General solutions for the $I/t$ response for reversible processes in the presence of product in a multipotential step experiment at planar and spherical electrodes whose areas increase with any power of time

Carmen Serna, Angela Molina *

Departamento de Química-Física, Universidad de Murcia, 30100 Murcia, Spain

Received 21 July 1998; received in revised form 12 November 1998; accepted 19 February 1999

Abstract

General explicit expressions are presented for the current $I_p$ corresponding to the $p$th step of any sequence of potential steps $E_1, E_2, \ldots, E_p$, when both oxidised and reduced species are present initially. These equations are applicable to reversible processes at planar and spherical electrodes whose areas increase with any power of time ($A(t) = A_0 t^z$, $z = 0$ for planar and spherical static electrodes and microelectrodes, and $z = 2/3$ for the DME). For an SMDE we have also considered those situations in which the diffusion coefficient values of both species are not equal and the reaction product is amalgamated initially into the electrode. As an example of the application of these equations, we have analysed the influence of the presence of the reaction product in multistep chronoamperometry for an SMDE and also when microhemispheres are used by considering that the diffusion coefficients are equal and the product is soluble in the electrolytic solution. All equations are applicable to any single, double or multipotential step techniques and also to linear sweep and cyclic voltammetry and polarography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Multipulse; SMDE; DME; Presence of product; Amalgamation; Microelectrodes; Reversible process

1. Introduction

It is a well known fact that in depth knowledge of the behaviour of reversible electrode processes is of fundamental interest to electrochemists [1–4]. In the study of these processes with a given electrochemical technique it is of great interest to introduce the assumption that both electroactive species, A and B, are present initially with concentrations $c_{A}^*$ and $c_{B}^*$, for the following reasons:

1. It permits a greater in depth study of electrochemical reversibility, since the anodic and cathodic currents depend on the relative concentrations of each oxidation state [2]. Moreover, this situation is the more general case of which the situations in which $c_{B}^* = 0$ and the reduced species has a constant activity (for example, deposition of metals) are special instances [5].

2. Because some ions (for example, the tetrathionate ion) are disproportionated partly into two electroactive species whose interconversion at the electrode surface must necessarily be analysed starting from this assumption [Ref. [6] and therein].

3. For the speciation study of metals, since the introduction of this assumption will make it possible to determine the concentration of both species A and B from accurate electrochemical experimental data obtained from double, triple or multipotential step techniques [7]. The use of atomic methods would, in contrast, lead to our obtaining the global concentrations of the different ionic species.

However, although the initial presence of both electroactive species was taken into account in some of the
first papers on dc polarography and the Kalousek switch methods [8], most of the solutions later deduced for reversible processes in non stationary multipotential step polarography or voltammetry suppose that only one species (either A or B) is present initially. An exception to the above has been given in recent papers [5,6] which deal with cyclic voltammetry when the reaction product is present initially in the electrolytic solution by considering planar diffusion. In spherical diffusion the general multiplet problem when the reaction product is present initially has to date never been solved analytically. Indeed, in Ref. [5] the authors have written under Discussion that ‘it would be very difficult to adapt the present treatment to cover spherical diffusion’.

Given this state of affairs, the aim of this work is to present the analytical general explicit equations corresponding to the response of a reversible electrode process in any multipotential step technique (i.e. from single pulse techniques through to sweep techniques). These solutions have been derived for the more general case of spherical electrodes whose areas increase with any arbitrary power of time (i.e. \( A(t) = A_0 t^a \)). Thus, from these general equations the following particular cases have been deduced: (a) DME with the expanding sphere electrode model (by making \( z = 2/3 \)); (b) SMDE and microspheres (by making \( z = 0 \)); (c) DME with the expanding plane electrode model (by making \( z = 2/3 \) and \( r_0 \to \infty \)); (d) planar electrodes (by making \( z = 0 \) and \( r_0 \to \infty \)).

In the cases b, c and d we have supposed that diffusion coefficients are not equal and in the case of an SMDE we have also analysed the presence of amalgamation.

For all the cases considered, easily manageable analytical solutions have been found, which show that the initial concentrations of A and B, \( c_0^A \) and \( c_0^B \), affect the addend of the \( I_p \) current corresponding to the first potential step applied in a different manner from that in which they affect those currents corresponding to the remaining potential steps.

We have included in a brief summary the expressions corresponding to the current \( I_p \) for \( p \geq 1 \) deduced when any sequence of potential steps \( E_1, E_2, \ldots, E_p \) is applied to the electrodes mentioned above. By making \( p = 1 \) in any equation of Table 1, we deduce the \( I_1(E_1, t_1) \) expression corresponding to single pulse voltammetry or polarography. If \( p = 2 \) in any equation of Table 1, we can deduce \( I_2(E_1, E_2, t_1, t_2) \) and by combining \( I_2 \) and \( I_1 \) we obtain the current signals corresponding to any double pulse voltammetry, polarography or chronamperometry. If \( p = 3 \) in any equation of Table 1, we can obtain the current signals corresponding to any triple pulse technique by combining \( I_1, I_2, \) and \( I_3 \). For much greater values of \( p \), we can obtain a whole set of currents \( I_1, I_2, \ldots, I_p \) and from these we obtain multipotential chronamperometries, square wave, staircase and also linear sweep or cyclic voltammetries or polarographies.

Finally, as an example, we apply these equations to the study of the influence of the presence of product in the electrolytic solution or in the electrode in multistep chronoamperometry at spherical electrodes. In the particular situation in which the diffusion coefficient of both species are equal and the product is soluble in the electrolytic solution, it is easy to obtain the concentrations of both species by using microelectrodes when the steady state is reached.

Table 1

<table>
<thead>
<tr>
<th>Solutions obtained for the current corresponding to any potential step when both reduced and oxidised species are present initially (( c_0^A \neq 0 ) and ( c_0^B \neq 0 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_1^A = c_0^A - K_A c_0^A ) for the first potential step ( (j = 1) )</td>
</tr>
<tr>
<td>( c_j^A = (c_0^A + c_0^B) ) for the following potential steps ( (j &gt; 1) )</td>
</tr>
</tbody>
</table>

DME with the expanding sphere electrode, \( D_A = D_B = D \) and B soluble in the electrolytic solution: Eq. (4) with \( z = 2/3 \).

| \( I_{p,\text{exp. sphere}} = nFA_0 \sqrt{2 \pi} \sqrt{t_1} \sum_{j=1}^{p} (\frac{D_j}{2} \int_{0}^{t_1} c_j^A \left( \frac{1}{\sqrt{t_1}} + \frac{\sqrt{\pi D_j}}{r_0} \frac{1 + K_j}{1 + j K_j} \right) \right) + \frac{h_j^N (\frac{t_1}{t_1})^2 z^2}{y t_1} \) |

Static spherical electrode, \( D_A \neq D_B \) and B soluble in the electrolytic solution (upper sign) or in the electrode (lower sign): Eq. (17).

| \( I_{p,\text{static sphere}} = nFA_0 \sqrt{\frac{D_A}{\pi}} \sum_{j=1}^{p} Z_j c_j^A \left( \frac{1}{\sqrt{t_1}} + \frac{\sqrt{\pi D_A}}{r_0} \frac{1 + K_j}{1 + j K_j} \right) \) |

Static spherical electrode, \( D_A = D_B = D \) and B soluble in the electrolytic solution: Eq. (4) with \( z = 0 \) or Eq. (17) with \( y = 1 \) and upper sign.

| \( I_{p,\text{static sphere}} = nFA_0 \sqrt{\frac{D_A}{\pi}} \sum_{j=1}^{p} Z_j c_j^A \) |

Microhemisphere steady state, \( D_A = D_B = D \) and B soluble in the electrolytic solution: Eq. (21) and also by making \( r_0 < \sqrt{\pi D t_j / 50} \) in Eq. (20) or in Eq. (17) with \( y = 1 \) and upper sign or in Eq. (4) with \( z = 0 \).

| \( I_{p,\text{microhemisphere}} = nFA_0 \sqrt{\frac{D_A}{\pi}} \sum_{j=1}^{p} Z_j c_j^A \left( \frac{1}{\sqrt{t_1}} + \frac{\sqrt{\pi D_A}}{r_0} \frac{1 + K_j}{1 + j K_j} \right) \) |

DME with the expanding plane electrode model, \( D_A \neq D_B \): Eq. (26).

| \( I_{p,\text{DME}} = nFA_0 \sqrt{\frac{D_A}{3 \pi}} \sum_{j=1}^{p} c_j^A \left( \frac{1}{\sqrt{t_1}} \right)^{3/2} \) |

Plane electrode, \( D_A \neq D_B \): Eq. (28).

| \( I_{p,\text{plane}} = nFA_0 \sqrt{\frac{D_A}{\pi}} \sum_{j=1}^{p} Z_j c_j^A \) |
2. Equations corresponding to the multipotential step problem

2.1. Analytical equations corresponding to a reversible charge transfer reaction when A and B species are present initially in the solution in spherical electrodes whose areas increase with any power of time, \( A(t) = A_d t^z \)

2.1.1. Expanding sphere electrode model with any power of time, \( A(t) = A_d t^z \), \( z \geq 0 \), \( D_A = D_B = D \) and both species soluble in the solution

If we suppose that any sequence of \( p \) successive potential steps \( (E_1, E_2, \ldots, E_p) \) is applied to an expanding spherical electrode whose area increases with any power of time, the surface concentrations of species A and B, which are both initially present with bulk concentrations \( c_A^* \) and \( c_B^* \) when \( D_A = D_B = D \), fulfil

\[
c_A^* + c_B^* = c_A^p(r, t) + c_B^p(r, t); \quad \text{for } r \geq r_0
\]

\[
c_A^p(r_0) = \frac{K_j(c_A^* + c_B^*)}{1 + K_j}
\]

\[
c_B^p(r_0) = \frac{c_A^* + c_B^*}{1 + K_j}
\]

In these conditions, considering as far as the second order spherical correction, we deduce the following expression for the current corresponding to the \( p \)th potential step, \( I_{jp} \),

\[
(I_{p, \text{exp.sphere}})_{j=1} \quad \text{no amalgamation}
\]

\[
\mu = nF(A(t))
\]

\[
\sqrt{\frac{D}{\pi}} \sum_j \frac{e_j^* Z_j t_{jp}}{t_{ip}} \left( \frac{t_{jp}}{t_{ip}} \right)^{\frac{1}{2}} + \sqrt{\frac{D}{\pi}} \left( \frac{t_{jp}}{t_{ip}} \right)^{\frac{1}{2} \cdot \xi_j}
\]

\[
+ h_j(\frac{t_{jp}}{t_{ip}})^{\frac{1}{2} \cdot \xi_j}, \quad p \geq 1
\]

where

\[
c_i^* = c_A^* - K_j c_B^*
\]

\[
c_j^* = c_A^* + c_B^* \quad j > 1
\]

and \( t_{ip} \) is the time elapsed between the beginning of the application of the \( j \) potential step and the end of the application of the \( p \) potential step,

\[
t_{jp} = \sum_{m=j}^{p} t_m
\]

\[
t_{pp} \equiv t_p
\]

\[
t_{ip} \equiv t
\]

with \( t_m \) being the duration of any potential step, \( E_m \), and \( t \) being the total time of the experiment.

\[
A(t_p) = A(t) = A_d t^z
\]

\[
z = 0 \quad \text{correspond to a static plane or spherical electrode of constant area } A_0
\]

\[
z = 2/3 \quad \text{correspond to a DME of time } - \text{dependent area } A_0 t^{2/3}, \text{ with } A_0 = 4\pi \left( \frac{3m}{4\pi\delta} \right)^{2/3}
\]

\[
\mu_0(\frac{t_{jp}}{t_{ip}}) = \sqrt{\frac{(2z + 1)t_{jp}}{t_{ip}}} \cdot \sqrt{1 - (1 - \frac{t_{jp}}{t_{ip}})(2z + 1)}
\]

\[
\mu_2(\frac{t_{jp}}{t_{ip}}) = 1 - \frac{3z(7z - 2)}{128} \left( \frac{t_{jp}}{t_{ip}} \right)^2 + \frac{z(z - 4)(7z + 2)}{264} \left( \frac{t_{jp}}{t_{ip}} \right)^3 + \cdots
\]

\[
\bar{z}_j = \frac{2}{r_0} \sqrt{2z + 1}
\]

\[
\bar{z}_j = \frac{2}{r_0} \sqrt{2z + 1}
\]

\[
Z_j = \frac{1}{1 + K_j} - \frac{1}{1 + K_j}; \quad j > 1
\]

\[
Z_1 = \frac{1}{1 + K_j}
\]

\[
K_j = \exp(nF(E_j - E^0)/RT)
\]

When species B is not present initially, \( c_B^* = 0 \), Eq. (4) becomes that deduced previously in Eq (10) of Ref. [9].

The expressions corresponding to a DME and to an SMDE can be easily obtained by respectively making \( z = 2/3 \) and \( z = 0 \) in Eq. (4). Moreover, if we make \( z = 2/3 \) and \( r_0 \rightarrow \infty \) (\( \bar{z}_j = 0 \)), Eq. (4) becomes that corresponding to a DME with the expanding plane electrode model and by making \( z = 0 \) and \( r_0 \rightarrow \infty \) (\( \bar{z}_j = 0 \)), Eq. (4) is transformed into that corresponding to a static plane electrode (see Section 2.2).

In expanding spherical electrodes (\( z > 0 \)) when \( D_A \neq D_B \) and/or species B is amalgamated into the electrode, we have not found general simple solutions to the multistep problem. This is due to the fact the surface concentrations of A and B for a given potential, \( E_m \), are complicated functions of time (see Eqs (42–44) in Ref. [10] for \( z = 2/3 \)).
2.1.2. Static sphere electrode (SMDE). $D_A \neq D_B$ and reaction product soluble in the solution or in the electrode (amalgamation)

In this case, the analytical expression corresponding to $I_p$ can be easily deduced when $D_A = D_B$ by making $z = 0$ in Eq. (4).

In the more general situation when $D_A \neq D_B$, we have solved the problem when both species are present initially and when species B is soluble in the electrolytic solution or in the electrode (amalgamation). Under these conditions, the surface concentrations of A and B corresponding to the $p$th potential step are complicated functions of time. However, when only the first order spherical correction is taken into account, they fulfill the following general relation

$$
\gamma c_A^*(r_0, t) + c_B^*(r_0, t) = \gamma c_A^* + c_B^* + \frac{(\gamma + 1)}{\gamma} \sum_{j=1}^{p} c_j^* Z_j \xi_j
$$

(12)

with

$$
c_j^* = c_A^* - K_j c_B^* \quad \quad c_j^* = \frac{\gamma c_A^* + c_B^*}{\gamma} \quad \quad j > 1
$$

(13)

$$
\gamma = \frac{D_A}{D_B}
$$

(14)

$$
Z_j = \frac{1}{1 + \gamma K_j} - \frac{1}{1 + \gamma K_{j-1}} \quad \quad j > 1
$$

(15)

$$
Z_1 = \frac{1}{1 + \gamma K_1}
$$

(16)

$$
\xi_j = \frac{2 \sqrt{D_A t_{jp}}}{r_0}
$$

(17)

In Eq. (12) and henceforth when two signs appear, the upper sign refers to a reaction product which is soluble in the electrolytic solution, whilst the lower sign corresponds to a product soluble in the electrode.

Under these conditions, the superposition principle can be applied and the current corresponding to any potential step is given by

$$
I_{p, \text{static sphere}} = n F A_0 \sqrt{D_A / \pi} \sum_{j=1}^{p} Z_j \left\{ c_j^* \left[ \frac{1}{\sqrt{t_{jp}}} \right] + \frac{\pi D_A}{r_0} \left( 1 + K_j \right) \left[ \frac{1}{1 + \gamma K_j} \right] \right\} + \frac{\pi D_A}{r_0} S_p^{(j)}
$$

(18)

where $A_0$ is the constant area of the spherical electrode ($4 \pi r_0^2$) and,

$$
S_p^{(j)} = \sum_{m=1}^{j-1} c_m^* Z_m \left( \frac{t_m}{t_{mp}} \right) \quad \text{for } j \geq 2
$$

$$
S_p^{(1)} = 0
$$

$$
\frac{w(t_{mp})}{w(t_{2mp})} = \frac{2}{\sqrt{\pi}} \left[ \arcsin \left( \frac{t_{mp}}{t_{mp} - 2} \right) \right]
$$

(19)

If $c_B^* = 0$, Eq. (17) coincides with that deduced previously in Ref. [11].

2.1.3. Microelectrodes

When $D_A = D_B = D$ (i.e. $\gamma = 1$) and both species are soluble in the electrolytic solution, Eq. (17) (and also Eq. (4) with $z = 0$) becomes

$$
(I_{p, \text{static sphere}})_{\gamma = 1} \quad \text{no amalgamation}
$$

$$
= n F A_0 D / \pi \sum_{j=1}^{p} Z_j c_j^* \left[ \frac{1}{\sqrt{t_{jp}}} + \sqrt{\pi D} \right]
$$

(20)

where $c_j^*$ and $Z_j$ are given by Eq. (5) and Eq. (10), respectively.

Eq. (20) is the exact solution of the multistep problem when A and B species are present initially in the solution and, therefore, this equation is applicable to spherical electrodes of any radius, including micro and ultramicroelectrodes [9]. Thus, when the condition $r_0 \leq \sqrt{\pi D r_{50}}$ is fulfilled [3], the steady state is reached and Eq. (20) in the following simpler expression becomes dependent only on the potential of the last pulse, $E_p$ (see Eq. (11))

$$
(I_{p, \text{microsphere}})_{\gamma = 1} \quad \text{no amalgamation}
$$

$$
= n F A_0 D / \pi \sum_{j=1}^{p} Z_j c_j^* \left[ \frac{1}{1 + K_j} \right]
$$

(21)

with $A_0 = 2 \pi r_0^2$.

2.2. Analytical equations corresponding to a reversible charge transfer reaction when A and B species are present initially in the solution and $D_A \neq D_B$ in planar electrodes whose areas increase with any power of time, $A(t) = A_0 t^z$; $z \geq 0$

In this case, for the $p$th potential step, the surface concentrations of species A and B fulfil

$$
c_A^p(0) = \frac{K_p (\gamma c_A^* + c_B^*)}{1 + \gamma K_p}
$$

(22)

$$
c_B^p(0) = \frac{\gamma c_A^* + c_B^*}{1 + \gamma K_p}
$$

(23)

for any power of time, $z$, in such a way that

$$
\gamma c_A^p(0) + c_B^p(0) = \gamma c_A^* + c_B^*
$$

(24)

Under these conditions, the superposition principle
can be applied [9] and we deduce the following expression for the current corresponding to the \( p \)th potential step

\[
I_p = nFA(t_{jp}) \frac{D_A}{\pi} \sum_{j=1}^{p} c_j^* Z_j \left( \frac{t_{jp}}{t_{1p}} \right) ^{7/3}
\]

where \( c_j^* \) and \( Z_j \) are given by Eq. (13) and Eq. (15), respectively.

This equation for \( D_A = D_B = D \) \((\gamma = 1)\) can be deduced by making \( r_0 \to \infty \left( \xi_j = 0 \right) \) in Eq. (4).

The general Eq. (25) for a DME with the expanding plane electrode model \((z = 2/3)\) is transformed to

\[
I_{p,\text{DME}} = nFA_d t_{1p}^{7/6} \frac{7D_A}{3\pi} \sum_{j=1}^{p} c_j^* Z_j \left[ 1 - \left( 1 - \frac{t_{jp}}{t_{1p}} \right) ^{7/3} \right] ^{-1/2}
\]

If species B is not present initially \((c_B^* = 0)\), Eq. (26) becomes that previously deduced by us (Eq (39) with \( z = 2/3 \) in Ref. [12]), which can be written as

\[
(I_{p,\text{DME}})_{c_B^* = 0} = nFA_d \frac{7D_A}{3\pi} c_A^* \sum_{j=1}^{p} Z_j \left[ 1 - \left( 1 - \frac{t_{jp}}{t_{1p}} \right) ^{7/3} \right] ^{-1/2}
\]

For a plane electrode \((z = 0)\) Eq. (25) is simplified to

\[
I_{p,\text{plane}} = nFA_d \frac{D_A}{\pi} \sum_{j=1}^{p} c_j^* Z_j \left( \frac{t_{jp}}{t_{1p}} \right) ^{7/3}
\]

which coincides for \( p = 2 \) with that previously deduced by Kambara for two potential steps [13].

Moreover, if \( c_B^* = 0 \), Eq. (28) becomes

\[
(I_{p,\text{plane}})_{c_B^* = 0} = nFA_d c_A^* \frac{D_A}{\pi} \sum_{j=1}^{p} \frac{Z_j}{t_{1p}}
\]

which coincides with Eq (39) with \( z = 0 \) in Ref. [12].

To deduce Eqs (26–29) we have taken into account that, from Eq. (8a),

\[
\begin{align*}
    h_{z=0}^{00} \left( \frac{t_{jp}}{t_{1p}} \right) &= 1 \\
    h_{z=2/3}^{00} \left( \frac{t_{jp}}{t_{1p}} \right) &= \sqrt{\frac{7t_{jp}/t_{1p}}{3[1 - (1 - t_{jp}/t_{1p}) ^{7/3}]}}
\end{align*}
\]

3. Results and Discussion

In Table 1 as a brief summary we show the general equations for the current \( I_p \) corresponding to the \( p \)th potential step of the sequence \( E_1, E_2, \ldots, E_p \).

As an example of the application of any of these expressions, Fig. 1 shows the influence of the initial presence of the reaction product B, \( c_B^* \neq 0 \), on the current time curves deduced for four potential steps under conditions of cathodic \((I_{1,\text{lim}}, I_{3,\text{lim}})\) and anodic \((I_{2,\text{lim}}, I_{4,\text{lim}})\) limiting currents \((E_1 = E_3 \to \infty, E_2 = E_4 \to \infty, t_1 = t_2 = t_3 = t_4 = 1 \text{ s}, \gamma = 0.8, \sqrt{D/r_0} = 0.15 \text{ s}^{-1/2})\). The values of \( c_B^*/c_A^* \) are: \((-) 0; (\cdots) 0.5; (\cdots\cdots) 1\).
and

\[ I_0 = nF_Ac^*_A\sqrt{D_A/\pi} \]  

(33)

The \( I_{p,\text{lim}}/I_0 \) versus \( t \) curves plotted in Fig. 1a correspond to a reaction product soluble in the electrolytic solution, whereas the curves of Fig. 1b correspond to a reaction product amalgamated into the electrode. From these curves it is interesting to note that \( I_{1,\text{lim}} \) is not influenced by the initial presence of B (in the solution or in the electrode) nor by the amalgam formation (in agreement with Eq. (31)), whereas \( I_{3,\text{lim}} \) is affected notably by both effects. The two anodic limiting currents, \( I_{5,\text{lim}} \) and \( I_{4,\text{lim}} \), are affected considerably by the presence of B and also by the amalgamation. Moreover, by comparing Figs 1a and b, it is clear that the presence of B increases the absolute values of the currents in the curves corresponding to \( p > 1 \), although this effect is more apparent when amalgamation does not exist since the diffusion field of species B is less restricted in this case.

Fig. 2 shows the effects of the electrode radius and the presence of species B on the \( I_{p,\text{lim}}/I_0 \) versus \( t \) curves when the product is soluble in the electrolytic solution for four potential steps identical to those indicated in Fig. 1. Fig. 2a and b correspond to a microhemisphere \((A_0 = 2\pi r_0^2)\) with \(3 \times 10^{-3}\) and \(8 \times 10^{-5}\) cm of the radius, respectively. As can be seen from this figure an increase of the relation \( c_B^*/c_A^* \) has a greater effect on the anodic than on the cathodic curves. Moreover, a comparison between Fig. 2a and b shows that when \( r_0 \) decreases the influence of the relation \( c_B^*/c_A^* \) on the cathodic currents becomes ever less. On the other hand, the influence of this ratio on the anodic currents is accentuated when \( r_0 \) decreases. From these figures the tendency of the currents to be independent of time as \( r_0 \) decreases can be observed. Thus, from Fig. 2b it is clear that when \( t_p \geq 0.5\) s steady state currents are obtained for this value of the electrode radius \((8 \times 10^{-5}\) cm), in such a way that the values of \( c_B^*/c_A^* \) and \( c_B^* \) can be calculated easily from the cathodic and anodic curves, respectively, since these limit currents fulfil (see Eq. (21))

\[
\begin{align*}
I_{1,\text{lim}} &= I_{3,\text{lim}} = \frac{2\pi nF_A D c^*_A}{r_0} \\
\frac{I_{1,\text{lim}}}{I_0} &= \frac{I_{3,\text{lim}}}{I_0} = \frac{\sqrt{\pi D}}{r_0} 
\end{align*}
\]  

(34) 

and

\[
\begin{align*}
I_{2,\text{lim}} &= I_{4,\text{lim}} = \frac{2\pi nF_A D c^*_B}{c_A^* r_0} \\
\frac{I_{2,\text{lim}}}{I_0} &= \frac{I_{4,\text{lim}}}{I_0} = -\frac{\sqrt{\pi D} c^*_B}{r_0 c_A^*} 
\end{align*}
\]  

(35)

with

\[ I_0 = 2r_0^2nF_Dc^*_A\sqrt{\pi D} \]  

(36)

Finally, it is clear that by combining equations corresponding to \( I_p \) for \( p = 1, 2, 3, \ldots\) any multipulse technique can be applied to the study of a reversible process when both species with different oxidation states are initially present. So, for example, the expression for the \( I_p \) corresponding to staircase voltammetry or cyclic staircase voltammetry can be obtained easily by making \( t_1 = t_2 = \ldots = t_p = \tau \) and \( v = |\Delta E|/\tau \), \( v \) being the scan rate, with \( \Delta E = E_j - E_{j-1} = \text{constant} (j \geq 2) \) in Eqs. (4) and (17) or Eq. (25). To obtain the equations corresponding to linear sweep voltammetry or cyclic voltammetry we must introduce the condition \( |\Delta E| \leq 0.01\) mV in the above equations [9].

Acknowledgements

The authors greatly appreciate the financial support provided by the Dirección General de Investigación Serna, A. Molina / Journal of Electroanalytical Chemistry 466 (1999) 8–14 13

![Fig. 2. Influence of \( c_B^* \) and \( r_0 \) on the \( I_{p,\text{lim}}/I_0 \) versus \( t \) curves for a microhemisphere when \( D_A = D_B = D \) and the product is soluble in the electrolytic solution (Eq. (20)). \( D = 10^{-5}\) cm\(^2\) s\(^{-1}\). The values of \( r_0 \) are \(3 \times 10^{-3}\) cm (curves a) and \(8 \times 10^{-5}\) cm (curves b). The values of \( c_B^*/c_A^* \) are: (——) 0; (····) 0.5; (—–····) 1; (········) 1.5. Other conditions as Fig. 1.](image-url)
Científica y Técnica (Project Number PB96-1095). The authors are indebted to Professor H.S. White for many helpful suggestions which have improved this work considerably.

References