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Convolution Voltammetry of Metal Complexes

by

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SUMMARY

The application of convolution potential voltammetry to questions of metal complexation is described. Theoretical relations are derived to show that the theories developed for polarographic boundary conditions by DeFord and Hume hold, provided the complexes are labile. Equations are also given for inert and quasilabile complexes. Stability constants for the PbCl$_x$ and CdCl$_x$ systems are reported, illustrating the use of convolution techniques with linear scan voltammetry and with anodic stripping voltammetry. Advantages of convolution techniques are discussed.
INTRODUCTION

The current interest in trace metal speciation has led to renewed efforts at obtaining precise stability constants for metal complexes, including those of possible environmental significance. Electroanalytical methods, particularly those at a stationary electrode such as the hanging mercury drop electrode (HMDE), have been used in the bulk of these studies (e.g., [1]).

One problem in using the HMDE for metal speciation studies is the shape of the current peak produced: a relatively broad, asymmetric waveform even in the reversible case. Identification of the peak potential can be difficult in the best of conditions, and may be impossible when several electroactive species are present, because of peak overlap [2]. Since the major source of error in a determination of metal complex stability constants has been shown to be the measurement of peak potentials [3], the precision of the results can be significantly affected.

A second problem inherent in the use of an electrochemical method to determine stability constants is the treatment of the lability of the metal complex(es) present in the solution [4,5]. Theoretical analysis of this problem is made difficult by the lack of a simple, closed form expression for linear potential scan voltammetry, the simplest waveform to treat both instrumentally and mathematically.

We wish to report the application of convolution voltammetry
to studies of metal speciation at the hanging mercury drop electrode. We have examined both linear scan voltammetry and linear scan anodic stripping voltammetry using numerical convolution techniques coupled with computer controlled instrumentation. To demonstrate the applicability of the method, we have determined the stability constants for the cadmium and lead chloride systems.

**THEORY**

**Linear scan voltammetry (LSV)**

Previous workers [6,7] have outlined the use of convolution integrals of the current with \( t^{-1/2} \), either by use of RC ladder circuits [8,9], or by digitization of waveforms and subsequent numerical processing of scans on large computers [10]. We perform the convolution immediately after the potential scan, and have found that it is more convenient to convolute the current with the potential, so that we define:

\[
m(E) = \pi^{-1/2} \int_{E_1}^{E} \frac{i(\gamma) \, d\gamma}{\sqrt{E-\gamma}}
\]  

(1)

and

\[
e(E) = \left( \frac{\partial m(E)}{\partial E} \right)
\]  

(2)

where \( E \) is the potential applied to the electrode, \( E_1 \) is the initial
potential of the experiment, and \( i \) is the current as a function of the potential. The expression for \( m(E) \) is equivalent to the semi-integral used by Saveant [6,10] and Oldham [7,8], while the expression for \( e(E) \) is equivalent to the semiderivative used by Goto [9]; since the scan is linear, our expressions differ from those of previous workers only by \( \sqrt{\nu} \), the root of the scan rate.

We consider first the case where no complexes are present. Using our definitions, and the approach of Oldham [11] for the usual electrode reaction:

\[
\text{Ox} + ne^- = \text{Red} \tag{3}
\]

the surface concentrations for the oxidized and reduced species are respectively:

\[
C_O(E) = C^*_O - (nF\nu^{1/2}D_O^{1/2})^{-1} m(E) \tag{4}
\]

\[
C_R(E) = (nF\nu^{1/2}D_R^{1/2})^{-1} m(E) \tag{5}
\]

where \( n \) is the number of electrons transferred, \( A \) is the surface area of the electrode, \( F \) is Faraday's constant, \( D_O \) and \( D_R \) are the diffusion constants of the chemical species, and \( C^*_O \) is the concentration of oxidized species in the bulk solution. For a reversible reaction, we obtain the expression for the shape of the
wave:

\[ E = E_{1/2}^R + \frac{RT}{nF} \ln \left( \frac{m^* - m(E)}{m(E)} \right) \]  

(6)

where

\[ E_{1/2}^R = E^0 + \frac{RT}{nF} \ln \left( \frac{D_o}{D_R} \right)^{1/2} \]  

(7)

\[ m^* = (D_o^2)^{1/2} nF A C_0^* \]  

(8)

and \( E^0 \) is the standard electrode potential; these equations are analogous to the expressions obtained by Oldham [11].

The shape of the semidifferential wave, obtained by differentiation of equation 6, is:

\[ e(E) = \left( \frac{n^2F^2A_n^*}{4RT} \right) \sech^2 \left[ \frac{nF}{2RT} (E - E_{1/2}^R) \right] \]  

(9)

Note that it is centered at \( E_{1/2}^R \), and is a symmetric peak.

For the case of one complex, which we assume to be electroinactive, we have the reaction:

\[ M X_L^{(n-Lp)} + k_b \]  

\[ \frac{M^{n+} + L X^p - n e^-}{k_f} \]  

(10)

where \( M \) is the metal, \( X \) is the ligand and \( M X_L^{(n-Lp)} \) is the complex.
We define the equilibrium constants as:

\[ K = \frac{k_f}{k_b} = \frac{1}{\beta L [X]^L} \]  

(11)

Where \( \beta L \) is the stability constant of the complex, and \( k_f \) and \( k_b \) are the forward and backward exchange rate constants of the ligand, respectively. For large excesses of ligand, the reaction may be considered pseudo-first-order, since \( K \) is nearly constant. This is identical to the case of a first order chemical reaction preceding the electrochemical reaction, first examined by Saveant and Vianello [12]. By recasting their treatment in terms of convolution integrals, we obtain, defining \( M^{n+} \) as ox, and \( M^o \) as red:

\[ C_o(E) = C_o^* \left( \frac{nFA}{\nu} \right)^{-1/2} \int_{E_i}^{E} \left\{ \left( \frac{1}{1+K} + \frac{\exp[-k(E-\nu)]}{1+K} \right) \frac{i(\nu) d\nu}{\sqrt{E-\nu}} \right\} \]  

(12)

and

\[ C_R(E) = \left( \frac{nFA}{\nu} \right)^{1/2} D_R^{1/2} \left( m(E) \right)^{-1} \]  

(13)

where \( k = (k_f + k_b)/\nu \).  

(14)

These equations contain the effects of complex lability upon the shape and position of the semi integral wave.

Examination of equation 12 leads to three cases:
Case 1 -- Inert Complexes

For inert complexes, the exchange rate is slow, and we let \( k \) approach zero. Then equation [12] reduces to:

\[
C_o(E) = C_{ox}^* - \left( nF \Delta \nu_0^{1/2} D_0^{1/2} \right)^{-1} m(E) \tag{15}
\]

which, upon substitution into the Nernst equation, gives an unshifted wave of height proportional to the concentration of the uncomplexed metal, because of the speed of the electrochemical measurement relative to the kinetics of ligand exchange.

Case 2 -- Labile Complexes

For rapid exchange rates, we let \( k \) approach infinity, and equation 12 reduces to:

\[
C_{ox}(E) = \frac{K}{1+K} \left[ C_{tot}^* - (nFAD_{ox}^{1/2} \Delta \nu_0^{1/2})^{-1} m(E) \right] \tag{16}
\]

where \( C_{tot}^* \) is the total analytical concentration of metal in solution. Substitution of equation 6 into the Nernst equation yields a wave of height proportional to \( C_{tot}^* \), shifted from the wave observed for a "free" metal ion:

\[
E = E^R_{1/2} + \frac{RT}{nF} \ln \left( \frac{m^* - m(E)}{m(E)} \right) + \frac{RT}{nF} \ln \left( 1 + K^{-1} \right) \tag{17}
\]

so that, using the half-wave point on the semiintegral, or at the
peak maximum on the semiderivative wave we obtain:

\[
\Delta E_{1/2} = E_{1/2, \text{free}} - E_{1/2, \text{complexed}} = \frac{RT}{nF} \ln\left(1 + \beta_L [X]^L\right)
\] (18)

Equation 18 reduces to the Lingane equation [13] for cases where \(\beta_L [X]^L \gg 1\).

For the labile case, one may calculate the concentration of the complex at the electrode surface, and show that, in fact:

\[
\frac{[MX_L^{(n-Lp)^+}]}{[M^{n+}]} = K
\]

Thus, the species are always in equilibrium.

The above treatment can be extended to \(N\) labile complexes in equilibrium at the electrode surface. By similar arguments:

\[
\Delta E_{1/2} = \frac{RT}{nF} \ln F_0(L)
\]

(20)

where \(F_0(L)\) is defined by:

\[
F_0(L) = 1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 + \ldots
\]

(21)

and is the DeFord-Hume function [14]. This expression is identical to that found by DeFord and Hume for an analogous situation in classical polarography, where the diffusion layer is renewed.
Case 3 -- Quasiliability

Here $k$ is finite, and dependent upon the scan rate. One can fit both $k$ and $K$ to the results of a number of runs, analogous to that done by Carney for nitriloacetic acid complexes of Cd and Pb\[15\], or one can use the scan rate dependence of $k$ to force the reaction into either the labile or inert regimes.

These three cases are analogous to those proposed by Davison, using reaction layer theory [4], and by Van Leeuwen [5]. Use of convolution potential voltammetry allows a simple test of the kinetic control of the process in the shape of the semiintegral and semidifferential waves, and their variation with scan rate. Labile complexes will show "normal" semiintegral and semidifferential waves, shifted from the "free"-ion position, while inert complexes will not shift, but will decrease in height. Quasi-labile complexes will show a broadening of the semiderivative peak into a waveform somewhat similar to that of a normal LSV wave; this effect will be more pronounced with increasing scan rate.

Anodic Stripping Voltammetry Using Linear Scans (ASV).

The same equations for LSV apply to linear scan ASV provided the boundary conditions governing reactant transport remain valid. The problem then reduces to a pseudo-first order chemical reaction (complexation) following the electrode process. For the equations to apply to ASV, the following boundary conditions must be met:

(i) the initial potential of the scan must be well below the
half-wave potential for oxidation;

(ii) the concentration of reduced species must be homogenous within the mercury drop;

(iii) the concentration of oxidized species in solution must be small compared to the concentration of reduced metal in the drop; and

(iv) the concentration of ligand in the system must be greatly in excess of that of the metal ion.

For many speciation studies involving ASV, these conditions can be met, and one may judge the lability of the complex by its response to scan rate, as well as determine its stability constant by the methods developed here for LSV. For labile complexes, the DeFord-Hume relation applies to convolution ASV.

A difficulty arises, however, in ASV studies involving very small amounts of strongly complexing ligand, in that the reaction is no longer pseudo-first order in metal ion. For quasilabile systems, this effect complicates the treatment.

EXPERIMENTAL

Reagents. For the LSV runs, reagent grade NaClO₄, Cd(NO₃)₂,
Na₂EDTA, and NaCl were used as received. The pH of the solutions was adjusted with reagent grade HClO₄. Solutions for ASV analysis were prepared by electrolyzing filtered solutions of reagent grade NaClO₄ and NaCl at -1.5 V vs. the SCE over a mercury pool cathode for
three days under argon. These solutions were stored in thoroughly
treated Teflon® bottles. Water for the runs was taken from a
leached all-vitreous silica still and stored in pre-leached 5-L
linear polyethylene containers. No electrochemically active
impurities were observed when 5 ml each of the purified NaCl and
NaClO₄ solutions were added to 25 ml of the water, plated at the
HMDE for 20 minutes at -1.00 V vs. the SCE, and subsequently stripped.
The Pb(NO₃)₂ used was reagent grade, added just before the ASV
scans with an Eppendorf pipette utilizing pre-leached tips. The
pH for the ASV runs was adjusted with ultrapure HClO₄ (Ventron).

Cell and Electrodes. The cell used for all runs was the standard
Princeton Applied Research (PAR) polarographic cell and cell holder,
thermostatted to 20.0°C. The cell was thoroughly leached between
runs for the ASV experiments, using Transistor® grade HNO₃
(Mallinckrodt). The working electrode was a PAR #9323 HMDE, con-
taining triply distilled mercury, precleaned by passage through a
pinhole. The reference electrode was an Ag|AgCl electrode with
a 1.0M NaClO₄/0.1M NaCl bridge solution; the potential of this
electrode was observed to be +40 mV vs. the SCE for the LSV experi-
ment, and +44 mV for the ASV experiment. The counter electrode was
a length of heavy-gauge platinum wire. Solutions were degassed with
purified argon before scans were taken, using a PAR gas inlet tube,
with only Teflon® tubing contacting the solution. Magnetic stirring
was used for the ASV runs.
Equipment. A conventional three-electrode potentiostat (PAR 173) was used, along with a linear scan generator (PAR 175). These were controlled by Digital Equipment Corporation MINC-11B computer with data acquisition via a 25 kHz, 12-bit analog-to-digital converter coupled to a PAR 179 current-to-voltage converter. The LSI-11/2 processor used has 30 K words of usable memory as well as two double density floppy disk units for data and program storage. Computer control of the scans was achieved by coupling the PAR 175 to the 16-bit digital output module of the MINC system. A programmable clock was used for all timing, and a 12-bit digital-to-analog converter was used to control plating potentials for the ASV runs.

Computer Programs. Control of the LSV and ASV experiments was performed by MACRO-11 assembly language subroutines linked to a FORTRAN driver. Data were stored on disks for processing, which consisted of digital filtering using the fast Fourier transform [16] and semiintegration by a FORTRAN program employing the method of Huber [17], as given by Nicholson and Olmstead [18]. The FORTRAN program then numerically differentiated the semiintegral wave to produce the semiderivative wave. Potential shift vs. ligand concentration curves were analyzed using a polynomial regression routine supplied by Digital Equipment Corporation; this routine was previously checked by us with known data and found to behave properly. Species distributions were calculated from our results using MINEQL [19].

Procedure. LSV Runs: For the complexations studies, solutions of
NaCl were made up to an ionic strength of 0.99 ± 0.01 with NaClO₄, and Cd(NO₃)₂ was added to make the final solutions 1.2 x 10⁻⁴ M in Cd²⁺. The pH was adjusted with HClO₄ to 5.00, and the solution was degassed. Ten LSV scans were taken from -0.400 to -0.900 V vs. the Ag|AgCl electrode, averaged, and digitally filtered. The filtered scans were then semi integrated and differentiated to yield the semiderivative scan. It was observed that the order of filtering and semi integration made no difference in the value obtained for the half-wave potential which was obtained via a parabolic interpolation routine. Studies of the peakshape of the CdEDTA wave were done with a solution containing 10⁻⁴ M Cd²⁺ and Na₂EDTA, adjusted to pH 4.0 with HClO₄. The scan rate was varied, and the data taken as before.

**ASV Runs:** To purified solutions of NaCl and NaClO₄, of total ionic strength 2.22 ± 0.3 enough Pb(NO₃)₂ was added to give a final Pb²⁺ concentration of 4.4 x 10⁻⁷ M, (to insure that the Kₛₚ (1.0 x 10⁻⁵) for PbCl₂ would not be exceeded) and the pH was adjusted to 4.00. The solutions were degassed, then stirred for 15 seconds at a potential of -0.131 V vs. the Ag|AgCl electrode to establish a reproducible flux. The potential was changed to -1.000 V and held for 600 seconds. Six seconds before the end of the plating period, stirring was halted. The potential was changed to the rest potential of -0.800 V vs. the SCE, where it was held for 15 seconds to insure a homogenous amalgam. Stripping them took place at a
rate of 1.00 V/sec, and the resultant voltammogram was recorded, after which the potential was then held at -0.135 V for 60 seconds to remove all remaining Pb from the drop. The potential was then changed to the rest potential, held there for 15 seconds, and a second stripping voltammogram was performed and recorded. Both this background scan and the ASV scan were stored on disk. Subsequent processing began with the numerical subtraction, point by point, of the background scan from the ASC scan to remove capacitative and other background currents [19]. The rest of the processing took place as in the LSV scans.

The precision in obtaining half-wave potentials was observed to be about 0.3 mv; in changing plating times from 60 seconds to 600 seconds during some preliminary studies for our ASV runs, we could distinguish the shift (~0.3 mv) of peak potential with the logarithm of the plating time, as predicted by pseudopolarographic theory [20].

RESULTS AND DISCUSSION

System Characterization

Scan Rates. A sample LSV scan and the resulting semiderivative are shown in Figure 1. For our scans, 512 data points were taken, with the maximum available scan rate (100 V/s) being limited by the interrupt latency time of the LSI 11/2 microcomputer and the throughput of the analog-to-digital converter; higher scan rates are possible
at the cost of lowering the resolution of voltage. ASV scan rates were limited to scan rates below 20 V/s to obtain reproducible background-subtracted waves. Figure 2 shows the ASV and background scans, and it also illustrates the resulting semiderivative. Removal of the larger background currents in ASV is necessary to obtain well-shaped semiderivatives at moderate scan rates.

Effects due to the sphericity of the electrode have been observed by others in convolution potential voltammetry [6]. Because our scan rates are relatively fast, we anticipate relatively small effects on the semiintegral due to electrode sphericity, with these effects being most prominent well after the $E_{1/2}$ value [6]. The main effect will be a slight altering of the baseline past the peak in the semidifferential scan. We performed a series of experiments on the same solution, using different drop sizes, ranging from 0.27 to 0.57 mm in radius. No shift in the potential of the peak maximum of the semidifferential peak was observed. We have therefore not corrected our data for sphericity. The effects of uncompensated resistance were minimized by careful location of the reference electrode adjacent to the working electrode.

**Peak Shapes.** The reversible, 2-electron semidifferential waveform is predicted to have a peak width (at half-height) of 45.4 mv [21]. For our studies of cadmium and lead, we observed widths of 45.6 mv for cadmium and 47.5 mv for lead, indicating a good degree of
reversibility. Analysis of the raw LSV and ASV scans also indicated both systems to be reversible at the scan rates used for our complexation studies. Both the cadmium and lead systems in chloride were observed to be labile, in that the semiderivative peak shape and width was invariant to scan rate, as shown in Figure 3. The cadmium-EDTA system, however, was observed to be quasilabile in that the shape of the semiderivative peak was strongly dependent upon the scan rate, as predicted by equations 11-13. This dependence is illustrated in Figure 4. For scan rates below 200 mv/s, we were able to obtain symmetric semiderivative waves for the system, indicating that the complex is somewhat labile. Studies of this complex have shown that the rate constant for dissociation of Cd EDTA is 10.8 sec⁻¹ [22].

It should be noted that the ability to scan rapidly is a distinct advantage of the numerical generation of semiintegral and semidifferential waves. The RC ladder network of Oldham [8] can be expected to induce distortions at higher scan rates via time constant effects. For studies of the kinetics of complex dissociation by convolution voltammetry, these effects are particularly damaging, since any evaluation of kinetics will involve a fit of the peak widths to scan rate.

Stability Constants. Tables 1 and 2 list the data observed for the CdCl\(_{2-x}\) systems, respectively. From these data, a fit of the calculated DeFord-Hume \(F_1\) function to a second-degree polynomial in \([Cl^-]\) for cadmium and a second-degree polynomial in \([Cl^-]\) for lead; other models
were investigated, but rejected because they either gave negative stability constants or gave constants with considerably larger errors (and correspondingly poorer fit parameters) than those reported here. The stability constants produced by these fits are reported in Tables 3 and 4. These results have not been corrected for ionic strength effects because no good literature data on mixed NaCl-NaClO₄ electrolytes could be found. Other work on these systems is compared with our results in Tables 3 and 4; agreement is quite good. Figure 5 shows the calculated distribution of species in the two systems with chloride.

The agreement of values obtained using rapid-scan convolution potential voltammetry with slower, more tedious techniques is encouraging. The advantage of being able to obtain peak shifts through examination of peak maxima and to avoid the use of thin-film electrodes, while still retaining fairly narrow peaks makes the technique quite attractive for studies involving multi-metal systems, or where the thin-film electrode is easily fouled [4]. Further, since no RC circuitry is used, no distortions are introduced into the scan, allowing kinetic information to be obtained in quasilabile systems.
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CREDIT

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    (1958) 141.
24. R.M. Smith and A. Martell, Critical Stability Constants, v. 4,
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$^a$Potential relative to the Ag|AgCl electrode

pH = 5.01 ± .05, I = .99 ± .01M, Sensitivity = 10μA/full scale, scan rate = 1.0 V/s, drop radius = .61mm, T = 20.0 ± .9°C.
Table 2: Potential Shifts and DéFord-Hume Functions for Lead in Chloride

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<td>195</td>
<td>89.3</td>
<td>38.6</td>
</tr>
<tr>
<td>2.26</td>
<td>-.4949</td>
<td>-79.3</td>
<td>533</td>
<td>235</td>
<td>98.7</td>
<td>39.0</td>
</tr>
</tbody>
</table>

pH = 3.99 ± .06, I = 2.22 ± 0.04M, Sensitivity = 1.0μA/Ful scale, drop radius .58mm, scan rate = 1.0 V/s, T = 20.0 ± .5°C.

aPotential is relative to the Ag|AgCl electrode.
Table 3: Stability Constants for Cadmium Chloride Complexes

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature</th>
<th>Medium</th>
<th>Log $\beta_n$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>differential</td>
<td>25</td>
<td>1M(NaClO$_4$)</td>
<td>$\beta_1$ 1.34</td>
<td>23</td>
</tr>
<tr>
<td>pulse polarography</td>
<td></td>
<td></td>
<td>$\beta_2$ 1.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_3$ 1.49</td>
<td></td>
</tr>
<tr>
<td>potentiometry</td>
<td>25</td>
<td>1M(NaClO$_4$)</td>
<td>$\beta_1$ 1.33</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_2$ 1.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_3$ 1.53</td>
<td></td>
</tr>
<tr>
<td>polarography</td>
<td>25</td>
<td>1M</td>
<td>$\beta_1$ 1.35</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_2$ 1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_3$ 1.5</td>
<td></td>
</tr>
<tr>
<td>polarography</td>
<td>25</td>
<td>0.76M(NaClO$_4$)</td>
<td>$\beta_1$ 1.46</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_2$ 1.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_3$ 1.96</td>
<td></td>
</tr>
<tr>
<td>convolution potential voltammetry</td>
<td>20</td>
<td>1M(NaClO$_4$)</td>
<td>$\beta_1$ 1.44 ± .08</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_2$ 1.46 ± .05</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_3$ 1.66 ± .03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(multiple regression coeff. = 0.996)</td>
<td></td>
</tr>
</tbody>
</table>
Table 4: Stability Constants for Lead Chloride Complexes

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature</th>
<th>Medium</th>
<th>$\log \beta_n$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>potentiometry</td>
<td>25</td>
<td>3M (NaClO$_4$)</td>
<td>$\beta_1$ 1.05</td>
<td>25</td>
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<td></td>
<td></td>
<td></td>
<td>$\beta_2$ 1.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_3$ 1.83</td>
<td></td>
</tr>
<tr>
<td>potentiometry</td>
<td>25</td>
<td>3M (NaClO$_4$)</td>
<td>$\beta_1$ 1.16</td>
<td>25</td>
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<td>$\beta_2$ 1.7</td>
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</tr>
<tr>
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<td></td>
<td>$\beta_3$ 1.97</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_4$ 0.7</td>
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</tr>
<tr>
<td>cyclic voltammetry</td>
<td>23</td>
<td>0.7M (KNO$_3$)</td>
<td>$\beta_1$ 0.96</td>
<td>26</td>
</tr>
<tr>
<td>polarography</td>
<td>25</td>
<td>3M</td>
<td>$\beta_1$ 1.17 $\pm$ .03</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_2$ 1.7 $\pm$ .1</td>
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<tr>
<td></td>
<td></td>
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<td>$\beta_3$ 1.4 $\pm$ .2</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>$\beta_4$ 1.2 $\pm$ .2</td>
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</tr>
<tr>
<td>convolution potential voltammetry</td>
<td>20</td>
<td>2.22M(NaClO$_4$)</td>
<td>$\beta_1$ 1.09 $\pm$ .18 This Work</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>$\beta_2$ 1.02 $\pm$ .10</td>
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<td></td>
<td>$\beta_3$ 1.59 $\pm$ .01</td>
<td></td>
</tr>
</tbody>
</table>

(multiple regression coeff. = 0.999)
Figure Captions

Figure 1. LSV wave for cadmium and its resulting semiderivative wave. Supporting electrolyte is 1M KNO₃.

Figure 2. (a) ASV wave; (b) background scan; (c) background-subtracted wave; (d) resulting semiderivative wave.

Figure 3. Peakshape dependence of the semiderivative wave for cadmium in chloride on scan rate.

Figure 4. Peakshape dependence of the semiderivative wave for cadmium in EDTA on scan rate.

Figure 5. Species distribution of cadmium and lead in chloride media as a function of chloride concentration.

\[ \text{pH} = 5.00, \ K_{sp} (\text{PbCl}_2) = 1.0 \times 10^{-5}, \ I = 1.00 \ \text{for Cd}^{2+}, \ I = 2.22 \ \text{for Pb}^{2+}. \]
Figure 1.

Volts vs SCE

XBL 804-713
Figure 2.
Figure 4.

Cd/EDTA

Scaled semi-derivative of current

Volts vs. S.C.E.

0.5 V/s

2 V/s

10 V/s

20 V/s
Figure 5.

Percent of species present vs. [Cl\(^-\)].

- Cd\(^{+2}\)
- CdCl\(^+\)
- CdCl\(_3\)^-
- CdCl\(_2\)
Figure 5.
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