CHRONOPOTENTIOMETRY WITH PROGRAMMED CURRENT AT THE DROPPING MERCURY ELECTRODE

PART IV. THEORETICAL RELATIONSHIPS FOR A CATALYTIC MECHANISM

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ABSTRACT

The chronopotentiometric response for the catalytic mechanism has been examined when a programmed current of the form \( I = I_0 t^{m+1/6} \) \((m > 0)\) is applied to the DME. Procedures of quantitative kinetic data analysis in order to determine the kinetic parameters of the chemical reaction and of the charge-transfer reaction are proposed. With this purpose, it follows that values of \( m > \frac{1}{6} \) and \( m = 0 \) are the most appropriate.

INTRODUCTION

In Parts I–III of this series [1–3] we have shown that DME chronopotentiometry with a current–time function (ctf) of the form \( I = I_0 t^{m+1/6} \) \((m > 0)\) is a very appropriate technique for the study of electrode processes. In turn, in the present paper, we shall examine the chronopotentiometric response for a catalytic mechanism and develop procedures of quantitative kinetic data analysis in order to determine the kinetic parameters of the chemical reaction and of the charge-transfer reaction (ctf). On the other hand, the existing relation with the response obtained at a stationary plane electrode (which has already been derived [4–7]) is also analysed.

THEORY

The catalytic mechanism may be written (see refs. 1 and 2 for notation/definitions)

\[
A + n e^{-} \xrightleftharpoons{k_1}{k_2} \text{B; \quad B} \xrightarrow{k_3} \text{A}
\]

If a ctf of the form \( I(t) = I_0 t^{m+1/6} \) \((m > 0)\) [1] is applied to the DME, the surface concentrations, \(c_A(0, t)\) and \(c_B(0, t)\), can be obtained by following the same derivational pattern previously adopted in Parts II and III of this series [2,3]. Thus, we
have

$$c_A(0, t) = \xi^* (1 - (1 + K)N(m, t)G_m(\chi)/(1 + K))$$

(1)

$$c_B(0, t) = \xi^* (K + (1 + K)N(m, t)G_m(\chi))/(1 + K)$$

(2)

where

$$\xi^* = c_A^* + c_B^*$$

(3)

$$N(m, t) = N_0 \tau^m/P_{bm}/\tau$$

(4)

$$N_0 = \sqrt{12/\tau D}(I_0/nFA_0\xi^*)$$

(5)

$$p_2 = 2\Gamma(1 + z)/\Gamma(1 + z/2)$$

(6)

$$G_m(\chi) = p_{bm}/\tau e^{-\chi} \sum_{j=0}^1 j! p_{bm}^{(j+1-\chi)/\tau}$$

(7)

$$\chi = k_1; \quad k = k_1 + k_2$$

(8)

$$K = k_2/k_1$$

(9)

From eqn. (1) it follows that the transition time $\tau$ is obtained by writing $c_A(0, t) = 0$, i.e.

$$(\tau/\tau_0)^m = 1/(1 + K)G_m(\chi_\tau); \quad \chi_\tau = k\tau$$

(10)

where $\tau_0$ is the transition time which would be observed in the absence of the chemical reaction and is given by

$$\tau_0^m = p_{bm}/\tau N_0$$

(11)

In turn, the potential–time function is

$$\left(\frac{1}{\theta(m, t)}\right)^{1/2} \left(\frac{1}{1 + K} \frac{1}{N(m, t)} - (1 + K)G_m(\chi)\right)$$

$$- \left(\frac{K}{N(m, t)} + (1 + K)G_m(\chi)\right)^{1/2}$$

(12)

with

$$\theta(m, t) = \theta_{0}\tau/\tau_{bm/\tau}$$

(13)

$$\theta_0 = 12k_1/\tau D$$

(14)

$$\eta(t) = (nF/RT \ln 10) (E(t) - E^0)$$

(15)

If the ctr is reversible ($k_1 \to \infty$), eqn. (12) is simplified to

$$\eta(t) = \log \left(\frac{1 - (1 + K)N(m, t)G_m(\chi)}{K + (1 + K)N(m, t)G_m(\chi)}\right)$$

(16)

Conversely, if the ctr is totally irreversible ($k_1 \ll 1$), eqn. (12) becomes

$$\eta(t) = \frac{1}{\alpha} \log \left(\frac{1 - (1 + K)N(m, t)G_m(\chi)}{(1 + K)N(m, t)(\theta(m, t))^{1/2}}\right)$$

(17)

RESULTS AND DISCUSSION

In the cases where a transition time is observed (see below), we may determine the kinetic parameters of the chemical reaction from working curves of $(\tau/\tau_0)^m$ vs. $\chi$, (eqn. 10). In Fig. 1 we have represented these curves for $m = \frac{1}{2}, m = 1$ and different values of $K$. If the chemical reaction is irreversible, these plots allow us to obtain the $k_1$-value. Conversely, if $K = 0$, we must know the equilibrium constant in order to determine $k_1$ and $k_2$.

This may be accomplished analogously to that previously described for the CE mechanism [2], and so from eqns. (5), (10) and (11) we find

$$\lim_{t_0 \to \infty} \left(\frac{I_0}{I(t)}\right)^m = \sqrt{\frac{12}{\tau D}} \frac{nFA_0\xi^*}{1 + K} \frac{p_{bm}/\tau}{p_{bm/\tau}}$$

(18)

Hence, we may obtain the $K$-value from the limit of $I_0/\tau^m$ at values of $I_0$ which are sufficiently large.

However, if we take into account the behaviour of $G_m(\chi)$ for $\chi \gg 1$ [2], i.e.

$$G_m(\chi) = \sqrt{7}/12\chi p_{bm}/\tau$$

(19)

it follows from eqns. (1), (4) and (19) that if $0 < m < \frac{1}{2}$ the existence of a transition time depends on the values of $k, K$ and $\tau_0$. Thus, for $m = \frac{1}{2}$ one finds that a $\tau$ exists.

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**Fig. 1**: $(\tau/\tau_0)^m$ vs. $\chi$, (eqn. 10). (---) $m = \frac{1}{2}$; (---) $m = 1$. K-values shown on the curves.
only if the condition
\[ k_i/(1 + K)^2 < 1.20/\tau_0 \]  
(20)
is verified.

When this condition is not accomplished, it follows that, although \( t \) increases, no \( \tau \) will be observed, because \( E(t) \) tends towards a constant value which depends on \( N_0, K, k_1 \) and \( \theta_0 \). Thus, if \( K = 0 \) and the ctc is reversible, from eqns. (16) and (19) one obtains \((m = \frac{1}{2})\)
\[ E(t) = E^0 + (RT/nF) \ln \left( \frac{1}{N_0} \right)(12k_1/7)^{1/2} \]
\( t \to 1 \)
\[ \ln \left( \frac{1}{N_0} \right)(12k_1/7)^{1/2} \]

In turn, if \( k_1 \ll 1 \) we have
\[ E(t) = E^0 + \frac{RT}{2anF} \ln \theta_0 + \frac{RT}{anF} \ln \left( \frac{1}{N_0} \right) - \frac{(7/12k_1)^{1/2}} \]
\( t \to 1 \)

Conversely, for \( m > \frac{1}{2} \), it is readily shown (see eqns. 1, 4 and 19) that if \( t \) increases there is always a value of \( t = \tau \) for which \( c_\alpha(0, \tau) = 0 \). Hence, we may, under these conditions, use the working curves of Fig. 1 regardless of the \( k \)-values. This different behaviour of the potential–time curves \( E(t) \) for \( m \ll \frac{1}{2} \) and \( m > \frac{1}{2} \) is shown in Figs. 2 and 3, where we have plotted \( \Delta E = E(t) - E^0 \) vs. \( t \) for \( N_0 = 1 \, \text{s}^{-m}, k_1 = \infty, K = 0 \) and different values of \( m \). In Fig. 2, eqn. (19) is verified \((k = 0.5 \, \text{s}^{-1}, \tau_0 = 2.05 \, \text{s})\) and therefore, a value of \( \tau \) is obtained, both for \( m = \frac{1}{2} \) and \( m = 1 \) (the \( E/t \) curves for \( m = 0 \) will be discussed below). Conversely, in Fig. 3 \( k_1 \) is equal to \( 3 \, \text{s}^{-1} \) (> \( 1.20/\tau_0 \)) and hence, a transition time is observed only for \( m = 1 \). However, it is interesting to show that for \( m = \frac{1}{2} \) and \( t \gg 1 \), \( E(t) \) takes a constant value (defined by eqn. 21), and under these conditions we may obtain \( k_1 \) if \( E^0 \) is known.

In Table 1 we have presented the approximate maximum values of \( k_1 \) that may be obtained for different values of \( m \) and \( \tau \). As mentioned above, for \( m \ll \frac{1}{2} \) no transition time will be observed if the \( k_1 \)-values are larger than those given in this table. However, for \( m = 1 \) there is always a \( \tau \)-value regardless of \( k_1 \), although, since \( \tau \)

![Fig. 2. E/t curves for a reversible process \( (\theta_0 = \infty) \). \( N_0 = 1 \, \text{s}^{-m}, n = 1, T = 298 \, \text{K}, k_1 = 0.5 \, \text{s}^{-1}, K = 0 \); \( m \)-values shown on the curves. The dashed lines show the transition time for the \( m = \frac{1}{2} \) and \( m = 1 \) cases.](image1)

![Fig. 3. E/t curves for a reversible process; \( k_1 = 3 \, \text{s}^{-1} \). The dashed lines show the transition time for \( m = 1 \). Other conditions as Fig. 2.](image2)

<table>
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<th>( \tau_0/\text{s} )</th>
<th>( k_1/\text{s}^{-1} )</th>
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TABLE 1
Approximate maximum values of \( k_1 \) \((K = 0)\), as a function of \( \tau_0 \) and \( m \)
must be within the drop lifetime, the available range of \( k_r \)-values is also limited to those given in Table 1. In any case, note how for a given value of \( \tau_d \), the available range of \( k_r \)-values is much greater for \( m = 1 \) (especially if \( \tau_d < 1 \)) than for \( m \leq 1 \).

The effects of chemical reversibility on the \( E/t \) curves are shown in Fig. 4 for \( m = 1 \), \( k = 50 \) s\(^{-1}\) and different values of \( K \). Note that as \( K \) increases the \( \eta \)-values become lower, in accordance with eqn. (10). In fact, for \( K \to \infty \), \( c^* \to 0 \) and therefore, if \( I_0 \) is set, no current takes place under these conditions (\( \tau = 0 \)).

Regarding the influence exerted by the ctr on the \( E/t \) curves, it follows that the classification previously given for the CE and EC mechanisms [2,3] is also valid in this case and hence, further discussion is not given here.

Finally, we shall analyse the \( E/t \) curves for \( m = 0 \). In this case eqn. (12) becomes

\[
\frac{10^{n(t)}}{W_0 \chi^{1/2}} = \frac{1}{1 + K} \left[ \frac{1}{N} - (1 + K)G_0(\chi) \right]
- \left( \frac{K}{N} + (1 + K)G_0(\chi) \right) 10^{n(t)}
\]

(23)

where

\[ W_0 = \frac{3\pi k_i^2}{7Dk} \]

(24)

\[ N = e^{1/2} N_0/2 \]

(25)

In Fig. 5 we have plotted \( \eta(\chi) vs. \log \chi \) for \( \alpha = 0.5 \), \( N_0 = 0.05 \) and different values of \( K \) and \( W_0 \). Note how in this case no transition time exists, because \( E(t) \) increases with \( t \), starting from an initial value which is equal to \( (1 - (1 + K)N)/(K + (1 + K))N \) if the ctr is reversible (see Figs. 2 and 3), while \( E(0) = -\infty \) if the ctr presents non-Nernstian behaviour. Under these conditions, the curves given in Fig. 5 have two asymptotes defined by

\[
[\eta(\chi)] = \frac{1}{2\alpha} \log \chi + \frac{1}{2\alpha} \log W_0 + \frac{1}{\alpha} \log \frac{1 - N(1 + K)}{N(1 + K)}
\]

(26)

\[
[\eta(\chi)] = \left\{ \begin{array}{ll}
\log \left( \frac{1}{N} \left( \frac{3\pi}{7} \right)^{1/2} \right) + \frac{1}{2} \log(k_i t); & K = 0 \\
-\log K; & K = 0
\end{array} \right.
\]

(27a)

(27b)

From eqns. (27) it follows that the behaviour of \( E(t) \) for \( t \gg 1 \) is different, depending on whether or not \( K = 0 \). In the former case, \( E(t) \) increases continuously with \( t \), while if \( K = 0 \) \( E(t) \) tends towards a constant value which is equal to \( E^0 = RT \).
In \(K/mF\). In any case, eqns. (27) allows us to determine \(E^0\) if the value of \(k_1\) (or \(K\)) is known. In turn, dependence of \(\eta(\chi)\) on \(\log \chi\) for \(\chi \ll 1\) is \(\alpha\) and \(k_\alpha\) to be determined. However, if \(k \gg 1\), eqn. (26) is valid only for \(t \ll 1\), and in order to avoid this difficulty we may use an analogous procedure to that described for the CE mechanism [2]. Thus, by plotting \(\eta(\chi^*)\) vs. \(\log \chi^*\), where

\[
\chi^* = \chi^{1/2} (1 - N(1 + K)G_0(\chi))/N(1 + K)
\]

it follows that the asymptote to this curve for \(\chi^* \ll 1\) is

\[
[\eta(\chi^*)] = (1/\alpha) \log \chi^* + (1/2) \log W_0
\]

Equation (28) allows \(\alpha\) and \(k_\alpha\) to be obtained through measurements of \(E(t)\) with \(t\)-values larger than those required in eqn. (26) (see ref. 2 for details).

In short, working curves of \((\tau/\tau_0)^m\) vs. \(\chi\) are appropriate in order to obtain the kinetic parameters of the chemical reaction (especially for \(m > \frac{1}{2}\)). In turn, \(E/t\) curves for \(m = 0\) allow us to determine the corresponding parameters of the cfr.

**Chronopotentiometry at stationary plane electrodes (SPE)**

As previously for the CE and EC mechanisms [2,3], it follows that the expressions derived above for the catalytic mechanism are also readily adapted for a SPE by following the suggestions made in ref. 2. In particular, if a constant current is applied to a SPE no transition time is obtained if

\[
k_1 > \frac{\pi}{4\tau_0} \quad (K = 0)
\]

which is an equivalent expression to eqn. (20). In turn, one finds that regardless of the \(k\)-values a transition time is always obtained if a cfr increasing with any positive time power is used.

**Conclusions**

In addition to the characteristics in common with the CE and EC mechanisms [2,3], DME chronopotentiometry for the catalytic mechanism shows the following features:

1. For \(0 < m < \frac{1}{2}\) the existence of a transition time depends on the values of \(k\), \(K\) and \(\tau_0\). Conversely, if \(m > \frac{1}{2}\) one finds that a transition time is always obtained, regardless of the \(k\)-values (at stationary electrodes this condition is fulfilled for a cfr increasing with any positive time power).

2. The rate constants of the chemical reaction can be determined in a similar way by using dc polarography [8] or DME chronopotentiometry (compare the working curves of Fig. 1 with the corresponding plots of \(i/i_a\) vs. \(\chi\)) [8].

3. If the cfr is irreversible, analysis of the \(E/t\) curves by using a cfr with \(m = 0\) provides a method for the determination of \(\alpha\) and \(K\). As showed for the CE and EC mechanisms, this procedure has no correspondence with controlled-potential methods.

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**References**