Study of the Behavior of an EC Mechanism Using Cyclic and Derivative Chronopotentiometric Techniques with Spherical Electrodes

Manuela López-Tenes, Juana María Molina, Ángela Molina*
Departamento de Química Física, Facultad de Química, Universidad de Murcia, Espinardo, 30100 Murcia, Spain
*e-mail: amolina@um.es
Received: April 7, 2003
Final version: June 30, 2003

Abstract
The theory for an EC mechanism in chronopotentiometric techniques – reversal chronopotentiometry, cyclic chronopotentiometry and reciprocal derivative chronopotentiometry – is developed. The equations of this article are valid for spherical electrodes of any size and present a compact and easy-to-manage form. Methods for determining kinetic parameters of the chemical reaction are proposed and the influence of the electrode radius is discussed. We conclude that large errors in the determination of these parameters are committed if electrode sphericity is neglected. Reciprocal derivative chronopotentiometry has been applied in its traditional form (dt/dE vs. E), and in a more recently proposed modality consisting of plotting dt1/2/dE vs. E. These techniques are very convenient for studying an EC mechanism since the response is obtained in the form of peaks which are quantitatively related to the kinetic parameters of the chemical reaction. A comparison of the chronopotentiometric methods analyzed leads us to conclude that working curves based on the dt1/2/dE vs. E curves are more suitable to obtain accurate values of the rate constants of the chemical reaction.

Keywords: EC mechanism, Cyclic chronopotentiometry, Reciprocal derivative chronopotentiometry, Kinetic parameters, Spherical electrodes

1. Introduction
The electrode reaction scheme in which the charge transfer is followed by a homogeneous chemical reaction has received increasing attention in the scientific literature, not only in the field of electrochemistry but also in general chemistry and biochemistry, since it appears in many experimental systems of interest in biomedical science, industrial synthesis and electrochemical technologies [1–6].

The theoretical study of the EC mechanism has been made in the literature by means of several electrochemical techniques [7–9] and, among them, the chronopotentiometric methods have proved to be very useful for determining precise kinetic data [10]. Indeed, the chronopotentiometric techniques in which the current sign is reversed, as in the case of current reversal and cyclic chronopotentiometry, can be used to determine the kinetic parameters of the chemical reaction in an EC mechanism from measurements of transition times [7–9, 11–14]. Most studies on this subject with the above-mentioned techniques have been carried out for planar diffusion [7–9, 11–13] and more recently, for spherical electrodes of conventional size [14].

In this article we have developed the theory for the general case of an EC mechanism with reversible chemical reaction in several chronopotentiometric techniques like chronopotentiometry with current reversal, cyclic chronopotentiometry and reciprocal derivative chronopotentiometry. The equations deduced here present the innovation of having a compact form, which makes them applicable to spherical electrodes of any size.

From this broad perspective we have carried out a general survey of the behavior of the EC mechanism in these techniques and we propose methods for determining kinetic parameters of the chemical reaction, analyzing the influence of the electrode sphericity. We have concluded that the electrode radius greatly influences the working curves and this fact leads to large errors in the determination of kinetic parameters when a spherical electrode is used and the equations for planar diffusion are being considered.

Among the techniques analyzed in this article, the more recently developed reciprocal derivative chronopotentiometry has been shown to be a powerful, alternative tool for the study of an EC mechanism, since the curves obtained present characteristic peaks that are highly dependent on the kinetic parameters of the chemical reaction.

These peaks are scarcely affected by capacitative effects on account of their being obtained from the central zone of the E-t curves. Moreover, this derivative technique is very simple to apply, and it presents high reproducibility in the measure of the peak potentials and peak heights, thus affording simple diagnosis criteria for the electrode process analyzed [15].

In this article we have applied reciprocal derivative chronopotentiometry both in its traditional form, i.e., by plotting the reciprocal of the time derivative of the chronopotentiogram versus the measured potential (dt/dE vs. E), and in a more recently proposed modality consisting of plotting dt1/2/dE vs. E. These techniques are very convenient for studying an EC mechanism since the response is obtained in the form of peaks which are quantitatively related to the kinetic parameters of the chemical reaction.

A comparison of the chronopotentiometric methods analyzed leads us to conclude that working curves based on the dt1/2/dE vs. E curves are more suitable to obtain accurate values of the rate constants of the chemical reaction.

Keywords: EC mechanism, Cyclic chronopotentiometry, Reciprocal derivative chronopotentiometry, Kinetic parameters, Spherical electrodes
vs. E curve) [10, 16–18], and in the form proposed in recent articles, which consists of plotting the \( dI/dE \) vs. E curve [15, 19]. The latter gives a practically identical signal to that obtained in differential pulse voltammetry when electrode processes with reversible charge transfer reactions are studied under planar diffusion conditions. We have confirmed that \( dI/dE \) vs. E curves offer much better possibilities than the other techniques considered in determining the chemical kinetic constants.

2. Theory

The reaction scheme for the EC mechanism can be written as

\[
O + ne^{-} \rightarrow \text{R} + k_{1}^{-1} \rightarrow Z
\]  

To study this reaction mechanism, we will apply \( k \) successive, alternating sign current steps to a spherical electrode of any size, as below (cyclic chronopotentiometry)

\[
\begin{align}
I_{o} & , \quad 0 \leq t_{1} \leq t_{1} \\
-I_{o} & , \quad 0 \leq t_{2} \leq t_{2} \\
& \vdots \\
(-1)^{j+1}I_{o} & , \quad 0 \leq t_{j} \leq t_{j} \\
& \vdots \\
(-1)^{k+1}I_{o} & , \quad 0 \leq t_{k} \leq t_{k}
\end{align}
\]  

\[\text{(II)}\]

without the balance being recovered in the electrode-solution interphase before application of second and subsequent current steps. For the sake of simplicity, equal absolute value currents have been assumed. In Scheme II, \( t_{j} \) and \( t_{i} \) are, respectively, the time of application and the transition time of the \( j \)th step (\( j = 1 \) to \( k \)). Thus, by following the procedure indicated in the Appendix, we have obtained the equations for the surface concentrations of species participating in the EC process, for any \( j \)th current step:

\[
\frac{c_{O}^j(t_{o}, t)}{c_{O}} = 1 - N_{EC} \left\{ t_{ij}^{1/2} S_{O}(\xi_{O}^{(j)}) + 2 \sum_{n=2}^{j} (-1)^{n+1} t_{n}^{1/2} S_{O}(\xi_{O}^{(n)}) \right\}
\]  

\[\text{(1)}\]

\[
\frac{c_{R}^j(t_{o}, t)}{c_{O}} = \frac{1}{1 + K} \left\{ K \frac{c_{R}^{'} + c_{Z}^{'}}{c_{O}} + \gamma N_{EC} \left\{ t_{ij}^{1/2} [KS_{R}(\xi_{R}^{(j)}) + T_{R}(\xi_{R}^{(j)}, \chi^{(j)})] + 2 \sum_{n=2}^{j} (-1)^{n+1} t_{n}^{1/2} [KS_{R}(\xi_{R}^{(n)}) + T_{R}(\xi_{R}^{(n)}, \chi^{(n)})] \right\} \right\}
\]  

\[\text{(2)}\]

\[
\frac{c_{Z}^j(t_{o}, t)}{c_{O}} = \frac{1}{1 + K} \left\{ K \frac{c_{R}^{'} + c_{Z}^{'}}{c_{O}} + \gamma N_{EC} \left\{ t_{ij}^{1/2} [S_{R}(\xi_{R}^{(j)})] - T_{R}(\xi_{R}^{(j)}, \chi^{(j)})] + 2 \sum_{n=2}^{j} (-1)^{n+1} t_{n}^{1/2} [S_{R}(\xi_{R}^{(n)})] - T_{R}(\xi_{R}^{(n)}, \chi^{(n)})] \right\} \right\}
\]  

\[\text{(3)}\]

where \( c_{R}^{'} (i = O, R \text{ or } Z) \) is the initial concentration of species \( i, t_{o} \) is the radius of the spherical electrode and \( K \) is the equilibrium constant of the chemical reaction, given by

\[
K = k_{2} / k_{1} = c_{R}^{'} / c_{Z}^{'}
\]  

\[\text{(4)}\]

Also:

\[
N_{EC} = 2I_{o}/(nFAD_{a}^{1/2}c_{o})
\]  

\[\text{(5)}\]

\[
\gamma = (D_{C}/D_{a})^{1/2}
\]  

\[\text{(6)}\]

where \( t_{n} = t_{n-1} + \ldots + t_{j} \)  

\[\text{(7)}\]

\[t_{ij} = t_{j}\]

\[\text{(8)}\]

\[
S_{i}(\xi_{i}^{(j)}) = \frac{1}{\xi_{i}} \left( 1 - \exp \left( \frac{\xi_{i}^{(j)}}{2} \right) \right)
\]  

\[\text{(9)}\]

\[
T_{R}(\xi_{R}^{(j)}, \chi^{(j)}) = \exp \left( -\chi^{(j)} \right) \frac{1}{4} \left( \frac{\xi_{R}^{(j)}}{\xi_{R}} \right)^{2} \times \left\{ \exp \left( \frac{\xi_{R}^{(j)}}{2} \right) \right\} \right.
\]  

\[\text{(10)}\]

In the above equations, \( n, F, A \) and \( D_{a} \) have their usual meanings and variables \( \xi_{i}^{(j)} \) and \( \chi^{(j)} \) are given by Equations A48 and A49 in the Appendix on changing \( t_{ij} \) in these equations for \( t_{n} \) (Eq. 7).

Note that the surface concentrations (Eqs. 1–3) depend on the functions \( S_{i}(\xi_{i}^{(j)}) \) and \( T_{R}(\xi_{R}^{(j)}, \chi^{(j)}) \), which in these expressions obey two very different phenomena. While the function \( S_{i}(\xi_{i}^{(j)}) \) is a consequence of the diffusion, due to the variations of the species concentrations, and is identical to that obtained for a simple E mechanism, the function \( T_{R}(\xi_{R}^{(j)}, \chi^{(j)}) \) appears only in the expressions for species which are also involved in the homogeneous chemical reaction and, therefore, it has a purely kinetic character. The function \( S_{i}(\xi_{i}^{(j)}) \) is multiplied by \( K \) in the equation corresponding to the surface concentration of species \( R \) (Eq. 2) and hence, the EC process will have a major kinetic character the lower \( K \) is. In contrast, for \( K \gg 1 \) it will become a simple E mechanism.
It is worthwhile highlighting that, due to the compact form of Equations 9 and 10, the solutions presented in this article are valid for spherical electrodes of any size. These equations simplify in the following particular cases:

- For planar electrodes \((r_0 \to \infty\), i.e., \(\xi_0^n \to 0\)),

\[
S_{\xi_0^n} = 1/\pi^{1/2}
\]  

(11)

\[
T_R(\xi_0^n \to 0, \chi_n^i) = \frac{erf(\chi_n^i/2)}{2(\chi_n^i)^{1/2}}
\]  

(12)

- For ultramicroelectrodes \((r_0 \to 0\), i.e., \(\xi_0^n \gg 1\)),

\[
S_{\xi_0^n} = T_R(\xi_0^n \gg 1, \chi_n^i) = 1/\xi_0^n
\]  

(13)

The expressions corresponding to the transition time of the \(j\)th current step \((j > 1)\) for the EC mechanism can be obtained by making \(c_{\text{O}}^r(r_0, t_j) = 0\) in Equation 1 if \(j\) is odd, and \(c_{\text{R}}^r(r_0, t_j) = 0\) in Equation 2 if \(j\) is even. Thus, we find

\[
\tau_{j}^{\text{odd}} = \frac{1 - N_{\text{EC}}(\xi_0^n)^{1/2}}{2N_{\text{EC}}(\xi_0^n)} \sum_{n=0}^{j-1} (-1)^n r_n^{1/2} S_{\xi_0^n}(\xi_0^n)
\]  

(14)

\[
\tau_{j}^{\text{even}} = \frac{K_{\text{EC}}^{\text{O}} c_{\text{R}}^{2} + K_{\text{EC}}^{\text{R}} c_{\text{O}}^{2} + \gamma N_{\text{EC}}(r_0 + r_1)^{1/2}}{2\gamma N_{\text{EC}}(K_{\text{R}}^{\text{O}} + K_{\text{R}}^{\text{R}})} \sum_{n=0}^{j-1} (-1)^n r_n^{1/2} S_{\xi_0^n}(\xi_0^n) + T_R(\xi_0^n, \chi_n^i)
\]  

(15)

For \(j = 1\) (constant current chronopotentiometry), from Equation 1 we obtain

\[
\tau_{1}^{\text{odd}} = 1/N_{\text{EC}}(\xi_0^n)
\]  

(16)

In the particular case \(j = 2\) (current reversal chronopotentiometry), Equation 15 leads to the following expression

\[
\tau_{2}^{\text{odd}} = \frac{K_{\text{EC}}^{\text{O}} c_{\text{R}}^{2} + K_{\text{EC}}^{\text{R}} c_{\text{O}}^{2} + \gamma N_{\text{EC}}(r_1 + r_2)^{1/2}}{2\gamma N_{\text{EC}}(K_{\text{R}}^{\text{O}} + K_{\text{R}}^{\text{R}})} \sum_{n=0}^{j-1} (-1)^n r_n^{1/2} S_{\xi_0^n}(\xi_0^n) + T_R(\xi_0^n, \chi_n^i)
\]  

(17)

which, in the case \(\xi_0^n \to 0\) (planar electrode), is equivalent to that obtained by Dračka in reference [11].

The potential-time response corresponding to the EC mechanism can be deduced by substituting the expressions obtained for the surface concentrations of the oxidized and the reduced species, \(c_{\text{O}}(r_0, t_j)\) and \(c_{\text{R}}(r_0, t_j)\) for the \(j\)th current step (Eqs. 1 and 2) in the Butler-Volmer equation:

\[
(1 - \delta)^{(i-1)} I_0 / nF = k^n e^{-\delta \mu(\xi(t)) - \xi(t)} c_{\text{O}}(r_0, t_j)
\]

\[
- k^n e^{-\delta \mu(\xi(t)) - \xi(t)} c_{\text{R}}(r_0, t_j)
\]

(18)

where \(E(t)\) is the time-dependent potential, \(E^\circ\) is the formal potential of the electrode reaction, \(k^n\) is the apparent heterogeneous rate constant of charge transfer at \(E^\circ\) and \(\alpha\) is the charge transfer coefficient.

3. Results and Discussion

One of the major achievements of this paper is that the solutions deduced here are really valid for any size of the spherical electrode considered. This constitutes a generalization of the results presented in previous papers on constant current chronopotentiometry, current reversal chronopotentiometry and cyclic chronopotentiometry [14, 20, 21], where small spherical electrodes \((r_0 < 0.006 \text{ cm})\) were not included. The generalization arises from the compact form that we have given for series \(S_{\xi_0^n}(\chi_n^i)\) and \(T_R(\xi_0^n, \chi_n^i)\) (Eqs. 9 and 10), which appear in expressions for the surface concentrations.

We have also studied the EC mechanism using a recently developed derivative chronopotentiometric technique that has been shown to be a powerful tool for obtaining the characteristic parameters of the chemical reaction following the charge transfer (see Section 3.5).

3.1. Constant Current Chronopotentiometry

In constant current chronopotentiometry, only one current step \((j = 1)\) is applied to a spherical electrode of any size. For conventional sized spherical electrodes, the study of the EC mechanism has been carried out in references [20, 21]. The transition time \(\tau_1\) is identical to that of a simple charge transfer reaction (Eq. 16), and therefore, no information about kinetic parameters of the chemical reaction can be obtained from its measurement. Under these conditions, it is necessary to study the whole potential-time curve. As can be deduced from Equation 13, if \(r_0 \to 0\), the surface concentrations (Eqs. 1 – 3) become independent of time. Therefore, there is not any transition time when spherical ultramicroelectrodes are used.

3.2. Current Reversal Chronopotentiometry

In current reversal chronopotentiometry two successive current steps of different sign are applied to a spherical electrode of any size \((j = 1, 2)\). In this case, the transition time \(\tau_2\), corresponding to an EC mechanism for the second current step, does depend explicitly on the characteristic parameters of the chemical reaction (Eq. 17), and hence, measurements of \(\tau_2\) can be used to obtain this information (see Section 3.5).

**Electroanalysis** 2004, 16, No. 11

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
In Figure 1 we have plotted the variation with time of the surface concentrations of species R (Fig. 1a) and Z (Fig. 1b), for a reversible chemical reaction with $K = 1$ and for different values of $k_1 + k_2$, when a spherical electrode with $r_0 = 0.01$ cm is used (Eqs. 2 and 3). In this figure we observe that for very small values of the rate constants ($k_1 + k_2 \leq 10^{-3}$ s$^{-1}$), the surface concentration of species Z (Fig. 1b) is zero for any current step applied, as corresponds to an immobile chemical equilibrium. However, the surface concentration of species R (Fig. 1a) increases during the first current step, attaining its maximum value at $t_1 = \tau_1$, and then decreases until zero during the second current step, reaching the reverse transition time, $\tau_2$, which coincides logically with that of a simple E process ($\tau_{2,k}$). For higher values of $k_1 + k_2$, the mobility of the chemical equilibrium increases and a similar behavior is observed for species R and Z, i.e., the surface concentration increases during the first current step and decreases during the second. As can be observed in Figure 1a, the reverse transition time $\tau_2$ first decreases when $k_1 + k_2$ increases (see curve with $k_1 + k_2 = 1$ s$^{-1}$), and then starts to increase for higher values of the rate constants (see curve with $k_1 + k_2 = 100$ s$^{-1}$) in such a way that in the limit case $k_1 + k_2 \gg 100$ s$^{-1}$, the reverse transition time would again be that corresponding to an E process. An EC mechanism is therefore easily detected from measurements of the reverse transition time $\tau_2$, since it is always less than that corresponding to a simple charge transfer reaction.

In Figure 2 we have plotted the potential-time curves corresponding to an EC process with $k_1 + k_2 = 15$ s$^{-1}$, for several values of the equilibrium constant $K$, when a spherical electrode with $r_0 = 0.05$ cm is used (Eq. 18). The figure shows that the reverse transition time becomes greater as $K$ increases, and the system tends to behave as an E mechanism, as can be deduced from Equation 2. For an irreversible chemical reaction ($K = 0$), the reverse transition time $\tau_2$ becomes so small that a vertical asymptote is observed when the current is reversed. This is due to the transformation of species R, which appears during the application of the first current step, into electroinactives species Z.

This case $K = 0$ is of great interest, since the influence of the chemical reaction on the process is maximum. The behavior described in Figure 2 for $K = 0$ obviously depends also on the value of the rate constant $k_1$. As can be observed in Figure 3, where the potential-time curves for an EC mechanism with $K = 0$ and several values of $k_1$ are plotted, a vertical asymptote appears when the current is reversed, for values of $k_1 > 10$ s$^{-1}$.

3.3. Cyclic Chronopotentiometry

In cyclic chronopotentiometry, successive current steps are applied according to Scheme II. Their sign is alternately changed at a time which may be less than or equal to the
transition time corresponding to the $j$th current step, $t_j$. We will consider that the current is reversed when $t_j$ is reached, which is actually the most common case in practice.

Figure 4 shows the variation of the surface concentrations of species O and R for an EC mechanism when five constant current steps are applied to a spherical electrode (Fig. 4a), as well as the typical potential-time response for this mechanism in a cyclic chronopotentiometric experiment (Fig. 4b). In these figures, the values of the transition times (see dotted lines) can be observed (odd transition times $t_1\text{,} t_3$, and $t_5$, reached when surface concentration of species O becomes zero, and even transition times $t_2$ and $t_4$, for $c_{O}(r_0,t_j) = 0$, with $j = 2, 4$).

In cyclic chronopotentiometry it is of great interest to study the variation of the transition time ratios, defined with respect to the transition time of the first electrochemical reaction, $t_1$, as

$$a_j = \frac{t_j}{t_1}$$

(19)

with the number of alternating current steps applied, $j$, since this allows us to characterize the electrode process [12, 13]. It is useful to plot these transition time ratios vs. $j$ for the EC mechanism, as well as those for an E mechanism, which is taken as reference.

As can be deduced from Equation 15, the transition time obtained for an EC mechanism when an oxidation process takes place ($j$ even) is given as a function of the equilibrium and rate constants of the chemical reaction, but the transition time does not depend explicitly on these parameters when an odd current step is applied (Eq. 14). Thus, in the following sections, we will analyze odd and even transition time ratios separately. On account of its enormous practical interest, we pay special attention to the case in which the chemical reaction following the charge transfer reaction is irreversible ($K = 0$, i.e. $k_z = 0$).

Electroanalysis 2004, 16, No. 11

Fig. 3. Potential-time curves for an EC mechanism with $K = 0$ in current reversal chronopotentiometry when a spherical electrode is used (Eq. 18). The values of $k_1$ (in s$^{-1}$) are shown on the curves $T = 298$ K, $n = 1$. Other conditions as in Figure 1.

Fig. 4. Variation with time of the surface concentrations of species O (solid line) and R (dashed line) (Fig. 4a) and potential-time curves (Fig. 4b) for an EC mechanism in cyclic chronopotentiometry ($j = 1, 2, 3, 4, 5$) when a spherical electrode is used (Eqs. 1, 2 and 18). $k_1 + k_2 = 15$ s$^{-1}$, $T = 298$ K, $n = 1$. Other conditions as in Figure 1.

Fig. 5 shows the influence of the rate constant $k_1$ on the variation of the transition time ratios with the number of current steps applied in a spherical electrode with $r_0 = 0.01$ cm. We have plotted $a_j$ vs. $j$ in Figure 5a ($j$ odd) and in Figure 5b ($j$ even). In both figures it can be observed that ratios $a_j$ move between two limit situations: for small values of the rate constant ($k_1 < 10^{-3}$ s$^{-1}$), the transition time ratios are logically identical to those obtained for an E mechanism. For large values of $k_1$ (> $10$ s$^{-1}$), the initial reduction process gives rise to the first transition time ($t_1$), but the fast transformation of electroactive species R into electroinactive species Z leads to a second and subsequent transition times which are near to zero. Thus, the transition time ratios also tend to zero. In this case, an EC mechanism is easily detectable. It follows that, in order to characterize an EC mechanism with irreversible chemical reaction it is convenient to increase the rate constant, which can be done by modifying the experimental conditions if the chemical reaction is of pseudo-first order [13].

The existence of an EC mechanism can also be shown if we change the current density applied to the electrode, $N_{EC}$ (Eq. 5), since a decrease of this variable has the same effect on these curves as an increase of the chemical rate constant, (see Figure 6 for $k_1 = 10^{-1}$ s$^{-1}$). Moreover, a variation of the
current density has practically no influence on a simple E process [22]. Consequently, the variation of $N_{EC}$ allows us, not only to show the existence of possible kinetic complications in the electrode process, but also to observe the typical behavior described for an EC mechanism, even for small values of $k_1$.

3.4. Reciprocal Derivative Chronopotentiometry

In this section we will show the response corresponding to an EC mechanism in reciprocal derivative chronopotentiometry with constant current in its traditional form, i.e., by plotting the reciprocal of the time derivative of the chronopotentiogram versus the measured potential ($dE/dt$ plot) for an EC mechanism, even for small values of $k_1$.

The behavior described for the $dE/dt$ vs. $E$ and $dE/dt^2$ vs. $E$ curves have been obtained from the $E$ vs. $E$ and $E$ vs. $t^2$ responses in current reversal chronopotentiometry, which were numerically differentiated by using a finite-difference formula of the fifth degree [23].

In Figure 7 we have represented the reciprocal derivative chronopotentiograms ($dE/dt^2$ vs. $E$ in Figure 7a and $dE/dt$ vs. $E$ in Figure 7b) for an EC mechanism with $K = 0$ and for several values of the rate constant $k_1$, when a planar electrode is used. The figure shows how, as $k_1$ increases, cathodic peaks move towards more positive potentials, and their heights ($|h_{cat}|$) increase. This effect is much more considerable in Figure 7a than in Figure 7b, since the heights of the peaks corresponding to a $dE/dt^2$ vs. $E$ curves increase strongly and the peaks become narrower and more asymmetric as $k_1$ increases, while those corresponding to a $dE/dt$ vs. $E$ curve become independent of $k_1$ for $k_1 > 10^{-1}$.

However, the position of the anodic peak hardly depends on the value of $k_1$, while the peak height ($h_{an}$) diminishes when the rate constant increases.

The behavior described for the $dE/dt$ vs. $E$ and $dE/dt^2$ vs. $E$ curves leads to an easy detection of a chemical reaction following the charge transfer since for a reversible E process the relations $|h_{cat}/h_{an}|_{plane} = 3$ [10, 24] and $|h_{cat}/h_{an}|_{sphere} |d\theta|= 1.73$ [25], while for an EC mechanism these relations are always greater than above, and they increase with $k_1$.

3.5. Determination of Kinetic Parameters of the Chemical Reaction

The chronopotentiometric techniques in which the current sign is reversed at least once, can be used to determine the
kinetic parameters of the chemical reaction in an EC mechanism from measurements of transition times. Thus, by using reversal (Section 3.2), cyclic (Section 3.3) and reciprocal derivative (Section 3.4) chronopotentiometry, several methods can be proposed to obtain this kinetic information.

In current reversal chronopotentiometry, since the reverse transition time depends on the kinetic parameters of the chemical reaction (Eq. 17), it is possible to make working curves, like those plotted in Figure 8, from which we can obtain the rate constants $k_1$ and $k_2$, once $K$ is determined [14]. In this figure, we have represented $(t_2^2 + t_1^2)^{1/2}$ for several values of $r_0$ and for two values of the equilibrium constant: $K = 0$ (Fig. 8a) and $K = 0.5$ (Fig. 8b). Thus, from measurements of $t_1$ and $t_2$, the value of $k_1 + k_2$ can be immediately determined from the abscissa corresponding to the value of the transition time ratios represented. As can be observed in Figures 8a and 8b, the electrode radius has a large influence on the working curves and this leads to important errors in the determination of kinetic parameters when a spherical electrode is used and the equations for planar diffusion are being considered. It is of great interest, therefore, to deduce equations that take into account the sphericity of the electrode. Moreover, when working curves for a planar electrode are of the form shown in Figure 8b ($K = 0.5$), the use of spherical electrodes permits an easier and much more accurate determination of the rate constants.

In cyclic chronopotentiometry, the study of the transition time ratios can also be used to calculate the rate constants of the chemical reaction coupled to the charge transfer in an EC mechanism, (see references [12, 13]). The value $k_1 + k_2$ is determined by comparing theoretical working curves $q_j$ vs. $j$ with the experimental one. This method is complementary and can be more advantageous than that described above for current reversal chronopotentiometry, since in this last case we obtain all the kinetic information from just one measurement of $t_1$ and $t_2$. However, in cyclic chronopotentiometry we can apply as many current steps as we consider necessary [13].

In Figure 9 we have plotted the variation with $j$ of the transition time ratios $q_j$ corresponding to an EC mechanism with $K = 0$, for several values of the electrode radius, and for two values of the rate constant $(k_1 = 10^{-1} \text{s}^{-1}$ and $k_2 = 10 \text{s}^{-1})$. As can be observed, a decrease in the electrode radius acts in the same way as an increase in the chemical rate constant (Fig. 5) and hence, we conclude again that the use of equations taking into account the electrode sphericity is imperative in order to obtain accurate values for the kinetic parameters of the chemical reaction, when spherical electrodes are used. The effect exerted by the sphericity...
decreases as $k_1$ increases, as a result of $t_2$ and following transition times tending to zero.

In reciprocal derivative chronopotentiometry, both the peak heights and the peak potentials are dependent on the value of the rate constants of the chemical reaction, as shown in Figure 7. Thus, this dependence can be used to determine these kinetic parameters. In Figure 10 we have plotted the working curves corresponding to the variation of the cathodic peak height $|\theta_{\text{cal}}|$ (Fig. 10a) and the cathodic peak potential ($E_{\text{p, cal}}$) (Fig. 10b) with $k_1$, obtained from curves $d^2t_1/2dE$ vs. $E$, for $K = 0$ and three values of the electrode radius. As can be observed in Figures 10a and 10b, and according to results shown in Figure 7a for a planar electrode, there is an univocal correspondence between the values of height peak and potential peak with the rate constant $k_1$, which makes this parameter easy to determine. It is also observed in Figure 10a that the use of spherical electrodes is not advisable for determining high values of $k_1$. From Figure 10 we conclude that the working curves obtained from the use of this new modality of reciprocal derivative chronopotentiometry are undoubtedly, of those considered in this article, the most useful and reliable in obtaining the kinetic information of the chemical reaction in an EC mechanism.

4. Conclusions

1. Compact and easy-to-manage equations corresponding to the application of current reversal and cyclic chronopotentiometry at spherical electrodes have been deduced and checked, showing that electrode radius has a great influence on the responses of these techniques, in such a way that important errors are committed in the determination of kinetic parameters of the chemical reaction when a spherical electrode is used and the equations for planar diffusion are considered. Thus, the possibility of having equations that take into account the sphericity of the electrode is of great interest.

2. The use of reversal current chronopotentiometry and cyclic chronopotentiometry in spherical electrodes as the SMDE is very useful for the study of the EC mechanism since homogeneous kinetic parameters can be obtained by using the working curves given in this article.

3. Two different forms of applying the reciprocal derivative chronopotentiometry are proposed and discussed. In both cases the $dt/dE$ vs. $E$ and $d^2t_1/2dE$ vs. $E$ curves present peaks whose height and position are strongly dependent on the rate constants of the chemical reaction. Thus, this dependence has been used to propose working curves leading to the determination of these kinetic parameters.
4. A comparison of the chronopotentiometric methods analyzed leads us to conclude that working curves based on the $d^2I/dE$ vs. $E$ curves are more suitable to obtain accurate values of the rate constants of the chemical reaction.

5. Appendix

For a spherical electrode of any size, the mass transport to the electrode surface when the $j$th ($j = 1$ to $k$) current step is applied is described by the differential equation system

$$
\begin{align*}
\delta_0 c'O & = 0 \\
\delta_R c'R & = -k_1 c'R + k_2 c'_Z \\
\delta_Z c'_Z & = k_1 c'R - k_2 c'_Z 
\end{align*}
$$

(A1)

with $\delta_i$ ( $i = O$, $R$ or $Z$) being the operator for Fick’s second law given by

$$
\delta_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right)
$$

(A2)

where $D_i$ is the diffusion coefficient of species $i$ and $r$ is the distance from the center of the electrode to any point in the solution.

The boundary value problem is given by:

$$
\begin{align*}
t_j = 0, r & \geq r_0 \\
t_j > 0, r & \to \infty \end{align*}
$$

$$
c'_O(r, t_j) = c'^{-1}_O(r, t_j), c'_R(r, t_j)
$$

$$
= c'^{-1}_R(r, t_j), c'^{-1}_Z(r, t_j)
$$

(A3)

$$
t_j > 0, r = r_0 : D_O \left( \frac{\partial c'_O}{\partial r} \right)_{r = r_0} = -D_R \left( \frac{\partial c'_R}{\partial r} \right)_{r = r_0} = \frac{(-1)^{j+1} I_0}{nFA}
$$

(A4)

$$
D_Z \left( \frac{\partial c'_Z}{\partial r} \right)_{r = r_0} = 0
$$

(A5)

where $c'^{-1}_i(r, t)$ ($i = O$, $R$ or $Z$) are the solutions for the $(j - 1)$th current step.

When the first current step ($j = 1$) is applied, by introducing the variables:

$$
\zeta'(r, t_1) = c'_k(r, t_1) + c'_Z(r, t_1)
$$

(A6)

$$
\phi'(r, t_1) = (c'_k(r, t_1) - Kc'_Z(r, t_1))e^{(k_1 + k_2)t_1}
$$

(A7)

and with the assumption

$$
D_O + D_R = D_Z
$$

(A8)

the differential equation system (Eqs. A1) and the boundary value problem (Eqs. A3 – A5) are transformed into

$$
\delta_0 c'_O = \delta_R c'_R = \delta_Z c'_Z = 0
$$

(A9)

$$
t_1 = 0, r \geq r_0 \\
t_1 > 0, r \to \infty \end{align*}
$$

$$
\left\{ \begin{array}{l}
c'_O = c'_R, c'_R = c'_Z, \phi' = 0
\end{array} \right.
$$

(A10)

$$
t_1 > 0, r = r_0 : D_O \left( \frac{\partial c'_O}{\partial r} \right)_{r = r_0} = -D_R \left( \frac{\partial c'_R}{\partial r} \right)_{r = r_0} = \frac{I_0}{nFA}
$$

(A11)

$$
\left( \frac{\partial \phi'}{\partial r} \right)_{r = r_0} = -e^{(k_1 + k_2)t_1} = \frac{I_0}{nFA D_R}
$$

(A12)

By supposing that $c'_O$, $\zeta'$, and $\phi'$ have the form:

$$
c'_O(r, t_1) = c'_R + \sum_{p = 0}^q \alpha_{p,q}(s'_R)(\zeta'_O)^p(\phi')^{q/2}
$$

(A13)

$$
\zeta'(r, t_1) = (c'_R + c'_Z) + \sum_{p = 0}^q \rho_{p,q}(s'_R)(\zeta'_R)^p(\phi')^{q/2}
$$

(A14)

$$
\phi'(r, t_1) = \sum_{p = 0}^q \delta_{p,q}(s'_R)(\zeta'_R)^p(\phi')^{q+1/2}
$$

(A15)

where

$$
s'_i = \frac{r - r_0}{2\sqrt{D_i t_1}} \quad (i = O, R)
$$

(A16)

$$
\zeta'_i = \frac{2\sqrt{D_i t_1}}{r_0} \quad (i = O, R)
$$

(A17)

$$
\chi' = (k_1 + k_2)t_1
$$

(A18)

and using the dimensionless parameters method [26] to solve the differential equation system (Eqs. A9), we obtain the following solutions:

$$
\alpha_{p,q}(s'_R) = \rho_{p,q}(s'_R) = 0 \quad \text{unless} \quad q = 1
$$

(A19)

$$
\alpha_{0,1}(s'_R) = -\frac{N_{EC} c'_D}{(k_1 + k_2)^{1/2}} \left\{ \frac{\psi_3(s'_R)}{p_3} \right\}
$$

(A20)

$$
\alpha_{1,1}(s'_R) = -\frac{N_{EC} c'_D}{(k_1 + k_2)^{1/2}} \left\{ \frac{\psi_3(s'_R)}{2} - \psi'_0(s'_O) \right\}
$$

(A21)

$$
\alpha_{1,2}(s'_R) = -\frac{N_{EC} c'_D}{(k_1 + k_2)^{1/2}} \left\{ \psi_3(s'_R) - \frac{p_3 \psi'_1(s'_R)}{2} + \frac{p_3 \psi'_1(s'_R)}{4} \right\}
$$

(A22)

$$
\alpha_{1,3}(s'_R) = -\frac{N_{EC} c'_D}{(k_1 + k_2)^{1/2}} \left\{ \frac{15}{32} \psi'_4(s'_R) - \psi'_2(s'_R) + \frac{\psi'_0(s'_O)}{2} \right\}
$$

(A23)
\[ \rho^{\prime,1}_{p,q}(s^1_R) = -\gamma \alpha^{\prime,1}_{p,q}(s^1_R) \]  
(\text{A24})

\[ \delta_{t=4}^{(1)}(s^1_R) = \frac{\gamma N_{EC}^0 \Psi_{2p+1}(s^1_R)}{2q!(k_1 + k_2)^{1/2}} \left\{ \frac{2q + 1}{2q + 2} \Psi_{2p+2}(s^1_R) - \Psi_{2p}(s^1_R) \right\} \]  
(\text{A25})

\[ \rho^{\prime,1}_{p,q}(s^1_R) = \frac{\gamma N_{EC}^0}{4q!(k_1 + k_2)^{1/2}} \times \left\{ \frac{4(q + 1)}{p_{2p+3}} \Psi_{2p+2}(s^1_R) - 2p_{2q} \Psi_{2p+1}(s^1_R) + p_{2q} \Psi_{2p+1}(s^1_R) \right\} \]  
(\text{A26})

\[ \delta^{(1)}_{t=4}(s^1_R) = \frac{\gamma N_{EC}^0}{4q!(k_1 + k_2)^{1/2}} \times \left\{ \frac{8q^3 - 32q^2 + 40q + 15}{(2q + 4)(2q + 2)} \Psi_{2p+4}(s^1_R) \right. \]  
(\text{A27})

\[ - (6q + 4) \Psi_{2p+2}(s^1_R) + (6q + 2) \Psi_{2p}(s^1_R) \]  
(\text{A28})

where \( \gamma \) is given by Equation 6 and functions \( \alpha^{\prime,1}_{p,q}(s^1_R) \) are given by Equations A19–A23 on changing \( s_0^0 \) for \( s^1_R \) (Eq. A16). \( \psi(s^1_i) \) (i = O, R) are the Koutecky functions and \( p_m = \Gamma(1 + m/2)/\Gamma((1 + m)/2) \).

By using the superposition principle in the way indicated in [14, 27] we deduce that, for \( j > 1 \), the solution for the differential equation system (Eqs. A1) can be written as

\[ c^{(1)}_{t=1}(r, t) = c^{(1)}_{t=1}(r, t) + c^{(1)}_{t=1}(r, t) \]  
(\text{A29})

\[ c^{(1)}_{t=1}(r, t) = c^{(1)}_{t=1}(r, t) + c^{(1)}_{t=1}(r, t) \]  
(\text{A30})

\[ c^{(1)}_{t=1}(r, t) = c^{(1)}_{t=1}(r, t) + c^{(1)}_{t=1}(r, t) \]  
(\text{A31})

where

\[ c^{(1)}_{t=1}(r, t) = \delta^{(1)}_{t=1}(r, t) + \sum_{m=1}^{j-1} \delta^{(m)}_{t=1}(r, t) \]  
(\text{A32})

Now, we define the functions

\[ \zeta = c^1_R + c^1_Z = \zeta^{(1)} + \zeta^{(1)} \]  
(\text{A33})

\[ \phi^{(1)} = (c^1_R - k c^1_Z) \exp(k_1 + k_2 t) = \phi^{(1)} + \dot{\phi} \]  
(\text{A34})

with

\[ \zeta^{(1)} = \zeta^{(1)}(r, t) + \sum_{m=1}^{j-1} \delta^{(m)}_{t=1}(r, t) \]  
(\text{A35})

\[ \dot{\phi}^{(1)}(r, t) = \delta^{(1)}_{t=1}(r, t) \]  
(\text{A36})

where \( t \) is given by

\[ t = t_1 + t_2 + \cdots + t_j \]  
(\text{A37})

the boundary value problem (Eqs. A3–A5) has the generalized form:

\[ t_j = 0, r \geq r_0 \]  
(\text{A38})

\[ t_j > 0, r \to \infty \]  
(\text{A39})

\[ (\partial_t \tilde{c}^{(1)}_{t=1})_{r=\infty} = -D_0 \left( \frac{\partial \tilde{c}^{(1)}_{t=1}}{\partial r} \right)_{r=r_0} = \frac{2I_0}{nFAD_R} \]  
(\text{A40})

Therefore, if we suppose that

\[ \delta^{(1)}_{t=1}(r, t) = \sum_{p,q=0}^{\infty} \delta^{(1)}_{p,q}(s^1_R) (\hat{\zeta}^1)^p(\chi)^{q/2} \]  
(\text{A41})

\[ \tilde{c}^{(1)}_{t=1}(r, t) = \sum_{p,q=0}^{\infty} \delta^{(1)}_{p,q}(s^1_R) (\hat{\zeta}^1)^p(\chi)^{q/2} \]  
(\text{A42})

\[ \tilde{c}^{(1)}_{t=1}(r, t) = \sum_{p,q=0}^{\infty} \delta^{(1)}_{p,q}(s^1_R) (\hat{\zeta}^1)^p(\chi)^{q/2} \]  
(\text{A43})

the solutions can be expressed in the general form

\[ \alpha^{(1)}_{p,q}(s^1_R) = 2(-1)^{p+1} \alpha^{(1)}_{p,q}(s^1_R) \]  
(\text{A44})

\[ \rho^{(1)}_{p,q}(s^1_R) = -\gamma \alpha^{(1)}_{p,q}(s^1_R) \]  
(\text{A45})

\[ \delta^{(1)}_{p,q}(s^1_R) = 2(-1)^{p+1} e^{(k_1 + k_2) t} \sum_{n=0}^{\infty} \delta^{(1)}_{p,q}(s^1_R) \]  
(\text{A46})

where

\[ s_i = \frac{r - r_0}{2\sqrt{D_0 t_j}} (i = O, R) \]  
(\text{A47})

\[ \zeta_i = 2\sqrt{D_0 t_j} (i = O, R) \]  
(\text{A48})

\[ \chi = (k_1 + k_2)t_j \]  
(\text{A49})

In the particular case \( s_1 = 0 \), from Equations A6, A7, A13–A15, A29–A31, and [28, 29], we obtain the surface
concentrations of species involved in an EC mechanism, which are given by Equations 1–3 in theory.

6. Acknowledgements

The authors greatly appreciate the financial support provided by the Dirección General Científica y Técnica (Project No. BQU2000-0231), and by the Fundación Séneca (Projects 00696/CV/99 and AR 28-02698/FS/02). Also J. M. Molina thanks Fundación Séneca for the grant received.

7. References