Square wave voltammetry for a pseudo-first-order catalytic process at spherical electrodes

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Received 30 November 1999; received in revised form 20 March 2000; accepted 21 March 2000

Abstract

A theoretical equation corresponding to square wave voltammetry for a pseudo-first-order catalytic mechanism at spherical electrodes of any radius is presented. The effects of the electrode sphericity are analysed. Methods for calculating equilibrium and rate constants of the chemical reaction are proposed and applied to the system Fe(III)–triethylamine | Fe(II)–triethylamine in the presence of hydroxylamine. The advantages of this equation for analytical purposes are laid out. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Catalytic mechanism; Spherical electrodes; Microelectrodes; Multipotential step; Square wave voltammetry

1. Introduction

Theoretical expressions for square wave voltammetry have been derived and tested experimentally by Zeng and Osteryoung [1] for a pseudo-first-order catalytic process in planar electrodes, supposing irreversible chemical behaviour, \( K_0 = 0 \).

In a recent paper we have deduced easy analytical equations for the above mentioned mechanism which are applicable to any multipotential step electrochemical technique with planar and spherical electrodes and which consider that the chemical equilibrium constant can take any value [2]. In this work we apply these equations to square wave voltammetry at spherical electrodes of any size, including microelectrodes, and we discuss the importance of considering the sphericity effects when square wave voltammetry is used for analytical purposes. The dependence of the forward, reversal and net square wave current on the equilibrium and rate constants of the chemical reaction is evaluated.

From equations given in this paper, the equilibrium and rate constants of the chemical reaction can be evaluated. When the kinetic steady state is reached, an easily manageable analytical expression is presented, which shows that the effects of the electrode sphericity assume greater importance as the square wave potential increases in the determination of the rate constants. Analytical advantages of the use of spherical electrodes in square wave voltammetry are discussed and it is also pointed out that the sphericity effects increase as the square wave frequency diminishes. Also it is precisely the low square wave frequencies that are the most desirable in minimising the double layer effects.

The complex of Fe(III) with triethylamine (TEA) has been used for the experimental verification of the theoretical equations obtained in this work for the response of a catalytic mechanism in square wave voltammetry. The reduced form of this complex (Fe(II)–TEA) is re-oxidized in the presence of hydroxylamine through a pseudo-first-order reaction. We have also applied the above methods for determining the rate constant to this system and we have compared the experimental and the theoretical responses.

2. Experimental

The computer-driven potentiostat was designed and constructed by Quiceltron (Spain). Square wave generation and data acquisition were performed using i-
SBXDD4 and DAS16-330i boards (ComputerBoars, USA), respectively. Data acquisition and square wave generation were independent tasks carried out using two different time scales and different but connected routines. For square wave generation we have used an interrupt service routine programmed for this purpose triggered by the 8254 counter in the computer. Data acquisition was under the control of the on-board FIFO buffer. The interrupt service routine was responsible for changes in the potential values and for reading the acquisition counter and status. Hence, the use of appropriate programming techniques allows a large data oversampling (very useful for digital filtering) and almost complete versatility in the selection of amplitude and frequency of the square wave along 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 opening times in this valve allowed the use of mercury drops of radii varying from 0.01 to 0.05 cm. The electrode radius for a given opening time was determined by weighing a large number of drops. The standard deviation in each series of radius determination was always lower than 0.5%. The reference electrode was $\text{Ag}\mid \text{AgCl} \mid 0.1 \text{M KCl}$.

The working solutions of Fe(III) complexed with triethylamine (TEA) and different amounts of $\text{NH}_2\text{OH}$ were prepared following the procedure given by Zeng and Osteryoung [1].

The diffusion coefficient of complexed Fe(III) was determined by chronoamperometric measurements in a solution which did not contain NH$_2$OH. A value of $(5.00 \pm 0.05) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was obtained. The E° value of this experimental system was determined from the peak potential in the square wave voltamograms, giving E° = -1025 ± 1 mV. All experiments begin at a potential (usually -0.75 V) at which no faradaic processes take place. The same potential was used to ensure mechanical stability of the drops over 2 s before the voltammetric scan.

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

In all the experiments the temperature was kept constant at $(20 \pm 0.2)^\circ \text{C}$.

3. Theory

In a previous paper we deduced the general voltammetric theory corresponding to a pseudo-first-order catalytic mechanism in spherical electrodes of any size [2]. The scheme of this mechanism is given by

$$A + n \text{e}^- \rightarrow B$$

$$B + Z \stackrel{k_1}{\underset{k_2}{\rightleftharpoons}} A + P$$

where A and B are the electroactive species and Z and P are electroinactive species in the whole range of applied potentials, which should be in high excess with respect to A and B species, and in such a way that $k_1 = k_2 c_Z^2$ and $k_2 = k_1 c_P^2$ are both pseudo-first-order rate constants (with $c_p$ being the bulk concentration of the i species).

For the above mechanism, the equation for the current $I_m$ measured at the end of the mth potential corresponding to any sequence of potential steps $E_1$, $E_2$, ..., $E_m$, is given by

$$I_m = nF A_0 D \xi^* \left[ \sum_{-m}^{m} f(\chi_{jm}) \sqrt{\frac{k_1 + k_2 Z_j}{D}} \right. + \left. \frac{1 - K_jm}{r_0(1 + K)(1 + J_m)} \right]$$

where $D_A = D_B = D$ is the diffusion coefficient of species A and B, $K$ is the equilibrium constant of the chemical reaction ($K = k_2/k_1 = c_B^* (c_A^*)$), $r_0$ and $A_0$ are the electrode radius and area, respectively, and

$$\xi^* = c_A^* + c_B^*$$

$$Z_j = \left\{ \begin{array}{ll}
1 - \frac{K_j}{1 + K j (1 + J_m)} & j \geq 1 \\
1 & j = 1
\end{array} \right.$$

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

$$\chi_{jm} = (k_1 + k_2)t_{jm}$$

$$t_{jm} = \sum_{k=-j}^{m} t_k$$

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

It should be noted that the electrode sphericity affects only the potential pulse considered (mth), such as occurs in the case of a reversible E mechanism [3] under the same conditions (i.e. $D_A = D_B = D$).

It is of interest to point out that, for any value of the equilibrium constant, when $k_1 + k_2 \rightarrow 0$ ($\chi_{jm} \rightarrow 0$) a catalytic process (Eq. (1)) behaves as an E process in which both electroactive species are initially present in the solution with $c_A^*$ and $c_B^*$ values in a ratio $(c_B^*/c_A^*)$ equal to the equilibrium constant of the catalytic process, $K$ (see Eq. (20) in Ref. [3]).

3.1. Square wave voltammetry at spherical electrodes

Eq. (1) can be easily applied to square wave voltammetry by taking into account that, in these techniques, a sequence of potential pulses of the same duration, $t_p$, given by [4,5]
is applied, where $\Delta E_s$ is the staircase potential and $E_{sw}$ the square wave amplitude, in agreement with the scheme given by Osteryoung [4,5] (Fig. 1). The pulse width, $t_p$, coincides with the half period of the staircase ($t/2$).

The current is measured at the end of each potential pulse, i.e. at nominal times $t_p$ and $2t_p$ in each cycle and the net current for the $m$th cycle of the square wave is given by

$$\Delta I_m = I_{2m} - I_{2m-1}$$

for each cycle of the square wave.

The index potential for the voltammogram, in line with Refs. [4,6], is chosen at the midpoint of each square wave cycle in order to ensure that, for a catalytic process with a reversible charge transfer reaction, the experimental peak potential occurs at $E_{p} \equiv E^*$ (as we are supposing $D_A = D_B = D$). Thus, the index potential, $E$, is given by

$$E = E_{2m} - E_{2m-1} = E_{in} - m\Delta E_s - E_{sw}$$

The dimensionless square wave currents, $\psi_f$, $\psi_r$, and $\Delta \psi$, are defined as

$$\psi_f = \frac{I_f}{nFA_0q^{+}} \sqrt{\frac{E_p}{D}}$$
$$\psi_r = \frac{I_r}{nFA_0q^{+}} \sqrt{\frac{E_p}{D}}$$
$$\Delta \psi = \frac{\Delta I}{nFA_0q^{+}} \sqrt{\frac{E_p}{D}}$$

such that, from Eqs. (1) and (8) or (9) and taking into account that

$$t_{jm} = (m - j + 1)t_p$$

we write $\Delta \psi$ for a spherical electrode as

$$\Delta \psi = \Delta \psi_{pl} + \Delta \psi_{sph}$$

with $\Delta \psi_{pl}$ and $\Delta \psi_{sph}$ being the planar and spherical contribution to the total net current $\Delta \psi$, which are given by

$$\Delta \psi_{pl} = \sqrt{\frac{2}{r_0}} \left( \sum_{j=1}^{m-1} \left( f(2m - j) \chi_{t_p}^j \right) - f((2m - j + 1) \chi_{t_p}^j) Z_j - f(\chi_{t_p}^j Z_{2m}) \right)$$

$$\Delta \psi_{sph} = -\sqrt{\frac{D t_p}{r_0}} Z_{2m}$$

where

$$\chi_{t_p}^j = (k_1 + k_2) t_p$$

From Eqs. (13) and (14) we deduce that the sphericity $(\sqrt{D t_p/r_0})$ is operative only at the two potential pulses which intervene in the $m$th square wave cycle (i.e. $E_{2m-1}$ and $E_{2m}$ through $Z_{2m}$). So, for planar electrodes ($r_0 \rightarrow \infty$) $\Delta \psi_{sph} = 0$ and Eqs. (13) and (14) coincide when $K = 0$ with that previously deduced by Zeng and Osteryoung [1].

From Eqs. (1) and (8) or (9) we can distinguish two different steady states: a first kinetic steady state which is reached when $f(\chi_{t_p}^j) \rightarrow 1$ ($\chi_{t_p}^j \geq 1.9$), for which we obtain

$$\Delta I_{ss} = nFA_0D_s c^{+} \left[ \sqrt{\frac{k_1 + k_2}{D}} + \frac{1}{r_0} \right] \left[ \frac{1}{1 + J_{2m-1}} - \frac{1}{1 + J_{2m}} \right]$$

This equation is formally analogous to that previously obtained by us in differential pulse voltammetry (Eq. (15) in Ref. [8]) since only two pulses are involved.

The second steady state (non kinetic) is reached when $1/r_0 \geq 50f(\chi_{t_p}^j)/((k_1 + k_2)/D$ (microelectrodes or ultramicroelectrodes) [2]. In this case, the catalytic process loses its identity and behaves like a reversible $E$ process with the two electroactive species initially present in the solution and it is fulfilled that

$$\Delta I_{ss} = \frac{nFA_0D_s c^{+}}{r_0} \left[ \frac{1}{1 + J_{2m-1}} - \frac{1}{1 + J_{2m}} \right]$$
4. Results and discussion

The sphericity effects on the dimensionless forward, \( \psi_f \), and reversal, \( \psi_r \), currents and on the net current, \( \Delta \psi \), when conventional spherical electrodes are used (i.e. electrodes of radius \( r_0 > 10^{-3} \) cm at time pulse \( t_p < 0.1 \) s for which the sphericity \( \sqrt{Dt_p/r_0} < 1 \) by supposing \( D \approx 10^{-5} \) cm² s⁻¹) are shown in Fig. 2 for \( K = 0 \) for \( \sqrt{Dt_p/r_0} = 0 \) (planar electrodes) and \( \sqrt{Dt_p/r_0} = 0.354 \) at two different values of \( \chi_{tp} \). These effects for \( \psi_f \) and \( \psi_r \), are greatest in the zone of the voltammograms corresponding to the cathodic limit current (Fig. 2(a)). The influence of these effects on the voltammograms corresponding to the net current \( \Delta \psi \) (Fig. 2(b)) is highest in the peak current region, which is that of greatest analytical use. The relative influence of the sphericity decreases when \( k_1 \) (and therefore \( \chi_{tp} \)) increases. Evidently, this influence is greater when spherical electrodes of smaller radii are used.

Fig. 3 shows that the effects of sphericity increase in absolute form when the square wave amplitude, \( E_{sw} \), increases.

In our experimental study we have used working solutions of the complex Fe(III)–TEA. The reduced form of this complex (Fe(II)–TEA) is oxidized chemically by hydroxylamine in a pseudo-first-order reaction (if the appropriate experimental conditions are achieved) as has been indicated by Koryta [7]. This experimental system has also been studied by Zeng and Osteryoung [1].

Fig. 4 shows the influence of the square wave frequency \((1/2t_p)\) on the sphericity effects when \( r_0 = 4.87 \times 10^{-2} \) and \( 8.25 \times 10^{-3} \) cm, for this experimental system for which \( k_1 \approx 2.85 \) s⁻¹ and \( K = 0 \) (see below). In this case it may be of interest to increase the \( t_p \) value in order to increase the kinetic effects, which is highly desirable from an analytical point of view since, for values of \( k_1 \) of this order, a catalytic process behaves like an E process for small values of time [8]. In this situation, this figure clearly shows that sphericity effects increase with \( t_p \) and these must be taken into account.

Fig. 5 shows the square wave voltammograms obtained by assuming that the chemical reaction is reversible (this case has not been considered in Refs. [1,4–6]). The curves on this figure show that for a given value of \( k_1 \), reversibility and sphericity amplify the \( \Delta \psi \) response notably (Fig. 5(b)). Another interesting consequence of the chemical reversibility on the forward and reversal voltammograms is that when \( k_0 \), the \( \psi_f \) and \( \psi_r \), currents (Fig. 5(a)) reach a value other than zero at the beginning of the experiment (\( E \ll E^0 \)). This is due to the initial presence of B species in the bulk solution.
4.1. Methods for the experimental determination of the equilibrium and the rate constants

In accordance with the above discussion, a catalytic irreversible process \((K = 0)\) can be easily characterised through a simple visual inspection of the anodic plateaux of the forward and reverse curves, \(\psi_f\) and \(\psi_r\), which always take the constant value of zero. Therefore, according to Fig. 4, the value of the equilibrium constant for the system \(\text{Fe(III)}|\text{TEA}|\text{Fe(II)}|\text{TEA}\) is \(K = 0\).

The equilibrium constant, \(K\), can be easily determined from measurements of the cathodic and anodic limit plateaux of the direct and/or reversal currents \(I_f\) and \(I_r\), when the kinetic steady state has been reached, as

\[
\frac{(I_{f/r})_{\text{cathodic plateau}}}{nFA_0D\zeta^*} = \left(\sqrt{\frac{k_1 + k_2}{D}} + \frac{1}{r_0}\right) \frac{1}{1 + K}
\]  

\((18)\)

The determination of the equilibrium constant is immediate by dividing Eqs. (18) and (19).

For the determination of the rate constants we can distinguish two situations:

1. The kinetic steady state is not reached. In this case, we can determine the rate constants by fitting the experimental curves to the theoretical ones obtained from Eq. (13). This procedure has been applied to the system \(\text{Fe(III)}|\text{TEA}|\text{Fe(II)}|\text{TEA}\) in the presence of 0.04 M hydroxylamine. Under these conditions, we have obtained a value of the pseudo-first-order rate constant of \(k_1 = 2.85 \pm 0.05 \text{ s}^{-1}\).

Fig. 6 shows the experimental \(I_f, I_r\), and \(\Delta I\) curves (points) obtained for the above system for three different electrode radii and the theoretical curves (solid lines) calculated from Eqs. (11)–(14) with \(k_1 = 2.85 \text{ s}^{-1}\). The excellent agreement between the experimental and theoretical curves underlines the good applicability of the theory developed in this paper.
2. The kinetic steady state is reached.

Under these conditions, the rate constants can be determined directly from measurement of the peak current, since from Eq. (16) it can easily be deduced that

$$\Delta I_{\text{peak}}^{\text{ss}} = nF A_0 D \xi^* \left( \sqrt{\frac{k_1 + k_2}{D} + \frac{1}{r_0}} \right) \tanh \left( \frac{nF E_{\text{sw}}}{2RT} \right)$$

(20)

This equation is identical to Eq. (34) in Ref. [8], corresponding to differential pulse voltammetry, if we change $E_{\text{sw}}$ for $|\Delta E|$.

Eq. (20) provides a simple way to determine the rate constants for spherical electrodes or microelectrodes of any radius, as

$$k_1 + k_2 = D \left( \frac{\Delta I_{\text{peak}}^{\text{ss}}}{nF A_0 D \xi^* \tanh(nF E_{\text{sw}}/2RT)} - \frac{1}{r_0} \right)^2$$

(21)

Note that the determination of the rate constants under these conditions is independent of the staircase potential and clearly shows that the effects of the electrode sphericity on the value of the rate constants determined are greater when $E_{\text{sw}}$ increases.

The experimental system Fe(III)–TEA reaches a stationary state if the hydroxylamine concentration is increased and the square wave frequency is decreased. Hence, for working solutions containing 0.1 M hydroxylamine, the net square wave current becomes independent of the square wave frequency for frequencies lower than 5 Hz, showing that a kinetic steady state is reached. Fig. 7 shows an example of these steady state square wave voltammograms obtained for three different values of the electrode radius. By applying Eq. (21) we have obtained $k_2 = 7.50 \pm 0.05 \text{ s}^{-1}$. From the values of $k_1$ obtained in this paper, values of $k_1$ in the range 143–150 s$^{-1}$ M$^{-1}$ are obtained, which are in very reasonable agreement with the values reported at 25°C by Zeng and Osteryoung [1] (151 s$^{-1}$ M$^{-1}$) and Koryta [7] (190 s$^{-1}$ M$^{-1}$).

5. Conclusions

The theoretical equations derived in this paper for spherical electrodes of any radius present, among others, the following advantages when analysing a catalytic process: Eqs. (14) and (16) and Figs. 2–7 show that the effects of the electrode sphericity are, in general, important in SWV. It is, therefore, highly desirable to have equations that are applicable to an SMDE of any radius instead of those corresponding to planar geome-
try, which have been used in Ref. [1] to analyse the behaviour of a catalytic mechanism in an SMDE.

The sphericity effects are highest in the peak current region, which is that of greater analytical interest. These effects increase as the square wave frequency \(1/T\) decreases.

For analysis, fast catalytic reactions are of great interest since in this case the kinetic steady state is reached and the easy analytical equations proposed in this paper (Eqs. (20) and (21)) can be applied.

In the case of catalytic reactions that are not so fast, for the enhancement of kinetic effects and to avoid the double layer effects it is necessary to work at the lowest square wave frequencies possible. Evidently, the consideration of the sphericity effects \(\sqrt{D_{p}/r_0}\) at these frequencies (\(<10\) Hz) is imperative.

Acknowledgements

The authors greatly appreciate the financial support provided by the Dirección General de Investigación Científica y Técnica (Project No. PB96-1095) and the Fundación Séneca (Expedient No. 00696/CV/99).

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