in the ternary AlCl₃-NaCl-KCl (66-20-14 mol %) melt (4). However, the value of $\Delta E^\circ$ calculated in the present study is almost identical in magnitude to the value reported previously (4). The larger equilibrium constant observed in the present study indicates that the acidic, low temperature chloroaluminate melts tend to stabilize low oxidation state species even more strongly than inorganic chloroaluminate melts of similar composition. This enhanced stability appears to originate primarily from the decreased temperature at which these molten salts may be employed.

A Nernst plot for the Fe(III)/Fe(II) couple is shown in Fig. 13. Data for this plot, given in Table II, were obtained by coulometric oxidation of a solution containing Fe(II) at a potential of 2.10V.
The data were corrected for the effect of background current due to slight oxidation of the melt.

Iron(III) chloride dissolved readily in the melt to give a yellow-orange solution. The rest potential of a glassy carbon or tungsten indicator electrode in a 13.9 mM solution of Fe(III) was 2.11V. The rest potential could be observed to decrease and the color of the solution to fade over a period of several days. The anodic limit of the pure melt was established with linear sweep voltammetry at a glassy carbon electrode to be ca. 2.2V. The proximity of the Fe(III) solution rest potential to the anodic limit of the melt suggested that the instability of the solution resulted from slow oxidation of the melt by Fe(III). Only freshly prepared Fe(III) solutions were used in this study.

Iron(II) chloride was soluble in the melt and gave a clear to faintly salmon colored solution. Deposition of iron from solutions containing Fe(II) was accompanied by nucleation as previously observed during copper deposition. However, in this case overpotentials cathodic of aluminum deposition (0.0V) were required to initiate nucleation on glassy carbon or tungsten electrodes. For this reason, the electrochemical behavior of Fe(II) was not considered further.

Cyclic voltammograms for the reduction of Fe(III) at glassy carbon and tungsten electrodes are shown in Figs. 14 and 15. As the scan rate was increased, an increase in $E^a_p - E^c_p$ was noted and the waves became more drawn out. At very slow scan rates, $E^a_p - E^c_p$ began to approach values expected for a one electron reversible process. Voltammetric behavior of this type has been attributed to a quasireversible charge transfer process (14). An estimate of the standard potential for the Fe(III)/Fe(II) couple, obtained from the average of $E^a_p$ and $E^c_p$, was 2.06V. This value was in good agreement with that determined from the Nernst plot (see above).

Galus and Adams (15) describe a RDE technique attributed to Levich (16) which can be employed to estimate rate constants for the Fe(III)/Fe(II) system. This technique requires that only Fe(III) be present. Using their procedure, the heterogeneous rate constant for the reduction of an oxidized species, $k_f$, is calculated from the intercepts of $1/i$ vs $1/\omega^2$ plots according to Eq. 2

$$
\frac{1}{i} = \frac{1}{n F k_f C_0^b} + \frac{1.61 V^{1/6}}{n F D^{1/4} C_0^{1/2}} \frac{1}{\omega^2}
$$

The method is applicable provided that the electrode reaction is first order and that measurements are made at large overpotential (15). The standard heterogeneous rate constant, $k_s$, and cathodic transfer...
coefficient \( a \), can be determined from a plot of \( E \) vs \( \ln k_f \) as indicated by Eq. 3 if the standard potential is known.

\[
k_f = b_s \exp \left( \frac{-a n F E}{RT} \right)
\]  

This technique was ideally suited to the present investigation since the anodic limit of the melt precluded a rigorous study of Fe(II) oxidation in our melt system.

An \( i \) vs \( E \) curve for the reduction of Fe(III) obtained at constant rotation rate with a glassy carbon electrode is shown in Fig. 16. To exclude possible interferences from melt decomposition, data for this and subsequent curves were not taken at potentials anodic of 2.10V. In addition, concentrations of Fe(III) were kept high, i.e., equal to or greater than \( 10^{-2} \text{M} \), to ensure that the observed current accurately represented the current resulting from Fe(III) reduction. Plots of \( i \) vs \( \omega^{\frac{1}{2}} \) constructed from data measured at selected potentials on both the ascending and plateau portions of the \( i \) vs \( E \) wave are shown in Fig. 17. In this figure, the current can be observed to transition from charge transfer control (2.00V) to mass transport control (1.00V), confirming the quasireversible nature of the Fe(III)/Fe(II) electrode reaction.

Figure 18 shows plots of \( 1/i \) vs \( 1/\omega^{\frac{1}{2}} \) as a function of applied potential. These plots were linear indicating that the Fe(III)/Fe(II) electrode reaction was first order (17). Similar results have been obtained for this electrode reaction in aqueous solution (15, 18, 19). Diffusion coefficients were calculated from the slopes of \( 1/i \) vs \( 1/\omega^{\frac{1}{2}} \) plots constructed with data taken at potentials corresponding to the plateau of the \( i \) vs \( E \) wave. The average value of the diffusion coefficient, obtained at Fe(III) concentrations of 10.6, 13.7, and 13.9mM with the kinematic viscosity of the melt taken as 0.1263 cm\(^2\)/sec (1), is \( 3.5 \times 10^{-7} \) cm\(^2\)/sec. This value compared well with the Cu(II) diffusion coefficient.

Potential dependent values of \( k_f \) were determined from the intercepts of \( 1/i \) vs \( 1/\omega^{\frac{1}{2}} \) plots constructed at potentials corresponding to the ascending portion of the polarographic wave. A plot of \( \ln k_f \) vs \( E \) for these data is shown in Fig. 19. The standard heterogeneous rate constant, \( k_s \), for the Fe(III) reduction process at 30.0°C was determined from the intercept of this plot at the standard potential. The cathodic transfer coefficient, \( a \), was calculated from the slope of the plot according to Eq. 3. Both values, determined with a glassy carbon rotating disc electrode (GC-RDE), are given in Table III.

For comparative purposes, \( k_s \) was estimated for Fe(III) reduction using a method which was more or less independent of the rotating disc electrode technique. Values of \( k_s \) were determined from the increase in \( E_p^A - E_p^C \) with increase in scan rate using cyclic voltammetry according to the procedure described by Nicholson (14). Estimates of \( k_s \) determined in this fashion at glassy carbon (GC) and tungsten (W) electrodes are given in Table III. The good agreement found between GC-RDE and GC...
determined values of $k_s$ was not anticipated, because it was necessary to begin cyclic voltammetric sweeps at potentials well into the melt decomposition region in order to obtain reproducible values of $E_{p^a} - E_{p^c}$ at each scan rate.

Table III. Kinetic Data for the Fe(III)/Fe(II) System at 30°C

| $k_s$ (cm/sec) | $\alpha$ |
|---------------|----------|
| GC-RDE        | GC       | W       |
| (1.6 ± 0.3)x 10^{-4} | (1.3 ± 0.2)x 10^{-4} | (0.49 ± 0.03)x 10^{-4} | 0.38 ± 0.01 |

Comparison of $k_s$ for Fe(III) reduction at glassy carbon and tungsten electrodes reveals that $k_s$ for Fe(III) reduction at a tungsten electrode is only 38% of the value obtained at glassy carbon. However, a fundamental comparison of the difference in $k_s$ is not warranted since there may be gross differences in the electrode surface areas due to blockage, etc.

It is also difficult to make rigorous comparisons between $k_s$ for Fe(III) reduction in aqueous solutions and that measured in the molten salt used in the present study owing to the fundamental differences in the media and the slight temperature difference (30°C vs 25°C). Nonetheless, for the sake of a qualitative comparison selected values of $k_s$ for the Fe(III)/Fe(II) electrode reaction and $\alpha$ determined in aqueous media at various electrodes are reported in Table IV. On a qualitative basis, the value of $k_s$ and $\alpha$ appear to agree well with values previously reported.
Table IV. Comparison of Kinetic Data for the Fe(III)/Fe(II) System.

| Electrolyte | Electrode | $k_s$ (cm/sec) | $\alpha$ | Ref. |
|-------------|-----------|----------------|---------|------|
| 1M H$_2$SO$_4$ | Pt        | $4.3 \times 10^{-3}$ | 0.46    | (15) |
| 1M H$_2$SO$_4$ | C-paste   | $5.4 \times 10^{-5}$ | -       | (15) |
| 9M LiCl-O.1M HCl | C-paste | $2.2 \times 10^{-4}$ | -       | (15) |
| 1M HClO$_4$ | Pt        | $9.0 \times 10^{-3}$ | 0.50    | (18) |
| 1M H$_2$SO$_4$ | Au        | $1.0 \times 10^{-4}$ | -       | (20) |
| AlCl$_3$-MPC* | GC        | $1.6 \times 10^{-4}$ | 0.38    | This work (30°C) |

*AlCl$_3$-N-methylpyridinium chloride (67-33 mol%)
LIST OF SYMBOLS

$C_b$ Concentration of oxidized material in bulk melt (mol/cm$^3$)
$D$ Diffusion coefficient (cm$^2$/sec)
$E$ Potential (V)
$E^\circ$ Standard electrode potential (V)
$E_p$, $E_c$ Polarographic half-wave potential (V)
$E_{p_a}$, $E_{p_c}$ Anodic and cathodic peak potentials (V)
$F$ Faraday Constant
$i$ Current (A)
$i_d$ Polarographic diffusion current (A)
$i_L$ Rotating disc electrode limiting current (A)
$i_{p_a}$, $i_{p_c}$ Anodic and cathodic voltammetric peak currents (A)
$k_f$ Heterogeneous forward rate constant (cm/sec)
$k_s$ Standard heterogeneous rate constant (cm/sec)
$M$ Molarity (mol/liter)
$n$ Number of electrons in charge transfer step
$R$ Cell resistance (Ω); Gas constant
$t$ Time (sec)
$T$ Temperature (K)
$\alpha$ Transfer coefficient
$v$ Sweep rate (V/sec)
$\omega$ Rotation rate (rad/sec)

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Fig. 1 Polarogram constructed from current-time transients for the reduction of Cu(II) at a glassy carbon electrode at 30°C. Cu(II) concentration was 25.4 mM; current was measured at 3 sec.

Fig. 2 Polarogram constructed from current-time transients for the reduction of Cu(II) at a tungsten electrode at 30°C. Cu(II) concentration was 25.4 mM; current was measured at 3 sec.

Fig. 3 Dependence of the polarographic diffusion current at a glassy carbon electrode on the Cu(II) concentration at 30°C.

Fig. 4 Cyclic voltammograms at 30°C; A. melt background at a glassy carbon electrode, sweep rate was 0.050V/sec, B. Cu(II) at a glassy carbon electrode, Cu(II) concentration was 13.2 mM, sweep rate was 0.020V/sec, C. Cu(II) at a tungsten electrode, Cu(II) concentration was 9.52 mM, sweep rate was 0.020V/sec.
Fig. 5 Variations of the limiting current at a glassy carbon rotating disc electrode with square root of the rotation rate as a function of temperature. Potential was 1.6 V; Cu(II) concentration was 9.52 mM, ○ 30°C, ● 40°C, □ 50°C, ■ 60°C, △ 70°C.

Fig. 6 Current-time transients for Cu(I) reduction at a glassy carbon electrode at 30°C. Cu(I) concentration was 9.14 mM.

Fig. 7 Current-time transients for Cu(I) reduction at a tungsten electrode at 30°C. Cu(I) concentration was 9.14 mM.

Fig. 8 Current-time transients for Cu(I) reduction at a platinum electrode at 30°C. Cu(I) concentration was 9.14 mM.
Fig. 9 Plot of the current from the ascending portion of the transients in Fig. 6 vs square root of time; ○ 0.15 V, ● 0.25 V.

Fig. 10 Plot of the current from the ascending portion of the transients in Fig. 7 vs square root of time; ○ 0.50 V, ● 0.55 V.

Fig. 11 Nernst plot for the Cu(II)/Cu(I) couple.

Fig. 12 Nernst plot for the Cu(I)/Cu couple. Cu(I) concentration was in units of molarity.
Fig. 13 Nernst plot for the Fe(III)/Fe(II) couple.

Fig. 14 Cyclic voltammogram of the Fe(III)/Fe(II) couple at a glassy carbon electrode at 30.0°C. Sweep rate was 0.002 V/sec.

Fig. 15 Cyclic voltammogram of the Fe(III)/Fe(II) couple at a tungsten electrode at 30.0°C. Sweep rate was 0.002 V/sec.

Fig. 16 Current-potential curve for the reduction of Fe(III) at a glassy carbon rotating disc electrode at 30.0°C. Fe(III) concentration was 13.9 mM; rotation rate was 209 rad/sec.
Fig. 17 Plot of the current versus the square root of the rotation rate for the reduction of Fe(III) at a glassy carbon electrode at 30.0°C. Fe(III) concentration was 13.9 mM; ○ 1.00 V, ● 1.80 V, □ 1.90 V, ■ 1.97 V, and △ 2.00 V.

Fig. 18 Plot of the reciprocal current versus the square root of the rotation rate for the reduction of Fe(III) at a glassy carbon electrode at 30.0°C. Fe(III) concentration was 13.9 mM; ○ 2.00 V, ● 1.98 V, □ 1.95 V, ■ 1.90 V, △ 1.80 V, and △ 1.00 V.

Fig. 19 Plot of the rate constant for Fe(III) reduction as a function of applied potential at 30.0°C. ○ 10.6 mM Fe(III), □ 13.9 mM Fe(III), and △ 13.7 mM Fe(III).