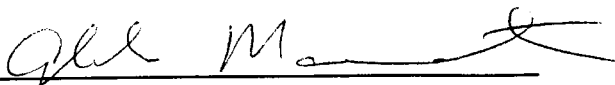


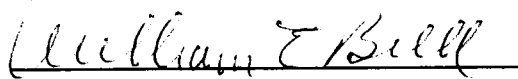
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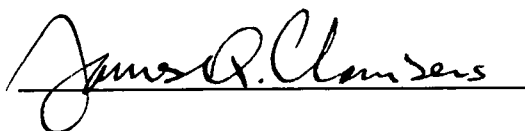
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ELECTROCHEMICAL INVESTIGATIONS
IN BASIC ALKALI CHLOROALUMINATE MELTS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Chaolan Hu

August 1991

To

My Parents

胡之德 谢秀君

To

My Husband

徐希翔

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ABSTRACT

Alkali chloroaluminate melts, such as the $\text{AlCl}_3/\text{NaCl}$ melt, have drawn considerable interest as aprotic media for chemical, electrochemical and various spectroscopic studies. These melts are characterized by relatively low melting points, large decomposition potentials, and a wide optical transparency range. The acid-base properties of these melts can be varied over a wide range by changing the melt composition.

The utility of ultramicroelectrodes for electrochemical studies in $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melts has been demonstrated by using iron(III) chloride as a probe system. Cyclic voltammetric and normal pulse voltammetric results obtained at a tungsten disk ultramicroelectrode were compared to the results obtained at a conventional tungsten disk electrode. Several improvements resulting from the use of ultramicroelectrodes with respect to conventional electrodes were observed in this research.

The electrochemical and spectroscopic studies of $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ and $\text{K}_2[\text{ReCl}_6]$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt are also reported in this thesis. UV-visible absorption spectroscopic studies reveal that $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ are stable in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. Cyclic voltammetry (CV), normal pulse voltammetry (NPV), and controlled potential electrolysis were used to study the reduction of these species. Cyclic voltammograms and normal pulse voltammograms exhibit two

reduction waves. The first reduction peak of $[\text{Re}_2\text{Cl}_8]^{2-}$ involves an EC mechanism in which $[\text{Re}_2\text{Cl}_8]^{2-}$ is first reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$. The species $[\text{Re}_2\text{Cl}_8]^{3-}$ is not stable in this melt and is converted to some unknown species. Electrochemical and spectroscopic results suggest that the initial reduction of $[\text{ReCl}_6]^{2-}$ involves an ECEC mechanism in which $[\text{ReCl}_6]^{2-}$ is first reduced to $[\text{ReCl}_6]^{3-}$. This species is unstable in the melt and dimerizes to give $[\text{Re}_2\text{Cl}_8]^{2-}$, which has a reduction potential more positive than that of $[\text{ReCl}_6]^{2-}$, and therefore is immediately reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$ which is converted to some unknown species. Finally, the addition of Re_3Cl_9 to the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt produced $[\text{ReCl}_6]^{2-}$ and an unknown solid.

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CHAPTER I

INTRODUCTION

Alkali chloroaluminate melts have drawn considerable interest as aprotic media for chemical, electrochemical and various spectroscopic studies (1). These melts are characterized by relatively low melting points, large decomposition potentials, and a wide optical transparency range. In addition, the acid-base properties of these melts can be varied over a wide range by changing the melt composition; mixtures that contain a molar excess of AlCl_3 are designated as acidic melts, while those containing a molar excess of the alkali chloride are denoted as basic.

Ultramicroelectrodes have been used increasingly of late, because they offer several improvements with respect to conventional electrodes. Previously impossible experiments have been made possible with ultramicroelectrodes, for example, some complex electrochemical behavior can be observed at very high scan rates (10^5 V/sec) (2). However, experimental difficulties are often encountered because it is difficult to obtain a reproducible electrode surface. Although electrochemical studies of iron(III) in different chloroaluminate melts have been reported, ultramicroelectrodes have not been used to study this system.

The main purpose of this investigation is to study the electrochemistry of a known system, iron trichloride, at an ultramicroelectrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. In addition, the electrochemical behavior of the $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ species has been investigated previously in high temperature and room temperature melts, but not in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. The research described in this thesis concerns the electrochemical and spectroscopic behavior of the $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ species at a glassy carbon disk electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.

A. Review of the Literature

1. Properties of Molten Salts

Various aspects of molten salts, such as thermodynamic properties, reactions, electrochemistry and various spectroscopic data, have been reviewed (3). Fundamental concepts dealing with the general chemistry of solvent media have been extended to molten salts (4). In general, molten salts are characterized by high thermal stabilities, low vapor pressures and highly ionic environments; such solvents are very useful in many applications and can be used at temperatures well above the ambient range.

The room temperature chloroaluminate melts are obtained by combining AlCl_3 and certain organic halide salts, such as N-1-butylpyridinium chloride (BPC) and 1-methyl-3-

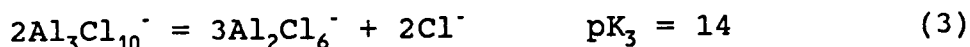
ethylimidazolium chloride (MEIC). Some useful reviews about room temperature melts have been published (5,6). These ionic liquids exhibit some favorable properties, such as low liquidus temperatures, low vapor pressures, good thermal stabilities and moderately high electrical conductivities.

Alkali chloroaluminate melts have drawn considerable interest as aprotic ionic media for chemical, electrochemical and various spectroscopic studies (1). Advantages of these systems over other halide melts are (3):

- 1) They have lower melting points than alkali chloride melts. From the phase diagram for the $\text{AlCl}_3\text{-NaCl}$ system, the freezing point of the compound NaAlCl_4 is $156.7 \pm 0.1^\circ\text{C}$ (7).
- 2) They have high electrical conductivities and large decomposition potentials, which is good for electrochemical studies.
- 3) They are clear and colorless liquids, which is good for spectroscopic studies.
- 4) The acidities of these systems can be varied by adjusting the molar ratio of AlCl_3/MCl , where M is an alkali element.
- 5) These melt systems can stabilize low oxidation states of many elements.

The fact that chloroaluminates exhibit adjustable Lewis acid-base properties makes them very useful for chemical studies. For the $\text{AlCl}_3\text{-NaCl}$ system, melts with more than 0.5 molar fraction of AlCl_3 are referred to be acidic, whereas those with less than 0.5 molar fraction of AlCl_3 are termed

basic. Neutral melts have 0.5 molar fraction of AlCl_3 . The acid-base concept for molten salts was first introduced by Flood and Forland (8); the Lewis acid and base concept was adapted to molten chloroaluminates by Tremillon and Letisse (9). Torsi and Mamantov (10,11), and Osteryoung and coworkers (12) have studied Lewis acid-base properties of chloroaluminates in more detail. Several equilibrium reactions have been reported; however, the best fit between an experiment and the calculation is provided by the following (3):



Al_2Cl_7^- is considered to be an acidic species, and Cl^- is a basic species. K_1 values for several inorganic chloroaluminates have been tabulated by Torsi and Mamantov (11), and can be expressed as:

$$K_1 = [\text{X}(\text{Al}_2\text{Cl}_7^-)][\text{X}(\text{Cl}^-)] / [\text{X}(\text{AlCl}_4^-)]^2 \quad (4)$$

where X is the mole fraction.

The acid-base properties of the chloroaluminate melts near the neutral point can also be expressed in terms of pCl^- :

$$\text{pCl}^- = \text{pK}_1 - \log[\text{X}(\text{AlCl}_4^-)]^2 / [\text{X}(\text{Al}_2\text{Cl}_7^-)] \quad (5)$$

According to this equation, pCl^- for the neutral $\text{AlCl}_3/\text{NaCl}$ melt is about 3.53. pCl^- for the 2:1 $\text{AlCl}_3/\text{NaCl}$ melt is about 7, where AlCl_4^- and Al_2Cl_7^- are present in

approximately equal concentrations forming a buffer system.

2. Chemistry and Electrochemistry of Iron Chlorides in Molten Halides

Various aspects of the chemistry of iron chlorides, such as synthesis, thermodynamic properties, bonding and structure have been reviewed (13-15). The oxidation states of iron in its halogen compounds are almost always +3 and +2.

Iron trichloride is a very hygroscopic dark green compound having a hexagonal lattice structure (13). Its vapor is dimeric (16); the proportion of the dimer relative to the monomer decreases with increasing temperature. Electron diffraction studies have confirmed the dimeric nature of iron trichloride vapor (17). Iron trichloride is thermally unstable, decomposing slowly above about 200°C and rapidly above 300°C. Its thermodynamic properties (13) and the dependence of the sublimation pressure on the temperature (18,19) have been reported. Iron trichloride reacts ligands to form complexes.

The electrochemistry of the Fe^{2+}/Fe and $\text{Fe}^{3+}/\text{Fe}^{2+}$ couples has been studied in both high temperature and ambient temperature chloroaluminates. The electrochemical behavior of the Fe^{2+}/Fe and $\text{Fe}^{3+}/\text{Fe}^{2+}$ couples in the neutral $\text{AlCl}_3\text{-NaCl}$ melts has been investigated using potentiometry, pulse polarography, and cyclic voltammetry (20). The Fe^{2+}/Fe couple showed typical deposition/stripping behavior, while the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple

exhibited some irreversibility. The deposition process was concentration independent (concentration of FeCl_3 was in the range of 5 mM), while the stripping process involved two different electrode reactions which were consistent with the low solubility of FeCl_2 in the neutral melt (20).

The electrochemistry of iron(III) at a conventional glassy carbon and tungsten electrodes in molten AlCl_3 -BPC was reported by Osteryoung and coworkers (21,22), who indicated that FeCl_4^- was the dominant species in the basic AlCl_3 -BPC melt. The Fe(II) oxidation was reversible in the basic melt using rotating disk electrode measurements, and the electron transfer for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple was found to be irreversible in acidic melts.

The electrochemistry of iron species in AlCl_3 -BPC melt has been reported by Hussey and coworkers (23,24). The results indicated that the charge transfer for the reduction of Fe(III) was only quasi-reversible at glassy carbon and tungsten electrodes in a 2:1 melt. Values of the standard heterogeneous rate constant, diffusion coefficient and the standard potential were reported. A potentiometric titration procedure was employed to study iron(II) and iron(III) in the basic AlCl_3 -BPC melt. The results indicated that iron(II) and iron(III) were complexed as FeCl_4^{2-} and FeCl_4^- , respectively, in this melt.

3. Chemistry and Electrochemistry of Re(III) and Re(IV)

Halides

In recent years, cluster compounds have received a great deal of attention (25). The structure and bonding of various trinuclear and dinuclear rhenium compounds have been studied by X-ray diffraction, infrared, UV and other spectroscopic techniques (25-35). The preparation of cluster compounds of rhenium has been reviewed (25).

Rhenium trichloride is purple in color; it has been shown to exist as the trinuclear cluster Re_3Cl_9 . Most structural parameters of the Re_3Cl_9 unit are very similar to those of the other trinuclear rhenium clusters (25). The bonding in the rhenium trinuclear clusters has been discussed in terms of valence bond theory (31), and the molecular orbital method (33,34).

UV spectra have been used to study the behavior of the Re_3Cl_9 species in various melts (36,37). According to Bailey and coworkers, Re_3Cl_9 is stable in molten dimethyl sulfone, but when chloride ion is added, trinuclear rhenium is partially converted to the octachlorodirhenate(III) ion $[\text{Re}_2\text{Cl}_8]^{2-}$, with the concurrent formation of an unidentified product. Re_3Cl_9 disproportionates to $[\text{ReCl}_6]^{2-}$ and Re metal in the LiCl-KCl melt at 450-550°C (38). Hussey and coworkers have examined the spectrum of the rhenium trinuclear clusters in the basic AlCl_3 -MEIC melt (37). They found that the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ species was formed after Re_3Cl_9 dissolved in this melt.

The electrochemistry of the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ species in the basic AlCl_3 -MEIC has been reported (37). The trimeric, metal-metal bonded rhenium(III) complex $[\text{Re}_3\text{Cl}_{12}]^{3-}$ exists after Re_3Cl_9 is dissolved in this melt. This species in the basic AlCl_3 -MEIC melt can be reduced to form a species of the type $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$ at a glassy carbon electrode in a reversible one-electron transfer process with an $E_{1/2}$ of about -0.34 V versus the Al(III)/Al couple in the 66.7/33.3 mol% melt at 40°C.

As mentioned above, when Re_3Cl_9 is added in the LiCl-KCl eutectic, Re_3Cl_9 disproportionates to rhenium metal and Re(IV) (38). The fact that Re metal can be electrodeposited in this melt was confirmed. The redox potential of the Re(IV)/Re(III) couple in the LiCl-KCl melt at 500°C is - 0.358 V versus the standard Pt(II)/Pt(0) reference (38).

The species $[\text{Re}_2\text{Cl}_8]^{2-}$ is blue-green. It contains a quadruple metal-metal bond. The electronic transitions associated with each of the bands in the UV-visible spectrum of the $[\text{Re}_2\text{Cl}_8]^{2-}$ species have been discussed in detail by Cotton and coworkers (39). The electrochemistry of the $[\text{Re}_2\text{Cl}_8]^{2-}$ species in acetonitrile and dichloromethane at 25°C has been reported (40). The reaction $[\text{Re}_2\text{Cl}_8]^{2-} + e^- = [\text{Re}_2\text{Cl}_8]^{3-}$ is quasireversible with an $E_{1/2} = - 0.840$ V vs SCE. $[\text{Re}_2\text{Cl}_8]^{3-}$ is unstable in these solvents, and decomposes to an unknown compound.

The electrochemistry of the $[\text{Re}_2\text{Cl}_8]^{2-}$ species has also been investigated in the basic AlCl_3 -MEIC melt (37). $[\text{Re}_2\text{Cl}_8]^{2-}$ is stable in this melt, and can be reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$ at a glassy carbon electrode in a reversible one-electron reaction, with an $E_{1/2} = -0.58$ V in the 49.0/51.0 mol% (AlCl_3 -MEIC) melt versus the Al^{3+}/Al couple in the 66.7/33.3 mol% melt at 40°C. The $[\text{Re}_2\text{Cl}_8]^{3-}$ species is stable in this medium.

The species K_2ReCl_6 is yellow-green in color. Its preparation and structure have been reviewed by Canterford and Colton (25). UV-visible spectra for $[\text{ReCl}_6]^{2-}$ in various solvents have been summarized (41,42). Resonance Raman spectra of the $[\text{ReCl}_6]^{2-}$ species have been reported by Bosworth and Clark (43). The electrochemistry of the $[\text{ReCl}_6]^{2-}$ species has been studied in different media. Hussey and coworkers conducted a detailed investigation of the $[\text{ReCl}_6]^{2-}$ species in the basic AlCl_3 -MEIC melt at 40°C, from which they determined that the monomeric rhenium(IV) chloride complex, $[\text{ReCl}_6]^{2-}$, is stable in the basic AlCl_3 -MEIC melt, and that it could be reduced to $[\text{ReCl}_6]^{3-}$ at a glassy carbon electrode in a reversible process with an $E_{1/2} = -0.87$ V in the 49.0/51.0 mol% melt versus the $\text{Al(III)}/\text{Al}$ couple in the 66.7/33.3 mol% melt (42). Bailey and Nobile found that $[\text{ReCl}_6]^{2-}$ decomposed partially to give rhenium metal and volatile ReCl_5 in the LiCl-KCl melt at 450-550°C; the rest of the $[\text{ReCl}_6]^{2-}$ species could be reduced to Re metal in a four-electron transfer process (38). Heath et al. (44) reported half wave potentials

vs S.C.E. for the $[\text{ReCl}_6]^{0/1-}$, $[\text{ReCl}_6]^{1-/2-}$, and $[\text{ReCl}_6]^{2-/3-}$ redox couples in CH_2Cl_2 which are 2.35 V, 1.33 V, and -1.12 V, respectively.

B. Review of Basic Principles

1. Cyclic Voltammetry (CV) with Conventional Disk Electrodes

Cyclic voltammetry has become a powerful tool for initial electrochemical studies of new systems, and is very useful for obtaining information about quite complicated electrode reactions (45). This method, as applied to the reaction



involves several assumptions:

- 1) The solution is static.
- 2) Semi-infinite linear diffusion is the only form of mass transport.
- 3) The solution has only species O (or only R) initially.

To obtain a cyclic voltammogram, the potential of a stationary working electrode in an unstirred solution containing an electroactive species is swept linearly with time at a certain scan rate. The potential sweep is begun at an initial potential at which no electrode reaction occurs and the potential is swept linearly in a negative direction for a reduction. In this process, species O is reduced at the electrode, and the ions in the bulk solution diffuse toward the electrode surface because a concentration gradient is

produced between the surface of the electrode and the solution. As the potential becomes more negative, the surface concentration of O is reduced, and the current increases. As the potential moves past the standard potential, the surface concentration of species O drops to about zero, mass transfer of species O to the surface reaches a maximum rate, and the current will then decrease. Following the above process, the potential sweep is switched in a positive direction. For a reversible reaction the reversal current-potential curve has a shape similar to that of the forward peak. The resulting voltammogram shows a duck-shaped current-potential curve. The peak current for a simple reversible process follows the Randles-Sevcik equation (45):

$$i_p = 0.4463nFAC(nF/RT)^{1/2}v^{1/2}D^{1/2} \quad (7)$$

where A (cm²) is the electrode surface area, D (cm²/sec) is the diffusion coefficient of species O, C (mol/cm³) is the concentration of species O, v (V/sec) is the scan rate, T (K) is the temperature, R (8.314 J/mol.K) is the molar gas constant, F (96484.5 coulombs) is the Faraday constant, and n is the number of electrons transferred. The peak potential (E_p) for a reversible process is independent of the scan rate and the concentration of the solution; it is related to the half wave potential (E_{1/2}) (45):

$$E_p - E_{1/2} = -1.109(RT/nF) \quad (8)$$

The relationship between E_p and E_{p/2} can also be used as a convenient diagnosis for a reversible wave as (45):

$$E_p - E_{p/2} = 2.2(RT/nF) \quad (9)$$

Furthermore, $i_{pa}/i_{pc} = 1$, where i_{pa} and i_{pc} are the anodic and cathodic peak currents, is often used as a criterion to determine whether the system is simple and reversible. The theory of cyclic voltammetry has been extended to irreversible systems (46-48), multicomponent systems, multistep charge transfers (49), electrode reactions with coupled homogeneous chemical reactions (50-52) and adsorption of reactants and products (53,54).

2. Normal Pulse Voltammetry (NPV) with Conventional Disk Electrodes

In the analysis of a system using normal pulse voltammetry, certain conditions are required: semi-infinite diffusion, unstirred solution, a planar electrode and only species O (or R) present initially in solution. Normal pulse voltammetry, first performed by Barker and Gardner, is one of the electrochemical methods used to obtain an i - E curve (55). Initially, the electrode is held at a potential E_1 , where Faradaic processes do not occur. The potential is then stepped to another value E_2 , for a set interval, followed by a return to the initial value E_1 . The Faradaic current on the plateau follows the modified Cottrell equation (45):

$$i_d = nFAD^{1/2}C/\pi^{1/2}(\tau - \tau')^{1/2} \quad (10)$$

where $(\tau - \tau')$ is time (sec) measured for the pulse width, and i_d is the limiting current; the other parameters are the same

as mentioned before.

One advantage in using normal pulse voltammetry is that greater sensitivity (10^{-6} - 10^{-7} M) is obtained with respect to conventional polarography (10^{-5} M) (56,57). The relationship between current at any time t and the limiting current i_d is as follows (45):

$$i = i_d / (1 + \delta \theta) \quad (11)$$

where i_d is the steady state current, i is the current at time t , δ is $(D_o/D_R)^{1/2}$, and θ is $C_o(0,s) / C_R(0,s)$, where $C_o(0,s)$ is the concentration of species O at the electrode surface at fixed time (s) , and $C_R(0,s)$ is a concentration of species R at the electrode surface. In addition, a plot of the potential E vs $\log[(i_d - i)/i]$ is linear, since for a reversible system the Nernst equation applies (45):

$$E = E_{1/2} + (RT/nF) \ln[(i_d - i)/i] \quad (12)$$

The slope of this curve can be used to determine the number of electrons transferred. NPV is a useful analytical tool to study the behavior of a chemical system. It has been used in studies with solid electrodes, which have proven to be especially useful in molten salt studies (20,58,59).

3. The Behavior of Ultramicroelectrodes

The use of ultramicroelectrodes in electrochemical studies is a relatively new area that has received much attention recently (2). The electrochemical behavior at ultramicroelectrodes differs greatly from that at conventional

microelectrodes, and ultramicroelectrodes are more in use today because they offer significant improvements (2):

1) Capacitance and charging current can be reduced to insignificant proportions. The capacitance arises from the structure of ions in the double layer (45). In the absence of Faradaic events, the electrochemical cell has electrical characteristics similar to a resistor-capacitor series network (2). In most cases, the charging current is (2):

$$i_c = vC_d \quad (13)$$

where v is the scan rate; C_d is the capacitance.

The charging current is the major interference in electrochemical measurements, so it is very important to reduce this effect. Because the magnitude of the double layer capacitance is proportional to the electrode area (59), it is much reduced at the ultramicroelectrode relative to the conventional electrode, and therefore the charging current decreases according to equation 13 (p. 13). In this way, the ratio of the Faradaic to charging current becomes larger with ultramicroelectrodes under the steady state conditions (60).

2) The iR drop can be reduced at small electrodes. Solution resistance can severely distort electrochemical data, and if reduced, better results can be obtained. An expression for the resistance at an inlaid microdisk electrode with a remote reference electrode is (2):

$$R = \rho/4r_0 \quad (14)$$

where R is the resistance, ρ is the resistivity, and r_0 is

the radius of the electrode. The limiting current for an inlaid ultramicrodisk electrode follows the equation (2):

$$i_d = 4nFDcR_0 \quad (15)$$

From equations 14 and 15, iR drop is a constant ($nFDC\rho$) for a inlaid disk electrode. The iR drop has been estimated by Wightman and coworkers (61).

3) The rate of mass transfer increases as the electrode size decreases, thus a steady state of mass transfer can be established quickly. As a result, an ultramicroelectrode can be used to obtain voltammograms at very high scan rates (10^5 V/sec) (62-66), whereas those with conventional electrodes have been limited to the millisecond or lower time.

Due to the above advantages, ultramicroelectrodes have been used as micro-probes, for non-planar diffusion current response studies, for working in highly resistive media, and for the studies of more complex chemical processes. (50,66).

4. Theories of Cyclic Voltammetry and Normal Pulse Voltammetry at Ultramicroelectrodes

a. Theory of cyclic voltammetry at ultramicroelectrodes

An expression for linear voltammograms at ultramicroelectrodes is presented by Aoki et al. (67). For large scan rates, cyclic voltammograms at very small disk electrodes have the characteristics of CVs at a large planar electrode. With small scan rates, the plateau characteristic for cyclic voltammograms can be observed, while the limiting

current in cyclic voltammetry is given by equation 15 (p. 15). In addition, for reversible processes under steady state conditions, the current on the rising part of the voltammetric wave follows equation 12 (p. 13).

The limiting current at ultramicroelectrodes is larger than that which would be obtained for linear diffusion at ultramicroelectrodes. The increase in the current results from non-linear diffusion taking place in the vicinity of an edge or a part of the electrode with small curvature (67). Based on the above concept, Galus et al. attempted to express an equation for the total peak current in linear sweep voltammetry at ultramicroelectrodes as the sum of the linear and non-linear components (68). However, this approach only holds for some limiting cases. Later Heinze (69) calculated cyclic voltammograms with the aid of a two dimensional simulation based on the fact that the peak current and the peak potential depended on various parameters, such as electrode radius, scan rate, and diffusion coefficient (69). However, this method failed to consider the behavior at a very small electrode and very slow scan rates, and that the diffusion coefficient was sometimes difficult to obtain. Aoki et al. derived an empirical equation in a further improvement (67). It is as follows:

$$\begin{aligned} (I_m RT) / (4n^2 F^2 Cr_0^3 v) = & 0.34p^{-2} \exp(0.66p) + 0.66p^{-2} - \\ & 0.13p^{-2} \exp(-11/p) + 0.351/p \end{aligned} \quad (16)$$

Where I_m is the maximum current, p is $[(nFr_0^2 v)/(RTD)]^{1/2}$, and

the other parameters are as mentioned before. In this equation it is assumed that the Nernst equation holds at the electrode surface. A plot of dimensionless maximum current vs p is an asymptotic line as in Figure 1. From this Figure it can be seen that the upper line is similar to the voltammetric behavior when only linear diffusion is considered, but it is larger. A possible reason is the edge effect (67). When n , C , v , a , I_m are known, a diffusion coefficient can be estimated using this equation. When the edge effect is very small, the relationship between maximum current and p can be simplified to (67):

$$I_m/(4nFCDr_0) = 0.351p \quad (17)$$

A plot of dimensionless maximum current vs p is linear, with an intercept of zero (dashed line in Figure 1).

b. Theory of normal pulse voltammetry.

For normal pulse voltammetry the decay in faradaic current is less time dependent at ultramicroelectrodes (58,2) than that at conventional microelectrodes. The steady state nature of the current at ultramicroelectrodes was studied first by Saito (70). The limiting current for an ultramicro disk electrode follows equation 15 (p. 15). A plot the potential vs $\ln[(i_d - i)/i]$ is linear with a slope $(RT)/(nF)$, from which the number of electrons transferred can be calculated.

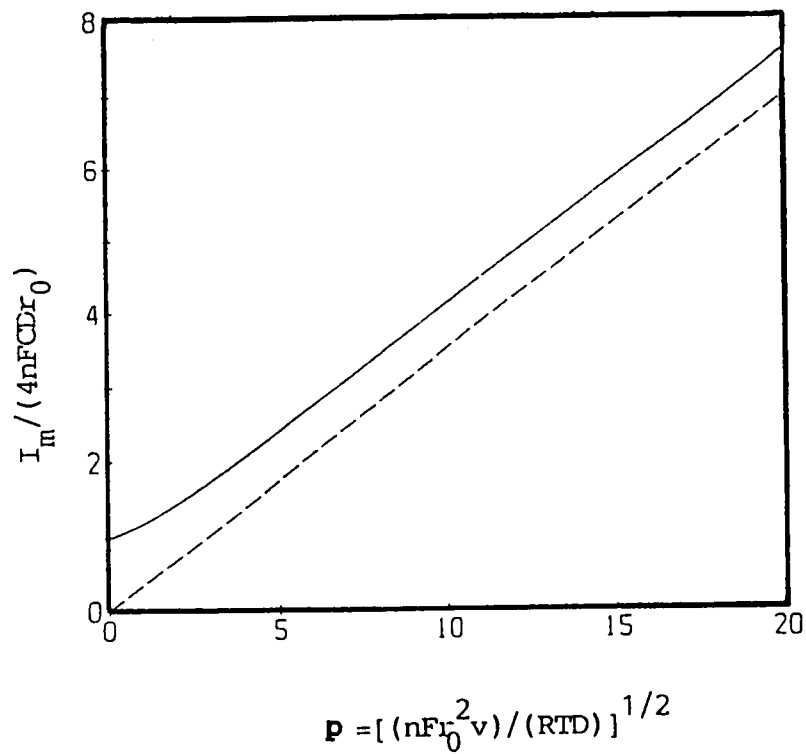


Figure 1. Plots of dimensionless maximum current vs p (solid line) and the corresponding asymptotic line, (dashed line) given by equation 17.

C. Proposed Research

This thesis includes two projects. The first project deals with the electrochemical studies of iron trichloride in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at a conventional tungsten working electrode and at a tungsten ultramicroelectrode working electrode. The purpose of this project is to compare the electrochemical behavior of FeCl_3 observed at a conventional tungsten working electrode with that seen at a tungsten ultramicroelectrode. The second project is the study of the electrochemical behavior of the rhenium complexes $[\text{ReCl}_6]^{2-}$ and $[\text{Re}_2\text{Cl}_8]^{2-}$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt for comparison with earlier results obtained by Hussey and coworkers in the basic AlCl_3 -MEIC melt, as well as with previous studies in the LiCl-KCl eutectic.

CHAPTER II

EXPERIMENTAL

A. Materials

1. Melt Preparation

Anhydrous AlCl_3 (Fluka Chemical Corp., 99.0%) was purified by double distillation in vacuo as follows: AlCl_3 was heated with aluminum metal (m5N from Alfa Products) and a small amount of NaCl at 210°C in a sealed evacuated pyrex three bulb tube. The AlCl_3 was distilled by raising one end of the distillation tube out of the furnace; this procedure was repeated twice. NaCl (Mallinckrodt, Inc., reagent grade) was dried under vacuum for 4 days at 400°C . The $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt was prepared by weighing appropriate amounts of AlCl_3 and NaCl, with a slight excess of NaCl, in the dry box, placing the mixture in a pyrex tube containing aluminum metal, and heating for at least one day at 180°C in a rocking furnace. Following this procedure, the melt was allowed to freeze, and was stored in a sealed pyrex ampule. The purity of the melts was checked by voltammetry as follows: the potential was swept from a point at which no current flowed to the cathodic and anodic potential limits of the melt. If cyclic voltammograms do not contain reduction waves except the cathodic and anodic limits of the melt, the melt can be

considered to contain no electroactive impurities. If the melts were found to be impure, they were repurified by the following scheme. The melt was sealed under vacuum in a purification vessel containing two large aluminum electrodes, and heated to 225-250 °C (20); then the melt was electrolyzed for at least 24 hrs at a current density of 1.5 mA cm⁻². This procedure overcomes the limitation incurred by using only Al metal; if electrolysis were not performed, the surface of the Al metal would become coated by a film of impurities, and the process to displace the impurities would not be continuous. Using two large Al electrodes instead of Al metal results in a continuously fresh aluminum surface and enhances the efficiency of purification. Following electrolysis the melt was filtered through a glass frit, cooled, frozen and stored in a clean melt tube. The purity of the melt was again checked by voltammetry as mentioned above.

2. Transition Metal Halide Compounds

Iron(III) chloride (Cerac Co., 99.9%) was used without further purification. The compounds ReCl₃ and K₂ReCl₆ (Aesar Co., 99.9%) were used as received. The compound [(C₄H₉)₄N]₂[Re₂Cl₈] was provided by Dr. C. L. Hussey at the University of Mississippi.

B. Apparatus

1. Electrochemical Cell

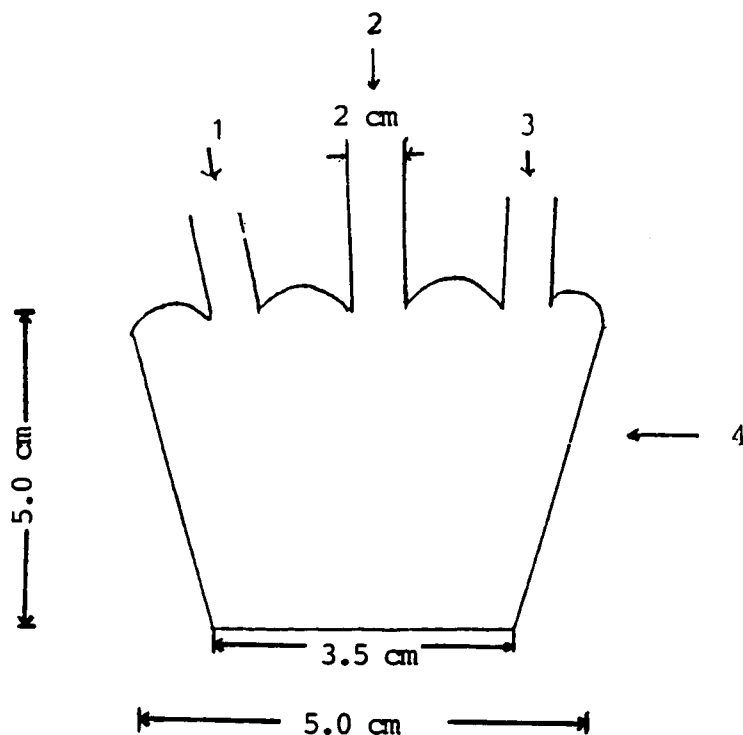
A typical electrochemical cell used is shown in Figure 2. Tungsten electrodes of two different diameters (0.5 mm and 25 μm) and a glassy carbon electrode (diameter 0.3 cm) were used as the working electrodes, each sealed in pyrex to present a circular disk of area $5.1 \times 10^{-6} \text{ cm}^2$ in the case of the 25 μm wire, and $1.96 \times 10^{-3} \text{ cm}^2$ in the case of 0.5 mm, 0.071 cm^2 in the case of the 0.3 cm glassy carbon rod. An aluminum wire with the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt was employed as the reference electrode, which was separated from the bulk solution by a fine pyrex frit to avoid any reaction between the electrode and any oxidizing solutes in the solution. A platinum wire electrode was used as the counter electrode.

2. Furnace

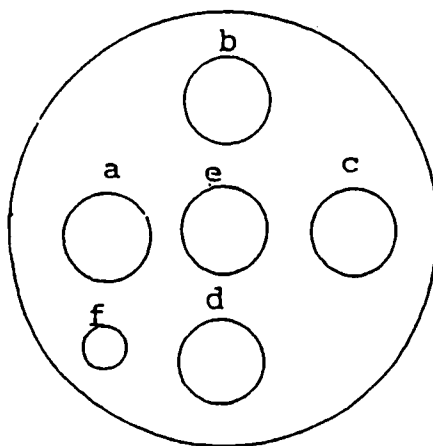
A 5 inch inner diameter tube furnace was used, and a precision temperature controller (Model 124 115V 60CY 0°C - 500°C) was employed to control the temperature of the furnace to $\pm 1^\circ\text{C}$. An Omega chromel-alumel thermocouple (Model 115KC) was used to measure the temperature.

3. Instrumentation for Voltammetry

Cyclic voltammograms were obtained utilizing a PAR (Princeton Applied Research) Model 174A Polarographic Analyzer



Side View



Top View

Figure 2. The electrochemical cell for studies in chloroaluminates.

1 for a; 2 for b, e, and d; 3 for c; reference electrode; 4: cell; a and b: working electrode; c and d: reference electrode; e: counter electrode; f: thermocouple.

with a PAR 175 Programmer, a Houston 2000 X-Y Recorder, and a PAR Model 273 Potentiostat/Galvanostat. Normal pulse voltammograms were obtained with a PAR Model 174 Polarographic Analyzer and the same X-Y Recorder.

4. Dry Box

A vacuum Atmospheres Model HE-43-2 DRI LAB was used. The dry box system includes a Model HE63 Pedatrol automatic pressure controller, a Model HE-493 DRY-TRAIN moisture/oxygen getter, a Sargent Welch Model 1402 Duo-Seal rotary vacuum pump, and Panametrics Model 700 Hygrometer. Typical moisture level in the dry box was <1ppm. A Cahn Model TA 4200 analytical balance was employed for weighings in the dry box.

C. Procedures

1. Ultramicroelectrode Preparation

Ultramicroelectrode preparation involved the following steps: a) Several 0.5 cm length tungsten wires (Aesar Co.) of 25 μm diameter were cleaned by heating in 1:1 HCl for at least 1 hour, rinsed with distilled water and dried in the oven. b) Several 16 cm long pieces of 7 mm pyrex tubes into which 5 cm long pieces of 5 mm pyrex had been sealed were prepared by the glass shop. The glass was heated in 1:1 HCl for one hour, rinsed with distilled water, and dried in the oven. c) Tungsten wires (25 μm diameter from Morton Thiokol Inc.)

were attached to 17 cm long pieces of 0.25 mm diameter tungsten wire (Morton Thiokol Co.) using silver ink (Engelhard). Following attachment, the wires were placed in the oven to allow the ink to dry.

d) After drying, the smaller diameter tungsten wire was threaded into the larger diameter end of the glass tube until the tungsten wire was in the small diameter pyrex tube. The larger tungsten wire, used for electrical contact, was sealed in the glass, but the glass tube was not completely closed. This is done only to set the position of the tungsten wire so that it cannot move freely. Tungsten was used for the electrical connection because it seals well in glass.

e) The end of the small diameter tube was sealed by flame. The end of the larger diameter tube was connected to a vacuum line and then the small end was gradually heated in a moderate flame to soften the glass.

f) After sealing the electrodes, the best surface was selected by viewing the electrode under a Transmission Electron Microscope (Hitachi H-600). Then a section of the glass tube containing the 25 μm wire was cut using the saw in the glass shop.

g) Pretreatment of the tungsten electrodes involved polishing first with 240, 400, 600 grit silicon carbide powder, and then with 1.0, 0.3, and 0.05 μm alumina. The polished electrodes were placed into 1:1 HCl for 2 hours, rinsed with water, treated in the ultrasonic bath in distilled water for 15

minutes, and dried in the vacuum oven for at least two hours before use.

2. Electrochemical Procedures

The electrochemical cells were heated in 1:1 HCl for two hours, rinsed with distilled water, rinsed with dry acetone and then rinsed with double distilled water. All samples and solvents were added to the cell in the dry box. The electrodes were fixed in the cell using Acethred connectors with viton o-rings. The reference electrodes were previously cleaned with 1:1 HCl, then rinsed with distilled water and dried in oven. The Pt wire electrodes were previously heated to glowing in a flame, placed into 1:1 HCl, rinsed with distilled water and dried in the oven. Melt volumes were estimated using melt density data (71,72).

The controlled potential electrolysis experiments employed a glassy carbon cup working electrode with large surface area. The reference and counter electrodes were both composed of aluminum wires separated from the bulk solution by a fine frit.

3. Cyclic Voltammetric Measurements

Voltammetric measurements involved the following steps:

- (1) The background current versus potential characteristics were examined to obtain the largest potential window between the cathodic and anodic limits of the solvent melt at each

indicator electrode for every melt.

(2) The sample was added to the solution, and the initial potential at which no current was observed was measured. Current-potential curves were begun at this initial potential. All voltammograms were recorded at various scan rates. Good reproducibility was obtained by waiting several minutes and then allowing the system to return to equilibrium conditions.

4. Normal Pulse Voltammetric Measurements

Normal pulse voltammograms were obtained by using the PAR Model 174 Polarographic Analyzer. All parameters, such as scan rate, step time, and others, were determined before every run.

5. UV-Visible Measurements

HP 8452 Photodiode Array UV-vis Spectrophotometer was used to record electronic absorption spectra. 1 mm path length quartz cells which were fitted with airtight Teflon caps were used to contain the solutions under study. A background absorption spectrum of the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt is shown in Figure 3.

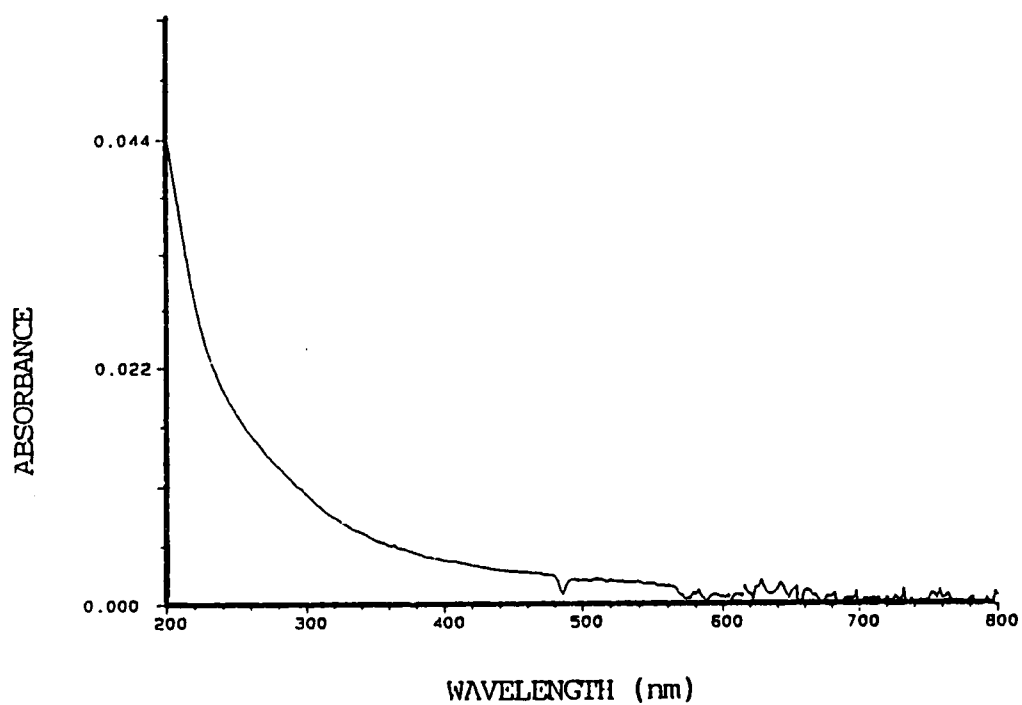


Figure 3. Background absorption spectrum of the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 180°C .
Path length: 0.1 cm.

CHAPTER III

RESULTS AND DISCUSSION

A. Electrochemistry of FeCl_3 in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt

Electrochemical studies of FeCl_3 in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt were carried out in a typical cell as discussed in the experimental section (See Figure 2) (p. 23). A conventional tungsten disk electrode ($1.96 \times 10^{-3} \text{ cm}^2$) and a tungsten disk ultramicroelectrode ($5.1 \times 10^{-6} \text{ cm}^2$) were used as working electrodes. An aluminum wire in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt which was separated from the bulk solution by a fine frit, was used as the reference electrode. A platinum wire was employed as the counter electrode. The solution of FeCl_3 in the saturated $\text{AlCl}_3/\text{NaCl}$ melt was yellow-orange; the FeCl_3 was observed to be completely dissolved in this melt. Typical background cyclic voltammograms over the whole potential region at the conventional tungsten electrode, the ultramicroelectrode and a glassy carbon electrode are shown in Figures 4 and 5. The melt appeared to contain no electroactive impurities.

The following discussion involves the study of the electrochemical behavior of FeCl_3 in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt using cyclic voltammetry and normal pulse voltammetry at the conventional and ultramicro tungsten disk electrodes. More attention will be paid to the experimental results of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in this melt.

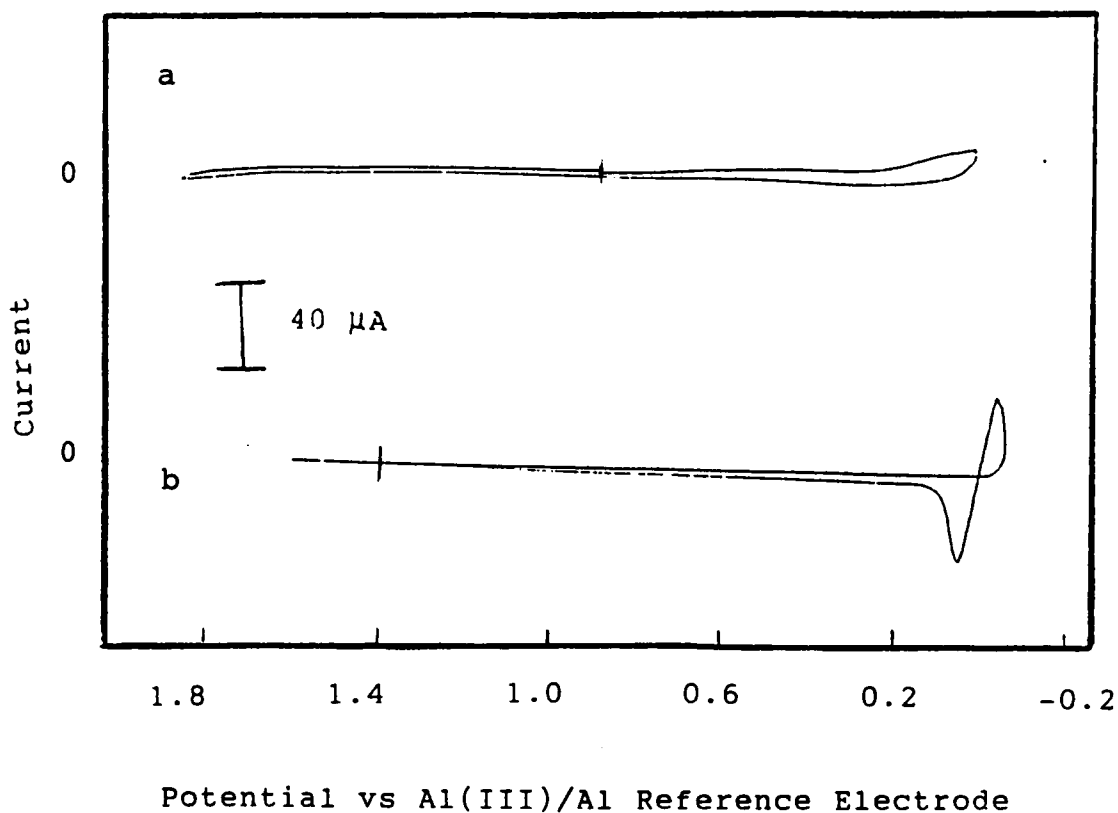
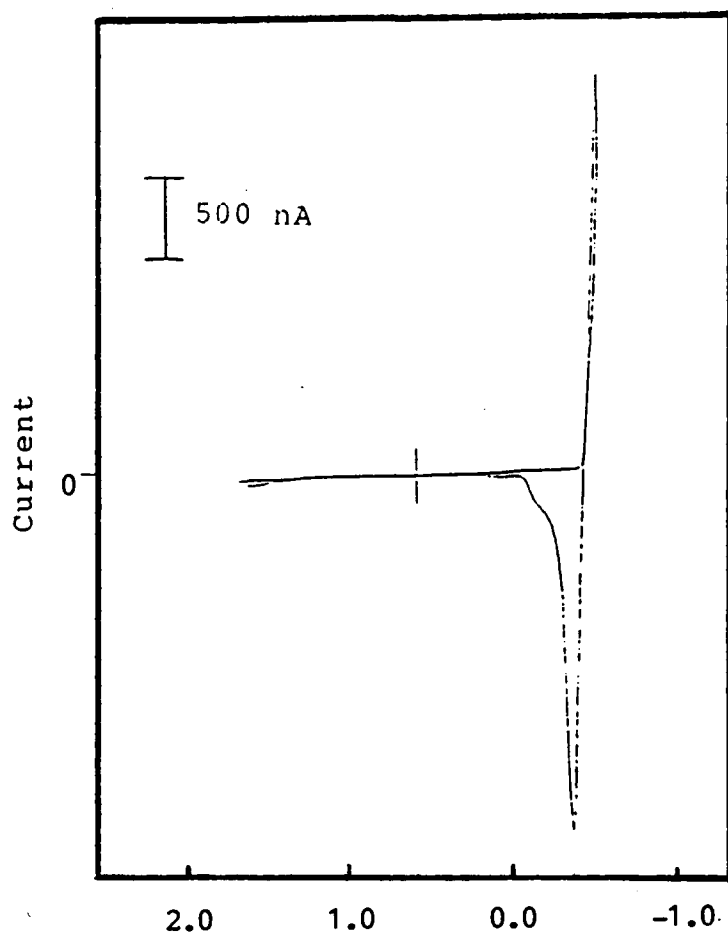


Figure 4. Background cyclic voltammograms for the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C for two working electrodes. Scan rate: 0.5 V/sec ; (a) the conventional tungsten electrode; (b) the glassy carbon electrode; electrode area: 1.96×10^{-3} and 0.071 cm^2 , respectively.



Potential vs Al(III)/Al Reference Electrode

Figure 5. Background cyclic voltammogram for the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C for the tungsten ultramicroelectrode.

Scan rate: 0.5 V/sec; electrode area:

$5.1 \times 10^{-6} \text{ cm}^2$.

a. Electrochemistry of FeCl_3 in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ Melt at the Conventional Tungsten Disk Electrode

Cyclic voltammetric studies of the reduction of FeCl_3 in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt were carried out at different scan rates. Voltammetric studies extended over the potential region from 1.5 V to 0.2 V; the potential region from 1.5 V to 1.0 V was examined in detail for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple. Cyclic voltammograms (CVs) were initiated from a potential of 1.34 V.

CVs were obtained at various scan rates from 10 mV/sec to 500 mV/sec. Figure 6 is a typical cyclic voltammogram for the overall electrochemical redox reaction of Fe(III) at a conventional tungsten disk electrode at 175°C with a Fe(III) concentration of 1.85×10^{-2} M at a scan rate of 50 mV/sec. This figure shows that the overall reduction of Fe(III) at this scan rate involves two reduction waves. The peak potential of the first reduction wave which is attributed to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple is 1.16V. The second wave at the peak potential of 0.32 V shows the typical deposition and stripping behavior for the Fe^{2+}/Fe couple. A shoulder is seen at 0.47 V, possibly due to the underpotential deposition of iron. A similar cyclic voltammogram of FeCl_3 in the neutral $\text{AlCl}_3/\text{NaCl}$ melt was reported by Osteryoung and coworkers (see Figure 7) (20). Figure 8 shows the cyclic voltammograms at the scan rates 100, 200, and 500 mV/sec under the same conditions as those in Figure 6. Figure 9 shows the cyclic voltammograms for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple at scan rates of 100, 200, and 500 mV/sec at

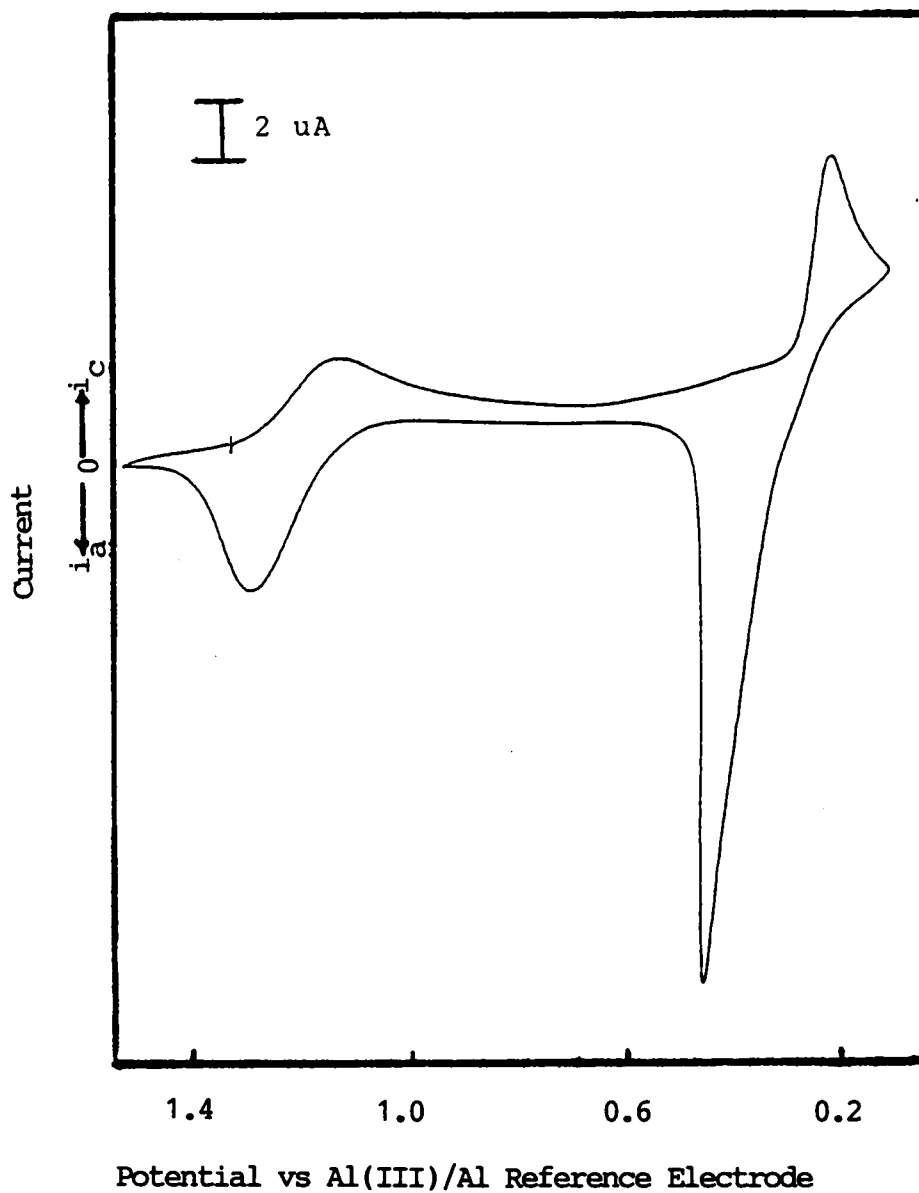


Figure 6. Cyclic voltammogram of FeCl_3 at a conventional tungsten electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.
 Electrode area: $1.96 \times 10^{-3} \text{ cm}^2$; Fe(III) concentration: $1.85 \times 10^{-2} \text{ M}$; scan rate: 50 mV/sec .

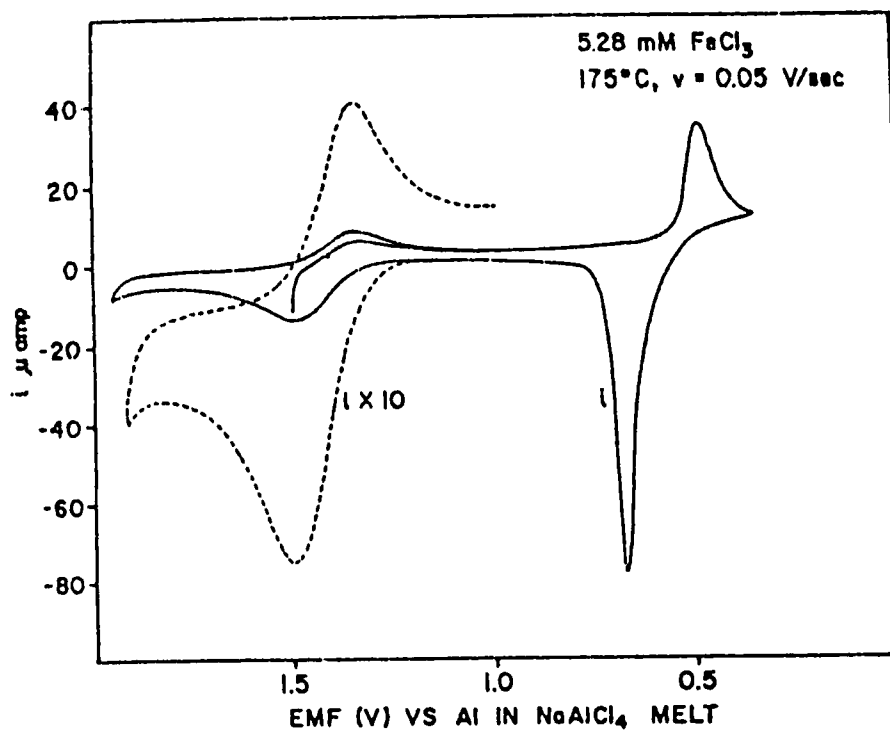


Figure 7. Cyclic voltammogram of FeCl_3 at a tungsten electrode at 175°C in NaAlCl_4 . Dashed curve: scale expanded by 10.

Electrode area: $1.79 \times 10^{-2} \text{ cm}^2$; Fe(III) concentration: $5.28 \times 10^{-3} \text{ M}$; scan rate: 50 mV/sec (20).

Reference electrode is the Al(III)/Al couple in an equimolar $\text{AlCl}_3/\text{NaCl}$ melt.

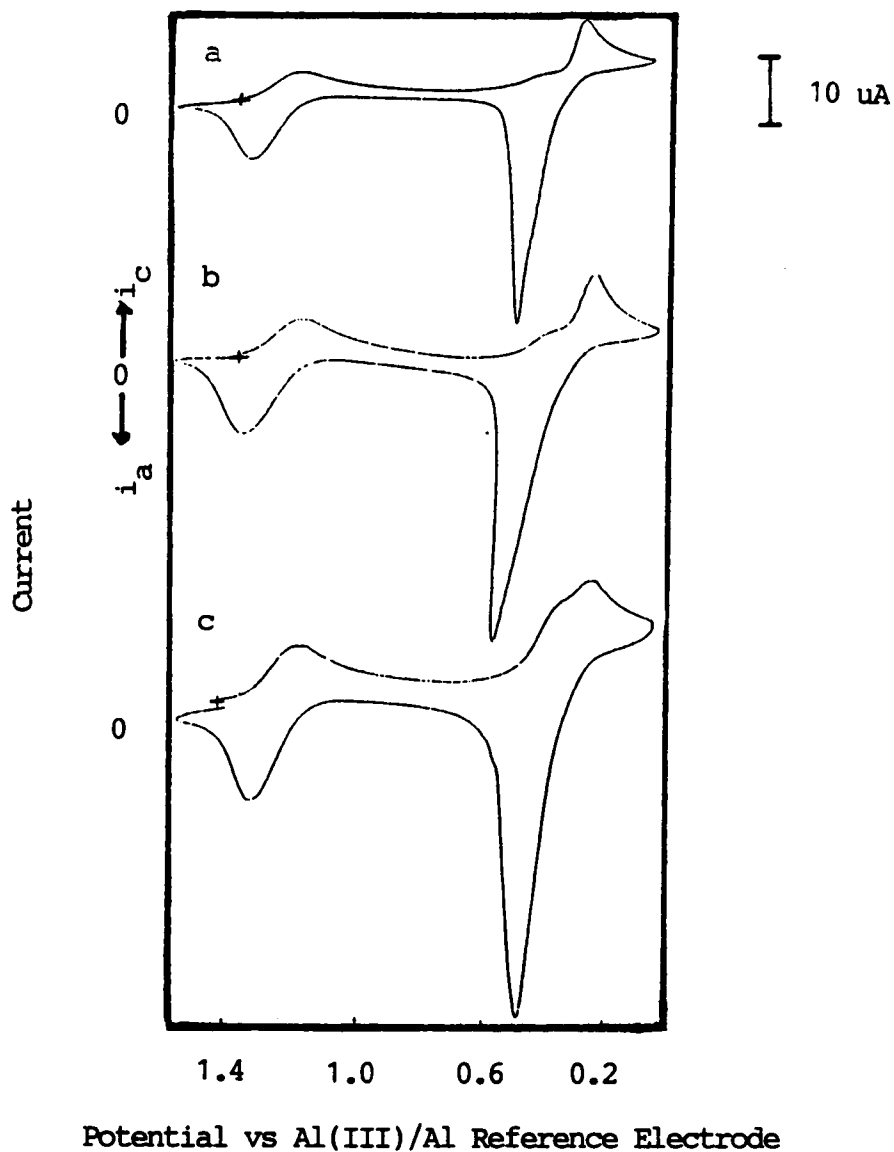


Figure 8. Cyclic voltammograms of Fe(III) at a conventional tungsten electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. Electrode area: $1.96 \times 10^{-3} \text{ cm}^2$; Fe(III) concentration: $1.85 \times 10^{-2} \text{ M}$; scan rate: (a) 100 mV/sec, (b) 200 mV/sec, (c) 500 mV/sec.

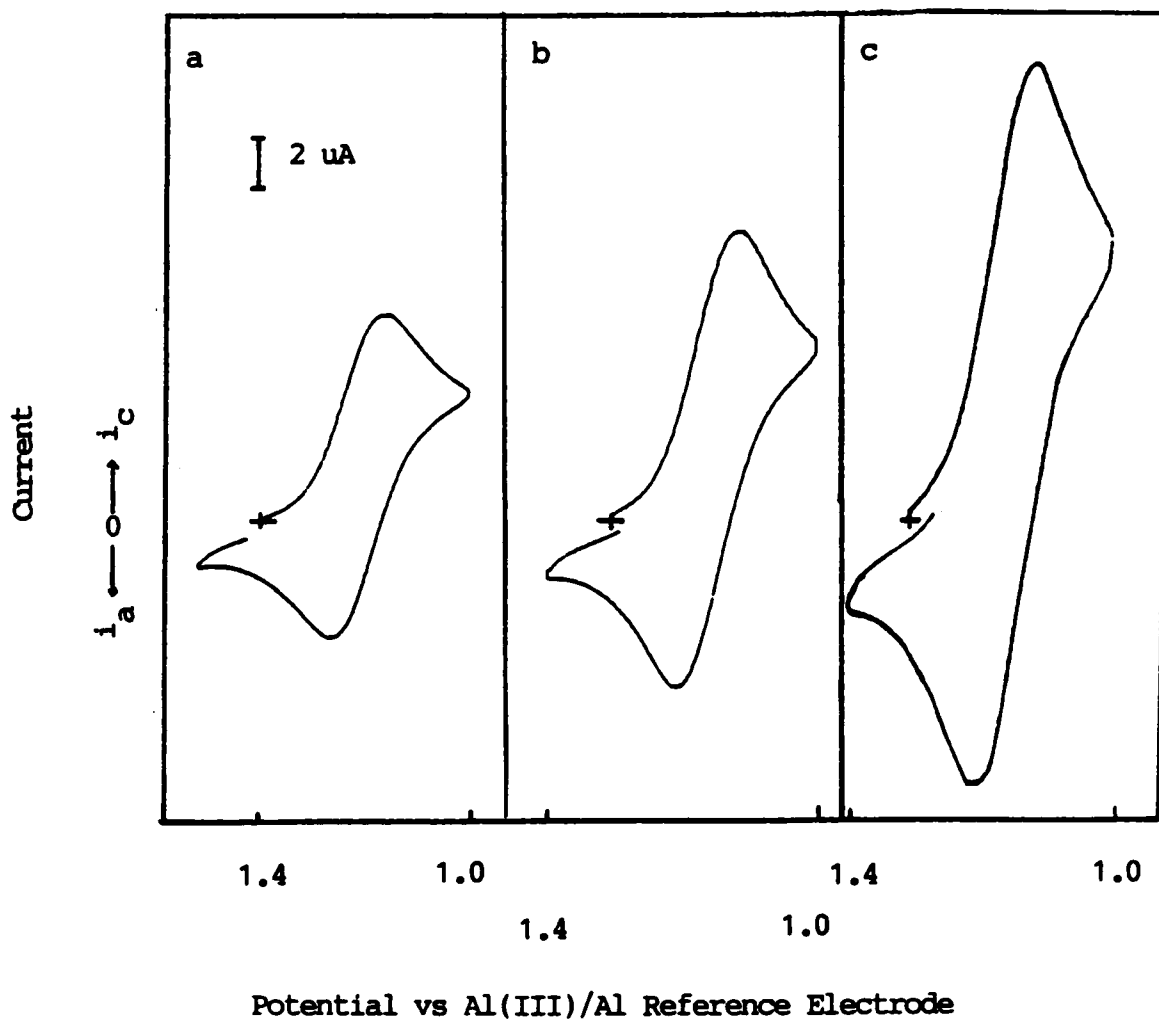


Figure 9. Cyclic voltammograms for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple at a conventional tungsten electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. Electrode area: $1.96 \times 10^{-3} \text{ cm}^2$; Fe(III) concentration: $1.85 \times 10^{-2} \text{ M}$; scan rate: (a) 100 mV/sec, (b) 200 mV/sec, (c) 500 mV/sec.

a conventional tungsten working electrode at 175°C with a Fe(III) concentration of 1.85×10^{-2} M. From these cyclic voltammograms, a series of electrochemical parameters can be obtained. These parameters are summarized in Table 1. For the $\text{Fe}^{3+}/\text{Fe}^{2+}$ reduction peak, a plot of the peak current vs the square root of the scan rate is linear as shown in Figure 10. The parameter i_{pa}/i_{pc} was obtained using the Nicholson equation (45):

$$i_{pa}/i_{pc} = (i_{pa})_0/i_{pc} + 0.485[(i_{sp})_0/i_{pc}] + 0.086 \quad (18)$$

where i_{pc} is the cathodic peak current; i_{pa} is the anodic peak current; $(i_{pa})_0$ is the uncorrected anodic peak current with respect to the baseline, while $(i_{sp})_0$ is the current at the point at which the potential sweep is reversed. For all the scan rates employed, the i_{pa}/i_{pc} was about unity. Values for $E_{1/2}$ at different scan rates were obtained using the equation (45):

$$E_{1/2} = (E_{pa} + E_{pc})/2 \quad (19)$$

Over the range of the scan rates that were employed, a constant $E_{1/2}$ of 1.21 V was obtained. The peak separation was 100 mV which is slightly larger than the theoretical value of 84 mV for a reversible, one-electron redox system at 175°C (20). The peak potential separation between cathodic and anodic peaks does not change with the scan rate. Cyclic voltammetric behavior of this type is ascribed to an essentially reversible charge transfer process. Equation 7 (p. 11) was used to estimate the diffusion coefficient.

Table 1: Electrochemical data for the Fe(III)/Fe(II) couple
in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C

Scan rate (V/sec)	i_{pc} (A) $\times 10^{-6}$	i_{pa} (A) $\times 10^{-6}$	E_{pc} (V)	E_{pa} (V)	$E_{\text{pa}} - E_{\text{pc}}$ (V)	$E_{1/2}$ (V)	$i_{\text{pa}}/i_{\text{pc}}$	$D \times 10^{-6}$ (cm^2/sec)
0.02	2.90	2.98	1.16	1.26	0.10	1.21	1.03	6.35
0.05	4.40	4.86	1.16	1.26	0.10	1.21	1.10	6.67
0.10	6.40	6.97	1.16	1.26	0.10	1.21	1.09	6.14
0.20	9.00	10.03	1.16	1.26	0.10	1.21	1.11	6.50
0.50	15.20	16.20	1.16	1.26	0.10	1.21	1.07	6.43
								$\bar{D}$ 6.42

$$E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$$

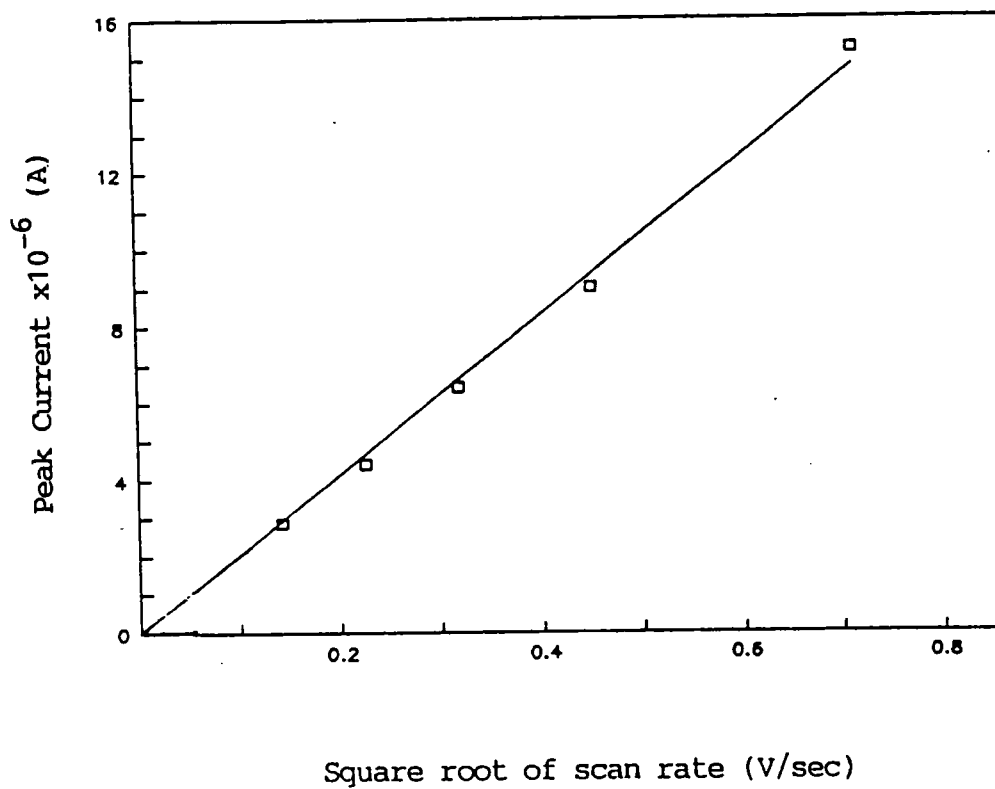


Figure 10. A plot of i_p vs the square root of the scan rate for the Fe(III)/Fe(II) couple at a conventional tungsten electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.

Electrode area: $1.96 \times 10^{-3} \text{ cm}^2$; Fe(III) concentration: $1.85 \times 10^{-2} \text{ M}$.

The diffusion coefficient values obtained with this equation at different scan rates are summarized in Table 1 (p. 38). An average diffusion coefficient of 6.42×10^{-6} cm²/sec was calculated. This value is in reasonable agreement with an average diffusion coefficient of $9.1 \pm 0.9 \times 10^{-6}$ cm²/sec reported in literature for Fe(III) in a 1:1 AlCl₃/NaCl melt at 175°C (20).

Normal pulse voltammetric studies were conducted with a solution containing 9.8×10^{-3} M of FeCl₃ using the conventional tungsten disk working electrode at 175°C. Typical voltammograms are shown in Figure 11. The reduction wave for the Fe³⁺/Fe²⁺ couple was observed at various pulse widths. A plot of the limiting current vs $1/t^{1/2}$, where t is the pulse width, is linear (See Figure 12). An average diffusion coefficient was calculated to be 8.85×10^{-6} cm²/sec from the Cottrell equation. This value is in good agreement with the value from the literature ($9.1 \pm 0.9 \times 10^{-6}$ cm²/sec) (20). Some electrochemical parameters for the Fe(III)/Fe(II) couple are summarized in Table 2. A plot of the potential vs $\ln[(i_d - i)/i]$ is shown in Figure 13. The straight line through the data points of this reduction step has the theoretical slope $(RT)/(nF)$ corresponding to a 0.9 electron reversible charge transfer process. The half wave potential of 1.25 V is obtained.

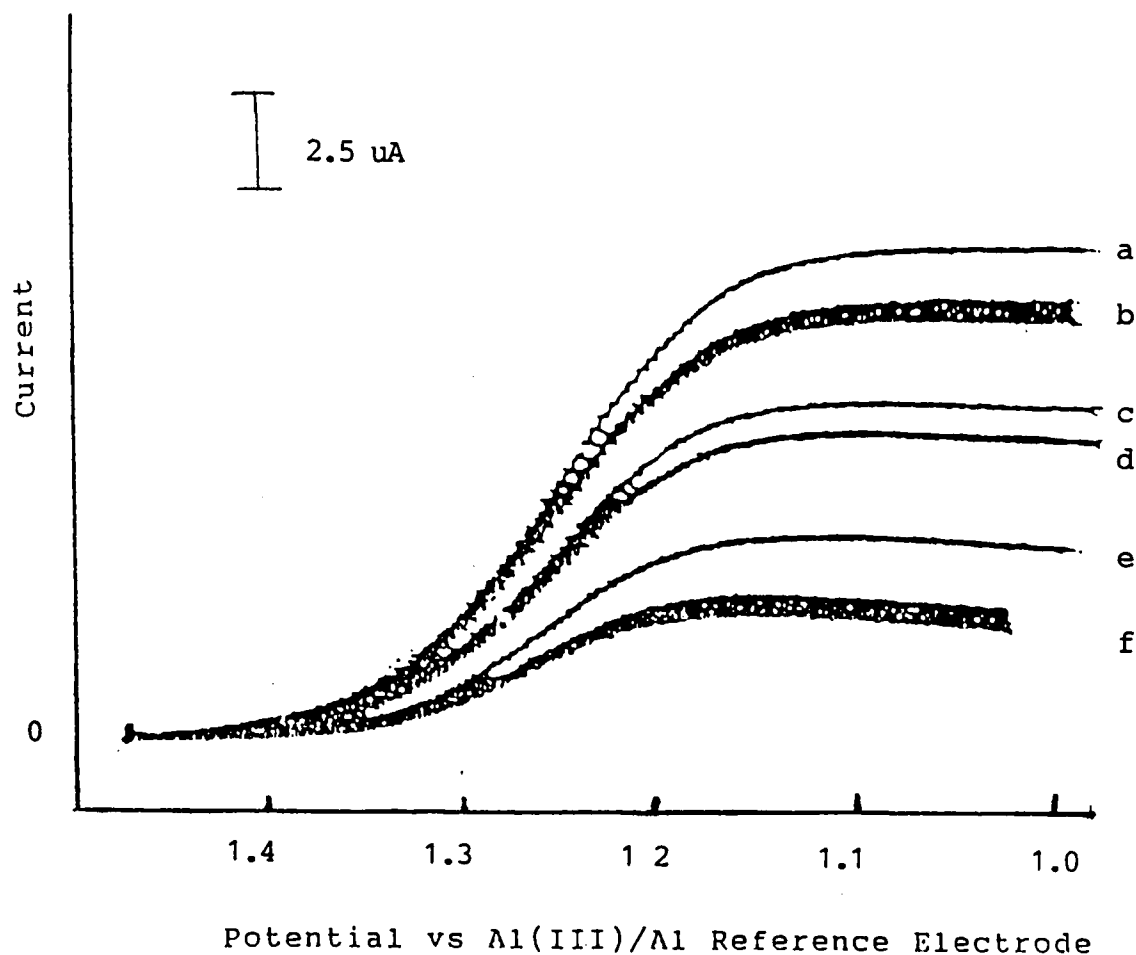


Figure 11. Normal pulse voltammograms for the Fe(III)/Fe(II) couple at a conventional tungsten electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. Electrode area: $1.96 \times 10^{-3} \text{ cm}^2$; Fe(III) concentration: $9.8 \times 10^{-3} \text{ M}$; pulse width: (a) 57 ms, (b) 77 ms, (c) 95 ms, (d) 115 ms, (e) 175 ms, (f) 272 ms; scan rate: 1 mV/sec; drop time: 0.5 s.

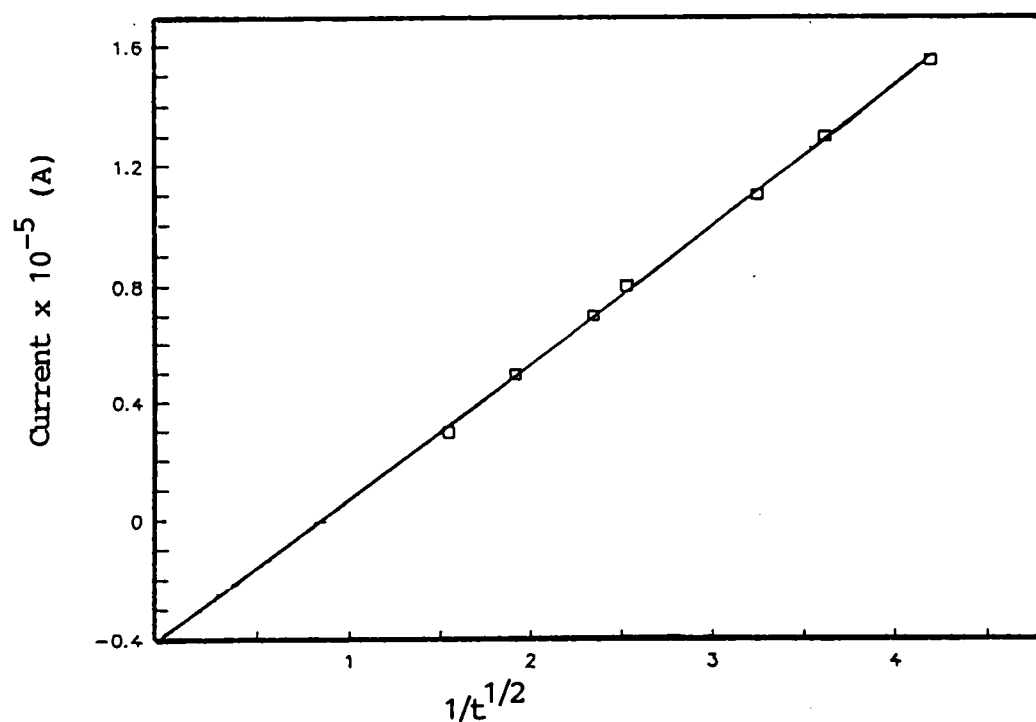


Figure 12. A plot of the limiting current vs $1/t^{1/2}$ at a conventional tungsten electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.

Electrode area: $1.96 \times 10^{-3} \text{ cm}^2$; Fe(III)
concentration: $9.8 \times 10^{-3} \text{ M}$.

Table 2: Normal pulse voltammetric results for
the Fe(III)/Fe(II) couple in the
AlCl₃/NaCl_{sat} melt at 175°C

Pulse width t(s)	i _d (A)x10 ⁻⁶	(1/t) ^{1/2} (1/s)	it ^{1/2} (A s ^{1/2})x10 ⁻⁶
0.42	3.00	1.54	1.94
0.27	5.00	1.92	2.61
0.18	7.00	2.34	2.99
0.16	8.00	2.52	3.17
0.10	11.00	3.24	3.40
0.08	13.00	3.60	3.61
0.06	15.50	4.19	3.70

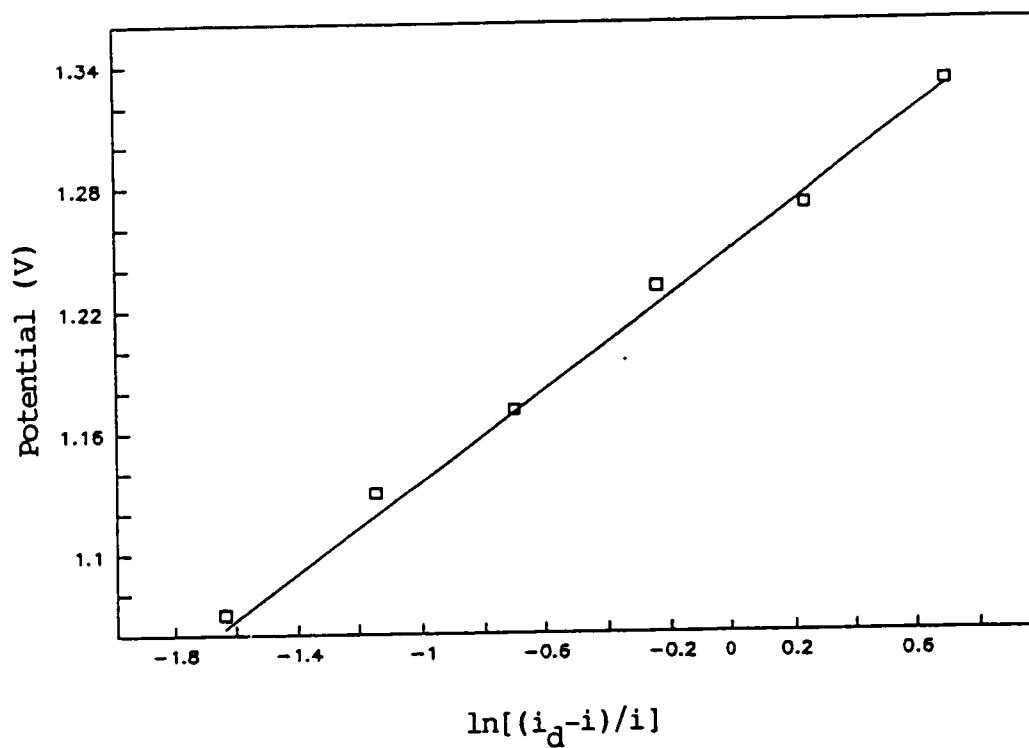


Figure 13. A plot of the potential vs $\ln[(i_d - i)/i]$ at a conventional tungsten electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.
 Electrode area: $1.96 \times 10^{-3} \text{ cm}^2$; Fe(III) concentration: $9.8 \times 10^{-3} \text{ M}$; pulse width: 57 ms.

b. Electrochemistry of FeCl_3 in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ Melt at the Tungsten Disk Ultramicroelectrode

The potential region from 1.75 to 1.0 V was examined by cyclic voltammetry to study the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple at the ultramicroelectrode. Cyclic voltammograms were obtained at various scan rates from 1 mV/sec to 500 mV/sec at 182°C , for the FeCl_3 concentration of 1.39×10^{-2} M. Cyclic voltammograms at these scan rates reveal that the limiting current plateau is observed at the lower scan rates at this ultramicroelectrode. Figure 14 shows cyclic voltammograms for the $\text{Fe(III)}/\text{Fe(II)}$ couple at scan rates of 50, 100, 200, and 500 mV/sec. From these cyclic voltammograms, a series of electrochemical parameters were obtained and summarized in Table 3. Figure 15 shows that the relationship between the peak current and the square root of the scan rate is linear at the different scan rates. In this figure, the experimental values are shown as symbols and the value obtained by the linear least squares fit is shown as a solid line. However, the intercept is not zero, which may be due to the edge effect at the small electrode (67). To calculate the diffusion coefficient of FeCl_3 using data obtained with the ultramicroelectrodes, a computer program using GW-BASIC language was written based on equation 16 (p. 16). The program to calculate diffusion coefficients is summarized in Appendix 1. An average diffusion coefficient of 5.2×10^{-6} cm^2/sec was obtained, which is smaller than the literature

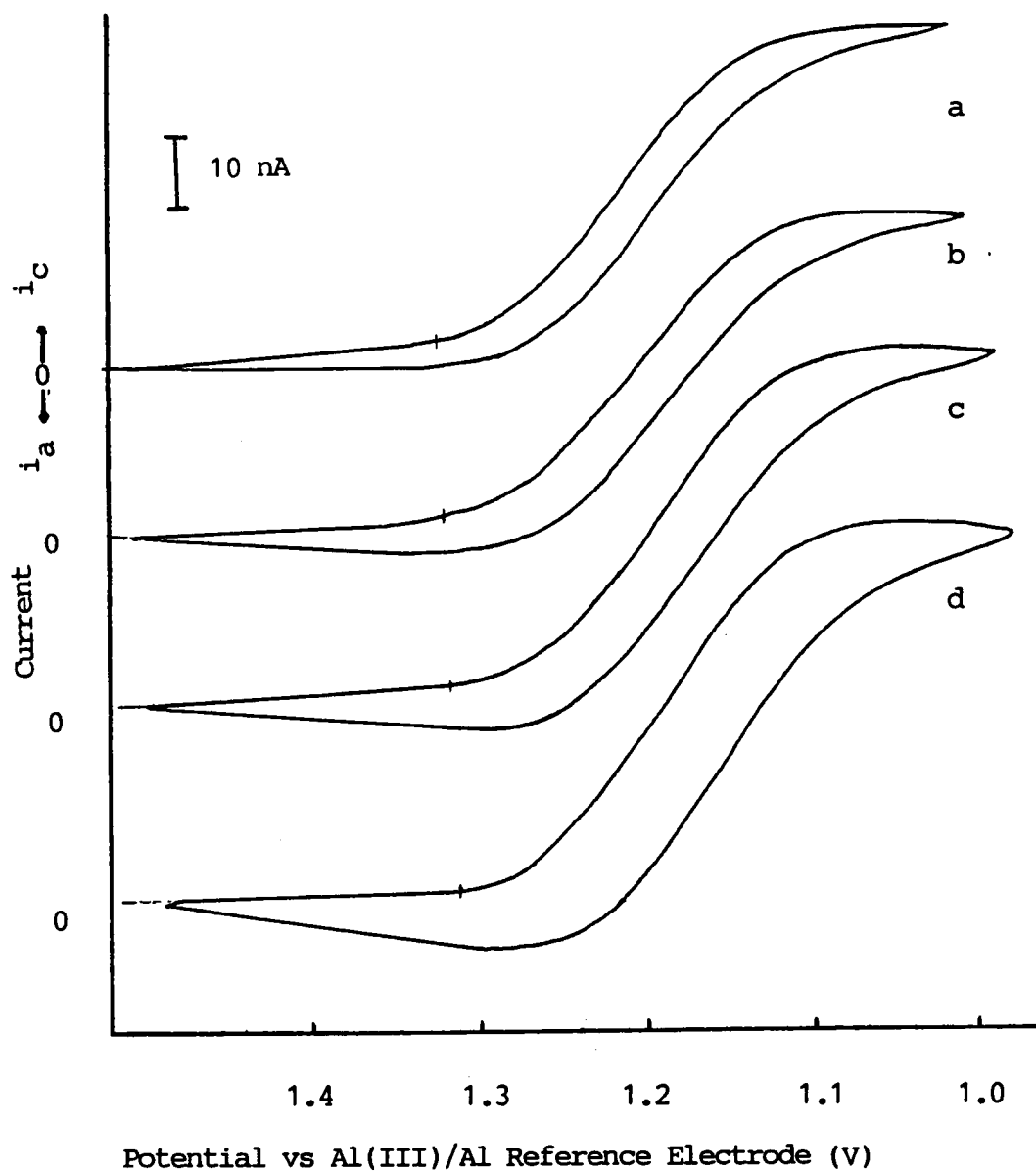


Figure 14. Cyclic voltammograms for the Fe(III)/Fe(II) couple at a tungsten disk ultramicroelectrode at 182°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. Electrode area: $5.1 \times 10^{-6} \text{ cm}^2$; Fe(III) concentration: $1.39 \times 10^{-2} \text{ M}$; scan rate: (a) 50 mV/sec, (b) 100 mV/sec, (c) 200 mV/sec, (d) 500 mV/sec.

Table 3: Electrochemical data for the Fe(III)/Fe(II) couple at a tungsten disk ultramicroelectrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 182°C

I_m (nA)	scan rate v (V/sec)	$E_{1/2}$ (V)	$D \times 10^{-6}$ (cm^2/sec)
33.0	0.001	1.20	5.12
33.5	0.005	1.19	5.36
36.5	0.010	1.20	5.36
38.0	0.020	1.19	5.42
40.0	0.050	1.20	5.35
41.5	0.100	1.20	5.26
44.5	0.200	1.20	4.85
49.5	0.500	1.21	4.86
$\bar{D}$			5.2

$E_{1/2}$ is obtained by measureing manually the potential at $1/2 I_m$.

The program to calculate D values is in the Appendix.

I_m is the maximum current.

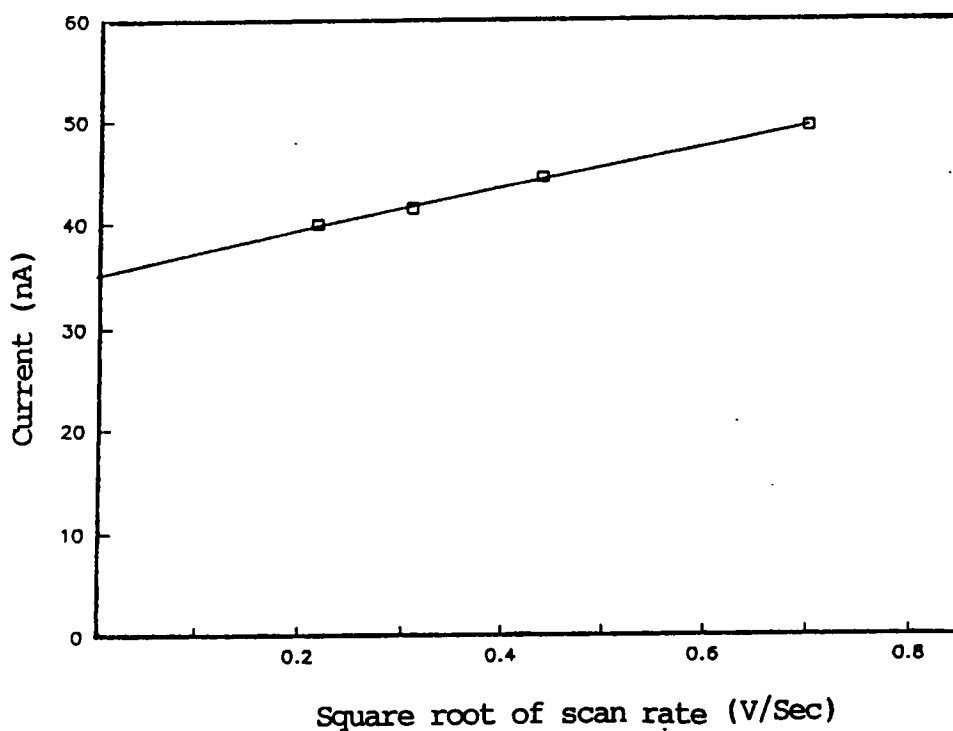


Figure 15. A plot of the maximum current vs the square root of scan rate at a tungsten disk ultramicroelectrode at 182°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.
 Electrode area: $5.1 \times 10^{-6} \text{ cm}^2$; Fe(III) concentration: $1.39 \times 10^{-2} \text{ M}$.

value (20), however, it is in good agreement with the value of 6.42×10^{-6} cm²/sec obtained from equation 7 (p. 11) at the conventional tungsten disk electrode. At scan rates less than 500 mV/sec, the limiting current at the ultramicroelectrode is still found to exhibit steady state behavior. From Figure 14 (p. 46), it appears that voltammograms obtained with the ultramicroelectrode at higher scan rates approached the characteristics of planar diffusion. Figure 16 is the cyclic voltammogram at a scan rate of 1 mV/sec, showing a curve which is similar to the normal pulse voltammogram. Obviously, the predominant mode of diffusion to the electrode is the steady state. According to equation 15 (p. 15), the diffusion coefficient was determined to be 4.92×10^{-6} cm²/sec. This value is in good agreement with the value obtained from equation 16 (p. 16). For a reversible system at low scan rates at an ultramicroelectrode, the Nernst equation should be applicable. A plot of potential vs $\ln[(i_d - i)/i]$ should give a slope of RT/nF (see Figure 17). When n was calculated in this manner, a value of 1.06 was obtained, which indicated that the reduction involved one electron. The half wave potential is 1.18 V.

Figure 18 is the normal pulse voltammogram of Fe(III) in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. The diffusion coefficient of 1.1×10^{-5} cm²/sec was calculated using equation 15 (p. 15). This value is in good agreement with the literature value ($9.1 \pm 0.9 \times 10^{-6}$ cm²/sec). A plot of the potential vs

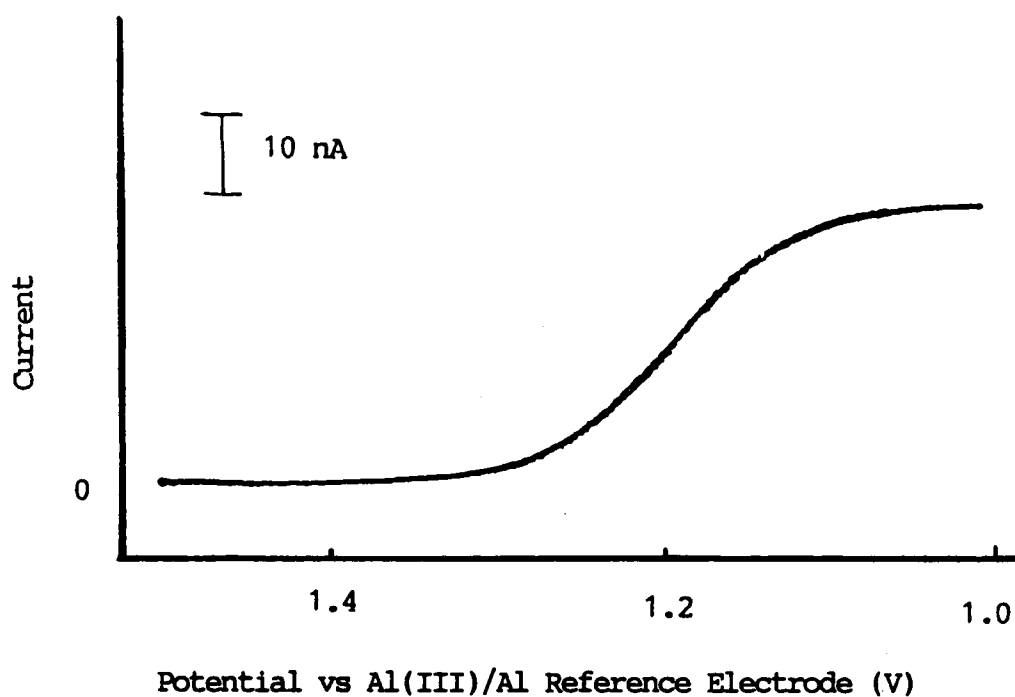


Figure 16. Cyclic voltammogram at a tungsten disk ultramicroelectrode at 182°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.
 Electrode area: $5.1 \times 10^{-6} \text{ cm}^2$; Fe(III) concentration: $1.39 \times 10^{-2} \text{ M}$; scan rate: 1 mV/sec.

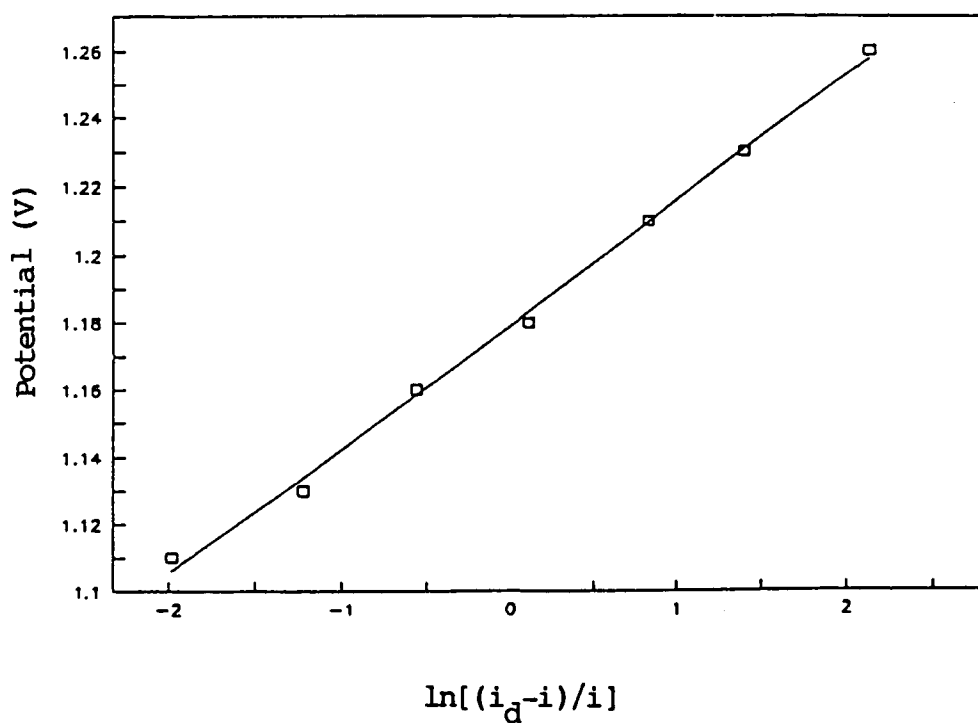


Figure 17. A plot of potential vs $\ln[(i_d - i)/i]$ at a ultramicro tungsten disk electrode at 182°C in the $\text{AlCl}_3/\text{NaCl}$ melt.

Electrode area: $5.1 \times 10^{-6} \text{ cm}^2$; Fe(III) concentration: $1.39 \times 10^{-2} \text{ M}$; scan rate: 1 mV/sec.

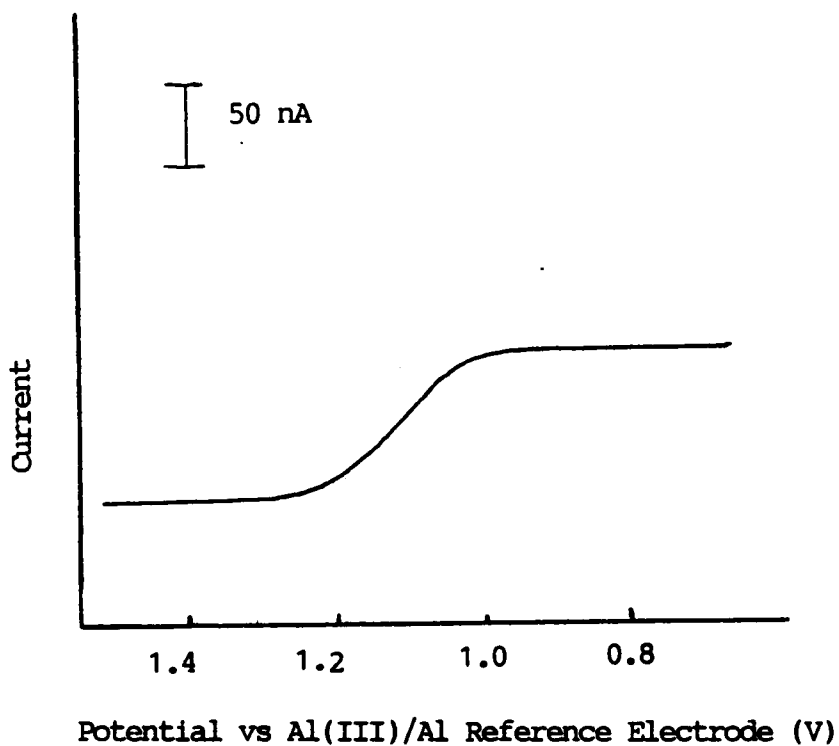


Figure 18. Normal pulse voltammogram of the Fe(III)/Fe(II) couple at a tungsten disk ultramicro electrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.

Electrode area: $5.1 \times 10^{-6} \text{ cm}^2$; Fe(III) concentration: $1.85 \times 10^{-2} \text{ M}$; scan rate: 1 mV/sec; pulse width: 57 ms; drop time: 1 sec.

$\ln[(i_d - i)/i]$ is shown in Figure 19. The calculated n-value was 0.93. The half wave potential is 1.17 V.

c. Comparison of the Electrochemical Behavior of FeCl_3 at the Conventional Electrode and Ultramicroelectrode

The electrochemical behavior of the Fe(III)/Fe(II) couple at both the conventional tungsten disk electrode and tungsten ultramicroelectrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt has been investigated using cyclic voltammetry and normal pulse voltammetry. The Fe(III)/Fe(II) couple was found to be reversible. Diffusion coefficient values for Fe(III) at 175°C using different methods are tabulated in Table 4. It can be noted that diffusion coefficient values obtained from NP are in good agreement with the literature value of $9.1 \pm 0.9 \times 10^{-6} \text{ cm}^2/\text{sec}$ (20). Plots of the peak current vs the square root of the scan rate at both the conventional tungsten disk electrode and the tungsten ultramicroelectrode at the different scan rates are linear. Cyclic voltammograms at an ultramicroelectrode at lower scan rates exhibit a plateau, whereas at higher scan rates peak-shaped voltammograms are obtained. The calculation from equation 15 (p. 15) to obtain the diffusion coefficient for the ultramicroelectrode is relatively easy compared with that for the conventional electrode from equation 7 (p. 11). According to experimental results, the base line of the cyclic voltammograms at the ultramicroelectrode is more flat than that at the conventional

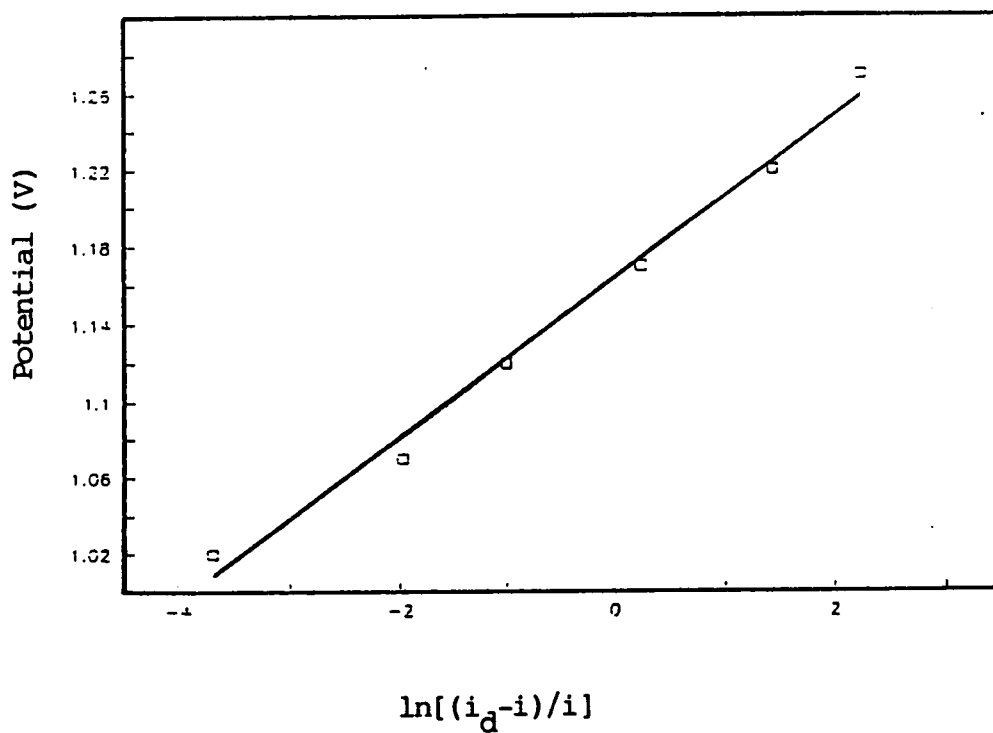


Figure 19. A plot of potential vs $\ln[(i_d - i)/i]$ at a tungsten disk ultramicroelectrode at 175°C in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt.
 Electrode area: $5.1 \times 10^{-6} \text{ cm}^2$; Fe(III) concentration: $1.85 \times 10^{-2} \text{ M}$.

Table 4: The half wave potential and diffusion coefficient of Fe(III) in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at both the conventional and ultramicroelectrodes

Electrode	Technique	D (cm^2/sec)	$E_{1/2}$ (V)
CTDE	CV	6.4×10^{-6}	1.21
	NP	8.85×10^{-6}	1.25
UTDE	CV	5.2×10^{-6}	1.20
	NP	1.1×10^{-5}	1.18

CTDE is a conventional tungsten disk electrode.

UTDE is an ultramicro tungsten disk electrode.

CV is cyclic voltammetry.

NP is normal pulse voltammetry.

electrode. The iR drop is reduced at the ultramicroelectrode. Steady states of mass transfer can be quickly established at the ultramicroelectrode. For this system, the steady state behavior could be observed at a scan rate less than 500 mV/sec at the ultramicroelectrode.

B. Electrochemical and Spectroscopic Studies of Re(III) and Re(IV) in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ Melt

a. Electrochemical and Spectroscopic Studies of $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ Melt

The dissolution of $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt at 175°C produced a blue-green solution. An absorption spectrum of this solution is shown in Figure 20. The wavelengths and the molar absorptivities of the bands that appear in this spectrum are collected in Table 5, as are literature data (37) for solutions of this compound dissolved in basic $\text{AlCl}_3\text{-MEIC}$ melts. The spectroscopic data originating from Figure 20 are in fairly good agreement with the literature data, indicating that $[\text{Re}_2\text{Cl}_8]^{2-}$ is stable in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt at this temperature.

Cyclic voltammograms of $[\text{Re}_2\text{Cl}_8]^{2-}$ (1.09×10^{-3} M) in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt, at various scan rates ranging from 20 mV/sec to 6 V/sec, were obtained covering the electrochemical window of the melt. Typical cyclic voltammograms obtained at a glassy carbon disk electrode vs the Al(III)/Al couple in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at three scan rates (50, 100, 500 mV/sec) at

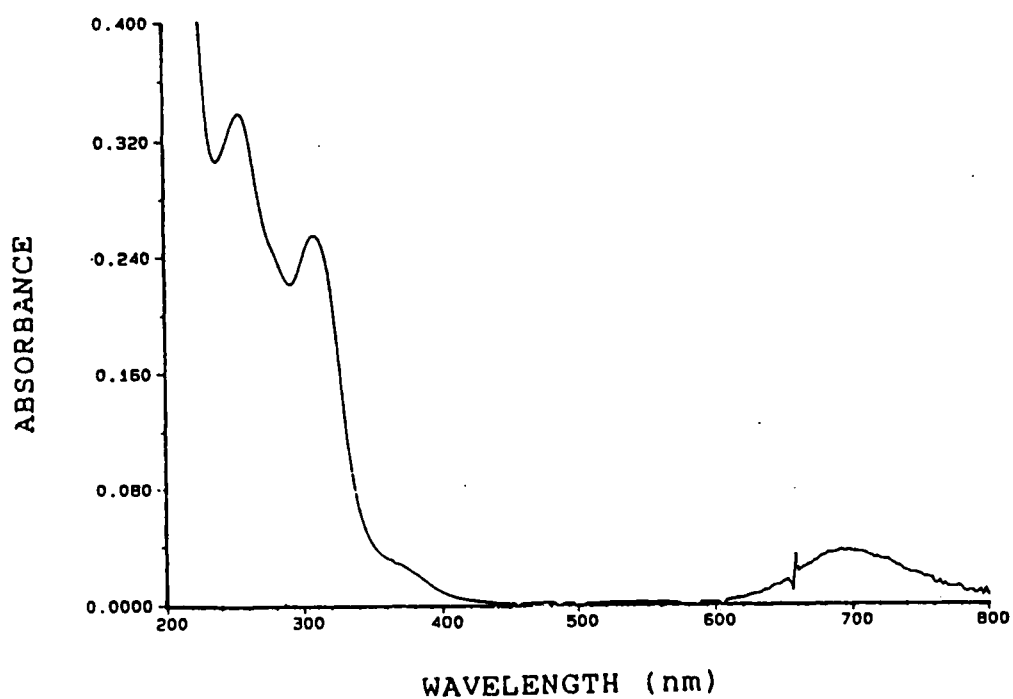


Figure 20. Absorption spectrum of $[\text{Re}_2\text{Cl}_8]^{2-}$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C . $[\text{Re}_2\text{Cl}_8]^{2-}$ concentration: 3.8×10^{-4} M; path length: 0.10 cm.

Table 5: Spectroscopic Data for Selected Rhenium Compounds

Solute	Solvent	Wavelength, nm(ϵ , M ⁻¹ cm ⁻¹)	Relative intensity*	Ref.
[Bu ₄ N] ₂ [Re ₂ Cl ₈]	49.0/51.0	253(1.0x10 ⁴), 316(1.0x10 ⁴)	4.6 : 4.6 : 1	37
	AlCl ₃ /MEIC	[360 ^{a,b}], 688(2.3x10 ³)		
[Bu ₄ N] ₂ [Re ₂ Cl ₈]	AlCl ₃ /NaCl _{sat}	254(8.1x10 ³), 308(6.1x10 ³)	10.3 : 7.7 : 1	This work
		[364(8.1x10 ²)], 694(7.9x10 ²)		
K ₂ ReCl ₆	49.0/51.0	263(9.4x10 ³), 283(1.5x10 ⁴)	2.9 : 4.7 : 1	42
	AlCl ₃ /MEIC	[300 ^{sh}], 322(3.2x10 ³)		
K ₂ ReCl ₆	AlCl ₃ /NaCl _{sat}	262(4.5x10 ³), 282(5.9x10 ³)	2.1 : 2.6 : 1	This work
		324(2.1x10 ³)		

a Broad band composed of two or more maxima. b Very weak. sh Shoulder.

* Ratios of molar absorptivities of bands not included in square brackets.

175°C are shown in Figure 21. These voltammograms exhibit two reduction waves. The peak potential of the first reduction wave shifts from 0.92 V to 0.79 V, and that of the second reduction wave shifts from 0.40 V to 0.33 V when scan rates change from 20 mV/sec to 500 mV/sec. The second reduction wave is associated with an oxidation wave having a peak potential which shifts from 0.46 V to 0.51 V at scan rates from 20 mV/sec to 500 mV/sec. Some electrochemical parameters for the first and second waves are summarized in Table 6. A plot of the peak current vs the square root of the scan rate for the first wave is linear (see Figure 22). This indicates that the electron transfer process for the first wave is diffusion controlled. It can be noted from Table 6 that E_{pc} shifts cathodically as the scan rate increases, and this shift is more evident at low scan rates than at high ones. A plot of the rate of the potential shift ($\frac{\Delta E_p}{\Delta \log v}$) vs scan rate is shown in Figure 23. This plot can be rationalized qualitatively if the electron transfer process giving rise to the first wave is a reversible charge transfer followed by an irreversible chemical reaction (48). In such a situation, the peak potential can be obtained from the following equation (48):

$$E_p = E_{1/2} - (RT/nF) [0.780 - \ln(k_f/a)^{1/2}] \quad (20)$$

where k_f is the rate constant of the chemical reaction, and a is $(nFv)/(RT)$. This equation indicates that when k_f/a is small, the peak potential is independent of k_f/a ; when k_f/a

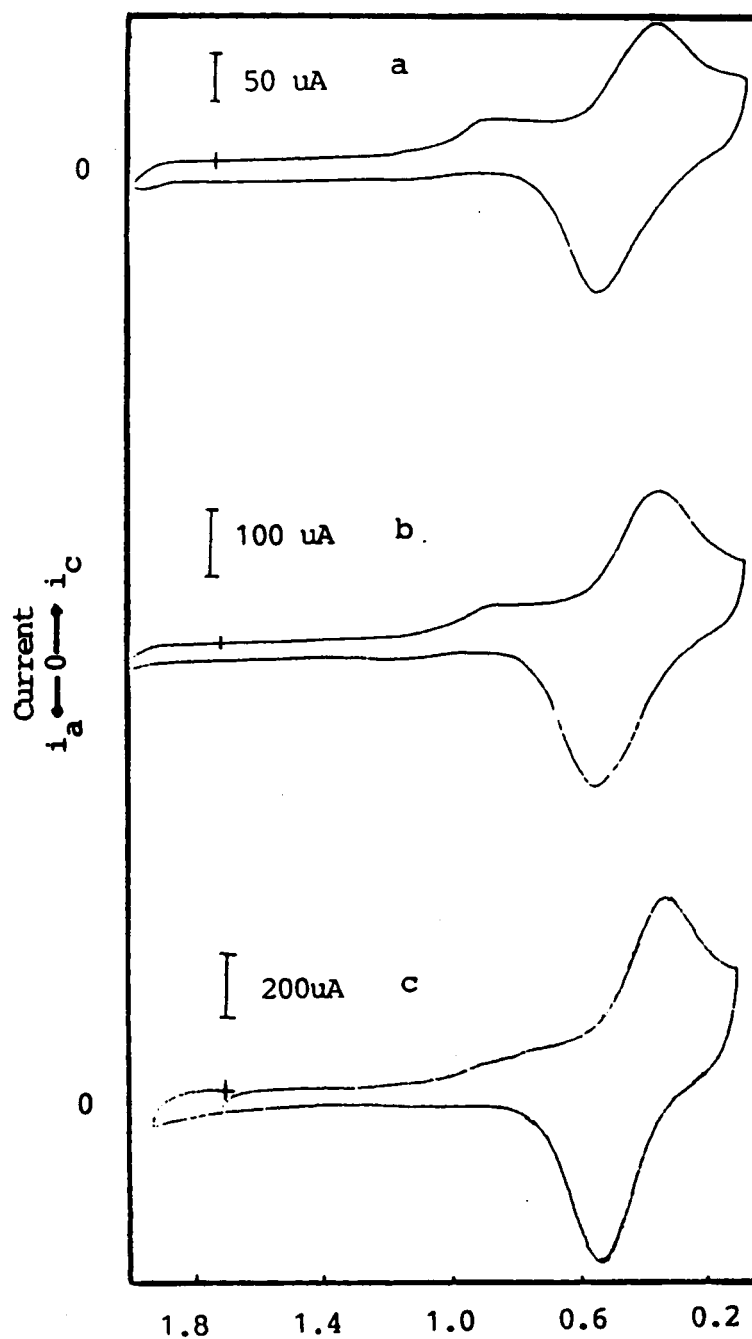


Figure 21. Potential vs Al(III)/Al Reference Electrode (V)
Cyclic voltammograms of $[\text{Re}_2\text{Cl}_8]^{2-}$ at a glassy carbon electrode at three different scan rates in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C .
Electrode area: 0.071 cm^2 ; $[\text{Re}_2\text{Cl}_8]^{2-}$ concentration: $1.09 \times 10^{-3} \text{ M}$; scan rate: (a) 0.05 V/sec , (b) 0.1 V/sec , (c) 0.5 V/sec .

Table 6: Electrochemical parameters for $[\text{Re}_2\text{Cl}_8]^{2-}$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C

scan rate (V/sec)	$(E_{\text{pc}})_1$ (V)	$(E_{\text{pc}/2})_1$ (V)	$(E_{\text{pc}/2} - E_{\text{pc}})_1$ (V)	$(i_{\text{pc}}/C)_1$ (A/M)	$(E_{\text{pc}})_2$ (V)	$(E_{\text{pa}})_2$ (V)	$(E_{1/2})_2$ (V)
0.02	0.92	1.00	0.08	0.023	0.40	0.46	0.43
0.05	0.83	0.91	0.08	0.040	0.36	0.50	0.43
0.10	0.80	0.88	0.08	0.059	0.36	0.50	0.43
0.20	0.79	0.88	0.09	0.075	0.35	0.51	0.43
0.50	0.79	0.90	0.11	0.077	0.33	0.51	0.42

$(E_{1/2})_2 = (E_{\text{pc}} + E_{\text{pa}})/2$.
 1 and 2 designate for the first and second reduction peaks, respectively.
 $[\text{Re}_2\text{Cl}_8]^{2-}$ concentration: 1.09×10^{-3} M.

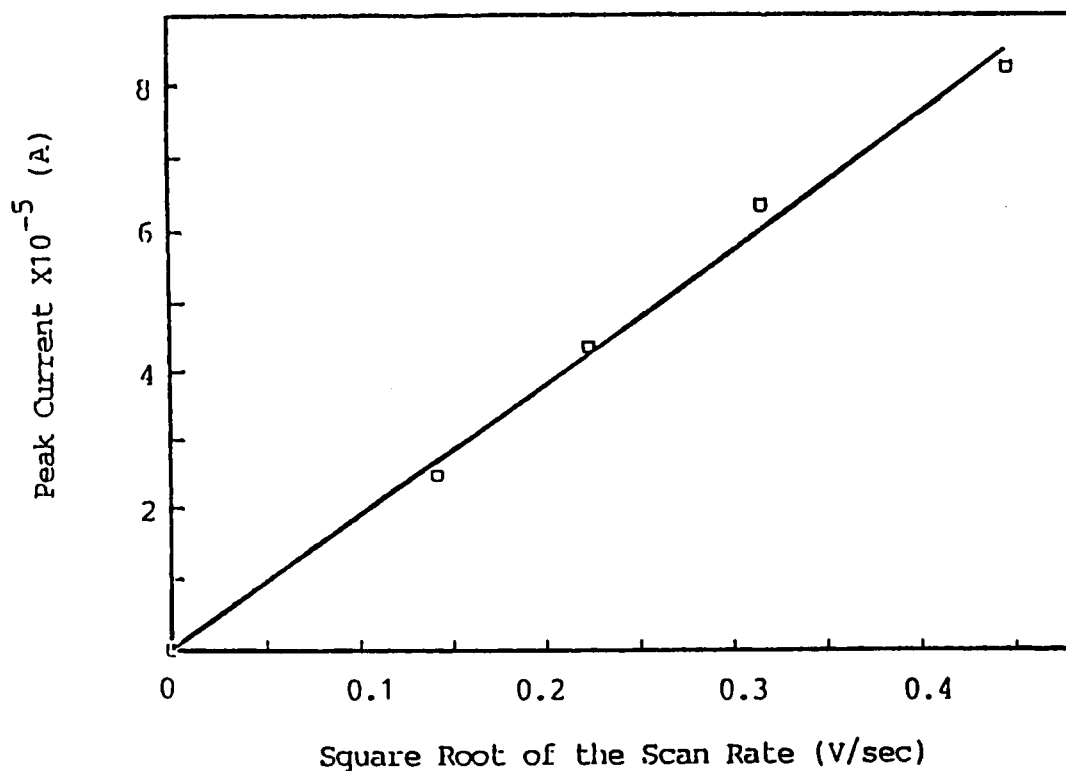


Figure 22. A plot of the peak current vs the square root of the scan rate for the first wave of $[\text{Re}_2\text{Cl}_8]^{2-}$ at a glassy carbon electrode at 175°C .

Electrode area: 0.071 cm^2 ; $[\text{Re}_2\text{Cl}_8]^{2-}$
concentration: $1.09 \times 10^{-3} \text{ M}$.

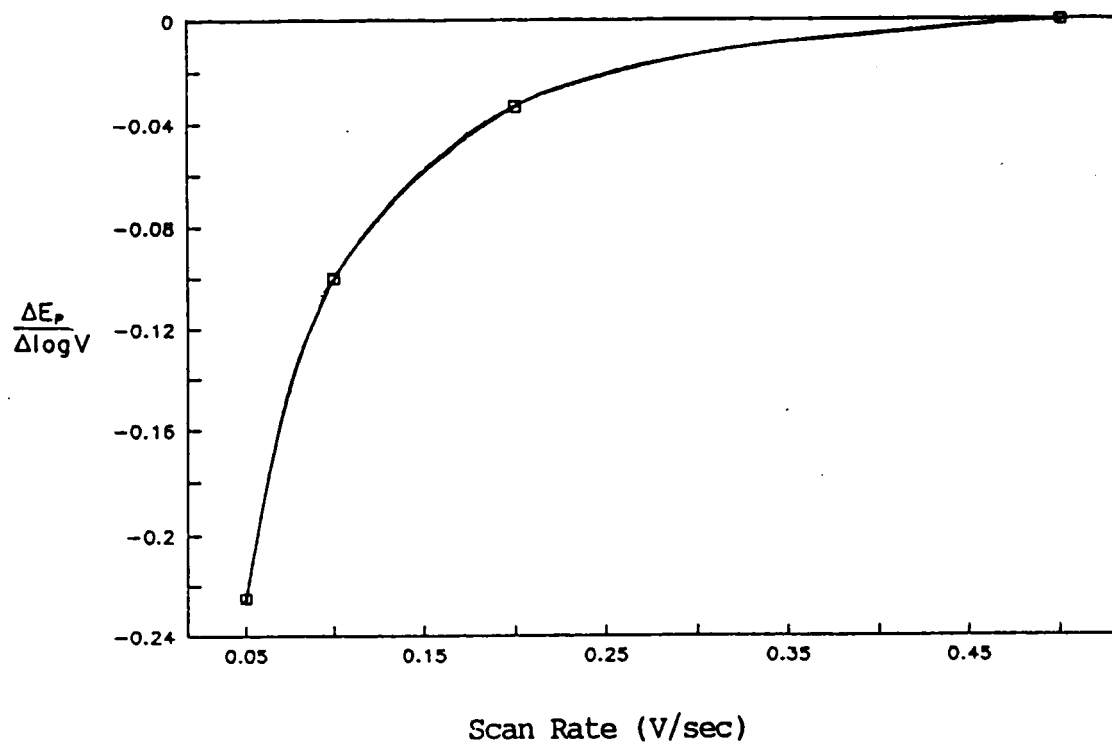


Figure 23. A plot of the rate of the peak potential shift vs scan rate for the first reduction step.

becomes large, the cyclic voltammogram has the same form as that seen for the irreversible case; an increase in the kinetic parameter k_f/a causes an anodic shift in the wave (48). CVs show that there is no oxidation wave associated with the first reduction wave. This is the case at large values of k_f/a .

The value of $E_p - E_{p/2}$ for this wave was 80 mV (see Table 6) (p. 61) at low scan rates, which is close to the theoretical value (72 mV) for a simple reversible one-electron charge transfer followed by an irreversible chemical reaction process at this temperature. $E_p - E_{p/2}$ can be calculated by the equation (73):

$$E_p - E_{p/2} = -(48/n)(T/298). \quad (21)$$

It can be seen from Table 6 (p. 61) that the half wave potential of the second wave is 0.43 V; the cathodic to anodic peak separation of this wave increases with increasing scan rate. Because the first peak is not well-defined, it is difficult to measure the peak current of the second peak.

Normal pulse voltammetric studies were conducted at 175°C with a solution containing 8.5×10^{-4} M of $[\text{Re}_2\text{Cl}_8]^{2-}$ using a glassy carbon disk working electrode. The normal pulse voltammogram is shown in Figure 24. It can be seen from this figure that there are two reduction waves. The half wave potential of the first wave is 0.92 V; it was measured from a plot of the potential vs $\ln[(i_d - i)/i]$, shown in Figure 25. Figure 25 shows a straight line with a slope of 0.05, from

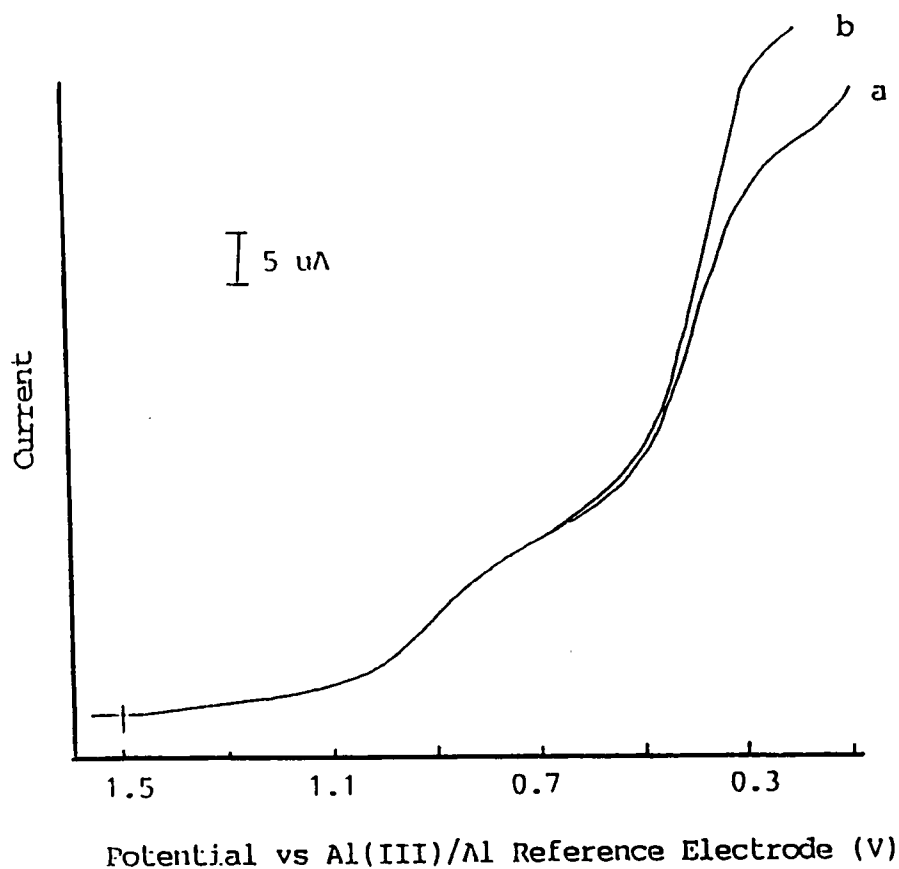


Figure 24. The normal pulse voltammogram of $[\text{Re}_2\text{Cl}_8]^{2-}$ at a glassy carbon electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C . Electrode area: 0.071 cm^2 ; scan rate: 2 mV/sec ; drop time: 5 sec ; pulse width: 57 msec ; $[\text{Re}_2\text{Cl}_8]^{2-}$ concentration: $8.5 \times 10^{-4}\text{ M}$; (a) the first run, (b) the second run.

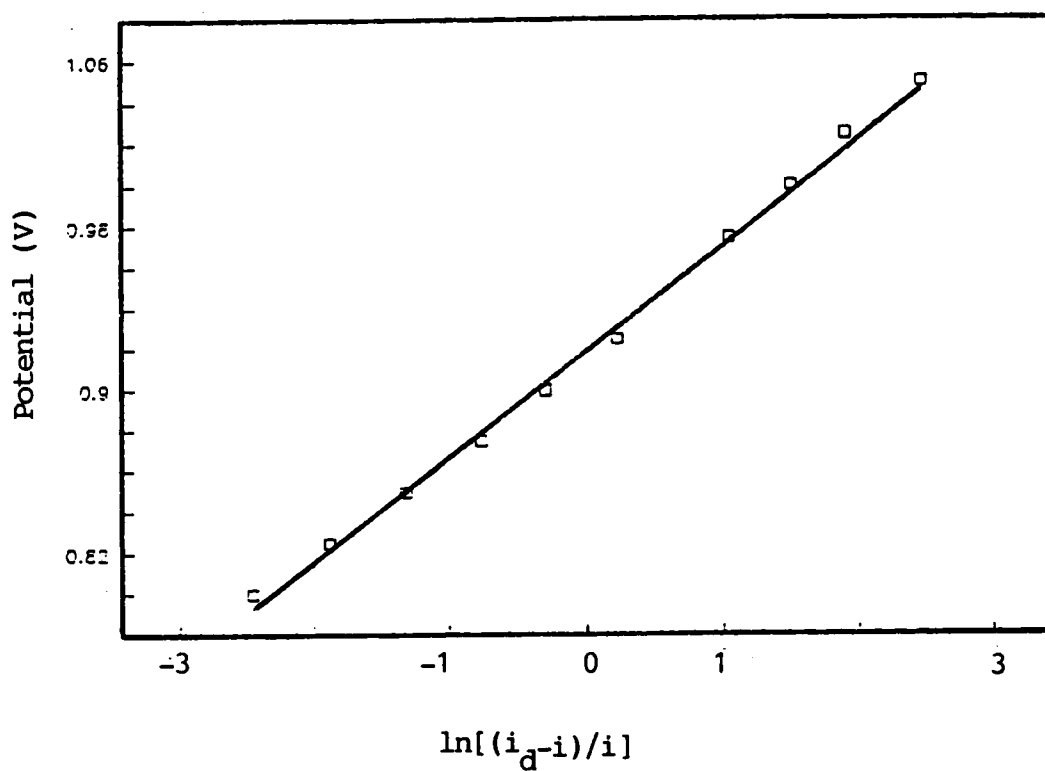


Figure 25. A plot of the potential vs. $\ln[(i_d - i)/i]$ of $[\text{Re}_2\text{Cl}_8]^{2-}$ for the first reduction wave.

which the number of electrons for this process was calculated to be 0.8. This result suggests that the first wave is due to a one-electron transfer process. The non-integral n value indicates that this electron transfer process is either irreversible, or that it is coupled with chemical reactions. Normal pulse voltammetry was also used to examine the second reduction wave of the $[\text{Re}_2\text{Cl}_8]^{2-}$ species. However, reliable results were not obtained, since the limiting current of the second wave increased on successive scans (see Figure 24b) (p. 65).

Controlled potential electrolysis at a glassy carbon cup electrode was carried out at a potential of 0.75 V in order to obtain the product of the first reduction process. An Al wire electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt which was separated from the bulk solution by a fine frit was employed as the reference electrode. Following electrolysis of 24 hours, the solution had turned yellow and some black particles were observed. An absorption spectrum of the resulting solution is shown in Figure 26. This spectrum does not match the spectrum of $[\text{Re}_2\text{Cl}_8]^{3-}$ or any other spectrum in the literature known for Re(IV) or Re(III) compounds. Figure 27 shows the cyclic voltammogram at a scan rate of 100 mV/sec taken after the electrolysis. It is apparent that the first reduction wave at 0.80 V has disappeared. Also, it is noted that the peak potential for the second reduction has shifted from about 0.36 V to 0.16 V.

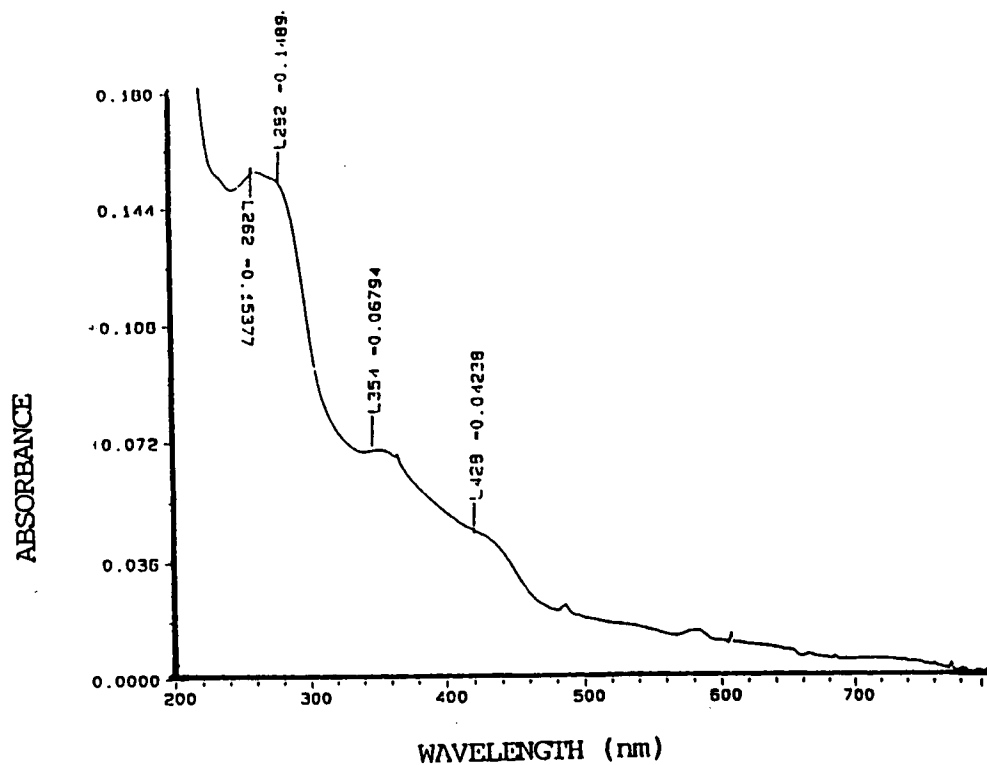
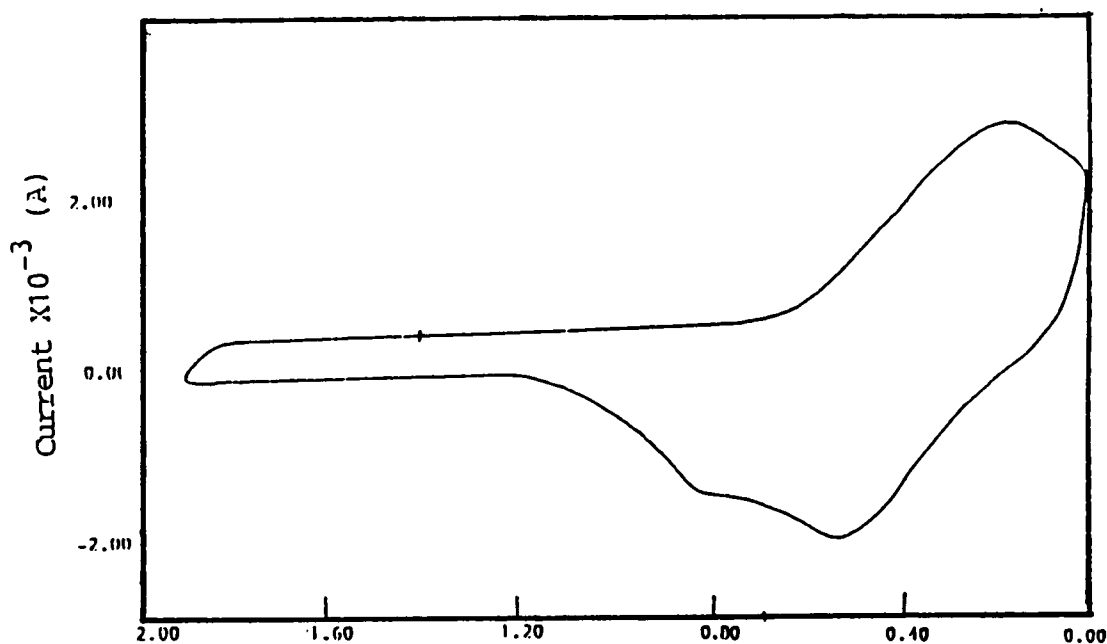


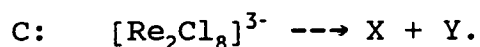
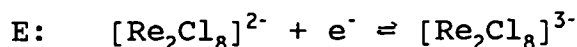
Figure 26. Absorption spectrum of $[\text{Re}_2\text{Cl}_8]^{2-}$ after reduction at 0.75 V in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C .
Path length: 0.10 cm; $[\text{Re}_2\text{Cl}_8]^{2-}$ concentration: 1.09×10^{-3} M.



Potential vs Al(III)/Al Reference Electrode (V)

Figure 27. Cyclic voltammogram of $[\text{Re}_2\text{Cl}_8]^{2-}$ after reduction at 0.75 V at a glassy carbon electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C. Electrode area: 0.071 cm²; $[\text{Re}_2\text{Cl}_8]^{2-}$ concentration: 1.09×10^{-3} M; scan rate 100 mV/sec.

The CVs indicate that the electron transfer process for the first reduction wave is a reversible charge transfer followed by a rapid irreversible chemical reaction, while normal pulse voltammetry indicates that the first reduction wave is due to a one electron transfer process. The following EC mechanism is proposed for the first reduction process:

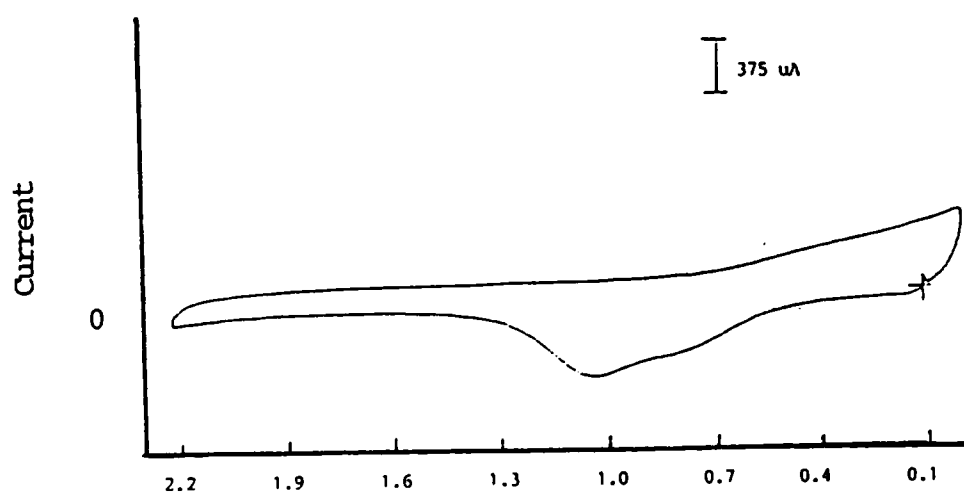


The fact that $[\text{Re}_2\text{Cl}_8]^{3-}$ decomposes to an unknown compound in acetonitrile and dichloromethane has been reported by Cotton and Pedersen (40).

In a separate experiment, controlled potential electrolysis (24 hours) was conducted at a potential of 0.15 V in order to generate the product of the second reduction process. After 24 hours of electrolysis, the solution became light brown, and some black particles were observed. Figure 28 shows the cyclic voltammogram obtained after the electrolysis at the scan rate of 500 mV/sec. In this figure an oxidation peak at 1.05 V was observed. An absorption spectrum for the product of the second peak is given in Figure 29. Unfortunately, this product could not be identified.

b. Electrochemical and Spectroscopic Studies of K_2ReCl_6 in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ Melt

The dissolution of K_2ReCl_6 in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt at



Potential vs Al(III)/Al Reference Electrode (V)

Figure 28. Cyclic voltammogram of $[\text{Re}_2\text{Cl}_8]^{2-}$ after reduction at 0.15 V at a glassy carbon electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ at 175°C .
 Electrode area: 0.071 cm^2 ; $[\text{Re}_2\text{Cl}_8]^{2-}$ concentration: $1.09 \times 10^{-3} \text{ M}$;
 scan rate: 500 mV/sec.

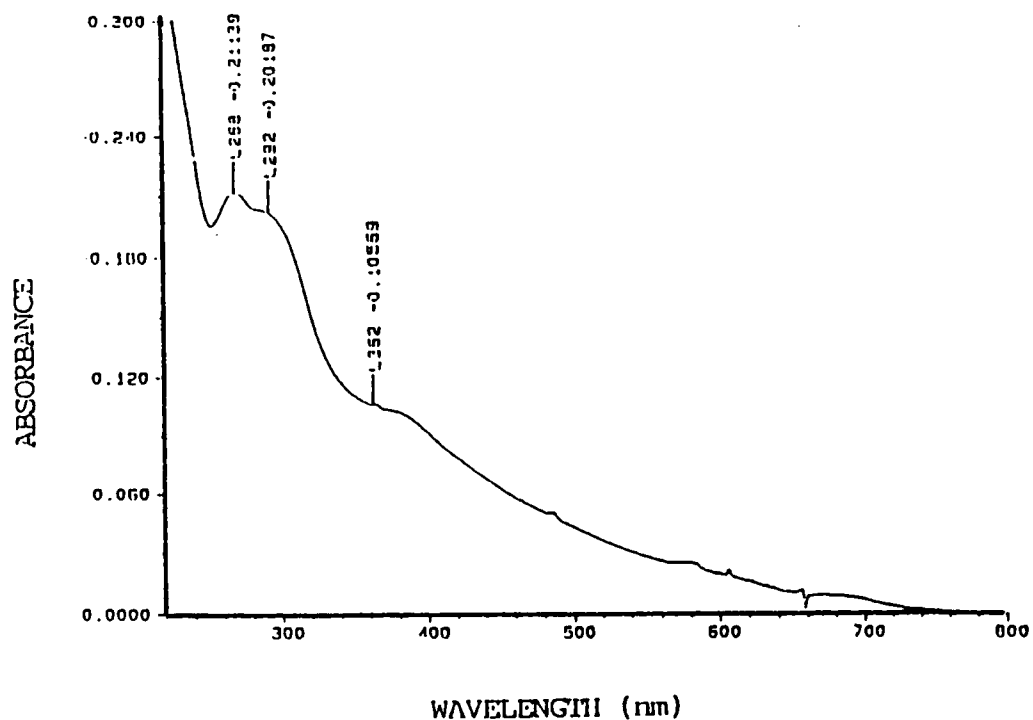


Figure 29. Absorption spectrum of $[\text{Re}_2\text{Cl}_8]^{2-}$ after reduction at 0.15 V in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C .
 Path length: 0.10 cm, $[\text{Re}_2\text{Cl}_8]^{2-}$
 concentration: 1.09×10^{-3} M.

175°C results in a clear green-yellow solution. An absorption spectrum of this solution is shown in Figure 30. The wavelengths and molar absorptivities of the bands in this spectrum are summarized in Table 5 (p. 58). Literature data for solutions of this compound dissolved in the basic AlCl_3 -MEIC melt are also given in this table. The spectroscopic data originating from Figure 30 are in reasonable agreement with the literature data, indicating that $[\text{ReCl}_6]^{2-}$ is stable in AlCl_3 - NaCl_{sat} melt at this temperature.

The cyclic voltammograms for a solution of 2.5×10^{-3} M $[\text{ReCl}_6]^{2-}$ at 175°C were obtained using a glassy carbon electrode at various scan rates from 20 mV/sec to 6 V/sec. Figure 31 shows voltammograms for this solution at scan rates of 50, 100, and 500 mV/sec. These voltammograms exhibit two reduction waves at about 0.83 V and 0.39 V at a scan rate of 100 mV/sec, along with one oxidation wave at about 0.54 V. It is noted that these cyclic voltammograms are similar to those of $[\text{Re}_2\text{Cl}_8]^{2-}$ (see Figure 21) (p. 60) except that the first reduction wave is better defined. Some electrochemical parameters for both waves are summarized in Table 7. Plots of the peak currents for both the first peak and the second peak vs the square root of the scan rate are linear (see Figures 32 and 33). The peak current of the second reduction wave was measured by establishing the baseline, in which each point obeys the Cottrell equation. Of interest is that $(i_{\text{pc}})_1/C$ for the $[\text{ReCl}_6]^{2-}$ species was 1.8 times as large as $(i_{\text{pc}})_1/C$ for the

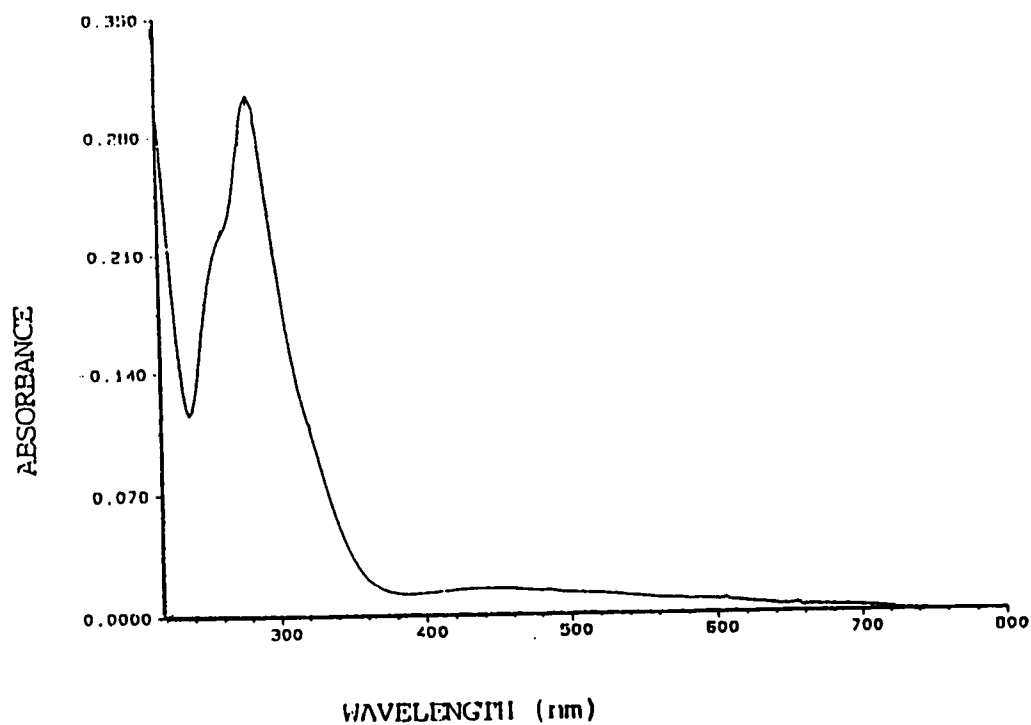


Figure 30. Absorption spectrum of $[\text{ReCl}_6]^{2-}$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C . $[\text{ReCl}_6]^{2-}$ concentration: $5.1 \times 10^{-4} \text{ M}$; path length: 0.10 cm.

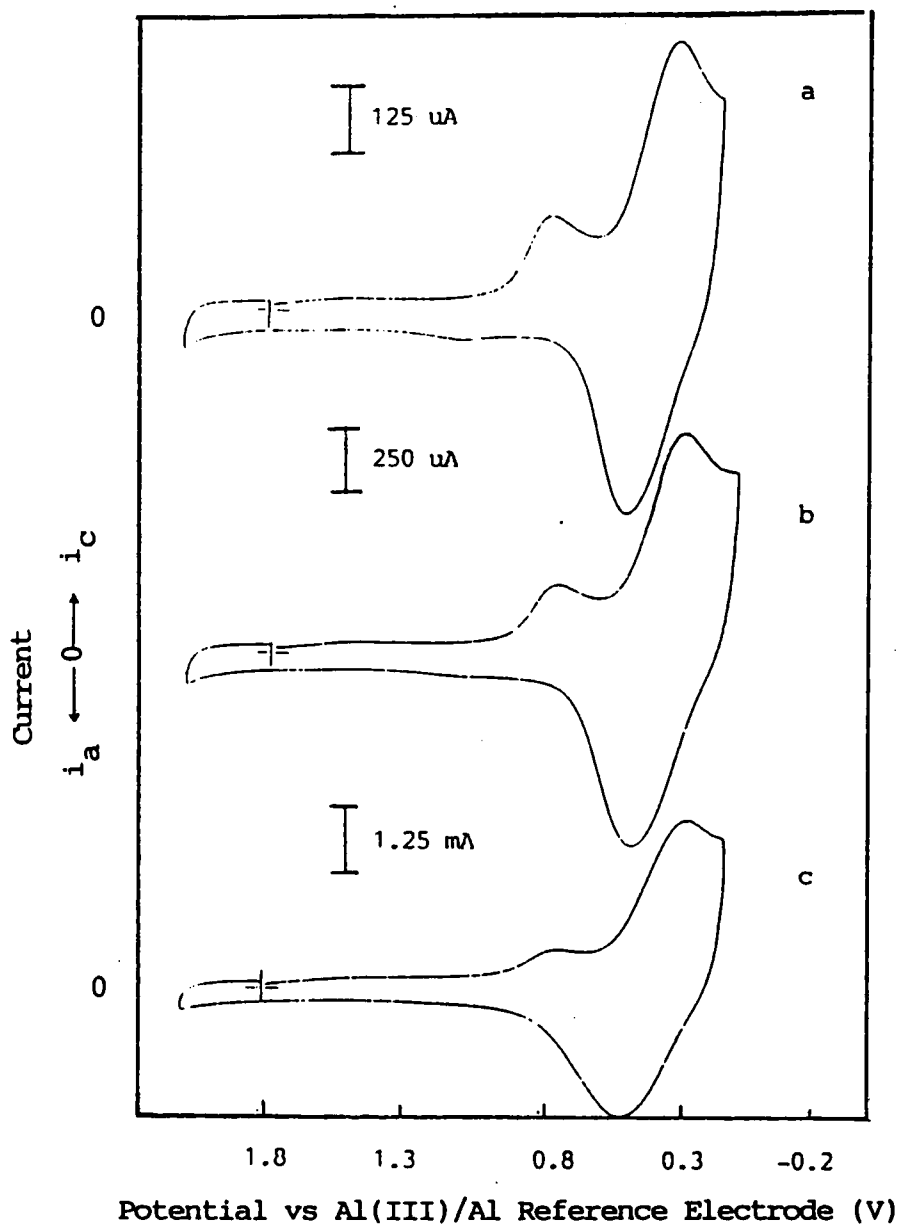


Figure 31. Cyclic voltammograms of $[\text{ReCl}_6]^{2-}$ at a glassy carbon electrode at three different scan rates in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C . Electrode area: 0.071 cm^2 ; $[\text{ReCl}_6]^{2-}$ concentration: $2.5 \times 10^{-3} \text{ M}$; scan rate: (a) 0.05 V/sec , (b) 0.1 V/sec , (c) 0.5 V/sec .

Table 7: Electrochemical parameters for $[\text{ReCl}_6]^{2-}$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C

scan rate (V/sec)	$(E_{\text{pc}})_1$		$(E_{\text{pc}/2})_1$		$(E_{\text{pc}/2} - E_{\text{pc}})_1 (i_{\text{pc}}/C)_1$		$(E_{\text{pc}})_2$		$(E_{1/2})_2$		$(i_{\text{pc}})_2$	
	(V)	(V)	(V)	(V)	(V)	(A/M)	(V)	(V)	(V)	(V)	(A)	(A)
0.02	0.86	0.97	0.09	0.09	0.041	0.043	0.55	0.49			1.6×10^{-4}	
0.05	0.84	0.93	0.09	0.09	0.064	0.41	0.54	0.48			3.7×10^{-4}	
0.10	0.83	0.93	0.10	0.10	0.096	0.39	0.54	0.47			6.4×10^{-4}	
0.20	0.81	0.91	0.10	0.10	0.130	0.37	0.55	0.46			1.1×10^{-3}	
0.50	0.80	0.89	0.09	0.09	0.160	0.34	0.56	0.45			2.2×10^{-3}	

$(E_{\text{p}/2})_2 = (E_{\text{pc}} + E_{\text{pa}})/2$.
 1 is for the first reduction wave, 2 is for the second wave.
 $[\text{ReCl}_6]^{2-}$ concentration: 2.5×10^{-3} M.

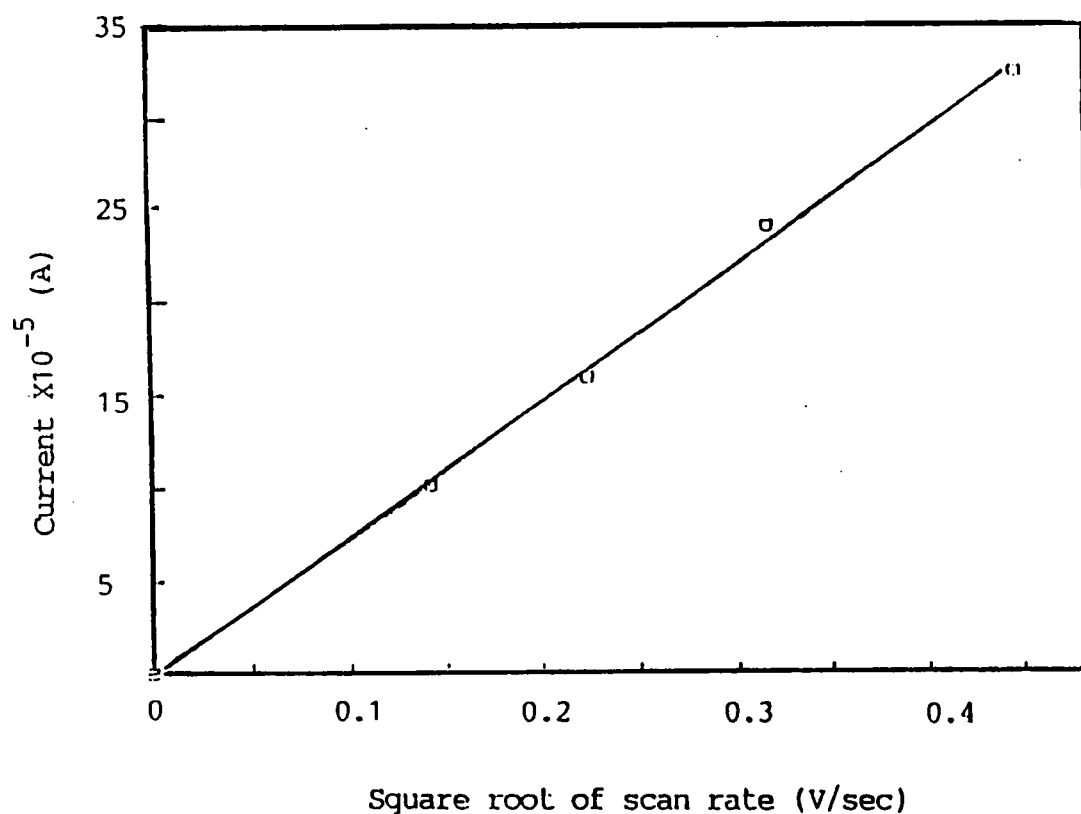


Figure 32. A plot of the peak current vs the square root of scan rate for the first wave of $[\text{ReCl}_6]^{2-}$ at a glassy carbon electrode at 175°C. Electrode area: 0.071 cm²; $[\text{ReCl}_6]^{2-}$ concentration: 2.5×10^{-3} M.

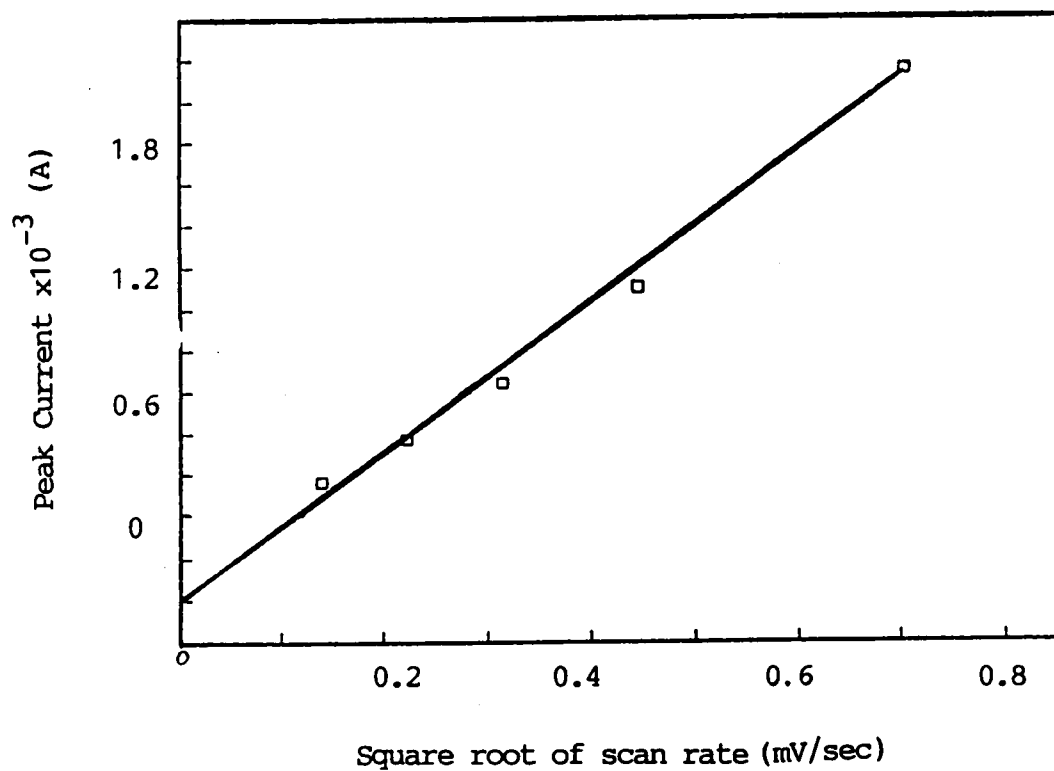


Figure 33. A plot of the peak current vs the square root of scan rate for the second wave of $[\text{ReCl}_6]^{2-}$ at a glassy carbon disk electrode at 175°C .

Electrode area: 0.071 cm^2 ; $[\text{ReCl}_6]^{2-}$ concentration: $2.5 \times 10^{-3} \text{ M}$.

$[\text{Re}_2\text{Cl}_8]^{2-}$ species (see Tables 6 and 7) (p. 62 and 77). The Stokes-Einstein products ($D\eta/T$) for two species in the basic AlCl_3 -MEIC melt are very similar. They are 2.1×10^{-10} , and $2.0 \times 10^{-10} \text{ g cm s}^{-2} \text{ K}^{-1}$ for $[\text{ReCl}_6]^{2-}$ and $[\text{Re}_2\text{Cl}_8]^{2-}$ species (37,42), respectively. Furthermore, the experimental conditions for the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]$ species were similar. The differences in these $(i_{pc})_1/C$ values may be due to the fact that more than one electron is involved in the case of $[\text{ReCl}_6]^{2-}$.

There is no oxidation wave associated with the first reduction wave, even when the potential sweep was reversed immediately after the peak using larger scan rates. This indicates that the first reduction process may be either irreversible or coupled with chemical processes (73).

Cyclic voltammograms for the $[\text{ReCl}_6]^{2-}$ species were also obtained for several concentrations of $[\text{ReCl}_6]^{2-}$ at four different scan rates ranging from 20 mV/sec to 500 mV/sec. Results of these experiments are summarized in Table 8. It can be noted that the voltammetric peak potential shifts in the positive direction with increasing Re(IV) concentration, while the peak current increases with increasing solute concentration. The anodic shift of the peak potential with increasing solute concentration may be caused either by a mechanism involving reversible charge transfer followed by a reversible or an irreversible dimerization, or by a disproportionation reaction following a reversible charge

Table 8: Electrochemical parameters for the first reduction wave of $[\text{ReCl}_6]^{2-}$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 180°C

Conc.	E(50)	E(100)	E(200)	E(500)	i(50)	i(100)	i(200)	i(500)
(mM)	(V)	(V)	(V)	(V)	(uA)	(uA)	(uA)	(uA)
5.8	0.770	0.760	0.745	0.710	115	160	230	270
8.1	0.850	0.820	0.785	0.750	210	285	390	425
11.9	0.860	0.840	0.805	0.760	285	400	600	1050
16.6	0.890	0.860	0.835	0.800	520	575	1015	2250
20.5	0.905	0.860	0.830	0.770	575	750	1275	2300
25.0	0.910	0.860	0.835	0.770	900	1250	2200	4250

$i(X)$ is the peak current at the scan rate of X .

$E(X)$ is the peak potential at the scan rate of X .

Conc. is the concentration of $[\text{ReCl}_6]^{2-}$ in the solution.

transfer (73-80). Plots of the peak potential vs $\ln C$ are shown in Figure 34. The reasons for the differences in the slopes of these plots are not obvious. A plot of the peak current vs concentration for the first reduction wave at a scan rate of 100 mV/sec is linear, and is shown in Figure 35. Because of this result, the possibility of a disproportionation reaction following a reversible charge transfer can be eliminated (73). A plot of the peak current of the second reduction wave vs concentration at scan rate of 100 mV/sec is also linear (see Figure 36).

Normal pulse voltammetric studies were conducted at 175°C with a solution containing 1.06×10^{-3} M $[\text{ReCl}_6]^{2-}$ using a glassy carbon disk working electrode. The normal pulse voltammogram is shown in Figure 37. It can be seen from this figure that there are two reduction waves. The half wave potentials of the first and the second reduction waves are 0.76 V and 0.39 V, respectively. A plot of the potential vs $\ln[(i_d - i)/i]$ for the first reduction wave is shown in Figure 38. This figure shows a straight line with a slope of 0.03, from which the number of electrons for this process was calculated to be 1.3. This value is 1.6 times larger than that obtained from normal pulse voltammetric results for the $[\text{Re}_2\text{Cl}_8]^{2-}$ species (p. 65). A plot of the potential vs $\ln[(i_d - i)/i]$ for the second reduction wave is also linear, as shown in Figure 39. This figure gives a slope of 0.045, from which the number of electrons transferred for the second wave was calculated to be

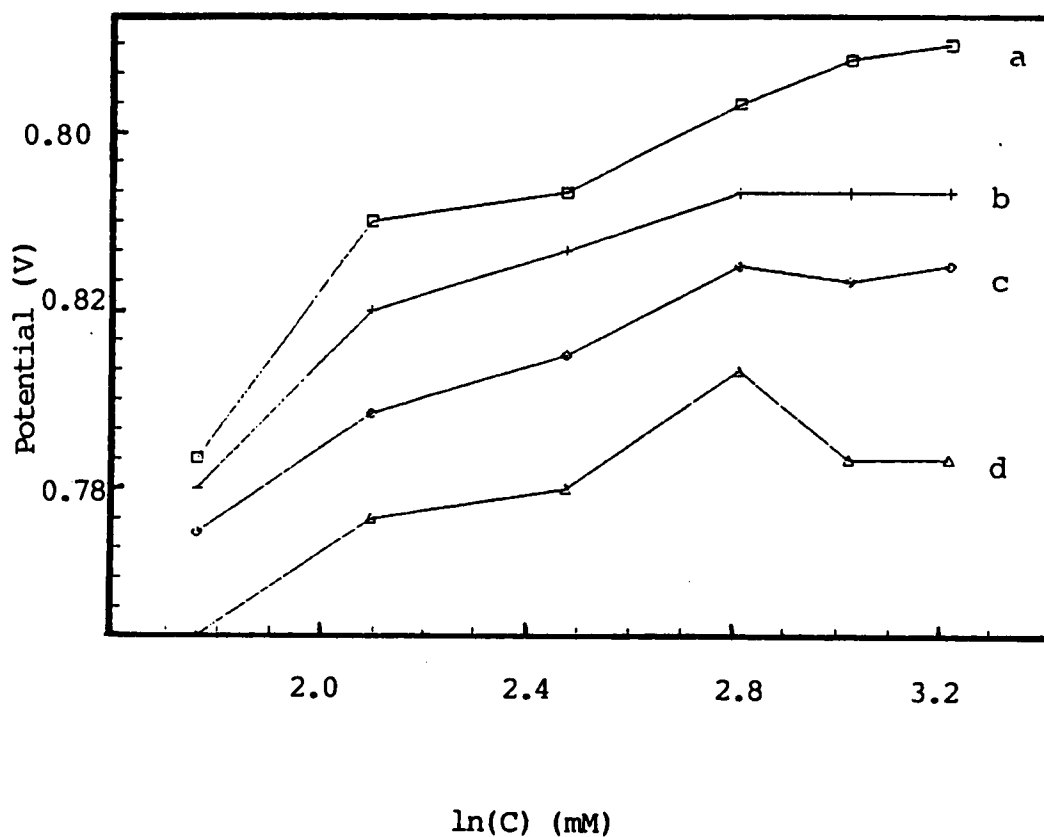


Figure 34. Plots of the peak potential vs $\ln C$ for the first reduction wave of $[\text{ReCl}_6]^{2-}$ in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 180°C . Electrode area: 0.071 cm^2 ; a: scan rate 50 mV/sec; b: scan rate 100 mV/sec; c: scan rate 200 mV/sec; d: scan rate 500 mV/sec.

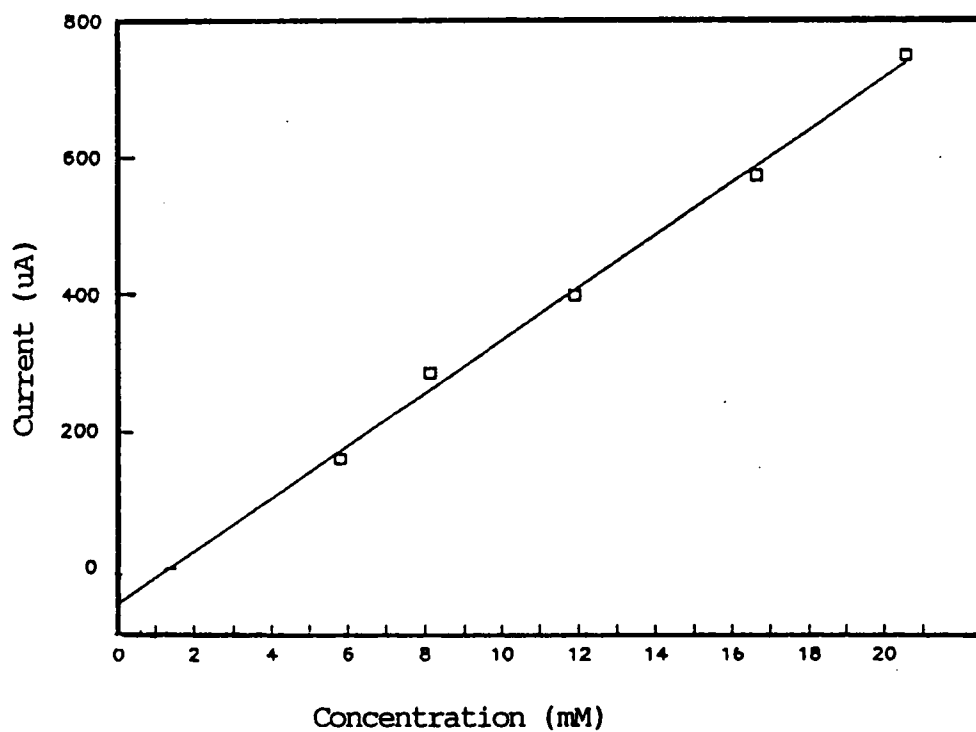


Figure 35. A plot of the peak current of the first reduction wave vs $[\text{ReCl}_6]^{2-}$ concentration in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 180°C at scan rate of 100 mV/sec . Electrode area: 0.071 cm^2 .

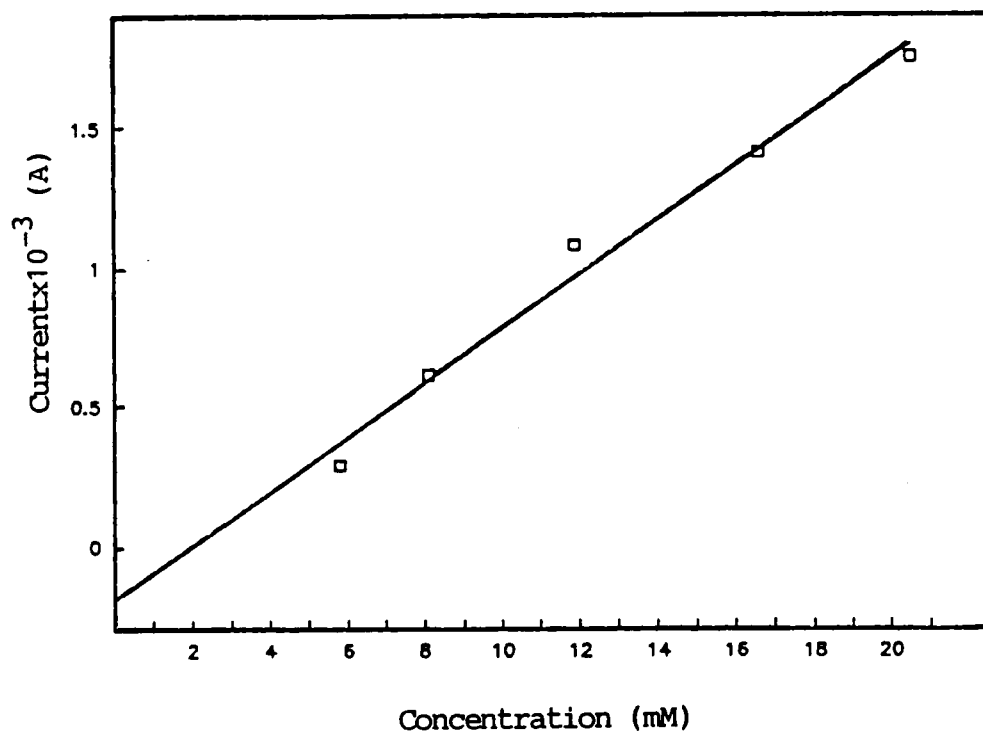


Figure 36. A plot of the peak current of the second peak vs $[\text{ReCl}_6]^{2-}$ concentration in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 180°C .
Electrode area: 0.071 cm^2 .

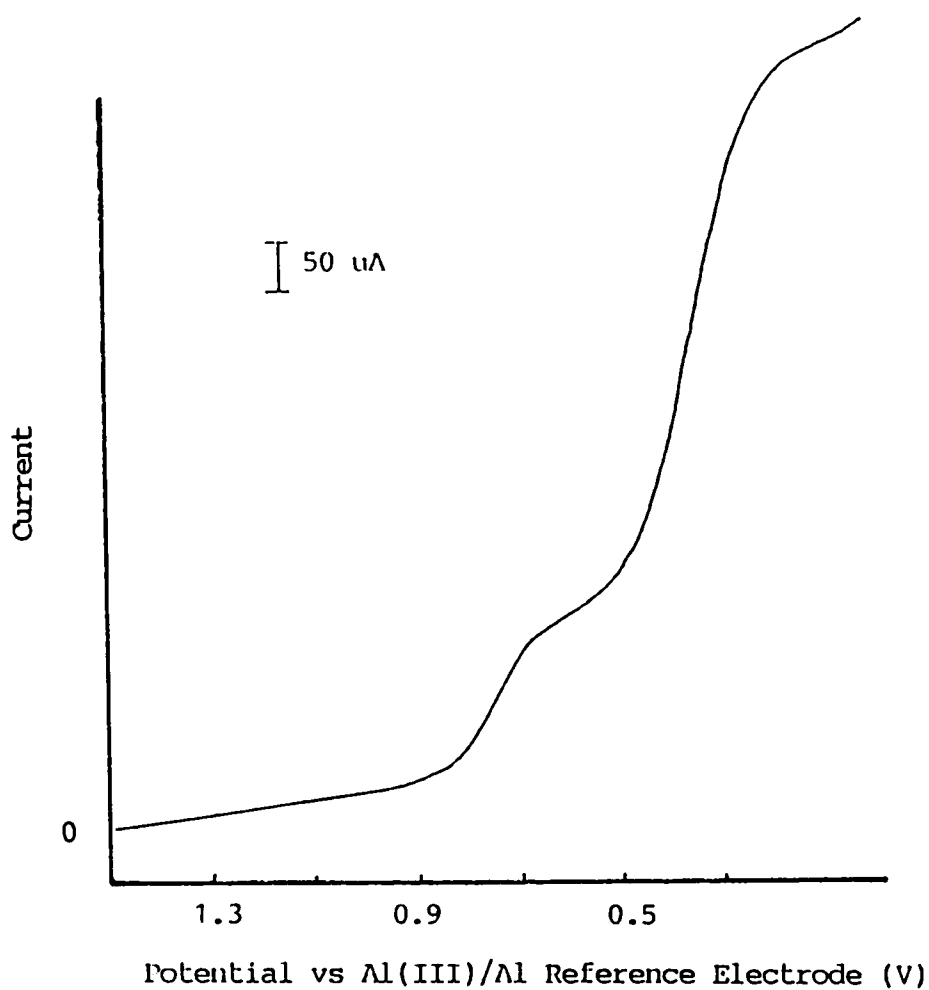


Figure 37. The normal pulse voltammogram of $[\text{ReCl}_6]^{2-}$ at a glassy carbon electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C . Electrode area: 0.071 cm^2 ; scan rate 2 mV/sec ; drop time: 5 sec ; pulse width: 95 msec ; $[\text{ReCl}_6]^{2-}$ concentration: $7.7 \times 10^{-3} \text{ M}$.

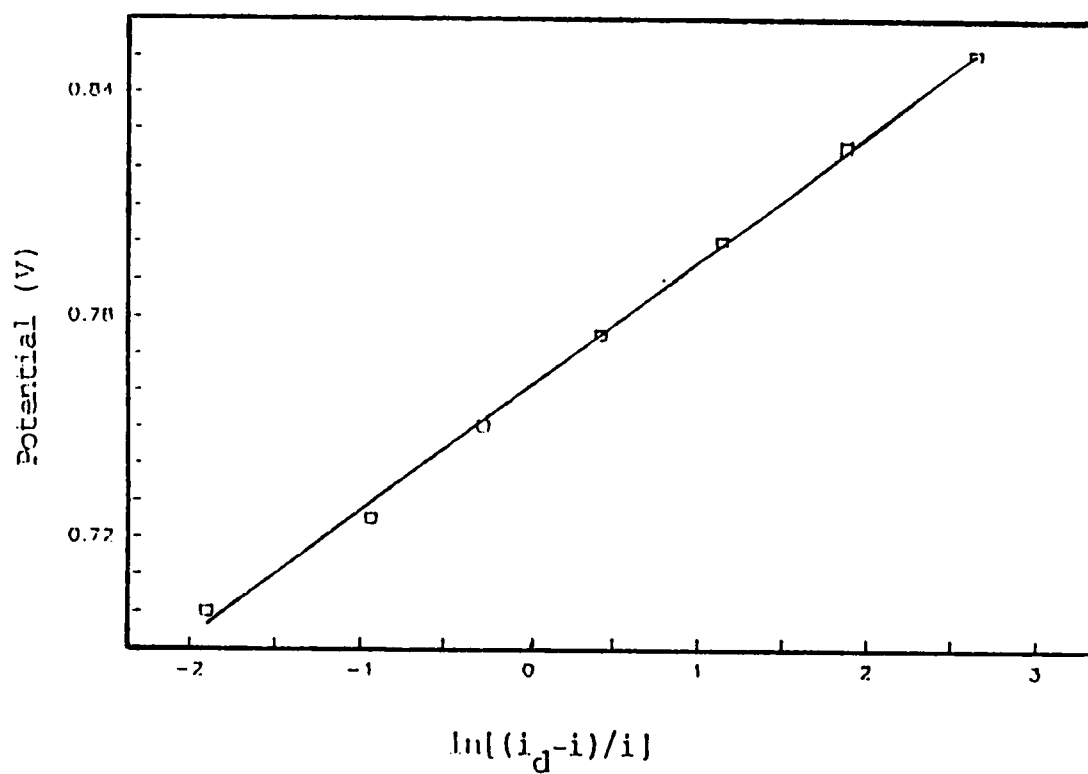


Figure 38. A plot of the potential vs $\ln[(i_d - i)/i]$ for the first reduction wave of $[\text{ReCl}_6]^{2-}$.

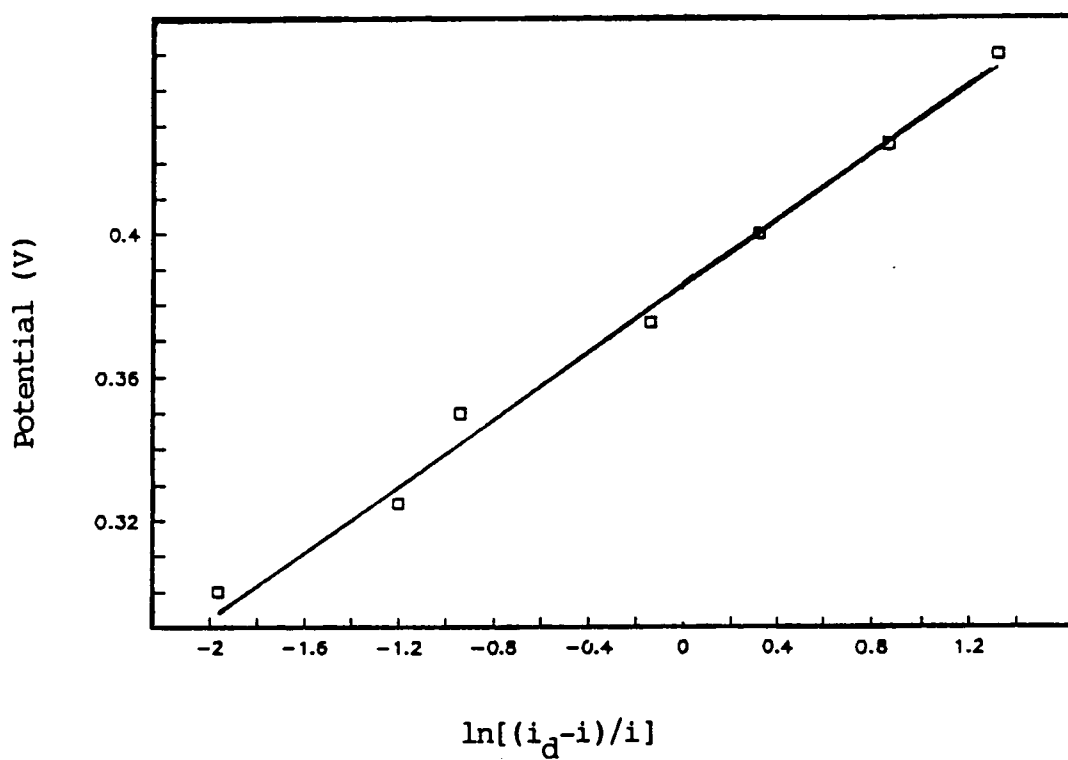
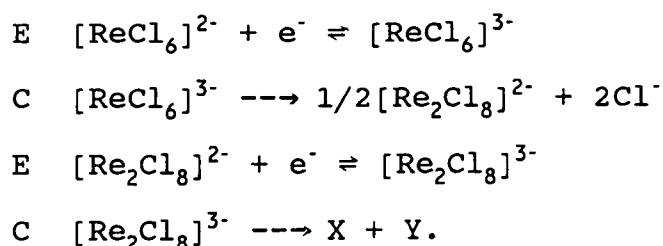


Figure 39. A plot of the potential vs $\ln[(i_d - i)/i]$ for the second reduction wave of $[\text{ReCl}_6]^{2-}$.

0.86, while the current of the second reduction wave is about four times as large as that of the first reduction wave.

The controlled potential electrolysis was carried out at 0.65 V at a $[\text{ReCl}_6]^{2-}$ concentration of 7.7×10^{-3} M. After 24 hours of electrolysis, the solution was yellow or yellow-green in color, and some black particles were observed. An absorption spectrum for this solution after the reduction is given in Figure 40. This spectrum matches neither that of $[\text{Re}_2\text{Cl}_8]^{2-}$ nor of any other spectrum in the literature known of or Re(IV) and Re(III) compounds. However, this spectrum is in fair agreement with the spectrum seen in Figure 26 (p. 68), indicating that the products of the first reduction for solutions of $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ may be the same. Following electrolysis, the solution was examined by cyclic voltammetry; a typical cyclic voltammogram is shown in Figure 41. This figure is similar to Figure 27 (p. 69). This supports the contention that the first reduction wave products for both $[\text{ReCl}_6]^{2-}$ and $[\text{Re}_2\text{Cl}_8]^{2-}$ may be the same.

Based on the above observations, the following mechanism for the first reduction peak of $[\text{ReCl}_6]^{2-}$ dissolved in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt is proposed:



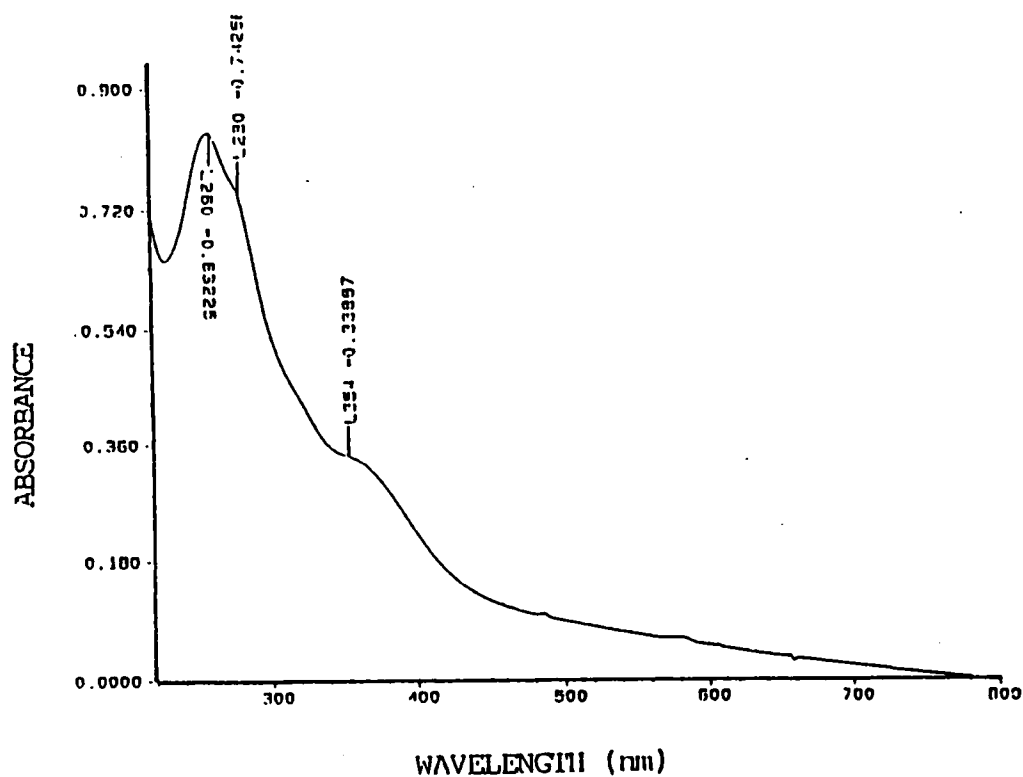
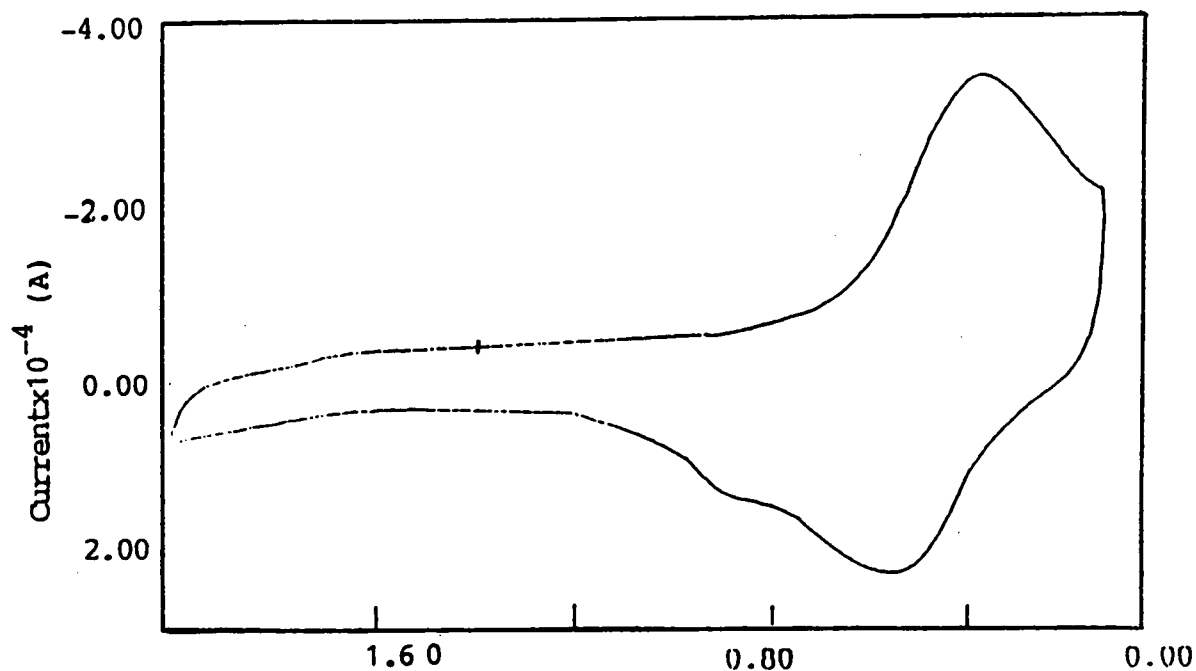


Figure 40. Absorption spectrum of $[\text{ReCl}_6]^{2-}$ after reduction at 0.65 V in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C .
 $[\text{ReCl}_6]^{2-}$ concentration: $7.7 \times 10^{-3} \text{ M}$; path length: 0.10 cm.



Potential vs Al(III)/Al Reference Electrode (V)

Figure 41. Cyclic voltammogram of $[\text{ReCl}_6]^{2-}$ after reduction at 0.65 V at a glassy carbon electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt at 175°C. Electrode area: 0.071 cm^2 ; $[\text{ReCl}_6]^{2-}$ concentration: 7.7×10^{-3} M; scan rate: 100 mV/sec.

In this scheme, $[\text{ReCl}_6]^{2-}$ is first reduced to $[\text{ReCl}_6]^{3-}$ through a one-electron process. $[\text{ReCl}_6]^{3-}$ is unstable in the solution and dimerizes to give $[\text{Re}_2\text{Cl}_8]^{2-}$, which has a reduction potential more positive than that of $[\text{ReCl}_6]^{2-}$, and therefore is immediately reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$ followed by a chemical process to give species X and Y. Because a total of 1.5e is needed to convert $[\text{ReCl}_6]^{2-}$ to $1/2[\text{Re}_2\text{Cl}_8]^{3-}$, the peak current for the reduction of $[\text{ReCl}_6]^{2-}$ would be expected to be higher than that for the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$ to $[\text{Re}_2\text{Cl}_8]^{3-}$ process. Also, this reduction scheme results in the same final product that was observed for the reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$.

In addition, Re_3Cl_9 was selected as a system to study. When Re_3Cl_9 was added to a $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt at 175°C , it slowly dissolved and gave a yellow-green solution and a black precipitate. A spectrum of this yellow-green solution, after the precipitate was separated from the solution, showed identical features to the spectrum obtained for $[\text{ReCl}_6]^{2-}$. Cyclic voltammograms for this solution were also identical to those obtained for $[\text{ReCl}_6]^{2-}$. These results indicate that Re_3Cl_9 is unstable in this melt and decomposes to $[\text{ReCl}_6]^{2-}$ and some other rhenium species. Thus, the behavior of Re_3Cl_9 in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt is very different from that obtained in basic room temperature melts. In a basic room temperature melt, Re_3Cl_9 dissolves to form $[\text{Re}_3\text{Cl}_{12}]^{3-}$, which is then converted to $[\text{Re}_2\text{Cl}_8]^{2-}$ when the temperature is higher than 175°C (37). However, the behavior of Re_3Cl_9 in the $\text{AlCl}_3\text{-}$

NaCl_{sat} melt is somewhat similar to that observed in a LiCl-KCl melt, in which Re_3Cl_9 decomposed to give $[\text{ReCl}_6]^{2-}$ and rhenium metal (38).

c. Comparison of the Electrochemical Behavior of $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ at a Glassy Carbon Electrode in the Basic $\text{AlCl}_3\text{-EMIC}$ and the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ Melts

The above results show that the electrochemical behavior of the $[\text{Re}_2\text{Cl}_8]^{2-}$, Re_3Cl_9 , and $[\text{ReCl}_6]^{2-}$ species in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt at 175°C is different from that observed for these compounds in basic $\text{AlCl}_3\text{-MEIC}$ melt at 40°C and the LiCl-KCl eutectic melt at $450\text{-}550^\circ\text{C}$. The complex $[\text{Re}_2\text{Cl}_8]^{2-}$ is stable in the basic $\text{AlCl}_3\text{-MEIC}$. It can be reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$ at a glassy carbon electrode in a reversible one-electron transfer reaction; the half-wave potential in the 49.0/51.0 mol % melt vs the Al(III)/Al couple in the 66.7/33.3 mol % melt at 40°C is -0.58 V . Even though $[\text{Re}_2\text{Cl}_8]^{2-}$ is also stable in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt at 175°C , and can be reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$ at a glassy carbon electrode, the $[\text{Re}_2\text{Cl}_8]^{3-}$ species is not stable in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt at 175°C . When Re_3Cl_9 was added to the basic $\text{AlCl}_3\text{-MEIC}$ melt, it produced $[\text{Re}_3\text{Cl}_{12}]^{3-}$, which could be reduced in a reversible one-electron transfer process to form a species of the type $[\text{Re}_3\text{Cl}_{12-x}]^{(4-x)-}$, in which x may be 1. When the temperature was increased to above 175°C , the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ species was irreversibly converted to $[\text{Re}_2\text{Cl}_8]^{2-}$. $[\text{Re}_3\text{Cl}_9]$ is unstable in the LiCl-KCl eutectic melt at 450-

550°C, and disproportionates to $[\text{ReCl}_6]^{2-}$ and Re metal (38). This behavior is similar to that in the basic AlCl_3 -NaCl melt at 175°C. In the LiCl-KCl eutectic melt at 450-550°C, $[\text{ReCl}_6]^{2-}$ is reduced to rhenium metal via a four-electron transfer process (38). On the other hand, in the AlCl_3 -NaCl_{sat} melt at 175°C, the electrochemical behavior of $[\text{ReCl}_6]^{2-}$ appears to be much more complicated. The monomeric rhenium chloride complex $[\text{ReCl}_6]^{2-}$ is stable in the basic AlCl_3 -MEIC melt and can be reduced to $[\text{ReCl}_6]^{3-}$ in a reversible one electron transfer reaction with a half wave potential of -0.87 V in the 49.0/51.0 mol% melt vs. the Al(III)/Al couple in the 66.6/33.7 mol% melt. $[\text{ReCl}_6]^{2-}$ slowly decomposed to ReCl_5 and ReCl_3 in LiCl-KCl melt at 450-550°C (38); the latter further disproportionated to rhenium metal and $[\text{ReCl}_6]^{2-}$ (38).

The species $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ exhibit an additional multielectron voltammetric reduction process at more negative potentials in the basic AlCl_3 -MEIC and AlCl_3 -NaCl_{sat} melts. However, no definite explanation for the large peak can be given so far.

As summarized above, the behavior of these rhenium compounds in the AlCl_3 -NaCl_{sat} melt appears to be intermediate to that seen in the room temperature melt (AlCl_3 -MEIC) and in the high temperature melt (LiCl-KCl). Whether $[\text{Re}_2\text{Cl}_8]^{2-}$ and Re_3Cl_9 are stable or not depends on the temperature and the molten salt system. The electrochemical behavior for these compounds is different in the different molten salts.

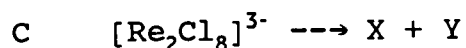
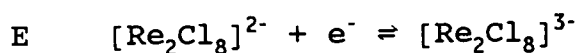
CHAPTER IV

SUMMARY

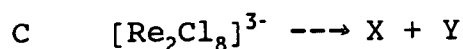
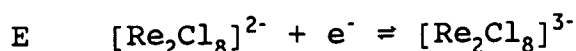
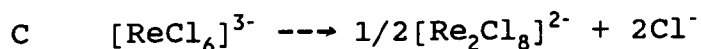
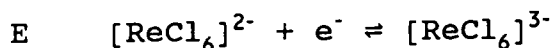
In this research, the utility of ultramicroelectrodes for electrochemical studies in $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melts has been demonstrated by using iron(III) chloride as a probe system. Cyclic voltammetric and normal pulse voltammetric results obtained at a tungsten disk ultramicroelectrode were compared to the results obtained at a conventional tungsten disk electrode. These results are consistent with those reported in the literature (20). In general, the advantages of using microelectrodes over conventional electrodes, such as reduced iR drop and rapidly established steady states of mass transfer, were also observed in this research.

In the second part of this research, the electrochemistry and absorption spectroscopy of the dimeric rhenium (III) chloride complex $[\text{Re}_2\text{Cl}_8]^{2-}$ and the monomeric rhenium complex $[\text{ReCl}_6]^{2-}$ were studied in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. The species $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ are stable in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt. Electrochemical methods included cyclic voltammetry, normal pulse voltammetry, and controlled potential electrolysis. Cyclic voltammograms of $[\text{Re}_2\text{Cl}_8]^{2-}$ are similar to those of $[\text{ReCl}_6]^{2-}$; both exhibit two reduction waves. The peak potentials of the first and second reduction waves of $[\text{Re}_2\text{Cl}_8]^{2-}$ occur at about 0.80 V and 0.36 V, respectively. The

first reduction peak involves an EC mechanism in which $[\text{Re}_2\text{Cl}_8]^{2-}$ is first reduced to $[\text{Re}_2\text{Cl}_8]^{3-}$, which is not stable in this melt and is converted to some unknown species. The mechanism for the first reduction wave is represented as follows:



The peak potentials for $[\text{ReCl}_6]^{2-}$ are about 0.83 V and 0.39 V, respectively. Electrochemical and spectroscopic results suggested that the first reduction of $[\text{ReCl}_6]^{2-}$ involves an ECEC mechanism as follows:



The addition of Re_3Cl_9 to the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt produced the monomeric rhenium(IV) complex $[\text{ReCl}_6]^{2-}$ and some unknown solid species.

The second reduction waves for both $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ were much larger than their respective first reduction waves, indicating that these waves may be due to multielectron voltammetric reduction processes.

The electrochemical behavior of $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{ReCl}_6]^{2-}$ at a glassy carbon electrode in the $\text{AlCl}_3/\text{NaCl}_{\text{sat}}$ melt appears to be intermediate to that seen in the room temperature ($\text{AlCl}_3/\text{MEIC}$) and in the high temperature (LiCl/KCl) melts.

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APPENDIX

APPENDIX 1

```

10 ' This is a short program
20 ' using Newton-Raphson method
30 ' to solve nonlinear equations.
40 '
50 ' Nov. 20,1990
60 '
70 F = 96485: r = 8.314: n = 1
80 a = .00125
   INPUT "file name: "; F$
81 OPEN F$ FOR OUTPUT AS #1
90 INPUT "Im"; im: im = im * 1E-09
100 t = 455: C = .0000139
120 INPUT "scan rate"; v
130 '
140 ' finish the input
150 '
160 C = (im * r * t) / (4 * n * n * F * F * C * a * a * a * v)
170 '
180 DEF FNF (p) = -C * p * p + .34 * EXP(-.66 * p) + .66 - .13
   * EXP(-11 / p) + .35 * p
190 DEF FNDF (p) = -2 * C * p - .34 * .66 * EXP(-.66 * p) -
   .13 * 11 * EXP(-11 / p) / (p * p) + .35
200 '
210 INPUT "initial value p"; p
220 '
230 INPUT "error allowed"; TOL
240 ITMAX = 100
250 '
260 ' iteration loop
270 '
280 POLD = p
290 FP = FNF(p)
300 DFP = FNDF(p)
310 '
320 FOR I = 1 TO ITMAX
330 p = p - FP / DFP
340 FP = FNF(p): DFP = FNDF(p)
350 IF ABS((p - POLD) / p) < TOL GOTO 400
360 POLD = p
370 PRINT I, p, FP, DFP
380 NEXT I
390 PRINT "fail to converge"
400 PRINT "solution="; p
401 d = n * F * a * a * v / (r * t * p * p): PRINT "Diffusion
Coef.="; d
   PRINT #1, d
   GOTO 90
   CLOSE #1
410 END

```

VITA

Chaolan Hu was born on June 17, 1963 in Lanzhou, the People's Republic of China. She graduated from the First High School, Lanzhou, in 1981. In 1982, she entered Lanzhou University in Lanzhou and received the B. S. degree in Chemistry in 1986. She was wed to Dr. XiXiang Xu in 1990.