A THEORETICAL INVESTIGATION OF DOUBLE POTENTIAL STEP TECHNIQUES AS APPLIED TO THE FIRST ORDER, ONE-HALF REGENERATION MECHANISM AT PLANAR ELECTRODES: CHRONOAMPEROMETRY, CHRONOCOULOMETRY AND CHRONOABSORPTOMETRY

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ABSTRACT

Analytic solutions for the current, charge, and optical responses of a first-order "one-half" regeneration mechanism following double potential step excitation are reported. Polynomial approximations to the resulting working curves are developed.

INTRODUCTION

The first order, one-half regeneration mechanism is of current interest among electroanalytical chemists as it appears to be a limiting case for more complex mechanisms encountered in the study of the follow-up chemical reactions between aromatic hydrocarbon cation radicals and purposely added nucleophiles. The electrooxidative coupling reactions of 9,10-diphenylantra- cene (DPA) with nucleophiles such as water [1–3], dimethylformamide [4], and pyridine [5] have been extensively studied and now appear to proceed via one-half regeneration mechanisms. During the course of our own experimental investigations of this type of follow-up chemical reaction, we carried out the complementary theoretical study to predict current, charge and optical absorbance responses for double potential step excitation of the one-half regeneration mechanism.

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THEORETICAL RESULTS AND DISCUSSION

The first order one-half regeneration mechanism is classically represented [6–8] by:

\[ A \pm n_1e \xrightleftharpoons{E^0_1} B \tag{1a} \]

\[ B + Z \stackrel{k'}{\rightarrow} \frac{1}{2} A + C \tag{2} \]

The electrochemical reaction is assumed to be perfectly reversible in the electrochemical sense at the potentials applied during the experiment; species Z and C are electroinactive participants at these potentials; species Z is in sufficient excess so that pseudo first order behavior is observed and the totally irreversible step in eqn. (2) has an effective rate constant \( k = k'[Z] \).

It is somewhat difficult to envision the mechanism, as written, pertaining to the observed results for organic reactions such as those obtained for DPA [1–5]. In these cases the evidence seems to indicate that after the electrode process, eqn. (1), the mechanism proceeds as:

\[ B + Z \rightarrow B' \tag{3a} \]

\[ B + B' \stackrel{k_2^0}{\rightarrow} A + C \tag{4a} \]

In the particular case of DPA\(^+\) reacting in the presence of water Sioda [1] and others [2,3] have proposed the mechanistic scheme:

\[ \text{DPA} - e \xrightleftharpoons{E^0_1} \text{DAP}^+ \tag{1b} \]

\[ \text{DPA}^+ + H_2O \xrightarrow{k_1^0} \text{DPA(OH)}^+ + H^+ \tag{3b} \]

\[ \text{DPA}^+ + \text{DPA(OH)}^+ \rightarrow \text{DPA} + \text{DPA(OH)}^+ \tag{4b} \]

\[ \text{DPA(OH)}^+ \text{appears to undergo a further, very rapid, follow-up reaction [1–5] \}

\[ \text{DPA(OH)}^+ + H_2O \rightarrow \text{DPA(OH)}_2 + H^+ \tag{4c} \]

which in more general terms can be expressed as

\[ C + Z \rightarrow D \tag{4d} \]

For this mechanism, if the reagent Z is again in great excess relative to A and if \([B']/k_2^0 \gg k_1^0 [Z]\), then the diffusion—kinetic relationships for a planar electrode can be written as
\[ \frac{\partial [A]}{\partial t} = D_A (\frac{\partial^2 [A]}{\partial x^2}) + k_1^0 [Z] [B] \] (5)

\[ \frac{\partial [B]}{\partial t} = D_B (\frac{\partial^2 [B]}{\partial x^2}) - 2k_1^0 [Z] [B] \] (6)

These diffusion—kinetic relationships are the same as those resulting from
the classical model of eqns. (1) and (2) with the exception that now \( k = 2k_1^0 [Z] \).

The diffusion—kinetic equations, initial conditions and boundary values
for the model of eqns. (1) and (2) have been previously given by Guidelli and
Cozzi [6] as well as by Delmastro and Booman [7,8] for the more complex
spherical diffusion case. Consequently, the boundary value problem will not
be further stated here. It should be noted that the optical responses to be
derived for the product species \( C \) assume that it is stable on the time scale
of the experiment. If the effective rate of the reaction in eqn. (4a) is not zero,
as for example in the DPA cases studied [1–5], then the result will be errone-
ous. However, if the rate of this reaction is much greater than the rate of for-
mation of \( C \), again as seems to be the case for the DPA reactions quoted
above, then the response calculated here for \( C \) should be a good representa-
tion for the optical response of the final product \( D \). It is also obvious that
now two moles of \( Z \) are required for formation of a single mole of the final
product \( D \).

Bearing these differences in mind it is relatively easy to show from the
results of previous workers [6–8] that the planar diffusion current for a
single potential step can be represented in the Laplace plane by

\[ \bar{I}(s) = 2nFAC_A^* D_A^{1/2} [(s + k)^{1/2}/s^{1/2} \{s^{1/2} + (s + k)^{1/2}\}] \] (7)

so that one can immediately write

\[ \bar{C}_B(0,s) = 2C_A^* (D_A/D_B)^{1/2}[1/\{s^{1/2} \{s^{1/2} + (s + k)^{1/2}\}\}] \] (8)

By using the usual definitions for the absorbance of \( B \), \( \bar{A}_B (0,s) \) is given by

\[ \bar{A}_B (0,s) = \epsilon_B C_A^* D_A [1/s(s + k)^{1/2} - 1/(s + k) s^{1/2}]/k \] (9)

The charge response is merely eqn. (7) divided by \( s \). In the time plane, the
responses are

\[ i(t) = 2nFAC_A^* (D_A/t\pi)^{1/2} [2 - (1 - e^{-kt})/kt] \] (10)

\[ A_B(t) = 2\epsilon_B C_A^* (D_A t/\pi)^{1/2} e^{-kt} [2_1 F_1 (1/2,3/2,kt) - (1 - F_1 (-1/2,1/2,kt))/kt] \] (11)

\[ Q(t) = 2nFAC_A^* (D_A t/\pi)^{1/2} [2 + (1 - e^{-kt})/kt - (\pi/kt)^{1/2} \text{erf}(kt)^{1/2}] \] (12)

\[ C_B(0,t) = C_A^* (D_A/D_B)^{1/2} e^{-kt} [2_1 F_1 (1/2,1,kt) - F_1 (1/2,2,kt)] \] (13)
Responses for double potential step

The surface concentration of B in the Laplace plane valid for the double potential step is computed in the usual manner by multiplying eqn. (13) by $e^{-\alpha t} \, dt$ and integration from zero to $\tau$ [9]. Considerable effort is saved, and an insight into the nature of the kinetic processes is obtained by noting that the first term in eqn. (13) is twice the surface concentration term for the e.c. case [10]. With this in mind, the Laplace plane form for the surface concentration of B becomes

$$
\bar{C}_B(0,s) = C^*_A (D_A/D_B)^{1/2} \left[ 2\bar{C}_B(0,s)_{EC} - \int_0^\tau \mathbf{1}_F(1/2,2,kt) \, e^{-(s+k)t} dt \right] \tag{14}
$$

The second term in eqn. (14) represents in effect the surface concentration of B which is lost in forming the electro-inert product or products. Expressing this lost surface concentration transform by $\bar{C}_B(0,s)$ and carrying out the integration

$$
\bar{C}_B(0,s) = C^*_A (D_A/D_B)^{1/2} \left[ \sum_{n=0}^\infty \left( \frac{1}{2} \right)_n \frac{(k)^n}{(2)_n} \frac{k^n}{(s+k)^{n+1}} - \sum_{n=0}^\infty \frac{\Gamma(n+\frac{1}{2})}{\Gamma(n+2)} \times \frac{(k)^n}{(s+k)^{n+1}} \mathbf{1}_F(\frac{n+\frac{1}{2}}{2},n+2,kt) \, e^{-(s+k)t} \right] \tag{15}
$$

The first series in eqn. (15) may be eliminated by a knowledge of the properties of hypergeometric functions [11]. Defining $y = k/(s + k)$

$$
\sum_{n=0}^\infty \frac{(1/2)_n}{(2)_n} y^n = \sum_{n=0}^\infty \frac{(1/2)_n}{(2)_n n!} y^n = 2 \mathbf{1}_F(\frac{1}{2},1,2,y) = \frac{2}{1 + (1 - y)^{1/2}} = \frac{2s + k}{s^{1/2} + (s+k)^{1/2}} \tag{16}
$$

Following the procedures utilized in a previous paper in this series [10], it can be shown that the Laplace plane forms of current, charge, and optical responses are given by

$$
\bar{i}(s) = -nFAC^*_A (D_B(s+k))^{1/2} C_B(0,s) \tag{17}
$$

$$
\bar{Q}(s) = -nFAC^*_A \left[ (D_B(s+k))^{1/2}/s \right] \bar{C}_B(0,s) \tag{18}
$$

$$
\bar{A}_B(s) = \epsilon_B (D_B/s + k)^{1/2} \bar{C}_B(0,s) \tag{19}
$$

At this point in the derivation, one is faced with two choices. In the first, the surface concentration of B can be evaluated in terms of the results previously obtained for the e.c. mechanisms in conjunction with eqn. (10). Combining eqns. (14)–(16) with the previously published results for the e.c. case [10], it can be shown that
\[ \bar{C}_B(0,s) = \mathcal{C}_A^*(D_A/D_B)^{1/2} \left[ \frac{2}{(s+k)^{1/2}} \left( \frac{1}{s^{1/2}} - \frac{1}{s^{1/2} + (s+k)^{1/2}} \right) \right] - \]
\[
\sum_{n=0}^{\infty} \frac{\Gamma(n+\frac{1}{2})k^n e^{-(s+k)t}}{n!(s+k)^{n+1}} \left[ \frac{1}{n+1} \left\{ \frac{1}{(n+1/2,n+2,k\tau)} - 2_1F_1(n+1/2,n+1,k\tau) \right\} \right] \]

Reversion of eqns. (17), (18), and (19) to the time plane using the series form of eqn. (21) yields eqns. (23), (25), and (27).

\[ \bar{Q}(t > \tau) = 2nFAC^* \left( D_A/\pi \right)^{1/2} \left[ t^{1/2} \left( 2 + \frac{1-e^{-kt}}{kt} \right) - \frac{1}{(t-\tau)^{1/2}} \frac{2\phi_1(k,t,\tau)}{(k\tau)_{1/2}} \right] \]

\[ = 2nFAC^* \left( D_A/\pi \right)^{1/2} \left[ t^{1/2} \left( 2 + \frac{1-e^{-kt}}{kt} \right) - \frac{1}{(t-\tau)^{1/2}} \phi_8(k,t,\tau) \right] \]

\[ (t-\tau)^{1/2} \left( 2\phi_2(k,t,\tau) - \phi_9(k,t,\tau) \right) \]

\[ = 2nFAC^* \left( D_A/\pi \right)^{1/2} \left[ t^{1/2} \left( 2 + \frac{1-e^{-kt}}{kt} \right) - \frac{1}{(k\tau)_{1/2}} \right] \]

\[ (t-\tau)^{1/2} \phi_{10}(k,t,\tau) \]
\[ A_B(t > \tau) = 2e_B C_A^*(D_A/\pi)^{1/2} \left[ \frac{e^{-kt} t^{1/2}}{kt} \left( 2_{1}F_{1}(1/2, 3/2, kt) + \right. \right. \\
\left. \left. (1 - 1_{1}F_{1}(-1/2, 1/2, kt)) \right) - (t - \tau)^{1/2} \left( 2\phi_3(k, t, \tau) - \phi_1(k, t, \tau) \right) \right] \]

\[ = 2e_B C_A^*(D_A/\pi)^{1/2} \left[ \frac{e^{-kt} t^{1/2}}{kt} \left( 2_{1}F_{1}(1/2, 3/2, kt) + \frac{(1 - 1_{1}F_{1}(-1/2, 1/2, kt))}{kt} \right) \right. \]

\[ (t - \tau)^{1/2} \phi_2(k, t, \tau) \]

The functions \( \phi_1(k, t, \tau), \phi_2(k, t, \tau), \) and \( \phi_3(k, t, \tau) \) have been defined previously [9,10,13]. The remaining functions are given by

\[ \phi_7(k, t, \tau) = e^{-kt} \sum_{n=0}^{\infty} \frac{(k(t - \tau))^n}{n!(n+1)} \, 1_{1}F_{1}(n + 1/2, n + 2, k\tau) \]

\[ \phi_8(k, t, \tau) = e^{-kt} \sum_{n=0}^{\infty} \frac{(k(t - \tau))^n (2n + 1)}{n!(n+1)} \, 1_{1}F_{1}(n + 3/2, n + 2, k\tau) \]

\[ \phi_9(k, t, \tau) = e^{-kt} \sum_{n=0}^{\infty} \frac{(k(t - \tau))^n}{n!(n+1)(2n+1)} \, 1_{1}F_{1}(n + 1/2, n + 2, k\tau) \times \]

\[ (1, n + 3/2, k(t - \tau)) \]

\[ \phi_{10}(k, t, \tau) = e^{-kt} \sum_{n=0}^{\infty} \frac{(k(t - \tau))^n}{n!(n+1)} \, 1_{1}F_{1}(n + 3/2, n + 2, k\tau) \times \]

\[ (1, n + 3/2, k(t - \tau)) \]

\[ \phi_{11}(k, t, \tau) = e^{-kt} \sum_{n=0}^{\infty} \frac{(k(t - \tau))^n}{n!(n+1)(2n+1)} \, 1_{1}F_{1}(n + 1/2, n + 2, k\tau) \]

\[ \phi_{12}(k, t, \tau) = e^{-kt} \sum_{n=0}^{\infty} \frac{(k(t - \tau))^n}{n!(n+1)} \, 1_{1}F_{1}(n + 3/2, n + 2, k\tau) \]

The optical response function for the electro-inert product C may be obtained from a knowledge of the charge and the optical response of B.

\[ A_C(t > \tau) = \epsilon_C \{ Q(t > \tau)/nFA - A_B(t > \tau)/\epsilon_B \} \]

Response characteristics

The method of choice for analyzing the various double potential step responses \( G(k, t, \tau) \) is to form the corresponding response ratio:

\[ |R_G(k\tau, \theta)| = |[G(k, \theta, \tau) - G(k, \tau + \theta, \tau)]/G(k, \theta, \tau)| \]
Fig. 1. Double potential step chronoamperometric working curves, \(|i_c/i_a|\) vs. \((kT)^{1/2}\) for the half-regeneration mechanism, calculated from eqn. (23), is solid line. The circles were obtained from the explicit finite difference simulation (300 time increments in each half-cycle) for this mechanism. The values of \(\theta\) used are 0.032, 0.099, 0.333, 0.667 and 1.000 \(\tau\).

where the responses are measured at \(t = \theta\) and at \(t = \tau + \theta\) where \(\theta \leq \tau\). The most commonly used form is \(\theta = \tau\) (i.e., the responses are measured at \(\tau\) and \(2\tau\)) although Shain has suggested using variable \(\theta\)'s for double potential step current measurements [9] and the use of the ratio \(|i_c/i_a|\).

The current response ratio \(|i_c/i_a|\) for a number of values of \(\theta\) from 0.016 \(\tau\) to 1.00 \(\tau\) was computed using eqn. (23), and the results are shown as a solid line in Fig. 1. The circles represent the results obtained by finite difference simulation of this mechanism and, as can be seen, the correspondence with the analytic solution is excellent. The charge and optical response ratios for species B and C are given in Fig. 2 for \(\theta = \tau\), the circles again representing the finite difference simulations; once again, the correspondence between the methods is quite good.

Great care should be exercised when using working curves to establish reaction mechanisms. For example, the forward step charge and current responses for the "one-half" regeneration mechanism will be identical to the corresponding responses obtained for the pre-kinetic case with an equilibrium constant of unity [7,8] where \(k = k_f + k_b\). The optical responses, on the other hand, are different for the two mechanisms as are the faradaic ratios in the double step experiment. This is due to the fact that the flux of species A is identical for the two mechanisms, but the spatial distribution and surface flux of species B in solution are different. A good fit of experimental data to one type of
working curve for a given mechanism does not constitute a valid proof of the mechanistic path. Generally, the products of the reaction should be established and then all mechanisms which could yield these products should be investigated using a variety of techniques. Certain candidate mechanisms can be rejected for failure to conform to the experimental results. When only one mechanism remains, then some degree of confidence can be placed in the assignment. The ability to investigate effectively a number of candidate mechanisms requires that a large number of working curves be available in a convenient, accurate, and rapidly accessible form.

**Polynomial approximations to working curves and analytic functions**

Working curves such as Figs. 1 and 2 are helpful in obtaining a feeling for the nature of the response in question but are of limited use in practical data analysis. The analytic functions themselves while being exact representations of the response in question are such complex and slowly convergent entities that their evaluation on a desk calculator or even a small mini-computer is very time consuming.

A viable alternative to these two representation forms is to express the relevant \( \phi_n(k, t, \tau) \) and \( R_G(k\tau, \theta) \) functions for charge, and optical properties
of B and C as polynomial approximations in terms of \((k\tau)^{1/2}\). In this way, the working curves can be speedily and accurately regenerated. In order to conserve space, these functions will only be presented for \(\theta = \tau\) as this seems to be the most useful condition.

Table 1 represents the coefficients to the three response ratios as well as \(\phi_8(k, \tau, 2\tau), \phi_{10}(k, \tau, 2\tau), \phi_{12}(k, \tau, 2\tau), e^{-k\tau}I_F(1/2, 3/2, k\tau),\) and \(IF_1(-1/2, 1/2, k\tau)\). The polynomial representation of these five functions and three response ratios were cast into the form

\[
P(X) = Y_0 + A e^{-\Delta X \cdot X^2} \left( B_0 + X(B_1 + X(B_2 + \ldots X^*B_N)) \ldots \right) \tag{36}
\]

where \(X = (k\tau)^{1/2}\) in eqn. (36). The terms \(Y_0\) and \(A e^{-\Delta X \cdot X^2}\) in eqn. (36) are used to reduce the effective range and modify the shape of function. This modified shape function was then treated by a polynomial least-squares fit procedure to establish the values of the \(B_i\) coefficients. With the exception of the \(IF_1(a, b, k\tau)\) functions, the polynomials are defined for the range

<table>
<thead>
<tr>
<th>(R_B(k\tau, \tau))</th>
<th>(R_C(k\tau, \tau))</th>
<th>(R_Q(k\tau, \tau))</th>
<th>(\phi_8(k, 2\tau, \tau))</th>
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<tr>
<th>(\phi_{12}(k, 2\tau, \tau))</th>
<th>(\phi_{10}(k, 2\tau, \tau))</th>
<th>(e^{-k\tau}IF_1(0.5, 1.5, k\tau))</th>
<th>(IF_1(-0.5, 0.5, k\tau))</th>
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<td>(B_7) 0.2495500(--1)</td>
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0.1 \leq (k\tau)^{1/2} \leq 2.0. The $F_1(a, b, k\tau)$ functions are defined over the range $0.1 \leq (k\tau)^{1/2} \leq 3.0$ since these must be defined for values at $2\tau$ as well as at $\tau$. The $B_i$ coefficients, $Y_0$, $A$ and $\Delta X$ for these polynomials are given in Table 1. The resulting approximations, formula, and coefficients yield values of $P(X)$ having relative errors of less than 0.05% over the range of $k\tau$ cited above.

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