# CONVOLUTION VOLTAMMETRY OF METAL COMPLEXES

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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 stability constants may be directly related to the shift in the peak potential of the semiderivative wave, 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 linear scan anodic stripping voltammetry. Advantages of convolution techniques are discussed.

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 (h.m.d.e.), have been used in the bulk of these studies (e.g., [1]).

One problem in using the h.m.d.e. 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]. Because 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.

This paper reports the application of convolution voltammetry to studies of metal speciation at the hanging mercury drop electrode. Both linear scan

voltammetry and linear scan anodic stripping voltammetry were examined using numerical convolution techniques coupled with computer-controlled instrumentation. To demonstrate the applicability of the method, the stability constants for the cadmium and lead chloride systems were determined.

THEORY

*Linear scan voltammetry (l.s.v.)*

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]. In this work, the convolution was performed immediately after the potential scan, so that it is more convenient to convolute the current with the potential. The semi-integral, $m(E)$, is defined as

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

and the semiderivative, $e(E)$, as: $e(E) = \delta m(E)/\delta E$, 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 effectively equivalent to the semi-integral used by Savéant [6, 10], Oldham [7, 8] and co-workers, while the expression for $e(E)$ is equivalent to the semi-derivative used by Goto and Ishii [9]; since the scan is linear, these expressions differ from those of previous workers only by $\nu^{1/2}$, the root of the scan rate.

When these definitions, and the approach of Goto and Oldham [11] for the usual electrode reaction where no complexes are present (Ox + ne⁻ = Red), are used, the surface concentrations for the oxidized and reduced species are, respectively

$$C_o(E) = C_o^* - (nFA\nu^{1/2}D_o^{1/2})^{-1} m(E) \tag{2}$$

$$C_R(E) = (nFA\nu^{1/2}D_R^{1/2})^{-1} m(E) \tag{3}$$

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, the expression obtained for the shape of the wave is

$$E = E_{1/2}^R + \frac{RT}{nF} \ln \left[ (m^* - m(E))/m(E) \right] \tag{4}$$

where $E_{1/2}^R = E^0 + RT(nF)^{-1} \ln(D_o \, D_R^{-1})^{1/2}$, $m^* = (D_o \, \nu)^{1/2} nFAC_o^*$, and $E^0$ is the standard electrode potential; these equations are analogous to the expressions obtained by Goto and Oldham [11].

The shape of the semidifferential wave, obtained by differentiation of eqn. (4) is

$$e(E) = [n^2F^2A\nu^{1/2}C_o^* \, (4RT)^{-1} \, D_o^{1/2}] \, \text{sech}^2 \, [nF(2RT)^{-1} \, (E - E_{1/2}^R)] \tag{5}$$

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

For the case of one complex, assumed to be electroinactive, the reaction

$$MX_L^{(n-Lp)^+} \underset{k_f}{\overset{k_b}{\rightleftharpoons}} M^{n+} + L \, X^{p-} \overset{ne^-}{\rightleftharpoons} M^0 \tag{6}$$

may be written, where M is the metal, X is the ligand and $MX_L^{(n-Lp)^+}$ is the complex. The equilibrium constants are defined as $K = k_f/k_b = 1/\beta_L[X]^L$, 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 Savéant and Vianello [12]. By recasting their treatment in terms of convolution integrals, defining $M^{n+}$ as ox, and $M^0$ as red, the following equations are obtained

$$C_o(E) = C_o^* - (\pi D_o \nu)^{-1/2} \, (nFA)^{-1} \int_{E_i}^{E} \{((K)/(1+K)) + (\exp[-k(E-\gamma)])/$$

$$(1+K)\} \, i(\gamma)d\gamma \times (E-\gamma)^{-1/2} \tag{7}$$

and

$$C_R(E) = (nFA\nu^{1/2}D_R^{1/2})^{-1} \, m(E) \tag{8}$$

where $k = (k_f + k_b)/\nu$. These equations contain the effects of complex lability upon the shape and position of the semi-integral wave.

Examination of eqn. (7) leads to three cases:

*Case 1, Inert complexes.* For inert complexes, the exchange rate is slow, and $k$ approaches zero. Then eqn. (7) reduces to

$$C_o(E) = C_o^* - (nFA\nu^{1/2}D_o^{1/2})^{-1} \, m(E) \tag{9}$$

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, $k$ approaches infinity, and eqn. (7) reduces to

$$C_{ox}(E) = [K/(1 + K)] \, [C_{tot}^* - (nFAD_{ox}^{1/2} \, \nu^{1/2})^{-1} \, m(E)] \tag{10}$$

where $C_{tot}^*$ is the total analytical concentration of metal in solution. Substitution of eqns. (8) and (10) into the Nernst equation yields a wave of height proportional to $C_{tot}^*$, shifted from the wave observed for a "free" metal ion

$$E = E_{1/2}^R + RT(nF)^{-1} \ln [(m^* - m(E))/(m(E))^{-1}] + RT(nF)^{-1} \ln (1 + K^{-1}) \tag{11}$$

so that, using the half-wave point on the semi-integral, or at the peak maximum on the semiderivative wave

$$\Delta E_{1/2} = E_{1/2,\,\text{free}} - E_{1/2,\text{complexed}} = RT(nF)^{-1} \ln (1 + \beta_L[X]^L) \qquad (12)$$

Equation (12) 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

$$[MX_L^{(n-p)^+}][M^{n+}]^{-1} = K \qquad (13)$$

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

$$\Delta E_{1/2} = RT(nF)^{-1} \ln F_o(X) \qquad (14)$$

where $F_o(X)$ is defined by: $F_o(X) = 1 + \beta_1[X] + \beta_2[X]^2 + \beta_3[X]^3 + \cdots$. This expression is identical to that found by DeFord and Hume for an analogous situation in classical polarography, where the diffusion layer is renewed [14].

*Case 3, Quasi-lability.* Here $k$ is finite, and dependent upon the scan rate. One can often fit both $k$ and $K$ to the results of a number of runs, analogously to the method used by Carney [15] for nitroloacetic acid complexes of Cd and Pb, 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 semi-integral and semidifferential waves, and their variation with scan rate. Labile complexes will show "normal" semi-integral and semidifferential waves, shifted from the "free"-ion position, while inert complexes will not shift, but will decrease in height. Quasilabile complexes will show a broadening of the semiderivative peak into a waveform somewhat similar to that of a normal l.s.v. wave; this effect will be more pronounced with increasing scan rate.

*Anodic stripping voltammetry using linear scans (a.s.v.)*

The same equations for linear scan voltammetry apply to linear scan a.s.v. anodic stripping voltammetry provided that 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 a.s.v., the boundary conditions that must be met are that : (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 homogeneous within the mercury drop; (iii) the concentration of oxidized species in solution must be small compared to the con-

centration 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 a.s.v., 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 l.s.v. For labile complexes, the DeFord—Hume relation applies to convolution a.s.v.

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

## EXPERIMENTAL

### Reagents

For the l.s.v. runs, reagent-grade $NaClO_4$, $Cd(NO_3)_2$, $Na_2EDTA$, and $NaCl$ were used as received. The pH of the solutions was adjusted with reagent-grade perchloric acid. Solutions for a.s.v. study were prepared by electrolysing filtered solutions of reagent-grade $NaClO_4$ and $NaCl$ at $-1.5$ V (vs. s.c.e.) 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 $NaClO_4$ solutions were added to 25 ml of the water, plated at the h.m.d.e. for 20 min at $-1.00$ V (vs. s.c.e.), and subsequently stripped. The lead nitrate used was reagent grade, added just before the a.s.v. scans with an Eppendorf pipette utilizing pre-leached tips. The pH for the a.s.v. runs was adjusted with ultrapure perchloric acid (Ventron).

### Equipment 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 a.s.v. experiments, using Transistar-grade nitric acid (Mallinckrodt). The working electrode was a PAR 9323 h.m.d.e., containing triply-distilled mercury, precleaned by passage through a pinhole. The reference electrode was an Ag/AgCl electrode with a 1.0 M $NaClO_4$/0.1 M $NaCl$ bridge solution; the potential of this electrode was observed to be $+40$ mV vs. s.c.e., for the l.s.v. experiment, and $+44$ mV for the a.s.v. 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 a.s.v. runs.

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 30K 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 a.s.v. runs.

*Computer programs*

Control of the l.s.v. and a.s.v. 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 semi-integration by a FORTRAN program employing the method of Huber [17], as given by Nicholson and Olmstead [18]. The FORTRAN program then numerically differentiated the semi-integral wave to produce the semiderivative wave. Potential shift vs. ligand concentration curves were analyzed by 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*

For the complexation with l.s.v. studies, solutions of NaCl were made up to an ionic strength of $0.99 \pm 0.01$ with $NaClO_4$, and cadmium nitrate was added to make the final solutions $1.2 \times 10^{-4}$ M in $Cd^{2+}$. The pH was adjusted with perchloric acid to 5.00, and the solution was degassed. Ten l.s.v. scans were taken from $-0.400$ to $-0.900$ V (vs. Ag/AgCl), 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 peak shape of the CdEDTA wave were done with a solution containing $10^{-4}$ M $Cd^{2+}$ and $10^{-2}$ M $Na_2EDTA$, adjusted to pH 4.0 with perchloric acid. The scan rate was varied, and the data taken as before.

The a.s.v. studies of metal complexation used purified solutions of NaCl and $NaClO_4$, of total ionic strength $2.22 \pm 0.3$, to which enough lead nitrate was added to give a final $Pb^{2+}$ concentration of $4.4 \times 10^{-7}$ M (insuring that the $K_{so}$ ($1.0 \times 10^{-5}$) for lead chloride would not be exceeded) and the pH adjusted to 4.00. The solutions were degassed, then stirred for 15 s at a potential of $-0.131$ V (vs. Ag/AgCl) to establish a reproducible flux. The potential was changed to $-1.000$ V and held for 600 s; 6 s before the end of the plating period, stirring was halted. The potential was changed to the rest potential of $-0.800$ V vs. s.c.e., where it was held for 15 s to insure a homogeneous amalgam. Stripping then took place at a rate of $1.00$ V s$^{-1}$,

and the resultant voltammogram was recorded, after which the potential was held at —0.135 V for 60 s to remove all remaining lead from the drop. The potential was then changed to the rest potential and held there for 15 s, and a second stripping voltammogram was performed and recorded. Both this background scan and the a.s.v. scan were stored on disk. Subsequent processing began with the numerical subtraction, point by point, of the background scan from the a.s.v. scan to remove capacitative and other background currents [19]. The rest of the processing took place as in the l.s.v. scans.

The precision in obtaining half-wave potentials was observed to be about 0.3 mV; in changing plating times from 60 s to 600 s during some preliminary studies for the a.s.v. runs, the shift (ca. 0.3 mV) of peak potential with the logarithm of the plating time could be distinguished, as predicted by pseudo-polarographic theory [20, 21].

## RESULTS AND DISCUSSION

### Scan rates

A sample l.s.v. scan and the resulting semiderivative are shown in Fig. 1. For these scans, 512 data points were taken, with the maximum available scan rate (100 V s$^{-1}$) 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. A.s.v. scan rates were limited to below 20 V s$^{-1}$ to obtain reproducible background-subtracted waves. Figure 2 shows the a.s.v. and background scans, and also illustrates the resulting semiderivative. Removal of the larger background currents in a.s.v. is necessary to obtain well-shaped semiderivatives at moderate scan rates.

Effects due to the sphericity of the electrode have been observed by
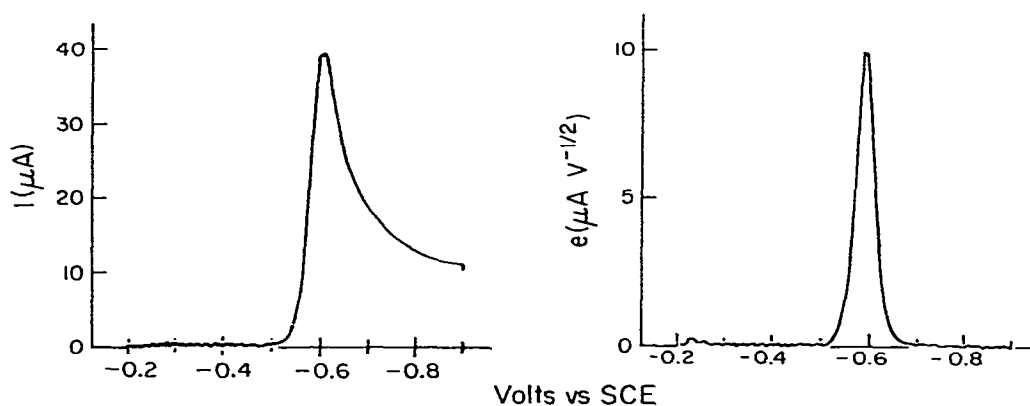
Fig. 1. Linear scan voltammetry wave for cadmium and its resulting semiderivative wave. Supporting electrolyte is 1 M KNO$_3$.
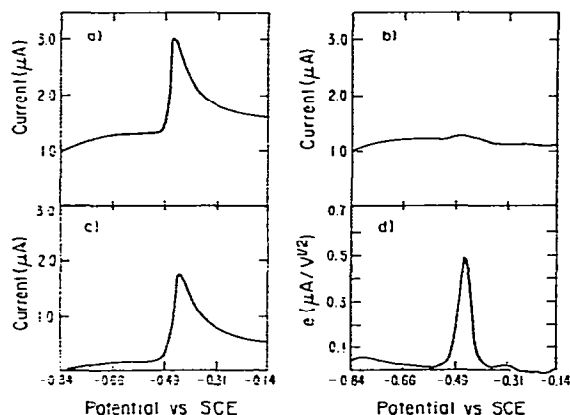
Fig. 2. Numerical generation of semiderivative wave in anodic stripping voltammetry. (a) A.s.v.; (b) background scan; (c) background-subtracted wave; (d) resulting semiderivative wave.

others in convolution potential voltammetry [6]. Because the scan rates used here are relatively fast, relatively small effects on the semi-integral caused by electrode sphericity may be expected, 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. A series of experiments were performed 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. The data have therefore not been corrected 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 [22]. In the studies of cadmium and lead, widths of 45.6 mV for cadmium and 45.5 mV for lead were observed, indicating a good degree of reversibility. Analysis of the raw l.s.v. and a.s.v. scans also indicated both systems to be reversible at the scan rates used for the 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 Fig. 3. The cadmium—EDTA system, however, was observed to be quasi-labile in that the shape of the semiderivative peak was strongly dependent upon the scan rate, as predicted by eqns. (7) and (8). This dependence is illustrated in Fig. 4. For scan rates below 200 mV s$^{-1}$, symmetric semiderivative waves were obtained for the system, indicating that the complex is somewhat labile. Studies of this complex have shown that the rate constant for dissociation of CdEDTA is 10.8 s$^{-1}$ [23].
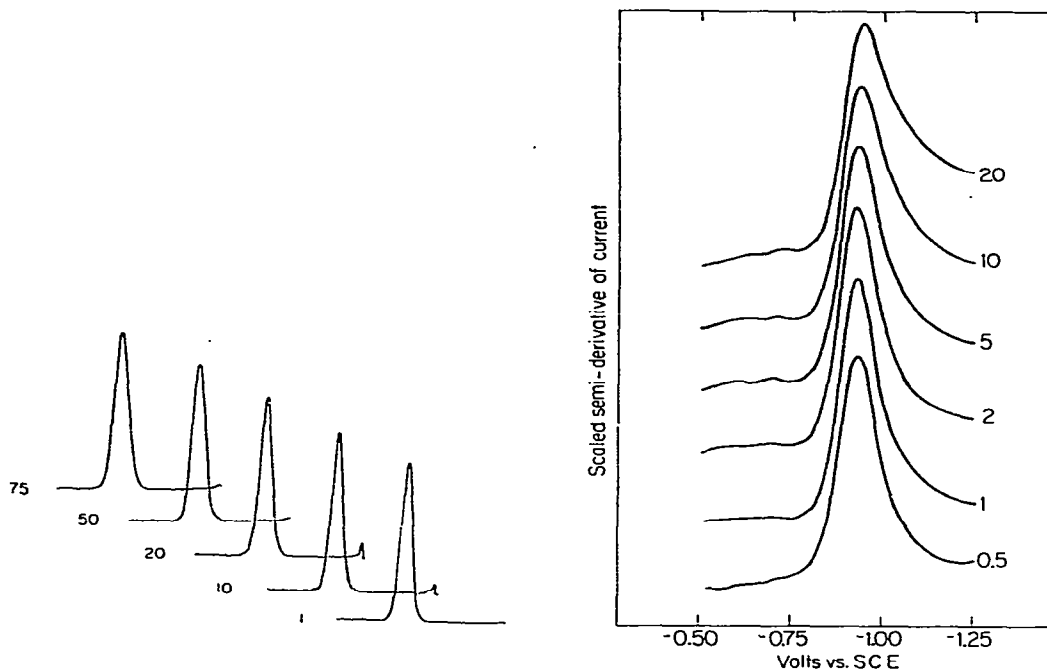
Fig. 3. Peak-shape dependence of the semiderivative wave for cadmium in chloride on scan rate. The numbers on the waves represent scan rate in V s$^{-1}$.

Fig. 4. Peak-shape dependence of the semiderivative wave for cadmium in EDTA on scan rate. The numbers on the waves represent scan rate in V s$^{-1}$.

It should be noted that the ability to scan rapidly is a distinct advantage of the numerical generation of semi-integral 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 $CdCl_x^{2-x}$ and $PbCl_x^{2-x}$ 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. Polynomials used were weighted with simple $1/F_0$ functions as described by Momoki et al. [24] and Varga [25], but unweighted fits were also attempted. 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

TABLE 1

Potential shifts and DeFord—Hume functions for cadmium in chloride[a]

| $[Cl^-]$ (M) | $E_p(V)$[b] | $\Delta E_{1/2}$(mV) | $F_0$ | $F_1$ | $F_2$ | $F_3$ |
|---|---|---|---|---|---|---|
| 0 | —0.6175 | 0 | — | — | — | — |
| 0.107 | —0.6375 | —18.2 | 4.23 | 30.3 | 28.0 | — |
| 0.191 | —0.6429 | —25.4 | 7.47 | 34.0 | 35.3 | — |
| 0.301 | —0.6504 | —32.9 | 13.5 | 41.9 | 48.4 | — |
| 0.398 | —0.6547 | —37.2 | 19.0 | 45.4 | 45.6 | 42.8 |
| 0.481 | —0.6588 | —41.3 | 26.3 | 52.7 | 52.8 | 50.4 |
| 0.588 | —0.6625 | —45.0 | 35.3 | 58.4 | 53.0 | 41.6 |
| 0.703 | —0.6665 | —49.0 | 48.4 | 67.5 | 57.3 | 40.9 |
| 0.783 | —0.6699 | —52.4 | 63.4 | 79.7 | 67.0 | 49.1 |
| 0.995 | —0.6758 | —58.3 | 101 | 100.7 | 53.9 | 45.5 |

[a]pH 5.01 ± 0.05; I = 0.99 ± 0.01 M; sensitivity 10 $\mu$A/full scale; scan rate 1.0 V s$^{-1}$, drop radius 0.61 mm; T = 20.0 ± 0.9°C. [b]Potential relative to the Ag/AgCl electrode.

TABLE 2

Potential shifts and DeFord—Hume functions for lead in chloride[a]

| $[Cl^-]$ (M) | $E_p(V)$[a] | $\Delta E_{1/2}$(mV) | $F_0$ | $F_1$ | $F_2$ | $F_3$ |
|---|---|---|---|---|---|---|
| 0 | —0.4156 | — | — | — | — | — |
| 0.207 | —0.4338 | —18.2 | 4.23 | 15.6 | 15.7 | — |
| 0.464 | —0.4484 | —32.8 | 13.4 | 26.8 | 31.2 | 35.2 |
| 0.691 | —0.4568 | —41.2 | 26.1 | 36.4 | 34.8 | 35.2 |
| 0.895 | —0.4651 | —49.5 | 50.4 | 55.2 | 48.0 | 41.9 |
| 1.13 | —0.4717 | —56.1 | 84.9 | 73.8 | 54.0 | 38.3 |
| 1.60 | —0.4828 | —67.2 | 11.6 | 127 | 71.8 | 38.3 |
| 1.85 | —0.4880 | —72.4 | 206 | 167 | 83.6 | 39.2 |
| 2.04 | —0.4907 | —75.6 | 309 | 195 | 89.3 | 38.6 |
| 2.26 | —0.4949 | —79.3 | 533 | 235 | 98.7 | 39.0 |

[a]pH 3.99 ± 0.06; I = 2.22 ± 0.04 M; sensitivity 1.0 $\mu$A/full scale; drop radius 0.58 mm, scan rate 1.0 V s$^{-1}$; T = 20.0 ± 0.5° C. [b]Potential is relative to the Ag/AgCl electrode.

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—NaClO$_4$ electrolytes could be found. Other work on these systems is compared with the present 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

TABLE 3

Stability constants for cadmium chloride complexes

| Method | Temp. | Medium | Log $\beta_n$ | Ref. |
|---|---|---|---|---|
| Differential pulse polarography | 25 | $NaClO_4$ (1 M) | $\beta_1$ 1.34 $\beta_2$ 1.75 $\beta_3$ 1.49 | 26 |
| Potentiometry | 25 | $NaClO_4$ (1 M) | $\beta_1$ 1.33 $\beta_2$ 1.69 $\beta_3$ 1.53 | 26 |
| Polarography | 25 | $NaClO_4$ (1 M) | $\beta_1$ 1.35 $\beta_2$ 1.7 $\beta_3$ 1.5 | 27 |
| Polarography | 25 | $NaClO_3$ (0.76 M) | $\beta_1$ 1.46 $\beta_2$ 1.83 $\beta_3$ 1.96 | 27 |
| Convolution potential voltammetry | 20 | $NaClO_4$ (1 M) | $\beta_1$ 1.44 ± .08 $\beta_2$ 1.46 ± .05 $\beta_3$ 1.66 ± .03 | This work[a] |

[a]Multiple regression coefficient = 0.996.

TABLE 4

Stability constants for lead chloride complexes

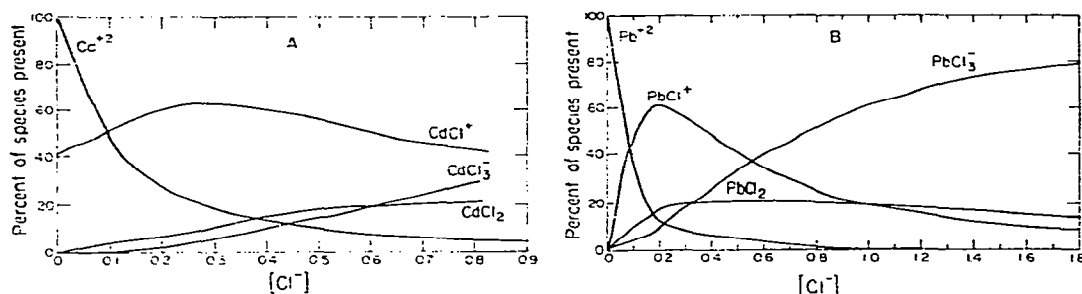| Method | Temp. | Medium | Log $\beta_n$ | Ref. |
|---|---|---|---|---|
| Potentiometry | 25 | 3 M ($NaClO_4$) | $\beta_1$ 1.05 $\beta_2$ 1.51 $\beta_3$ 1.83 | 28 |
| Potentiometry | 25 | 3 M ($NaClO_4$) | $\beta_1$ 1.16 $\beta_2$ 1.7 $\beta_3$ 1.97 $\beta_4$ 0.7 | 28 |
| Cyclic voltammetry | 23 | 0.7 M ($KNO_3$) | $\beta_1$ 0.96 | 29 |
| Polarography | 25 | 3 M | $\beta_1$ 1.17 ± .03 $\beta_2$ 1.7 ± .1 $\beta_3$ 1.4 ± .2 $\beta_4$ 1.2 ± .2 | 27 |
| Convolution potential voltammetry | 20 | 2.22 M ($NaClO_4$) | $\beta_1$ 1.09 ± .18 $\beta_2$ 1.02 ± .10 $\beta_3$ 1.59 ± .01 | This work[a] |

[a]Multiple regression coefficient = 0.999.

Fig. 5. Species distribution of cadmium (A) and lead (B) in chloride media as a function of chloride concentration. pH 5.00, $K_{SO}$ (PbCl$_2$) = 1.0 × 10$^{-5}$, I = 1.00 for Cd$^{2+}$, I = 2.22 for Pb$^{2+}$.

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 quasi-labile systems.

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