PULSE POLAROGRAPHY

PART VIII. THEORY FOR ELECTRODE PROCESSES WITH FIRST-ORDER REGENERATION MECHANISMS

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ABSTRACT

A theoretical study of the limiting current in pulse polarography is given for first-order regeneration mechanisms: fractional regeneration and catalytic regeneration (regeneration > 1). Rigorous equations for the current have been derived, taking into account both the expanding plane electrode and the expanding sphere electrode models. In addition, the corresponding asymptotic solutions which show the behavior of the current when the rate constant values are large, have been derived by using the steady-state approximation.

INTRODUCTION

We have shown in this series of papers [1–6] that normal pulse polarography is a suitable technique for the study of electrode processes with chemical reactions coupled to the charge transfer step. Thus, the pulse polarographic responses for the catalytic [1,2], CE [3,4] and ECE [5,6] mechanisms have been obtained. In turn, the theory of regeneration mechanisms has been already proposed for different electrochemical techniques [7–17], although, in pulse polarography this theory has not as yet been developed. Hence, we present in this paper a theoretical study for first-order regeneration mechanisms: fractional regeneration and catalytic regeneration (regeneration > 1). Equations derived in this paper are valid both in the context of the expanding plane electrode and the expanding sphere electrode. In addition, the behavior of the current for large values of the rate constant, has been obtained from the corresponding asymptotic solutions, which have been derived by using the steady-state approximation. The notation/definitions are the same as in our previous papers [4,5].

THEORY

Consider the reaction scheme:

\[ aA + ane^- \rightarrow bB \]

\[ B \rightarrow hA + \text{other products} \]  \hspace{1cm} (I)

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where \( n \) is the number of electrons transferred per molecule of \( A \), \( k \) is a first-order rate constant and \( h \) may take on any positive value. In turn, when \( a \) and \( b \) take on the values 1 and 2 we have the case of a dimerization on the electrode surface.

If \( \delta \) is the operator:

\[
\delta = \frac{\partial}{\partial t} - \frac{\partial}{\partial r}\left(\frac{b^2}{r}\right) + \frac{\gamma^3}{\partial^3 r}
\]

the boundary value problem with the assumption \( D_A = D_B = D \) is described by

\[
\delta c_A = h c_B \quad \delta c_B = -c_B \quad t = 0, \quad r > \gamma t^{1/3}
\]

\[
t > 0, \quad r \to \infty \quad c_A = c_A^* \quad c_B = 0
\]

\[
t > 0, \quad r = \gamma(t_1 + t)^{1/3}:
\]

\[
b \left( \frac{\partial c_A}{\partial r} \right) = -a \left( \frac{\partial c_B}{\partial r} \right)
\]

\[
c_A = 0 \quad c_B = 0
\]

where \( t \) is the time elapsed between potential application and measurement of the instantaneous limiting current, and \( t_1 \) the time of the drop growth prior to potential application.

Introducing the variables:

\[
\phi = c_B e^{\gamma t}
\]

\[
\delta = c_B + c_A^*/h
\]

and proceeding according to our previous papers \([4,6]\) it is possible to deduce the solution of the problem described by eqns. (1)–(6). Thus, we have:

**Expanding plane electrode**

If \( p \) is the regeneration fraction defined by

\[
p = h b / a
\]

one finds:

\[
\frac{\partial}{\partial t} = 1 + p S
\]

where \( i_{d.p} \) is the diffusion current in the expanding plane electrode \([18]\), i.e.

\[
i_{d.p} = nF q \sqrt{D \pi i c_A^* f(a)}
\]

\[
f(a) = 1 + \frac{1}{2} a + \frac{1}{2} a^2 + \ldots = \sum_{i=0} a_i a_i
\]

\[
a = t / (t_1 + t)
\]

and

\[
S = \sum_{i=0} A_i, a_i \chi^m
\]

\[
\chi = kt
\]

In addition,

\[
-A_{j,m} = \frac{a_j}{f(a)} \left( \frac{1}{m!} + Q_{j,m} \right) + p \sum_{i=1}^{m-1} \frac{A_{j,i}}{(m-i)!}
\]

\[
Q_{j,m} = -\frac{p_2 m \delta j o}{p_0 m!} + \sum_{i=0}^{j-1} H_{j,m i} \Delta_{j,m}
\]

\[
+ (p - 1) \sum_{i=1}^{m-1} \frac{1}{(m-i)!} \sum_{n=0}^{j} e_{n,i} F_{j,n,i,m}
\]

\[
p_n = \frac{2 \Gamma \left(\frac{1+n}{2}\right)}{\Gamma \left(\frac{1+n}{2}\right)}
\]

\[
H_{j,m i} = B_{j,m i} F_{j,n,i,m} - B_{j,m i}
\]

\[
\Delta_{j,m} = \delta_{j,0} m! p_0 \sum_{i=1}^{m-1} \sum_{i=1}^{m-1} \frac{1}{(m-i)!} \sum_{n=0}^{j} \frac{a_n e_{n,i} F_{j,n,i}}{B_{j,n,i}}
\]

\[
- \sum_{i=0}^{j} F_{j,n,i,m} \Delta_{j,m}
\]

\[
e_{j,m} = \frac{1}{m!} \left( 1 - P_{2m} \delta j o \right) - \sum_{i=1}^{m-1} \frac{1}{(m-i)!} \sum_{n=0}^{j} e_{n,n,i} F_{j,n,i,m} + \sum_{i=0}^{j} G_{j,m}
\]

\[
F_{j,n,i,m} = \frac{a_j F_{j,n,i} p_{2m}}{a_j B_{j,n,i} p_{2i}}
\]

\[
F_{j,n,i} = \frac{a_n}{a_j B_{j,n,i}} \left( p B_{j,n,i} - (p - 1) B_{j,n,i} F_{j,n,i} p_{2m} / p_{2i} \right)
\]

\[
G_{j,m} = \frac{1}{a_j} \left( p_{2m} F_{j,n,i,m} / B_{j,n,i} - a_j e_{n,m} B_{j,n,i} \right)
\]

In these equations \( B_{j,n,i} \) and \( F_{j,n,i,m} \) are polynomials (or quotient of polynomials) in \( m \) which depend on the \( i \) and \( j \) values. They have been defined previously \([4,6]\). Note that eqns. (14)–(22) are analogous to those given previously for the CE \([4]\) and ECE \([6]\) mechanisms if in the corresponding equations of these references we replace the equilibrium constant \( K \) by \( p(1-p) \).
Expanding sphere electrode

In this case the expression for the current is

\[ i / i_{d,e} = 1 + p S_e \]  
(23)

where \( i_{d,e} \) is the diffusion current in the expanding sphere electrode [18]:

\[ i_{d,e} = i_{d,p} \left( 1 + \frac{\sqrt{\pi}}{2} \xi g(\alpha) \right) \]  
(24)

\[ g(\alpha) = \frac{1 - \frac{\alpha}{4} a^2 - \frac{\alpha^2}{45} a^3 \ldots}{1 + \frac{\alpha}{12} a^2 + \ldots} \]  
(25)

and \( \xi \), the spherical correction parameter, being defined by

\[ \xi = 2(Dt)^{1/2}\gamma(t_1 + t)^{1/3} \]  
(26)

In addition:

\[ S_e = \frac{S + \xi T}{1 + \frac{\sqrt{\pi}}{2} \xi g(\alpha)} \]  
(27)

\[ T = \sum_{m=0}^{\infty} A_{lm}^1 \chi^m \]  
(28)

As before, the \( A_{lm}^1 \) coefficients in the power series \( T \) are also defined as previously [4,6] if in the corresponding equations of these references we replace \( K \) by \( p/(1 - p) \).

Particular cases

Equations (8) and (23) are valid for all the values of \( p \), although it is convenient to take into consideration three different cases:

1) \( h < a/b \), i.e., \( p < 1 \). In this case the regeneration of \( A \) is only partial. Thus, when \( h = a/2b \) \( p = 1/2 \) we have the one-half regeneration mechanism. In turn, when the regeneration fraction \( p = 0 \), eqns. (8) and (23) give \( i = i_0 \), which is in agreement with the value of the limiting current for an EC mechanism.

2) \( h = a/b \). Now \( p = 1 \) and scheme (1) is coincident with the catalytic mechanism. Under these conditions the equations for the current given above adopt a simpler form, which was derived in Part III of this series [1].

3) \( h > a/b \). In this case the regeneration fraction \( p > 1 \), and therefore the regeneration of \( A \) is more than total. Examples of this have been reported [10,19].

Asymptotic solutions

The power series in eqns. (12) and (28) are unconditionally convergent for all the values of \( \chi \), although convergence is slow when \( \chi \gg 1 \). Under these conditions we find some computation difficulties when \( p \neq 1 \), which are due to the "oscillating" behavior of these power series [2]. Conversely, if \( p = 1 \) the corresponding equation for the current (see eqns. 1 and 2 in ref. 2) does not show these computation difficulties [2]. In any case, it is useful to obtain the corresponding asymptotic solutions which are derived by using the steady-state approximation and following the procedures utilized in two previous papers in this series [3,5]. Thus, we find:

(1) \( p < 1 \):

\[ i / i_{d,p} = \frac{1}{1 - p} \left( 1 + \frac{G(\alpha, \chi)}{f(\alpha)} \right) \]  
(29)

where

\[ G(\alpha, \chi) = \sum_{m=1}^{\infty} \frac{(-1)^m \prod_{i=1}^{m} p_{-i}}{1 - \frac{\alpha}{3} \chi^m} \left[ 1 - \frac{m + 1}{3(m - 1)} \alpha \right. \]  
\[ - \frac{(m + 1)(2m - 7)}{18(m - 1)(m - 3)} \alpha^2 - \frac{5(m + 1)(m - 4)}{81(m - 1)(m - 5)} \alpha^3 \]  
\[ - \frac{(m + 1)(16m^2 - 204m + 725m - 693)}{1944(m - 1)(m - 3)(m - 5)(m - 7)} \alpha^4 \ldots \]  
(30)

\( \chi = 2(1 - p)^{1/2} \) \( \alpha \) \( \chi \) \( \alpha \)

(2) \( p = 1 \):

\[ i / i_{d,p} = \frac{\sqrt{\pi} \chi / \alpha}{f(\alpha)} \]  
(31)

(3) \( p > 1 \):

\[ i / i_{d,p} = \frac{1}{(p - 1) f(\alpha)} \sum_{m=0}^{\infty} \frac{\chi^{m+1}}{m + 1} \left[ 1 - \frac{m + 1}{3(m + 2)} \alpha \right. \]  
\[ - \frac{m(m + 9)}{18(m + 2)(m + 4)} \alpha^2 - \frac{5m(m + 5)}{81(m + 2)(m + 6)} \alpha^3 \]  
\[ - \frac{5m(16m^2 + 252m + 1181m + 1638)}{1944(m + 2)(m + 4)(m + 6)(m + 8)} \alpha^4 \ldots \]  
(32)

with

\( \chi = 2(p - 1)^{1/2} \) \( \alpha \) \( \chi \) \( \alpha \)

If \( \alpha \ll 1 \), eqn. (33) becomes:

\[ i / i_{d,p} = \frac{1}{2(p - 1) f(\alpha)} \left[ 1 + \frac{1}{\sqrt{\pi}} e^{-\chi^2/4} \sum_{n=0}^{\infty} \frac{\chi^{2n+1}}{(2n + 1)!} \right] \]  
(35)

In this equation, for \( \chi \) sufficiently large, the second term within the bracket is practically equal to unity and therefore:

\[ i / i_{d,p} = \frac{\sqrt{\pi} \chi}{(p - 1) f(\alpha)} \]  
(36)
or, taking into account eqn. (34),

\[ \frac{i}{i_{d,p}} \approx \frac{2\sqrt{\pi \chi}}{f(\alpha) \rho} e^{(1-\frac{1}{\rho}) \chi} \]  

(37)

**RESULTS AND DISCUSSION**

The calculations have been carried out as previously [4,6]. With this purpose we have written eqns. (8) and (23) in an equivalent form which are more appropriate for computation. These expressions are given in the Appendix. Figure 1 shows the behavior of the \(i/i_{d,p}\) values computed with the rigorous theory (eqn. A1) as a function of \(\chi\) for \(\alpha = 0.001\) and some cases of regeneration: partial \((p = 1/2, 3/4)\), total \((p = 1)\) and more than total \((p = 5/4)\). If one compares these values with those from the asymptotic solutions, one finds that there is a good agreement with the rigorous theory if \(\chi_a > 4(1-p)^2\) (note that, unlike \(\chi_a\), it is not possible to assign a fixed value to \(\chi\) because \(\chi\) depends on \(p\)). Plots for other values of \(\alpha\) are similar to Fig. 1, and from them one can easily find the \(h\) value if the fraction regeneration is known.

In addition, it follows from these plots that when \(p < 1\) and the values of \(\chi\) are sufficiently large, \(i/i_{d,p}\) increases toward a maximum value \((I_m)\), which is in agreement with eqns. (29)–(30). According to these equations \(I_m\) is equal to \(1/(1-p)\). Hence, the fraction regeneration can be calculated if one knows \(I_m\).

With this purpose, we must bear in mind that according to eqns. (8)–(13) \(i/i_{d,p}\) depends on \(\alpha\) and \(\chi\). Hence, plots of \(i/i_{d,p}\) vs. \(\chi\) must be obtained for different values of \(\alpha\). However, it is readily verified that if \(\alpha \ll 1\) the dependence of these plots regarding \(\alpha\) is small. Under these conditions, and in order to obtain \(I_m\), it is sufficient to check — within the same plot — the constancy of \(i/i_{d,p}\) for different values of \(t\). Conversely, if the condition \(\alpha \ll 1\) cannot be invoked when \(t\) is changed, then we must examine the constancy of \(i/i_{d,p}\) in different plots.

On the other hand, we have in Fig. 1 that, when \(p > 1\), \(i/i_{d,p}\) increases continuously with \(\chi\). However, this rise is different for \(p = 1\) and \(p > 1\). Thus, when \(p = 1\) it follows from eqn. (32) that if \(\chi >> 1\), \(f(\alpha) i/i_{d,p}\) increases linearly with \(t^{1/2}\). This fact provides a test in order to determine \(p\). In addition, the value of \(h\) is also easily calculated from the corresponding plot.

Finally, when \(p > 1\) it follows from eqn. (37) that \(i/i_{d,p}\) rises exponentially for large values of \(\chi\). Under conditions where eqn. (37) remains valid, a plot of

\[ \ln \left( \frac{f(\alpha) i}{2\sqrt{\pi t} i_{d,p}} \right) \]  

vs. \(t\)

is a straight line whose slope and intercept allows \(p\) and \(k\) to be calculated.

Regarding the influence exerted by the electrode sphericity, this is shown for the half-regeneration mechanism in Fig. 2. In this figure we have represented the

![Fig. 2. Dependence of the ratio \(i/i_{d,p}\) on \(\chi\) for the half-regeneration mechanism \((p = 1/2)\). Values of \(\alpha\) and \(\xi(K)\) are given on the curves (those corresponding to \(\alpha = 1\) are the same as \(\alpha = 0.5\); \(\xi(K)\) = Koutecký's spherical correction parameter in dc polarography [20] \[\xi = (7/3)^{1/2}a^{1/2}\xi(K)\].](image-url)
values of $i/i_{d,e}$ vs. $\chi$ computed from eqn. (23) for three values of $\alpha$ and several of $\xi$ [values obtained with the expanding plane electrode ($\xi = 0$) are also included]. According to this plot, for a given value of the $i/i_0$ relationship, one finds that the value of $k$ obtained by using the curves for the expanding plane electrode are always lower than those calculated with the expanding sphere electrode. This fact has been also described for the CE and ECE mechanisms [4,6]. In addition, this plot also shows that in both electrode models the $i/i_0$ relationship tends toward its maximum value more rapidly as $\alpha$ becomes smaller.

APPENDIX

For computation purposes it is useful to write eqns. (8) and (23) as:

\[
i/i_{d,p} = e^{-\chi}(1 + S_1)
\]

\[
S_1 = \sum_{j=0} B_{1,m}a_j\chi^m
\]  

\[
B_{1,m} = \frac{\delta_{1,0} + p}{m!} \sum_{i=1}^m \frac{A_{1,i}}{(m-i)!}
\]

\[
i/i_{d,e} = e^{-\chi}(1 + S_{1,e})
\]

\[
S_{1,e} = \frac{S_1 + \xi T_1}{1 + \frac{\xi T_1}{2}}
\]

\[
T_1 = \sum_{j=0} B_{1,m}a_j\chi^m
\]

\[
B_{1,m} = \frac{\delta_{1,0} + a_j}{mlp_0} + p \sum_{i=1}^m \frac{A_{1,i}}{(m-i)!}
\]

REFERENCES