The electrochemistry and coordination chemistry of cobalt and molybdenum solute species were studied in the room temperature chloroaluminate melt, aluminum chloride-\(N-(n\)-butyl)pyridinium chloride (\(\text{AlCl}_3\)-BPC). Cobalt(II) was readily introduced into acidic and basic \(\text{AlCl}_3\)-BPC melts by dissolution of \(\text{CoCl}_2\). Reduction of Co(II) at a glassy carbon electrode in 2:1 molar ratio melt was accompanied by codeposition of aluminum, but this effect decreased with decreasing acidity of the melt. Evidence was found which indicated that deposition of cobalt metal in 2:1 molar ratio \(\text{AlCl}_3\)-BPC melt is preceded by monolayer formation. The \(\text{CoCl}_4^{2-}\) species was electro-inactive in 0.8:1.0 \(\text{AlCl}_3\)-BPC melt. Potentiometric measurements on the cell \(\text{Co} | \text{Co}^{2+} \text{AlCl}_3\)-BPC | fritted disc : 2:1 molar ratio \(\text{AlCl}_3\)-BPC | Al were used to determine formation constants for the reaction \(\text{Co}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{CoCl}_4^{2-}\) in BPC rich \(\text{AlCl}_3\)-BPC melt as a function of temperature. Molybdenum(V) was conveniently introduced into 2:1 \(\text{AlCl}_3\)-BPC melt by dissolution of \(\text{MoCl}_5\); however, \(\text{MoCl}_5\) and \(\text{MoCl}_4\) appeared to oxidize BPC rich melt. Four reduction waves with peak potentials of 1.91, 1.10, 0.34, and 0.11 V versus Al were observed during reduction of Mo(V) at a glassy carbon electrode in 2:1 \(\text{AlCl}_3\)-BPC melt. The first reduction wave corresponds to the reversible one-electron reduction of Mo(V) to Mo(IV) and appears to be preceded by a chemical step, possibly dissociation of a dimeric Mo(V) species. The potential of the Mo(V)/Mo(IV) electrode reaction was linearly dependent on the melt pCl, and data for this correlation show that this reaction involves a single chloride ion.

INTRODUCTION

Mixtures of aluminum chloride and \(N-(n\)-butyl)pyridinium chloride (\(\text{AlCl}_3\)-BPC) form a molten salt system of adjustable Lewis acidity. One of the most unusual properties of this molten salt system is that it is liquid close to room temperature over the range of compositions from 2:1 to 1:1.33 \(\text{AlCl}_3\)-BPC (1). Recent studies have shown that the distribution of chloroaluminate melt species in the \(\text{AlCl}_3\)-BPC system
is quite different from that of related AlCl₃-NaCl melts (2). This species distribution can in fact be represented by a single equilibrium reaction

\[ 2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \quad K \]  

with a value of \( K \approx 3.8 \times 10^{-13} \) at 30°C (3).

In recent papers we reported the electrochemistry of the Cu(II)/Cu(I) and Cu(I)/Cu (4), and Fe(III)/Fe(II) (5) electrode reactions in AlCl₃-BPC and a closely related room temperature chloroaluminate melt, aluminum chloride-N-methylpyridinium chloride. In order to gain further insight into the electrochemical behavior of transition metal ions in AlCl₃-BPC melts, cobalt(II) and molybdenum(V) solutes were investigated. The electrochemistry and spectroscopy of Co(II) have been examined in inorganic chloroaluminate melts by several workers (6-13). Thus, data that have been obtained for Co(II) in the AlCl₃-BPC molten salt system can be compared to data concerning Co(II) solutes in inorganic chloroaluminates. Molybdenum electrochemistry has also been examined in an inorganic chloroaluminate melt and found to be extremely complex (14). Results are presented in this paper which show that the chemistry and electrochemistry of Mo(V) in AlCl₃-BPC melt vary substantially from that reported in inorganic chloroaluminate melts (14).

EXPERIMENTAL SECTION

The preparation and purification of the AlCl₃-BPC melt are detailed in a previous publication (15). Anhydrous CoCl₂, 99.9%, was obtained from CERAC, Inc. Samples of anhydrous CoCl₂ were also obtained from Alfa Products and used in some experiments. Anhydrous MoCl₅ was purchased from Alfa Products, and anhydrous MoCl₄, 99.5% was acquired from CERAC, Inc.

All experiments were conducted in a dry nitrogen atmosphere inside a Kewaunee Scientific Equipment Corp. drybox equipped with a 3 cfm inert gas purifier for removing moisture and oxygen. Cyclic voltammetry was performed using an AMEL model 551 potentiostat/galvanostat equipped with an AMEL model 566 function generator. Cyclic voltammograms were recorded using a Houston model 100 X-Y recorder. Resistance compensation was applied during cyclic voltammetric measurements. The potentiostat was equipped with an AMEL model 731 digital integrator during coulometric generation of Co(II).

The electrochemical cell and glassy carbon working electrode, geometric area = 0.07 cm², were similar to those used in previous studies (4, 5). A glassy carbon crucible (Tokai) was used as the working electrode during controlled potential electrolysis experiments. A spiral wire cobalt metal working electrode was fashioned from 0.25 mm cobalt wire (Alfa Products, m2N7). The electrode was dipped briefly into concentrated HNO₃ followed by similar treatment with concentrated HCl. The electrode was rinsed thoroughly with distilled H₂O.

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and dried in an oven prior to use. All potentials were referenced to an aluminum wire immersed in 2:1 AlCl₃-BPC melt, separated from the bulk melt compartment by a fine porosity frit.

The electrochemical cell temperature was maintained to within ±0.2°C of the desired temperature with a thermistor-controlled furnace. The furnace consisted of an insulated aluminum block containing a Vulcan Electric 150 watt cartridge heater. Regulated current to power the furnace was provided by an Ace Glass temperature controller.

RESULTS AND DISCUSSION

Voltammetry of cobalt(II) in AlCl₃-BPC melt.—Anhydrous CoCl₂ was readily soluble in the acidic (AlCl₃ rich) and basic (BPC rich) AlCl₃-BPC melt. Solutions of CoCl₂ in basic melt were aquamarine while acidic solutions were deep blue in color. A cyclic voltammogram for the reduction of Co(II) in 2:1 AlCl₃-BPC melt at a glassy carbon electrode is shown in Fig. 1a. The reduction peak potential for deposition of cobalt metal from the 2:1 AlCl₃-BPC melt shifts negatively by about 160 mV for each order of magnitude increase in scan rate. In addition, the reverse scan in Fig. 1a exhibits a hysteresis-like effect. Chronoamperometric current-time curves for Co(II) reduction in 2:1 AlCl₃-BPC exhibit maxima with induction times dependent on the applied potential, as depicted in Fig. 2. These electrochemical data suggest that deposition of cobalt metal on glassy carbon from 2:1 AlCl₃-BPC melt is controlled by the rate of nucleation during the initial phases of deposit formation (16). Similar behavior has been reported for deposition of copper (4) and aluminum (17) at glassy carbon in room temperature chloroaluminate melts.

Two stripping peaks, located at ca. 0.8 and 0.5 V, which correspond to reoxidation of material deposited on the electrode surface are also evident in Fig. 1a. The peak at 0.5 V may be due to reoxidation of aluminum codeposited with cobalt, since the Co(II) reduction process at 0.1 V is very close to the potential for reduction of Al₂Cl₇⁻ at glassy carbon at ca. -0.15 V (17). As the melt is made less acidic by successive additions of BPC and the Al₂Cl₇⁻ ion concentration is reduced, the peak attributed to reoxidation of deposited aluminum at 0.5 V begins to decrease (Fig 1b), and the large featureless reduction wave observed at 0.13 V in Fig. 1a begins to broaden and split into a well-defined reduction wave at 0.25 V and a broad indistinct wave at 0.13 V. Reversal of the scan after the first reduction wave considerably diminishes the oxidation wave at 0.5 V. After further decrease in the Al₂Cl₇⁻ concentration it is possible to obtain a deposition-stripping voltammogram that can be attributed solely to deposition and reoxidation of cobalt metal (Fig. 1c).

If the acidity of the melt is further decreased to the 1:1 AlCl₃-BPC composition, the melt becomes cloudy and some of the Co(II) precipitates from the melt, presumably as CoCl₂. Similar behavior for Co(II) has been reported in inorganic chloroaluminate melts (10).
No reduction or reoxidation wave was observed for Co(II) in basic AlCl₃-BPC mixtures over the available potential range. Thus, Co(II) may be electroinactive at the glassy carbon electrode when complexed as CoCl₄²⁻, or it may be reduced at potentials negative of the electrochemical window of the melt.

Predeposition of cobalt metal on glassy carbon.—An additional feature present in the voltammogram shown in Fig. 1a is a small wave at about 0.35 V. The presence of this peak was independent of the source of Co(II), i.e., the peak was present after the addition of anhydrous CoCl₂ from two different commercial sources or generation of Co(II) from a cobalt wire electrode by controlled potential electrolysis. This peak was not present in pure AlCl₃-BPC melt prior to addition of Co(II). An expanded scale, multiple scan cyclic voltammogram which encompasses this reduction peak but avoids the main deposition process is shown in Fig. 3. Cyclic scans which include this reduction wave reveal an associated stripping process at about 0.8 V. Several cycles are necessary before the area of this stripping peak begins to approximate that of the original reduction process. The potential at which the stripping peak is observed is proximate to the peak for stripping of cobalt metal as shown by comparison of Figs. 1a and 3.

Similar deposition and stripping of a monolayer or less of aluminum metal positive of the main deposition-stripping process in acidic AlCl₃-BPC melt was observed in previous studies and attributed to an underpotential deposition process (17). Integration of the area under the voltammetric predeposition peak (first scan) shown in Fig. 3 with respect to charge was undertaken at several concentrations of Co(II). These results are presented in Table I and indicate that the charge under this peak may correspond to as much as one monolayer of deposited cobalt metal. Thus, deposition of cobalt metal on glassy carbon would seem to be preceded by predeposition of a monolayer of the metal. The amount of predeposited cobalt appears to recede at high concentrations of Co(II). Formation of a complete monolayer is most favorable at low Co(II) concentrations. This observation contrasts with results reported by Hills et al (18) for monolayer formation during the reduction of Ni(II) and Ag(I) in LiCl-KCl eutectic. These workers reported that monolayer formation was relatively independent of the substrate ion concentration.

In the present case this process could hardly be described as underpotential deposition in the thermodynamic sense, because $E^\circ_m$ for the Co(II)/Co couple (Table II) is positive of the predeposition wave by about 0.5 V. In addition, the reported $E_1/2$ value for Co(II) reduction in an inorganic chloroaluminate melt (8) is also significantly positive of the potential reported for this predeposition wave. A complete explanation of this phenomenon awaits further studies.
Table I. Effect of Concentration on the Predeposition of Cobalt Metal at Glassy Carbon

| Co(II) Concentration (M) | Cobalt Metal (moles) | % Monolayer Coverage |
|--------------------------|----------------------|----------------------|
| $12.6 \times 10^{-3}$    | $2.72 \times 10^{-10}$ | 92                   |
| $21.1 \times 10^{-3}$    | $2.46 \times 10^{-10}$ | 83                   |
| $30.1 \times 10^{-3}$    | $2.33 \times 10^{-10}$ | 79                   |
| $51.7 \times 10^{-3}$    | $1.88 \times 10^{-10}$ | 63                   |

*Assuming that the geometrical area of the electrode represents its true area, 2.96 x 10$^{-10}$ moles of cobalt metal are required per monolayer.

Table II. Standard Potential Data for the Co(II)/Co Couple in 2:1 AlCl$_3$-BPC Melt

| $E^\circ (V)$ | Molar Fraction | Slope of Nernst Plot | t(°C) |
|--------------|----------------|----------------------|-------|
| 0.935±0.002  | 0.960±0.002    | 0.032±0.001          | 40.0  |
| 0.886±0.002  | 0.914±0.002    | 0.036±0.001          | 100.0 |

Potentiometric titration studies.- The nature and strength of the coordination of Co(II) was further probed in the acidic and basic AlCl$_3$-BPC melts using a potentiometric titration procedure. Potential measurements were made on the cell

Co | Co(II) dill, AlCl$_3$-BPC fritted disk : 2:1 molar ratio AlCl$_3$-BPC | Al (2)

as a function of the ratio of AlCl$_3$ to BPC in the left-hand compartment. There is at present no information about the external transport numbers of the various ionic species in room temperature chloroaluminate melts with which to estimate the magnitude of the liquid junction potential for this cell. However, very little shift in the cyclic voltammetric half-peak potential for the ferrocenium/ferrocene couple was observed in a similar cell with wide variation in the AlCl$_3$-BPC melt composition (1). Based on this indirect evidence, corrections for the liquid junction were assumed small and ignored in all calculations.

Figure 4 shows a plot of the cell potential for the cell depicted in Eq. 2 as a function of the apparent mole fraction of AlCl$_3$, $X_{AlCl_3}$, in the left-hand cell compartment. The cell potential is relatively independent of $X_{AlCl_3}$ in the acidic melt composition region despite variation of $X_{AlCl_3}$ from 0.66 to approximately 0.55. Substantial changes in the ion mole fractions for the ionic melt constituents Al$_2$Cl$_7^-$, AlCl$_4^-$, and Cl$^-$ take place over this composition interval. Subsequent analysis of the cell potential data with variation of the logarithm of the ion mole fractions of Al$_2$Cl$_7^-$, AlCl$_4^-$, and Co$^{2+}$
revealed a linear correlation only for the plot involving the ion mole fraction of Co$^{2+}$.

Further decrease in $X_{\text{AlCl}_3}$ to about 0.51 results in precipitation of CoCl$_2$ as previously described. When $X_{\text{AlCl}_3}$ is decreased to approximately 0.49 the CoCl$_2$ precipitate redissolves. Plots of the cell potential as a function of the negative logarithm of the chloride ion mole fraction, $X^-_{\text{Cl}}$, (Fig. 5) obtained by variation of $X_{\text{AlCl}_3}$ from 0.49 to 0.44 are linear and exhibit slopes of 127±4 and 154±2 mV at 40.0 and 100.0°C. These slopes are consistent with theoretical slopes of 124 and 148 mV for fourth-power dependence of the cell potential on $X^-_{\text{Cl}}$.

These potentiometric studies indicate that the predominant Co(II) ion equilibrium reaction in chloride rich AlCl$_3$-BPC melt may be represented by the expression given in Eq. 3.

$$\text{Co}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{CoCl}_4^{2-} \quad K_f$$

The relationship between the potential of the cell depicted in Eq. 2 and $X^-_{\text{Cl}}$ in the left-hand compartment of the cell is given by the Nernst equation represented by Eq. 4.

$$E = E^o_X + \frac{RT}{2F} \ln X^-_{\text{CoCl}_4} - \frac{RT}{2F} \ln K_f - \frac{RT}{2F} \ln X^-_{\text{Cl}}$$

In deriving this expression, the activities of the various species have been replaced by their mole fractions, $E^o_X$ is the standard potential of the Co(II)/Co couple on the mole fraction scale in 2:1 AlCl$_3$-BPC melt, and $K_f$ is the formation constant for the cobalt chloro-complex.

Values of $K_f$ for the process represented by Eq. 3 may be calculated at each value of $E$ and $X^-_{\text{Cl}}$ shown in Fig. 5 using Eq. 4 if $E^o_X$ is known and $X^-_{\text{CoCl}_4}$ can be estimated. Estimates of $E^o_X$ for the Co(II)/Co couple at 40.0 and 100.0°C were obtained from the intercepts of Nernst plots. Data with which to construct these plots were acquired by anodizing a cobalt electrode and coulometrically monitoring the Co(II) concentration. Values of $E^o_X$ are summarized in Table II. The observed potentials, various ion mole fractions, and calculated $K_f$ values for a representative calculation at 40.0°C are listed in Table III. Table IV contains the results of an additional determination of $K_f$ at 100.0°C. Values of $K_f$ for cobalt chlorocomplex formation in inorganic chloroaluminate melts are also included in this table for comparison.

The values of $K_f$ observed in AlCl$_3$-BPC melt are larger by many orders of magnitude than those observed in inorganic chloroaluminate melts, and they show a very slight reduction in magnitude with increased temperature. These results are consistent with the decreased ionic field strength of the N-(n-butyl)pyridinium cation resulting from its larger ionic radius relative to that of alkali metal cations. The reaction depicted in Eq. 3 is much more favorable from an electrostatic
point of view since the N-(n-butyl)pyridinium cation can exert only weak electrostatic attraction for melt chloride ion. The effect observed is quite similar to that proposed to account for the increased extent of Al$_2$Cl$_7^-$ ion formation in molten chloroaluminates when the cation ionic field strength is decreased (3, 19).

Table III. Potentials, Species Mole Fractions, and Calculated Formation Constants for Titration of 3.71 x 10$^{-3}$ M CoCl$_2$ in 0.8:1 AlCl$_3$-BPC Melt at 40.0°C

| E (V) | $X_{Cl^-}^a$ | $X_{CoCl_4^{2-}}$ | $X_{CoCl_4^{3-}}^b$ | $K_f$  |
|-------|-------------|-----------------|-----------------|------|
| -0.338 | 1.01 x 10$^{-1}$ | 3.87 x 10$^{-4}$ | 9.98 x 10$^{-2}$ | 2.27 x 10$^{+2}$ |
| -0.324 | 8.63 x 10$^{-2}$ | 3.87 x 10$^{-4}$ | 8.55 x 10$^{-2}$ | 1.60 x 10$^{+2}$ |
| -0.318 | 7.34 x 10$^{-2}$ | 3.87 x 10$^{-4}$ | 7.26 x 10$^{-2}$ | 1.90 x 10$^{+2}$ |
| -0.306 | 6.11 x 10$^{-2}$ | 3.87 x 10$^{-4}$ | 6.04 x 10$^{-2}$ | 1.69 x 10$^{+2}$ |
| -0.295 | 4.98 x 10$^{-2}$ | 3.87 x 10$^{-4}$ | 4.90 x 10$^{-2}$ | 1.72 x 10$^{+2}$ |
| -0.278 | 3.96 x 10$^{-2}$ | 3.87 x 10$^{-4}$ | 3.61 x 10$^{-2}$ | 1.63 x 10$^{+2}$ |
| -0.257 | 2.34 x 10$^{-2}$ | 3.87 x 10$^{-4}$ | 2.27 x 10$^{-2}$ | 2.14 x 10$^{+2}$ |

$^a$ Chloride ion mole fraction in excess of the 1:1 AlCl$_3$-BPC melt composition
$^b$ Excess chloride ion minus amount complexed with CoCl$_2$

Table IV. Cobalt Chlorocomplex Formation Constants in Chloroaluminate Melts

| Melt System | t (°C) | log $K_f$ | Ref. |
|-------------|--------|-----------|------|
| AlCl$_3$-LiCl | 300 | 6.5 | 13 |
| AlCl$_3$-NaCl | 300 | 11.2 | 13 |
| AlCl$_3$-CsCl | 400 | 19.7 | 13 |
| AlCl$_3$-BPC | 40 | 42.3±0.1 | this work |
| AlCl$_3$-BPC | 100 | 41.3±0.1 | this work |

Voltammetry of Mo(V) in AlCl$_3$-BPC melt.—Molybdenum(V) chloride dissolved readily in acidic AlCl$_3$-BPC melt to give a reddish-purple solution. It was possible to dissolve considerable amounts of MoCl$_5$ in the melt, and solutions with concentrations exceeding 100 mM could be readily obtained.

Figure 6 shows a cyclic voltammogram for the reduction of MoCl$_5$ at a glassy carbon electrode in 2:1 AlCl$_3$-BPC melt. Four reduction waves with peak potentials of 1.91, 1.10, 0.34, and 0.11 V are evident. Reversal of the voltammetric scan immediately after the first reduction wave at 1.91 V results in an oxidation wave at 1.97 V. The shape of this cyclic voltammogram suggests that it may arise from a reversible or quasi reversible redox process. If the voltammetric scan is reversed at 0.4 V a small oxidation wave at 1.78 V can be observed.
prior to the oxidation wave at 1.97 V. Reversal of the voltammetric scan at 0.0 V results in the appearance of an additional ill-defined oxidation wave slightly negative of the wave at 1.78 V. The reduction waves at 1.10, 0.34, and 0.11 V and associated oxidation waves were not subjected to additional study during this investigation.

Cyclic voltammetric data for the first redox process depicted in Fig. 6 are summarized in Table V. The average value of \( E_{p}^{a} - E_{p}^{c} \) presented in this table for scan rates less than 0.5 V/sec is about 63 mV. This value compares favorably with the theoretically predicted value of 62 mV for a one-electron reversible electrode reaction at 40.0°C. Values for \( E_{p}^{c} - E_{1/2}^{c} \) average about 31 mV and likewise compare well with the theoretical value expected for this parameter under the same conditions, 30 mV. However, a quasireversible, multielectron charge transfer process cannot be ruled out based on this data alone.

Table V. Cyclic Voltammetric Data for the Reduction of 12.9 mM MoCl₅ in 2:1 AlCl₃-BPC Melt at 40.0°C

| \( V \) (V/sec) | \( E_{p}^{c} \) (V) | \( E_{p}^{a} - E_{p}^{c} \) (V) | \( E_{p}^{c} - E_{1/2}^{c} \) (V) | \( i_{p}^{c}/\sqrt{v^{1/2}} \) (A sec^{1/2}/V^{1/2}) | \( i_{p}^{a}/i_{p}^{c} \) |
|----------------|----------------|-----------------|----------------|----------------|-----------------|
| 0.01           | 1.910          | 0.060           | -0.030         | 2.2 x 10^{-4}  | 1.00            |
| 0.05           | 1.906          | 0.064           | -0.031         | 2.2 x 10^{-4}  | 1.07            |
| 0.20           | 1.908          | 0.066           | -0.032         | 2.2 x 10^{-4}  | 1.13            |
| 0.50           | 1.910          | 0.063           | -0.030         | 2.3 x 10^{-4}  | 1.20            |
| 2.00           | 1.912          | 0.069           | -0.028         | 2.3 x 10^{-4}  | 1.24            |
| 5.00           | 1.908          | 0.082           | -0.032         | 2.3 x 10^{-4}  | 1.28            |

A convenient method for determining the number of electrons involved in the charge transfer process, \( n \), involves comparison of the voltammetric current function, \( i_{p}^{c}/\sqrt{v^{1/2}} \), with chronoamperometric values of \( \sqrt{v^{1/2}} \) according to Eq. 5 (20):

\[
i_{p}^{c}/\sqrt{v^{1/2}}/\sqrt{v^{1/2}} = 86.31(n/T)^{1/2}
\]

Calculations based on this equation yielded a value of 0.9 for \( n \), confirming that the first redox process depicted in Fig. 6 corresponds to a one electron charge transfer reaction. In addition the voltammetric peak current at a fixed scan rate of 50 mV/sec was linearly dependent on the molar concentration of MoCl₅ (Fig. 7). Combined together, this data suggests that Mo(V), introduced into the melt by addition of MoCl₅, undergoes a one-electron reduction to Mo(IV).

Values of \( i_{p}^{c}/\sqrt{v^{1/2}} \) shown in Table V are relatively constant with scan rate; but the peak current ratio, \( i_{p}^{a}/i_{p}^{c} \), calculated using Nicholson's empirical method (21), increases with increasing scan rate. This behavior is usually associated with a chemical step which precedes the charge transfer reaction (22). An equilibrium process that can be proposed for this chemical step is the dissociation...
equilibrium between electroinactive Mo(V) dimer and electroactive Mo(V) monomer. Dimeric Mo(V) species are well known (23).

Similar cyclic voltammetric experiments were undertaken after additions of MoCl₅ or MoCl₆ to 0.8:1 AlCl₃-BPC melt. However, a very large reduction wave was observed at ca. 0.7 V (vs. Al in the 2:1 AlCl₃-BPC melt) after these additions. A similar voltammetric wave was obtained after pure melt was saturated with chlorine gas. From these results, it was concluded that both MoCl₅ and MoCl₆ oxidize BPC rich AlCl₃-BPC melt, and that the molybdenum species which remained in the melt after these additions possessed an oxidation state less than four. The instability of Mo(V) in BPC rich AlCl₃-BPC melt contrasts sharply with its stability in NaCl saturated AlCl₃-NaCl melt at 175°C (14).

Variation of the average of the anodic and cathodic peak potentials for the Mo(V)/Mo(IV) electrode process, \( (E_p^{a}+E_p^{c})/2 \), was studied using cyclic voltammetry as \( x_{AlCl_3} \) was varied from 0.664 to 0.516. A linear plot was obtained for \( (E_p^{a}+E_p^{c})/2 \) as a function of the negative logarithm of the chloride concentration or \( pCl^- \) (Fig. 8). The slope of this plot was 59±6 mV and was in excellent agreement with the 62 mV theoretical slope expected for an electrode reaction involving a single chloride ion. The overall sequence for the one-electron reduction of Mo(V) in AlCl₃ rich AlCl₃-BPC melt can therefore be summarized by the reactions depicted in Eqs. 6 and 7.

\[
\text{Mo(V)}_2 \rightleftharpoons 2\text{Mo(V)} \quad (6)
\]
\[
\text{Mo(V)} + e^- \rightleftharpoons \text{Mo(IV)} + Cl^- \quad (7)
\]

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LIST OF SYMBOLS

- \( E \): potential (V)
- \( E_{1/2} \): polarographic half-wave potential (V)
- \( E_M^o \): standard electrode potential, molar scale (V)
- \( E_X^o \): standard electrode potential, mole fraction scale (V)
- \( E_p^a, E_p^c \): anodic and cathodic voltammetric peak potentials (V)
- \( F \): faraday (C)
- \( i \): current (A)
- \( i_p^a, i_p^c \): anodic and cathodic voltammetric peak currents (A)
- \( K \): equilibrium constant
- \( K_f \): formation constant
\( M \)  
\( n \)  
\( R \)  
\( t \)  
\( T \)  
\( X_{AlCl_3} \)  
\( X_{Al_2Cl_7^-} \)  
\( X_{AlCl_4^-} \)  
\( X_{Co^{2+}} \)  
\( X_{Cl^-} \)  
\( v \)  
molarity (moles/liter)
number of electrons in charge transfer step
gas constant (joules/mole K)
time (sec) or temperature (°C)
temperature (K)
apparent mole fraction of AlCl_3
ion mole fractions of Al_2Cl_7^- and AlCl_4^-
ion mole fractions of Co^{2+} and Cl^-
voltammetric sweep rate (V/sec)

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Figure 1. Cyclic voltammograms for 5 mM Co(II) at a glassy carbon electrode at 40.0°C; sweep rates are 0.020 V/sec. (a) 2:1 AlCl₃-BPC melt (b) 1.33:1 AlCl₃-BPC melt (c) 1.14:1 AlCl₃-BPC melt.
Figure 2. Current-time transients for Co(II) reduction at a glassy carbon electrode (area = 0.071 cm²) at 40.0°C; Co(II) concentration was 1.26 x 10⁻² M. (a) 0.050 V (b) 0.025 V (c) 0.0 V (d) -0.050 V.

Figure 3. Multiple cyclic voltammograms of the Co(II) predeposition-stripping process at a glassy carbon electrode (area = 0.071 cm²) in 2:1 AlCl₃-BPC melt at 40.0°C; Co(II) concentration was 5.17 x 10⁻² M; sweep rate was 0.200 V/sec.

Figure 4. Dependence of the potential of the cell depicted in Eq. 2 on the apparent mole fraction of AlCl₃.
Figure 5. Dependence of the potential of the cell depicted in Eq. 2 on the Cl⁻ ion mole fraction. The apparent mole fraction of AlCl₃ in the left-hand cell compartment was varied from 0.49 to 0.44; 100.0°C (upper line) and 40.0°C (lower line).

Figure 6. Cyclic voltammogram for the reduction of Mo(V) at a glassy carbon electrode in 2:1 AlCl₃-BPC melt. Sweep rate was 50 mV/sec; Mo(V) concentration was 12.9 mM; and temperature was 40.0°C.

Figure 7. Variation of the voltammetric peak current for reduction of Mo(V) at a glassy carbon electrode in 2:1 AlCl₃-BPC melt with the concentration of Mo(V). Sweep rate was 50 mV/sec; temperature was 40.0°C.
Figure 8. Plot of the average of the anodic and cathodic voltammetric peak potentials for the Mo(V)/Mo(IV) electrode process versus the melt pCl. Sweep rate was 50 mV/sec; temperature was 40.0°C.