Short communication

Chronopotentiometry at the dropping mercury electrode when the current is a power and/or exponential function of time: study of the second step of an EE mechanism with widely separated standard potentials

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1. Introduction

We have previously developed a theory for the use of a programmed current which can be expressed by the general form \( I(t) = I_0 t^\gamma e^{-\alpha t} \) for a single charge transfer reaction [1]. The aim of this investigation was to carry out a general study of the concentration profiles, the surface concentrations and the potential–time response corresponding to the second step of an EE mechanism in a dropping mercury electrode (DME) when the programmed current is applied after a blank period \( t_b \). For the DME we have chosen the more rigorous expanding sphere electrode model and, from the general equations derived, the models corresponding to the expanding plane electrode and also to static electrodes, such as the SMDE and the static plane electrode, can be deduced as particular cases.

For this study we have supposed that the diffusion coefficients of the three species implicated are not equal. This supposition has never been considered in the literature for this mechanism studied by chronopotentiometric techniques with spherical diffusion [2–4], owing to the fact that, under these conditions, the analytical resolution of this problem is considerably more complicated, since the additivity principle proposed by Murray and Reilley [5] cannot be applied.

We have analysed the behaviour of the concentration profiles of three species implicated in the EE mechanism during the second step. Moreover, we show that the relation between transition times of the two steps is strongly dependent on the values of diffusion coefficients of the different species under spherical diffusion, contrary to the situation occurring under planar diffusion.

Finally, we studied the influence of the electrode sphericity and the kinetic parameters of both steps in the potential–time response and we also propose methods to calculate the kinetic parameters of the second step, \( k_{21} \) and \( \alpha_2 \), for a totally irreversible process, and the half-wave reversible potential for a totally reversible process.

2. Theory

The stepwise reduction of a species A according to the scheme

\[
\begin{align*}
A + n_1 e^- & \xrightleftharpoons[k_{\text{rin}}]{k_{\text{bi}}} B \\
B + n_2 e^- & \xrightleftharpoons[k_{\text{rin}}]{k_{\text{bi}}} C
\end{align*}
\]

when a programmed current of the form

\[ I(t) = I_0 t^\alpha e^{-\alpha t} \]  \hspace{1cm} (1)

is applied to a DME, can be treated for the case in which the substances A and B are reduced at sufficiently different potentials to yield a potential–time curve exhibiting two steps. The potential–time response for the first step is not influenced by the second step because it occurs when the transition time for species A has already been reached. This response is given in Ref. [1].

The programmed current applied, given by Eq. (1), is very general and is reduced to a power function of time when \( \alpha = 0 \), to an exponential function of time when \( \alpha = 0 \) and to a current step when \( \alpha = \omega = 0 \). In general, this programmed current must be used after a blank period \( t_b \) if it is applied to dynamic electrodes such as the DME [6].
The boundary value problem associated with the second step is given by
\[ \delta c_h^{\infty} = \delta c_b^{\infty} = \delta c_c^{\infty} = 0 \]  
\[ t' = 0, \quad r > r_0, \quad t' > 0, \quad r \to \infty \]  
\[ c_A^\infty(r, t') = c_A^\infty(r, t_1) \]  
\[ c_B^\infty(r, t') = c_B^\infty(r, t_1) \]  
\[ c_C^\infty(r, t') = 0 \]  
\[ t' > 0, \quad r = r_0 \]  
\[ c_A^h(r_0, t') = 0 \]  
\[ (n_1 + n_2)D_A \left( \frac{\partial c_A^h}{\partial r} \right)_{r=r_0} + n_2 D_B \left( \frac{\partial c_B^h}{\partial r} \right)_{r=r_0} = \frac{I(t)}{FA(t_1)} \]  
\[ D_A \left( \frac{\partial c_A^h}{\partial r} \right)_{r=r_0} + D_B \left( \frac{\partial c_B^h}{\partial r} \right)_{r=r_0} + D_C \left( \frac{\partial c_C^h}{\partial r} \right)_{r=r_0} = 0 \]  
where
\[ t_1 = t_1 + t \]  
\[ t = t_1 + t', \quad 0 \leq t' \leq t_{11} \]  
where \( t_1 \) is the blanking period, \( t_1 \) has its zero at the instant the drop starts to grow, \( t = 0 \) corresponds to the start of application of the current and \( t' \) is measured from the first transition time \( t_{11} \).

In Eqs. (3) and (4), \( c_A^\infty(r, t_1) \) and \( c_B^\infty(r, t_1) \) are the concentrations of A and B species deduced for step 1 (see Eqs. (18) and (19) in Ref. [1]) and \( \delta c_h \) in Eq. (2) is the operator corresponding to the expanding sphere electrode model [7]
\[ \delta_h = \frac{\partial}{\partial t} - D_A \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{a^2}{3r^2} \frac{\partial}{\partial r} \]  
where the subscript \( h \) refers to species A, B or C.

Using chronopotentiometric techniques it is not possible to analyse the total potential–time response corresponding to an EE mechanism under conditions different to those given by Eqs. (3)–(8). This is because the situation described by Eqs. (3)–(8) is the only one in which the time evolution of the system can be unmistakably deduced. In intermediate situations (i.e. when the reduction of B occurs before the whole transition time of A, \( t_{11} \), has been reached), it is not possible to establish the boundary value problem for the second step and, therefore, the total potential–time response cannot be analysed rigorously using chronopotentiometry.

By following the dimensionless parameters method we obtain the corresponding concentration profiles of species A, B and C for the second step. From these profiles, we deduce the corresponding surface concentrations, which are given by
\[ c_A^h(r_0, t') = 0 \]  
\[ c_B^h(r_0, t') = c_B^\infty(r_0, t_1) + \gamma_{AB} c_A^\infty(r_0, t_1) G_B \]  
\[ c_C^h(r_0, t') = -\gamma_{AC} c_A^\infty(r_0, t_1) G_C \]
where \( c_A^\infty(r_0, t) \) and \( c_B^\infty(r_0, t) \) are given in Ref. [1] (Eqs. (18) and (19)), and the series \( G_h \) with \( h = B \) or \( C \), is given by
\[ G_h = 1 - (1 - \gamma_{hA}) \left( \frac{2 \xi_{hA}^\infty}{\sqrt{\pi}} \left( \frac{1}{2} - \frac{1}{27} \lambda^6 + \ldots \right) \right) \]  
\[ - \left( \frac{\xi_{hA}^\infty}{4} \left( 1 + \frac{1}{12} \lambda^3 + \ldots \right) \right) \]
\[ \gamma_{hA} = \sqrt{D_A / D_h} \]  
\[ \xi_{hA}^\infty = 2(D_A t_1') / r_0 \]  
\[ \lambda = (t'/t_1')^{1/3} \]
Note that Eqs. (12) and (13) are valid for determining the potential–time response corresponding to a programmed current given by Eq. (1) for different electrodes and for any value of diffusion coefficients of participating species. So, Eqs. (12) and (13) deduced for a DME with the expanding sphere electrode model become those corresponding to an SMDE by making \( t_1 \to t \) (\( \lambda = 0 \)). Moreover, if we make \( r_0 \to \infty \) (\( \xi_{hA}^\infty = 0 \) in Eqs. (12) and (13), they become those corresponding to a DME with the expanding plane electrode model. Finally, when \( \xi_{hA}^\infty = 0 \) and \( \lambda = 0 \) these equations become those corresponding to a static planar electrode.

The series \( G_h \) is only effective under spherical diffusion (\( \xi_{hA}^\infty = 0 \)) and when the diffusion coefficients of species A, B and C are different. This case has never been contemplated in the literature because under these conditions the additivity principle cannot be applied [5] and resolution of the problem becomes more difficult. In contrast, under planar diffusion (\( \xi_{hA}^\infty = 0 \)) and under spherical diffusion when \( D_A = D_B = D_C \) (\( \gamma_{AB} = \gamma_{AC} = 1 \)), the \( G_h \) series becomes equal to unity (see Eq. (14)). Under these conditions, Eqs. (12) and (13) in this paper coincide with those previously obtained in the literature for current–time functions which are particular cases of those used in this work. So, for static sphere electrodes when \( D_A = D_B = D_C \), Eqs. (12) and (13) coincide with those obtained by Murray and Reiley [5] for a power current (\( I(t) = I_0 t^n \)), with those obtained by Hurwitz [2] when \( u = 1/2 \) and \( w = 0 \) (\( I(t) = I_0 t^{1/2} \)) and with that obtained by Jain et al. [4] when \( u = w = 0 \). For static plane electrodes (\( \xi_{hA}^\infty = 0 \)) and any value of \( D_A, D_B \) and \( D_C \), Eqs. (12) and (13) coincide with those obtained by Murray [3] for an exponential current
\( I(t) = I_0 e^{\omega t} \) and with those obtained by Berzins and Delahay [8] when \( \omega = \omega = 0 \) (step current).

When the concentration of intermediate B is zero at the electrode surface, the transition time of the second step \( \tau_{\text{ii}} \) is reached. The expression for \( \tau_{\text{ii}} \) can be easily deduced by making \( c_B^0(r_0, \tau_{\text{ii}}) = 0 \) in Eq. (12), so we obtain for a DME

\[
\left( \tau_1 + \tau_{\text{ii}} \right) e^{\nu/2} = \frac{(G_B)_{\text{ii}}}{(G_A)_{\text{ii}}} \frac{(S_{\text{DME,A}})_{\text{ii}}}{(S_{\text{DME,B}})_{\text{ii}}} \tag{18}
\]

where \((G_B)_{\text{ii}}\) and \((S_{\text{DME,A}})_{\text{ii}}\) are the values of \( G_B \) and \( S_{\text{DME,A}} \) corresponding to \( t = \tau_{\text{ii}} \) and the series \( S_{\text{DME,B}} \) \( (h = A \text{ or } B) \) in this equation and hereinafter is a series which is given by Eq. (20) in Ref. [1]. Moreover, \( N_i \) is given by

\[
N_i = 2I_0/n_1 F D_A^{-1/2} A_0 c_A^* \tag{19}
\]

The units of \( N_i \) are \( s^{-1} \), since \( I_0 \) is given in A \( s^{-1} \) and \( A_0 \) depends on time for a DME.

Eq. (18) is very much simplified for a DME with the expanding plane electrode model and for static electrodes such as SMDE and plane electrodes. So, for a static plane electrode, by making \( t_1 = \tau_{\text{ii}} \) and \( \xi_{\text{ii}}^i = 0 \), Eq. (18) becomes

\[
\left( \tau_1 + \tau_{\text{ii}} \right) e^{\nu/2} = \frac{n_1 + n_2}{n_1 N_1^* (S_{\text{PE}})_{\text{ii}}} \tag{20}
\]

where

\[
N_1^* = 2I_0/nFAC_A^{-1} D_A^{-1} \tag{21}
\]

and the series \( S_{\text{PE}} \) is given by Eq. (43) in Ref. [1]. Note that the units of \( N_1^* \), which appear in the case of static electrodes (planar or spherical), are \( s^{-1/2} \).

The potential–time response for the first step is given by Eq. (28) in Ref. [1]. The general expression for this response associated with the reduction of B under these conditions is given by

\[
\frac{I(t_1 + t')}{FA(t_1 + t' + t')} = n_1 \left[ k_{b, \text{ii}} c_B^0(r_0, t') - k_{b, \text{ii}} c_C^0(r_0, t') \right] \tag{22}
\]

An analytical expression for this response can be easily obtained by introducing Eqs. (12) and (13) in Eq. (22),

\[
\frac{n_1}{n_2} e^{\omega t} \frac{N(u, t, t_1)}{S_{\text{DME,B}}} \frac{\partial \left( \frac{1}{(n_1 + n_2) \times 10^{-5} \eta(t)} \right)}{\eta_{\text{ii}}}
= \gamma_{\text{AB}} \frac{n_1 + n_2}{n_1} G_B \{ 1 - N(u, t, t_1) S_{\text{DME,A}} \}
+ \gamma_{\text{AB}} \frac{n_1 + n_2}{n_1} G_B \{ 1 - N(u, t, t_1) S_{\text{DME,A}} \}
+ \frac{n_1}{n_2} e^{\omega t} \frac{N(u, t, t_1)}{S_{\text{DME,B}}} \frac{\partial \left( \frac{1}{(n_1 + n_2) \times 10^{-5} \eta(t)} \right)}{\eta_{\text{ii}}}
= \gamma_{\text{AB}} \frac{n_1 + n_2}{n_1} G_B \{ 1 - N(u, t, t_1) S_{\text{DME,A}} \}
+ \frac{n_1}{n_2} e^{\omega t} \frac{N(u, t, t_1)}{S_{\text{DME,B}}} \frac{\partial \left( \frac{1}{(n_1 + n_2) \times 10^{-5} \eta(t)} \right)}{\eta_{\text{ii}}}
\]

where

\[
N(u, t, t_1) = N_i^i t e^{\nu/2} / t_i^{2/3} \tag{24}
\]

\[
\gamma_{\text{ii}}(t) = \frac{4 (k_{b, \text{ii}})^2}{D_A} \tag{25}
\]

\[
\eta_{\text{ii}} = \frac{n_1 F}{RT \ln 10} \{ E(t) - E_{\text{ii}} \} \tag{26}
\]

3. Discussion

3.1. Concentration profiles

Fig. 1 shows the concentration profiles of species A, B and C for the second step of an EE mechanism \( (t > t_1) \) when a constant current is applied to a static spherical electrode for two different values of electrode radius. When the whole electrolysis time \( (t_1 + t') \) and/or the electrode sphericity increases, the concentration gradient in the vicinity of the electrode of species A diminishes while those of species B and C increase in agreement with Eq. (8).

At the surface of the electrode, from Eqs. (12) and (13) for the DME with the expanding plane electrode model \( (\xi_{\text{ii}} = 0) \) and for a static plate electrode \( \{ t_1 \Rightarrow (t_1 + t') \) and \( \xi_{\text{ii}}^i = 0 \) \} the following relation can be deduced

\[
c_A(x = 0, t) + \frac{1}{\gamma_{\text{AC}}} + c_C(x = 0, t) \tag{27}
\]

\[
\frac{1}{\gamma_{\text{AC}}} + c_C(x = 0, t) = c_A^* \tag{27}
\]

Fig. 1. Concentration profiles of species A (-----), B (-----) and C (-----) corresponding to the second step of an EE mechanism for an SMDE. \( N_1 = 2.5 \, \text{s}^{-1/2}, \, I(t) = I_0 \) \( (u = \omega = 0), \, \gamma_{\text{AB}} = \gamma_{\text{AC}} = 1.0 \). The values of \( r_0 \) (cm) and \( t_1(s) \) are: (1) 0.06, 0.4145; (2) 0.015, 0.5187.
where

\[ E_{1/2}^{II} = E_0^{II} + \frac{RT}{n_{II}F} \ln \left( \frac{D_C}{D_B} \right) \]  

(31)

\[ S_{II}^{n_{II}} = \frac{N(u, t, \tau) f_1}{(n_1 + n_{II})/n_1} G_B \left\{ 1 - N(u, t, \tau) f_1 \right\} \]  

(32)

From this equation it is possible to deduce \( E_{1/2}^{II} \) for the second step by plotting \( E(t) \) vs. \( \ln S_{II}^{n_{II}} \).

For a second totally irreversible step (%2 < 1 cm s\(^{-1}\)) we obtain

\[ E(t) - E_0^{II} = \frac{RT}{\alpha_{II} n_{II} F} \ln \frac{k_{III,n_{II}} F A_0 c_A^*}{I_0} + \frac{RT}{\alpha_{II} n_{II} F} \ln S_{II}^{n_{II}} \]  

(33)

where

\[ S_{II}^{n_{II}} = \gamma_{AB} N_i e^{-\omega t} \frac{G_B}{\omega} \]  

(34)

In this case, by plotting \( E(t) - E_0^{II} \) vs. \( \ln S_{II}^{n_{II}} \), a straight line is obtained from the slope of which \( P \) and intercept \( O \) it is possible to determine the values of \( k_{III,n_{II}} \) and \( \alpha_{II} \), since

\[ P = \frac{RT}{\alpha_{II} n_{II} F} \]  

(35)

\[ O = \frac{RT}{\alpha_{II} n_{II} F} \ln \frac{k_{III,n_{II}} F A_0 c_A^*}{I_0} \]

Fig. 5. Dependence of \( E(t) - E_0^{II} \) on \( \ln S_{II}^{n_{II}} \) (Eq. (33)) for a DME.

\( I(t) = I_{ee} \omega \) (\( \omega = 1 \), \( \omega = 1 \) s\(^{-1}\)), \( N_i = 3.5 \times 10^{-3} \), \( \alpha_{II} = 0.5 \). The values of \( k_{III,n_{II}} \) in cm s\(^{-1}\): are: (a) \( 10^{-7} \), (b) \( 10^{-4} \), (c) \( 10^{-5} \). Other conditions as for Fig. 3.

Fig. 5 shows the variation of \( E(t) - E_0^{II} \) vs. \( \ln S_{II}^{n_{II}} \), for different values of \( k_{III,n_{II}} \). It is important to take into account (as is indicated in Ref. [1]) that the degree of reversibility of both electrode processes diminishes when the exponents \( u \) and \( \omega \) of the applied current \( I(t) \) decrease. So, in order to determine \( k_{III,n_{II}} \), \( \alpha_{II} \), \( k_{III,n_{II}} \) and \( \alpha_{II} \), when \( 10^{-3} < k_i < 10^{-2} \) cm s\(^{-1}\) it is suitable to use programmed currents with small values of \( u \) and \( \omega \) (\( u = -1/6 \) and \( \omega = -0.1 \) or \( u = -1/3 \) and any value of \( \omega \)) on condition that fulfillment of Eq. (33) is guaranteed.

For \( 10^{-2} < k_i < 1 \) cm s\(^{-1}\) we must use Eq. (23), which has no explicit form and, therefore, the \( k_{III,n_{II}} \) and \( \alpha_{II} \) determination must be carried out by a non-linear regression analysis in a similar way to that described in Ref. [10].

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References

Nomenclature

\[ c^h_i(r, t_i) \] concentration profiles of species \( h \) and 
\[ c^h_{ii}(r, t') \] steps respectively
\[ E^0, k^{h,1}, \alpha^1 \] thermodynamic and kinetic parameters of 
\[ E_{ii}^0, k^{h,ii}, \alpha^ii \] the first and second steps
\[ D^h \] diffusion coefficient of species \( h \) (A, B or C)
\[ a \] \( (3m_{hg}/4\pi d)^{1/3} \)
\[ m_{hg} \] and \( d \) rate of flow and density of mercury
\[ t_i \] blank period used only for a DME
\[ \tau_{11}, \tau_{ii} \] transition times of the first and second steps
\[ t \] time elapsed between current application and measurement of the potential \( t \leq \tau_1 \) for the first step and \( t = \tau_1 + t' \) for the second step
\[ t_s \] total time \( t_s = t_i + t \)
\[ I_0 \] value of \( I(t) \) at \( u = \omega = 0 \)
\[ r \] distance from the centre of the spherical electrode
\[ r_0 \] electrode radius at time \( t_i (r_0 = a t_i^{1/3}) \) for a DME, or constant electrode radius for an SMDE
\[ A(t_i) \] time dependent electrode area of a DME \( A(t_i) = A_0 t_i^{2/3} \)
\[ A_0 \] \( (4\pi)^{2/3}(3m_{hg}/d)^{2/3} \) in \( \text{cm}^2 \ s^{-2/3} \)
\[ A \] electrode area \( A = A_0 t_i^{2/3} \) when \( t_i \gg t \) (static spherical or planar electrodes)
\[ \delta^ii \] \( 2 D^h a^i / r_0 \)
\[ \delta_{0, h} \] \( 2 D^h a^i / r_0 \)
\[ \Delta E \] \( E^0 - E_{ii}^0 \)

Other definitions are conventional