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Rigorous Analytical Solution for EC Mechanism in Normal Pulse Voltammetry at Spherical Electrodes and Microelectrodes

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Electrochemical processes involving a follow-up homogeneous chemical reaction are very common and largely examined in the literature. A rigorous analytical solution for chronoamperometry and Normal Pulse Voltammetry is presented in this paper, applicable to spherical electrodes of any size. From this solution, the technique is analyzed as a useful electrochemical way to characterize homogenous chemical reactions from potential-dependent chronoamperometry experiments. The validity of existing approximate solutions is also checked by comparison with the rigorous results, demonstrating that they cannot be used for large electrodes and/or slow chemical reactions.

Keywords: EC mechanism, Normal Pulse Voltammetry, rigorous solution, half-wave potential, microelectrode

1. INTRODUCTION

The study of homogenous chemical reactions coupled to oxidation-reduction processes at electrode surfaces is a major subject in Electrochemistry as well as other scientific fields, such as biomedicine and chemical synthesis. In particular, the common case of homogenous reactions involving the electrogenerated species has been extensively examined by means of different electrochemical techniques: cyclic voltammetry [1], chronoamperometry [2,3], square wave voltammetry [4-6], chronocoulometry [7], chronopotentiometry [8].

Examples of these systems include the electroreduction/oxidation of metal complexes [9,10] and organic compounds (ascorbic acid, aminophenols, azines and certain radicals) followed by reactions of additions, substitutions, dimerizations, disproportionation,..[11-21].

Numerical approaches to this problem are frequently laborious and mathematically demanding, and the analytical solutions existing in the literature generally assumes simplifying hypothesis (steady-state conditions [22-24]) which limit their applicability.

In this context, we present an explicit and analytical rigorous solution for EC mechanism in potential-dependent chronoamperometry, valid for spherical electrodes of any size including microelectrodes. The expression is given as series of two dimensionless parameters, related to the electrode sphericity and to the kinetics of the homogenous chemical reaction.

In general, the characterization of subsequent homogenous reactions involves the elucidation of the mechanism of reaction, as well as the determination of the rate constants and the half-wave potential of the redox system.

Useful diagnostic criteria for the mechanism type are here discussed, based on the variation of the half-wave potential with the chemical kinetics and the electrode size. Besides, from the fitting of experimental and theoretical chronoamperograms the simultaneous determination of the rate constants and the half-wave potential is possible [25,26]. So, it is of great interest to have at our disposal a rigorous solution, which permits us an accurate determination of these parameters without any limitation, in such a way that the time range of investigation is extended towards short times and fast kinetics.

Finally, two approximate solutions are checked by comparison with the rigorous results, pointing out that for slow chemical kinetics, short pulse durations and/or medium-sized microelectrodes they involve significant errors.

2. THEORY

Let us consider an electrochemical process giving rise to a reactive species that undergoes a homogenous first or pseudo-first order chemical reaction:

$$\left.\begin{array}{ll} \mathrm{A} + ne^- \rightleftarrows \mathrm{B} & \quad (\mathrm{E}) \\ \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{C} & \quad (\mathrm{C}) \end{array}\right. \qquad \text{(I)}$$

where k_1 and k_2 are the rate constants of the homogeneous reaction and the equilibrium constant is given by:

$$K = \frac{k_2}{k_1} = \frac{c_{\mathrm{B}}^*}{c_{\mathrm{C}}^*} \qquad (1)$$

where c_i^* $(i \equiv B, C)$ are the bulk concentrations of species *B* and *C*, respectively.

The mass transport of the different species towards or from the electrode surface is described by the following diffusive-kinetic differential equation system:

$$\hat{\Lambda} c_A = 0 \qquad (2)$$

$$\hat{\Lambda} c_B + k_1 c_B - k_2 c_C = 0 \tag{3}$$

$$\hat{\Lambda} c_C - k_1 c_B + k_2 c_C = 0 \tag{4}$$

where $\hat{\Lambda}$ is the diffusion operator corresponding to Fick’s second law for spherical diffusion:

$$\hat{\Lambda} = \frac{\partial}{\partial t} - D\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] \tag{5}$$

assuming equal diffusivities for all the species.

The boundary value problem, when assuming that the electrochemical reaction behaves as reversible, is given by:

$$\left.\begin{array}{l} t = 0,\ r \geq r_0 \\ t > 0,\ r \to \infty \end{array}\right\} \qquad c_{\mathrm{A}}(r,t) = c_{\mathrm{A}}^*,\ c_{\mathrm{B}}(r,t) = c_{\mathrm{B}}^*,\ c_{\mathrm{C}}(r,t) = c_{\mathrm{C}}^* \tag{6}$$

$$t > 0,\ r = r_0\}$$

$$D\left(\frac{\partial c_{\mathrm{A}}(r,t)}{\partial r}\right)_{r=r_0} = -D\left(\frac{\partial c_{\mathrm{B}}(r,t)}{\partial r}\right)_{r=r_0} \tag{7}$$

$$\left(\frac{\partial c_{\mathrm{C}}(r,t)}{\partial r}\right)_{r=r_0} = 0 \tag{8}$$

$$c_{\mathrm{A}}(r_0,t) = e^{\eta} c_{\mathrm{B}}(r_0,t) \tag{9}$$

with:

$$\eta = \frac{nF}{RT}\left(E - E^{0'}\right) \tag{10}$$

where n, F, R, T, E and $E^{0'}$ have their usual meanings.

To solve the above problem, we introduce two variables, ζ and ϕ, defined as:

$$\zeta(r,t) = c_{\mathrm{B}}(r,t) + c_{\mathrm{C}}(r,t) \tag{11}$$

$$\phi(r,t) = \left[c_{\mathrm{B}}(r,t) - K c_{\mathrm{C}}(r,t)\right] e^{\chi} \tag{12}$$

with:

$$\chi = \kappa t \tag{13}$$

where $\kappa = k_1 + k_2$.

By means of the mathematical procedure described in reference [27], we solve the problem obtaining the following expression for the current corresponding to an EC mechanism:

$$\frac{I}{I_d(t)}=\frac{1+K-\mu K e^{\eta}}{(1+K)(1+e^{\eta})}\left(1+\frac{\sqrt{\pi D t}}{r_0}\right)+\frac{\sqrt{\pi}}{2}\frac{e^{\eta}}{(1+K)(1+e^{\eta})}\left(S^{p}+S^{sphe}\right) \tag{14}$$

with:

$$S^{p}=\sum_{j=1}^{\infty}a_{0j}\cdot p_{2j}\cdot\chi^{j} \tag{15}$$

$$S^{sphe}=\sum_{i=1,j=1}^{\infty}\left(a_{ij}\cdot p_{i+2j}+a_{i-1,j}\right)\xi^{i}\chi^{j} \tag{16}$$

$$I_d(t)=nFA\sqrt{\frac{D}{\pi t}}c_A^{*} \tag{17}$$

and

$$\mu=\frac{\zeta^{*}}{c_A^{*}} \tag{18}$$

where $\zeta^{*}=c_B^{*}+c_C^{*}$ and $a_{i,j}$ and p_x are defined in the *Appendix*.

3. RESULTS AND DISCUSSION

From the rigorous solution here deduced, the effects of the kinetics and the electrode sphericity on the current of an electrochemical process followed by an irreversible chemical reaction ($K=0$) are studied in Figure 1. Thus, we have plotted the normalized current ($I^{N}=I/I_d(\infty)$) versus the sphericity parameter ($\xi=2\sqrt{Dt}/r_0$), the kinetic parameter ($\chi=\kappa t$) and the applied potential, being $I_d(\infty)=4\pi r_0\,n\,F\,D\,c_{\mathrm{A}}^{*}$.

In general, according to Eq. (14) the response of an EC mechanism depends on ξ and χ values, as well as on the applied potential. With respect to the influence of the kinetics of the homogenous reaction (χ), in Figure 1.a we can see that the maximum influence is observed at potential values around the half-wave potential ($\mathrm{E}_{1/2}$), this influence being null under cathodic limit conditions ($\mathrm{E}\to-\infty$) (see black curves in Figure 1.a). Thus, for a given potential value the current increases with χ, which can be understood by considering that the electrogenerated species is removed in the follow-up homogenous reaction so that an additional current flows to fulfil the concentration ratio given by the nernstian condition (Eq. (9)) [14,21].

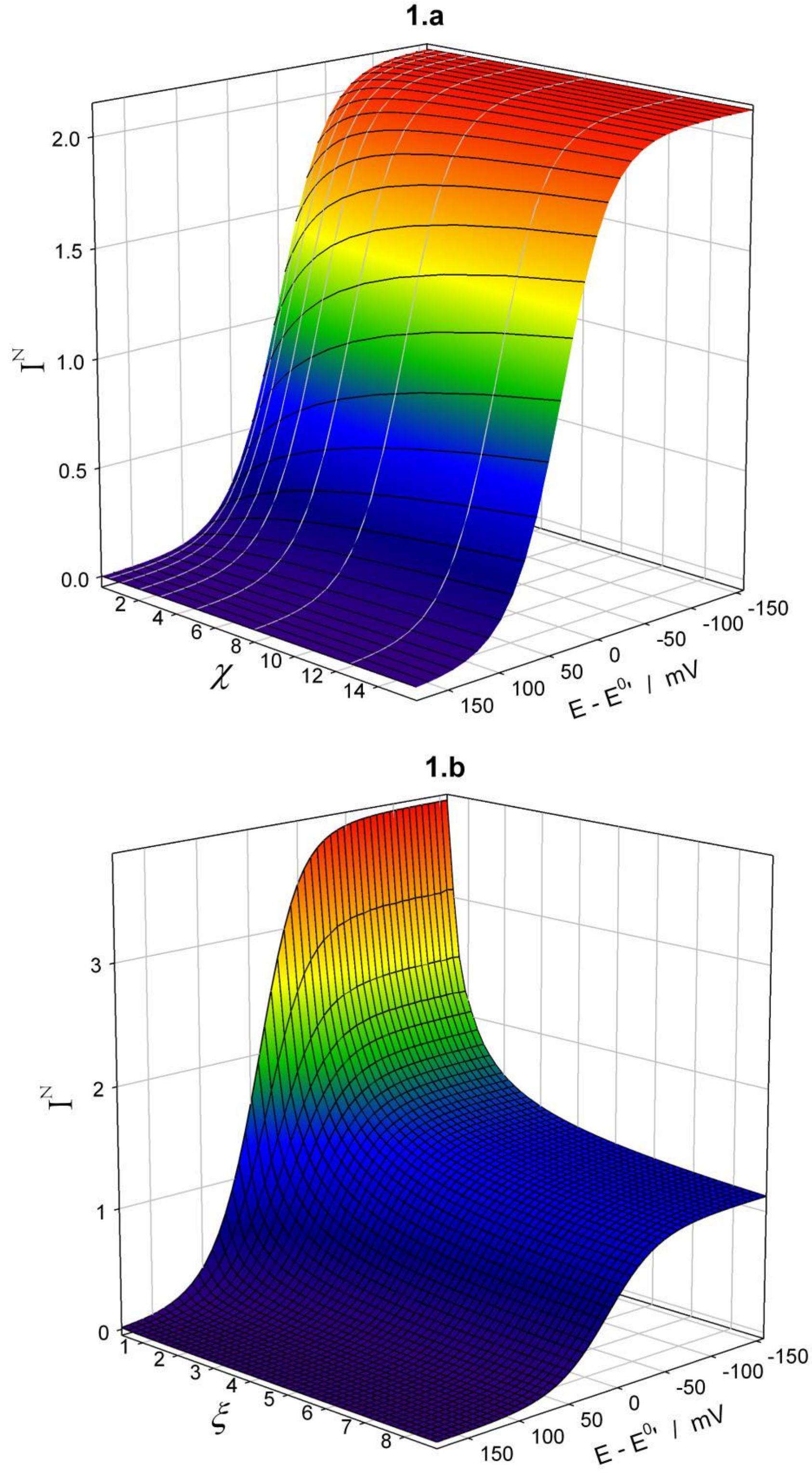

Figure 1. I^N - χ - E (Figure 1.a) and I^N - ξ - E (Figure 1.b) curves for EC mechanism. $K = 0$, $\zeta^* = 0$. **(a)** $\xi = 1$; **(b)** $\chi = 10$.

The current varies between two extreme situations, corresponding to the cases of very slow (inert equilibrium, $\chi \rightarrow 0$) and very fast (full-labile equilibrium, $\chi \rightarrow \infty$) chemical reactions. In the first case, the chemical equilibrium is "frozen" so that there is not interconversion of species *B* and *C* and the response of the system tends to that of a simple electron transfer process (E mechanism):

$$I^N(\chi \rightarrow 0) = \frac{1}{1+e^{\eta}}\left(1+\frac{2}{\sqrt{\pi}\xi}\right) \tag{19}$$

When the subsequent chemical reaction is very fast ($\chi \rightarrow \infty$), the equilibrium is maintained at any time and distance from the electrode surface, and the expression for the current is given by:

$$I^N(\chi \rightarrow \infty) = \frac{(1+K)}{1+K\,(1+e^{\eta})}\left(1+\frac{2}{\sqrt{\pi}\xi}\right) \tag{20}$$

Under cathodic limit conditions ($\eta \rightarrow -\infty$), the expression for the current is always equivalent to that corresponding to an E mechanism regardless of the chemical kinetics, since it only depends on species *A*.

Concerning the electrode sphericity (Figure 1.b), the value of the normalized current decreases with ξ, that is, when the electrode radius decreases, tending to a constant value when r_0 value is very small.

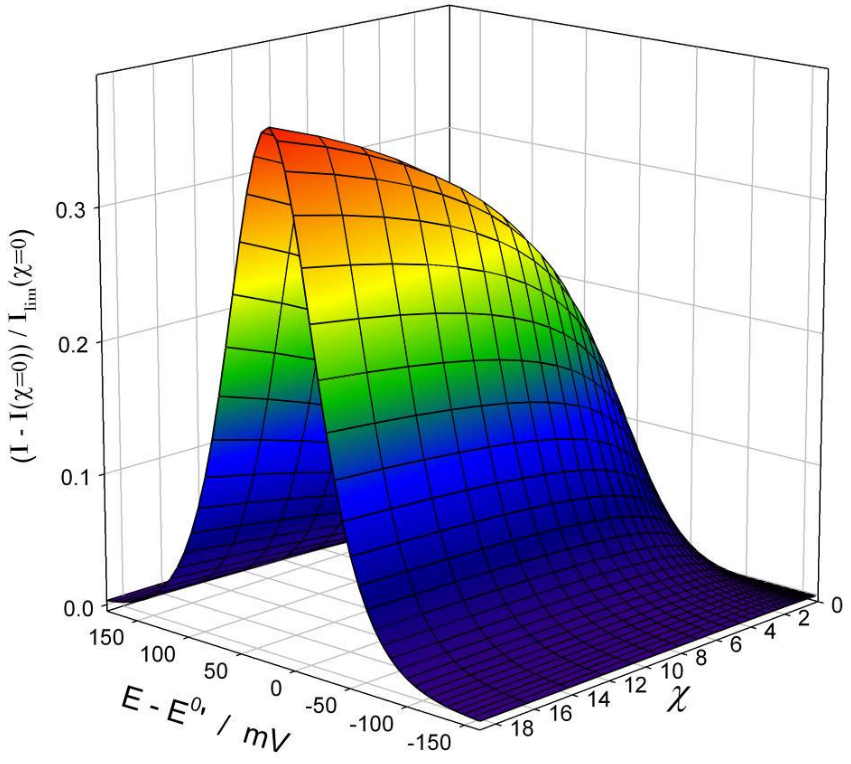

Figure 2. Difference between the currents of EC and E ($\chi = 0$) mechanisms versus the applied potential and χ. $\xi = 1$. Other conditions as in Figure 1.

Figure 2 shows the difference between the currents of EC and E mechanisms *versus* the applied potential and the kinetic parameter χ. A peak-shaped curve is obtained so that the sensitivity to the follow-up chemical step is highest around the half-wave potential. Therefore, this potential region (around +20 mV from the formal potential for the conditions considered in the figure) is the most appropriate for the study of EC mechanism by single step chronoamperometry.

In accordance with all the above it is very important the study of the position of the wave, that is, the analysis of the behaviour of the half-wave potential ($E_{1/2}$) since its experimental determination is easy and it contains information about the chemical reaction [23]. Thus, in Figure 3 we study the dependence of $E_{1/2}$ with χ and ξ for different mechanisms of reaction.

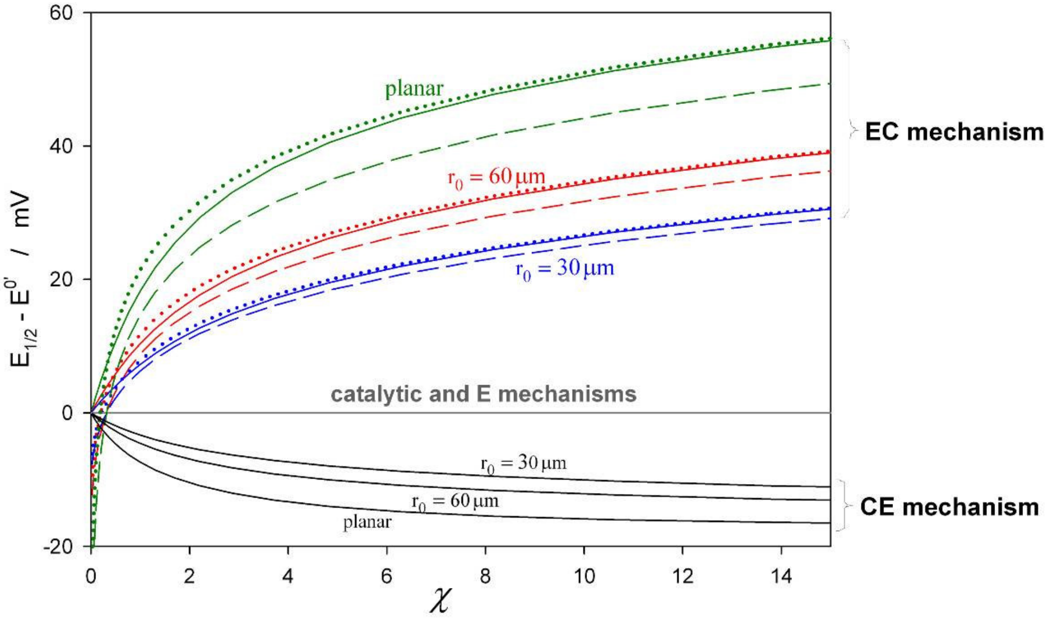

Figure 3. Variation of the half-wave potential ($E_{1/2}$) with χ for EC mechanism ($K = 0$, coloured lines,), CE mechanism ($K = 1$, black lines, ref. [27]) and catalytic and E mechanisms (grey line, ref. [23]). For the case of EC mechanism the different curve traces correspond to the results obtained from the rigorous solution (———, Eq. (14)), the kinetic steady state approximation (··············, [22,28]) and the diffusive-kinetic steady state approximation (— — — —, [23]). $t = 1s$, $D = 10^{-5} cm^2/s$. Other conditions marked on the curves.

In the case of EC mechanism, we have plotted the data obtained from the rigorous solution (solid line) together with the results from the kinetic steady state (dotted line) [22,28] and the diffusive-kinetic steady state (dashed line) [23] approximate solutions. The first approximation assumes that the perturbation of the chemical equilibrium (ϕ, eq. (12)) does not depend on time (i.e., $\partial \phi(r,t)/\partial t = 0$), and the second one supposes, along with kinetic steady state, that (pseudo)species $\zeta(= c_B + c_C)$ and A present a time-space dependence similar to that obtained when no homogenous reaction takes place, i.e., they have a purely diffusive behaviour (see ref. [23]).

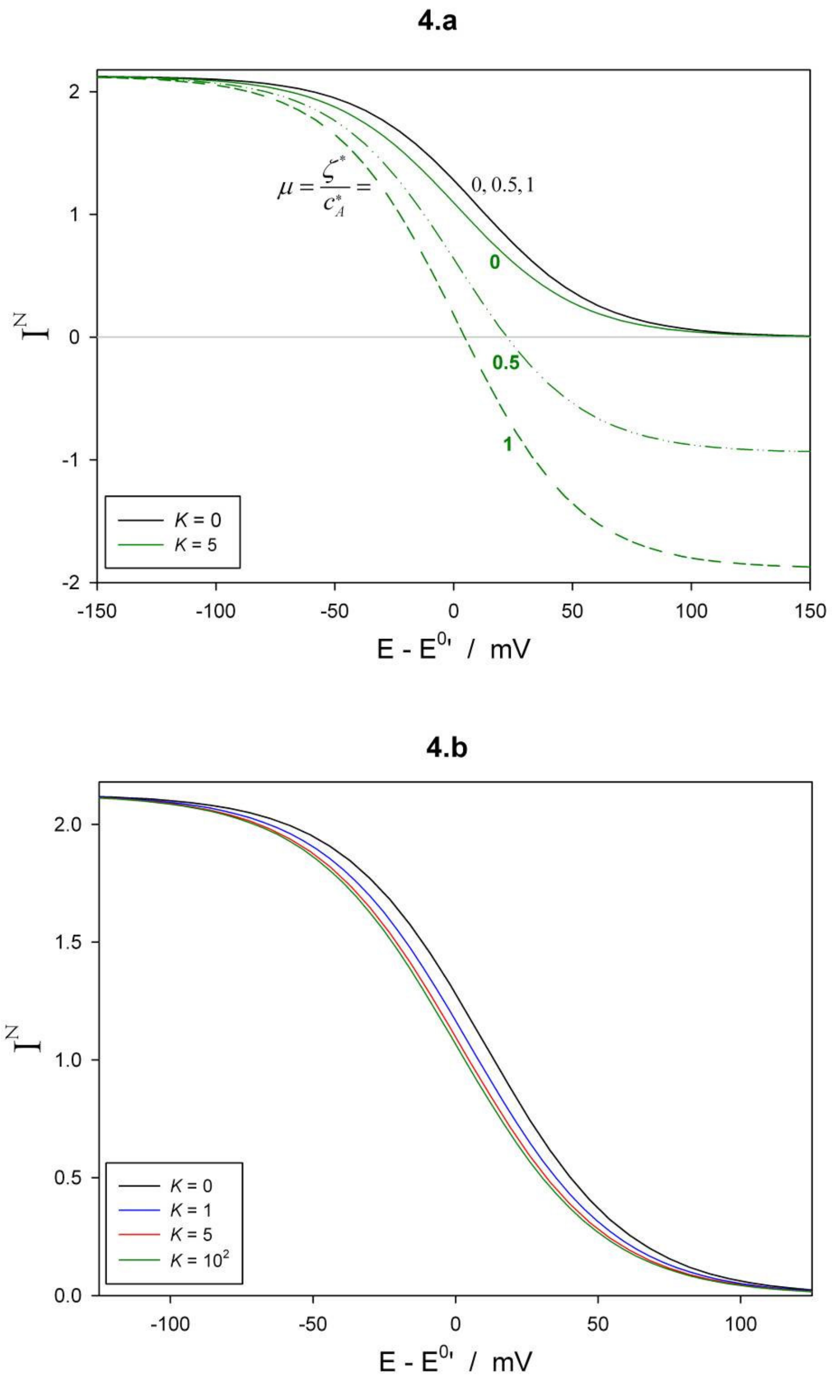

Figure 4. Effect of the initial concentration of species *B* and *C* ($\mu = \zeta^* / c_A^*$, Figure 4.a) and the equilibrium constant value (*K*, Figure 4.b) on I^N - E curves of EC mechanism. $\xi = 1$, $\chi = 1$. **(a)** Two equilibrium constants are considered: $K = 0$ (black line) and $K = 5$ (green lines); μ values marked on the curves. **(b)** $\mu = 0$; K values indicated on the panel.

We can see that $E_{1/2}$ is sensitive to the chemical kinetics (χ), the electrode radius and the type of mechanism under consideration. Thus, for an EC mechanism $E_{1/2}$ varies towards more positive values as χ and r_0 increase, whereas for a CE mechanism (black solid lines) the shift takes place towards more negative values and for a catalytic or E mechanism (grey solid line), the value of $E_{1/2}$ is independent of χ and r_0, taking the same value from planar electrodes to microelectrodes [23]. Therefore, the shift of $E_{1/2}$ with χ (either varying the rate constants through pH,… or the pulse duration) and with the electrode radius can be simple and useful diagnostic criteria.

When the chemical kinetics is very slow ($\chi \to 0$), the half-wave potential tends to the value corresponding to the electroreduction of species A ($E_{1/2} = E^{0'}$). For fast chemical kinetics, a simple expression for the half-wave potential is derived from the diffusive-kinetic steady state approximation [23]:

$$E_{1/2}(\chi >> 1) = E^{0'} + \frac{RT}{nF}\ln\frac{(1+K)\left(1/r_0 + \sqrt{\kappa/D}\right)}{\left(1/r_0 + 1/\sqrt{\pi D t}\right) + K\left(1/r_0 + \sqrt{\kappa/D}\right)} \qquad (21)$$

The above equation includes the dependence of $E_{1/2}$ with kinetic and geometrical variables, and indicates that in the case of very fast kinetics ($\kappa \to \infty$) the half-wave potential tends to a value which only depends on the equilibrium constant: $E_{1/2}(\kappa \to \infty) = E^{0'} + \frac{RT}{nF}\ln\left(\frac{1+K}{K}\right)$.

We have also checked the validity of the two approximate solutions above-mentioned, by comparison with the rigorous results. Figure 3 shows that for small χ values (short pulse duration and/or slow chemical reaction) and not too small electrode radius, the approximate solutions diverge from the rigorous one dealing to significant errors. So, under these conditions they are not suitable for accurate characterization of EC systems.

To conclude, in Figure 4.a we study the case at which species *B* and *C* are initially present ($\mu = \zeta^* / c_A^* \neq 0$) and, therefore, the complete anodic-cathodic wave. Obviously, for an irreversible chemical reaction ($K = 0$, black line) the initial concentration of these species has no influence on the voltammogram since the chemical equilibrium is fully displaced to the electroinactive species. For $K \neq 0$ (green lines), the anodic current increases with μ and the null-current potential (equilibrium potential) shifts towards less positive values, according to the equation:

$$E_c = E^{0'} + \frac{RT}{nF}\ln\left(\frac{c_A^*}{c_B^*}\right) = E^{0'} + \frac{RT}{nF}\ln\left(\frac{1+K}{\mu K}\right) \qquad (22)$$

In Figure 4.b the effect of the equilibrium constant on the voltammograms is plotted, showing that the increase of *K* value gives rise to a shift of the wave towards less positive potentials.

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Appendix

In order to tackle the problem presented here, it is convenient to define:

$$u_{\mathrm{A}}(r,t)=\frac{c_{\mathrm{A}}(r,t)\,r}{c_A^*\,r_0} \tag{A1}$$

$$u_{\zeta}(r,t)=\frac{\zeta(r,t)\,r}{c_A^*\,r_0} \tag{A2}$$

$$u_{\phi}(r,t)=\frac{\phi(r,t)\,r}{c_A^*\,r_0} \tag{A3}$$

in such a way that it is fulfilled that:

$$\left.\begin{aligned}\frac{\partial u_{\mathrm{A}}(r,t)}{\partial t}&=D\frac{\partial^2 u_{\mathrm{A}}(r,t)}{\partial r^2}\\ \frac{\partial u_{\zeta}(r,t)}{\partial t}&=D\frac{\partial^2 u_{\zeta}(r,t)}{\partial r^2}\\ \frac{\partial u_{\phi}(r,t)}{\partial t}&=D\frac{\partial^2 u_{\phi}(r,t)}{\partial r^2}\end{aligned}\right\} \tag{A4}$$

and the boundary value problem is given by:

$$\left.\begin{aligned}t=0,\ r\geq r_0\\ t>0,\ r\to\infty\end{aligned}\right\}\qquad u_A(r,t)=\frac{r}{r_0},\quad u_{\phi}(r,t)=0,\quad u_{\zeta}(r,t)=\mu\frac{r}{r_0} \tag{A5}$$

$$t>0,\ r=r_0\}$$

$$\left(\frac{\partial u_{\mathrm{A}}(r,t)}{\partial r}\right)_{r=r_0}-\frac{u_{\mathrm{A}}(r_0,t)}{r_0}=-\left[\left(\frac{\partial u_{\zeta}(r,t)}{\partial r}\right)_{r=r_0}-\frac{u_{\zeta}(r_0,t)}{r_0}\right] \tag{A6}$$

$$e^{\chi}\left[\left(\frac{\partial u_{\zeta}(r,t)}{\partial r}\right)_{r=r_0}-\frac{u_{\zeta}(r_0,t)}{r_0}\right]=\left[\left(\frac{\partial u_{\phi}(r,t)}{\partial r}\right)_{r=r_0}-\frac{u_{\phi}(r_0,t)}{r_0}\right] \tag{A7}$$

$$(1+K)\,e^{\chi}u_{\mathrm{A}}(r_0,t)=e^{\eta}\left[K\,e^{\chi}u_{\zeta}(r_0,t)+u_{\phi}(r_0,t)\right] \tag{A8}$$

In order to apply Koutecky's dimensionless parameters method [29,30], we introduce the following variables:

$$s=\frac{r-r_0}{2\sqrt{Dt}} \tag{A9}$$

$$\xi=\frac{2\sqrt{Dt}}{r_0} \tag{A10}$$

and by means of the mathematical procedure described in reference [27] we obtain the expression for the current given by eq. (14) where:

$i=0$ **(Planar Electrode)**

$$a_{00}=\frac{\mu e^{\eta}+(1+K)(1+\mu)}{(1+K)(1+e^{\eta})} \tag{A11}$$

$$a_{0j}=\frac{1}{j!}\left(\frac{1+K}{e^{\eta}}+\left(\frac{p_0}{p_{2j}}+\frac{1+K}{e^{\eta}}\right)(\mu-a_{00})-K\,a_{00}\right)-\frac{1}{e^{\eta}}\sum_{n=1}^{j-1}\left(1+K+e^{\eta}\left(K+\frac{p_{2n}}{p_{2j}}\right)\right)\frac{a_{0n}}{(j-n)!} \tag{A12}$$

$i>0$ **(Spherical corrections)**

$j=0$

$$a_{i0}=b_{i0}=0 \tag{A13}$$

$j\geq 1$

$$a_{1j}=\frac{(\mu-a_{00})}{j!}\left(\frac{1}{p_{1+2j}}-\frac{p_0}{p_{2j}}\right)+\sum_{n=1}^{j}\frac{a_{0n}}{(j-n)!}\left(\frac{p_{2n}}{p_{2j}}-\frac{1}{p_{1+2j}}\right)-\frac{1}{e^{\eta}}\sum_{n=1}^{j-1}\left(1+K+e^{\eta}\left(K+\frac{p_{1+2n}}{p_{1+2j}}\right)\right)\frac{a_{1n}}{(j-n)!} \tag{A14}$$

$$a_{i>1,j}=-\frac{b_{i-1,j}}{p_{i+2j}}-\sum_{n=1}^{j}\frac{a_{i-1,n}}{(j-n)!\,p_{i+2j}}-\frac{1}{e^{\eta}}\sum_{n=1}^{j-1}\left(1+K+e^{\eta}\left(K+\frac{p_{1+2n}}{p_{1+2j}}\right)\right)\frac{a_{in}}{(j-n)!} \tag{A15}$$

where

$$b_{1j}=\frac{(\mu-a_{00})}{j!}\left(\frac{1}{p_{1+2j}}-\frac{p_0}{p_{2j}}\right)+\sum_{n=1}^{j}\frac{a_{0n}}{(j-n)!}\left(\frac{p_{2n}}{p_{2j}}-\frac{1}{p_{1+2j}}\right)-\sum_{n=1}^{j}\frac{a_{1n}\,p_{1+2n}}{(j-n)!\,p_{1+2j}} \tag{A16}$$

$$b_{ij}=-\frac{b_{i-1,j}}{p_{i+2j}}-\sum_{n=1}^{j}\frac{a_{i-1,n}}{(j-n)!\,p_{i+2j}}-\sum_{n=1}^{j}\frac{a_{in}\,p_{i+2n}}{(j-n)!\,p_{i+2j}} \tag{A17}$$

and

$$p_x=\frac{2\Gamma\left(1+\frac{x}{2}\right)}{\Gamma\left(\frac{1+x}{2}\right)}\qquad x\geq 0 \tag{A18}$$

where $\Gamma(x)$ is the Euler Gamma function.

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