Full Paper

Steady State Reciprocal Derivative Chronopotentiometry with Programmed Currents at Microelectrodes

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Abstract
Equations corresponding to the application of Reciprocal Derivative Chronopotentiometry with programmed currents to spherical and disk microelectrodes under steady state conditions have been deduced. Traditional stationary \( \frac{d}{dt} \) \( E \) curves for a current time function of the form \( I(t) = I_0 u(t) \), \( u > 0 \), and the new \( \frac{dI}{dE} \) \( E \) curves, which do not depend on the particular characteristics of the applied programmed current \( I(t) \) are shown for any degree of reversibility of the electrode process. The evolution from transient to steady state for both derivative techniques has been analyzed. Criteria for characterizing reversible and totally irreversible stationary derivative curves, together with easy methods for determining thermodynamic and kinetic parameters of the charge transfer process from the measure of peak parameters are proposed. The validity of the theoretical predictions has been experimentally tested with hexachloroiridate(IV) reversible oxidation and with iron(III) irreversible reduction in aqueous media.

Keywords: Steady state, Reciprocal derivative chronopotentiometry, Microelectrodes, Programmed current

1. Introduction
In a recent paper [1], we analyzed the application of Chronopotentiometry with programmed current at microelectrodes, since these present great advantages for carrying out electrochemical measurements as their use greatly reduces the magnitude of undesired effects such as the charge current and the ohmic drop of potential [1 – 10].

In this paper, we present the application of Reciprocal Derivative Chronopotentiometry with programmed current to microelectrodes under steady state conditions. This technique, which is based on the plotting of the reciprocal of the time derivative of the chronopotentiogram versus the measured potential (\( \frac{dt}{dE} \) vs. \( E \) curve) [11], has been much used in recent years for the study of different electrode processes because the response obtained presents a characteristic peak that is quantitatively related to the kinetic and thermodynamic parameters of the electrode process, and is scarcely affected by the capacitative effects since it has been obtained from the central zone of the \( E \) vs. \( t \) curve. This derivative technique is very simple to apply, it presents high reproducibility in measuring the peak potentials and peak heights, even in highly resistive media [12], very high sensitivity [13 – 20], and it affords simple diagnosis criteria for the electrode processes analyzed [21 – 25].

Traditionally, the current perturbation employed for Reciprocal Derivative Chronopotentiometry has been the constant current or current step. However, when a constant current is applied to an electrode of small size, a potential variable with time is not obtained as occurs in electrodes of conventional size and, therefore, constant current is not useful at microelectrodes [1, 26 – 27]. In order to apply this technique at microelectrodes we have employed time variable currents, which allows us to obtain an \( E \) vs. \( t \) response, from which the transition time can be measured [1].

Here we have used a power current time function \( I(t) = I_0 u(t) \), \( u > 0 \), in order to obtain, on the one hand, the traditional \( \frac{dt}{dE} \) vs. \( E \) curves and, on the other, the new modality of this technique in which the response is the reciprocal derivative of the potential with respect to the applied current time function, \( I(t) \), versus the potential measured \( E \), i.e., the \( \frac{dI}{dE} \) vs. \( E \) curve. This stationary response is completely general and does not depend on the particular characteristics of the applied programmed current \( I(t) \). Moreover, these curves are similar to those obtained in Derivative Voltammetry (DV), Differential Pulse Voltammetry (DPV) and Square Wave Voltammetry (SWV).

We have also analyzed the evolution from “transient” to “steady state” of both \( \frac{dt}{dE} \) vs. \( E \) and \( \frac{dI}{dE} \) vs. \( E \) responses at spherical microelectrodes for any degree of reversibility of the electrode process, deducing the limit electrode radius values for which these curves can be considered as practically identical to those corresponding to stationary conditions. Moreover, easy criteria to determine kinetic and thermodynamic parameters of the process from values of peak parameters of the stationary \( \frac{dI}{dE} \) vs. \( E \) and \( \frac{dt}{dE} \) vs. \( E \) curves are presented.

Equations deduced in this paper have been experimentally tested for the reversible oxidation of \( K_2\text{IrCl}_6 \), and the totally irreversible reduction of \( \text{FeCl}_3 \), in aqueous solutions.
at different gold disk microelectrodes. We have determined kinetic and thermodynamic parameters for these experimental systems from the analysis of the stationary \( dI/dE \) vs. \( E \) curves, obtaining values which are in good agreement with those in the literature.

2. Experimental

The computer driven potentiostat-galvanostat was designed and constructed by Quiceltron (Spain).

Pulse and waveform generation and data acquisition were performed using i-SBXDD4 and DAS16-330i (Computer-Boards, USA) boards, respectively. All computer programmes were written in our laboratory.

A three electrode cell was employed in the experiments. Gold disk microelectrodes of different radii \( (r_0 = 12.5 \times 10^{-4}, 5 \times 10^{-4} \text{ and } 2.5 \times 10^{-4} \text{ cm}) \) served as working electrodes. The counter electrode was a Pt foil and the reference electrode was a Ag/AgCl, KCl 1.0 M. In the experimental chronopotentiometric measurements, different digital noise filters of the instrument supported software were used.

FeCl\(_3\), HClO\(_4\), K\( _2\)IrCl\(_6\), and KNO\(_3\) were of Aldrich, reagent grade. All chemical reagents were used without further purification.

Nitrogen gas was passed through solutions for de-aeration for 15 minutes prior to measurements.

The diffusion coefficient of IrCl\(_3\) was determined by chronoamperometric measurements of IrCl\(_3\) in KNO\(_3\) 0.25 and 0.125 M, respectively, and of Fe\(^3+\) in HClO\(_4\) 0.5 M solutions at a gold electrode of \( r_0 = 5 \times 10^{-2} \text{ cm} \), obtaining the following values: \( D_{\text{IrCl}_3} = (9.01 \pm 0.05) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \), \( D_{\text{Fe}^{3+}} = (6.55 \pm 0.05) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \), and \( D_{\text{K}_{2}\text{IrCl}_6} = (1.74 \pm 0.02) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \), which are in line with previous results in the literature (see [28, 29]). We have also determined the formal potential of FeCl\(_3\) from current reversal chronopotentiometric measures at a gold disk electrode of \( r_0 = 5 \times 10^{-2} \text{ cm} \) by following the procedure indicated in [30], and obtaining the value \( E^* = 0.508 \pm 0.001 \text{ V} \) (vs. Ag/AgCl), KCl 1.0 M, which is in line with results in [31].

In the chronoamperometric experiments, we have applied programmed anodic (negative) currents for the oxidation of the IrCl\(_3^+\) system and cathodic (positive) ones for the reduction of the Fe\(^{3+}\) system.

All the kinetic and thermodynamic data were obtained using the K\( _2\)IrCl\(_6\)/KNO\(_3\) 0.25 M and FeCl\(_3\)/HClO\(_4\) 0.5 M systems corresponding to series of five replicates of the \( dI/dE \) vs. \( E \) curves. The results obtained are the mean of the five experimental values. The errors correspond to the standard deviation.

3. Reciprocal Derivative Chronopotentiometric Curves Under Steady State Conditions

Let us consider a simple charge transfer process, \( \text{A} + ne^- \leftrightarrow \text{B} \), which takes place at a spherical or disk microelectrode of radius \( r_0 \) under steady state conditions. In general, when a time dependent potential \( E(t) \) is applied, a current-potential response (\( I(E) \text{ curve} \)) is obtained. On the other hand, when chronopotentiometric methods are used and a current time function \( I(t) \) is applied, it is interesting to obtain both the potential-time \( (E-t) \) and the current-potential \( (I-E) \) responses.

Note that, under steady state conditions, it is possible to obtain a time dependent potential (or \( E-t \) curve) since the applied current varies with time, whereas when a constant current is applied to a microelectrode under these conditions, a constant potential is obtained [1]. Therefore, the application of programmed currents is necessary when microelectrodes are used.

In this paper we analyze two different modalities of Derivative Chronopotentiometry depending on which is the curve that will be differentiated with respect to the measured potential:

- In the first modality we obtain the reciprocal derivative of the \( E-t \) curves (\( dI/dE \) vs. \( E \) responses), which depends on the characteristics of the programmed current applied. We consider in this case that the current applied varies with a power of time of the form \( I(t) = I_0 t^u \), with the exponent \( u > 0 \).

- In the second modality we obtain the derivative of the \( I-E \) curves (\( dI/dE \text{ vs. } E \) curves), with \( I \) being the applied current and \( E \) the measured potential), which is independent of the characteristics of the applied programmed current. Therefore, in this case we could consider a generic current \( I(t) = I_0 f(t) \), with \( f(t) \) being any function of time.

3.1. \( dI/dE \text{ vs. } E \) Curves for a Power Current Time Function

In this case, the expression of the \( E-t \) curve corresponding to the application of a power time current of the form \( I(t) = I_0 t^u \) to a spherical electrode of any radius is given by the following equation:

\[
\frac{I_0 t^u}{4 \pi r_0^2 n F k} = e^{\gamma \mu (\gamma \phi/r_0)} \left[ 1 - \frac{I_0}{I_0(\infty)} I_{A^+} \right] - \gamma^2 \frac{I_0}{I_0(\infty)} I_{A^-} e^{(\gamma-\gamma)\mu} f(t)
\]

\[\text{J}_{A^+}, \text{J}_{A^-} \text{ with } i = A \text{ or } B, \text{ is given by Equations 8 and 9 in [32]:}\]

\[
J_{A^+} = \frac{t^u \mu!}{(\sqrt{D_IF/r_0})^\mu} \left[ -e^{(\mu \sqrt{D_IF/r_0})^2} \text{erfc} \left( \sqrt{D_IF/r_0} \right) \right]
\]

\[+ \sum_{j=0}^{n} \left( \frac{D_IF/r_0)^{2j}}{j!} - 2 \sum_{j=0}^{n} \left( \frac{D_IF/r_0)^{2j-1}}{(j-1)!} p_{2j-2} \right) \]

for \( u = 0, 1, 2, 3... \)
\[ J_{\alpha i} = \frac{2\alpha^i(u + 1/2)!}{(\sqrt{D_i r_0})^{3/2} p_{2u+1}} \times \left[ e^{\left(\frac{\sqrt{D_i r_0}}{2}\right)^2} \text{erfc}\left(\frac{\sqrt{D_i r_0}}{2}\right) + 2 \sum_{j=0}^{u-1/2} \left(\frac{\sqrt{D_i r_0}}{2}\right)^{2j} \right] \]

where \( r \) is the transition time corresponding to the application of a power current time function under steady state conditions [32].

In the particular case of a reversible process (\( k'\to\infty \)), the \( \frac{d\eta}{dE} \) vs. \( E \) curve given by Equation 7, takes the following simplified form:

\[ \frac{d\eta}{dE} = -\frac{nF}{uRT} \frac{\gamma^2 e^\eta}{1 + (1 + \gamma^2 e^\eta)^{1/\alpha}} \]

whereas if the charge transfer process is totally irreversible (\( k' < 0.1 \text{ cm s}^{-1} \), see below), Equation 7 becomes:

\[ \frac{d\eta}{dE} = -\frac{anF}{uRT} \frac{(\gamma e^{-\alpha})^\frac{1}{\alpha}}{(1 + \frac{\gamma e^{-\alpha}}{\gamma e^{-\alpha}})^{1/\alpha}} \]

In this case, the \( \frac{d\eta}{dE} \) vs. \( E \) curves show a characteristic peak, whose peak potential, \( E_p \), and peak height, \( \gamma = (d\eta/dE)|_{E_p} \), formulas are shown in Table 1 for reversible and totally irreversible electrode processes. As can be observed from Equations 1.1–1.4 in this Table, both peak potentials and peak heights depend on the value of the time exponent, \( u \), in the current applied.

### 3.2. \( \frac{dI}{dE} \) vs. \( E \) Curves for any Programmed Current

The \( \frac{dI}{dE} \) vs. \( E \) curve when any current time function \( I(t) = I_0 f(t) \) is applied to a spherical or disk microelectrode (with \( f(t) = e^{\omega t} \), \( \omega \), etc.), is obtained by differentiating the expression for the stationary state \( I \sim E \) curve [1], obtaining:

\[ \frac{dI}{dE} = -\frac{nF}{RT} \frac{(\gamma e^{-\alpha})(\gamma e^{-\alpha})}{1 + \frac{\gamma e^{-\alpha}}{\gamma e^{-\alpha}})^{1/\alpha}} \]

In Equations 1–8, \( D_i \) is the diffusion coefficient of \( i \) species (\( i = A \) or \( B \)), \( k' \) and \( \alpha \) are the heterogeneous rate constant and the charge transfer coefficient of the electrode process, respectively. \( E^\circ \) is the formal potential of the electroactive couple and \( \tau \) is the transition time corresponding to the application of a power current time function under steady state conditions [32].

In the particular case of a reversible electrode process (\( k'\to\infty \)), \( \frac{dI}{dE} \) vs. \( E \) curve following simplified form:

\[ \frac{dI}{dE} = -\frac{nF}{RT} \frac{\gamma^2 e^\eta}{1 + (1 + \gamma^2 e^\eta)^{1/\alpha}} \]

\[ \gamma_p = \frac{\gamma^2 e^\eta}{1 + \frac{\gamma e^{-\alpha}}{\gamma e^{-\alpha}})^{1/\alpha}} \]

\[ \gamma_p = -\frac{anF}{RT} \frac{\tau}{1 + \frac{\gamma e^{-\alpha}}{\gamma e^{-\alpha}})^{1/\alpha}} \]

Table 1. Peak potentials (\( E_p \)) and peak heights (\( \gamma_p = (dI/dE)|_{E_p} \)) of the stationary \( dI/dE \) vs. \( E \) responses for reversible and totally irreversible charge transfer process calculated from Equations 10 and 11, respectively, corresponding to the application of a power current time function of the form \( I(t) = I_0 f(t) \) to a spherical or disk microelectrode. \( E^\circ_{\text{micro}} = E^\circ + (RT/nF) \ln(1/\gamma^2) \) and \( E^\circ_{\text{micro}} = E^\circ + (RT/anF) \ln(1/\gamma) \) and \( \gamma \). The expression for \( \tau \) is given in Equation 9.

<table>
<thead>
<tr>
<th></th>
<th>( E_p )</th>
<th>( \gamma_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reversible</strong></td>
<td>( E^\circ_{\text{micro}} + \frac{RT}{nF} \ln u )</td>
<td>( \gamma^2 e^\eta )</td>
</tr>
<tr>
<td><strong>Totally irreversible</strong></td>
<td>( E^\circ_{\text{micro}} + \frac{RT}{anF} \ln u )</td>
<td>( \gamma e^{-\alpha} )</td>
</tr>
</tbody>
</table>

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\frac{1}{I_d(\infty)} \frac{dI}{dE_{\text{rev}}} = - \frac{nF}{RT} \left( \frac{\gamma^2 e^\theta}{1 + \gamma^2 e^{2\theta}} \right) \quad (13)

whereas if the charge transfer process is totally irreversible (\(k' < 0.1 \text{ cm s}^{-1}\)), Equation 10 becomes:

\frac{1}{I_d(\infty)} \frac{dI}{dE_{\text{irr}}} = - \frac{anF}{RT} \left( \frac{\chi e^{-an\theta}}{1 + \chi e^{-an\theta}} \right) \quad (14)

The expressions of the peak potential, \(E_p\), and the peak height, \(y_p\), are given in Equations 2.2 – 2.4 of Table 2.

Table 2. Peak potentials (\(E_p\)) and peak heights (\(y_p\)) of the stationary \(dI/dE\) vs. \(E\) responses for reversible and totally irreversible charge transfer processes calculated from Equations 13 and 14, respectively, according to the application of a constant value of the ratio \(I_d/I_d(\infty)\), \(I_d(\infty)\) is given by Equation 6.

<table>
<thead>
<tr>
<th>Reverse</th>
<th>Reversible (E_p^\text{rev} = E_p^\text{micro} \quad (2.1))</th>
<th>(y_p^\text{rev} = - \frac{nF}{4RT} \quad (2.2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Totally irreversible</td>
<td>(E_p^\text{irr} = E_p^\text{micro} \quad (2.3))</td>
<td>(y_p^\text{irr} = \frac{anF}{4RT} \quad (2.4))</td>
</tr>
</tbody>
</table>

Note that, in this case, and independently of the reversibility of the process (see Equations 12 – 14), neither peak potentials nor peak heights given in Equations 2.1 – 2.4 depend on the applied current varies with time, \(R(t) = I_0 \cdot f(t)\). So, for instance, the \(dI/dE\) vs. \(E\) curves are independent of the value of \(I_0\) and of the exponents \(u\) and \(\omega\) for programmed currents of the form \(I_0 e^{\omega t}\) and \(I_0 e^{\omega t}\), respectively. Moreover, these curves are similar to those obtained in Derivative Voltammetry (DV), Differential Pulse Voltammetry (DPV) and Square Wave Voltammetry (SWV).

In the case of a quasi-irreversible process, the peak potential can be obtained by solving the following equation:

\[(1 - \gamma^2 \theta^{-1}) \gamma^2 (\theta e^{\theta})^2 + \left[ (\theta + \gamma^2) \alpha^2 - 4\alpha + 1 \right] \theta e^{\theta} - \alpha^2 \theta = 0 \quad (15)\]

where:

\[\theta = e^{-\eta_p} \quad (16)\]

\[\eta_p = \frac{nF}{RT} (E_p - E^\text{rev}) \quad (17)\]

If we suppose \(D_\lambda = D_{\mu p}\), i.e., \(\gamma = 1\), Equation 15 takes the following simpler form:

\[(1 - \theta^{-1})(\theta e^{\theta})^2 + [(\theta + \gamma^2) \alpha^2 - 4\alpha + 1] \theta e^{\theta} - \alpha^2 \theta = 0 \quad (18)\]

The \(E_p\) and \(y_p\) values can be obtained by numerically solving Equation 15 or Equation 18, by using, for instance, the bisection method.

4. Results and Discussion

4.1. Theoretical Results and Discussion

In Figures 1 and 2 we have studied the evolution from transient to steady state responses, by considering the influence exerted by the electrode radius. These Figures show the theoretical \(dI/dE\) vs. \(E\) and \(dI/dE\) vs. \(E\) curves have been obtained by differentiating Equation 1 numerically, and have been calculated for a constant value of the ratio \(I_d/I_d(\infty)\), i.e., of the ratio \(I_d/I_d(\infty)\).

The curves in Figure 2 indicate that, as the electrode radius decreases, both \(dI/dE\) vs. \(E\) and \(dI/dE\) vs. \(E\) curves have been obtained by differentializing Equation 1 numerically, and have been calculated for a constant value of the ratio \(I_d/I_d(\infty)\), i.e., of the ratio \(I_d/I_d(\infty)\). From Figure 1 it can be observed that, as the electrode radius decreases, both \(dI/dE\) vs. \(E\) and \(dI/dE\) vs. \(E\) curves become practically coincident. This indicates that, in agreement with Equations 10 and 13, the steady state has been reached.

From the curves in Figure 2 it can be shown that, for totally irreversible processes, peak heights of both \(dI/dE\) vs. \(E\) and \(dI/dE\) vs. \(E\) curves decrease with the electrode radius until steady state is reached, where they become practically independent of \(r_0\), in agreement with Equations 1.2 and 2.3 of Tables 1 and 2, respectively. Under these conditions, peak potentials depend on the electrode radius on account of the parameter \(x = k' \cdot r_0/D_\lambda\) (see Equations 1.3 and 2.3 of Tables 1 and 2), such a way that these curves are shifted to more cathodic potentials with the increase of \(r_0\) (see Equations 11 and 14).

Under these conditions we have established that, by using electrodes with radii \(r_0 \leq 1.5 \times 10^{-4} \text{ cm}\), steady state responses are obtained for time values \(t \geq 0.05 \text{ s}\), with an error of less than 5%, independently of the reversibility of the process, and therefore, the numerical \(dI/dE\) vs. \(E\) and \(dI/dE\) vs. \(E\) curves obtained by differentiating Equation 1 coincide with those calculated from Equations 10, 13 and Equations 11, 14, for reversible and totally irreversible processes, respectively.

In Figure 3 we have studied the influence of the reversibility of the electrode process on the theoretical \(dI/dE\) vs. \(E\) (Figure 3.a, see Equation 7) and \(dI/dE\) vs. \(E\) curves (Figure 3.b, see Equation 12), under steady state conditions. These curves have been calculated for the application of a
linear current time function $I(t) = I_0 t$ to a spherical electrode of radius $r_0 = 1 \times 10^{-4}$ cm with $I_0/I_0(\infty) = 0.75$.

From this Figure it can be shown that the peak heights of the $dI/dt$ vs. $E$ and $dI/dE$ vs. $E$ curves decrease with the heterogeneous rate constant $k''$, in such a way that the process can be considered as totally irreversible when the peak heights in both derivative curves become independent of $k''$, as in Equations 1.4 and 2.4 in Tables 1 and 2, respectively. This behavior can be observed in these conditions for $k'' \leq 10^{-1}$ cm s$^{-1}$ [1, 26].

In Figure 4 we have plotted the theoretical $dI/dE$ vs. $E$ curves, calculated by differentiating Equation 1, corresponding to the application of a power current time function of the form $I(t) = I_0 t^u$; with $u = 1$ (solid lines) and $u = 2$ (dashed lines), to spherical electrodes of different radii, for a reversible (Figure 4.a) and a totally irreversible ($k'' = 10^{-5}$ cm s$^{-1}$, Figure 4.b) electrode process. From these curves it can be observed that the decrease of the electrode radius makes the curves corresponding to different values of the exponent $u$ become coincident, whatever the reversibility degree of the electrode process was. This independence of the $dI/dE$ vs. $E$ curve with the exponent $u$ indicates that the steady state has been reached.

Once we can assure that we are under steady state conditions ($r_0 \leq 1.5 \times 10^{-4}$ cm), the determination of the kinetic and thermodynamic parameters of the electrode process can be carried out easily using equations in Table 2 for the peak parameters of $dI/dE$ vs. $E$ curves.
4.2. Experimental Results and Discussion

We have experimentally studied the reversible oxidation of K₃IrCl₆ in KNO₃ and the totally irreversible reduction of FeCl₃ in aqueous acidic solution at different gold disk microelectrodes in order to determine the conditions under which stationary state is attained.

Figures 5 and 6 show the experimental \( \frac{dI}{dE} \) vs. \( E \) curves obtained for the reversible oxidation of K₃IrCl₆ in aqueous acidic solution at different gold disk microelectrodes in order to determine the conditions under which stationary state is attained.

In Figure 5 we have experimentally verified the theoretical prediction shown in Figure 4. In order to obtain the curves in this Figure we have applied power programmed currents of the form \( I(t) = I_{0}t^{u} \) for two values of the exponent \( u \): 0.5 (solid lines) and 0.75 (dashed lines). This Figure shows the evolution of the \( dI/dE \) vs. \( E \) curves from transient to steady state as the electrode radius decreases. This evolution is indicated by the lesser influence of the exponent \( u \) in the power current applied on these \( dI/dE \) vs. \( E \) curves, independently of the degree of reversibility of the electrode process. Thus, in order to show this behavior clearly we have calculated the relative difference between the peak heights, \( y_{p} \), of the \( dI/dE \) vs. \( E \) curves obtained for the two values of the exponent \( u \) used in each microelectrode and we have found that, for the reversible IrCl₆³⁻ system, this difference decreases from 13.2% to 0.9% for the microelectrode of \( r_{0} = 12.5 \times 10^{-3} \) cm to 0.9% for the microelectrode of \( r_{0} = 2.5 \times 10^{-3} \) cm, whereas in the case of the irreversible Fe³⁺ system, it decreases from 13.9% to 0.4%.

![Graph](image-url)
Figure 6 shows the application of two programmed currents which vary in a different way with time: a power current time function, \( I(t) = I_0 t^u \), with \( u = 0.75 \) (solid lines), and an exponential current time function, \( I(t) = I_0 e^{\omega t} \), with \( \omega = 0.5 \) s\(^{-1}\) (dashed lines). In this Figure we have also plotted the \( \frac{dI}{dE} \) vs. \( E \) curve obtained by differentiating the voltammetric \( I - E \) curve, corresponding to Cyclic Voltammetry for a sweep rate \( |v| = 0.1 \) V s\(^{-1}\) (dotted lines). Note that the chronopotentiometric and voltammetric \( \frac{dI}{dE} \) vs. \( E \) responses are logically different if we are not in stationary conditions (see curves A in Figures 6.a and 6.b). However, when the stationary state has been reached it is observed that the responses obtained for the power and the exponential current becomes coincident (see curves B in Figure 6.a and 6.b). Moreover, these responses tend to be similar to those corresponding to the derivative of the cyclic voltammogram. This fact shows again that steady state has been reached since, in these conditions, the \( \frac{dI}{dE} \) vs. \( E \) curves are even independent of the electrochemical method employed to obtain them.

Therefore, from the measurement of the peak parameters of the \( \frac{dI}{dE} \) vs. \( E \) curves of Figure 5 corresponding to the microelectrode of \( r_0 = 2.5 \times 10^{-4} \) cm, we can obtain the thermodynamic and kinetic parameters of the systems under study by applying equations of Table 2. Thus, once the values of the diffusion coefficients of \( \text{IrCl}_3^+ \) and \( \text{IrCl}_2^+ \) have been obtained (see experimental section), we have determined the formal potential of the reversible system \( \text{K}_3\text{IrCl}_6^{5-} + \text{KNO}_3^{0.25} \) M from the measurement of the peak potential, according to Equation 2.1 in Table 2, obtaining the value \( E' = 0.710 \pm 0.002 \) V (vs. Ag/AgCl/KCl 1.0 M), which is in good agreement with that reported in the literature [28]. On the other hand, we have used Equations 2.3 – 2.4 in Table 2 for the \( \frac{dI}{dE} \) vs. \( E \) curves

Fig. 3. Theoretical – \( \frac{dI}{dE} \) vs. \( E \) (Figure 3a) and \( -\frac{d(I(t)(\infty))}{dE} \) vs. \( E \) (Figure 3b) curves in steady state conditions (see Equations 5 and 10), corresponding to the application of a linear current time function, \( I(t) = I_0 t \), to a spherical microelectrode of radius \( r_0 = 10^{-4} \) cm. Values of \( k' \) (in cm s\(^{-1}\)) appear on the curves. Other conditions as in Figure 2.
to obtain the charge transfer coefficient and the heterogeneous rate constant of the Fe\(^{3+}\) reduction in HClO\(_4\) media, once the values of the diffusion coefficient of oxidized species and the formal potential of the electroactive couple are known (see experimental section). From equations in Table 2 it can be deduced that,

\[
\alpha = \frac{4RT}{nF} \gamma_p^{\infty} \tag{19}
\]

\[
\ln k^{\infty} = \frac{D_a}{r_0} \exp \left(-4\gamma_p^{\infty} \left( E_p^{\infty} - E^\circ \right) \right) \tag{20}
\]

and by using Equations 19 and 20 we have obtained the following values: \(\alpha_{\text{FeCl}_3/\text{HClO}_4} = 0.70 \pm 0.01, \) and \(\ln (k^{\infty}_{\text{FeCl}_3/\text{HClO}_4}/\text{cm s}^{-1}) = -6.0 \pm 1.0.\) These results are in line with the literature [29].

Fig. 4. Theoretical \(-d(I(t)/I_{d(\infty)})/dE vs. E\) curves for reversible \((k^{\infty} = 10^6 \text{cm s}^{-1}, \text{Figure 4a})\) and totally irreversible \((k^{\infty} = 10^{-5} \text{cm s}^{-1}, \text{Figure 4b})\) electrode processes, corresponding to the application of a power current time function, \(I(t) = I_0 t^u\), for two values of the exponent \(u\): 1 (solid lines) and 2 (dashed lines), to spherical electrodes of different radii. Values of \(r_0\) (in cm) appear on the curves. Other conditions as in Figure 2.

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5. Conclusions

Reciprocal Derivative Chronopotentiometry with programmed currents in microelectrodes under steady state conditions is presented, under two different modalities: the traditional $dI/dE$ vs. $E$ curves, which depend on the form of the programmed current applied, and the $dI/dE$ vs. $E$ curves, which do not depend on the particular characteristics of the applied current $I(t)$. These derivative signals lead to well defined peaks, whose height and position are directly related with analytical concentration and kinetic and thermodynamic information, respectively, of the systems under study, whereas the most frequently used steady state voltammetry lead to sigmoidal curves which require a more complex analysis. Moreover, stationary $dI/dE$ vs. $E$ curves are similar to those obtained by means of potentiostatic techniques, such as, Derivative Voltammetry, Differential Pulse Voltammetry and Square Wave Voltammetry.

We have analyzed the evolution of both derivative techniques from transient to steady state. In the case of reversible electrode processes, both stationary $dI/dE$ vs. $E$ curves become independent of the electrode radius, whereas for totally irreversible processes, the stationary $dI/dE$ vs. $E$ curves show peak heights independent of the electrode radius whose peak potentials vary linearly with $\ln(r_0)$, as in equations in Tables 1 and 2.

We have determined that, by using electrodes with radii $r_0 < 1.5 \times 10^{-4}$ cm, stationary responses can be obtained for...
$t > 0.05$ s, with an error of less than 5%, independently of the degree of reversibility of the process. Moreover, electrode processes behave as more irreversible the lower the electrode radius. Under the above conditions, both $\frac{dI}{dE}$ vs. $E$ and $\frac{dI}{dE}$ vs. $E$ curves of an electrode process coincide with those corresponding to totally irreversible behavior for $k^+ < 10^{-3}$ cm s$^{-1}$.

Stationary $\frac{dI}{dE}$ vs. $E$ and $\frac{dI}{dE}$ vs. $E$ curves allows us to determine easily the kinetic and thermodynamic parameters of the electrode process under study from measurements of peak potentials and peak heights, as we have experimentally verified for the reversible oxidation of K$_3$IrCl$_6$ system, and for the irreversible reduction of FeCl$_3$ system, by using programmed currents of the form $I(t) = I_0 e^{-\omega t}$ and $R(t) = I_0 e^{-\omega t}$.

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7. References

