Study of a catalytic mechanism in double potential step techniques at spherical electrodes

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Abstract

An analytical complete solution corresponding to the double potential step problem for the catalytic mechanism at spherical electrodes is presented. This solution is applicable to double potential step chronoamperometry, differential normal pulse voltammetry (DNPV), differential pulse voltammetry (DPV) and reverse pulse voltammetry (RPV). The effects of the sphericity of the electrode on the \( I/t \) and \( I/E \) responses are analysed. The equations deduced in this paper allow us to calculate smaller rate constant values than those that can be calculated by using microelectrodes when only steady state is considered. Methods for calculating kinetic and thermodynamic parameters for the catalytic mechanism in all the above mentioned techniques are proposed and applied to the system Ti (IV) oxalate complex in the presence of hydroxylamine at spherical electrodes of different radii. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In recent papers we have developed a simple, general and rigorous theory corresponding to a catalytic mechanism given by the scheme,

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

\[
B + Z \overset{k_1}{\underset{k_2}{\rightleftharpoons}} A + P
\]

in the multipotential step technique at planar [1] and spherical electrodes and microelectrodes [2]. In these papers the expression for the current corresponding to any potential step of a determined sequence of applied potentials is given by a simple sum of terms of the same general expression. Therefore, this expression is applicable to any multipotential step technique.

The aim of this paper is to apply these results in order to obtain the rigorous analytical solution for the catalytic mechanism in spherical diffusion applicable to any double potential step technique without restrictions in the values of the duration of both potential steps since previous analytical treatments of this mechanism in double potential step techniques have considered only planar diffusion [3–5]. Thus, we have deduced the responses involved with this mechanism in double potential step chronoamperometry, differential normal pulse voltammetry (DNPV), differential pulse voltammetry (DPV) and reverse pulse voltammetry (RPV). The potential-time waveforms for DNPV and RPV techniques are shown in Fig. 1, in which the dashed lines represent a delay time between each pair of pulses in order for the equilibrium to be re-established. The waveform for DPV technique is similar to that for DNPV, but with the restriction \( t_2 \ll t_1 \). We have applied DNPV and DPV techniques with the potential being scanned both in the negative (\( \Delta E < 0 \)) and in the positive (\( \Delta E > 0 \)) direction.

It is also demonstrated for any spherical electrode of any size that a catalytic process with a reversible homogeneous reaction and an equilibrium constant \( K \) in double potential step techniques behaves, when the rate constants \( k_1 + k_2 \to 0 \), as a simple E process with both electroactive species present initially in the solution whose concentrations \( c_B^* \) and \( c_A^* \) are in a ratio equal to \( K \).
We have analysed the effects of the size of the spherical electrode \( r_0 \) in the response obtained in each one of the double potential step techniques mentioned above. Moreover, we have also analysed the advantages of steady state and non steady state responses when spheres of different size are used.

We show that, under most conditions, when determining rate constants \( k_1 + k_2 < 3 \text{ s}^{-1} \) it is convenient to use double potential step techniques with long values of \( t_1 \) and \( t_2 \) (such as double potential step chronoamperometry and DNPV) in order to enhance the difference between the responses corresponding to a catalytic mechanism and to a simple E process. However, for \( k_1 + k_2 \geq 3 \text{ s}^{-1} \), the information concerning the kinetic reaction can be deduced from DPV and RPV techniques in spherical electrodes. In the RPV technique an appropriate selection of the values of \( t_2 \) permits the determination of a wide range of rate constants.

From equations deduced in this paper it is possible to use double potential step techniques in microspheres without the need to work under conditions in which the steady state approximation can be used. This allows us to calculate smaller rate constant values than those that can be calculated by using microelectrodes when only steady state is considered [6–9].

The behaviour of many of the equations deduced in this paper has been contrasted through the experimental study of the system Ti(IV) oxalate complex in the presence of hydroxylamine in spherical electrodes of different radii.

Finally, we propose methods for calculating kinetic \((k_1 \text{ and } k_2)\) and thermodynamic \((K \text{ and } E^{\circ})\) parameters for a catalytic mechanism in all the double potential step techniques analysed in this paper.

### 2. Experimental

The computer-driven potentiostat was designed and constructed by Quiceltron (Spain). Pulse generation and data acquisition were performed using i-SBXDD4 and DAS16-330i boards (ComputerBoards, USA), respectively. Data acquisition and waveform generation were independent tasks which have been carried out using two different time scales and different but connected routines. For waveform generation we have used an interrupt service routine programmed for this purpose and triggered by the 8254 counter in the personal computer. Data acquisition was under the control of the on-board pacer which usually runs at the maximum sampling rate and data were stored in the on-board FIFO buffer. The interrupt service routine was called a variable number of times in each potential step and was responsible for changes in the potential values and for reading of the acquisition counter and status. Hence, the use of appropriate programming techniques allows a large data oversampling (very useful for digital filtering) and an almost complete versatility in the selection of time and amplitude for potential pulses with a very good acquisition synchronisation.

A static mercury drop electrode (SMDE) was constructed using a DME, EA 1019-1 (Metrohm) to which a home-made valve was sealed. Different open times in this valve allowed the use of mercury radii varying from 0.01 to 0.05 cm. The electrode radius for a given open time was determined by weighing a large number of drops. The reference electrode was Ag | AgCl | 1 M KCl.

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added. All other chemicals were Merck reagent grade and were used without further purification.

The diffusion coefficient of complexed Ti(IV) was determined by chronoamperometric measurements in a solution which did not contain NH$_2$OH. A value of $(5.85 \pm 0.02) \times 10^{-6}$ cm$^2$ s$^{-1}$ was obtained. For the determination of peak values in DNPV, we have used a second order polynomial fitting, taking the 8 points nearest to the maximum or minimum.

In all the experiments the temperature was kept constant at $(25 \pm 0.2) ^\circ$C.

3. Theory

The pseudo first order reversible catalytic process that we treat is given by the scheme (I), with Z and P being electroinactive species in all the range of applied potentials and $k_1 = k_1^c c^*_A$ and $k_2 = k_2^c c^*_B$ are both pseudo first order rate constants ($c^*_A$ being the bulk concentration of the i species).

We consider conditions of semi-infinite spherical diffusion and we assume that the diffusion coefficients of electroactive species A and B, $D_A$ and $D_B$, are equal and that the concentrations of electroactive species at the electrode surface are related by the Nernst equation when any potential step is applied. Let $\zeta^*$ be the sum of concentrations of oxidised and reduced species,

$$\zeta^* = c^*_A + c^*_B$$  

with $K$ being the equilibrium constant of the chemical reaction,

$$K = \frac{c^*_B}{c^*_A} = \frac{k_2}{k_1}$$  

In previous papers we have deduced the expression for the current corresponding to the $m$th potential step $E_m$ of any sequence of successive potential steps applied, $E_1$, $E_2$, ..., $E_m$, ... (see Eq. (17) in Ref. [2]), by applying the superposition principle [10], since it was demonstrated therein that the surface concentrations of species A and B have no memory of the previous potential steps, and are given by,

$$c^*_A(r_0) = \frac{J_{mA} \zeta^*}{1 + J_m}$$  

(3a)

$$c^*_B(r_0) = \frac{\zeta^*}{1 + J_m}$$  

(3b)

with $r_0$ being the radius of the spherical electrode and,

$$J_m = \exp((nF)RT) (E_m - E^\circ)$$  

(4)

By making $m = 1$ and $m = 2$ in Eq. (17) of Ref. [2] we deduce that when two successive potential steps $E_1$ and $E_2$ are applied to a spherical electrode during a time $t_1$ and $t_2$, respectively, with $t$ being the total time ($t = t_1 + t_2$), then the corresponding currents are given by:

$$I_1(t_1) = \sqrt{\frac{k_1 + k_2}{D} f(x_{11})} \frac{1 - KJ_1}{1 + K(1 + J_1)}$$  

$$+ \frac{1}{r_0} \frac{1 - KJ_1}{(1 + K)(1 + J_1)}$$  

(5)

for the first pulse and

$$I_2(t > t_1) = \sqrt{\frac{k_1 + k_2}{D} f(x_{12})} \frac{1 - KJ_1}{(1 + K)(1 + J_1)}$$  

$$+ \frac{1}{r_0} \frac{1 - KJ_1}{(1 + K)(1 + J_2)}$$  

(6)

for the second one, where

$$I_m = \frac{i_m}{nFAD_{12}}$$  

$m = 1, 2$

$$x_{ij} = (k_1 + k_2)t_{ij}$$  

$$t_{ij} = \sum_{k = i}^{j} t_k$$  

$$t_{ij} = t_j$$  

$$f(y) = \frac{e^{-y_0}}{\sqrt{\pi}y_0} + \text{erf}(\sqrt{y_0})$$  

(10)

$$f(y) \to 1 \text{ for } y_0 \gg 1$$  

(11)

$$f(y) \to \frac{1}{\sqrt{\pi}y_0^2} \text{ for } y_0 \ll 1$$  

(12)

Eqs. (5) and (6) are applicable to spherical electrodes for any value of $r_0$ (i.e. for $0 \leq r_0 \leq \infty$). These equations clearly show that the electrode radius affects only the terms corresponding to the potential pulse considered.

3.1. Particular cases

3.1.1. Planar approximation of a static mercury drop electrode

For $r_0 \to \infty$ (plane electrode), the last term of the right hand side of Eqs. (5) and (6) disappears and these equations are simplified to:

$$I_1^{\text{planar}}(t_1) = \sqrt{\frac{k_1 + k_2}{D} f(x_{11})} \frac{1 - KJ_1}{(1 + K)(1 + J_1)}$$  

(13)

and
\[ I_2^\text{planar} (t > t_1) = \frac{k_1 + k_2}{\sqrt{D}} \left[ f(x_{12}) \frac{1 - KJ_1}{(1 + K)(1 + J_1)} + f(x_{22}) \frac{J_1 - J_2}{(1 + J_1)(1 + J_2)} \right] \] (14)

Eqs. (13) and (14) are coincident with Eqs. (15) and (32) in Ref. [5] and with Eq. (57) in Ref. [1] with \( m = 1, 2 \).

3.1.2. Steady state approximations

For \( \chi_{11} > 1.90 \) and \( \chi_{22} > 1.90 \) Eq. (11) is fulfilled with an error margin of less than 1\%, in such a way that an \( I/E \) response independent of time (steady state) is reached. By introducing these conditions in Eqs. (5) and (6) we deduce

\[ I_m^\text{ss} = \frac{k_1 + k_2}{\sqrt{D}} \frac{1 - KJ_m}{r_0(1 + K)(1 + J_m)} \quad \text{for} \quad m = 1, 2 \] (15)

Eq. (15) corresponds to the first \( (m = 1) \) and second \( (m = 2) \) potential step under conditions of steady state and is applicable for a spherical electrode of any radius.

By making \( r_0 \to \infty \) in Eq. (15) we deduce the steady state currents corresponding to planar geometry, which are pure kinetic steady state currents,

\[ I_m^\text{planar,ss} = \frac{k_1 + k_2}{\sqrt{D}} \frac{1 - KJ_m}{(1 + K)(1 + J_m)} \quad \text{for} \quad m = 1, 2 \] (16)

Contrarily, by making \( r_0 \to 0 \) (ultramicroelectrodes), a non kinetic steady state is reached. So, from Eqs. (5)–(6) and/or Eq. (15) we deduce,

\[ I_m^\text{micro,ss} = \frac{1 - KJ_m}{r_0(1 + K)(1 + J_m)} \quad \text{for} \quad m = 1, 2 \] (17)

This steady state is reached for any value of \( E_m \) when \( \frac{k_1 + k_2}{D} \frac{1 - KJ_m}{r_0} \leq 50 \) [11]. In this case the kinetic term disappears and the catalytic mechanism behaves as an E process under the conditions given in Section 3.1.3.

3.1.3. Simple diffusion process when species A and B are present initially (E process)

By making \( k_1 + k_2 \to 0 \) \( (x_{11} \to 0, x_{12} \to 0 \) and \( x_{22} \to 0) \) in Eqs. (5) and (6), these equations become those corresponding to an E process when both electroactive species are initially present in the solution [12], with concentrations \( c^*_{A} \) and \( c^*_{B} \) being in a ratio equal to \( K \). So we can easily obtain (see Eqs. (2) and (12)),

\[ I_1^\text{E process} = \frac{1}{\sqrt{\pi D r_1}} \frac{c^*_{A} - c^*_{B} J_1}{1 + J_1} \] (18)

\[ I_2^\text{E process} = \frac{1}{\sqrt{\pi D r_2}} \left[ \frac{1}{1 + J_1} \frac{c^*_{A} - c^*_{B} J_1}{(1 + J_1)} + \frac{1}{1 + J_2} \frac{J_1 - J_2}{(1 + J_1)(1 + J_2)} \right] \] (19)

By comparing Eqs. (5) and (6) corresponding to a catalytic mechanism with Eqs. (18) and (19) for an \( E \) process, it can be seen that the term which includes the effect of the electrode sphericity (last term in the right hand side of Eqs. (5)–(6) and (18)–(19)) in a catalytic process is identical to that of an \( E \) process when both species are initially present with concentrations whose ratio \( c^*_A/c^*_B \) is precisely \( K \).

4. Results and discussion

In this section we will apply Eqs. (5) and (6), which correspond to the rigorous solutions for a catalytic mechanism in spherical diffusion in the double potential step to different techniques such as double potential step chronoamperometry, differential normal pulse voltammetry, differential pulse voltammetry and reverse pulse voltammetry.

In the following sections we will show the usefulness of the employment of spherical electrodes of different radii in order to characterise a catalytic mechanism.

4.1. Double potential step chronoamperometry at spherical electrodes

Fig. 2a shows the experimental chronoamperograms corresponding to a double potential step which have been obtained under conditions of diffusion control, i.e. \( (E_1 - E^\circ) \ll (RT/nF) \) \( (J_1 \to 0 \) in Eqs. (5) and (6), \( I_1 = I_{1,1} \) and \( (E_2 - E^\circ) \ll (RT/nF) \) \( (J_2 \to \infty \) in Eq. (6), \( I_2 = I_{2,2} \), at an SMDE with different values of the electrode radius. The experimental curves correspond to the system Ti(IV) oxalate complex in the presence of hydroxylamine.

From these curves it is clear that both anodic \( (i_{2,2}) \) and cathodic \( (i_{1,1}) \) currents increase in absolute value with \( r_0 \). However, for values of time for which currents independent of time are obtained (steady state currents), the anodic current \( i_{2,2} \) becomes independent of \( r_0 \) and tends to zero. This behaviour of \( i_{1,1} \) and \( i_{2,2} \) and also those of \( I_{1,1} \) and \( I_{2,2} \) can be easily deduced by making \( m = 1, J_1 \to 0, \) and \( m = 2, J_2 \to \infty \) in Eq. (15), respectively. So we deduce:

\[ I_{1,1}^* = \left( \frac{k_1 + k_2}{D} + \frac{1}{r_0} \right) \frac{1}{1 + K} \] (20)

\[ I_{2,2}^* = - \left( \frac{k_1 + k_2}{D} + \frac{1}{r_0} \right) \frac{K}{1 + K} \] (21)

From Eqs. (20) and (21), \( K, k_1 \) and \( k_2 \) can be easily calculated. So from Eq. (21) and Fig. 2a \( (I_{2,2}^* \to 0) \), we
deduce that \( K = 0 \) and by using Eq. (20), we have plotted in Fig. 2b the experimental values of \( I_{1,0} \) measured for various spherical electrodes of different size, versus \( 1/r_0 \), obtaining \( k_1 = (1.97 \pm 0.05) \) s\(^{-1}\) from the intercept of the straight line of Fig. 2b, which is in good agreement with the reported value in Ref. [4].

From the above method it is possible to calculate kinetic parameters from steady state currents. Note that if the electrode radius becomes very small (ultramicroelectrode), the second term of the right hand side of Eqs. (20) and (21) becomes greater and then the kinetic information of the \( I/t \) response is lost due to the microgeometrical steady state being reached.

It is also possible to determine the values of \( K, k_1 \) and \( k_2 \) from non steady state measurements. So, by introducing the conditions of limit currents (\( J_1 = 0 \) and \( J_2 \to \infty \)) in Eqs. (5) and (6) we obtain:

\[
I_{1,1} = \frac{Z_{11}}{D_{t_1}} f(x_{11}) \left( 1 \cdot \frac{1}{1 + K} \right) \left( 1 \cdot \frac{1}{r_0(1 + K)} \right)
\]

and

\[
I_{2,1} = \left[ \frac{Z_{12}}{D_{t_2}} f(x_{12}) - \frac{Z_{22}}{D_{t_2}} f(x_{22}) \right] - \frac{K}{r_0(1 + K)}
\]

From Eqs. (22) and (23) and Fig. 3b, c it is clear that for a pseudo first order catalytic mechanism, the plots of \( I_{1,1} \) versus \( 1/r_0 \) and \( I_{2,1} \) versus \( 1/r_0 \) at fixed values of \( t_1 \) and \( t_2 \) must be straight lines with slopes \( P_m \) \((m = 1 \) and \( 2) \) and intercepts \( O_m \) \((m = 1 \) and \( 2) \) which are given by,

\[
P_1 = \frac{1}{1 + K}
\]

\[
O_1 = \frac{Z_{11}}{D_{t_1}} f(x_{11}) \left( 1 \cdot \frac{1}{1 + K} \right)
\]

\[
P_2 = -\frac{K}{1 + K}
\]

\[
O_2 = \sqrt{\frac{Z_{12}}{D_{t_2}} \frac{f(x_{12})}{1 + K} - \frac{Z_{22}}{D_{t_2}} f(x_{22})}
\]

From the plots of \( I_{1,1} \) versus \( 1/r_0 \) and \( I_{2,1} \) versus \( 1/r_0 \) we have deduced the values of \( K = 0 \) from Fig. 3b and/or c \((P_1 \approx 1 \) and \( P_2 \approx 0, \) respectively) and \( k_1 = (1.95 \pm 0.05) \) s\(^{-1}\) from the intercepts \( O_1 \) and/or \( O_2 \) in cm\(^{-1}\) of Fig. 3b and/or c, respectively.

4.2. Differential normal pulse voltammetry and differential pulse voltammetry at spherical electrodes

4.2.1. Differential normal pulse voltammetry (DNPV) at spherical electrodes

Eqs. (5) and (6) can be used for both differential normal pulse voltammetry (DNPV) and differential pulse voltammetry (DPV) in spherical electrodes of any size. In these techniques the difference \( E_2 - E_1 = \Delta E \) is kept constant and the response \( \Delta I = I_2(t_2 + t_3) - I_1(t_1) \) is recorded versus \( E_1, \) with the potential being scanned both in the negative direction if \( \Delta E < 0, \) and in the positive direction, if \( \Delta E > 0. \) This response can be obtained easily, without restrictions on the times in DNPV and by making \( t_2 \ll t_1 \) in DPV. So by subtracting Eqs. (5) and (6) we deduce:
If we call $f$ Fig. 3. (a) Experimental current time curves for 1.04 mM Ti (IV) in 0.2 M H$_2$C$_2$O$_4$ curves are independent of the value of the equilibrium $D$ $0.377, 0.404, 0.431, 0.458$. Other conditions as in Figure 2b. (b) Dependence of the normalised limiting current corresponding to the first potential step, $I_{\text{cath}}$, on $1/\tau_0$ obtained from Figure 3a. The values of $\tau_1$ in increasing order (in s) are: 0.080, 0.107, 0.134, 0.161, 0.188, 0.215, 0.242, 0.269, 0.296, 0.323, 0.350, 0.377, 0.404, 0.431, 0.458. Other conditions as in Figure 2b. (c) Dependence of the normalised limiting current corresponding to the second potential step, $I_{\text{anod}}$, on $1/\tau_0$ obtained from Figure 3a. $\tau_1 = 0.5$ s. The values of $\tau_2$ in increasing order (in s) are: 0.080, 0.107, 0.134, 0.161, 0.188, 0.215, 0.242, 0.269, 0.296, 0.323, 0.350, 0.377, 0.404, 0.431, 0.458. Other conditions as in Figure 2b.

$$\Delta I_{\text{DNPV}} = \frac{J_1 - J_2}{(1 + J_1)(1 + J_2)} \frac{1}{r_0} + \frac{\sqrt{k_1 + k_2}}{D \left(1 + J_1 \right) \left(1 + J_2 \right)}$$

Eq. (28) can be written as:

$$\Delta I_{\text{DNPV}} = \frac{J_1 - J_2}{(1 + J_1)(1 + J_2)} \frac{1}{r_0} + \Delta I_{\text{DNPV}}^\text{plane}$$

where $\Delta I_{\text{DNPV}}^\text{plane}$ is the current obtained for a plane electrode.

For $\chi_{11}$ and $\chi_{22}$ higher than 1.90, a steady state is reached and Eq. (28) becomes $(f(\chi_{11}), f(\chi_{22})$ and $f(\chi_{12}) \to 1)$,

$$\Delta I_{\text{DNPV}}^\text{plane} = \frac{J_1 - J_2}{(1 + J_1)(1 + J_2)} \frac{1}{r_0} + \frac{\sqrt{k_1 + k_2}}{D}$$

Under these conditions the recorded $\Delta I_{\text{DNPV}}/E_1$ curves are independent of the value of the equilibrium constant $K$ for a given value of the sum of the rate constants.

Under conditions of steady state the values of the peak potentials and the corresponding peak currents are given by,

$$(E_{\text{cath}}^\text{ss})^\text{anod} = E^\circ + \frac{|\Delta E|}{2}$$

$$(\Delta I_{\text{p}}^\text{anod}) = \frac{1}{r_0} + \frac{\sqrt{k_1 + k_2}}{D} \tanh \left( \frac{nF|\Delta E|}{4RT} \right)$$

and therefore, the values of the formal potential $E^\circ$, and of $(k_1 + k_2)$ can be calculated easily from measurements of peak potentials and peak currents, respectively, under these conditions.

Fig. 4 shows the experimental DNPV voltammograms corresponding to the catalytic process of Ti (IV) in presence of hydroxylamine, under steady state conditions. In accordance with Eq. (33) the difference between cathodic and anodic peak potentials is always equal to the pulse amplitude $\Delta E$. Moreover, the formal potential obtained from these curves is $E^\circ = (-0.299 \pm 0.001)$ V. According with Eq. (34) the absolute values of the experimental anodic and cathodic peak currents are equal for each value of $r_0$. From these peak currents we have obtained a value of $k_1 = (1.95 \pm 0.05)$ s$^{-1}$.

Fig. 5 shows the theoretical DNPV voltammograms obtained for $k_1 + k_2 = 1$ s$^{-1}$, $r_0 = 5 \times 10^{-2}$ cm for three values of the equilibrium constant $K = 0, 1$ and 10 with
Fig. 4. Experimental differential normal pulse voltammograms for 1.04 mM Ti (IV) in 0.2 M H$_2$C$_2$O$_4$, 0.07 M HCl, 0.1 M H$_2$O$_2$. The values of the electrode radii (in cm) are: a) 0.00825, b) 0.0116, c) 0.0161, d) 0.0267 and e) 0.0385. Other conditions as in Figure 2b.

$t_1 = t_2 = 0.5$ s (Fig. 5a) and $t_1 = t_2 = 2.0$ s (Fig. 5b). From this figure it is clear that while an increase of $K$ at fixed ($k_1 + k_2$) hardly affects the position of the anodic and cathodic peaks, both anodic and cathodic DNPV voltammograms are shifted towards more positive DNPV currents in Fig. 5a. However, for values of $t_1$ and $t_2$ which fulfil $\chi_{11} > 1.90$ and $\chi_{22} > 1.90$, $K$ has no influence on the voltammogram, since the steady state has been reached (Fig. 5b). This last effect becomes stronger when $r_0$ decreases, in agreement with Eq. (32).

Moreover, when the potential is scanned both in the negative and positive directions, the cathodic and anodic limiting currents calculated when $E_1 \rightarrow -\infty$ and $E_1 \rightarrow \infty$, respectively, are given by:

$$(\Delta I_{\text{DNPV}})^{\text{cath}}_{\text{limit}} = \frac{1}{1 + K} \sqrt{\frac{k_1 + k_2}{D}} [f(\chi_{12}) - f(\chi_{11})]$$  (35)

$$(\Delta I_{\text{DNPV}})^{\text{anod}}_{\text{limit}} = -\frac{K}{1 + K} \sqrt{\frac{k_1 + k_2}{D}} [f(\chi_{12}) - f(\chi_{11})]$$  (36)

It can be demonstrated easily that the function $\Delta I_{\text{DNPV}}(E_1 - E^\circ) - (\Delta I_{\text{DNPV}})^{\text{cath}}_{\text{limit}}$ is symmetrical with respect to the origin. Therefore, the DNPV voltammograms fulfil the following condition for any value of $E_1$:

$$\Delta I_{\text{DNPV}}(E_1 - E^\circ)^{\text{cath}}_{\text{limit}} - (\Delta I_{\text{DNPV}})^{\text{cath}}_{\text{limit}} = -[(\Delta I_{\text{DNPV}}(E_1 - E^\circ))^{\text{anod}}_{\text{limit}} - (\Delta I_{\text{DNPV}})^{\text{anod}}_{\text{limit}}]$$  (37)

Thus, as the anodic and cathodic peak potentials fulfil

$$(E_p)^{\text{cath}}_{\text{limit}} - E^\circ = -((E_p)^{\text{anod}}_{\text{limit}} - E^\circ)$$  (38)

by introducing Eqs. (35), (36) and (38) in Eq. (37) we deduce the following expression for the subtraction of the peak currents,

$$(\Delta I_p)^{\text{cath}}_{\text{limit}} - (\Delta I_p)^{\text{anod}}_{\text{limit}} = \frac{1}{1 + K} \sqrt{\frac{k_1 + k_2}{D}} [f(\chi_{12}) - f(\chi_{11})]$$  (39)

which is independent of the electrode radius.

Eqs. (37)–(39) are applicable regardless of whether the steady state has been reached or not.

From Eq. (38) the formal potential can be easily calculated since,

$$E^\circ = \frac{(E_p)^{\text{cath}}_{\text{limit}} + (E_p)^{\text{anod}}_{\text{limit}}}{2}$$  (40)
The chemical kinetic parameters $K, k_1$ and $k_2$ can be determined from Eq. (39) by making measurements of the difference of the peak currents ($\Delta I_p$) under conditions of non steady state at two different values of the pair of times $t_1$ and $t_2$ and by using any standard numerical procedure. These kinetic parameters can also be calculated from measurements of the cathodic and anodic limiting currents ($\Delta I_{DNPV}^{limit}$) (see Eqs. (35)–(36)).

4.2.2. Differential pulse voltammetry (DPV) at spherical electrodes

This technique is analogous to DNVP but with $t_2 \ll t_1$, so by taking into account that $t_1 + t_2 \approx t_1, z_{12} \approx z_{11}$ and $f(z_{12}) \approx f(z_{11})$ Eq. (28) is simplified to:

$$\Delta I_{DPV} = \frac{J_1 - J_2}{(1 + J_1)(1 + J_2)} \left[ \frac{1}{r_0} + \frac{k_1 + k_2}{D} f(x_{22}) \right]$$

By imposing the condition $d(\Delta I_{DPV})/dE_1 = 0$ on the DPV currents corresponding to the negative and positive scans, the following values are obtained for the peak potentials and the peak currents,

$$E_p^{cath} = E^0 + \frac{\Delta E}{2}$$

and

$$E_p^{anod} = \pm \left( \frac{1}{r_0} + \frac{k_1 + k_2}{D} f(x_{22}) \right) \tanh \left( \frac{nF}{4RT} \Delta E \right)$$

Eq. (42) coincides with that obtained in Ref. [4] for a catalytic process in planar electrodes. Moreover, Eq. (43), which is valid for a spherical electrode of any radius when the steady state has not been reached, shows that the peak currents in DPV voltammograms are independent of the equilibrium constant for a fixed value of $k_1 + k_2$. From Eqs. (42) and (43) $E^0$ and $k_1 + k_2$ can be calculated easily.

Moreover, for the DPV technique

$$\Delta I_{DPV}^{cath} = (\Delta I_{DPV}^{lim})_{cath} = 0$$

is fulfilled (see Eqs. (35) and (36) with $f(z_{12}) \approx f(z_{11})$). Therefore, the peak currents fulfil (see Eqs. (37) and (43)),

$$\Delta I_p^{cath} = - (\Delta I_p)^{anod}$$

Condition (45) is also fulfilled in the DNPV technique under steady state conditions (see Eq. (34)), and also in the particular case in which $K = 1$ (see Eq. (39)).

Fig. 5 shows the theoretical DPV voltammograms with $t_1 = 1$ s and $t_2 = 0.030$ s (Fig. 6a) and the theoretical DNPV voltammograms with $t_1 = t_2 = 1$ s (Fig. 6b) corresponding to a catalytic mechanism with $K = 0$ and $k_1 = 3$ s$^{-1}$, and to an E process ($k_1 \rightarrow 0$ according to the conditions given in Section 3.1.3) at different values of the electrode radius. These figures show the enhancement of the DNPV and DPV responses when $r_0$ decreases. By comparing Fig. 6a and b it can also be deduced that, although the peak currents for a catalytic process given by Eq. (43) are always greater in absolute value than those corresponding to a simple E process given by [13],

$$\Delta I_p^{E \rightarrow Process} = \left( \frac{1}{r_0} + \frac{1}{\sqrt{\pi D t_2}} \right) \tanh \left( \frac{nF}{4RT} \Delta E \right)$$
the difference between both responses becomes smaller when $t_2$ and/or $k_1$ decreases according to Eq. (12) (see also Fig. 7). So, from Fig. 6a it is clear that in DPV, this difference is very small and is scarcely affected by the value of the rate constant $k_1$ when $k_1 \leq 3 \text{ s}^{-1}$, as is shown in Fig. 7a. However, in DNPV with $t_1 = t_2 = 1 \text{ s}$ (Fig. 6b) the difference between both mechanisms is much greater and increases strongly with $k_1$ as can be seen in Fig. 7b.

From the above we can conclude that DNPV is more adequate than DPV in characterising a catalytic process with any value of $K$ for values of the sum of the rate constants $k_1 + k_2 \leq 3 \text{ s}^{-1}$.

On the contrary, for $k_1 + k_2 > 3 \text{ s}^{-1}$, the DPV technique is very useful both in conventional spherical electrodes as well as in microelectrodes, since by using Eq. (43) of this paper, it is not necessary to work under steady state conditions when microelectrodes are used. This fact enables us to determine lower rate constants than those that can be calculated when only the steady state is considered [6,7,9].

So, for example, from Eq. (43) corresponding to the peak current in DPV we can determine rate constants which fulfil the following non steady state condition

$$\sqrt{\frac{k_1 + k_2}{D}} f((k_1 + k_2) t_2) \gtrsim \frac{1}{r_0}$$

in such a way that if $t_2 \approx 0.05 \text{ s}$ and $D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, the rate constants that can be calculated when microelectrodes of radius $r_0 \approx 10^{-3} \text{ cm}$ are used are $k_1 + k_2 \gtrsim 3 \text{ s}^{-1}$ since for $k_1 + k_2 < 3 \text{ s}^{-1}$ the difference between a simple $E$ process and a catalytic process is slight (less than 10%). In the same way, when microelectrodes of radius $r_0 \approx 10^{-4} \text{ cm}$ are used, we can calculate rate constants $k_1 + k_2 \gtrsim 35 \text{ s}^{-1}$ when the above conditions are considered.

From the above results and also from Fig. 6a and b, we can deduce that the relative difference between an $E$ process and a catalytic mechanism is more obvious when the electrode size ($r_0$) increases, although the absolute difference between both responses is independent of $r_0$ for any value of $E_1$ according to Eqs. (5)–(6) and (18)–(19).

Fig. 8 shows the enhancement suffered by the current density obtained in DPV with the electrode sphericity (solid line: planar electrode ($r_0 \to \infty$) and dashed line: spherical electrode with $r_0 = 10^{-4} \text{ cm}$) for a catalytic process with $K=1$ and different values of $k_1 + k_2$.

4.3. Reverse pulse voltammetry at spherical electrodes

In reverse pulse techniques the second potential step is applied under conditions of a first step controlled by diffusion ($E_1 \to -\infty, J_1 \to 0$) and $E_2$ is scanned in the positive direction. With these conditions in Eq. (6) we obtain:

$$I_{RPV} = \frac{1 - KJ_2}{(1 + K)(1 + J_2)} \frac{1}{r_0} + \sqrt{\frac{k_1 + k_2}{D}} \frac{f(x_{12})}{1 + K} \frac{J_2 f(x_{22})}{1 + J_2}$$

with

$$I_{RPV} = I_2(t_2 + t_1)$$
The cathodic and anodic limiting currents are given respectively by:

\[
(I_{RXV}^{\text{limit}})_{\text{cath}} = \frac{1}{1 + K} \left\{ \frac{1}{r_0} + \sqrt{\frac{k_1 + k_2}{D}} f(x_{12}) \right\} \\
(I_{RXV}^{\text{limit}})_{\text{anod}} = -\frac{K}{1 + K} \left\{ \frac{1}{r_0} + \sqrt{\frac{k_1 + k_2}{D}} f(x_{12}) \right\}
\]  

(50)  

(51)

As can be deduced easily from Eqs. (50) and (51), both anodic and cathodic currents increase in absolute value when \( r_0 \) decreases. Moreover, for an irreversible chemical reaction \( (K = 0) \) the anodic limiting current is independent of \( r_0 \) according to Eq. (51).

Moreover, \( E^0 \) can be determined taking into account that, by making \( E_2 = E^0 \) \( (J_2 = 1) \) in Eq. (48) we obtain:

\[
I_{RXV}(E^0) = \frac{1}{2}[(I_{RXV}^{\text{limit}})_{\text{cath}} - (I_{RXV}^{\text{limit}})_{\text{anod}}]
\]  

(52)

as in the case of a simple E process [14].

Moreover, it is fulfilled that

\[
(I_{RXV}^{\text{limit}})_{\text{cath}} + (I_{RXV}^{\text{limit}})_{\text{anod}} = \frac{1}{r_0} + \sqrt{\frac{k_1 + k_2}{D} f(x_{22})}
\]  

(53)

From Eq. (53) it is also possible to use microelectrodes in order to determine rate constants of the order of \( k_1 + k_2 \geq 3 \text{ s}^{-1} \), from measurements of the sum of both cathodic and anodic limiting currents through a reasoning analogous to that shown in Section 4.2.2 for DPV.

Fig. 9 shows the influence of \( t_2 \) on the experimental RPV voltammograms. In this figure the strong influence of \( t_2 \) on the anodic currents owing to the presence of the catalytic process is evident. By using Eq. (53) we have determined \( k_1 = (1.90 \pm 0.05) \text{ s}^{-1} \).

Under conditions of steady state, from Eqs. (48), (50)–(51) we deduce:

\[
I_{RXV}^{\text{ss}} = \frac{1 - KJ_2}{(1 + K)(1 + J_2)} \frac{1}{r_0} \left\{ \frac{1}{1 + K} \sqrt{\frac{k_1 + k_2}{D}} \right\} f(x_{12})
\]  

(54)

\[
(I_{RXV}^{\text{limit}})^{\text{ss}})_{\text{cath}} = \frac{1}{1 + K} \left\{ \frac{1}{r_0} + \sqrt{\frac{k_1 + k_2}{D}} \right\}
\]  

(55)
Fig. 9. Experimental reverse pulse voltammograms for 1.04 mM Ti (IV) in 0.2 M H$_2$C$_2$O$_4$ 0.07 M HCl 0.1 M NH$_2$OH. $r_0 = 0.0226$ cm, $t_1 = 1.5$ s, $T = 298$ K. The values of $t_2$ (in s) are: a) 0.020, b) 0.030, c) 0.040, d) 0.050, e) 0.060, f) 0.070, g) 0.080, h) 0.090 and i) 0.100. Other conditions as in Figure 4.

\[
(I_{\text{RPV limit,ss}})^{\text{anod}} = -\frac{K}{1+K}\left\{\frac{1}{r_0} + \sqrt{\frac{k_1+k_2}{D}}\right\} 
\]

Note that, under these conditions, by adding both anodic and cathodic absolute currents

\[
(I_{\text{RPV limit,ss}})^{\text{cath}} + |(I_{\text{RPV limit,ss}})^{\text{anod}}| = \frac{1}{r_0} + \sqrt{\frac{k_1+k_2}{D}} 
\]

is obtained.

The $K$ value can be easily deduced by subtracting or dividing the cathodic and anodic currents.

5. Conclusions

The use of double potential step techniques at spherical electrodes is very advantageous in characterising a catalytic process both in steady state and in non steady state conditions.

We have shown the usefulness of carrying out double potential step chronoamperometry experiments at different values of the electrode radius to obtain the kinetic ($k_1$ and $k_2$) and thermodynamic ($K, E^o$) parameters of a catalytic process.

Under most conditions, the DNPV technique is more advantageous than DPV for determining rate constants $k_1 + k_2 < 3$ s$^{-1}$ because it gives rise to an enhancement of the difference between the responses corresponding to an E process and to a catalytic mechanism.

The RPV technique in spherical electrodes with an appropriate selection of the values of $t_2$ allows the determination of a wide range of rate constants.

The experimental catalytic reduction of Ti (IV) in the presence of hydroxylamine has been studied through double potential step chronoamperometry, DNPV and RPV. The catalytic rate constant for this system has been calculated by using the above techniques, with very close values being obtained in all cases.

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