Lawrence Berkeley National Laboratory

Recent Work

Title

CONVOLUTION VOLTAMMETRY OF METAL COMPLEXES

Permalink

<https://escholarship.org/uc/item/86x297g4>

Authors

Toman, J.J.
Corn, R.M.
Brown, S.D.

Publication Date

1980-04-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to *Analytica Chimica Acta*

CONVOLUTION VOLTAMMETRY OF METAL COMPLEXES

J. J. Toman, R. M. Corn and S. D. Brown

April 1980

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUL 9 1980

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

LBL-10820 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Convolution Voltammetry of Metal Complexes

by

J.J. Toman, R.M. Corn and S.D. Brown^{*}

Department of Chemistry
University of California
Berkeley, California 94720

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

Pages: 31

Tables: 4

Figures: 5

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:

$$m(E) = \pi^{-1/2} \int_{E_i}^E \frac{i(\gamma) d\gamma}{\sqrt{E-\gamma}} \quad (1)$$

and

$$e(E) = \left(\frac{\partial m(E)}{\partial E} \right) \quad (2)$$

where E is the potential applied to the electrode, E_i 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 $v^{1/2}$, 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:

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

$$C_O(E) = C_O^* - (nFAv^{1/2}D_O^{1/2})^{-1} m(E) \quad (4)$$

$$C_R(E) = (nFAv^{1/2}D_R^{1/2})^{-1} m(E) \quad (5)$$

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:

$$E = E_{1/2}^R + \frac{RT}{nF} \ln \left(\frac{m^* - m(E)}{m(E)} \right) \quad (6)$$

where

$$E_{1/2}^R = E^0 + \frac{RT}{nF} \ln \left(\frac{D_o}{D_R} \right)^{1/2} \quad (7)$$

$$m^* = (D_o v)^{1/2} nFA C_o^* \quad (8)$$

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

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

$$e(E) = \left(n^2 \frac{F^2 A v^{1/2} C_o^*}{4RT} D_o^{1/2} \right) \operatorname{sech}^2 \left[\frac{nF}{2RT} (E - E_{1/2}^R) \right] \quad (9)$$

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:

where M is the metal, X is the ligand and $MX_L^{(n-Lp)+}$ is the complex.

We define the equilibrium constants as:

$$K = \frac{k_f}{k_b} = \frac{1}{\beta_L [X]^L} \quad (11)$$

Where β_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^0 as red:

$$C_o(E) = C_o^* - \frac{(\pi D_o \nu)^{-1/2}}{nFA} \int_{E_i}^E \left\{ \left(\frac{K}{1+K} \right) + \frac{\exp [-k(E-\gamma)]}{1+K} \right\} \frac{i(\gamma) d\gamma}{\sqrt{E-\gamma}} \quad (12)$$

and

$$C_R(E) = \left(nFA \nu^{1/2} D_R^{1/2} \right)^{-1} m(E) \quad (13)$$

$$\text{where } k = (k_f + k_b)/\nu. \quad (14)$$

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 I -- Inert Complexes

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

$$C_o(E) = C_{ox}^* - \left(nFAv^{1/2}D_o^{1/2} \right)^{-1} m(E) \quad (15)$$

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:

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

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:

$$E = E_{1/2}^R + \frac{RT}{nF} \ln \left(\frac{m^* - m(E)}{m(E)} \right) + \frac{RT}{nF} \ln (1 + K^{-1}) \quad (17)$$

so that, using the half-wave point on the semiintegral, or at the

peak maximum on the semiderivative wave we obtain:

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

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:

$$\frac{[MX_L^{(n-Lp)+}]}{[M^{n+}]} = K \quad (19)$$

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:

$$\Delta E_{1/2} = \frac{RT}{nF} \ln F_0(L) \quad (20)$$

where $F_0(L)$ is defined by:

$$F_0(L) = 1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 + \dots \quad (21)$$

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 -- Quasilability

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 semi-differential 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 NaClO_4 , $\text{Cd}(\text{NO}_3)_2$, Na_2EDTA , and NaCl were used as received. The pH of the solutions was adjusted with reagent grade HClO_4 . Solutions for ASV analysis were prepared by electrolysing filtered solutions of reagent grade NaClO_4 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 pre-leached 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 Transistar® grade HNO₃ (Mallinckrodt). The working electrode was a PAR #9323 HMDE, containing 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 experiment, 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 couples 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 $0.99 \pm .01$ with NaClO_4 , and $\text{Cd}(\text{NO}_3)_2$ was added to make the final solutions $1.2 \times 10^{-4} \text{ M}$ in Cd^{+2} . The pH was adjusted with HClO_4 to 5.00, and the solution was degassed. Ten LSV scans were taken from -0.400 to -0.900 V vs. the $\text{Ag}|\text{AgCl}$ electrode, averaged, and digitally filtered. The filtered scans were then semiintegrated and differentiated to yield the semiderivative scan. It was observed that the order of filtering and semiintegration 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 $10^{-4} \text{ M Cd}^{+2}$ Na_2EDTA , adjusted to pH 4.0 with HClO_4 . The scan rate was varied, and the data taken as before.

ASV Runs: To purified solutions of NaCl and NaClO_4 , of total ionic strength 2.22 ± 0.3 enough $\text{Pb}(\text{NO}_3)_2$ was added to give a final Pb^{+2} concentration of $4.4 \times 10^{-7} \text{ M}$, (to insure that the K_{sp} (1.0×10^{-5}) for PbCl_2 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 $\text{Ag}|\text{AgCl}$ 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 $E_{1/2}^R$ 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 semi-differential 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_x^{2-x} systems, respectively. From these data, a fit of the calculated DeFord-Hume F_1 function to a second-degree polynomial in $[\text{Cl}^-]$ for cadmium and a second-degree polynomial in $[\text{Cl}^-]$ 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.

ACKNOWLEDGEMENTS

We are pleased to recognize the assistance of C.M. Phillips, who calculated the distributions of species, and of N. Edelstein, who provided access to the potentiostat.

CREDIT

This research was supported by the Office of Nuclear Waste Isolation and by the Division of Chemical Sciences under Contract No. W-7405-Eng-48, both affiliated with the U.S. Department of Energy.

REFERENCES

1. H. Bilinski, R. Huston and W. Stumm, *Anal. Chim. Acta*, 84 (1976) 157.
2. T.M. Florence, *J. Electroanal. Chem.*, 27 (1970) 273.
3. L.N. Klatt and R.L. Rouseff, *Anal. Chem.*, 42 (1970) 1234.
4. W. Davison, *J. Electroanal. Chem.*, 87 (1978) 395.
5. H.P. Van Leeuwen, *J. Electroanal. Chem.*, 99 (1979) 93.
6. J.C. Imbeaux and J.M. Savéant, *J. Electroanal. Chem.*, 44 (1973) 169.
7. M. Grenness and K.B. Oldham, *Anal. Chem.*, 44 (1972) 1121.
8. K.B. Oldham, *Anal. Chem.*, 45 (1973) 39.
9. M. Goto and D. Ishii, *J. Electroanal. Chem.*, 61 (1975) 361.
10. J.M. Savéant and D. Tessier, *J. Electroanal. Chem.*, 77 (1977) 225.
11. M. Goto and K.B. Oldham, *Anal. Chem.*, 45 (1973) 2043.
12. J.M. Savéant and E. Vianello, *Electrochim. Acta*, 8 (1963) 905.
13. J. J. Lingane, *Chem. Rev.*, 29 (1941) 1.
14. D. D. DeFord and D.N. Hume, *J. Amer. Chem. Soc.*, 73 (1951) 5321.
15. J.H. Carney, *Anal. Chem.*, 47 (1975) 2267.
16. J.W. Hayes, D.E. Glover, D.E. Smith and M.W. Overton, *Anal. Chem.*, 45 (1973) 277.
17. R.S. Nicholson and M.C. Olmstead, in J.S. Matlson, H.B. Mark and H.C. McDonald (Eds.), *Electrochemistry*, Dekker, New York, 1972.

18. A. Huber, *Monatsh. Math. Phys.* 47 (1939) 240.
19. S.D. Brown and B.R. Kowalski, *Anal. Chim. Acta*, 107 (1979) 13.
20. (a) M.S. Shuman and J.L. Cromer, *Anal. Chem.*, 51 (1979) 1546, and
(b) S.D. Brown and B.R. Kowalski, *Anal. Chem.*, 51 (1979), 2133.
21. P. Dalrymple-Alford, M. Goto and K.B. Oldham, *J. Electroanal. Chem.*, 85 (1977) 1.
22. N. Tanaka, R. Tamamushi and M. Kodana, *Z. Phys. Chem., N.F.* 14 (1958) 141.
23. G.A. Heath and G. Hefter, *J. Electroanal. Chem.*, 84 (1977) 295.
24. R.M. Smith and A. Martell, *Critical Stability Constants*, v. 4, Plenum Press, New York, 1976.
25. Special Publication No. 25, Supplement No. 1, part I, The Chemical Society, London, 1971.
26. L.M. Petrie and R.W. Baier, *Anal. Chem.*, 50 (1978) 351.

Table 1: Potential Shifts and DeFord-Hume Functions for Cadmium in Chloride

[Cl-]	E_p (v) ^a	$\Delta E_{1/2}$ (mv)	F_0	F_1	F_2	F_3
0	-.6175	0	-	-	-	-
.107	-.6375	-18.2	4.23	30.3	28.0	-
.191	-.6429	-25.4	7.47	34.0	35.3	-
.301	-.6504	-32.9	13.5	41.9	48.4	-
.398	-.6547	-37.2	19.0	45.4	45.6	42.8
.481	-.6588	-41.3	26.3	52.7	52.8	50.4
.588	-.6625	-45.0	35.3	58.4	53.0	41.6
.703	-.6665	-49.0	48.4	67.5	57.3	40.9
.783	-.6699	-52.4	63.4	79.7	67.0	49.1
.995	-.6758	-58.3	101	100.7	53.9	45.5

pH = $5.01 \pm .05$, I = $.99 \pm .01$ M, Sensitivity = 10 μ A/full scale, scan rate = 1.0 V/s, drop radius = .61mm, T = $20.0 \pm .9^\circ$ C.

^aPotential relative to the Ag|AgCl electrode

Table 2: Potential Shifts and DeFord-Hume Functions for Lead in Chloride

$[Cl^-]$	$E_p (v)^a$	$\Delta E_{1/2} (mv)$	F_0	F_1	F_2	F_3
0	-.4156	-	-	-	-	-
.207	-.4338	-18.2	4.23	15.6	15.7	-
.464	-.4484	-32.8	13.4	26.8	31.2	35.2
.691	-.4568	-41.2	26.1	36.4	34.8	35.2
.895	-.4651	-49.5	50.4	55.2	48.0	41.9
1.13	-.4717	-56.1	84.9	73.8	54.0	38.3
1.60	-.4828	-67.2	11.6	127	71.8	38.3
1.85	-.4880	-72.4	206	167	83.6	39.2
2.04	-.4907	-75.6	309	195	89.3	38.6
2.26	-.4949	-79.3	533	235	98.7	39.0

pH = $3.99 \pm .06$, I = $2.22 \pm 0.04M$, Sensitivity = $1.0\mu A/Full\ scale$, drop radius .58mm, scan rate = $1.0\ V/s$,
T = $20.0 \pm .5^\circ C$.

^aPotential is relative to the Ag|AgCl electrode.

Table 3: Stability Constants for Cadmium Chloride Complexes

<u>Method</u>	<u>Temperature</u>	<u>Medium</u>	<u>Log β_n</u>	<u>Ref.</u>
differential	25	1M(NaClO ₄)	β_1 1.34	23
pulse polarography			β_2 1.75	
			β_3 1.49	
potentiometry	25	1M(NaClO ₄)	β_1 1.33	23
			β_2 1.69	
			β_3 1.53	
polarography	25	1M	β_1 1.35	24
			β_2 1.7	
			β_3 1.5	
polarography	25	0.76M(NaClO ₄)	β_1 1.46	24
			β_2 1.83	
			β_3 1.96	
convolution potential voltammetry	20	1M(NaClO ₄)	β_1 1.44 $\pm$ .08	This work
			β_2 1.46 $\pm$ .05	
			β_3 1.66 $\pm$ .03	
				(multiple regression coeff. =
				0.996)

Table 4: Stability Constants for Lead Chloride Complexes

<u>Method</u>	<u>Temperature</u>	<u>Medium</u>	<u>Log β_n</u>	<u>Ref.</u>
potentiometry	25	3M (NaClO ₄)	β_1 1.05	25
			β_2 1.51	
			β_3 1.83	
potentiometry	25	3M (NaClO ₄)	β_1 1.16	25
			β_2 1.7	
			β_3 1.97	
			β_4 0.7	
cyclic voltammetry	23	0.7M (KNO ₃)	β_1 0.96	26
polarography	25	3M	β_1 1.17 $\pm$ .03	24
			β_2 1.7 $\pm$ .1	
			β_3 1.4 $\pm$ .2	
			β_4 1.2 $\pm$ .2	
convolution potential voltammetry	20	2.22M(NaClO ₄)	β_1 1.09 $\pm$ .18	This Work
			β_2 1.02 $\pm$ .10	
			β_3 1.59 $\pm$ .01	
(multiple regression coeff. = 0.999)				

Figure Captions

Figure 1. LSV wave for cadmium and its resulting semiderivative wave. Supporting electrolyte is 1M KNO_3 .

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.

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

Figure 1.

XBL 804-713

XBL 804-714

Figure 2.

Figure 3.

XBL 804-712

Figure 4.

XBL 7910 - 4541

XBL 804-707

Figure 5.

Figure 5.

XBL 804-706

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720