General analytical solution for a catalytic mechanism in potential step techniques at hemispherical microelectrodes: Applications to chronoamperometry, cyclic staircase voltammetry and cyclic linear sweep voltammetry

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Abstract

An easy, general analytical solution, applicable to any multipotential step technique for a catalytic process in planar and spherical electrodes (including ultramicrohemispheres), is presented. The solution has been deduced rigorously using the mathematical method described by Molina (A. Molina, J. Electroanal. Chem. 443 (1998) 163) based on the application of the superposition principle. In this paper it has been applied to multistep chronoamperometry, cyclic staircase voltammetry (CSCV) and cyclic linear sweep voltammetry (CLSV) by analysing the influence of the electrode radius and the equilibrium and rate chemical constants over the different \( I/t \) and \( I/E \) responses. Different voltammetric steady states (kinetic, microgeometrical and geometrical-kinetic) can be distinguished and methods for calculating the kinetic parameters of the chemical reaction are also proposed. In the case of an irreversible chemical reaction in linear sweep voltammetry our results are in agreement with those recently deduced by Diao and Zhang (G. Diao, Z. Zhang, J. Electroanal. Chem. 429 (1997) 67). © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The use of microelectrodes offers great advantages. Better use can be made of the electrochemical techniques since high quality experimental data are obtained which are barely distorted by the ohmic drop or the effects of the charge current [1–10]. Moreover, the study of a catalytic process in which the charge transfer reaction is followed by a homogeneous chemical reaction that regenerates the electroactive species is of great interest, as shown in recent papers [1,11–17].

In a previous paper [11], we developed a mathematical method based on the application of the superposition principle which gives a rigorous solution to the multistep problem for a catalytic process in planar diffusion. Thus, we deduced an easy, manageable analytical solution applicable to any multipotential step technique and also to cyclic linear sweep voltammetry.

In this paper we extend the above treatment to the spherical diffusion field and deduce another general analytical solution which can be applied both to planar and spherical electrodes, including hemispherical microelectrodes and ultramicroelectrodes. This equation presents the following advantages:

1. It permits a rigorous treatment of the catalytic mechanism in hemispherical microelectrodes (without considering the reaction layer approximation) for any value of the equilibrium constant of the homogeneous chemical reaction in any multistep
2. Theory

Let us consider a catalytic mechanism which can be described by the following scheme:

\[ A + ne^- \rightleftharpoons B \]

\[ k_1' \]

\[ B + Z \rightleftharpoons A + \text{Products} \]

\[ k_2' \]

where \( A \) and \( B \) are the electroactive species and \( Z \) and 'Products' are electroinactive species in the whole range of applied potentials, in such a way that \( k_1 = k_1^*c_B^* \) and \( k_2 = k_2^*c_{\text{products}} \) are both pseudo first order rate constants (\( c_B^* \) being the bulk concentration of the \( i \) species).

The solution corresponding to the above mechanism, when a first potential step \( E_1 \) is applied to a spherical electrode or microelectrode, has been deduced in the Appendix for a reversible charge transfer reaction and can be written as,

\[
\frac{I_1}{nFADc_B^*} = \left( \frac{1}{\sqrt{\pi}x_{11}} + \text{erf}(\sqrt{x_{11}}) \right) \left( k_1 + k_2 + 1 \right)
\]

\[
\frac{1 - KJ_1}{(1 + K)(1 + J_1)}
\]

(1)

where

\[ x_{11} = (k_1 + k_2)\tau_1 \]

(2)

with \( \tau_1 \) being the duration of the first potential step and \( k_1 \) and \( k_2 \) being the homogeneous pseudo first order rate constants. Moreover,

\[ K = k_2/k_1 = c_B^*/c_A^* \]

(3)

\[ \xi^* = c_A^* + c_B^* \]

(4)

\[ J_1 = \exp \left[ nF(E_1 - E_B)/RT \right] \]

(5)

with \( r_0 \) and \( A \) being the electrode radius and area, respectively.

Note that Eq. (1) is the exact solution to this problem and therefore is applicable for any value of the electrode radius. Thus, for example, for \( r_0 \rightarrow \infty \), the second term in the brackets disappears and \( I_1 \) corresponds under these conditions to the solution for planar diffusion [11]. For smaller values of \( r_0 \) the contribution of both terms inside the bracket must be carefully evaluated in order to analyse the weight of each of the two addends as a function of the values of \( x_{11} \), \((k_1 + k_2)\) and \( r_0 \). Thus, for values of \( x_{11} \) or \((k_1 + k_2)\) for which the first term might be ignored with respect to the second (ultramicroelectrodes), it is fulfilled that,

\[
\left( \frac{I_1}{nFADc_B^*} \right)_{r_0 \rightarrow 0} = \frac{1 - KJ_1}{r_0(1 + K)(1 + J_1)}
\]

(6)

We can consider that this result is valid if, in agreement with reference [7], it is fulfilled that,
\[
I_2 = \sum_{p=1}^{2} \left\{ \left( \frac{e^{-x_{p2}}}{\pi x_{p2}} + \text{erf}(\sqrt{x_{p2}}) \right) \sqrt{\frac{k_1 + k_2}{D} + \frac{1}{r_0}} \right\} Z_p
\]

with
\[
Z_1 = \frac{1 - KJ_1}{(1 + K)(1 + J_1)}
\]
\[
Z_2 = \frac{1}{1 + J_2} \frac{1}{1 + J_1}
\]
\[
J_2 = \exp[nF(E_2 - E^o)/RT]
\]
\[
Z_{p2} = (k_1 + k_2)t_{p2}
\]
\[
t_{12} = t_1 + t_2
\]
\[
t_{22} = t_2
\]

If we take into account that, like the planar diffusion case in reference [11], this is a linear problem and that the boundary value problem has the same general form for any \(m\)th potential step applied (\(m \geq 1\)) and also that this \(m\)th boundary value problem is independent of the previous solutions corresponding to the above potential steps \(E_1, E_2, \ldots, E_{m-1}\), we deduce that the current corresponding to the \(m\)th potential step can be obtained by applying the superposition principle as follows,

\[
I_m = \sum_{p=1}^{m} \left\{ \left( \frac{e^{-x_{pm}}}{\pi x_{pm}} + \text{erf}(\sqrt{x_{pm}}) \right) \sqrt{\frac{k_1 + k_2}{D} + \frac{1}{r_0}} \right\} Z_p
\]

with
\[
Z_1 = \frac{1 - KJ_1}{(1 + K)(1 + J_1)}
\]
\[
Z_p = \frac{1}{1 + J_p} \frac{1}{1 + J_{p-1}}; \quad p > 1
\]
\[
J_p = \exp[nF(E_p - E^o)/RT]
\]
\[
\chi_{pm} = (k_1 + k_2)t_{pm}
\]
\[
t_{pm} = \sum_{k=p}^{m} t_k
\]

Eq. (13) is the complete solution corresponding to any multistep problem for a catalytic mechanism in spherical diffusion. This equation converts to an even simpler form after some manipulations. Thus, taking into account that the second term inside the brackets is independent of time, Eq. (13) becomes,

\[
\frac{I_m}{nFAD_2^{*}} = \sum_{p=1}^{m} \left\{ \left( \frac{e^{-x_{pm}}}{\pi x_{pm}} + \text{erf}(\sqrt{x_{pm}}) \right) \sqrt{\frac{k_1 + k_2}{D} + \frac{1}{r_0}} \right\} Z_p
\]

\[
+ \frac{1 - KJ_m}{r_0(1 + K)(1 + J_m)}
\]

At certain times, it may be of interest to write the expression for \(I_m\) in a dimensionless form. In order to achieve this, both sides of Eq. (17) should be multiplied by \(r_0\) such that this equation becomes,

\[
\Phi_m = \sum_{p=1}^{m} \left\{ \left( \frac{e^{-x_{pm}}}{\pi x_{pm}} + \text{erf}(\sqrt{x_{pm}}) \right) \sqrt{A} \right\} Z_p
\]

\[
+ \frac{1 - KJ_m}{(1 + K)(1 + J_m)}
\]

where

\[
\Phi_m = \frac{I_m r_0}{nFAD_2^{*}}
\]
\[
A = \frac{k_1 + k_2}{D} r_0
\]

Eq. (17) is of great importance since, as can be seen, it is clearly shown that the electrode radius affects only the term corresponding to the last potential pulse \(E_m\). This situation is analogous to that found by us in a previous paper on the study of a reversible charge transfer reaction in multipotential step techniques [18]. This equation possesses the additional advantage of its simplicity, making it very easily programmable, as we shall see below.

3. Results and discussion

In the first place, we will analyse some particular cases of interest of Eq. (17) which corresponds to the rigorous solution for a catalytic mechanism in a multipotential step problem. Thus, we will discuss the existence of a steady state in planar geometry and in microhemispheres (Section 3.1), and we will compare it to the response obtained for a reversible mechanism (Section 3.2).

In the following sections, we will apply Eq. (17) to multistep chronocoulometry, cyclic staircasel sweep voltammetry and cyclic linear sweep voltammetry (Section 3.3). In the last case we will compare our results to those deduced by Diao and Zhang in a recent paper and which were applicable only to a catalytic process with \(K = 0\) in linear sweep voltammetry [1].

Finally, we propose methods for calculating the kinetic parameters of the chemical reaction (Section 3.4).
3.1. Attachment of steady state at planar, spherical electrodes and hemispherical microelectrodes.

Eq. (17) presents the following interesting particular cases

3.1.1. Planar electrodes and kinetic steady state (kss)

If we make \( r_0 \to \infty \) in Eq. (17), the last term disappears and we obtain,

\[
\left( \frac{I_m}{nFAD\zeta^*} \right)_{\text{planar}} = \frac{e^{-\chi_{pm}}}{\sqrt{\pi \chi_{pm}}} + \text{erf} \left( \sqrt{\chi_{pm}} \right) \left( \frac{k_1 + k_2}{D} \right) \frac{k_1 + k_2}{D} \quad (21)
\]

This equation is identical to that previously obtained by us (Eq. (62) in Ref. [11]).

It is interesting to point out that, by comparing Eqs. (21) and (17), it is quickly observed that the difference between the current time response of a catalytic process in planar and in spherical diffusion is due solely to the term \((1 - KI_m)/(1 + K)(1 + J_m)\).

The function in the brackets in Eq. (21) fulfills the following for \( \chi_{pm} \geq 1.27 \) (Fig. 1):

\[
e^{-\chi_{pm}} + \text{erf} \left( \sqrt{\chi_{pm}} \right) \to 1 \quad (22)
\]

By introducing Eq. (22) in Eq. (21) we deduce, after some simple manipulations, the following simpler expression:

\[
\left( \frac{I_m}{nFAD\zeta^*} \right)_{\text{kss}} = \frac{\sqrt{k_1 + k_2}}{D} \frac{1 - KI_m}{(1 + K)(1 + J_m)} \quad (23)
\]

From Eq. (23) we deduce that there exists a kinetic steady state which will be reached when the homogeneous chemical reaction is fast enough.

Under these conditions, the \( I/E \) response will practically correspond to a single sigmoid for any multipulse electrochemical technique applied (single pulse voltammetry, cyclic staircase or cyclic linear sweep voltammetry) and whatever the number of cycles of the same (Section 3.3).

3.1.2. Conventional spherical electrodes and mixed geometrical-kinetic steady state (gkss)

From Eq. (17) corresponding to spherical diffusion when \( \chi_{pm} \geq 1.27 \) we obtain:

\[
\left( \frac{I_m}{nFAD\zeta^*} \right)_{\text{gkss}} = -\frac{1 - KI_m}{(1 + K)(1 + J_m)} \left( \frac{k_1 + k_2}{D} + \frac{1}{r_0} \right) \quad (24)
\]

Eq. (24) clearly shows that for a determined sphere or hemisphere the steady state in a given experiment is, in general, a function of two contributions, one due to the spherical geometry for any value of the electrode radius and the other due to the rate of the homogeneous chemical reaction. This equation coincides with that deduced by Oldham [13] in the particular case of a cathodic limiting current \((J_m \to 0)\) and for an irreversible chemical reaction \((K = 0)\).

3.1.3. Ultramicrohemispheres and microgeometrical steady state (mgss)

In order to reach this steady state in a brief period of time, a very small electrode which must be finite in both dimensions is required.

This steady state can be obtained by making \( r_0 \to 0 \) in Eq. (17) or Eq. (24). So we obtain,

\[
\left( \frac{I_m}{nFAD\zeta^*} \right)_{\text{mgss}} = \frac{1 - KI_m}{(1 + K)(1 + J_m)} \quad (25)
\]

This equation shows that under these conditions we obtain a steady current dependent only on the potential applied in the \( m \)th step \( E_m \) and on the equilibrium constant of the homogeneous chemical reaction \( K \).

Note that, for \( K = 0 \), the \( I/E \) response deduced for a catalytic process is identical to that obtained under the same conditions for a reversible charge transfer process (see Eq. (24) in Ref. [18]). For Eq. (7) to be fulfilled and for the microgeometrical steady state to be reached, it is necessary to reduce the size of the electrode to a greater extent than in the case of a simple \( E \) mechanism (Section 3.2). Under any of the conditions of the three cases previously discussed, the \( I/t \) response of a given potential step is independent of the previous potential step sequence, i.e. the memory of the previous pulses is lost.
3.2. Comparison between the steady state in a catalytic mechanism and in a reversible E process

The steady state, in agreement with Diao and Zhang [1], will be reached earlier in a catalytic process than in a simple E process, as will be seen below. This fact can be easily deduced by comparing Eq. (17) of this paper with that corresponding to an E process.

To deduce the equation for $I_n$ corresponding to an E process it is sufficient to make $\chi_{pm} \to 0$ and $K = 0$ in Eq. (17), so we obtain (see Eq. (15)),

$$\left( \frac{I_n}{nFAD_C^*} \right)_E = \sum_{p=1}^{m} \left\{ \frac{1}{\sqrt{\pi \chi_{pm}}} \sqrt{\frac{k_1 + k_2}{D}} Z_p + \frac{1}{r_0(1 + J_m)} \right\}$$

which is evidently reached for lower values of $t_{on}$ (Eq. 15).

In the case of planar diffusion from Eq. (26) with $r_0 \to \infty$ it is evident that the steady state cannot be reached in a brief period of time for E process, while a pure kinetic steady state can be obtained in the case of a catalytic mechanism.

3.3. Multistep techniques

Eq. (17) is applicable to any multistep technique. In this paper we will analyse in greater detail its application to multistep chronoamperometry, cyclic staircase voltammetry (CSCV) and cyclic linear sweep voltammetry (CLSV) both in conventional electrodes (planar and spherical) and also in hemispherical microelectrodes and ultramicroelectrodes.

3.3.1. Multistep chronoamperometry

In order to show the application of Eq. (17) for any duration of the potential steps, in Figs. 2 and 3 we have represented the chronoamperograms corresponding to five potential steps obtained under conditions of cathodic and anodic limiting currents. Under these conditions, and taking into account that $E_1 = E_2 = -\infty$ and $E_3 = E_4 = +\infty$, the currents $I_m$ are limiting currents: $I_{1,lim}$, $I_{2,lim}$, ..., $I_{5,lim}$, $I_{6,lim}$, $I_{7,lim}$ and $I_{8,lim}$ being cathodic currents and $I_{5,lim}$ and $I_{6,lim}$ anodic ones and are given in the following general form,

$$\frac{I_{m,lim}}{nFAD_C^*} = \left\{ \left( \frac{e^{-\chi_{lim}}}{\pi \chi_{lim}} + \text{erf}(\sqrt{\chi_{lim}}) \right) \sqrt{\frac{k_1 + k_2}{D}} \right\}_{1 + K} + \sum_{p=1}^{m} \left\{ \frac{e^{-\chi_{pm}}}{\pi \chi_{pm}} + \text{erf}(\sqrt{\chi_{pm}}) \right\}_{k_1 + k_2} \left( -1 \right)^{p+1}$$

while for an E process this function is given by,

$$f(\chi_{pm})_{E} = \frac{1}{\sqrt{\pi \chi_{pm}}} \left( \frac{k_1 + k_2}{D} \right)_{1 + K}$$

In Fig. 1 we have plotted Eqs. (28) and (29) versus $\chi_{pm}$ and from these plots it is clear that $f(\chi_{pm})_{CAT}$ reaches a constant value for smaller values of $\chi_{pm}$ than does $f(\chi_{pm})_{E}$, and this explains why in spherical electrodes the steady state is reached earlier for a catalytic mechanism (mixed geometrical-kinetic steady state), than for an E mechanism (microgeometrical steady state).

On the other hand (and in agreement with Fig. 1), the microgeometrical steady state is more difficult to reach in a catalytic mechanism than in a pure E one since, in the first case condition (7) must be verified, while in an E mechanism the condition given below must be verified for any value of $E_m$ [7],

$$10 \sqrt{\frac{k_1 + k_2}{D}} r_0 < 1$$

In this case we have varied $m$ between 1 and 5, with $t_1 = t_2 = \ldots = t_5 = 1s$.

Note that Eq. (31) can be written in the following dimensionless way,

$$\phi_{m,lim} = \left\{ \left( \frac{e^{-\chi_{lim}}}{\pi \chi_{lim}} + \text{erf}(\sqrt{\chi_{lim}}) \right) \sqrt{\chi_{lim}} \right\}_{1 + K} + \sum_{p=1}^{m} \left\{ \frac{e^{-\chi_{pm}}}{\pi \chi_{pm}} + \text{erf}(\sqrt{\chi_{pm}}) \right\}_{k_1 + k_2} \left( -1 \right)^{p+1}$$

where $A$ is given by Eq. (20) and

$$\phi_{m,lim} = \frac{I_{m,lim} r_0}{nFAD_C^*}$$
In the case of a simple E process \((K = 0\text{ and } \chi_{pm} = 0)\), Eq. (32) becomes that corresponding to the diffusion currents, which is given by,
fact that when $K$ increases, the concentration of species A decreases and that of species B increases in the bulk of the solution). Fig. 2 shows that when $K \neq 0$, if the homogeneous rate constants increase, then both anodic and cathodic currents increase in absolute value, while for $K = 0$, the anodic currents slightly decrease when $k_1$ increases and the cathodic ones increase more with the rate constant than in the previous case. This behaviour is typical of a catalytic process and can be used to characterise it since, for example, in the case of an irreversible chemical reaction, the value of the rate constant $k_1$ can be varied by adding different amounts of the electroactive species Z. Moreover, it can be observed from this figure the tendency of the current $I_{m, \text{lim}}$ to be independent of time as the sum $(k_1 + k_2)$ increases, in such a way that these chronoamperograms are practically parallel to the time axis for $k_1 + k_2 > 10$ s$^{-1}$. This fact can be used to determine experimentally the value of $(k_1 + k_2)$ since under these conditions from Eq. (31) it can be easily deduced that the currents corresponding to the cathodic and anodic plateaus are given by

$$\frac{|I_{m, \text{lim}}|}{nFA\xi \phi \sqrt{D}} = \left(\sqrt{k_1 + k_2} + \sqrt{D}r_0\right) \frac{1}{1 + K}$$

for $m = 1, 3, 5, \ldots$ \hspace{1cm} (35)

and

$$\frac{|I_{m, \text{lim}}|}{nFA\xi \phi \sqrt{D}} = \left(\sqrt{k_1 + k_2} + \sqrt{D}r_0\right) \frac{K}{1 + K}$$

for $m = 2, 4, \ldots$ \hspace{1cm} (36)

respectively.

Therefore the calculation of $k_1$ and $k_2$ is immediate due to the fact that the equilibrium constant can be obtained by dividing Eqs. (36) and (35) and the rate constant can be obtained by taking into account that the sum of these equations is precisely $(\sqrt{k_1} + \sqrt{k_2}) + \sqrt{D}r_0$.

From Fig. 3 it is clear that for an irreversible catalytic process, the absolute value of the cathodic currents decreases with $r_0$ while the anodic ones are not affected by the value of the electrode radius in agreement with Eq. (31) for even $m$ (Fig. 3(a)). For a reversible catalytic process both anodic and cathodic currents increase in absolute value when $r_0$ decreases (Fig. 3(b)).

We have also found that, in general, the $I/t$ curves corresponding to a catalytic process are similar to those corresponding to an E mechanism for $r_0 < 1.5 \times 10^{-5}$ cm if $D = 7 \times 10^{-6}$ cm$^2$ s$^{-1}$ and $1 \leq (k_1 + k_2) \leq 100$ s$^{-1}$.

Fig. 4 shows the dimensionless $\Phi_{m, \text{lim}}/\chi_{pm}$ curves (Eq. (32)) calculated from different values of the dimensionless rate constant $A$ (Eq. (20)).

3.3.2. Cyclic staircase voltammetry (CSCV)

This section deals with the study of cyclic staircase voltammetry (CSCV) and analyses the behaviour of a catalytic process with this technique, one of the most commonly used experimentally together with cyclic linear sweep voltammetry (CLSV), which will be analysed in Section 3.3.3.

In CSCV all the potential pulses have the same height, $\Delta E$, whose sign may be positive or negative according to the potential sweep, as well as the same duration $\tau$. Therefore,

$$t_1 = t_2 = \ldots = t_m = \tau$$

$$t_{pm} = \sum_{k=p}^{m} t_k = (m + 1 - p)\tau$$

We define the potential sweep rate as

$$\nu = \frac{\Delta E}{\tau}$$

and

$$a = \frac{nF}{RT}$$

By introducing Eqs. (37)–(40) in Eq. (17) we deduce the dimensionless function of the current for spherical electrodes or microelectrodes, which is given by,
Fig. 5. Cyclic staircase voltammetry (one complete cycle, Eq. (41)). $D = 10^{-3}$ cm$^2$ s$^{-1}$, $n = 1$, $|\Delta E| = 10$ mV, $\tau = 0.10$ s, $E_i = +150$ mV, $T = 298.15$ K. The value of the equilibrium constant of the chemical reaction is $K = 0$. The values of the pseudo first order rate constant $k_i$ (in s$^{-1}$) are: (---) 0, (---) 3, (---) 5, (---) 10 and (O) 20. The values of $\sqrt{D}/r_0$ (in s$^{-1/2}$) are in the curves.

$$
\psi_m = \frac{nFA}{\sqrt{Da}} \sqrt{D} \sum_{\nu=1}^{m} \left( \frac{e^{-(k_1 + k_2)(m+1-p)\tau}}{\sqrt{\pi(k_1 + k_2)(m+1-p)\tau}} \right) \frac{k_1 + k_2}{D} \sqrt{k_1 + k_2} Z_p \left( \frac{1 + KJ_m}{r_0(1 + K)(1 + J_m)} \right)
$$

(41)

with

$$
\tau = \frac{nF |\Delta E|}{RT a}
$$

(42)

Eq. (41) will be used in CSCV and also in CLSV.

Fig. 5 shows the application of the above equation for CSCV to the study of the influence of the homogeneous rate constant $k_i$ corresponding to an irreversible catalytic process ($K = 0$), (a simple E process ($k_i = 0$) is included for comparison), in spherical electrodes of different radii including planar electrodes, for $|\Delta E| = 10$ mV and $\tau = 100$ ms ($v = 100$ mV s$^{-1}$). The main aim of this plot is to be able to determine when the voltammetric steady state is reached and when that voltammetric steady state has a pure microgeometrical character, a pure kinetic character or rather, as often occurs, it is a mixture of both. The use of CSCV is of great help in this analysis due to the fact that the voltammetric steady state is reached when the $\psi_m/E$ responses corresponding to the sweep towards both negative and positive potentials practically correspond to a single sigmoid (i.e., the $\psi_m/E$ response is dependent only on the applied potential $E_m$). From this figure, which shows four sets of curves each corresponding to one electrode radius and to different values of the rate constant $k_i$, it is clear that the voltammetric steady state is more easily obtained when $k_i$ increases and also when $r_0$ decreases, as is easily deduced from Eqs. (17) and (24).

Thus, in planar geometry (curves with $\sqrt{D}/r_0 = 0$), clearly the steady state is never reached for $\infty$ E process (dotted curve), while a voltammetric kinetic steady state is obtained for $k_i > 7$ s$^{-1}$. By applying Eqs. (17) and (24) we deduce from the set of curves with $\sqrt{D}/r_0 = 5$ and 10 s$^{-1/2}$ that the voltammetric steady state is reached for $k_i > 4$ s$^{-1}$ in the first case and for $k_i \geq 3$ s$^{-1}$ in the second. In both cases there is
a mixed voltammetric steady state (Eq. (24)). The microgeometrical voltammetric steady state should be reached at the limit \( r_0 \rightarrow 0 \). Thus, the set of curves in this figure corresponding to \( \sqrt{D/r_0} = 100 \text{ s}^{-1/2} \) shows that a catalytic process (with \( K = 0 \)) behaves like an E process for this value of the electrode radius \( (r_0 \approx 2.6 \times 10^{-5} \text{ cm if } D = 7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}) \) for \( k_i \leq 10 \text{ s}^{-1} \), which is in agreement with Eqs. (17) and (25). Therefore, the microgeometrical voltammetric steady state is obtained under these conditions. For \( k_i > 10 \text{ s}^{-1} \) the steady state is also a mixed steady state. All these values of \( k_i \) have been calculated with an average error margin of less than 3%.

Moreover, it is also clear from this figure that the voltammetric steady state (mixed) is reached earlier for a catalytic process than for an E process, whatever the electrode size.

It can also be concluded that the current measured to a given potential in the case of a catalytic process is always greater than that corresponding to a simple E process. The difference is greater the higher the rate constant of the homogeneous chemical reaction, except in the case of an ultramicroelectrode \( (r_0 < 10^{-5} \text{ cm}) \) for which both responses should be practically coincident (microgeometrical steady state).

Fig. 6 shows the influence of the sweep rate on a catalytic process with \( K = 0 \) in CSCV \( (\Delta E = 10 \text{ mV}) \). From the figure it is clear that for a given value of the microelectrode radius the voltammetric steady state (mixed or microgeometrical) is reached more quickly when the sweep rate decreases, which is in agreement with the predictions of Zoski et al. [3].

In Fig. 7 we show the influence of the equilibrium constant of the homogeneous chemical reaction \( K \), on these voltammograms in planar (Fig. 7(a)) and spherical (Fig. 7(b)) geometries. As can be seen when \( K \neq 0 \), the current reaches a value different from zero at the beginning of the experiment. This is due to the presence of species B in the bulk solution. This limit is easily deduced from Eq. (17) or Eq. (41). So, for \( r \rightarrow 0 \) and \( E_i \rightarrow \infty \), it is fulfilled that:

\[
(\psi_i),_{r \rightarrow 0, K > 0} = - \left( \frac{RT}{znF} \Delta E + \frac{D}{a r_0} \right) \frac{K}{1 + K} \quad (43)
\]

while \( (\psi_i),_{r \rightarrow 0} = 0 \) if \( K = 0 \).

Consequently, the first semicircle corresponding to the sweep towards negative potentials presents a cross point with the second semicircle corresponding to the sweep towards positive potentials. This behaviour can also be deduced from Eqs. (17) or (41) since when the potential again takes on highly positive values at the end of the second semicircle (again \( E_m \rightarrow \infty \)) the situation is different, but this new current can be clearly characterised if we suppose that the voltammetric steady state has been reached. By introducing the supposition of the voltammetric steady state (Eq. (24)) in Eqs. (17) or (41), we deduced, respectively,

\[
\left( \frac{L_m}{nFAD^2} \right)_{E_m \rightarrow \infty} = - \left( \frac{k_1 + k_2}{D} + \frac{1}{r_0} \right) \frac{K}{D} \quad (44)
\]

or

\[
(\psi_m)_{E_m \rightarrow \infty} = - \left( \frac{k_1 + k_2}{a} + \frac{D}{a r_0} \right) \frac{K}{1 + K} \quad (45)
\]

In the same way we deduced that, when the voltammetric steady state is reached at the end of the negative sweep (first semicircle), the value of this cathodic plateau is given by:

\[
(\psi_m)_{E_m \rightarrow - \infty} = \left( \frac{k_1 + k_2}{a} + \frac{D}{a r_0} \right) \frac{1}{1 + K} \quad (46)
\]

3.3.3. Cyclic linear sweep voltammetry (CLSV)

In order to apply Eq. (41) of this paper to cyclic linear sweep voltammetry (CLSV) it is necessary to introduce the condition \( | \Delta E | \rightarrow 0 \). We have checked that, according to Ref. [18], excellent results, independent of the \( | \Delta E | \) chosen, are obtained for values of \( | \Delta E | \leq 0.01 \text{ mV} \).

Note that, if \( K \neq 0 \), the current in CLSV tends to minus infinity at the beginning of the experiment while in CSCV it takes a constant value. This behaviour is easily deduced from Eq. (43), taking into account that in CLSV \( | \Delta E | \rightarrow 0 \).
Fig. 7. Cyclic staircase voltammetry (one complete cycle, Eq. (4)). $k_1 + k_2 = 1 \text{ s}^{-1}$. The values of $\sqrt{D/r_0}$ (in $\text{s}^{-1/2}$) are: (a) 0 and (b) 3. The values of the equilibrium chemical constant of the chemical reaction $K$ are on the curves. Other conditions as in Fig. 5.
Fig. 8. Cyclic linear sweep voltammetry (two complete cycles, Eq. (18)). $A = 1$. The values of the equilibrium chemical constant of the chemical reaction $K$ are: (a) 0 and (b) 1. The values of the dimensionless sweep rate $P$ (Eq. (48)) are: (---) 10 and (----) 20. Other conditions as in Fig. 5.
In Fig. 8 we have represented the dimensionless cyclic voltammograms $\Phi/\Theta$ deduced from Eq. (18), with $\Theta = (nF/RT)(E-E^\circ)$, with two complete cycles for $K = 0$ (Fig. 8(a)) and $K = 1$ (Fig. 8(b)). These curves have been deduced for two different values of the so-called dimensionless sweep rate in reference [1], $P$, which is given by,

$$P = \left( \frac{nFv^2}{RTD} \right)^{1.2} = \left( \frac{nFv}{RT} \frac{A}{(k_1 + k_2)} \right)^{1.2}$$

(47)

As has been pointed out in Fig. 8 the use of successive cycles in CLSV or in CSCV is advantageous, for example, in determining whether the chemical reaction is irreversible or not, since by increasing the sweep rate the differences between the first complete cycle and the second are shown both when $K = 0$ (Fig. 8(a)) and when $K \neq 0$ (Fig. 8(b)). To this extent, for a qualitative exploration of the process, CLSV could be of greater advantage than CSCV since these effects will be more notable in the former.

Finally we have compared our simple Eqs. (17) and (18) in this paper with the integral Eq. (30) in reference [1], which cannot be considered as a general analytical solution of this kind of problem on account of the following reasons:

1. This equation has a very complicated expression from which it is not possible to predict the general behaviour of the process (I) nor deduce limiting situations like those shown in the Sections 3.1 and 3.4 of this paper.

2. Secondly, this equation is applicable only in linear sweep voltammetry (LSV) and only when supposing that $K = 0$. This is a serious disadvantage since by using cyclic techniques it is possible to know whether the steady state has been reached or not through a simple visual inspection of the $I/E$ response (the properties of positive and negative sweeps are coincident).

3. Finally we have checked that our results are in agreement with those obtained by Diao and Zhang [1] in LSV. Thus, in Figs. 9 and 10 we have obtained the $\Phi/\Theta$ curves under the same conditions as those indicated in Figs. 1 and 2 in Diao and Zhang [1], respectively, but considering a whole cycle of potential sweep (CLSV).

The presence of the positive sweep in our curves (Figs. 9 and 10) clearly shows when it can be supposed that the voltammetric steady state has been reached.

3.4. Methods for calculating chemical kinetic parameters $k_1$, $k_2$, and $K$

The kinetic parameters of the chemical reaction can be calculated from multipotential step chronoamperometry (Section 3.3.1) and also by using cyclic staircase voltammetry (Section 3.3.2). So, Eqs. (45) or (46) can

Fig. 9. Cyclic linear sweep voltammetry (one complete cycle, Eq. (18)). $K = 0$. The values of the dimensionless sweep rate $P$ and of the dimensionless parameter $A$ are on the curves.
be used to calculate the rate constants \( k_1 \) and \( k_2 \), and also the equilibrium constant \( K \). Note that,

\[
\frac{|\psi_m|_{E_m \to -\infty}}{|\psi_m|_{E_m \to -\infty}} = \frac{1}{\sqrt{a \left( \sqrt{k_1 + k_2 + \frac{D}{r_0}} \right)}}
\]

It is clear that, for the calculation of the kinetic constants of the chemical reaction it is convenient to decrease the sweep rate. Fig. 7b shows that for a value of \( \sqrt{D/r_0} \approx 3 \text{ s}^{-1/2} \), the \( \psi_m/E \) response is a sigmoid whose anodic and cathodic plateaus fulfil Eqs. (45) and (46) respectively and therefore, the rate and equilibrium constants can be easily calculated from Eq. (48).

It is interesting to point out that in the cases where it is not possible to guarantee that the kinetic steady state has been reached (Eq. (24) is not applicable for the calculation of the rate constants \( k_1 \) and \( k_2 \)) it is better to use the general Eq. (21) corresponding to conventional plane electrodes. This is so since from Eqs. (17) and (48) it is deduced that when microelectrodes are used, the term depending on \( r_0 \) causes the kinetic contribution to the total current to decrease as \( r_0 \) decreases. Thus, under these conditions it is possible to obtain a practically sigmoidal \( \psi_m/E \) response, even when the chemical reaction has low rates and the kinetic steady state condition (\( f(x_{\text{eq}})_{\text{CAT}} \to 1 \), see Eq. (22)) is not applicable.

Fig. 11 shows the influence of the sweep rate on the different cyclic staircase voltammograms obtained with \( K \neq 0 \) for two very different values of \( (k_1 + k_2) \), 0.5 and 50 s\(^{-1}\) in plane electrodes (\( \sqrt{D/r_0} = 0 \)) and microelectrodes (\( \sqrt{D/r_0} = 10 \text{ s}^{-1/2} \)). As can be seen by combining the electrode size with the sweep rate, a steady state may or may not be obtained to characterise any catalytic process. As can be easily deduced from the Figure and from Eq. (41), a decrease of the electrode radius and an increase of the sweep rate both act to decrease the influence of the chemical reaction in the current potential response (\( \psi_m/E \) curve). For these reasons, in order to obtain the chemical kinetic parameters, for small values of \( (k_1 + k_2) \) conventional planar electrodes are more appropriate while, on the contrary, for values of \( (k_1 + k_2) > 1 \text{ s}^{-1} \), microelectrodes with a low sweep rate can be used in order to obtain experimental data of better quality.

All the applications analysed in this section in CSCV can be used with CLSV, although it should be made clear that in similar conditions, i.e. with the same sweep rate, the voltammetric steady state is reached somewhat more easily in CSCV than in CLSV. This fact is shown by comparing Fig. 12(a, b) obtained in CLSV with Fig. 11(a, b) corresponding to CSCV under the same condi-

Fig. 10. Cyclic linear sweep voltammetry (one complete cycle, Eq. (18)). \( K = 0 \). The values of the dimensionless sweep rate \( P \) and of the dimensionless parameter \( \Lambda \) are on the curves.
tions. This fact shows that it may be advantageous to use CSCV rather than CLSV to characterise a catalytic process, i.e., for calculating the rate and equilibrium constants of the chemical reaction. The rate constants can also be calculated by analysing the variation of the peak current with the sweep rate as indicated in Diao and Zhang [1]. But this method is not very practical due to the fact that the linear region corresponds to very high sweep rates for which a catalytic process behaves as a simple E process.

4. Conclusions

A general analytical equation for the \( I/t \) response corresponding to a catalytic mechanism for any value of the equilibrium constant has been obtained based on the superposition principle by applying the mathematical procedure described by [11]. This equation is easily programmable and is valid for any spherical electrode, including hemispherical ultramicroelectrodes \( (r_0 \to 0) \), and also for planar electrodes \( (r_0 \to \infty) \). Moreover, it can be applied to multistep chronoamperometry; double potential pulse techniques [19] (differential pulse (DPV), differential normal pulse (DNPV) and reverse pulse (RVP) voltammetries); triple potential pulse techniques [20] (double differential pulse (DDPV) and reverse differential pulse (RDPV) voltammetries); to multipulse techniques such as cyclic square wave (CSWV) and cyclic staircase voltammetry (CSCV), as well as to cyclic linear sweep voltammetry (CLSW).

As limit situations of this expression, it is possible to predict a ‘pure kinetic steady state’ for fast chemical reactions as observed in electrodes of planar geometry, a non kinetic steady state at hemispherical ultramicroelectrodes, which we have called the ‘micro-geometrical steady state’, and also the ‘mixed geometrical-kinetic steady state’ which should be expected for any microhemispheres and spheres of conventional size. The \( I/E \) response corresponding to an E process can also be deduced by making \( K = 0 \) and \( \chi_{pm} = 0 \) in Eq. (17). We also explain why a steady state is, in general, reached earlier for a catalytic mechanism than for a simple E mechanism as has been indicated in Diao and Zhang [1]. This is due to the fact that for a catalytic mechanism the achievement of a current independent of time is favoured by the existence of the homogeneous chemical reaction as is deduced from the comparison of Eqs. (17) and (26) and from Fig. 1.

We have analysed the approach to the steady state in different multistep techniques according to the electrode radius and to the equilibrium and the chemical rate constants.
Fig. 12. Cyclic linear sweep voltammetry (one complete cycle, Eq. (41)). |ΔE| = 0.01 mV, K = 1, k₁ + k₂ = 1 s⁻¹. The values of √D/ν₀ (in s⁻¹/²) are: a) 0 and b) 10. The values of the sweep rate ν (in mV s⁻¹) are: (→) 50, (---) 100, (⋯⋯) 1000 and (⋯⋯⋯) 10⁴. Other conditions as in Fig. 5.
We have compared the CSCV and CLSV techniques at the same sweep rate and we have also analysed the influence of the sweep rate on the response corresponding to a catalytic process in these two cyclic techniques. The use of these cyclic techniques is of great importance since through these we can ascertain whether the voltammetric steady state has been reached by a simple visual inspection of the I/E curves. In the case of linear sweep voltammetry (LSV) our results are in agreement with those obtained from Eq. (30) in Diao and Zhang [1].

In order to obtain the rate and equilibrium constant of the homogeneous chemical reaction, for small values of \((k_1 + k_2)\), conventional planar electrodes are more appropriate while on the contrary, for values of \((k_1 + k_2) > 1\) s\(^{-1}\), microhemi-spheres with a low sweep rate can be used in order to obtain experimental data of better quality.

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Appendix A

For the mechanism given by the reaction scheme (1), when a first potential step, \(E_1\), is applied to a spherical electrode, the differential equation system to solve is given by [21],

\[
\delta \phi^1 = \delta \xi^1 = 0
\]  
(A1)

where

\[
\delta = \frac{\partial}{\partial t_1} - D \left[ \frac{\partial^2}{\partial r^2} + 2 \frac{\partial}{\partial r} \right]
\]  
(A2)

and,

\[
\phi^1 = [c_A^1(r, t_1) - K c_b^1(r, t_1)] e^{(k_1 + k_2) t_1}
\]  
(A3)

\[
\xi^1 = c_A^1(r, t_1) + c_b^1(r, t_1)
\]  
(A4)

with \(K\) given by Eq. (3).

In the above equations we have supposed that the diffusion coefficients of species A and B are equal \((D_A = D_B = D)\).

Taking into account that for a reversible chemical reaction it is found that,

\[
c_A^1(r_0, t_1) - J_1 c_b^1(r_0, t_1)
\]  
(A5)

with \(J_1\) given by Eq. (5) and that the sum of the concentrations of A and B species remains constant for any values of the distance and time, i.e.

\[
\xi^1 = \xi^* = c_A^* + c_B^*
\]  
(A6)

the boundary value problem can be expressed only in terms of the variable \(\phi^1\) in the following way,

\[
t = 0; \quad r \geq r_0 \quad \phi^1 = 0
\]  
(A7)

\[
t > 0; \quad r \rightarrow \infty \quad \phi^1 = 0
\]  
(A8)

\[
t > 0; \quad r = r_0 \quad e^{-(k_1 + k_2) t_1} \phi^1(r_0, t_1) = \frac{1 - K J_1 \xi^*}{1 + J_1}
\]  
(A9)

The current corresponding to this potential step is given by

\[
\frac{I_1}{nF_A} = D \left( \frac{\partial c_A^1(r, t)}{\partial r} \right)_{r_0} = -D \frac{e^{-(k_1 + k_2) t_1}}{1 + K} \frac{\partial \phi^1}{\partial r} \bigg|_{r_0}
\]  
(A10)

By introducing the dimensionless parameters

\[
\chi_{11} = (k_1 + k_2) t_1
\]  
(A11)

\[
s_1 = \frac{r - r_0}{2 \sqrt{D t_1}}
\]  
(A12)

\[
\zeta_1 = \frac{2 \sqrt{D t_1}}{r_0}
\]  
(A13)

and adopting for \(\phi^1\) a solution of the form,

\[
\phi^1 = \sum_{i,j} \sigma_{i,j}(s_1) c_{i,j}^1 \chi_{11}^i
\]  
(A14)

Eqs. (A1), (A7) and (A8) transform into

\[
\sigma_{i,j}^n(s_1) + 2 s_1 \sigma_{i,j}^1(s_1) - 2(i + j) \sigma_{i,j}(s_1) = -\sum_{m=0}^{i-1} e_m(s_1) \sigma_{i-m-1,j}(s_1)
\]  
(A15)

\[
e_m = 2(1-i)^n s_1^n \quad \text{with} \quad e_m = 0 \quad \text{for} \quad i = 0
\]  
(A16)

\[
\xi^1 \rightarrow \infty; \quad \sigma_{i,j}(0) = 0 \quad \forall \ i,j
\]  
(A17)

\[
s_1 = 0;
\]  
(A18)

\[
\sigma_{i,j}(0) = 0 \quad \forall \ i \geq 1
\]  
(A19)

\[
\sigma_{0,j}(0) = \frac{(1 - K J_1 \xi^*)}{1 + J_1}
\]  
(A20)

Moreover, Eq. (A9) for the current becomes,

\[
\frac{I_1}{nF_A} = \frac{D}{1 + K} \frac{\sqrt{D}}{2 \sqrt{t_1} \ t_1} \sum_{i,j} \sigma_{i,j}(0) c_{i,j}^1 \chi_{11}^i
\]  
(A21)
By solving Eq. (A12) with conditions (A13) and (A14) we have deduced the expressions for \( \sigma_{i,s_i} \) functions and, from these expressions, those corresponding to the derivative in \( s_1 = 0 \), which are the following:

\[
\sigma_{0,0}(0) = \frac{(1 - K J_1 j^* p_{2j})}{1 + J_1 j!}
\]
(A16)

\[
\sigma_{0,i}(0) = \frac{(1 - K J_1 j^* 1)}{1 + J_1 j!}
\]
(A17)

\[
\sigma_{0,0}(0) = 0 \quad \text{for } i \geq 2
\]
(A18)

with

\[
p_{2j} = \frac{2 \Gamma(1 + j)}{\Gamma\left(1 + \frac{2j}{2}\right)}
\]
(A19)

Note that the functions \( \sigma_{i,s} \) which contribute to the current expression (equation (A15)) are null for \( i \geq 2 \) (spherical correction of higher order than the first).

By substituting Eqs. (A16)–(A18) in Eq. (A15) we obtain, for the current corresponding to the first potential step applied to a spherical electrode, the following exact expression,

\[
\frac{I_1}{nFAD} = \frac{(1 - K J_1 j^*)}{(1 + K)(1 + J_1)} \left\{ \frac{e^{-x_1}}{\sqrt{\pi D t_1}} + \sqrt{\frac{k_1 + k_2}{D}} \text{erf}(\sqrt{x_{11}}) + \frac{1}{r_0} \right\}
\]
(A20)

References