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MASTER

AN EQUATION FOR THE ANODIC STRIPPING
CURVES OF THIN MERCURY-FILM ELECTRODES

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ABSTRACT

A simple, but experimentally attainable model is used to derive the current-potential equation for anodic stripping from thin mercury-film electrodes under conditions of a linear potential scan. The magnitude of the mathematical approximations is evaluated and the model is demonstrated to be valid. The important features of this type of electrode are high sensitivity and very high resolution of current peaks.

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In one of the first descriptions (2) of the technique of trace analysis by anodic stripping voltammetry, a linear potential scan was used with a mercury plated, platinum microelectrode. This type of electrode has not received nearly as much attention as the hanging mercury drop electrode in the further development of stripping analysis. It has been reported that mercury plated electrodes are nonreproducible (2, 7), or at best require more care in maintenance and operation than a hanging mercury drop. There is also the strong possibility that interference will be found due to intermetallic compound formation, perhaps in the mercury layer or at the interface between the support metal and the mercury. It has been suggested (4) that this is the cause of the lack of reproducibility.

In spite of these difficulties with mercury plated electrodes, there is a basic advantage in their use. Sensitivity of a microelectrode in anodic stripping is closely related to its geometry; a figure of merit for any design is the surface to volume ratio of the mercury. On this basis, a sphere is the least efficient form and a very thin, unsupported film of mercury approaches the imaginary ideal. Within the limits of this point of comparison, mercury plated metals would certainly present an improvement over a hanging drop.

In a recent article (12) de Vries and van Dalen presented a detailed solution of the current-potential curve which would obtain with a linear, anodic voltage sweep initiated after deposition of a metal in a thin mercury film. The mathematical solution is complicated by the finite thickness of the mercury; the usual boundary condition of semi-infinite linear diffusion cannot be invoked. Computer analysis of the final equation, which is a non-linear Volterra integral equation of the second kind, was done for representative experimental values. Comparisons with experimental results were said to be in progress. The mathematical description of anodic stripping from this type of electrode is therefore on a par with previous work with hanging mercury drop electrodes; the general equation for the current-potential curve during stripping has been derived (9) and experimentally confirmed with excellent precision (11).

The purpose of this article is to present and substantiate a mathematical model for anodic stripping from mercury-film electrodes under such experimental conditions that broad, simplifying assumptions can be made. The result is a relatively simple equation which describes the current-potential curve and, of more importance, clearly shows the interrelation of experimental parameters.

EQUATION OF THE CURRENT-POTENTIAL CURVE

The model chosen to simplify the mathematical description is illustrated in Figure 1. There are two major departures from the previous treatments of anodic stripping (9, 12):

1. Diffusion in the mercury film is ignored.
2. The solution is stirred.

The first condition requires that the thickness of the mercury film, l , is much less than the diffusion region, δ , in the solution. Experimental values for l are of the order of 10^{-4} cm. The second condition insures that the first condition will hold during nearly the entire process. It is also very convenient to maintain the stirring, which is necessary during the deposition step.

On the basis of this model, a solution is sought for flux out of the mercury film as a function of time. The initial conditions are

$$C_o(x,0) = C_o^{\circ} = \text{solution concentration of metal ion}$$

$$C_R(o) = C_R^{\circ} = \text{metal concentration in mercury after deposition}$$

$$\frac{C_o^{\circ}}{C_R^{\circ}} = \exp \phi (E_i - E'^{\circ}) \quad \phi = nF/RT \quad (1)$$

and the boundary conditions are

$$\frac{C_o(o,t)}{C_R(t)} = \frac{C_o^{\circ}}{C_R^{\circ}} \exp \phi vt \quad (2)$$

$$C_o(\delta,t) = C_o^{\circ}$$

The initial potential, E_1 , is taken as the potential where the current is zero; time, t , is also referred to the same point since the potential scan rate, v , is linear with time. The potential at any time is given by $E = E_1 + vt$. C_R is a function only of time and it is assumed to be uniform through the mercury layer.

Fick's first law, flux = $-D_o \delta C / \delta x$, becomes for this model

$$\frac{d[l(C_R^o - C_R(t))]}{dt} = D_o \frac{C_o(o,t) - C_o^o}{\delta}$$

since the flux is positive and the concentration gradient is negative. Substitution for $C_o(o,t)$ is made from Equation 2 and the result is integrated. Separation of the variables is possible by following standard methods (3). For convenience, the following quantities are defined:

$$\psi = \frac{C_R(t)}{C_R^o}$$

$$y = \phi vt$$

$$H = \frac{D_o C_o^o}{\phi \delta l v C_R^o}$$

The solution for ψ , after evaluation of the integration constant, is differentiated with respect to y to obtain an expression proportional to flux:

$$\frac{d\psi}{dy} = H[\exp(-H \exp y)] [1 + (\exp y) (H - yH - \frac{H^2}{2!} \exp y + \frac{H^2}{2!} \exp y - \frac{H^3}{2.2!} \exp 2 y + \dots - \exp H + H^2 + \frac{H^3}{2.2!} + \dots)]$$

Examination of the contribution of each term of the two series for typical values of H and y , 10^{-2} and 0 to 7, respectively, leads to

$$\frac{d\psi}{dy} = H[\exp(-H \exp y)] [1 - (1 + y H) \exp y] \quad (3)$$

which has an error of less than 1% for $0 \leq y \leq 5.6$ (well beyond the peak anodic current, i_p) due to neglected terms. In view of the uncertainty with which the parameter H can generally be known, one further term can be dropped, leaving

$$\frac{d\psi}{dy} = H [\exp (-H \exp y)] [1 - \exp y] \quad (4)$$

The error here is -4% at the peak current, increasing to -15% when the current decays to $0.25 i_p$. Either of the two above equations can be substituted into the current expression

$$i = nFA\ell C_R^\circ \nu\phi \left| \frac{d\psi}{dy} \right| \quad (5)$$

and the combined equations permit the calculation of the anodic current-potential curve obtained during a linear, anodic potential scan.

A satisfactory solution for the peak anodic current is obtained from Equation 4 by determining y at the maximum value of $d\psi/dy$. This value of y is simply

$$y = \ln [(1 + H)/H] \approx \ln (1/H) \quad (6)$$

and can be substituted in the combination of 4 and 5. Noting that $(1/H) \gg 1$, there results

$$i_p = nFA\ell C_R^\circ \nu\phi/e \quad (7)$$

where e is the base of Napierian logarithms. This equation has an error of -3% due to approximations when $H = 10^{-2}$.

Also of interest is the potential, E_p , at i_p . This is obtained directly from Equation 6 using the Nernst equation (1) after substitution from the definitions of H and y .

$$E_p = E'^\circ + \frac{2.3}{\phi} \log \frac{\delta \ell \nu \phi}{D_o} \quad (8)$$

The following statements summarize the above equations and their implications:

1. Peak current is directly proportional to the initial metal concentration in the mercury. At constant stirring rate with a known deposition time, t_d , the current is therefore directly proportional to the metal ion concentration in solution since $lC_R^0 = D_O C_O^0 t_d / \delta$. It is assumed, of course, that C_O^0 is not appreciably altered by the deposition step. See reference (10) for a discussion of this point.

2. Peak current is directly proportional to potential scan rate. This is an interesting difference from the situation with a hanging mercury drop electrode where the peak current depends upon $v^{1/2}$. De Vries and van Dalen (12) found that i_p was a function of v^α where α was nearly 0.5 at $l = 10^{-2}$ cm. and approached a limiting value of 1 at $l = 4 \times 10^{-4}$ cm. This latter situation is similar to the condition assumed in this treatment: diffusion in the mercury film is negligible.

3. The peak current, as given by Equation 7 is independent of stirring rate, provided that decreases in δ do not cause H to increase beyond the limits noted.

4. The potential of the peak current is independent of concentration terms, all else constant.

5. The potential of the peak current depends upon the logarithm of the scan rate. Experimental variations in δ and l will have only a slight effect on E_p . Also E_p will generally be negative to E'^0 (or $E_{1/2}$ for many systems) since the argument of the logarithm in Equation 8 is almost always less than unity.

6. The anodic current peak occurs over a very narrow potential region. If $H = 10^{-2}$, $E_p - E_i = (120/n)$ mv ($T = 25^\circ$ C.) and current decays to less than 5% of i_p at $(40/n)$ mv beyond E_p .

It is apparent that the peak current has the same analytical significance as in other linear potential scan measurements.

In terms of the equations themselves, the simplifications introduce tolerable, but generally predictable errors. The parameter H embodies the experimental conditions in a simple term, so straightforward selection of conditions can be made. Comparison between calculated and experimental values then is a valid test of the assumptions in the model itself.

EXPERIMENTAL

The electrode used to test these equations was prepared by amalgamation of a nickel wire. Prior to dipping in mercury, the metal surface was cleaned cathodically in a chloride solution, very similar to the technique reported for the preparation of amalgamated platinum electrodes (8). Excess mercury was removed, leaving a typical thickness of 2.8×10^{-4} cm. as determined by weighing. The area of the exposed mercury film was 0.16 cm^2 .

Supporting electrolytes were purified by electrolysis or dithizone extraction until impurity peaks were negligible. Stirring of the cell solution was done with a magnetic bar driven by a synchronous motor. All electronic equipment was of conventional design (1,5). The current-potential curves were traced with an X-Y recorder.

COMPARISON OF EXPERIMENTAL RESULTS WITH CALCULATED VALUES

Typical current-potential curves for cadmium are shown in Figure 2. The points for the curve recorded at $v = 8.5 \text{ mv/sec}$ were calculated from Equations 4 and 5. The apparent thickness of the diffusion layer, δ , was determined by measuring the limiting cathodic current. C_R° was obtained either from E_i or by integration of the cathodic current during the deposition step. The diffusion coefficient was from polarographic measurements (6). Calculated values of current are expected to be low at i_p and beyond. The differences shown in Figure 2 are slightly higher than predicted from the neglected terms. It was found that the differences were related to the amount of excess mercury that collects at the bottom of the vertical wire electrode. A region of relatively thick mercury is formed which understandably decreases i_p and causes tailing.

The proportionality between i_p and cadmium ion concentration is compared in Figure 3 with values calculated from Equation 7. Since constant deposition time and stirring rate were used, C_R^0 in Equation 7 is directly proportional to C_0^0 . The shaded area represents the standard deviation of calculated i_p , largely due to uncertainty of l and δ . The standard deviation of the measured i_p values, which were taken in random order, are indicated by the lines above and below the open circles.

An indication of the departure from the assumed model is given by the dependence of i_p on v . Table I summarizes a series of measurements in terms of ratios of currents. The relation is also evident from Figure 1. Diffusion in the mercury film starts to play a noticeable role for this particular electrode at scan rates of 17.2 mv./sec. and higher. Electrodes were prepared that did not show significant deviation at the highest scan rate in Table I. The value of H decreases with increasing scan rate, so this effect is not due to an increasing error in the approximations.

The negligibility of the effect of stirring rate is indicated by the following peak currents, 16.0 and 16.1 μ amp. measured at respective values of δ of 4.8×10^{-3} and 6.4×10^{-3} cm. Effective values of δ were obtained from cathodic currents. In these measurements the same stirring rate was used during the time of deposition so that the same value of C_R^0 was obtained. Before starting the scan, the stirring rate was changed. Very large values of δ cause a departure from the model in that a linear time independent diffusion region is not maintained. Small values of δ produce errors in both the model and the approximations. The magnitude of these effects was very slight so that stirring rate is only of significance in the deposition step, as it is in all variations of anodic stripping voltammetry. It is certainly a convenience to continue the stirring during stripping. The avoidance of the "rest period" decreases the chance of chemical oxidation of reduced phase by traces of oxygen and other oxidizing impurities.

The peak currents of the measurements given in Figure 3 occurred at a potential of -0.620 ± 0.005 v. vs. AgCl(sat. KCl)/Ag. Thus E_p is a useful qualitative measurement in the same sense as is $E_{1/2}$. However, the provision that the approximations are acceptable must be observed.

In Table I the dependence of E_p on v is noted for the cadmium example. Calculated values of E_p are from Equation 8 with E'^0 taken as the polarographic half-wave potential (6), -0.595 v. vs AgCl(sat. KCl)/Ag.

The resolution of current peaks obtained with this type of electrode is rather remarkable, as shown in Figure 4. This combination of sensitivity and resolution is not matched by any of the other electrodes used with linear scan voltammetry and is perhaps better than A.C. polarography where the width of the peak is strongly dependent upon the transfer coefficient. A comparison between this electrode and the hanging mercury drop electrode is given in Figure 5. So that the conditions would be as close as possible, the stripping curve of the mercury-film electrode was calculated from the experimental data given by Shain and Lewinson (11); extrapolation of the curve was necessary in order to obtain a value for C_R^0 .

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TABLE I

Dependence of Peak Current and Potential on Scan Rate

 $H = 0.34/v$; $8 \times 10^{-5} \text{ M Cd(II)}$, 1 M KCl . 60 sec.deposition time. AgCl(sat. KCl)/Ag Reference Electrode

Scan Rate <u>mv/sec</u>	<u>Peak Current</u>		<u>Potential of Peak Current</u>	
	<u>Calculated</u> <u>ratio</u>	<u>Experimental</u> <u>ratio</u>	$-E_p$ <u>Calculated</u>	$-E_p$ <u>Experimental</u>
1.8	1	1	0.65	0.64
3.5	1.9	1.9	0.64	0.63
8.5	4.7	4.7	0.63	0.63
17.2	9.6	8.7	0.62	0.62
33.9	18.5	16.7	0.61	0.61
78.7	43.7	34.5	0.60	0.60

FIGURE CAPTIONS

Figure 1. Model for anodic stripping from a mercury-film electrode in stirred solution.

Figure 2. Current-potential curves for anodic stripping of Cd after 120 sec. deposition at -0.8 v.; 5×10^{-5} M Cd(II), 1 M KCl. Numbers indicate scan rate. Δ calculated points for curve measured at 8.5 mv./sec., based on $H = 1.6 \times 10^{-2}$

Figure 3. Peak anodic current vs. Cd(II) concentration in 1 M KCl. Deposition at -0.8 v. for 60 sec. Scan rate = 8.5 mv./sec, Shaded area based on standard deviations of δ and λ .

Figure 4. Anodic stripping of a mixture of ions at ca. 10^{-5} M in 1 M KCl after deposition time of 60 sec. Scan rate = 17.2 mv./sec.

Figure 5. Comparison of experimental (11) anodic stripping curve of 10^{-8} Tl(I) in 0.1 M KCl using hanging mercury drop electrode with calculated curve for mercury film electrode based on same data. Scan rate = 33.3 mv./sec.

fig 1

Fig 3

Fig. 4

Fig. 5