THE SPECTROELECTROCHEMICAL RESPONSE FOR FIRST-ORDER E.C. PROCESSES WITH ELECTRODE PRODUCT AND REACTANT ADSORPTION FOLLOWING DOUBLE POTENTIAL STEP EXCITATION

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ABSTRACT

The double potential step optical responses for the e.c. mechanism in the presence of electrode product and reactant adsorption have been described and their utility for the determination of chemical reaction rates discussed.

INTRODUCTION

In a previous report [1], analytical solutions were derived for the chronocoulometric response to a double potential step (DPS) excitation waveform for the homogeneous EC kinetic case where both electrode product and reactant are adsorbed on the electrode surface. This report discusses the complementary transmission spectroelectrochemical responses for this system under semi-infinite mass transport conditions only. The optical responses for the forward step in the absence of adsorption complications have been previously treated in the literature [2,3]. In addition several treatments of the optical responses for the DPS EC catalytic case [4–6] in the absence of adsorption and one paper dealing with the single potential step optical response for the non-kinetic case of reactant adsorption [7] have appeared. The double potential step optical responses are distinctly different from the purely faradaic responses, particularly when adsorption occurs. The nature of these differences in response and the utility of the optical method for the measurement of follow-up chemical reaction rates in the presence of reactant and product adsorption are developed here.

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GENERAL FORM OF THE THEORETICAL TREATMENT—ALL SPECIES ABSORB AT $\lambda$

Although the initial and boundary conditions for the EC kinetic scheme complicated by reactant and product adsorption:

$$\begin{align*}
\text{A}_{\text{ads}} & \rightarrow \text{e}^- \rightarrow \text{B}_{\text{ads}} \\
\text{A}_{\text{soln}} & \rightarrow \text{B}_{\text{soln}} \cdot k \rightarrow C_{\text{soln}}
\end{align*}$$

have been stated and discussed previously [1], they will be repeated here to facilitate the exposition.

$$\begin{align*}
c_A(x, 0) &= c_A^0; c_B(x, 0) = 0; c_C(x, 0) = 0 \\
\Gamma_A(t = 0) &= \Gamma_A^*; \Gamma_B(t = 0) = 0 \\
c_A(x \rightarrow \infty, t) &= c_A^0; c_B(x \rightarrow \infty, t) = 0; c_C(x \rightarrow \infty, t) = 0 \\
c_A(0, t \leq \tau) &= 0; \Gamma_A(t \leq \tau) = 0; \Gamma_B(t \leq \tau) = \Gamma_B^\$ \\
c_B(0, t > \tau) &= 0; \Gamma_A(t > \tau) = \Gamma_A^\$; \Gamma_B(t > \tau) = 0
\end{align*}$$

$$\begin{align*}
\frac{i}{nFA} &= D_A \left. \frac{\partial c_A(x, t)}{\partial x} \right|_{x = 0} \tag{6a} \\
- \frac{\partial \Gamma_A(t)}{\partial t} &= -D_B \left. \frac{\partial c_B(x, t)}{\partial x} \right|_{x = 0} + \frac{\partial \Gamma_B(t)}{\partial t} \tag{6b}
\end{align*}$$

All symbols have their previously defined meanings [1] except $\alpha$ which now stands for the electrode area in order to avoid confusion with the symbol for optical absorbance. The mass transport equations to be solved are the same as those for the purely faradaic situation treated earlier [1]. The adsorption equilibria in the above scheme are assumed to be linear and maintained at all times.

Since our objective here is merely to evaluate some of the many possible DPS spectroelectrochemical responses for this system, we will first set up the general problem with respect to the absorption spectroscopy of the various species and then choose an appropriately simplified situation for detailed discussion. We in no way intend to treat all possible cases in this short paper. Other workers should, however, find this treatment a useful starting point for the derivation of other responses for particular experimental situations.

In general the electronic absorption spectra of the five species in this system could be such that at the monitoring wavelength, $\lambda$, all contribute to the experimentally observable total absorbance change, $\Delta A_T(\lambda, t)$, upon application of the excitation waveform. The total absorbance change is defined
as [3]:

\[ \Delta A_T(\lambda, t) = A_T(\lambda, t) - A_T(\lambda, t = 0) \]  

(7)

where \( A_T(\lambda, t) \) is the total absorbance at time \( t \) and \( A_T(\lambda, t = 0) \) is the pre-perturbation value of the total absorbance. For the EC scheme complicated by the presence of \( A_{ads} \) and \( B_{ads} \), \( A_T(\lambda, t = 0) \) is given by:

\[ A_T(\lambda, t = 0) = A_0^\lambda(\lambda) + \epsilon_A^*(\lambda) \Gamma_A^* + A_{e\text{lectrode}}(\lambda) + A_{\text{solvent}}(\lambda) \]  

(8)

where \( A_0^\lambda(\lambda) \) is the absorbance of \( A_{\text{soln}} \) at \( t = 0 \), \( \epsilon_A^*(\lambda) \Gamma_A^* \) is the initial absorbance due to \( A_{ads} \) which has an extinction coefficient \( \epsilon_A^*(\lambda) \) in units of \( \text{mol}^{-1} \text{cm}^2 \), and \( A_{e\text{lectrode}}(\lambda) \) and \( A_{\text{solvent}}(\lambda) \) are possible background absorbances contributed by the optically transparent electrode (OTE) and the solvent respectively. For times less than the DPS switching time, \( \tau \), the total absorbance is:

\[ A_T(\lambda, t < \tau) = A_d^\lambda(\lambda, t < \tau) + A_d^B(\lambda, t < \tau) + A_\text{b}(\lambda, t < \tau) \]

(9)

There is no contribution from \( A_{ads} \) in eqn. (9) as a result of the boundary condition in eqn. (4). The superscripts \( d \) and \( a \) in eqn. (9) refer to solution phase diffusional and electrode surface adsorption contributions respectively. The Laplace plane representation of the surface concentration of \( B_{soln} \) is known [1]. \( A_d^\lambda(\lambda, t < \tau) \) is obtained from

\[ \bar{A}_B^d(\lambda, s) = \epsilon_B(\lambda) \int_0^\infty c_B(0, s) \exp\{-\sigma(s + k)^{1/2}\} \, dx \]  

(10)

which, in the time plane, yields:

\[ A_d^B(\lambda, t < \tau) = \epsilon_B(\lambda)[2e_A^0(D_A t/\pi)^{1/2} F_1(1,3/2, -kt) + (\Gamma_A^* - \Gamma_B^*) \exp -kt] \]

(11)

\( F_1(a, b, c) \) is a confluent hypergeometric function [8], \( \epsilon_B(\lambda) \) is the solution extinction coefficient of \( B \), and \( \Gamma_B^* \) is its surface excess. The absorbance contribution due to \( B_{ads} \) is given simply by:

\[ A_\text{b}(\lambda, t < \tau) = \epsilon_B^*(\lambda) \Gamma_B^* \]  

(12)

where \( \epsilon_B^*(\lambda) \) is the surface extinction coefficient appropriate to \( B_{ads} \). The solution absorbance of \( C \) can be most conveniently computed from the difference between the diffusional charge passed in the forward step [1] and the absorbance of \( B \) [9].

\[ \frac{A_c^d(\lambda, t < \tau)}{\epsilon_C(\lambda)} = \frac{Q(t < \tau)}{nF} - \frac{A_d^B(\lambda, t < \tau)}{\epsilon_B(\lambda)} \]  

(13a)
\[ A_C^d(\lambda, t \leq \tau) = \epsilon_C(\lambda) [2c_\lambda^0(D_A t/\pi)^{1/2} \{ 1 - I_1(1, 3/2, -kt) \} + (\Gamma_A^* - \Gamma_B^*) (1 - \exp - kt) ] \]  

(13b)

The remaining term in eqn. (9), \( A_A^d(\lambda, t \leq \tau) \), can be evaluated from the total mass balance expressed in terms of absorbance as follows:

\[
A_A^d(\lambda, t \leq \tau) = \left[ A_A^d(\lambda, t = 0) + \frac{\epsilon_A(\lambda) A_A^a(\lambda, t = 0)}{\epsilon_A^*(\lambda)} \right] - \left[ \frac{\epsilon_A(\lambda) A_B^a(\lambda, t \leq \tau)}{\epsilon_A^*(\lambda)} + \frac{\epsilon_A(\lambda) A_B^b(\lambda, t \leq \tau)}{\epsilon_B(\lambda)} + \frac{\epsilon_A(\lambda) A_C^b(\lambda, t \leq \tau)}{\epsilon_C(\lambda)} \right] \]

(14)

Substituting appropriately we find that the succeeding chemical reaction and the adsorption of A and B have no effect on \( A_A^d(\lambda, t \leq \tau) \):

\[
A_A^d(\lambda, t \leq \tau) = A_A^0(\lambda) - 2\epsilon_A(\lambda) c_\lambda^0(D_A t/\pi)^{1/2} \]

(15)

The general results for the forward step can be summarized in the form of \( A_T(\lambda, t \leq \tau) \) and \( \Delta A_T(\lambda, t \leq \tau) \) which are:

\[
A_T(\lambda, t \leq \tau) = [A_A^0(\lambda) + \epsilon_B^*(\lambda) \Gamma_B^* + A_{\text{electrode}}(\lambda) + A_{\text{solvent}}(\lambda)]
\]

(16a)

\[
+ 2c_\lambda^0(D_A t/\pi)^{1/2} \left\{ \left[ \epsilon_C(\lambda) - \epsilon_A(\lambda) \right] + \left[ \epsilon_B(\lambda) - \epsilon_C(\lambda) \right] I_1(1, 3/2, -kt) \right\} \]

(16b)

\[
+ (\Gamma_A^* - \Gamma_B^*) \left\{ \epsilon_C(\lambda) + [\epsilon_B(\lambda) - \epsilon_C(\lambda)] \exp - kt \right\} \]

(16c)

\[
\Delta A_T(\lambda, t \leq \tau) = [\epsilon_B^*(\lambda) \Gamma_B^* - \epsilon_A^*(\lambda) \Gamma_A^*] \]

(17)

In the limiting case of no adsorption eqns. (11) and (13b) reduce to previously published results [2]. Similarly eqns. (16) and (17) reduce to the results of Li and Wilson [3].

On the reverse step, \( t > \tau \), the total absorbance is given by:

\[
A_T(\lambda, t > \tau) = A_A^d(\lambda, t > \tau) + A_A^a(\lambda, t > \tau) + A_B^d(\lambda, t > \tau) + A_C^d(\lambda, t > \tau)
\]

(18)

\[
+ A_{\text{electrode}}(\lambda) + A_{\text{solvent}}(\lambda)
\]

This time there is no contribution to \( A_T(\lambda, t > \tau) \) due to B_{ads} as a result of the boundary condition in eqn. (5). The absorbance component due to adsorbed A is:

\[
A_A^a(\lambda, t > \tau) = \epsilon_A^*(\lambda) \Gamma_A^*
\]

(19)

\[
A_B^d(\lambda, t > \tau)
\]

is obtained from:

\[
\bar{A}_B^d(\lambda, s) = \epsilon_B(\lambda) \int_0^\infty \overline{c}_B(0, s) \exp \{-x(s + k)^{1/2}\} dx
\]

(20)
which, in the time plane, gives:

\[ A_\beta^d(\lambda, t > \tau) = \epsilon_B(\lambda)[2c_A^0(D_A/\pi)^{1/2}[t^{1/2}F_1(1, 3/2, -kt) - (t - \tau)^{1/2}\Phi_3(k, t, \tau)]] \]  

(21a)  

\[ + [2\epsilon_B(\lambda)/\pi](\Gamma_A^* - \Gamma_B^*) \exp(-kt) \sin^{-1}(\tau - t)^{1/2} \]  

(21b)

where

\[ \Phi_3(a, t, z) = \exp(-at) \sum_{n=0}^{\infty} \frac{(a(t - z))^n}{(2n + 1)!} F_1(n + 1/2, n + 1, az) \]  

(21c)

The optical response for species C is again available from the difference between the charge passed in the reverse step [1] and the amount of B present as obtained from the absorbance:

\[ A_c^d(\lambda, t > \tau) = 2\epsilon_C(\lambda)[c_0^0(D_A/\pi)^{1/2}[t^{1/2}(1 - F_1(1, 3/2, -kt)) - (t - \tau)^{1/2} \]  

\[ (\Phi_2(k, t, \tau) - \Phi_3(k, t, \tau)) + \frac{2}{\pi}(\Gamma_A^* - \Gamma_B^*) \exp(-kt) \]  

\[ \int_0^{(kt)^{1/2}} y^2 F_1(1, 3/2, y^2) dy/(kt - y^2)^{1/2} \]  

(22a)

\[ \Phi_2(a, t, z) = \exp(-at) \sum_{n=0}^{\infty} \frac{(a(t - z))^n}{(2n + 1)!} F_1(n + 1/2, n + 1, az) F_1(1, n + 3/2, a(t - z)) \]  

(22b)

A more detailed derivation of eqns. (21) and (22) has been given elsewhere [9]. \( A_\beta^d(\lambda, t > \tau) \) can now be evaluated from a total mass balance expression similar to eqn. (14) but appropriate for \( t > \tau \). Following this procedure we find

\[ A_\beta^d(\lambda, t > \tau) = A_\beta^0(\lambda) - \epsilon_A(\lambda)[2c_A^0(D_A/\pi)^{1/2}[t^{1/2} - (t - \tau)^{1/2}\Phi_2(k, t, \tau)]] \]  

\[ + \frac{2}{\pi}(\Gamma_A^* - \Gamma_B^*) \exp(-kt)[\sin^{-1}(\tau - t)^{1/2} + \]  

\[ 2\int_0^{(kt)^{1/2}} y^2 F_1(1, 3/2, y^2) dy/(kt - y^2)^{1/2}] \]  

(23)

The general results for the reverse step can now be summarized as \( A_T(\lambda, t > \tau) \) and \( \Delta A_T(\lambda, t > \tau) \):

\[ A_T(\lambda, t > \tau) = [A_\lambda^*(\lambda) + \epsilon_A^*(\lambda)\Gamma_A^* + A_{\text{electrode}}(\lambda) + A_{\text{solvent}}(\lambda)] \]  

(24a)
\[ + 2c_A^2(D_A t/\pi)^{1/2} \left[ (\varepsilon_C(\lambda) - \varepsilon_A(\lambda)) + (\varepsilon_B(\lambda) - \varepsilon_C(\lambda)) \right]_1 F_1(1, 3/2, -kt) \]  
(24b)

\[-2c_A^2(D_A/\pi)^{1/2}(t - \tau)^{1/2} \left[ [\varepsilon_C(\lambda) - \varepsilon_A(\lambda)] \Phi_2(k, t, \tau) + [\varepsilon_B(\lambda) - \varepsilon_C(\lambda)] \right] \]

\[ \Phi_3(k, t, \tau) \]  
(24c)

\[ + \frac{2}{\pi} (\Gamma_A^* - \Gamma_B^*) \exp(-kt) \left[ [\varepsilon_B(\lambda) - \varepsilon_A(\lambda)] \sin^{-1}(\tau - t)^{1/2} \right] \]

\[ + 2[\varepsilon_C(\lambda) - \varepsilon_A(\lambda)] \int_0^{(k\tau)^{1/2}} y^2 F_1(1, 3/2, y^2) dy (kt - y^2)^{1/2} \]  
(24d)

\[ \Delta A_T(\lambda, t > \tau) = (24b) + (24c) + (24d) \]  
(25)

**A SIMPLIFIED SPECTRAL SITUATION FOR DETAILED EVALUATION OF THE RESULTS**

The general theory of DPS transmission spectroelectrochemical responses for the adsorption complicated EC case presented above contains two adsorption parameters, and five spectral parameters in addition to the rate constant of the follow-up chemical reaction. Unfortunately, the presence of adsorption precludes a simple formulation of the total absorbance change involving only one spectral ratio parameter as was possible in the adsorption free case treated by Li and Wilson [3]. For the present situation at least three spectral ratio parameters analogous to:

\[ \theta = \frac{[\varepsilon_B(\lambda) - \varepsilon_C(\lambda)]}{[\varepsilon_C(\lambda) - \varepsilon_A(\lambda)]} \]

(26)

are needed for its description in addition to an adsorption ratio parameter:

\[ \phi = \frac{\Gamma_B^*}{\Gamma_A^*} \]

(27)

Furthermore the only obvious simplifications of \( A_T(\lambda, t < \tau) \) and \( A_T(\lambda, t > \tau) \) which occur in the very specialized instances where \( \varepsilon_A(\lambda) = \varepsilon_C(\lambda) \) and/or \( \varepsilon_C(\lambda) = \varepsilon_B(\lambda) \) and/or \( \varepsilon_A(\lambda) = \varepsilon_B(\lambda) \) result in the loss of kinetic information. Consequently presentation of all possible DPS spectroelectrochemical responses for this scheme is a formidable task.

We have, therefore, chosen a simplified spectral situation for the presentation of the responses as defined by the following parameter values:

\[ \varepsilon_A(\lambda) = 0; \varepsilon_B^*(\lambda) = 0; \varepsilon_C^*(\lambda) = 0 \]

\[ \varepsilon_B(\lambda) \neq 0; \varepsilon_C(\lambda) \neq 0 \]

(28)

\[ k \neq 0; \Gamma_A^* \neq 0; \Gamma_B^* \neq 0; \Gamma_B^* < \Gamma_A^* \]
This situation is likely to be encountered in dealing with the spectroelectrochemistry of planar, \( \pi \)-aromatic systems in nonaqueous solvents where \( A_{\text{soln}} \) usually absorbs in the u.v.; \( B_{\text{soln}} \) and \( C_{\text{soln}} \) absorb in the visible and/or near i.r.; and \( A_{\text{ads}} \) and \( B_{\text{ads}} \) have their absorption maxima generally shifted to higher energy with respect to their unadsorbed forms due to the electronic interaction with the electrode surface. By choosing this case for detailed discussion, we do not imply that cases where \( A_{\text{soln}} \) absorbs, such as the spectroelectrochemistry of biomolecules [6], are intractable. We have simply not chosen to deal with that case here in favor of detailing the effects of nonabsorptive adsorption on the measurement of the follow-up reaction rate in a typical situation. In specific instances simple corrections for the effects of finite values of \( \epsilon_A^*(\lambda)\Gamma_A^* \) and \( \epsilon_B^*(\lambda)\Gamma_B^* \) are possible and will be described.

For most purposes the optical responses are conveniently treated by a ratio method similar to that employed for the treatment of charge data [1]. The absorbance ratio for the \( j \)th species, \( R_j(k\tau) \) \( j = B \) or \( C \),

\[
R_j(k\tau) = \frac{|A_j(\tau) - A_j(2\tau)|}{|A_j(\tau)|} \quad (29)
\]

will be the form of data display. Three limiting cases of DPS responses will be presented: (1) EC kinetics — no adsorption; (2) adsorption of \( A \) and \( B \) — no EC kinetics; and (3) EC kinetics with adsorption of \( A \) and \( B \). Finally we will use the technique of polynomial approximation to the working curves, introduced by us [1], to summarize the theoretical results in a form quantitatively useful to other workers.

**EC kinetics with neither species \( A \) nor \( B \) adsorbed**

The response ratio working curves for \( B \) and \( C \) for this case are

\[
R_B(k\tau) = 1 - \frac{2^{1/2} \text{I}_1(1, 3/2, -2k\tau)}{\text{I}_1(1, 3/2, -k\tau)} - \Phi_3(k, 2\tau, \tau) \quad (30)
\]

\[
R_C(k\tau) = 1 - \frac{2^{1/2}[1 - \text{I}_1(1, 3/2, -2k\tau)] - \Phi_2(k, 2\tau, \tau) + \Phi_3(k, 2\tau, \tau)}{\text{I}_1(1, 3/2, -k\tau)} \quad (31)
\]

respectively, and are plotted in Fig. 1 where the open circles are values calculat ed by finite difference (FD) simulation of the system. Agreement between the FD simulation and the analytic results is excellent.

From Fig. 1 it can be seen that \( R_C(k\tau) \) has a wider dynamic range than \( R_B(k\tau) \) and is preferable for rate constant determinations if the spectroscopic conditions permit. The response for species \( B \) is obviously not as sensitive for mechanistic assignments since the irreversible nature of the path to form \( C \) effectively decouples it from the fate of \( C \). The form of \( R_B(k\tau) \) presented here will also apply to irreversible ECE, ECEC, ECECE, etc. systems if there is no adsorption [9].
Most of the experimental complications which can arise in this case, such as non-zero and potential dependent background absorbances can be treated by analogy with charge data treatment methods. Truly challenging situations can arise if it is not possible to find isolated bands for the individual species. There is no simple solution to problems of this sort. The optimal course of action is strongly dependent upon the exact nature of the problem. One general approach, which may be fruitful, involves the fact that the charge passed at any point in time is directly proportional to the total amount of species B plus C in solution as well as the amount of A consumed. This combination of charge and spectroscopic data may be used to arrive at a consistent set of rate constants.

Adsorption of both species A and B

Consider that the surface excess of B is somewhat less than the surface excess of A. In the forward step, the electrode process produces a concentration impulse of B at the electrode surface at \( t = 0 \) of magnitude \((\Gamma_A^* - \Gamma_B^*)\) in addition to the diffusional concentration. The reduction of the adsorbed A is responsible for the time independent term in charge. Some of the B is present on the electrode to produce the surface excess \( \Gamma_B^* \) and the remainder of the excess B is in solution at the surface and is free to diffuse as well as react to form C. The distribution of this excess B is given by \( c_B^a(x, t) \) for all times less than \( T \).

\[
c_B^a(x, t) = (\Gamma_A^* - \Gamma_B^*) \exp(-kt - x^2/4D_BT)/(\pi t)^{1/2}
\]  

(32)
When \( k \) is zero, this reduces to the contribution derived by Christie et al. [10] for the non-kinetic case. The optical response for \( B \), eqn. (11) shows a term \((\Gamma_A^* - \Gamma_B^*) \exp(-kt)\) that represents the amount of excess \( B \) which remains in solution, the remainder having reacted to form \( C \).

When the potential is switched at time \( \tau \), the surface excess of \( B \) is converted to \( A \), instantaneously producing another current transient. The surface excess of \( A \) must now be re-established, and some of the \( A \) will come from \( B \) in solution at the electrode surface since \( \Gamma_A^* > \Gamma_B^* \). At time equal to \( \tau \) there is in solution an amount of \( B \) given by \((\Gamma_A^* - \Gamma_B^*) \exp(-k\tau)\) in excess over the amount predicted by the simpler model, distributed according to eqn. (32). This material will continue to be depleted by the processes of: (i) diffusion to the electrode surface where it is converted to \( A \) and (ii) chemical reaction to form \( C \). The total amount of the excess \( B \) remaining in solution at any time after \( \tau \) is given by the \((2/\pi)(\Gamma_A^* - \Gamma_B^*) \exp(-kt) \sin^{-1}(\tau - t)^{1/2}\) term in eqn. (21b).

The optical ratio when adsorption occurs, \( R_B^\alpha(k, \phi, \beta, \tau) \), can be written as:

\[
R_B^\alpha(k, \phi, \beta, \tau) = \frac{R_B(k\tau) + \beta \tau^{-1/2}(1 - \phi)V(k\tau)(2 - \exp(-k\tau))}{1 + \beta \tau^{-1/2}(1 - \phi)2V(k\tau)}
\]  

(33)

The new parameters are defined by

\[
\beta \tau^{-1/2} = \pi^{1/2} \Gamma_A^* \tau^{-1/2}/2e_\lambda^0 D_A^{1/2} \quad 0 \leq \beta \tau^{-1/2} \leq 0.1
\]  

(34)

\[
\phi = \Gamma_B^*/\Gamma_A^*
\]  

(27)

\[
V(k\tau) = \exp(-k\tau)/2_1 F_1(1, 3/2, -k\tau)
\]  

(35)

The range of \( \beta \tau^{-1/2} \) is arbitrarily imposed but corresponds to realistic experimental conditions, whereas the range of \( \phi \) is imposed by the initial assumptions.

Species \( A \) and \( B \) adsorbed — no chemical kinetics

Before treating the case with chemical kinetics, it is instructive to examine the non-kinetic response. This can be formed by letting \( k \) equal zero in eqns. (32)–(35). The optical response with adsorption becomes

\[
R_B^\alpha(0, \phi, \beta, \tau) = \frac{2 - 2^{1/2} + \beta \tau^{-1/2}(1 - \phi)/2}{1 + (1 - \phi)\beta \tau^{-1/2}}
\]  

(36)

A comparison of eqn. (36) with the equivalent expression for the charge ratio given in ref. 1 shows two striking differences between the optical response for \( B \) and the charge response. The first is the obvious absence of contributions from the double layer which is one of the basic advantages of the optical method. An equivalent term could arise if the optical properties
of the solvent and/or electrolyte are sufficiently potential dependent, or if $\epsilon^*_a(\lambda)\Gamma^*_a$ and/or $\epsilon^*_b(\lambda)\Gamma^*_b$ are not negligible at the wavelength in question. The second difference is that the effects of adsorption reach a maximum at $\phi = 0.0$ and go to zero for equal adsorption of A and B. The properties of eqn. (36) are explored in Fig. 2. Within the range of the variables used, the lowest value of the response is 0.51 and the response asymptotically approaches the diffusion controlled value of 0.5858 as $\tau$ increases. This means that as expected the optical ratio for B is much less sensitive to adsorption effects than is the charge ratio under these conditions; however, we see that the

![Fig. 2. The effect of reactant and product surface excesses on the double potential step chronoabsorptometry response ratio for species B, $R_B^n(k, \phi, \beta, \tau)$ vs. log $\tau^{1/2}$ in the absence of chemical kinetics ($k = 0.0$) at a planar electrode. (1) Effect of reactant surface excess. No product adsorption. $\phi = 0; \beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (2) Effect of reactant surface excess. Reactant surface excess greater than product surface excess. $\phi = 0.5; \beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (3) Effect of reactant surface excess. Equal adsorption of reactant and product. $\phi = 1.0; \beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (4) Effect of product/reactant surface excess ratio. $\beta = 0.5$ s$^{1/2}; \phi$ values: (A) 1.0, (B) 0.75, (C) 0.50, (D) 0.25, (E) 0.00.]
optical method is not immune to the effects of adsorption.

The effects of finite values for $\epsilon^*_A(\lambda)\Gamma^*_A$ can be handled in a straightforward manner by noting that the absorbance prior to the initiation of the forward step will consist of $\epsilon^*_A(\lambda)\Gamma^*_A$ plus any background term. All that is required to correct the back step data for this contribution is to subtract the absorbance prior to the first step from the experimental back step data.

The effect of a finite value for $\epsilon^*_B(\lambda)\Gamma^*_B$ can be included by simply replacing $\phi$ in eqn. (36) with $\phi(1 - 2\epsilon^*_B(\lambda)/\epsilon^*_B(\lambda)$ in the numerator and $\phi(1 - \epsilon^*_B(\lambda)/\epsilon^*_B(\lambda)$ in the denominator.

Fig. 3. The effects of reactant and product surface excess on the double potential step chronoabsorptometry response ratio for species B, $R_B(k, \phi, \beta, \tau)$ vs. $\log \tau^{1/2}$ for an irreversible first-order EC mechanism at a planar electrode. $k = 2.0 \text{ s}^{-1}$. (1) Effect of reactant surface excess. No product adsorption. $\phi = 0; \beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (2) Effect of reactant surface excess. Reactant surface excess greater than product surface excess. $\phi = 0.5; \beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (3) Effect of reactant surface excess. Equal adsorption of reactant and product. $\phi = 1.0; \beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (4) Effect of product/reactant surface excess ratio. $\beta = 0.05 \text{s}^{1/2}; \phi$ values: (A) 1.0, (B) 0.75, (C) 0.50, (D) 0.25, (E) 0.00.
**EC case with species A and B adsorbed**

The response ratio for species B for this case, eqn. (33), is explored in Fig. 3 for the situation where the $e_A^*(\lambda)\Gamma_A^*$ and $e_B^*(\lambda)\Gamma_B^*$ terms can be considered negligible. Assuming that the adsorption effects are within the range of Fig. 3, the adsorption process will have a negligible effect on the accuracy of $k$ determined by this response provided that the data are evaluated in the range where the response ratio exceeds 0.75. The effect of finite $e_A^*(\lambda)\Gamma_A^*$ can be eliminated by the subtractive process previously discussed. Treatment of a finite $e_B^*(\lambda)\Gamma_B^*$ contribution is not as simple in this instance. If one has chronocoulometric charge data available it is possible to evaluate $\Gamma_A^*$ and $\Gamma_B^*$ for $kT \leq 0.01$, eqn. (11) will be approximately linear with square root of time, having a slope of $2e_A^0e_B(\lambda)D_A^1/\pi$ and an intercept $e_B(\lambda)(\Gamma_A^* - \Gamma_B^*) + e_B^*(\lambda)\Gamma_B^*$. In principle this information can be combined to evaluate the contribution from $e_B^*(\lambda)\Gamma_B^*$ which can then be subtracted from the forward step data. One expects that this would be implemented only as a last resort.

The response ratio for species C in the absence of significant $e_A^*(\lambda)\Gamma_A^*$ and $e_B^*(\lambda)\Gamma_B^*$ terms is given by:

$$R_C^*(k, \phi, \beta, \tau) = \frac{R_C(k\tau) + \beta\tau^{-1/2}[1 - \phi \{W(k\tau) - H(k\tau, 2\tau) + \frac{1}{2}\exp - 2k\tau\}]}{1 + \beta\tau^{-1/2}(1 - \phi)W(k\tau)}$$

$$W(k\tau) = \frac{(1 - \exp(-k\tau))}{1 - \_1F_1(1, 3/2, -k\tau)}$$

$H(k\tau, 2\tau)$ has been described previously [1]. The response for C is similar to that for B in that the effects of adsorption are cancelled when $\phi$ is unity. The behavior of eqn. (37) is explored in Fig. 4 which is analogous to Fig. 3. The effect of adsorption is much more pronounced in this ratio than for B or for the charge ratio (Figs. 2-4, ref. 1) at short $\tau$ values because of the small quantity of C normally produced. The effects of $e_A^*(\lambda)\Gamma_A^*$ can be eliminated as before. The effects of $e_B^*(\lambda)\Gamma_B^*$ can, in principle, be handled by recognizing that for $k\tau \leq 100$ eqn. (13b) predicts that a plot of $A_C(t < \tau)$ vs. square root of time produces a straight line with slope $2e_C(\lambda)e_0^2(D_A/\pi)^{1/2}$ and intercept $e_C(\lambda)(\Gamma_A^* - \Gamma_B^*) + e_B^*(\lambda)\Gamma_B^*$. If one knows $e_B(\lambda)$ and $e_C(\lambda)$ then this approach can also be used to eliminate the $e_B^*(\lambda)\Gamma_B^*$ effects for the species B data. The major difficulty with this extrapolation method is that the data must be collected for a period of at least five times, and preferably ten times, the length of the delay before collection in order to obtain an acceptable level of uncertainty in the intercept. A second extrapolation method is also possible if one knows the values of $e_B(\lambda)$ and $e_C(\lambda)$. If one adds the forward step data for B to $e_B(\lambda)/e_C(\lambda)$ times the corresponding data for C then the exponential and confluent hypergeometric time dependencies cancel out and
Fig. 4. The effects of reactant and product surface excess on the double potential step chronoabsorptometry response ratio for species C, $R_C^h(k, \phi, \beta, \tau)$ vs. log $\tau^{1/2}$ for an irreversible first-order EC mechanism at a planar electrode. $k = 2.00 \text{ s}^{-1}$. (1) Effect of reactant surface excess. No product adsorption. $\phi = 0$; $\beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (2) Effect of reactant surface excess. Reactant surface excess greater than product surface excess. $\phi = 0.5$; $\beta$ values (in s$^{1/2}$): (A) 0.00, (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (3) Effect of reactant surface excess. Equal adsorption of reactant and product. $\phi = 1.0$; $\beta$ values (in s$^{1/2}$): (A) 0.00; (B) 0.01, (C) 0.025, (D) 0.05, (E) 0.10. (4) Effect of product/reactant surface excess ratio. $\beta = 0.05 \text{ s}^{1/2}$; $\phi$ values: (A) 1.0, (B) 0.75, (C) 0.50, (D) 0.25, (E) 0.00.

an extrapolation of these data versus square root of time will yield a straight line with slope $2\epsilon_A^0\epsilon_B^0(D_A/\pi)^{1/2}$ and intercept $\epsilon_B^0(\lambda)(1 + \epsilon_B^0(\lambda)/\epsilon_C^0(\lambda)\Gamma_A^* + \epsilon_B^0(\lambda)(\Gamma_A^* - \Gamma_B^*)$ which is valid at all times. This method is probably only practical when experimental data are directly acquired with a computer.

POLYNOMIAL APPROXIMATIONS OF WORKING CURVES AND FUNCTIONS

Published working curves are useful in aiding the conceptualization of responses but are of little value to one who wishes to apply the work of other authors. Tables of values are more useful but can only describe the
functions at relatively few points. The most flexible presentation would seem to be one which allows the experimenter to duplicate the results of an author at any desired value of the independent variable, particularly if a computer is to be used in the data reduction process. Since the analytic functions encountered here are fairly complex and converge relatively slowly it will usually not be practical to evaluate the analytic functions themselves. An alternative approach is to present polynomial or other approximations to the functions over the most probable range of interest.

The functions encountered here can be reproduced, with a maximum absolute error of $5 \times 10^{-4}$ over the range specified, by simple polynomials in $kT$. These polynomials were generated by a least squares polynomial

**TABLE 1**

Polynomial coefficients

<table>
<thead>
<tr>
<th>Function $P(kT)$</th>
<th>$0 \leq kT \leq 1.0$</th>
<th>$1.0 \leq kT \leq 4.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_2(k, 2\tau, \tau)$</td>
<td>0.9999505(+0) 0.1329530(+1)</td>
<td>0.9585647(-2) 0.9533955(+0)</td>
</tr>
<tr>
<td></td>
<td>-0.5932597(+0) -0.3601724(+0)</td>
<td>0.2720781(+0) 0.4718329(-1)</td>
</tr>
<tr>
<td>$\Phi_3(k, 2\tau, \tau)$</td>
<td>0.9990200(+0) 0.1661001(+1)</td>
<td>0.4597059(-1) 0.2191498(+1)</td>
</tr>
<tr>
<td></td>
<td>-0.1528651(+1) -0.1151117(+1)</td>
<td>-0.9989358(+0) 0.2642317(+0)</td>
</tr>
<tr>
<td>$R_B(kT)$</td>
<td>0.585852(+0) 0.2494404(-2)</td>
<td>0.4484245(+0) 0.1151117(+1)</td>
</tr>
<tr>
<td></td>
<td>-0.318490(-1) -0.2191498(+1)</td>
<td>-0.3716767(+0) 0.2404404(-2)</td>
</tr>
<tr>
<td></td>
<td>-0.2006030(+0) 0.1258014(+1)</td>
<td>-0.3287122(-1) 0.1661001(+1)</td>
</tr>
<tr>
<td>$R_C(kT)$</td>
<td>0.8273558(+0) 0.12922290(+1)</td>
<td>0.2559223(-1) 0.1258014(+1)</td>
</tr>
<tr>
<td></td>
<td>-0.7816766(+0) -0.4168607(+0)</td>
<td>-0.3351159(+0) -0.4386857(-1)</td>
</tr>
<tr>
<td>$Y(kt)$</td>
<td>0.9992754(+0) 0.9366775(-2)</td>
<td>0.3802099(+0) 0.1315598(-1)</td>
</tr>
<tr>
<td></td>
<td>-0.7816766(+0) -0.4168607(+0)</td>
<td>-0.3351159(+0) -0.4386857(-1)</td>
</tr>
</tbody>
</table>

$^a 0.01 \leq kT \leq 1.00.$
fitting routine operating upon analytic data uniformly distributed with respect to $k\tau$. The polynomials are defined over two regions $0.0 \leq k\tau \leq 1.0$ and $1.0 \leq k\tau \leq 4.0$ and the appropriate polynomials must be used in each region. The polynomial coefficients are listed in Table 1. Note that the number in parentheses associated with each coefficient represents a power of ten multiplier for that coefficient. When no entry appears in a range this means that the entry to the left in the table also holds in the higher range.

As an example, the function $\Phi_2(k, 2\tau, \tau)$ in the range $1.0 \leq k\tau \leq 4.0$ can be evaluated by the FORTRAN STATEMENT

$$\text{PHI2} = 1.32953 - X*(0.95333955 + X*(0.3601724 - X*0.04718329)) \quad (39)$$

where $X$ is $(k\tau)^{1/2}$.

The function $\mathbf{1}_F(1, 3/2, -kt)$ can be efficiently evaluated over the range $0.0 \leq k\tau \leq 9.0$ by means of an auxiliary function

$$\mathbf{1}_F(1, 3/2, -kt) = \exp(-0.3136733kt)Y(kt) \quad (40)$$

with $Y(kt)$ being represented as a polynomial in $(kt)^{1/2}$ in Table 1.

CONCLUSIONS

Spectroscopic monitoring of the electrochemical reaction product B and the kinetic product C in a homogeneous EC kinetic process can yield valuable rate and mechanistic information even in some instances when adsorption on the electrode occurs. The chronoabsorptometric response of unadsorbed B is relatively insensitive to adsorption phenomena. The chronoabsorptometric response for C is more sensitive to adsorption than the analogous chronocoulometric response and is also sensitive to follow up steps of a chemical nature which would not be detected by monitoring the charge or the spectral properties of B.

Serious experimental difficulties can arise from adsorption of A and B on the electrode if the absorption bands of the adsorbed forms interfere with those of the solution forms of B and C, the obvious limiting case being when all light is absorbed at the electrode. It does appear that somewhat less catastrophic cases will still be tractable.

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