GENERAL EXPRESSION OF THE LINEAR POTENTIAL SWEEP
VOLTAMMOGRAM IN THE CASE OF DIFFUSIONLESS
ELECTROCHEMICAL SYSTEMS

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(Received 6th April 1978; in revised form 15th November 1978)

ABSTRACT
The equation of the linear potential sweep voltammogram is derived for any degree of
reversibility of the electrochemical reaction for the following methods: surface voltammetry
when both the oxidized and the reduced forms are strongly adsorbed, and a Langmuir iso-
therm is obeyed, thin layer voltammetry, and linear potential sweep coulometry. The results
are expressed in one mathematical form valid for the three cases. The transfer coefficient and
the rate constant of the electrochemical reaction can be deduced from an experimental study
of the variations of the peak potentials as a function of the sweep rate.

INTRODUCTION
As we have shown previously, the same mathematical formulation can be
used for the following three different linear potential sweep (l.p.s.) methods,
when certain conditions, ensuring in particular that control by diffusion is
absent, are fulfilled: (a) surface l.p.s. voltammetry, when both the oxidized and
the reduced forms are strongly adsorbed, and when a Langmuir isotherm is
obeyed [1-3], (b) thin layer l.p.s. voltammetry, when the sweep rate does not
exceed a certain limit [1,4]; and (c) l.p.s. coulometry [5], when the sweep rate
is small enough.

We have published in previous papers the theory of the reversible [2,6,7] and
totally irreversible [2,8] cases for l.p.s. surface voltammetry, and for a reversible
reaction in the case of l.p.s. coulometry [5]. The equations for the reversible and
completely irreversible reactions in thin layer l.p.s. voltammetry are well known
[4]. The general equation of the voltammogram for any degree of reversibility
has not however been derived yet. Such an equation would be useful for the
determination of the rate constant and of the transfer coefficient of the electro-
chemical reaction, as it is in the case of diffusion l.p.s. voltammetry [9]. (In ref.
10, Srinivasan and Gileadi considered a surface reaction corresponding to physi-
cal conditions different from those of case a; the mathematical formulation is
however the same and they derived the expression of the voltammogram for the
reversible and completely irreversible cases. They also gave a general differential
equation for the current, but only solved it numerically to obtain the shape of
the voltammogram in a few cases.)

We present in this paper a general expression for the voltammograms of the
systems described above, which we will designate as diffusionless systems, there-
by meaning that diffusion does not have to be taken into account in the mathe-
matical treatment of the problem: its only role is to homogenize the concentra-
tions in the case of thin layer voltammetry and l.p.s. coulometry. We will dis-
cuss the application of our results to the determination of the rate constant and
of the transfer coefficient of the reaction.

MATHEMATICAL FORMULATION

We shall consider the case of a reduction \( O + ne = R \). The potential \( E \) is given by
\[
E = E_i + vt
\]
\( v \) being the algebraic value of the sweep rate in \( V \, s^{-1} \).

(1) Surface voltammetry

We have shown previously \([2,3,6]\) that when a Langmuir isotherm is obeyed,
and when \( O \) and \( R \) are strongly adsorbed, the electrochemical reaction concerns
exclusively the adsorbed molecules, if the coverage is smaller than 1. A surface
standard potential \( E^{\circ} \) can be defined; its value is given by:
\[
E^{\circ} = E^0 - \frac{(RT/nF) \ln(b_O/b_R)}{\gamma}
\]
\( b_O \) and \( b_R \) being the adsorption coefficients of \( O \) and \( R \). We can thus write:
\[
i = nFAk_s\left\{\Gamma_O \exp[-\alpha nF(E - E^{\circ})/RT] - \Gamma_R \exp[(1 - \alpha)nF(E - E^{\circ})/RT]\right\}
\]
\( \Gamma_O + \Gamma_R = \Gamma_T \)  \hspace{1cm} (4)
\[i = -nFA \Gamma_O \frac{d\Gamma_O}{dt} \] \hspace{1cm} (5)
\( k_s \) is the rate constant of the electrochemical reaction (s\(^{-1}\)), \( \Gamma_O \) and \( \Gamma_R \) are the
surface concentrations of \( O \) and \( R \) (mol cm\(^{-2}\)), \( \Gamma_T \) is their constant sum, and \( A \) is
the area (cm\(^2\)). \( n, F, \alpha, R \) and \( T \) have their usual significance. \( i \) is here expressed
in Ampères.

The current can be defined by the dimensionless function
\[
\psi = \frac{i}{(F^2/RT)n^2aT^A}\Gamma_T = m[(\Gamma_O/\Gamma_T)\eta^{-\alpha} - (\Gamma_R/\Gamma_T)\eta^{1-\alpha}]
\] \hspace{1cm} (6)
with
\[m = \frac{(RT/F)(k_s/nv)}{\gamma} \] \hspace{1cm} (7)
\( \eta \) being defined by eqn. (12).

(2) Thin layer voltammetry

We have, if the sweep rate is so slow that the concentrations are uniform
throughout the cell:
\[
i = nFAk_{s,b}\left\{c_O \exp[-\alpha nF(E - E^0)/RT] - c_R \exp[(1 - \alpha)nF(E - E^0)/RT]\right\}
\]
\( c_O + c_R = c_T \) \hspace{1cm} (9)
\[i = -nFVdc_O/dt \] \hspace{1cm} (10)
\( k_{s,h} \) is the heterogeneous rate constant (cm s\(^{-1}\)), \( c_O \) and \( c_R \) are the concentrations (mol cm\(^{-3}\)), \( c_T \) is their constant sum, and \( V \) is the volume (cm\(^3\)).

(3) L.p.s. coulometry

Equation (8) is still valid, if \( c_O \) and \( c_R \) are replaced by \( c_{O}^s \) and \( c_{R}^s \), the concentrations at the surface of the electrode. Equations (9) and (10) still hold, \( c_O \) and \( c_R \) being the concentrations in the bulk of the solution. If the potential sweep is slow enough, \( c_O = c_{O}^s \) and \( c_R = c_{R}^s \), so that the problem is described by eqns. (8) to (10). In both cases, the current can be defined by the dimensionless function:

\[
\psi = \frac{i}{(F^2/RT)n^2vVc_T} = m[(c_O/c_R)\eta^{-\alpha} - (c_R/c_T)\eta^{1-\alpha}]
\]

with \( m = (RT/F)(Ak_{s,h}/Vn) \), \( \eta \) being defined by eqn. (12).

(4) General formulation of the problem

Let us designate by \( x_O, x_R \) and \( x_T \) the values of \( \Gamma_O \) or \( c_O, \Gamma_R \) or \( c_R, \Gamma_T \) or \( c_T \), by \( k \) the value of \( k_s \) or \( Ak_{s,h}/V \), and let

\[
\eta = \exp[(nF/RT)(E - E')]
\]

From the two systems of eqns. (1), (3--5) or (1), (8--10), we obtain the differential equations:

\[
d(x_O/x_T)/d\eta + m(1 + \eta)\eta^{-(1+\alpha)}(x_O/x_T) = m\eta^{-\alpha}
\]

\[
d(x_R/x_T)/d\eta + m(1 + \eta)\eta^{-(1+\alpha)}(x_R/x_T) = m\eta^{-(1+\alpha)}
\]

By solving one of these equations, we obtain the value either of \( x_O/x_T \) or of \( x_R/x_T \), and the value of \( \psi \) can be calculated by introducing it into eqn. (6) or (11), taking into account eqns. (4) or (9). The integration constant is determined by expressing the condition that when \( m \to 0 \), i.e. when the reaction becomes totally irreversible, the expression of \( \psi \) must be identical to the expression already calculated for this case [2,8]. This condition can be expressed by introducing the following approximations in the general expression of \( \psi \):

when \( m \to 0 \), for the cathodic curve \( \eta^{1-\alpha} \ll \eta^\alpha \) and \( \eta << 1 \), and for the anodic curve \( \eta^{-\alpha} << \eta^{1-\alpha} \) and \( \eta >> 1 \). The result of the calculations shows that it is more convenient, in order to obtain solutions in which the integration constant is zero, to start from eqn. (13) for the anodic curve and from eqn. (14) for the cathodic curve.

RESULTS AND DISCUSSION

(1) General expression of \( \psi \)

Proceeding as indicated above, we obtain for the cathodic curve:

\[
\psi_c = mn^{1-\alpha}(1 - m(1 + \eta)\exp[f(\eta)]) \int_0^\eta z^{-(1+\alpha)} \exp[-f(z)]dz
\]

and for the anodic curve:

\[
\psi_a = -mn^{-\alpha} \left[ \eta - m(1 + \eta)\exp[f(\eta)] \int_0^\eta z^{-\alpha} \exp[-f(z)]dz \right]
\]
with
\[ f(\eta) = \left[ \frac{m}{\alpha(1 - \alpha)} \right] \eta^{-\alpha} [1 - \alpha(1 + \eta)] \] (17)

\( f(z) \) represents the same function, with \( z \) replacing \( \eta \). \( m \) is negative for the cathodic curve and positive for the anodic curve.

(2) Limiting form when \( m \to 0 \) (totally irreversible reaction)

As stated above, when \( m \to 0 \), \( \eta^{1-\alpha} \ll \eta^{-\alpha} \) and \( \eta \ll 1 \) for the cathodic curve. The integration becomes possible and yields the simple equation:

\[ \psi_c = m\eta^{-\alpha} \exp(m\eta^{-\alpha}/\alpha) \] (18)

which is identical to the equation derived earlier [2,8]. (In refs. 2 and 8, the absolute value of \( m \) was used, instead of the algebraic value.)

In the same way, when \( \eta^{-\alpha} \ll \eta^{1-\alpha} \) and \( \eta \gg 1 \), we obtain from (16):

\[ \psi_a = -m\eta^{1-\alpha} \exp[-m\eta^{1-\alpha}/(1 - \alpha)] \] (19)

\( \psi_c \) passes through a maximum when \( \eta^{-\alpha} = -\alpha/m = \alpha/\lvert m \rvert \), so that the peak potential \( E_p \) is given by:

\[ E_p = E^i - \left( \frac{RT}{\alpha nF} \right) \ln[\alpha/\lvert m \rvert] \] (20)

\( E^i \) being equal to \( E^{i0} \) or \( E^0 \).

The maximum of \( \psi_a \) is obtained when: \( \eta^{1-\alpha} = (1 - \alpha)/m \), whence

\[ E_p = E^i + \left( \frac{RT}{(1 - \alpha)nF} \right) \ln[(1 - \alpha)/m] \] (21)

(3) Shape of the curves

When \( m \to \infty \) (\( \nu \to 0 \)), both the cathodic and the anodic peaks tend towards the “reversible peaks”, which are symmetrical with respect to the potential axis, and which have a symmetrical shape; the width at mid-height \( \delta_{0.5} \), which becomes independent of \( \alpha \), tends towards 90.6/\( n \) mV [1-3,5-7]. When \( m \to 0 \), the peaks tend towards the “totally irreversible peaks” (eqns. 18 and 19). The width of the cathodic peak is equal to 62.5/\( n \) mV, that of the anodic peak to 62.5/(1 - \( \alpha \))n mV [2,8].

(4) Determination of \( k_s(k_{s,h}) \) and \( \alpha \)

The most interesting experimental quantity is the difference \( \Delta E_p \) between the peak potential of the anodic and cathodic peaks. Figure 1 gives \( n(E_p - E^i) \) as a function of \( 1/m \), calculated from eqns. (15) and (16) by numerical integration (a Hewlett-Packard 9821 A calculator was used), and the corresponding variations of \( n \Delta E_p \) in the limiting case \( (m \to 0, \text{eqns. 20 and 21}) \). It can be seen that, whatever \( \alpha \), the relative error on \( n \Delta E_p \) when the limiting eqns. (18)—(21) are used instead of the general eqns. (15) and (16) remains smaller than about 2% when \( 1/m \) is larger than about 12 (see also Fig. 2). An experimental criterion has to be found, since \( m \) is not known: as shown in Fig. 1, the condition \( 1/m > 12 \) can be replaced by the experimental condition \( \Delta E_p > 200/n \) mV. Either \( n \) is known (e.g. for a 1e process) or it can be deduced from the width of the peak when \( \nu \to 0 \), as indicated above.
Fig. 1. $n(E_{p,c} - E^l)$ and $n(E_{p,a} - E^l)$ as a function of $1/m$. (Points) General eqns. (15) and (16). (Curves) Limiting eqns. (20) and (21). (1) $\alpha = 0.5$, (2) $\alpha = 0.8$.

(A) $\Delta E_p > 200/n$ mV. If values of $\Delta E_p/n$ larger than 200 mV can be obtained experimentally, $\alpha$ and $k$ ($k$ represents $k_s$ or $Ak_{s,h}/V$) can be easily determined by using eqns. (20) and (21). A graph of $E_p = f(\log v)$ yields two straight lines with a slope equal to $-2.3 \frac{RT}{nF}$ for the cathodic peak, and $2.3 \frac{RT}{(1 - \alpha)nF}$ for the anodic peak. Theoretical curves $E_p = f(\log(1/m)) = f(\log v + \log(nF/RTk))$ are shown in Fig. 2. An experimental plot having the form of these curves was given by Angerstein-Kozlowska et al. in a study of the adsorption of nitriles at a platinum electrode [11]. $\alpha$ can be determined from the slope of the straight lines, or also from the difference $\log v_a/v_c = \log m_c - \log m_a = \log[\alpha/(1 - \alpha)]$, or $\alpha/(1 - \alpha) = v_a/v_c$. $\alpha$ can also be calculated from the width of the peak (see above).

$k$ can be calculated with the help of the equation

$$\log k = \alpha \log(1 - \alpha) + (1 - \alpha) \log \frac{RT}{nFv} - \alpha(1 - \alpha)nF\Delta E_p/2.3 RT$$

which is valid for $n\Delta E_p > 200$ mV. It can also be deduced from the values of $v_a$ and $v_c$: according to eqns. (20) and (21), $\alpha/|m_c| = (1 - \alpha)/m_a = 1$ when
Fig. 2. Theoretical variations of \( n(E_p, \sigma - E^\dagger) \) as a function of \( \log(1/m) \) for \( \alpha = 0.7 \).

Fig. 3. Variations of the ratio \( y = |(E_{p,c} - E^\dagger)/(E_{p,a} - E^\dagger)| \) with \( n \Delta E_p \). The value of \( \alpha \) is indicated on each curve.
\[ E - E^i = 0, \] so that:
\[ k = \alpha nFv_e/RT = (1 - \alpha)nFv_a/RT \] (23)

\((B)\) \(\Delta E_p < 200/n\) mV. When the experimental conditions are such that values of \(n\Delta E_p\) smaller than 200 mV can only be attained, e.g. because the upper limit of the sweep rate has been reached, the limiting forms can no longer be used. \(\alpha\) can in principle be determined from the graph \(y = \frac{(E_{p,c} - E^i)/(E_{p,a} - E^i)}{f(v)}\) (Fig. 3), provided that \(E^i\) can be determined by extrapolation of the curves \(nE = f(v)\) (cf. Fig. 1). (In Fig. 3, the curves for \(\alpha > 0.5\) are shown; for \(\alpha < 0.5\) the ratio becomes \(1/y\).) In fact, as shown in Fig. 3, the determination of \(\alpha\) will not be precise, because a small error in the determination of \(E_{p,c}\) and \(E_{p,a}\) will cause a large error on the ratio \(y\). The relative error on \(y\) is
\[ \frac{\delta y}{y} = \frac{\delta (E_{p,c} - E^i)}{(E_{p,c} - E^i)} + \frac{\delta (E_{p,a} - E^i)}{(E_{p,a} - E^i)} \approx \frac{\delta (\Delta E_p)}{\Delta E_p} \]
if we assume in first approximation that \(E_{p,c} \approx E_{p,a}\). The error \(\Delta y/y\), calculated for an absolute error of 1 mV on \(E_p\), is indicated in Fig. 3. According to the result, only a very approximate value of \(\alpha\) can be deduced from the curves. If \(\alpha\)

![Figure 4. Variations of \(n\Delta E_p\) with \(1/m\). (1) \(\alpha = 0.5\), (2) \(\alpha = 0.8\), (3) \(\alpha = 0.85\), (4) \(\alpha = 0.9\).](image-url)
is not too different from 0.5, this will not however be an obstacle to the determination of $k$, as shown below.

Once $\alpha$ is known, the curves given in Fig. 4 can be used to determine $m$, hence $k$. As shown by these curves, when $0.3 < \alpha < 0.7$, the difference $\Delta E_p$ does not depend very much on $\alpha$ (a similar result has been reported in the case of diffusion voltammetry [9]): the relative error on $k$ is at the most about 6% when the curve for $\alpha = 0.5$ is used. Table 1 gives some values of $n\Delta E_p$ as a function of $1/m$ for $\alpha = 0.5$.

**EXPERIMENTAL VERIFICATION**

We have examined the behaviour of a series of molecules having a N=N double bond, benzo(c)cinnoline, phenazine, azobenzene, for which both the oxidized and the reduced forms are strongly adsorbed and follow a Langmuir isotherm when the superficial concentration is small enough [12]. The result of

![Graph](image)

Fig. 5. Voltammograms of benzo(c)cinnoline. (a) 0.4 V s$^{-1}$, (b) 6.67 V s$^{-1}$. Starting potential $-0.65$ V. $c = 3 \times 10^{-6}$ mol l$^{-1}$. 

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**TABLE 1**

<table>
<thead>
<tr>
<th>$m^{-1}$</th>
<th>0.5</th>
<th>0.75</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
<th>3.5</th>
<th>4</th>
<th>5</th>
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<tr>
<td>$n\Delta E_p$/mV ± 0.1</td>
<td>18.8</td>
<td>27</td>
<td>34.8</td>
<td>48.8</td>
<td>61.2</td>
<td>72.2</td>
<td>82.4</td>
<td>91.8</td>
<td>100.6</td>
<td>116.2</td>
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</table>

<table>
<thead>
<tr>
<th>$m^{-1}$</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n\Delta E_p$/mV</td>
<td>130</td>
<td>142.4</td>
<td>153.8</td>
<td>164</td>
<td>173.4</td>
<td>182</td>
<td>190</td>
<td>197.6</td>
<td>204.6</td>
</tr>
</tbody>
</table>
Fig. 6. \((E_p - E_l) = f(\log v)\) for benzo(c)cinnoline.

Fig. 7. (O) Experimental variations of \(E_p\) as a function of \(v\) for benzo(c)cinnoline. The theoretical curve has been calculated for \(\alpha = 0.5\) and \(k_s = 38.9 \text{ s}^{-1}\).
the study of benzo(c)cinnoline at pH 8.70 will be given here as an example. The width of the peak at mid-height tends towards 45 mV when \(v \to 0\), so that \(n = 2\), and the peaks become symmetrical (Fig. 5a). When \(v\) increases the difference between the peak potentials increases (Fig. 5b). Figure 6 gives the variations of \(E_{p,a}\) and \(E_{p,c}\) as a function of \(\log v\). The slope of the two oblique asymptotes is equal to 60 mV/log unit, and they intersect the horizontal asymptote \(E'\) at the same point; both results mean that \(\alpha = 0.5\). The value of \(\alpha\), calculated from the width of the peaks (Fig. 5b) is equal to 0.53. The value of \(k_s\) obtained from eqn. (23) with the values \(v_a = v_c = 1 \text{ V s}^{-1}\) is \(k_s = 38.9 \text{ s}^{-1}\). A comparison of the experimental and theoretical values of \(E_{p,a}\) and \(E_{p,c}\) is shown in Fig. 7.

EXPERIMENTAL

A Tacussel UAP4 unit and GSTP function generator were used for the experiments. The \(i - E\) curves were recorded on a Tektronix R 564B memory oscillograph and photographed. The experiments were carried out in water (Britton-Robinson buffer, supporting electrolyte NaCl 0.1 M).

The temperature was 25°C. The potentials refer to the saturated calomel electrode. The delay time was equal to 6 s.

CONCLUSION

As shown by our results, l.p.s. voltammetry appears as a convenient method for the determination of the characteristics (transfer coefficient and rate constant) of the electrochemical reaction in diffusionless electrochemical systems. The limiting values of the rate constant which can be determined depend on the limiting values of the sweep rate which can be used for each method: from less than 1 mV s\(^{-1}\) to more than 1000 V s\(^{-1}\) for surface voltammetry, very slow scan rates to about 1 mV s\(^{-1}\) for l.p.s. coulometry [5], and about 1 to 10 mV s\(^{-1}\) for thin layer voltammetry [4].

REFERENCES