REVERSAL AND CYCLIC CHRONOPOTENTIOMETRY WITH EXPONENTIAL CURRENT–TIME FUNCTIONS AT SPHERICAL ELECTRODES. REVERSIBILITY EFFECTS AND EXPERIMENTAL VERIFICATION

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General analytical solutions for the potential–time curves corresponding to a slow charge transfer reaction in reversal and cyclic chronopotentiometry with exponential current–time functions, $I(t) = I_0e^{wt}$, have been deduced. For obtaining these equations, the superposition principle can be applied. Our results are valid for planar and spherical electrodes of any size. We have evaluated the effects of electrode sphericity and of the reversibility of the process on the potential–time curves. The analysis of the successive potential–time responses allows to obtain accurate values of the thermodynamic and kinetic parameters of the process under study as well as to detect any possible kinetic complication. The validity of the theoretical solutions has been experimentally tested with the iron(III) trioxalate complex in aqueous solutions.

Keywords: Reversal chronopotentiometry; Cyclic chronopotentiometry; Exponential current; Spherical electrodes; Electrochemistry; Analytical solution.

General analytical equations for the potential–time curves corresponding to a simple charge transfer process in cyclic chronopotentiometry with exponential current–time functions have been derived and experimentally tested. These equations are applicable to planar electrodes and spherical electrodes of any size, and coincide with those previously derived when constant currents are used by making[1–4] $w = 0$. In order to obtain these equations, we have, in the first place, deduced the general potential–time response corresponding to current reversal chronopotentiometry with two successive exponential currents of alternating sign, and later we have demonstrated that the superposition principle can be applied even in this case, in which the current varies exponentially with time. By following a procedure similar to that indicated in previous papers[4,5], we have derived general expressions of the concentration profiles of both electroactive species par-

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ticipating in the electrode process and of the potential–time curves. The expressions are valid for any degree of reversibility, for any value of the diffusion coefficients, and for any number of exponential currents applied of the form $I(t_k) = (-1)^{k+1} I_0 \, e^{wt_k}$ with $w \geq 0$.

This solution is of great interest for using successive programmed currents of different sign since, when other current–time functions are used ($I(t) = I_0 t^u$, $I(t) = I_0 \cos(wt)$, ...), a general compact solution applicable to spherical electrodes of any radius could not be derived so far[4,6].

Our results indicate that when exponential current–time functions are used, the potential–time curves can reach the transition time, even if the electrode radius strongly decreases. However, when chronopotentiometry with constant currents is used, the potential–time response corresponding to the application of the first current tends to be time-independent and the following E/t responses tend to disappear as the electrode sphericity increases, and hence chronopotentiometric techniques with constant current cannot be used with spherical electrodes of small size[2,7,8].

Moreover, when the electrode radius decreases, the limits for which we can consider that the electrode process can behave as a reversible, quasi-reversible or totally irreversible change, and they become strongly dependent on the values of the electrode radius and on the exponent w in the programmed current applied.

We have experimentally tested the theoretical equations obtained in this paper by applying successive exponential current–time functions of the form $I(t_k) = (-1)^{k+1} I_0 \, e^{wt_k}$ to the iron(III) trioxalate complex in aqueous solutions using electrodes of different radii. Moreover, we have also determined the half-wave potential of the iron(III) trioxalate complex from the potential–time curves corresponding to the different cathodic and anodic programmed currents applied by using a simple procedure in which the plots corresponding to the successive currents must be superimposable. This method implies in itself a confirmation of the parameters obtained and it enables us to detect very easily any possible complications in the charge transfer process. For the above reasons we can conclude that reversal and cyclic chronopotentiometry with exponential currents are complete and simple techniques in characterising electrode processes.

EXPERIMENTAL

A 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 (ComputerBoards, U.S.A.) boards, respectively. All computer programmes were written in our laboratory.

In the chronopotentiometric experiments, the current switch was performed when the potential attained a predetermined value (cathodic or anodic) at which we assumed the transition time had already been reached. The necessary comparison was carried out by means of an interrupt service routine using the clock of the PC.

A three-electrode cell was employed in the experiments. A static mercury drop electrode (SMDE) served as a working electrode. The SMDE was constructed using a DME, EA 1019-1 (Metrohm), to which a home-made valve was sealed. The electrode radius of the SMDE was determined by weighing a large number of drops. The counter-electrode was a Pt foil and the reference electrode was an Ag|AgCl, 1.0 M KCl electrode. In the experimental chronopotentiometric measurements we have used different digital noise filters of the instrument supported software.

Iron(III) chloride and potassium oxalate (Merck) were of reagent grade. All chemical reagents were used without further purification.

Working solutions containing $[Fe(C_2O_4)_3]^{3-}$ were freshly prepared in order to avoid possible oxidation of the oxalate anion with Fe^{3+}. The value obtained for the redox potential of the iron(III) trioxalate complex corresponds to a series of five essays. The result obtained is the mean of the five experimental values. The error corresponds to the standard deviation.

The diffusion coefficient of $[Fe(C_2O_4)_3]^{3-}$ was determined by chronoamperometric measurements, obtaining the following value: $D_{[Fe(C_2O_4)_3]^{3-}} = (7.30 \pm 0.10) \times 10^{-6}$ cm^2 s^{-1}, which is in agreement with the values reported[9–11].

Nitrogen gas was passed through solutions for deaeration for 15 min prior to measurements.

THEORY

Application of a Programmed Current of the Form $I(t) = I_1 e^{wt}$

We will consider the following charge transfer process:

$$\mathrm{A} + n\mathrm{e}^- \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathrm{B} \qquad (I)$$

which takes place at the electrode-solution interface, where k_f and k_b are the heterogeneous rate constants of reduction (forward) and oxidation (backward) processes, respectively, and are given by[12,13]:

$$k_\mathrm{f} = k^{0'} \exp\left[\frac{-\alpha nF}{RT}\left(E(t) - E^{0'}\right)\right] \qquad (1)$$

$$k_b = k^{0'} \exp\left[\frac{(1-\alpha)nF}{RT}\left(E(t) - E^{0'}\right)\right] \tag{2}$$

with $k^{0'}$, α and $E^{0'}$ being, respectively, the apparent heterogeneous rate constant at $E^{0'}$, the charge transfer coefficient and the formal standard potential of the charge transfer process.

In order to obtain the expressions of the concentration profiles of electroactive species A and B, we must solve the following differential equations system

$$\left.\begin{aligned}\frac{\partial c_{A,1}(r,t)}{\partial t} &= D_A\left[\frac{\partial^2 c_{A,1}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial c_{A,1}(r,t)}{\partial r}\right]\\ \frac{\partial c_{B,1}(r,t)}{\partial t} &= D_B\left[\frac{\partial^2 c_{B,1}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial c_{B,1}(r,t)}{\partial r}\right]\end{aligned}\right\} \tag{3}$$

describing mass transport when we apply a current variable programmed exponentially with time, $I(t) = I_1 e^{wt}$, by taking into account the following boundary value problem that the solutions of the above system must fulfil:

$$\left.\begin{aligned}t &= 0; r \geq r_0\\ t &> 0; r \to \infty\end{aligned}\right\} \qquad \begin{aligned}c_{A,1}(r,t) &= c_A^*\\ c_{B,1}(r,t) &= c_B^*\end{aligned} \tag{4}$$

$$t > 0; r = r_0 \qquad D_A\left[\frac{\partial c_{A,1}(r,t)}{\partial r}\right]_{r=r_0} = -D_B\left[\frac{\partial c_{B,1}(r,t)}{\partial r}\right]_{r=r_0} \tag{5}$$

$$D_A\left[\frac{\partial c_{A,1}(r,t)}{\partial r}\right]_{r=r_0} = \frac{I_1 e^{wt}}{nFA}\ , \tag{6}$$

where c_A^* and c_B^* are the initial concentrations of both oxidised A and reduced B species, respectively, D_i the diffusion coefficient of the species i, i = A or B, and A the area of the stationary spherical electrode ($A = 4\pi r_0^2$, with r_0 being the electrode radius). In Eqs (*3*)–(*6*), $c_{A,1}(r,t)$, $c_{B,1}(r,t)$ are the solutions corresponding to the first exponential current applied. In all expressions appearing in this work, the subscript refers to the programmed current being considered (1, 2, ... j). By following the procedure proposed by Koutecký[14,15], the following expressions for the surface concentrations of electroactive species A and B are obtained:

$$\frac{c_{\mathrm{A},1}(r_0,t)}{c_{\mathrm{A}}^*} = 1 - N_s F(\xi_{\mathrm{A},1},\Omega_1) \tag{7}$$

$$\frac{c_{\mathrm{B},1}(r_0,t)}{c_{\mathrm{B}}^*} = \frac{c_{\mathrm{B}}^*}{c_{\mathrm{A}}^*} + \gamma N_s F(\xi_{\mathrm{B},1},\Omega_1)\ , \tag{8}$$

where

$$F(\xi_{i,j},\Omega_j) = \frac{1}{\xi_{0,i}} \frac{(\xi_{i,j})^2}{4\Omega_j - (\xi_{i,j})^2} \left\{ \exp\left(\frac{\xi_{i,j}}{2}\right)^2 \operatorname{erfc}\left(\frac{\xi_{i,j}}{2}\right) - \right.$$

$$\left. - \exp(\Omega_j)\left(1 - \frac{2\sqrt{\Omega_j}}{\xi_{i,j}} \operatorname{erf}\left(\sqrt{\Omega_j}\right)\right)\right\}$$

$$i = \mathrm{A} \text{ or } \mathrm{B};\ \ j = 1 \tag{9}$$

$$\xi_{i,1} = \frac{2\sqrt{D_i t}}{r_0} \qquad i = \mathrm{A} \text{ or } \mathrm{B} \tag{10}$$

$$N_s = \frac{2I_1}{nFA\sqrt{D_{\mathrm{A}}}\,c_{\mathrm{A}}^*} \tag{11}$$

$$\xi_{0,i} = \frac{2\sqrt{D_i}}{r_0} \qquad i = \mathrm{A} \text{ or } \mathrm{B} \tag{12}$$

$$\Omega_1 = wt \tag{13}$$

$$\gamma = \sqrt{\frac{D_{\mathrm{A}}}{D_{\mathrm{B}}}}\ . \tag{14}$$

Equations (*7*) and (*8*) are valid for spherical electrodes of any radius, including as limit cases, plane electrodes ($r_0 \to \infty$)[14,16,17] and spherical ultramicroelectrodes ($r_0 \to 0$)[7,14].

The transition time corresponding to the application of a programmed current $I(t) = I_1 \mathrm{e}^{wt}$ can be obtained by making $c_{\mathrm{A},1}(r_0, t = \tau_1) = 0$ in Eq. (*7*). Thus, the following nonexplicit expression for τ_1 is obtained:

$$F\left(\left(\xi_{A,1}\right)_{\tau_1}, \left(\Omega_1\right)_{\tau_1}\right) = \frac{1}{N_s} \tag{15}$$

where

$$\left(\xi_{i,1}\right)_{\tau_1} = \frac{2\sqrt{D_i \tau_1}}{r_0} \qquad i = \mathrm{A\ or\ B} \tag{16}$$

$$\left(\Omega_1\right)_{\tau_1} = w\tau_1 \ . \tag{17}$$

The potential–time curve corresponding to this first programmed current applied, $I_1\mathrm{e}^{wt}$, is given by

$$\frac{I_1 \mathrm{e}^{wt}}{nFAk^{0'} c_\mathrm{A}^*} \mathrm{e}^{\frac{\alpha nF}{RT}(E(t) - E^{0'})} =$$

$$= \left[1 - N_s F(\xi_{\mathrm{A},1}, \Omega_1)\right] - \mathrm{e}^{\frac{nF}{RT}(E(t) - E^{0'})} \left[\frac{c_\mathrm{B}^*}{c_\mathrm{A}^*} + \gamma N_s F(\xi_{\mathrm{B},1}, \Omega_1)\right]. \tag{18}$$

If the charge transfer process given by Eq. (*I*) is reversible ($k^{0'} \to \infty$), Eq. (*18*) takes the following simpler form:

$$E(t) = E_\mathrm{rev}^{1/2} + \frac{RT}{nF} \ln g_\mathrm{rev}^\mathrm{c} \tag{19}$$

with

$$E_\mathrm{rev}^{1/2} = E^{0'} + \frac{RT}{nF} \ln \frac{1}{\gamma} \tag{20}$$

$$g_\mathrm{rev}^\mathrm{c} = \frac{1 - N_s F(\xi_{\mathrm{A},1}, \Omega_1)}{c_\mathrm{B}^* / c_\mathrm{A}^* \gamma + N_s F(\xi_{\mathrm{B},1}, \Omega_1)} \ . \tag{21}$$

$E_\mathrm{rev}^{1/2}$ is the so called half wave reversible potential of the process[12,13].

If the charge transfer process given by Eq. (*I*) is totally irreversible, the general equation for the potential–time curve becomes

$$E(t) = E^{0'} + \frac{RT}{\alpha nF} \ln \frac{2k^{0'}}{N_s \sqrt{D_A}} + \frac{RT}{\alpha nF} \ln g^{c}_{irrev} \tag{22}$$

with

$$g^{c}_{irrev} = \frac{1 - N_s F(\xi_{A,1}, \Omega_1)}{e^{\Omega_1}} . \tag{23}$$

Current Reversal Chronopotentiometry

We will consecutively apply a second exponential current of the opposite sign, $-I_2 \, e^{wt_2}$, to the first current, without re-establishing the equilibrium of the electrode solution interface. This second current is applied in the time interval $0 \le t_2 \le \tau_2$, with τ_2 being the transition time corresponding to the oxidation of species B. Under these conditions, the total time is given by

$$t = \tau_1 + t_2 . \tag{24}$$

$c_{A,2}(r,t)$ and $c_{B,2}(r,t)$ are the solutions corresponding to the new current applied.

The differential equation system that describes the mass transport is

$$\left. \begin{aligned} \frac{\partial c_{A,2}(r,t)}{\partial t} &= D_A \left[\frac{\partial^2 c_{A,2}(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c_{A,2}(r,t)}{\partial r} \right] \\ \frac{\partial c_{B,2}(r,t)}{\partial t} &= D_B \left[\frac{\partial^2 c_{B,2}(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c_{B,2}(r,t)}{\partial r} \right] \end{aligned} \right\} . \tag{25}$$

The boundary value problem that the solutions of the differential equation system given by the equation system (*25*) for the second programmed current applied must fulfil is the following:

$$\left. \begin{aligned} t_2 &= 0; r \ge r_0 \\ t_2 &> 0; r \to \infty \end{aligned} \right\} \qquad \begin{aligned} c_{A,2}(r,t) &= c_{A,1}(r, t = \tau_1) \\ c_{B,2}(r,t) &= c_{B,1}(r, t = \tau_1) \end{aligned} \tag{26}$$

$$t_2 > 0; r = r_0 \qquad D_\mathrm{A}\left[\frac{\partial c_{\mathrm{A},2}(r,t)}{\partial r}\right]_{r=r_0} = -D_\mathrm{B}\left[\frac{\partial c_{\mathrm{B},2}(r,t)}{\partial r}\right]_{r=r_0} \tag{27}$$

$$D_\mathrm{B}\left[\frac{\partial c_{\mathrm{B},2}(r,t)}{\partial r}\right]_{r=r_0} = \frac{I_2 \mathrm{e}^{wt_2}}{nFA} . \tag{28}$$

Due to the linearity of the equation system (*25*), the solutions corresponding to the second programmed current, $c_{\mathrm{A},2}(r,t)$ and $c_{\mathrm{B},2}(r,t)$, can be expressed in the following manner:

$$\left.\begin{aligned} c_{\mathrm{A},2}(r,t) &= c_{\mathrm{A},1}(r,t) + \tilde{c}_{\mathrm{A},2}(r,t_2) \\ c_{\mathrm{B},2}(r,t) &= c_{\mathrm{B},1}(r,t) + \tilde{c}_{\mathrm{B},2}(r,t_2) \end{aligned}\right\} , \tag{29}$$

where $c_{\mathrm{A},1}(r,t)$ and $c_{\mathrm{B},1}(r,t)$ are the solutions found for the application of the first programmed current (given by Eqs (*7*) and (*8*)), and $\tilde{c}_{\mathrm{A},2}(r,t_2)$ and $\tilde{c}_{\mathrm{B},2}(r,t_2)$ are new unknown functions to be determined.

By taking into account Eqs (*3*)–(*6*) and (*29*), the system (*25*) and the boundary value problem given by Eqs (*26*)–(*28*) are transformed into

$$\left.\begin{aligned} \frac{\partial \tilde{c}_{\mathrm{A},2}(r,t_2)}{\partial t} &= D_\mathrm{A}\left[\frac{\partial^2 \tilde{c}_{\mathrm{A},2}(r,t_2)}{\partial r^2} + \frac{2}{r}\frac{\partial \tilde{c}_{\mathrm{A},2}(r,t_2)}{\partial r}\right] \\ \frac{\partial \tilde{c}_{\mathrm{B},2}(r,t_2)}{\partial t} &= D_\mathrm{B}\left[\frac{\partial^2 \tilde{c}_{\mathrm{B},2}(r,t_2)}{\partial r^2} + \frac{2}{r}\frac{\partial \tilde{c}_{\mathrm{B},2}(r,t_2)}{\partial r}\right] \end{aligned}\right\} \tag{30}$$

$$\left.\begin{aligned} t_2 &= 0; r \ge r_0 \\ t_2 &> 0; r \to \infty \end{aligned}\right\} \qquad \begin{aligned} \tilde{c}_{\mathrm{A},2}(r,t_2) &= 0 \\ \tilde{c}_{\mathrm{B},2}(r,t_2) &= 0 \end{aligned} \tag{31}$$

$$t_2 > 0; r = r_0 \qquad D_\mathrm{A}\left[\frac{\partial \tilde{c}_{\mathrm{A},2}(r,t_2)}{\partial r}\right]_{r=r_0} = -D_\mathrm{B}\left[\frac{\partial \tilde{c}_{\mathrm{B},2}(r,t_2)}{\partial r}\right]_{r=r_0} \tag{32}$$

$$D_\mathrm{B}\left[\frac{\partial \tilde{c}_{\mathrm{B},2}(r,t_2)}{\partial r}\right]_{r=r_0} = \frac{I_2 \mathrm{e}^{wt_2}}{nFA}\left(1 + \frac{I_1}{I_2}\mathrm{e}^{w\tau_1}\right) . \tag{33}$$

As can be seen, the differential equation system (*3*), whose solutions correspond to the first exponential current applied, $c_{\mathrm{A},1}(r,t)$ and $c_{\mathrm{B},1}(r,t)$, is identical to that corresponding to the new unknown partial solutions of the second exponential current applied, $\tilde{c}_{\mathrm{A},2}(r,t_2)$ and $\tilde{c}_{\mathrm{B},2}(r,t_2)$, given by Eq. (*30*). By following the procedure indicated in[1,4,5,14,15], we derive the expressions for $\tilde{c}_{\mathrm{A},2}(r_0,t_2)$ and $\tilde{c}_{\mathrm{B},2}(r_0,t_2)$.

From Eq. (*29*), we obtain the following expressions for the surface concentrations of both species A and B, corresponding to the application of the second exponential current:

$$\frac{c_{\mathrm{A},2}(r_0,t)}{c_\mathrm{A}^*} = 1 - N_s\left[F(\xi_{\mathrm{A},1},\Omega_1) - \left(\frac{I_2}{I_1} + \mathrm{e}^{w\tau_1}\right)F(\xi_{\mathrm{A},2},\Omega_2)\right] \tag{34}$$

$$\frac{c_{\mathrm{B},2}(r_0,t)}{c_\mathrm{A}^*} = \frac{c_\mathrm{B}^*}{c_\mathrm{A}^*} + N_s\gamma\left[F(\xi_{\mathrm{B},1},\Omega_1) - \left(\frac{I_2}{I_1} + \mathrm{e}^{w\tau_1}\right)F(\xi_{\mathrm{B},2},\Omega_2)\right], \tag{35}$$

where $F(\xi_{i,j},\Omega_j)$ is given by Eq. (*9*), with i = A or B, and j = 1 or 2.

Moreover:

$$\xi_{i,1} = \frac{2\sqrt{D_i t_{1,2}}}{r_0} \qquad i = \mathrm{A\ or\ B} \tag{36}$$

$$\xi_{i,2} = \frac{2\sqrt{D_i t_{2,2}}}{r_0} \qquad i = \mathrm{A\ or\ B} \tag{37}$$

$$\Omega_1 = wt_{1,2} \tag{38}$$

$$\Omega_2 = wt_{2,2} \tag{39}$$

$$t_{1,2} = \tau_1 + t_2 \tag{40}$$

$$t_{2,2} = t_2 \;. \tag{41}$$

Equations (*34*) and (*35*) are valid for spherical electrodes of any size, including as limit cases, plane electrodes ($r_0 \to \infty$) and spherical ultramicroelectrodes ($r_0 \to 0$).

The transition time for the second programmed current applied can be obtained by making $c_{\mathrm{B},2}(r_0, t = \tau_1 + \tau_2)$ in Eq. (*35*). Thus, for $t = \tau_1 + \tau_2$ the following nonexplicit expression must be fulfilled:

$$\frac{c_\mathrm{B}^*}{c_\mathrm{A}^*} + N_s \gamma F\left((\xi_{\mathrm{B},1})_{\tau_{1,2}}, (\Omega_1)_{\tau_{1,2}}\right) = \left(\frac{I_2}{I_1} + \mathrm{e}^{w\tau_1}\right) N_s \gamma F\left((\xi_{\mathrm{B},2})_{\tau_{2,2}}, (\Omega_2)_{\tau_{2,2}}\right) \qquad (42)$$

with $(\xi_{\mathrm{B},1})_{\tau_{1,2}}$ and $(\xi_{\mathrm{B},2})_{\tau_{2,2}}$ given by Eqs (*36*) and (*37*) with $t_{1,2} = \tau_1 + \tau_2$ and $t_{2,2} = \tau_2$, respectively, and $(\Omega_1)_{\tau_{1,2}}$ and $(\Omega_2)_{\tau_{2,2}}$ given by Eqs (*38*) and (*39*) with $t_{1,2} = \tau_1 + \tau_2$ and $t_{2,2} = \tau_2$.

If species B is not initially present in the solution ($c_\mathrm{B}^* = 0$), Eq. (*42*) takes the following simpler form:

$$\frac{F\left((\xi_{\mathrm{B},1})_{\tau_{1,2}}, (\Omega_1)_{\tau_{1,2}}\right)}{F\left((\xi_{\mathrm{B},2})_{\tau_{2,2}}, (\Omega_2)_{\tau_{2,2}}\right)} = \frac{I_2}{I_1} + \mathrm{e}^{w\tau_1}, \qquad (43)$$

where $F((\xi_{\mathrm{B},j})_{\tau_{j,2}}, (\Omega_j)_{\tau_{j,2}})$ is obtained by substituting $\xi_{\mathrm{B},j}$ by $(\xi_{\mathrm{B},j})_{\tau_{j,2}}$ and Ω_j by $(\Omega_j)_{\tau_{j,2}}$, with $j = 1$ or 2 in Eq. (*9*).

The potential–time curve corresponding to the second exponential current applied is given by

$$\frac{-I_2 \mathrm{e}^{wt_2}}{nFAk^{0'} c_\mathrm{A}^*} \mathrm{e}^{\frac{\alpha nF}{RT}(E(t) - E^{0'})} = \left\{1 - N_s \left[F(\xi_{\mathrm{A},1}, \Omega_1) - \left(\frac{I_2}{I_1} + \mathrm{e}^{w\tau_1}\right) F(\xi_{\mathrm{A},2}, \Omega_2)\right]\right\} -$$

$$- \mathrm{e}^{\frac{nF}{RT}(E(t) - E^{0'})} \left\{\frac{c_\mathrm{B}^*}{c_\mathrm{A}^*} + N_s \gamma \left[F(\xi_{\mathrm{B},1}, \Omega_1) - \left(\frac{I_2}{I_1} + \mathrm{e}^{w\tau_1}\right) F(\xi_{\mathrm{B},2}, \Omega_2)\right]\right\}. \qquad (44)$$

In the case of a reversible charge transfer process, $k^{0'} \to \infty$, general equation (*44*) becomes:

$$E(t) = E_\mathrm{rev}^{1/2} + \frac{RT}{nF} \ln g_\mathrm{rev}^\mathrm{a}, \qquad (45)$$

where $E_\mathrm{rev}^{1/2}$ is defined in Eq. (*20*) and

$$g^{\mathrm{a}}_{\mathrm{rev}} = \frac{1 - N_s\left[F(\xi_{\mathrm{A},1},\Omega_1) - \left(\frac{I_1}{I_2} + \mathrm{e}^{w\tau_1}\right)F(\xi_{\mathrm{A},2},\Omega_2)\right]}{\frac{c^*_{\mathrm{B}}}{\gamma c^*_{\mathrm{A}}} + N_s\left[F(\xi_{\mathrm{B},1},\Omega_1) - \left(\frac{I_1}{I_2} + \mathrm{e}^{w\tau_1}\right)F(\xi_{\mathrm{B},2},\Omega_2)\right]} \,. \tag{46}$$

When the electrode process is totally irreversible ($k^{0'} << 1$ cm s^{-1}), general equation (*44*) takes the following form:

$$E(t) = E^{0'} - \frac{RT}{(1-\alpha)nF}\ln\frac{2k^{0'}}{N_s\sqrt{D_{\mathrm{A}}}} - \frac{RT}{(1-\alpha)nF}\ln g^{\mathrm{a}}_{\mathrm{irrev}} \,, \tag{47}$$

where

$$g^{\mathrm{a}}_{\mathrm{irrev}} = \frac{\frac{c^*_{\mathrm{B}}}{c^*_{\mathrm{A}}} + N_s\gamma\left[F(\xi_{\mathrm{B},1},\Omega_1) - \left(\frac{I_1}{I_2} + \mathrm{e}^{w\tau_1}\right)F(\xi_{\mathrm{B},2},\Omega_2)\right]}{\mathrm{e}^{\Omega_2}} \,. \tag{48}$$

Cyclic Chronopotentiometry

In this section we will consider the application to the electrode of a series of *n* successive programmed currents of alternating sign which vary exponentially with time according to the following scheme:

$$\begin{array}{ll}
I_1\mathrm{e}^{wt_1} & 0 \le t_1 \le \tau_1 \\
-I_2\mathrm{e}^{wt_2} & 0 \le t_2 \le \tau_2 \\
. & . \\
. & . \\
. & . \\
(-1)^{k+1}I_k\mathrm{e}^{wt_k} & 0 \le t_k \le \tau_k \\
. & . \\
. & . \\
. & . \\
(-1)^{n+1}I_n\mathrm{e}^{wt_n} & 0 \le t_n \le \tau_n \,.
\end{array} \tag{49}$$

Here, I_k ($1 \le k \le n$) is the absolute value of the current amplitude of each exponential current applied, t_k is the time during which the k-th programmed current is applied, and τ_k is the transition time corresponding to the k-th programmed current applied. Therefore, the total time elapsed between the application of the first and k-th exponential current is given by

$$t = \tau_1 + \tau_2 + \ldots + \tau_{k-1} + t_k \ . \tag{50}$$

The mathematical treatment employed in the resolution of the differential equation systems that describe the mass transport to the electrode for the first and second exponential current applied can be generalized by induction. Thus, by applying the superposition principle[18–21], we can deduce that the concentration profiles of both electroactive species $c_{i,k}(r,t)$, i = A or B, for the k-th programmed current applied, take the following forms:

$$c_{\mathrm{A},k}(r,t) = c_{\mathrm{A},k-1}(r,t) + \tilde{c}_{\mathrm{A},k}(r,t_k) \quad k > 1 \tag{51}$$

$$c_{\mathrm{B},k}(r,t) = c_{\mathrm{B},k-1}(r,t) + \tilde{c}_{\mathrm{B},k}(r,t_k) \quad k > 1 \ , \tag{52}$$

where $c_{i,k-1}(r,t)$, i = A or B, are the solutions corresponding to the application of the (k – 1)-th exponential current applied:

$$c_{\mathrm{A},k-1}(r,t) = c_{\mathrm{A},1}(r,t) + \sum_{j=2}^{k-1} \tilde{c}_{\mathrm{A},j}(r,t_j) \tag{53}$$

$$c_{\mathrm{B},k-1}(r,t) = c_{\mathrm{B},1}(r,t) + \sum_{j=2}^{k-1} \tilde{c}_{\mathrm{B},j}(r,t_j) \ . \tag{54}$$

The differential equation system that describes the mass transport and its boundary value problem now takes the following form:

$$\left.\begin{aligned}\frac{\partial \tilde{c}_{\mathrm{A},k}(r,t_k)}{\partial t} &= D_{\mathrm{A}}\left[\frac{\partial^2 \tilde{c}_{\mathrm{A},k}(r,t_k)}{\partial r^2} + \frac{2}{r}\frac{\partial \tilde{c}_{\mathrm{A},k}(r,t_k)}{\partial r}\right] \\ \frac{\partial \tilde{c}_{\mathrm{B},k}(r,t_k)}{\partial t} &= D_{\mathrm{B}}\left[\frac{\partial^2 \tilde{c}_{\mathrm{B},k}(r,t_k)}{\partial r^2} + \frac{2}{r}\frac{\partial \tilde{c}_{\mathrm{B},k}(r,t_k)}{\partial r}\right]\end{aligned}\right\} \tag{55}$$

$$\left.\begin{aligned} t_k &= 0; r \geq r_0 \\ t_k &> 0; r \to \infty \end{aligned}\right\} \qquad \begin{aligned}\tilde{c}_{\mathrm{A},k}(r,t_k) = 0 \\ \tilde{c}_{\mathrm{B},k}(r,t_k) = 0\end{aligned} \tag{56}$$

$$t_k > 0; r = r_0$$

$$D_{\mathrm{A}}\left[\frac{\partial \tilde{c}_{\mathrm{A},k}(r,t_k)}{\partial r}\right]_{r=r_0} = -D_{\mathrm{B}}\left[\frac{\partial \tilde{c}_{\mathrm{B},k}(r,t_k)}{\partial r}\right]_{r=r_0} = \frac{(-1)^{k+1} I_k \mathrm{e}^{wt_k}}{nFA}\left(1 + \frac{I_{k-1}}{I_k}\mathrm{e}^{w\tau_{k-1}}\right). \tag{57}$$

By comparing equation system (*55*) and the boundary value problem (*56*) and (*57*) with Eqs (*30*) and (*31*)–(*33*), respectively, we deduce inmediately that it is possible to apply the superposition principle, and we can generalize the expressions for the surface concentrations corresponding to the application of *k* programmed currents, which vary exponentially with time, where *k* is any number,

$$\frac{c_{\mathrm{A},k}(r_0,t)}{c_{\mathrm{A}}^*} = 1 - N_s\left[F(\xi_{\mathrm{A},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\frac{I_{j-1}}{I_1}\left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{A},j},\Omega_j)\right] \tag{58}$$

$$\frac{c_{\mathrm{B},k}(r_0,t)}{c_{\mathrm{A}}^*} = \frac{c_{\mathrm{B}}^*}{c_{\mathrm{A}}^*} + N_s\gamma\left[F(\xi_{\mathrm{B},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\frac{I_{j-1}}{I_1}\left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{B},j},\Omega_j)\right], \tag{59}$$

where $F(\xi_{i,j},\Omega_j)$ is given by Eq. (*9*) with i = A or B, and $j = 1, 2, \ldots k$. Moreover

$$\xi_{i,j} = \frac{2\sqrt{D_i t_{j,k}}}{r_0} \qquad i = \mathrm{A\ or\ B}; \quad j = 1, 2, \ldots k \tag{60}$$

$$\Omega_j = wt_{j,k} \qquad j = 1, 2, \dots k \tag{61}$$

$$t_{j,k} = \sum_{p=j}^{k-1} \tau_p + t_k \tag{62}$$

$$t_{k,k} = t_k \ . \tag{63}$$

The expressions for the surface concentrations given in Eqs (*58*) and (*59*) allow to obtain, as particular cases, the solutions corresponding to a plane electrode of constant area and a spherical microelectrode. Thus, the function $F(\xi_{i,j},\Omega_j)$, given by Eq. (*9*) with i = A or B and $j = 1, 2, \dots k$, takes the following simpler form for the case of a plane electrode ($r_0 \to \infty$, $\xi_{i,j} \to 0$)

$$F(\xi_{i,j} \to 0, \Omega_j) = F_{\text{plane}}(\Omega_j) = \frac{1}{2\sqrt{w}} \exp(\Omega_j) \operatorname{erf}\left(\sqrt{\Omega_j}\right)$$

$$i = \text{A or B}; \quad j = 1, 2, \dots k \ , \tag{64}$$

whereas for the case of a spherical microelectrode, $F(\xi_{i,j},\Omega_j)$ becomes ($r_0 \to 0$, $\xi_{i,j} \to \infty$)

$$F(\xi_{i,j} >> 1, \Omega_j) = F_{\text{micro}}(\Omega_j) = \frac{1}{\xi_{0,i}} \exp(\Omega_j) \qquad i = \text{A or B}; \quad j = 1, 2, \dots k \ . \tag{65}$$

The expression for the transition time corresponding to the k-th exponential current applied, $(-1)^{k+1} I_k \mathrm{e}^{wt_k}$, can be obtained by making $c_{\text{A},k}(r_0, t = \tau_k) = 0$ for k odd, or $c_{\text{B},k}(r_0, t = \tau_k) = 0$ for k even, in Eqs (*58*) or (*59*), respectively. In this way, nonexplicit expressions for transition time are obtained:

a) k odd

$$\frac{1}{N_s} = F(\xi_{\text{A},1}, \Omega_1)_{\tau_{1,k}} + \sum_{j=2}^{k} (-1)^{j+1} \frac{I_{j-1}}{I_1} \left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}} \right) F(\xi_{\text{A},j}, \Omega_j)_{\tau_{j,k}} \tag{66}$$

b) k even

$$\frac{-c_{\text{B}}^*}{\gamma c_{\text{A}}^* N_s} = F(\xi_{\text{B},1}, \Omega_1)_{\tau_{1,k}} + \sum_{j=2}^{k} (-1)^{j+1} \frac{I_{j-1}}{I_1} \left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}} \right) F(\xi_{\text{B},j}, \Omega_j)_{\tau_{j,k}} \ . \tag{67}$$

The potential–time response corresponding to the *k*-th exponential current applied, $(-1)^{k+1} I_k \mathrm{e}^{wt_k}$, is given by

$$\frac{(-1)^{k+1} I_k \mathrm{e}^{wt_k}}{nFAk^{0'}} \mathrm{e}^{\frac{\alpha nF}{RT}(E(t)-E^{0'})} =$$

$$= \left\{1 - N_s\left[F(\xi_{\mathrm{A},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\frac{I_{j-1}}{I_1}\left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{A},j},\Omega_j)\right]\right\} - \mathrm{e}^{\frac{nF}{RT}(E(t)-E^{0'})} \times$$

$$\times \left\{\frac{c_\mathrm{B}^*}{c_\mathrm{A}^*} + N_s\gamma\left[F(\xi_{\mathrm{B},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\frac{I_{j-1}}{I_1}\left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{B},j},\Omega_j)\right]\right\}, \qquad (68)$$

which, for the case of a reversible electrode process, becomes ($k^{0'} \to \infty$):

$$E(t) = E_{\mathrm{rev}}^{1/2} + \frac{RT}{nF}\ln g_{\mathrm{rev}}\ , \qquad (69)$$

with $E_{\mathrm{rev}}^{1/2}$ given by Eq. (*20*) and

$$g_{\mathrm{rev}} = \frac{1 - N_s\left[F(\xi_{\mathrm{A},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\frac{I_{j-1}}{I_1}\left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{A},j},\Omega_j)\right]}{\frac{c_\mathrm{B}^*}{\gamma c_\mathrm{A}^*} + N_s\left[F(\xi_{\mathrm{B},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\frac{I_{j-1}}{I_1}\left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{B},j},\Omega_j)\right]}, \qquad (70)$$

whereas for a totally irreversible process, Eq. (*68*) becomes:

a) *k* odd (irreversible cathodic *E*/*t* curve)

$$E(t) = E^{0'} + \frac{RT}{\alpha nF}\ln\frac{2k^{0'}}{N_s\sqrt{D_\mathrm{A}}} + \frac{RT}{\alpha nF}\ln g_{\mathrm{irrev}}^{\mathrm{c}}\ , \qquad (71)$$

where

$$g_{\mathrm{irrev}}^{\mathrm{c}} = \frac{1 - N_s\left[F(\xi_{\mathrm{A},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\frac{I_{j-1}}{I_1}\left(\frac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{A},j},\Omega_j)\right]}{\frac{I_k}{I_1}\mathrm{e}^{wt_k}} \qquad (72)$$

b) *k* even (irreversible anodic *E*/*t* curve)

$$E(t) = E^{0'} - \frac{RT}{(1-\alpha)nF}\ln\frac{2k^{0'}}{N_s\sqrt{D_\mathrm{A}}} - \frac{RT}{(1-\alpha)nF}\ln g^{\mathrm{a}}_{\mathrm{irrev}} \qquad (73)$$

with

$$g^{\mathrm{a}}_{\mathrm{irrev}} = \frac{\dfrac{c^*_\mathrm{B}}{c^*_\mathrm{A}} + N_s\gamma\left[F(\xi_{\mathrm{B},1},\Omega_1) + \sum_{j=2}^{k}(-1)^{j+1}\dfrac{I_{j-1}}{I_1}\left(\dfrac{I_j}{I_{j-1}} + \mathrm{e}^{w\tau_{j-1}}\right)F(\xi_{\mathrm{B},j},\Omega_j)\right]}{\dfrac{I_k}{I_1}\mathrm{e}^{wt_k}}\,. \qquad (74)$$

RESULTS AND DISCUSSION

Current Reversal Chronopotentiometry with Exponential Currents of the Form $I(t_j) = (-1)^{j+1} I_0\, e^{wt_j}$

a) Transition Times

Figure 1 shows the variation with the electrode sphericity (through the parameter $\xi_{0,\mathrm{A}} = 2\sqrt{D_\mathrm{A}}/r_0$) of the transition times τ_1 (see Fig. 1a and Eq. (*15*)), τ_2 (see Fig. 1b and Eq. (*43*)), and of the ratio τ_2/τ_1 (see Fig. 1c), corresponding to the application of two successive exponential currents of the form $I(t) = I_0\mathrm{e}^{wt}$ and $I(t_2) = -I_0\mathrm{e}^{wt_2}$, to spherical electrodes. These curves have been obtained for different values of the exponent *w* in both programmed currents applied by assuming that $c^*_\mathrm{B} = 0$ and N_s = 1 $\mathrm{s}^{-1/2}$.

From Fig. 1a we can see that τ_1 always increases with $\xi_{0,\mathrm{A}}$, the more so the lower *w* is (see curves with *w* = 0.1 s^{-1}), whereas the τ_2 values shown in Fig. 1b remain practically constant with $\xi_{0,\mathrm{A}}$ for *w* > 0. Thus, the relationship τ_2/τ_1 decreases with $\xi_{0,\mathrm{A}}$ for any value of *w* in the applied currents and the decrease is the more evident, the lower is *w* (see Fig. 1c). It can also be observed that, for a given value of $\xi_{0,\mathrm{A}}$ (in Figs 1a and 1b we have marked $\xi_{0,\mathrm{A}}$ = 0.5 $\mathrm{s}^{-1/2}$), τ_1 and τ_2 increase if *w* decreases.

In the case corresponding to the application of two successive current steps of alternating sign (see curves with *w* = 0 in Figs 1a and 1b), we can see that τ_1 increases markedly with $\xi_{0,\mathrm{A}}$, to the extent that for $\xi_{0,\mathrm{A}}$ values larger than 1.6 $\mathrm{s}^{-1/2}$ we can consider τ_1 is not reached. A similar behaviour can be observed for τ_2, although the increase in τ_1 is more evident. The rela-

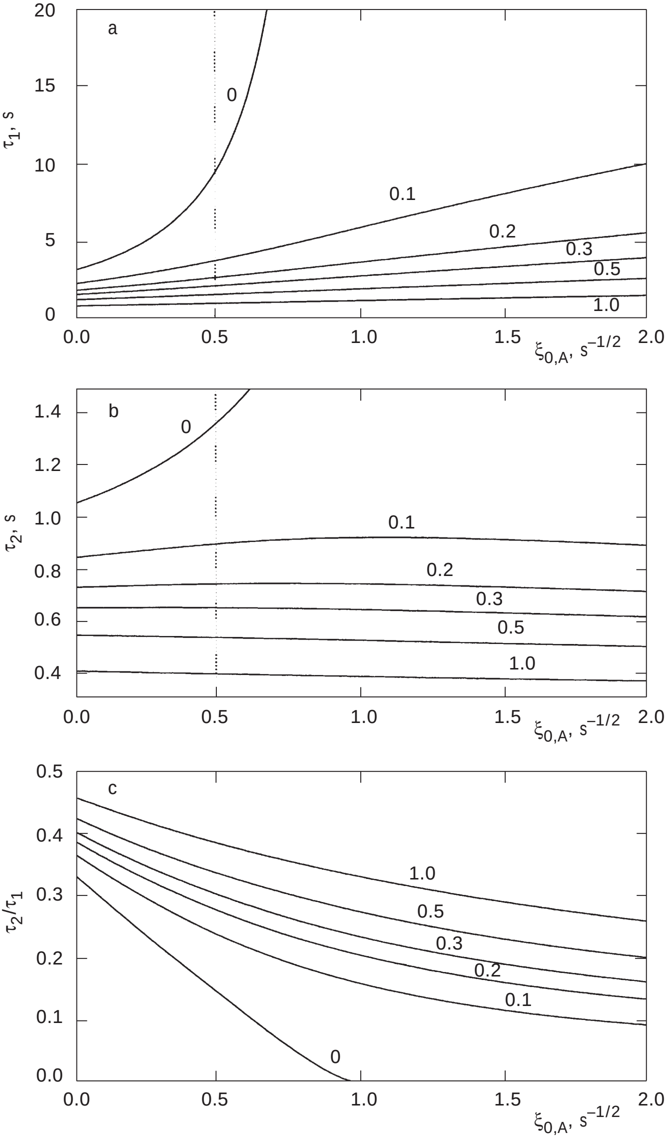

FIG. 1

Theoretical variation of τ_1 (a, Eq. (*15*)), τ_2 (b, Eq. (*43*)) and of the relationship τ_2/τ_1 (c) with the electrode sphericity, $\xi_{0,A}$, corresponding to the application of current reversal chronopotentiometry with exponential currents, $I(t) = I_0 e^{wt}$ and $I(t_2) = -I_0 e^{wt_2}$. $N_s = 1\ s^{-1/2}$, $D_A = 10^{-5}$ cm s^{-1}, $\gamma = 1$, $c_B^* = 0$. The values of the exponent w (in s^{-1}) in both programmed currents applied are shown on the curves tionship τ_2/τ_1 quickly decreases to values close to zero (see curve with $w = 0$ in Fig. 1c). This fact indicates that the use of current reversal chronopotentiometry with current steps is not suitable with spherical electrodes of small size.

b) Potential–Time Curves

Figure 2 shows the theoretical potential–time curves calculated from Eqs (*18*) and (*44*) corresponding to the application of current reversal chronopotentiometry with exponential currents, $I(t) = I_0 e^{wt}$ and $I(t_2) = -I_0 e^{wt_2}$, to a spherical electrode with $\xi_{0,A} = 0.2\ s^{-1/2}$. These curves have been obtained for different values of the heterogeneous rate constant of the charge transfer process, $k^{0'}$, with $\alpha = 0.5$, and they show that the decrease in $k^{0'}$, and, therefore, the increase of the irreversibility of the electrode process, makes the curves corresponding to the first cathodic current tend towards more negative potentials, whereas those corresponding to the second anodic programmed current are shifted towards more positive potentials. Hence, the separation between both responses increases. The variation of $k^{0'}$ logically does not affect the cathodic and anodic transition times, τ_1 and τ_2. If we analyze the dependence of the potential–time curves on the heterogeneous rate constant $k^{0'}$ with spherical electrodes of conven-

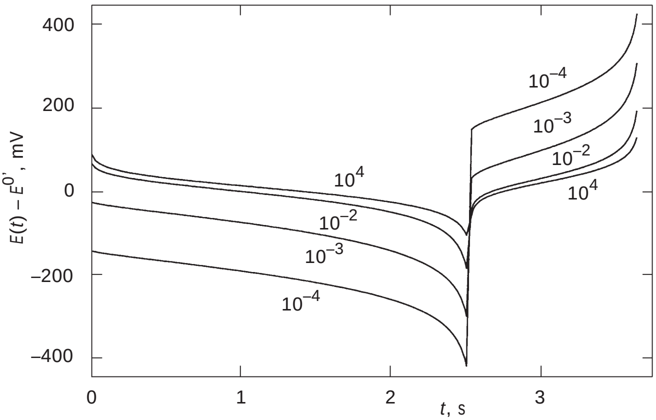

FIG. 2
Influence of $k^{0'}$ in the theoretical $E(t) - E^{0'}/t$ curves (Eqs (*18*) and (*44*)) corresponding to the application of current reversal chronopotentiometry with exponential currents, $I(t) = I_0 e^{wt}$ and $I(t_2) = -I_0 e^{wt_2}$, to a spherical electrode. $N_s = 0.5\ s^{-1/2}$, $w = 0.5\ s^{-1}$, $\xi_{0,A} = 0.2\ s^{-1/2}$, $n = 1$, $\alpha = 0.5$, $T = 298$ K. The values of $k^{0'}$ (in cm s^{-1}) are shown on the curves. For other conditions, see Fig. 1

tional size, we can deduce that the electrode process given by scheme (*I*) can be considered as quasireversible if $5 \times 10^{-3} \le k^{0'} \le 0.1$ cm s^{-1}. In this case we cannot use any simplification in the general equations (*18*) and (*44*) for the potential–time curves. If $k^{0'} \le 5 \times 10^{-3}$ cm s^{-1}, the results obtained with general Eqs (*18*) and (*44*) hardly differ from those obtained with simplified Eqs (*22*) and (*47*). Thus, under these conditions, the process can be considered as totally irreversible. Finally, if $k^{0'} \ge 0.1$ cm s^{-1} the electrode process behaves as reversible and is totally defined by simplified Eqs (*19*) and (*45*).

The limits discussed above for which we can consider the electrode process as reversible, quasireversible or totally irreversible are not valid when spherical electrodes of micrometric dimensions are used. Thus, the reversibility intervals of the process change with w and with the electrode radius such that a decrease in r_0 and/or an increase in w makes the potential–time response more irreversible.

In order to show this effect, in Fig. 3 we have plotted theoretical potential–time curves obtained with general equations (*18*) and (*44*), which are applicable to the electrode process for any value of $k^{0'}$ (solid lines), and with Eqs (*22*) and (*47*) (dashed lines), corresponding to a totally irreversible behaviour, for a process with $k^{0'} = 5 \times 10^{-3}$ cm s^{-1} with a spherical electrode for three values of the parameter $\xi_{0,\mathrm{A}} (= 2\sqrt{D_\mathrm{A}} / r_0)$. As is evident, on using

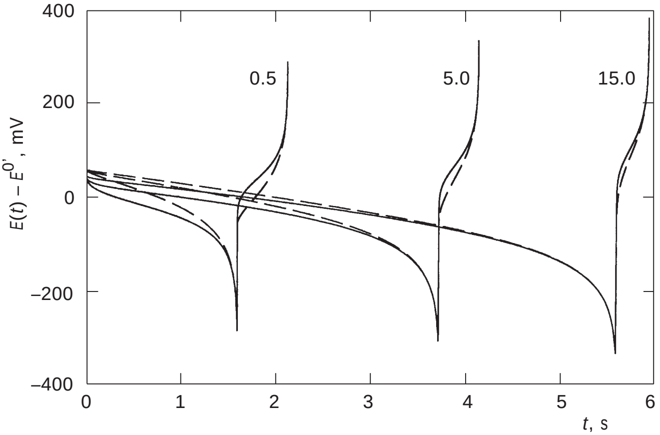

FIG. 3
Influence of the electrode sphericity on the theoretical cathodic and anodic potential–time curves corresponding to the application of current reversal chronopotentiometry with exponential currents, $I(t) = I_0 e^{wt}$ and $I(t_2) = -I_0 e^{wt_2}$, calculated from Eqs (*18*) and (*44*) (solid lines) for quasireversible processes, and Eqs (*22*) and (*47*) (dashed lines) for totally irreversible ones. $w = 0.5$ s^{-1}, $N_s = 1$ s$^{-1/2}$, $k^{0'} = 5 \times 10^{-3}$ cm s^{-1}, $\alpha = 0.5$. The values of $\xi_{0,\mathrm{A}}$ (= $2\sqrt{D_A} / r_0$), in s$^{-1/2}$, appear on the curves. For other conditions, see Fig. 2

electrodes of lower radius (higher $\xi_{0,A}$ values), this process behaves as totally irreversible (see curves with $\xi_{0,A}$ = 15 $s^{-1/2}$, r_0 = 4.2 × 10^{-4} cm if D_A = 10^{-5} cm^2 s^{-1}), and Eqs (*22*) and (*47*) can be used instead of Eqs (*18*) and (*44*) (which have no explicit form) in order to calculate kinetic parameters.

Thus, a quasireversible electrode process can behave as reversible or totally irreversible by changing the electrode radius and/or the value of *w* in the exponential applied current.

In Fig. 4 we have plotted the experimental cathodic and anodic chronopotentiograms for the reduction and subsequent reoxidation of 5 mM $[Fe(C_2O_4)_3]^{3-}$ in 0.25 M $K_2C_2O_4$ (pH 4.77) when current reversal chronopotentiometry with exponential currents, I_0e^{wt} and $-I_0e^{wt_2}$, w = 0.3 s^{-1}, are applied to a SMDE for two different values of the electrode radius, and the same value of N_s = 1.51 $s^{-1/2}$. From these curves, we can see that the effect exerted by the electrode sphericity is very important, reaching its maximum for *t* values close to the direct (τ_1) and reverse (τ_2) transition times. It can also be observed in this figure that the decrease in the electrode radius gives raises an increase in τ_1, whereas τ_2 remains practically unaltered. In such a way the ratio τ_2/τ_1 decreases, the fact that has been previously pointed out theoretically (see Fig. 1).

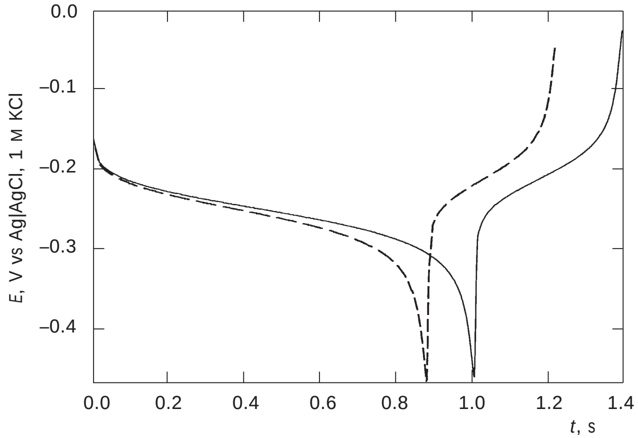

FIG. 4
Experimental $E(t)/t$ curves obtained for the application of current reversal chronopotentiometry with exponential currents, I_0e^{wt} and $-I_0e^{wt_2}$, to the system 5 mM $[Fe(C_2O_4)_3]^{3-}$ in 0.25 M $K_2C_2O_4$ (pH 4.77) in SMDE. $D_{[Fe(C_2O_4)_3]^{3-}}$ = 7.3 × 10^{-6} cm^2 s^{-1}, n = 1, T = 298 K, w = 0.3 s^{-1}, N_s = 1.51 $s^{-1/2}$. The values of r_0 (in cm) are: 0.0252 (solid line, I_0 = 7.8 μA), 0.0313 (dashed line, I_0 = 12.2 μA)

For totally irreversible processes, it is possible to obtain accurate values of thermodynamic ($E^{0'}$) and kinetic parameters (α and $k^{0'}$) of the charge transfer by following the procedure indicated in[1,4]. Thus, from the slopes and intercepts of the plots of $E(t)$ vs $\ln g^{\mathrm{c}}_{\mathrm{irrev}}$ (see Eq. (*22*)), and $E(t)$ vs $\ln g^{\mathrm{a}}_{\mathrm{irrev}}$ (see Eq. (*47*)), we can deduce these parameters, obtaining

$$\alpha = \frac{RT}{nFP_{\mathrm{c}}} \tag{75}$$

$$(1-\alpha) = -\frac{RT}{nFP_{\mathrm{a}}} \tag{76}$$

$$\ln k^{0'} = \frac{O_{\mathrm{c}} - O_{\mathrm{a}}}{P_{\mathrm{c}} - P_{\mathrm{a}}} + \ln \frac{N_s \sqrt{D_{\mathrm{A}}}}{2} \tag{77}$$

$$E^{0'} = \frac{O_{\mathrm{a}} P_{\mathrm{c}} - O_{\mathrm{c}} P_{\mathrm{a}}}{P_{\mathrm{c}} - P_{\mathrm{a}}}\ , \tag{78}$$

where O_i and P_i are the intercepts and slopes for the reduction (i = c) and oxidation (i = a) processes, respectively.

In the case of reversible electrode process, the half-wave potential can be immediately obtained from the intercepts of the plots of $E(t)$ vs $\ln g^{\mathrm{c}}_{\mathrm{rev}}$ for the application of a cathodic current $I(t) = I_0 \mathrm{e}^{wt}$ (Eq. (*19*)), or from the intercepts of the plots of $E(t)$ vs $\ln g^{\mathrm{a}}_{\mathrm{rev}}$ for the application of an anodic current $I(t) = -I_0 \mathrm{e}^{wt}$ (Eq. (*45*)). This linear regression has been applied to the current reversal chronopotentiograms obtained from a solution of 5 mM $[\mathrm{Fe(C_2O_4)_3}]^{3-}$ in 0.25 M $\mathrm{K_2C_2O_4}$ (pH 4.77) by applying two successive exponential currents of the form $I(t) = I_0 \mathrm{e}^{wt}$ and $I(t_2) = -I_0 \mathrm{e}^{wt_2}$, with I_0 = 7.87 μA and w = 0.25 $\mathrm{s^{-1}}$, in SMDE of radius r_0 = 0.025 cm. As is shown in Fig. 5, the straight lines corresponding to the cathodic ($E(t)$ vs $\ln g^{\mathrm{c}}_{\mathrm{rev}}$, black circles) and anodic ($E(t)$ vs $\ln g^{\mathrm{a}}_{\mathrm{rev}}$, white squares) programmed currents applied, are superimposable, in agreement with the theoretical results corresponding to Eqs (*19*) and (*45*) since the electrode behaves as plane and, therefore, in these equations, $\xi_{i,j} \to 0$, i = A or B, j = 1, 2. From the intercepts in Fig. 5 we have determined the following value for the reversible half-wave potential for this system: $E^{1/2}_{\mathrm{rev}}$ = (–0.244 ± 0.001) V vs Ag|AgCl, 1.0 M KCl, which is in agreement with previously reported values[9,22,23].

Cyclic Chronopotentiometry with Exponential Currents of the Form $I(t) = (-1)^{j+1} I_0 e^{wt_j}$

a) Transition Times

Figure 6 shows the influence of the electrode sphericity on the ratio $\tau_k(\text{odd})/\tau_1$ (see Eqs (*15*) and (*66*)), and on the ratio $\tau_k(\text{even})/\tau_2$ (see Eqs (*42*) and (*67*)), corresponding to the application of twenty successive exponential currents of alternating sign, $I(t) = (-1)^{j+1} I_0 \mathrm{e}^{wt_j}$, with $w = 0.5\ \mathrm{s}^{-1}$ and $N_s = 3\ \mathrm{s}^{-1/2}$, to spherical electrodes of different radii.

From these curves, we can observe a higher increase in the ratio $\tau_k(\text{even})/\tau_2$ with the number of programmed currents applied, when the electrode radius is greater, whereas the ratio $\tau_k(\text{odd})/\tau_1$ slightly decreases with the number of currents applied for high $\xi_{0,\mathrm{A}}$ values.

b) Current Potential Curves

In Fig. 7 we have experimentally studied the influence of *w* on the *E/t* curves obtained by applying seven programmed currents of the form $I(t_k) = (-1)^{k+1} I_0 \mathrm{e}^{wt_k}$ to the system 5 mM $[\mathrm{Fe(C_2O_4)_3}]^{3-}$ in 0.25 M $\mathrm{K_2C_2O_4}$ (pH 4.77) in SMDE with I_0 = 7.87 μA and different values of the exponent *w*.

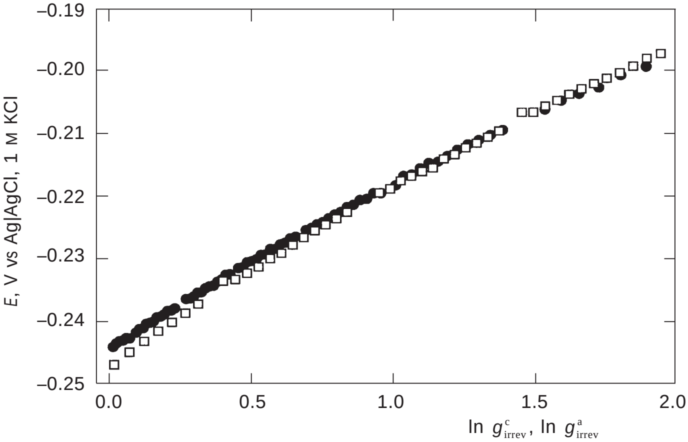

FIG. 5

Experimental dependence of $E(t)$ on ln $g^{\mathrm{c}}_{\mathrm{rev}}$ (●, see Eq. (*19*)), and on ln $g^{\mathrm{a}}_{\mathrm{rev}}$ (□, see Eq. (*45*)), for the system 5 mM $[\mathrm{Fe(C_2O_4)_3}]^{3-}$ in 0.25 M $\mathrm{K_2C_2O_4}$ (pH 4.77) in SMDE, corresponding to current reversal chronopotentiometry with two exponential currents of the form $I(t) = I_0 \mathrm{e}^{wt}$ and $I(t_2) = -I_0 \mathrm{e}^{wt_2}$. I_0 = 7.87 μA, $w = 0.25\ \mathrm{s}^{-1}$, r_0 = 0.025 cm. For other conditions, see Fig. 4

This figure shows that the increase in the exponent w causes a decrease in all the cathodic and anodic transition times, τ_k, with the differences being greater as the number of programmed currents applied grows. This behaviour is due to the increase in the current density with w.

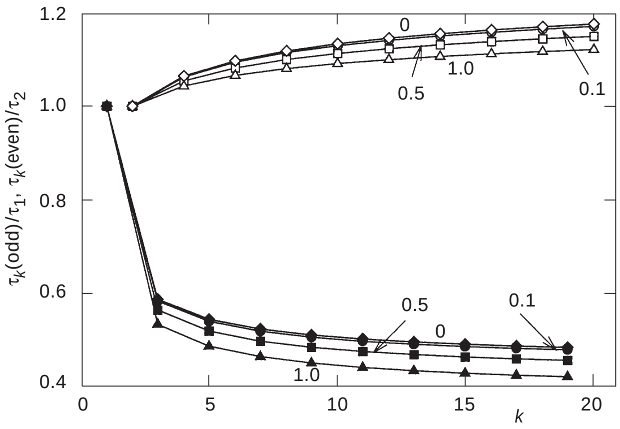

FIG. 6

Influence of the sphericity on the relationships τ_k(odd)/τ_1 (black symbols) and τ_k(even)/τ_2 (white symbols) corresponding to the application of twenty programmed currents of the form $I(t_k) = (-1)^{k+1} I_0 e^{wt_k}$, $w = 0.5\ s^{-1}$, $N_s = 3\ s^{-1/2}$, $n = 1$, $\gamma = 1$, $c_B^* = 0$. The values of $\xi_{0,A}$ (in $s^{-1/2}$) are on the curves

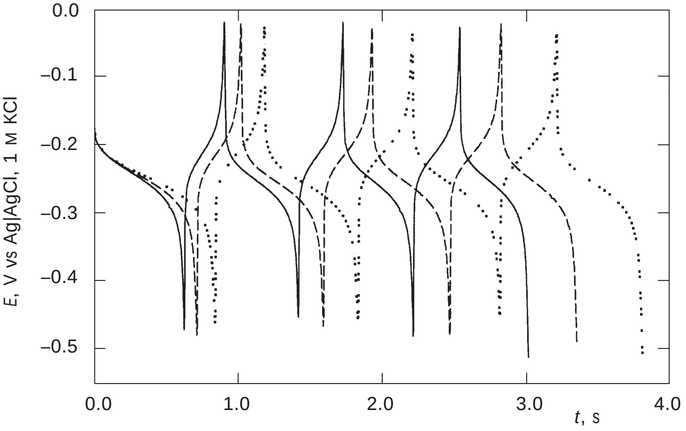

FIG. 7

Experimental E/t curves corresponding to the application of seven programmed currents of the form $I(t_k) = (-1)^{k+1} I_0 e^{wt_k}$ to the system 5 mM $[Fe(C_2O_4)_3]^{3-}$ in 0.25 M $K_2C_2O_4$ (pH 4.77) in SMDE. $r_0 = 0.025$ cm, $I_0 = 7.87$ μA. The values of w (in s^{-1}) are: 1 (solid lines), 0.75 (dashed lines) and 0.50 (dotted lines). For other conditions, see Fig. 4

Finally, we should point out that the application of cyclic chronopotentiometry with programmed currents of the form $(-1)^{j+1} I_0 e^{wt_j}$ to spherical electrodes of very small size (i.e., microelectrodes and ultramicroelectrodes), is not of interest since, as has been discussed in the previous section, the transition times τ_j, $j > 1$, are very small unless species B is initially present in the solution.

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