ANALYSIS OF THE CYCLIC VOLTAMMOGRAMS ASSOCIATED WITH DEPOSITION OR PRECIPITATION OF THE ELECTROCHEMICAL PRODUCT

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ABSTRACT

A reaction model is presented at cyclic voltammetry in which the whole of the product electrochemically generated is deposited or precipitated on an electrode surface in the forward potential scan and is dissolved in solution in the reverse scan. The boundary value problem corresponding to the reaction model is solved analytically, resulting in an integral equation with two parameters relevant to the adsorption equilibrium and kinetics. The voltamograms in the forward potential scan are composed of a diffusion wave and a surface wave due to adsorbed species. Those in the reverse scan consist of a surface wave for dissolution of the deposit. It is possible to evaluate the equilibrium parameter from variations of the peak current in the forward scan and those of the difference in peak potentials with the potential sweep rate.

INTRODUCTION

Adsorption processes occurring at an electrode surface give rise to complicated voltammetric or polarographic features because they involve not only charge-transfer reactions between non-adsorbed species and between adsorbed species but also cross reactions among adsorbed or non-adsorbed oxidized species and non- or adsorbed reduced species [1,2]. For a relatively simple adsorption–desorption process subject to a Langmuir isotherm, a quantitative treatment has been reported by Wopschall and Shain [3], and it has become a base for the understanding and analysis of adsorption behaviour. Interesting features of cyclic voltammograms are the appearance of a prewave and a postwave. It has been demonstrated [3] that a prewave is observed for strong adsorption of the product whereas a postwave...
appears for strong adsorption of the reactant. Effects of adsorption on the voltammetric waveforms have been comprehensively described in order to help in elucidating the complicated waveforms [2].

We have often observed an electrode reaction which produces a deposit, a sparingly soluble precipitate or a thin film on an electrode surface. A number of reports on such reactions can be found, even recently within a few months in this journal [4-14]. The cyclic voltammograms of this type of reaction are generally composed of a cathodic (anodic) peak with a diffusion tail and a bell-shaped anodic (cathodic) peak due to oxidation (reduction) or stripping of the deposit in the reverse potential scan. Because of the specific features of the cyclic voltammograms, it is readily possible to distinguish this reaction from other redox reactions between soluble species. When an adsorbed product by an electrochemical reaction has such a low solubility that the charge consumed by cathodic (anodic) electrolysis is equivalent to the amount of deposit on the electrode surface, it often forms a multi-layer under conventional experimental conditions. This is exemplified by the anodic deposition of silver sulphate on a silver electrode in a sulphate solution [15, 16]. Then the electrochemical behaviour is not dependent on mass transfer of the product but on the charge-transfer process of the deposit.

In this paper, we present a simple reaction model generating a product so sparingly soluble that most of the product is accumulated in a multi-layer form on the electrode surface without diffusing out to the solution. We further derive an expression for linear sweep or cyclic voltammograms of this model reaction by solving an appropriate boundary value problem involving the adsorption kinetics. This study was promoted by an attempt to elucidate quantitatively the voltammetric behaviour of tris–bipyridine cobalt(II) complex in ammonia buffer solution [14].

REACTION MODEL AND MATHEMATICAL FORMULATION

In Fig. 1, a reaction model is presented in which all the products generated electrochemically are adsorbed on the electrode surface in the positive potential scan and all the adsorbed products are stripped out in the negative scan. The reduced species, R, being soluble, diffuses from the bulk solution to the electrode and is adsorbed on the electrode surface through adsorption kinetics to produce Ra, where \( k_a \) and \( k_d \) are the adsorption and desorption rate constants, respectively. Ra

\[
\begin{align*}
R & \xrightarrow{\text{diffusion}} R_a \\
& \xrightarrow{k_a} Ra \\
& \xrightarrow{k_d} Ra \\
& \xrightarrow{\text{fast}} 0_a
\end{align*}
\]

Fig. 1. Reaction model in which the whole of the product generated electrochemically is deposited on the electrode surface.
is oxidized electrochemically to Oa under the adsorbed state. Since Oa is insoluble, it is accumulated on the electrode surface to yield a deposit as the reaction proceeds. Thus, the amount of Oa on the electrode may be equivalent to the faradaic charge consumed by the anodic electrode reaction. In this reaction mechanism, it is assumed that R is electroinactive in the potential domain of interest so long as it is in a soluble form. When the potential scan is reversed in the negative direction, the deposit is converted into Ra, discharging electricity equivalent to the deposit, and then disappears from the electrode by diffusion. The other possible reaction mechanism satisfying the equivalence of the amount of deposit and the faradaic charge would be an electrochemical reaction of R to O, which produces Oa. Soluble O might diffuse to the solution and hence the amount of deposit might be smaller than the charge. Therefore, a reaction mechanism that can retain the equivalence is well represented by the model in Fig. 1.

It is assumed that the charge-transfer reaction takes place so rapidly that the Nernst equation holds. Thus,

\[ \Gamma_{\text{Oa}} = \Gamma_{\text{Ra}} \exp(\xi) \]  

with

\[ \xi = \frac{nF}{RT}(E - E^\circ) \]  

where \( \Gamma_{\text{Oa}} \) and \( \Gamma_{\text{Ra}} \) are the surface concentrations of Oa and Ra, respectively; \( E \) is the potential; \( E^\circ \) is the formal potential of the charge-transfer reaction between Oa and Ra; \( n \) is the number of electrons transferred and the other symbols have their usual meaning. The rate of the adsorption, \( V \), is expressed by

\[ V = k_s(c_R)_a - k_d \Gamma_{\text{Ra}} \]  

where \( (c_R)_a \) denotes the concentration of R at the electrode surface. When the adsorption reaches equilibrium, we can introduce the following equilibrium constant, \( K \):

\[ K = \frac{[\Gamma_{\text{Ra}}]_\text{eq}}{[(c_R)_a]_\text{eq}} = k_s/k_d \]  

This is Henry's law. \( K \) has the dimension of length. By taking into account the material balance of Oa, Ra and R at the electrode surface, it follows that

\[ \frac{d\Gamma_{\text{Ra}}}{dt} = -i/nF + V \]  

\[ \frac{d\Gamma_{\text{Oa}}}{dt} = i/nF \]  

\[ -f + V = 0 \]  

where \( f \) is the flux of R due to diffusion from the bulk to the electrode, \( t \) is the electrolysis time and \( i \) is the current density defined to be positive as the anodic current. Equation (7) has been derived under the assumption that R is not adsorbed, namely that the surface excess of R does not vary with time, i.e. \( d(c_R)_a/dt = 0 \). In the solution, \( c_R \) obeys the time-dependent diffusion equation, whose solution satisfying the initial condition, \( c_R = c^* \), is given by [17]

\[ (c_R)_a = c^* - (\pi D)^{-1/2} \int_0^t f(u)(t-u)^{-1/2} du \]
where \( c^* \) is the bulk concentration of \( R \) and \( D \) is the diffusion coefficient. The electrochemical technique treated here is linear sweep or cyclic voltammetry. Thus

\[
E = E_i + \nu t
\]

or

\[
\xi = \xi_0 + (nF/RT)\nu t
\]

where \( \nu \) is the potential sweep rate, taken to be positive; \( E_i \) is the initial potential; and \( \xi_0 = (nF/RT)E_i \). When eqns. (9a) and (9b) are applied to the cyclic potential mode instead of the linear sweep mode, \( \nu t \) is replaced by \( \nu(2t_i - t) \) at a given potential \( E_i - nF \phi \). The initial conditions are given by

\[
\Gamma_{Ra} = c^*K \quad \text{at } t = 0
\]

\[
\Gamma_{On} = 0 \quad \text{at } t = 0
\]

We will solve the initial and boundary value problem given by eqns. (1)–(11). Summing eqns. (5), (6) and (7) and integrating the resulting equation by use of conditions (10) and (11) yields

\[
\Gamma_{Ra} + \Gamma_{On} = \int_{0}^{t} f(u) \, du + c^*K
\]

Eliminating \( \Gamma_{On} \) or \( \Gamma_{Ra} \) from eqns. (1) and (12) results in

\[
\Gamma_{Ra} = \left\{ \int_{0}^{u} f(u) \, du + c^*K \right\}/(1 + e^{\xi})
\]

\[
\Gamma_{On} = \left\{ \int_{0}^{u} f(u) \, du + c^*K \right\}/(1 + e^{-\xi})
\]

Inserting eqns. (7), (8) and (13) into eqn. (3) and changing the variables through the relations \( z = \xi + (nF/RT)u \) and

\[
g(\xi) = (RT/Kc^*nF\nu)f(t)
\]

we obtain

\[
1 - p \int_{\xi_i}^{t} g(z)(\xi - z)^{-1/2} \, dz = g(\xi) \Lambda + \left[ 1 + \int_{\xi_i}^{t} g(z) \, dz \right]/(1 + e^{-\xi})
\]

where

\[
p = (nF\nu/\pi RTD)^{1/2} K
\]

\[
\Lambda = k_0 RT/nF\nu
\]

The parameter \( \Lambda \) represents the dimensionless desorption rate constant. The parameter \( p \) denotes the ratio of the amount of \( Ra \) to a supply of \( R \) into the electrode by diffusion because \( p \) can be rewritten as \( (\text{const}) \times [\Gamma_{Ra}]_{eq} \nu/\{[(c_R)_{eq}]_{eq} e^{1/2} \}. Since eqn. (16) is an integral equation of Volterra type [18] with these two parameters, it can be solved formally by successive substitutions [18].
The current to be detected is expressed by eqn. (6). Differentiating eqn. (14) with respect to \( t \), inserting it into eqn. (6) and replacing \( f(t) \) by \( g(\xi) \) through use of eqn. (15), we obtain the expression for the dimensionless current density, \( \phi \):

\[
\phi = (i/nF) (RT/Kc \ast nFv) = C \left\{ 1 + \int_{\xi_i}^{\xi_f} g(z) \, dz \right\} \left[ \text{sech}(\xi/2) \right]^2/4 + g(\xi)/(1 + e^{-i}) \tag{19}
\]

where \( C \) represents 1 and \(-1\) for the positive and the negative scan, respectively. Equation (19) is composed of a surface wave expressed by \([\text{sech}(\xi/2)]^2/4\) and a flux term given by \( g(\xi)/(1 + e^{-i}) \). Furthermore, the surface wave is the sum of the wave due to the adsorbed species initially present on the electrode surface (expressed by \( 1 \) in eqn. 19) and the one due to the species accumulated during electrolysis (expressed by the integral of \( g(z) \)). Here, \( g(z) \) is given by the solution of integral equation (16), which includes both the diffusional flux, \( f \) (eqn. 8), and the adsorption kinetics (eqn. 3).

The above derivation is very similar to the technique employed for work on cyclic voltammetry for electrocatalysis at modified electrodes with very thin films [19]. The similarity is realized if the adsorbed couple is considered to play a role in electrocatalysing \( R \) in solution.

In order to evaluate \( g(\xi) \) numerically, we applied the product-integral method [20] to eqn. (16) by discretizing \( \xi - \xi_i \) into \( k \) divisions with the same width \( h \). Details of the derivation are given in the Appendix. Then \( g(\xi) \) or \( g_k \) is expressed by

\[
g_k = \left\{ 1 - 2h^{1/2}p \left( g_{k-1}/3 + \sum_{j=1}^{k-1} A_{k,j} \right) \right. \\
- \left[ 1 + (h/2) \left( g_{k-1} + \sum_{j=1}^{k-1} (g_j + g_{j-1}) \right) \right]/(1 + e^{-i}) \right\} \\
\times \left[ 1/A + (4/3)h^{1/2}p + (h/2)/(1 + e^{-i}) \right]^{-1} \tag{20}
\]

where

\[
A_{k,j} = \left\{ (g_j - g_{j-1})(k - j) + g_j \left\{ (k - j + 1)^{1/2} - (k - j)^{1/2} \right\} \right. \\
- \left\{ (g_j - g_{j-1}) \left\{ (k - j + 1)^{3/2} - (k - j)^{3/2} \right\} /3 \right. \\
\]

By starting with \( g_0 = 0 \) at \( \xi = \xi_i \), \( g_k \) or \( g(\xi) \) at \( \xi = \xi_i + kh \) can be evaluated from successive computation of eqns. (20) and (21). When \( h \) was taken to be less than 0.4, \( g_k \) could be evaluated within 0.3% error. The amount of charge supplied with the anodic current agreed with that in the negative scan after a potential reversal within 1%. This fact confirmed the numerical calculation.
Let us consider the voltammetric behaviour for the four limiting values of \( \Lambda \) and \( p \). Typical voltammograms belonging to these cases are shown in Figs. 2A–2C, where the dashed curves are the dimensionless flux \( g(\xi) \) computed from eqn. (20) and the solid curves are the dimensionless current calculated from eqns. (19) and (20).

(A) For large \( \Lambda \) and small \( p \) (Fig. 2A)

Since \( k_d \) is large in this case, the adsorption–desorption is assumed to be in equilibrium. Then eqn. (16) reduces to

\[
1 - p \int_{-\infty}^{\xi} g(z)(\xi - z)^{-1/2} \, dz = \left( 1 + \int_{-\infty}^{\xi} g(z) \, dz \right) / (1 + e^{-\xi})
\]

This equation can be derived directly by combining eqns. (1), (2) and (4)–(11) with

![Fig. 2. Cyclic voltammograms (solid curves) calculated from eqns. (19) and (20) and the dimensionless flux, \( g(\xi) \), evaluated from eqn. (20) for (\( \Lambda, p \)) = (A) (50, 0.1), (B) (50, 3) and (C) (0.3, 0.1). The bold arrow indicates the direction of the forward potential scan while a thin arrow indicates that of the reverse scan. The dotted curves represent surface waves due to adsorbed species initially present on the electrode surface, which is expressed by \( [\text{sech}(\xi/2)]^2/4 \).](image-url)
\( K = \Gamma_{Ra}(c_R) \), instead of eqn. (3). In other words, eqn. (22) is based on Henry's law. Consequently, \( \Gamma_{Ra} \) should be much smaller than the saturation value. Since Ra is not accumulated on the electrode surface, most of the Ra required for the charge transfer is supplied with the adsorption of R via diffusion. Thus, the overall process may be controlled by diffusion. Indeed, the steady-state approximation of eqn. (5) yields \( \dot{i}/nF = f \), which allows eqn. (8) to be rewritten as

\[
(c_R)_s = c^* - (\pi D)^{-1/2} \int_0^\infty [i(u)/nF](t - u)^{-1/2} \, du
\]  

(23)

This is an expression for the diffusion-controlled current. The reaction looks as if R in solution were electroactive to produce Oa directly. Since the redox couple determining potential is not O/R but Oa/Ra, it is predicted that the peak potential of the diffusion wave may vary with \( K \) or \( p \) according to \( \xi = \ln(\Gamma_{Oa}/K \Gamma_R) \). No matter how much Oa is accumulated on the electrode surface, Henry's law is still valid because it gives the relation between R and Ra rather than that between R and Oa. The anodic current is controlled by diffusion. The species Oa accumulated on the electrode surface yields the cathodic surface wave on the negative scan. It is the behaviour for this case that we are interested in.

(B) For large \( \Lambda \) and large \( p \) (Fig. 2B)

Since \( \Gamma_{Ra} \) exceeds \( (c_R)_s \), the surface wave (dotted curve) due to Ra initially present on the electrode surface contributes largely to the voltammogram. Curves of \( g(\xi) \) exhibit a diffusion tail at sufficiently positive and negative potentials because diffusion of R is a source of Ra. Too large values of \( p \) may cause divergences from Henry's law.

(C) For small \( \Lambda \) and small \( p \) (Fig. 2C)

Small values of \( \Lambda \) correspond to sluggish adsorption and hence make \( g(\xi) \) kinetically controlled. As a result, a sigmoidal portion with a plateau appears in the curve of \( g(\xi) \). In the reverse scan, \( g(\xi) < \phi(\xi) \) in the region \(-8 < \xi < -2\), because the desorption rate is slower than the potential sweep rate. Thus the amount of Ra reaches a maximum after passing through the cathodic peak of \( \phi(\xi) \).

(D) For small \( \Lambda \) and large \( p \) (similar to Fig. 2C)

The values of \( \Gamma_{Ra} \) are larger than those in case (C). Hence the ratio of \( g(\xi) \) to \( [\text{sech}(\xi/2)]^2/4 \) is smaller than that for case (C), being an extremely small diffusional flux.

From the above discussion, case (A) involves an interesting voltammogram, and hence the discussion is mainly directed to the voltammogram at small values of \( p \) and large values of \( \Lambda \) or infinite \( \Lambda \).
In Fig. 3, the dimensionless anodic peak current, \( \Phi_{pk} \), multiplied by \( p \), i.e. \( p\Phi_{pk} = (i/nFc^*)(RT/\pi nFvD)^{1/2} \), is plotted against \( p \) for several values of \( \Lambda \). For very large values of \( \Lambda \), \( p\Phi_{pk} \) has a linear relation to \( p \) with a slope of 0.22 and an intercept of 0.23. This relation can be rewritten as

\[
\frac{i_{pk}}{v^{1/2}} = 0.22 \left( \frac{nF^2}{RT} \right) K^* v^{1/2} + 0.408 nFe^* (DnF/RT)^{1/2}
\]

where \( i_{pk} \) is the peak current density. The plot of \( \frac{i_{pk}}{v^{1/2}} \) against \( v^{1/2} \) provides values of \( D \) from the intercept and values of \( K \) from the slope. Values of \( K \) determined by this plot may be helpful in imagining features of the adsorption because \( K \) represents a thickness. If 0.22 \( K^* \) and 0.408 in eqn. (24) are replaced by \( \Gamma \) and 0.446 [21], eqn. (24) is equivalent to the sum of the surface wave with surface concentration \( \Gamma^* \) and the diffusion wave [21]. Slight differences in the numerical coefficients are ascribed to the term of the integral of \( g(z) \) in eqn. (19), i.e. the effect of the accumulation of \( Oa \). Equation (24) is valid for \( \Gamma \log(p) > 5 \). When the values of \( \Lambda \) are small, the effect of adsorption kinetics is noticeable.

In Fig. 4, the anodic and cathodic peak potentials are plotted against \( \log(p) \) for several values of \( \Lambda \). The anodic peak potential shifts positively with a decrease in \( p \) when the values of \( \Lambda \) are large. For \( \Gamma > 3 \) and \( p < 1 \), the anodic peak potential, \( E_p^a \), is expressed approximately by

\[
E_p^a = E^o^* + (RT/nF) \left[ -2.3 \log(p) + 1.04 \right]
\]

This indicates that the peak potential shifts positively by \( 60/n \) mV at 25°C with a one-order decrease in \( p \) or a hundred-fold increase in \( v \), as has been discussed in the section relevant to Fig. 2A. Plots of \( E_p^a \) against \( \log(v) \) may fall on a straight line with a slope of \( 30/n \) mV at 25°C and an intercept of \( (30/n) \log(0.2(nF/RTD)K^2)/mV \), from which \( K \) can be estimated. As the values of \( \Lambda \) decrease, the variations of the anodic peak potential with \( p \) become small and they are insignifi-
cant for $\Lambda < 0.3$. On the contrary, the cathodic peak potential does not vary with $p$
and ranges from 0 to 0.6($RT/nF$) or 15/n mV at 25$^\circ$C when the potential is
reversed at $\xi = -15$. The cathodic peak potential shifts negatively as the reverse
potential becomes more positive. This dependence may be ascribed to the time of
the anodic electrolysis or the amount of the deposit rather than variations of
potentials. A large amount of deposit enhances the cathodic surface wave and
consequently the ideal bell-shaped surface wave is undistorted by the anodic
diffusion tail. In order to estimate $E^{\circ'}$ from the anodic peak potential, it may be
necessary to stop the potential sweep temporarily at an appropriate positive
potential. $E^{\circ'}$ thus evaluated may be similar to values determined by extrapolation
of $E^{\circ}$ to log($p$) = 0 in eqn. (25).

In conclusion, the reaction model in Fig. 1 provides an anodic diffusion wave
overlapped with the anodic surface wave and a cathodic surface wave due to
dissolution of the deposit. The amount of charge accumulated in the positive scan is
identical to that dissolved in the negative scan. When the adsorption–desorption is
in equilibrium, the equilibrium constant, being a significant factor of estimating the
extent of adsorption, can be estimated from the variations of the anodic peak
current and the peak potential with the potential sweep rate.

APPENDIX

The derivation of eqn. (20) from eqn. (16) is described in this appendix. We
divide $\xi - \xi_i$ into $k$ small divisions with the same width $h$ and let $g(\xi_i - jh)$ be $g_j$. It
is assumed that $g(\xi)$ is so smooth that $g(\xi)$ for $\xi_i + (j - 1)h < \xi < \xi_i + jh$ can be
approximated as an interpolation between $g_{j-1}$ and $g_j$. Then we have

$$ I = \int_{\xi_i}^{\xi_f} g(z)(\xi - z)^{-1/2} \, dz $$

$$ = \sum_{j=1}^{k} \int_{\xi_i}^{\xi_i + jh} \left( (g_j - g_{j-1})(\xi - \xi_i - jh)/h + g_j \right) (\xi - z)^{-1/2} \, dz \quad (A1) $$

Carrying out the integration in eqn. (A1) yields

$$ I = 2h^{1/2} \sum_{j=1}^{k} \left[ \left( (g_j - g_{j-1})(k-j) + g_j \right) \left( (k-j+1)^{1/2} - (k-j)^{1/2} \right) \right. $$

$$ \left. - \left( (g_j - g_{j-1})(k-j+1)^{3/2} - (k-j)^{3/2} \right)/3 \right] \quad (A2) $$

Applying the same procedure to the integral of $g(\xi)$, we have

$$ \int_{\xi_i}^{\xi_f} g(z) \, dz = \left( h/2 \right) \sum_{j=1}^{k} (g_j + g_{j-1}) \quad (A3) $$

Inserting eqns. (A2) and (A3) into eqn. (16) and solving the resulting equation with
respect to $g_{\xi}$ yields eqn. (20).
REFERENCES