Study of multistep electrode processes in double potential step techniques at spherical electrodes

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Abstract

Analytical solutions for reversible multistep electrode processes in double potential step techniques at spherical electrodes of any size, including plane electrodes and ultra-microelectrodes, are derived. These solutions are valid when the diffusion coefficients of all species are equal, and they are applicable for any number of the species initially present in the solution, for any values of the formal potentials of the different steps and for any duration of the two potential steps. In differential pulse voltammetry (DPV) and in additive differential pulse voltammetry (ADPV) the effects of the applied potential and of the electrode sphericity on the current are found to be separable and, therefore, the position of the peaks and the cross potentials are not dependent on the size of the electrode. The convenience of using ADPV in determining the formal potentials when some electrochemical steps are not completely separated is shown. It is also demonstrated that the reproportionation/disproportionation homogeneous reactions have no effect either on the surface concentrations nor on the currents in any multipotential step technique under the conditions considered here.

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1. Introduction

Recent papers by our laboratory have presented the analytical solutions deduced for a multistep reversible process at spherical electrodes in voltammetry with constant potential [1,2] and for a reversible EE process at planar electrodes in double potential step techniques [3,4]. These papers highlight, on the one hand, the convenience of using spherical electrodes, such as the SMDE, for the study of multistep processes and, on the other, the usefulness of the double pulse techniques in detecting and characterising these processes.

In this paper, we have derived the analytical expressions corresponding to the I/E response of reversible multistep electrode processes in double potential step techniques with spherical electrodes of any size, including planar electrodes and ultra-microelectrodes as limit cases, when the diffusion coefficients of all species implied in the process are equal.

The expression obtained for the current corresponding to the second potential step in spherical diffusion can be written in a very simple form as that corresponding to planar diffusion plus a term dependent on the electrode sphericity which is affected only by the last potential step applied.

The general analytical equations deduced here are applicable when several or all species are initially present in the solution, without restrictions on the values of the formal potentials and for any duration of the two potential steps applied, in such a way that they are applicable to any double potential step technique, including double pulse chronoamperometry. We have applied these solutions to differential pulse and additive differential pulse voltammetry (ADPV), which are the most useful in detecting and characterising this type of electrode processes, as has been shown in previous papers [3,4]. The ADPV is especially useful when two or more steps of the process are not completely
separated, since the ADP-curves provide an easy method to determine the formal potentials of all the electrochemical steps.

As is well known, the reproportionation/disproportionation homogeneous reactions coupled to the heterogeneous charge transfer steps in multistep electrode processes have no effect on the I/E curves if: (a) the heterogeneous steps are reversible, and (b) the diffusion coefficients of all species are equal [5]. Voltammetric experiments are not affected by these homogeneous reactions independently of whether the diffusion field is planar or spherical, as is shown in the present work and contrary to the affirmation made in Refs. [6,7], according to which, the lack of effects of these homogeneous reactions on the voltammetric response is also restricted to linear diffusion.

The reason why these homogeneous reactions have no influence on any single or multipotential step voltammetric technique in spherical diffusion under conditions (a) and (b) is that the expressions corresponding to the I/E curves for multistep processes in planar or ultramicrospherical diffusion are limit cases of those corresponding to spherical diffusion. Thus, the following is fulfilled:

The surface concentrations corresponding to any potential step are dependent only on the applied potential, and they are given by the same expressions as those corresponding to planar electrodes or to ultramicrohemispheres.

The current corresponding to any potential pulse is given as a sum of currents corresponding to single potential steps in the same way as occurs with planar electrodes and with ultramicrohemispheres.

A similar reasoning can be made for cylindrical electrodes and microelectrodes [8].

2. Theory

Let us consider a multistep mechanism, in which \( k \) reversible charge transfer reactions can take place according to the following scheme,

\[
\begin{align*}
\text{step} & \quad \quad \quad \text{formal potential} \\
1 & \quad O_1 + e^- \leftrightarrow O_2 & E_{1}^o \\
2 & \quad O_2 + e^- \leftrightarrow O_3 & E_{2}^o \\
& \quad \vdots & \vdots \\
j & \quad O_j + e^- \leftrightarrow O_{j+1} & E_{j}^o \\
& \quad \vdots & \vdots \\
k & \quad O_k + e^- \leftrightarrow O_{k+1} & E_{k}^o \\
\end{align*}
\]

(1)

We will suppose that the diffusion coefficients of the \( k+1 \) species participating in this process are equal and spherical semi-infinite diffusion to and from the surface of electrode takes place when a double potential step is applied.

The expression for the current corresponding to the first potential pulse, \( E_1^o \), applied during \( t_1 \) to a spherical electrode of any size for a \( k \)-step process has been deduced in Refs. [1,2] and is also given by Eq. (A12) herein. In this paper, for the same process, we have derived (see Appendix A) the expression for the current when a second potential step, \( E_1^H \), is applied to the electrode during a time \( t_2 \), which is given by Eq. (A28).

By introducing Eqs. (A7) and (A23) for the surface concentrations corresponding to the first and second potential step, respectively, into Eqs. (A12) and (A28) and taking into account Eq. (A6), we can rewrite these currents as

\[
I^I = FAE^o \left( \frac{D}{\pi t_1} \right)^{1/2} \left( 1 + \frac{\left( \pi D t_1 \right)^{1/2}}{r_0} \right) (X^I - X^\phi) 
\]

(1)

\[
I^H = FAE^o \left( \frac{D}{\pi t_2} \right)^{1/2} \left\{ \frac{t_2}{\left( t_1 + t_2 \right)^{1/2}} \right\} (X^I - X^\phi) 
\]

\[+ (X^H - X^I) + \frac{(\pi D t_1)^{1/2}}{r_0} (X^H - X^\phi) \]

(2)

where \( F, D, r_0 \) and \( A \) have their usual meaning, \( e^o \) is the sum of the initial concentrations of all species and \( X^o, X^d \) and \( X^H \) are given by

\[
X^\phi = \frac{1}{e^o} \left\{ c^o_{k+1} - \sum_{j=1}^{k-1} (k-j)c^o_j \right\} 
\]

(3)

\[
X^I = \frac{1}{1 + \sum_{j=1}^{k} \prod_{j'} J^I_{j'}} \left\{ 1 - \sum_{j=1}^{k-1} (k-j) \left( \prod_{j'=j}^{k} J^I_{j'} \right) \right\} 
\]

(4)

\[
X^H = \frac{1}{1 + \sum_{j=1}^{k} \prod_{j'} J^H_{j'}} \left\{ 1 - \sum_{j=1}^{k-1} (k-j) \left( \prod_{j'=j}^{k} J^H_{j'} \right) \right\} 
\]

(5)

\( J^I_j \) and \( J^H_j \) \((j = 1, 2, \ldots, k)\) are functions of the applied potentials \( E^d \) and \( E^H \), respectively, which are given by

\[
J^I_j = \exp \left( \frac{F(E^d - E^o)}{RT} \right) 
\]

(6)

\[
J^H_j = \exp \left( \frac{F(E^H - E^o)}{RT} \right) 
\]

(7)

The expressions for the currents \( I^I \) and \( I^H \) corresponding to the first and second applied potentials \( E^d \) and \( E^H \) (Eqs. (1) and (2)), can also be written as

\[
I^I = I^I_{\text{plane}} \left( 1 + \frac{\left( \pi D t_1 \right)^{1/2}}{r_0} \right) 
\]

(8)

\[
I^H = I^H_{\text{plane}} + \frac{FAE^o D}{r_0} (X^H - X^\phi) 
\]

(9)
where \( I_\text{plane} \) and \( I_\text{v, plane} \) are the currents corresponding to a planar electrode \((r_0 \to \infty)\), given by:

\[
I_\text{plane} = FAc^\circ \left( \frac{D}{\pi t_1} \right)^{1/2} (X^I - X^\phi) \tag{10}
\]

\[
I_\text{v, plane} = FAc^\circ \left( \frac{D}{\pi t_2} \right)^{1/2} \\
\times \left\{ \left( \frac{t_2}{t_1 + t_2} \right)^{1/2} (X^I - X^\phi) + (X^{II} - X^I) \right\} \tag{11}
\]

As can be observed in Eq. (9) for the current corresponding to the second potential step, the electrode radius affects only the term corresponding to the last potential step applied.

When \( r_0 \to \infty \) and \( k = 2 \), all the above equations obtained for the second potential step coincide with those deduced in Ref. [3] for an EE mechanism when planar electrodes are used.

2.1. Differential pulse techniques

2.1.1. Differential normal pulse voltammetry

In the double pulse technique differential normal pulse voltammetry (DNPV) two consecutive potential steps, \( E^I \) and \( E^{II} \), are applied during times \( t_1 \) and \( t_2 \), respectively, without restriction on the duration of either pulse, and the difference \( \Delta E = E^{II} - E^I \) is kept constant during the experiment. The currents \( I^I \) and \( I^{II} \) are measured at the end of each pulse and the difference \( \Delta I_{\text{DNPV}} = I^{II} - I^I \) is plotted versus \( E^I \). Thus, by subtracting Eqs. (2) and (1) we can obtain the expression for the response of a reversible multistep process in DNPV, which is given by

\[
\psi_{\text{DNPV}} = \left( \frac{t_2}{t_1 + t_2} \right)^{1/2} - \left( \frac{t_1}{t_1} \right)^{1/2} \right) (X^I - X^\phi) \\
+ \left( 1 + \frac{(\pi Dt_2)^{1/2}}{r_0} \right) (X^{II} - X^I) \tag{12}
\]

where

\[
\psi_{\text{DNPV}} = \frac{\Delta I_{\text{DNPV}}}{FAC^\circ (D/\pi t_1)^{1/2}} \tag{13}
\]

Note that Eq. (12) can also be written as

\[
\psi_{\text{DNPV}} = \psi_{\text{plane}}^{\text{DNPV}} + \frac{(\pi Dt_2)^{1/2}}{r_0} (X^{II} - X^I) \tag{14}
\]

where \( \psi_{\text{plane}}^{\text{DNPV}} \) is the normalised response corresponding to a planar electrode, given by

\[
\psi_{\text{DNPV}}^{\text{plane}} = \left( \frac{t_2}{t_1 + t_2} \right)^{1/2} - \left( \frac{t_1}{t_1} \right)^{1/2} \right) (X^I - X^\phi) \\
+ (X^{II} - X^I) \tag{15}
\]

The expressions for this response in the lower and upper limits can be deduced from Eq. (12) by making \( E^I \), \( E^{II} \to -\infty \) and \( E^I, E^{II} \to \infty \), respectively in Eqs. (4)–(7).

Thus, we obtain

\[
\psi_{\text{DNPV}}^{\text{II}} = \left( \frac{t_2}{t_1 + t_2} \right)^{1/2} - \left( \frac{t_1}{t_1} \right)^{1/2} \right) \frac{\sum_{j=1}^{k} (k - j + 1)c_j^r}{c^*} \tag{16}
\]

\[
\psi_{\text{DNPV}}^{I} = - \left( \frac{t_2}{t_1 + t_2} \right)^{1/2} - \left( \frac{t_1}{t_1} \right)^{1/2} \right) \frac{\sum_{j=1}^{k} (j - 1)c_j^r}{c^*} \tag{17}
\]

Note that these limit currents are dependent on the initial concentrations, whereas they remain independent of the electrode radius, \( r_0 \).

2.1.2. Differential pulse voltammetry

If we impose the condition \( t_2 \ll t_1 \), the first term in Eq. (12) can be suppressed and the expression for the current corresponding to differential pulse voltammetry (DPV) is obtained

\[
\psi_{\text{DPV}} = \left( 1 + \frac{(\pi Dt_2)^{1/2}}{r_0} \right) (X^{II} - X^I) \tag{18}
\]

Eq. (18) can also be written as

\[
\psi_{\text{DPV}} = \psi_{\text{plane}}^{\text{DPV}} \left( 1 + \frac{(\pi Dt_2)^{1/2}}{r_0} \right) \tag{19}
\]

with

\[
\psi_{\text{plane}}^{\text{DPV}} = (X^{II} - X^I) \tag{20}
\]

Note that both limit currents in the DPV are always null (see Eqs. (16) and (17) with \( t_2 \ll t_1 \)) and also that the signal in this technique is independent of which species are initially present in the solution (see Eq. (18)).

Moreover, in this technique the effects of sphericity, \((\pi Dt_2)^{1/2}/r_0\) (given by the first factor in Eq. (18)) and those of the applied potentials (given by the second factor in Eq. (18)), can be analysed independently in any reversible multistep process. Indeed, since this second factor, \((X^{II} - X^I)\), is identical to that obtained for a planar electrode (see Eq. (20)), the values of the peak potentials are identical for planar electrodes \((r_0 \to \infty)\) and for ultramicroelectrodes \((r_0 \to 0)\).

2.1.3. Ultramicrohemispherical electrodes

When \( r_0 \to 0 \) the expressions deduced for the response in the double pulse techniques DNPV and DPV (Eqs. (12) and (18)) are reduced to

\[
\Delta I_{\text{micro}}^{\text{DNPV}} = \Delta I_{\text{micro}}^{\text{DPV}} = \Delta I_{\text{SWV}}^{\text{micro}} = 2\pi F D_r c^*(X^{II} - X^I) \tag{21}
\]

where Eq. (13) with \( A = 2\pi r_0^2 \) has been introduced.
Note that as this response is the difference between two steady state currents, corresponding to two consecutive potential pulses, which are independent of time, and therefore independent of the previous history of the process, the signal given by DNPV or DPV in ultramicrohemispheres is identical to those obtained in square wave voltammetry (SWV), with the value of the difference between the two potential steps applied in DPV, $\Delta E = E^H - E^v$, being equal to twice the square wave amplitude, $E_{\text{SWV}}$, i.e. $\Delta E = 2E_{\text{SWV}}$. This behaviour for a reversible multistep electrode process is the same as that shown by a simple reversible E process and a catalytic mechanism [9,10].

2.2. Additive differential techniques

2.2.1. Additive differential normal pulse voltammetry

The additive differential normal pulse voltammetry (ADNPV) [11] is based on the addition of two responses obtained in DNPV, $\Delta I^\text{cat}_{\text{DNPV}}$ and $\Delta I^\text{an}_{\text{DNPV}}$, which correspond to the same first pulse potential, $E^1$, and different values for the potential applied to the second pulse, $E^H$ and $E^v$, respectively, which fulfil $|\Delta E| = -(E^H - E^v) = (E^H - E^v)$ with $\Delta E < 0$ for $I^\text{cat}_{\text{DNPV}}$ and $\Delta E > 0$ for $I^\text{an}_{\text{DNPV}}$ (see Ref. [11]),

$$\psi_{\text{ADNPV}} = 2\left(\frac{t_2}{t_1 + t_2}\right)^{1/2} \left[X^1 - X^\Phi\right]$$

$$+ \left(1 + \frac{(\pi D t_2)^{1/2}}{r_0}\right) \left[X^H \text{ cat} + X^H \text{ an} - 2X^1\right]$$

(22)

where

$$\psi_{\text{ADNPV}} = \psi_{\text{DPV}}^\text{cat} + \psi_{\text{DPV}}^\text{an} = \frac{I^H \text{ cat} + I^H \text{ an} - 2I^1}{\text{FAC}^*(D/\pi t_2)^{1/2}}$$

(23)

2.2.2. Additive differential pulse voltammetry (ADPV)

When $t_2 \ll t_1$ in Eq. (22), we obtain the simpler expression for the ADPV

$$\psi_{\text{ADPV}} = \left(1 + \frac{(\pi D t_2)^{1/2}}{r_0}\right) \left[X^H \text{ cat} + X^H \text{ an} - 2X^1\right]$$

(24)

2.3. DPV and ADPV for a multistep mechanism with well-separated waves

All the above expressions are applicable to any $k$-step reversible process without restriction on the values of the formal potential of each step.

The multistep mechanisms for which the values of the formal potentials verify that $E_1^H \gg \cdots E_k^H \gg \cdots \gg E_k^v$ always present well-separated $k$ responses. In this case, for the response corresponding to any step $s$ it is verified that

$$J_{p<s}^v = 0$$

$$J_s^p = \exp\left(\frac{F(E_s^p - E_s^v)}{RT}\right)$$ with $p = 1, \ldots, II$ (25)

$$J_{p>s}^v \rightarrow \infty$$

By introducing the above expressions in Eqs. (18) and (24) for the double pulse techniques DPV and ADPV, respectively, we obtain the responses corresponding to any step, whose expressions are given by

$$\psi_{\text{DPV}}(s-w) = \left(1 + \frac{(\pi D t_2)^{1/2}}{r_0}\right) \left(\frac{1}{1 + J_{I}^{\text{cat}}} - \frac{1}{1 + J_{I}^{\text{an}}}\right)$$

(26)

$$\psi_{\text{ADPV}}(s-w) = \left(1 + \frac{(\pi D t_2)^{1/2}}{r_0}\right) \times \left(\frac{1}{1 + J_{I}^{\text{cat}}} - \frac{2}{1 + J_{I}^{\text{an}}} + \frac{1}{1 + J_{I}^{\text{an}}}\right)$$

(27)

These equations for the normalised curves in both techniques are coincident with those corresponding to a simple E mechanism [11–13] and therefore, it is possible to deduce the expressions for the formal potentials of each step, obtaining

For DPV: $E_s^p = E_{\text{peak}}^p + \frac{\Delta E}{2}$

(28)

For ADPV: $E_s^p = E_{\text{cross}}$

(29)

where the upper and lower signs in Eq. (28) refer to the cathodic and anodic peaks, and $E_{\text{cross}}$ in Eq. (29) is the value of the potential at which the ADPV current changes in sign [4,11].

3. Results and discussion

The response of a multistep electrode process in differential double pulse techniques (DNPV, DPV, ADNPV and ADPV) has been previously analysed for the particular case of a two-step reversible process (EE mechanism) in planar diffusion [3,4]. In this section, we will apply the expressions deduced in this paper to analyse the effects of the electrode sphericity on the response of a $k$-step reversible process, with any value of $k$, in the above-mentioned techniques when spherical conventional electrodes and microelectrodes are used. We will also discuss the behaviour of these techniques when steady state responses are reached.

In Fig. 1 we have plotted the DNP curves calculated from Eqs. (12) and (13) for a two-step process ($k = 2$) with well-separated waves ($E_2^v - E_1^v = -200$ mV), by using $t_1 = t_2$ with three different values of these time pulses (0.05, 1 and 3 s) and for $r_0 = 5 \times 10^{-3}$ cm (Fig.
1a), \( r_0 = 2.5 \times 10^{-4} \text{ cm} \) (Fig. 1b) and \( r_0 = 10^{-5} \text{ cm} \) (Fig. 1c). This figure shows that the \( \Delta I_{\text{DNPV}} \) response tends to reach a steady state as the electrode radius decreases, in such a way that for \( r_0 = 2.5 \times 10^{-4} \text{ cm} \) (curves b) the steady state has been practically reached for \( t_1 = t_2 \geq 1 \text{ s} \) and for \( r_0 = 10^{-5} \text{ cm} \) (curves c) the steady state has been reached for \( t_1 = t_2 \geq 0.05 \text{ s} \).

Thus, under steady state conditions, i.e., when \( r_0 \leq \pi D t_p^{1/2} / 50 \) [14], with \( t_p \) being the duration of any potential step, the \( \Delta I/I \) curves of a multistep reversible process in DNPV and DPV are identical. Moreover, as has been pointed out in Section 2.1.3, under these conditions the above curves are also identical to that obtained in SWV when the square wave amplitude is
half the double pulse amplitude. This behaviour is shown in Fig. 1c and also in Fig. 2, which correspond to a four-step process with 
\[ E_2'^0 - E_1'^0 = -80 \text{ mV} \] 
where the steady state has been reached. As can be observed in Fig. 2, all the \( \Delta I/E \) curves corresponding to any differential pulse technique, both for a double pulse experiment (DNPV, DPV) or for a multipulse experiment (SWV), are indistinguishable. In this figure the influence of pulse amplitude \( \Delta E \) on the curves is shown. As can be deduced from it, when the \( \Delta E \) value decreases the \( \Delta I \) signal decreases and the voltammogram tends to separate into four peaks. This last behaviour of the \( \Delta I/E \) curves with the decrease in the \( \Delta E \) value is independent of the electrode sphericity and, therefore, of whether the steady state has been reached or not, and it makes it possible to detect at sight the existence of a multistep process with these techniques by acting on the experimental conditions. The differential pulse techniques are therefore more advantageous than single pulse techniques in detecting and characterising a multistep process, as has already been shown for the response in these techniques of an EE process with planar electrodes [3,4].

Fig. 2. Influence of pulse amplitude, \( \Delta E \), on the differential pulse voltammograms \( \Delta I/E_{DPV}/(E_3^f - E_1^f) \), for a reversible four-step mechanism (Eqs. (12) and (18) or Eqs. (21) and (13)). \( E_{j+1}^f - E_j^f = -80 \text{ mV} \) \((j = 1, 2, 3) \), \( t_1 = 1 \text{ s}, \ t_2 = 0.01 \text{ s}, r_0 = 10^{-4} \text{ cm} \). The values of \( \Delta E \) (in mV) are on the curves. Other conditions as in Fig. 1.

Fig. 3. Influence of electrode radius, \( r_0 \), on the differential normal pulse voltammograms \( \Delta I_{DNPV}/(E_3^f - E_1^f) \), for a reversible EE mechanism (Eq. (12)). \( E_2^f - E_1^f = -100 \text{ mV} \), \( t_1 = t_2 = 1 \text{ s} \). The values of \( r_0 \) (in cm) are on the curves. Other conditions as in Fig. 1.
The effects of electrode sphericity on the response of a multistep process have been analysed in Figs. 3 and 4 for a two-step mechanism in DNPV and for a three-step mechanism in DPV and ADPV, respectively. These figures show that, in agreement with Eqs. (14), (19) and (24), the decrease in the $r_0$ value always causes an enhancement in the $c$ signal. Due to the separability of the effects of the potential and the electrode sphericity, the $r_0$ value does not influence the position of the peaks nor the values of cross potentials.

In Fig. 4 we have plotted the DPV and ADPV curves for an EEE process for which we have supposed that the first and second steps are well-separated but the second and third are not well-separated ($E_1^0 - E_0^0 = 200$ mV, $E_2^0 - E_1^0 = -100$ mV, $t_1 = 2$ s, $t_2 = 0.02$ s. The values of $r_0$ (in cm) are on the curves. Other conditions as in Fig. 1.

Fig. 4. Comparison between $\psi_{DPV}(E^1 - E_1^0)$ and $\psi_{ADPV}(E^1 - E_1^0)$ curves for a reversible EEE mechanism (Eqs. (18) and (24), respectively). The circles correspond to the $E_j^0$ values ($j = 1, 2, 3$). $E_2^0 - E_1^0 = 200$ mV, $E_3^0 - E_2^0 = -100$ mV, $t_1 = 2$ s, $t_2 = 0.02$ s. The values of $r_0$ (in cm) are on the curves.

The usefulness of this method for evaluating the formal potentials of partially...
overlapped multistep reversible processes has been previously proved experimentally in Ref. [4] for the reduction of pyracine in aqueous acid media (EE process). These results again indicate the greater usefulness of the ADPV over other double pulse techniques.

Fig. 5 shows the dimensionless responses obtained in DPV (Fig. 5a) and ADPV (Fig. 5b) for a reversible process with six completely separated one-electron steps. The formal potentials (in mV) relative to AgQRE and the diffusion coefficient [15] are: $E_1^0 = -620$, $E_2^0 = -1020$, $E_3^0 = -1520$, $E_4^0 = -2010$, $E_5^0 = -2490$, $E_6^0 = -2860$, $D = 6.6 \times 10^{-6}$ cm$^2$ s$^{-1}$, $r_0 = 0.05$ cm. Other conditions as in Fig. 4.

4. Summary

(1) An analytical expression for the $I/E$ response of multistep reversible electrode processes in double potential step techniques at spherical electrodes of any size, including planar electrodes and ultramicroelectrodes as limit cases, has been derived and applied to DPV and ADPV.

(2) This expression shows that the electrode sphericity affects the current only in the term corresponding to the second potential step applied. This means that the formal potentials $E_j^0$ coincide with the cross potentials, and therefore they can be measured with great accuracy, as they can be easily obtained from a linear interpolation of the central zone of each curve.
analytical expressions for the responses in DPV and ADPV can be written as the products of two terms, one containing the effects of sphericity and the other with the effects of the applied potentials, and the effects can therefore be analysed independently. As a consequence, the values of the peak and cross potentials are independent of the electrode size and, thus, they are the same for planar electrodes and for ultramicroelectrodes.

(3) Differential pulse techniques are more advantageous than single pulse techniques in detecting a multistep reversible process, especially when the steps partially overlap, since a decrease in the pulse amplitude, $\Delta E$, tends to separate out the response for a $k$-step process into $k$ peaks, making it possible to detect the existence of a multistep process with these techniques at sight, by acting on the experimental conditions.

(4) Among double pulse techniques, ADPV is the most useful for the quantitative evaluation of formal potentials. This technique provides an easy method to determine them directly from the curves when some steps of the process partially overlap. Moreover, when all steps are well-separated, although, of course, the direct determination of the formal potentials is possible with any electrochemical technique, higher accuracy is achieved with ADPV.

(5) The solution electron-transfer reactions coupled to a multistep reversible process have no effect on any voltammetric response when the diffusion coefficients of all participating species are equal, as is the case considered in this work, regardless of whether the diffusion field is planar or spherical, as is shown in Appendix B.

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Appendix A

To deduce the expression for the current corresponding to the second potential step we must start out from the solutions of the problem for the first potential step applied to a spherical electrode, which were obtained in Refs. [1,2]. From these references, the differential equation system that describes the mass transport for a reversible $k$-step process and the boundary conditions can be summarised as follow,

$$\delta c_i(r, t) = 0 \quad i = 1, 2, \ldots, k + 1$$  \hspace{1cm} (A1)

where

$$\delta = \frac{\partial}{\partial t} - D \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right)$$  \hspace{1cm} (A2)

$$t = 0, \quad r \geq r_0$$

$$t > 0, \quad r \to \infty$$

$$c_i^0 = 0$$

for all $i \neq 0$.

$$t > 0, \quad r = r_0; \sum_{i=1}^{k+1} \left( \frac{\partial^2 c_i}{\partial r^2} \right)_{r=r_0} = 0$$  \hspace{1cm} (A4)

$$c_i^0(r_0, t) = J_i^0 c_{i+1}^0(r_0, t) \quad i = 1, 2, \ldots, k$$  \hspace{1cm} (A5)

with $J_i^0$ given by Eq. (6).

In this case in which the diffusion coefficients of all species are equal, the fulfilment of Eqs. (A1)–(A5) implies that [1,2]

$$\sum_{i=1}^{k+1} c_i^0(r_0) = \sum_{i=1}^{k+1} c_i^* = c^*$$  \hspace{1cm} (A6)

$$c_i^0(r_0) = \left[ \frac{c^*}{1 + k \sum_{j=1}^{k} (\prod_{j=1}^{k} J_j^0)} \right]^i; \quad i = 1, 2, \ldots, k$$  \hspace{1cm} (A7)

The independence of time of the surface concentrations leads to the following solutions for the concentration profiles of all species implied in a reversible $k$-step process (see eq. (37) in Ref. [2])

$$c_i^0(r, t) = c_i^0 + \left[ c_i^0(r_0) - c_i^0 \right] \frac{r_0}{r} \text{erfc} \left[ \frac{r - r_0}{2 \sqrt{D t}} \right]$$  \hspace{1cm} (A8)

$$i = 1, 2, \ldots, k + 1$$

which fulfil (see Eq. (A6))

$$\sum_{i=1}^{k+1} c_i^0(r, t) = c^*$$  \hspace{1cm} (A9)

From Eq. (A8), the derivative of the concentration of any species in the surface of the electrode is given by

$$\left( \frac{\partial c_i^0}{\partial r} \right)_{r=r_0} = \left( \frac{1}{(\pi D t)^{1/2}} + \frac{1}{r_0} \right) (c_i^0 - c_i^0(r_0))$$  \hspace{1cm} (A10)

$$i = 1, 2, \ldots, k + 1$$

This last equation implies that the contribution to the current due to any species in a multistep process under these conditions (spherical diffusion when the diffusion coefficients of all species are equal) present a depen-
idence with the potential applied, through \((c_i^r - c_i^l(r_0))\), identical to that corresponding to planar electrodes (see eqs. (9) and (11) in Ref. [2]), since the surface gradients of concentrations can be written as the product of two terms, one which contains the effects of time and the electrode radius, and another which contains those of the applied potential.

Thus, the expressions for the partial current due to any step \(j\) of the process and for the total current observed during the first potential pulse applied (see eqs. (13)–(15) in Ref. [1]) can be written as

\[
I_j^I(t) = FA \left( \frac{D}{\pi \tau} \right)^{1/2} \left( 1 + \frac{(\pi D t)^{1/2}}{r_0} \right) \sum_{i=1}^{k} (c_i^r - c_i^l(r_0)); \quad (A11)
\]

and

\[
I^I(t) = \sum_{j=1}^{k} I_j^I(t)
\]

\[
= FA \left( \frac{D}{\pi \tau} \right)^{1/2} \left( 1 + \frac{(\pi D t)^{1/2}}{r_0} \right) \sum_{j=1}^{k} (k - j + 1)
\]

\[
\times (c_j^r - c_j^l(r_0)) \quad (A12)
\]

When at time \(t_1\) a second potential step, \(E^{III}\), is applied during \(t_2\), the equation system to solve is given by

\[
\delta^I c_i^l(r, t) = 0; \quad i = 1, 2, \ldots, k + 1 \quad (A13)
\]

where the total time is now \(t = t_1 + t_2\), with \(t_1\) constant.

The boundary conditions for this second pulse are

\[
t_2 = 0, \quad r \geq r_0
\]

\[
t_2 > 0, \quad r \to \infty
\]

\[
\left\{ \begin{array}{l}
\partial^I c_i^l = c_i^r(r, t) \\
\quad i = 1, 2, \ldots, k + 1 \\
\end{array} \right. \quad (A14)
\]

\[
t_2 > 0, \quad r = r_0;
\]

\[
\sum_{i=1}^{k+1} \left( \frac{\partial^I c_i^l}{\partial r} \right)_{r=r_0} = 0 \quad (A15)
\]

\[
c_i^l(r_0, t) = J_i^l c_{i+1}^l(r_0, t) \quad i = 1, 2, \ldots, k \quad (A16)
\]

with \(J_i^l\) given by Eq. (7).

Due to the linearity of the operator \(\delta^I\), the solutions for the second potential step, \(c_i^l(r, t)\), can be expressed as

\[
c_i^l(r, t) = c_i^l(r, t) + \hat{c}_i^l(r, t_2) \quad i = 1, 2, \ldots, k + 1 \quad (A17)
\]

where \(c_i^l(r, t)\) are the solutions corresponding to the first potential step (Eq. (A8)).

Thus, the boundary value problem for this second potential step can be written in a simpler form, in terms of only the new unknown variables \(\hat{c}_i^l(r, t_2)\), by introducing Eq. (A17) in Eqs. (A13), (A14), (A15) and (A16) and taking into account Eqs. (A1)–(A5) for the first pulse,

\[
\hat{c}_i^l(r, t_2) = 0 \quad i = 1, 2, \ldots, k + 1
\]

\[
t_2 = 0, \quad r \geq r_0
\]

\[
t_2 > 0, \quad r \to \infty
\]

\[
\hat{c}_i^l = 0 \quad i = 1, 2, \ldots, k + 1 \quad (A19)
\]

\[
t_2 > 0, \quad r = r_0
\]

\[
\sum_{i=1}^{k+1} \left( \frac{\partial^l c_i^l}{\partial r} \right)_{r=r_0} = 0 \quad (A20)
\]

\[
\hat{c}_i^l(r_0, t) = J_i^l \hat{c}_{i+1}^l(r_0, t) + (J_i^l - J_i^l) c_{i+1}^l(r_0) \quad i = 1, 2, \ldots, k \quad (A21)
\]

As can be noted, the equation system and boundary conditions which must fulfill \(c_i^l(r, t)\) (Eqs. (A18)–(A21)) have the same form as those for \(c_i^l(r, t)\) (Eqs. (A1)–(A5)), with the only differences in the values of the initial conditions, which are \(c_i^l\) for the first pulse and zero for the second one, and in the surface conditions (Eq. (A5)) and (Eq. (A21)), which differ only in the additional terms \((J_i^l - J_i^l) c_{i+1}^l(r_0)\) in (Eq. (A21)) which, due to the independence of \(c_i^l(r_0)\) of time (Eq. (A7)), have constant values for given values of \(E^n\) and \(E^{III}\). Therefore, the partial solutions for the second pulse, \(\hat{c}_i^l(r, t_2)\), have an analogous form to that corresponding to the first one (Eq. (A8)), with surface values also independent of time. Taking into account Eqs. (A17)–(A21), these partial solutions are given by

\[
\hat{c}_i^l(r, t_2) = [c_i^l(r_0) - c_i^l(r_0)] \frac{2}{r} \frac{\text{erfc}(r - r_0)}{2 \sqrt{Dt_2}} \quad (A22)
\]

\[
i = 1, 2, \ldots, k + 1
\]

with \(c_i^l(r_0)\) given by Eq. (7) and \(\hat{c}_i^l(r_0)\) by

\[
\hat{c}_i^l(r_0) = \frac{c^* \prod_{j=1}^{k} J_j^l}{1 + \sum_{j=1}^{k} \left( \prod_{j=1}^{k} J_j^l \right)}; \quad i = 1, 2, \ldots, k \quad (A23)
\]

\[
\hat{c}_{k+1}^l(r_0) = \frac{c^*}{1 + \sum_{j=1}^{k} \left( \prod_{j=1}^{k} J_j^l \right)}
\]

Note that the surface concentrations are independent of the electrode sphericity and, therefore, are identical as those corresponding to planar electrodes or to ultramicroelectrodes.

In the same way as for the first potential pulse (Eqs. (A6) and (A9)), also for the second one it is fulfilled that

\[
\sum_{i=1}^{k+1} \hat{c}_i^l(r, t) = \sum_{i=1}^{k+1} c_i^l(r_0) = c^* \quad (A24)
\]

The derivative of Eq. (A22) in the surface of the electrode take a similar form to that obtained in the first pulse (Eq. (A10)),
(\frac{\partial c_i^{\text{II}}}{\partial r})_{r=r_0} = \left( \frac{1}{(\pi D t_2)^{1/2}} + \frac{1}{r_0} \right) \left( c_i^\text{I}(r_0) - c_i^{\text{II}}(r_0) \right) \quad \text{(A25)}

i = 1, 2, \ldots, k + 1

and, therefore, the partial current due to any step \( j \) (with \( j = 1 \) to \( k \)) of the \( k \)-step process when a second potential step is applied, which is given by

\[ I_j^{\text{II}}(t) = FAD \sum_{i=1}^j \left( \frac{\partial c_i^{\text{II}}}{\partial r} \right)_{r=r_0} \quad \text{(A26)} \]

can be expressed, taking into account Eqs. (A17), (A10) and (A25), in the following way

\[ I_j^{\text{II}}(t) = I_j^{\text{I}}(t) + FA \left( \frac{D}{\pi t_2} \right)^{1/2} \left( 1 + \frac{(\pi D t_2)^{1/2}}{r_0} \right) \times \sum_{i=1}^j \left( c_i^\text{I}(r_0) - c_i^{\text{II}}(r_0) \right) \quad \text{(A27)} \]

\[ j = 1, 2, \ldots, k \]

with \( I_j^{\text{I}}(t) \) given by Eq. (A11) with \( t = t_1 + t_2 \).

From Eq. (A27) and Eq. (A11) or (A12), the following expression for the current observed, \( I_j^{\text{II}}(t) \), during the second potential step is obtained,

\[ I_j^{\text{II}}(t) = \sum_{j=1}^k I_j^{\text{II}}(t) = FA \left( \frac{D}{\pi} \right)^{1/2} \left\{ \left( \frac{1}{(\pi D t_2)^{1/2}} + \frac{(\pi D t_2)^{1/2}}{r_0} \right) \sum_{j=1}^k (k-j+1) \right\}

\times \left( c_1^\text{I} - c_1^{\text{II}}(r_0) \right)

+ \left( \frac{1}{(\pi D t_2)^{1/2}} + \frac{(\pi D t_2)^{1/2}}{r_0} \right) \sum_{j=1}^k (k-j+1)(c_j^\text{I}(r_0) - c_j^{\text{II}}(r_0)) \quad \text{(A28)} \]

\[ \delta c_1 = -k_1 c_1 c_3 + k_{-1} c_2^2 \\
\delta c_2 = 2k_1 c_1 c_3 - 2k_{-1} c_2^2 - k_2 c_2 c_4 + k_{-2} c_3^2 \\
\vdots \\
\delta c_j = 2k_{j-1} c_{j-1} c_{j+1} - 2k_{-(j-1)} c_j^2 - k_{j-2} c_j c_{j+2} + k_{-(j-2)} c_{j+1}^2 - k_j c_{j+2} + k_{-j} c_{j+1}^2 \\
\vdots \\
\delta c_k = 2k_{k-1} c_{k-1} c_{k+1} - 2k_{-(k-1)} c_k^2 - k_{k-2} c_k c_{k+2} + k_{-(k-2)} c_{k+1}^2 - k_k c_{k+2} + k_{-k} c_{k+1}^2 \quad \text{(B1)} \]

where \( k_i \) and \( k_{-i} \) are the rate constants corresponding to any chemical step, \( i \), of Scheme (II), which obviously must be taken as zero if the subscript \( i \) is not in the range \( 1 \leq i \leq k-1 \). The boundary value problem for Scheme (I) is not affected by the existence of reactions indicated in Scheme (II) in any multipotential step technique.

As can be seen, this current is given by a sum of two terms corresponding to two single potential steps in the same way as occurs in planar electrodes \( (r_0 \rightarrow \infty) \) or in ultramicroelectrodes \( (r_0 \rightarrow 0) \).

It is also interesting to note that, as can be expected, the surface concentrations for any potential step applied fulfill the following (see Eqs. (A7) and (A23))

\[ \frac{c_{i+1}(r_0)^2}{c_i(r_0)c_{i+2}(r_0)} = \exp \left[ \frac{F}{RT} (E^{\text{III}}_i - E^{\text{III}}_{i+1}) \right] = K_i \quad \text{(A29)} \]

with \( K_i \) being the equilibrium constant for any of the reproportionation homogeneous reactions that may accompany a multistep process [16,17], whose lack of effect on the response in voltammetric techniques is considered in Appendix B.

Appendix B

By following a similar reasoning to that adopted in the appendix of Ref. [5] to show that the reproportionation reaction coupled to an EE process has no effect on the IIE response with planar diffusion when (a) the heterogeneous steps are reversible and (b) the diffusion coefficients of all species are equal, in this appendix we demonstrate that this behaviour is not exclusive to planar diffusion, as is stated in Refs. [6,7]. The same occurs in spherical diffusion for the reproporation homogeneous reactions that may accompany any multistep process if conditions (a) and (b) are fulfilled.

The \( k-1 \) reproporation reactions coupled to a \( k \)-step mechanism (Scheme (I)) can be summarised as [17].

\[ O_i + O_{i+1} \rightarrow 2O_j \quad \text{with} \quad i = 1, 2, \ldots, k-1 \quad \text{(II)} \]

By including these homogeneous reactions in Scheme (I), the differential equations that describe the mass transport to and from the electrode for the \( k+1 \) species implied are the sum of a diffusive contribution, which is the same as when only Scheme (I) is considered (Eqs. (A1) and (A2)), and a kinetic contribution due to the existence of Scheme (II). These equations can be written as
Thus, when a potential step is applied to the electrode, the problem is described by Eq. (B1) with the boundary conditions (Eqs. (A3)–(A5)), corresponding to a reversible multistep electrode process in which the diffusivities of all species are equal.

The relation between the observed current for a \( k \)-step process and the surface fluxes is given by (see Eqs. (13)–(15) in Ref. [5])

\[
I = FAD \sum_{j=1}^{k} \left( \sum_{i=1}^{j} \left( \frac{\partial c_i}{\partial r} \right)_{r=r_c} \right) = FAD \sum_{j=1}^{k} (k-j+1) \left( \frac{\partial c_j}{\partial r} \right)_{r=r_0} \tag{B2}
\]

This expression together with the surface condition Eq. (A4) suggests the introduction of the following two changes,

\[
\begin{align*}
C &= \sum_{j=1}^{k+1} c_j \\
W &= \sum_{j=1}^{k} (k-j+1)c_j
\end{align*}
\tag{B3}
\]

The differential equations for the mass transport in function of these two new variables are given by

\[
\begin{align*}
\delta C &= 0 \\
\delta W &= 0
\end{align*}
\tag{B4}
\]

where the contributions due to the reproportionation reactions have been cancelled.

The solutions of Eq. (B4) with the appropriate boundary conditions derived from Eqs. (A3)–(A5) are, therefore, the same as those corresponding to the multistep process (Scheme (I)) without taking into account the homogeneous reactions coupled (Scheme (II)). These solutions provide the expressions for the surface concentrations of all participating species and for the current, which consequently do not reflect the existence of the chemical reactions (Scheme (II)) at all, and are given by Eqs. (A7) and (A12), respectively.

Moreover, as in these conditions the surface concentrations are dependent only on the potential applied (Eq. (A7)), the problem to solve when considering the application of a second potential step has the same characteristics as that analysed above and, therefore, the same conclusion is valid for any double pulse, or even, multipulse technique.

Thus, we can conclude that the reproportionation reactions coupled to a reversible multistep process cannot be detected by any single, double or multipotential step technique when the diffusion coefficients of all species implied are equal, whether the diffusion field is planar, spherical or, even, cylindrical [8].

References