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Unified Theoretical Treatment of the E_{irrev} , CE, EC and CEC Mechanisms under Voltammetric Conditions

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Abstract

Via a thoughtful analysis it is demonstrated that the mathematical problem of the voltammetry of a simple charge transfer process of any reversibility degree at a macrointerface is totally equivalent to those of the CE, EC and CEC mechanisms such that they all can be reduced to a formally identical one-variable problem. The simplicity and generality of the resulting boundary value problem makes it very easy and rapid the study of the response in any voltammetric technique by analytical or numerical methods.

Keywords: Unified theoretical treatment; Reaction mechanisms; E_{irrev} , CE, EC and CEC voltammetry; Analytical methods; Numerical methods

1. Introduction

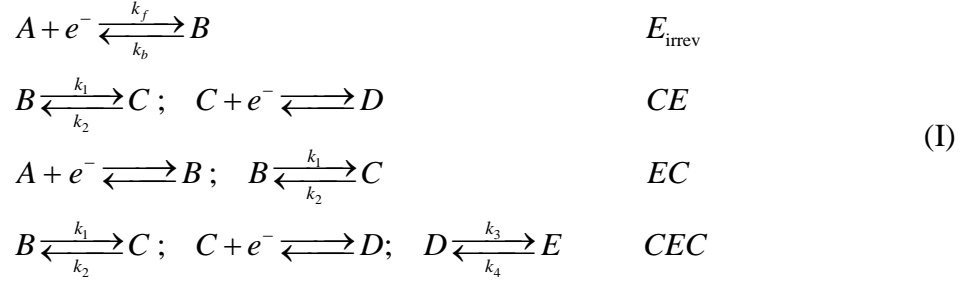
Through a thoughtful *a priori* analysis of the equations, the total equivalence between the boundary value problems (bvp) of a variety of charge transfer (CT) mechanisms in voltammetric techniques at macrointerfaces is demonstrated. This has enabled us to derive a very general theoretical framework for a number of electrochemical situations (namely, the E_{irrev} mechanism for any electrode kinetics and the CE, EC and CEC schemes when the coupled chemical reactions are not slow) pointing out that a formally identical bvp with only one differential equation applies in all cases. This obviously simplifies and speeds up importantly the resolution of the bvp and the analysis of the electrochemical signal.

The unique bvp of the E_{irrev} , CE, EC and CEC mechanisms holds in any voltammetric technique and regardless of whether the diffusion coefficients of the oxidized and reduced species are equal or not. Its resolution through appropriate analytical or numerical mathematical methods allows for the study of the current-potential-time response of all the above mechanisms at once, with a single mathematical expression or computer code. This contrasts with ‘brute force’ strategies where the original problem, which includes as many variables as participating species, is solved separately for each mechanism.

As an example, an exact analytical solution for the application of a constant potential pulse at a macroelectrode is derived as a function of a single dimensionless parameter that accounts for the influence of the electrochemical or chemical kinetics of the E_{irrev} , CE, EC and CEC mechanisms. Also, a simple numerical finite-difference approach on the basis of the common bvp has been employed to simulate very efficiently the cyclic voltammetry of such mechanisms.

2. Theory

The schemes for the E_{irrev} , CE, EC and CEC mechanisms can be written as:



where k_f and k_b are the heterogeneous rate constants of the forward (reduction) and backward (oxidation) processes, respectively. Species B in the CE mechanism, species C in the EC, and species B and E in the CEC are electro-inactive in the whole range of applied potentials. Also, k_1 and k_2 are the forward and backward rate constants, respectively, of the chemical reaction coupled to the charge transfer in the CE and EC mechanisms, and of the chemical reaction preceding the CT for a CEC process. In this last case, k_3 and k_4 are the forward and backward rate constants, respectively, of the chemical reaction following the CT [1–3]. Thus, we define

$$K_1 = \frac{k_2}{k_1} = \frac{c_B^*}{c_C^*} \tag{1}$$

$$\kappa_1 = k_1 + k_2 \tag{2}$$

$$K_2 = \frac{k_4}{k_3} = \frac{c_D^*}{c_E^*} \tag{3}$$

$$\kappa_2 = k_3 + k_4 \tag{4}$$

where K_1 and K_2 are the concentration-based equilibrium constants and c_i^* is the equilibrium concentration of species i (\equiv B, C, D, E).

In the CE, EC and CEC mechanisms, a Nernstian behaviour for the CT reaction will be assumed, as well as that the equilibrium perturbation functions remain under

steady state conditions according to the *kinetic steady state* approach (kss) [4,5] (see also Eq. (A13)) that yields accurate results for $\kappa t > 5$ [6].

2.1. Equal diffusion coefficients

By defining appropriate linear combination of the variables (concentrations, see Appendix A with $\gamma = 1$), and taking into account that when the diffusion coefficients of the species are equal it is fulfilled that [3]:

$$c_1(x,t) + c_2(x,t) = c_1^* + c_2^* \quad (5)$$

where c_1 and c_2 refer to the total concentration of oxidized and reduced species, respectively, in each mechanism (see Table 1 with $\gamma = 1$), then the bvp for the four mechanisms can be formulated in a general way with only one differential equation,

$$\hat{\delta}_1 c_1(x,t) = 0 \quad (6)$$

$$\left. \begin{array}{l} t = 0, \quad x \geq 0 \\ t \geq 0, \quad x \rightarrow \infty \end{array} \right\} c_1(x,t) = c_1^* \quad (7)$$

$$t > 0, x = 0$$

$$\left(\frac{\partial c_1(x,t)}{\partial x} \right)_{x=0} = \Lambda (A + B) [c_1(0,t) - c_1(0)_{\text{eq}}] \quad (8)$$

where $c_1(0)_{\text{eq}}$ is the surface concentration of c_1 under total equilibrium (electrochemical and chemical) conditions. The expressions for $c_1(0)_{\text{eq}}$ and the diffusion operator $\hat{\delta}_1$, together with the definitions of Λ , A and B are given in Table 1 making $\gamma = 1$ where necessary and with:

$$\eta(t) = \frac{F(E(t) - E^{0'})}{RT} \quad (9)$$

where $E^{0'}$ is the formal potential of the redox couple and other symbols have their usual meaning.

The above simple and general form for the bvp as a function of only one variable c_1 given by equations (6)-(8) greatly simplifies and speeds up its resolution, allowing us to obtain a formally-identical general solution for any of the mechanisms considered.

2.2. Unequal diffusion coefficients

As proven in Appendix A, when the diffusion coefficients of the oxidized and reduced species are different, the analysis of the bvp for the four mechanisms considered enables us to reduce them at first to a common two-variable problem:

$$\hat{\delta}_1 c_1(x, t) = \hat{\delta}_2 c_2(x, t) = 0 \quad (10)$$

$$\left. \begin{array}{l} t = 0, \quad x \geq 0 \\ t \geq 0, \quad x \rightarrow \infty \end{array} \right\} c_1(x, t) = c_1^*; \quad c_2(x, t) = c_2^* \quad (11)$$

$$t > 0, x = 0 \quad \left(\frac{\partial c_1(x, t)}{\partial x} \right)_{x=0} = -\frac{1}{\gamma^2} \left(\frac{\partial c_2(x, t)}{\partial x} \right)_{x=0} \quad (12)$$

$$\left(\frac{\partial c_1(x, t)}{\partial x} \right)_{x=0} = \Lambda(A + \gamma B) \left[\frac{A c_1(0, t) - B c_2(0, t)}{A + \gamma B} \right] \quad (13)$$

where $\hat{\delta}_i$ ($i \equiv 1, 2$) and other definitions can be found in Table 1.

2.2.1. Simplification to a one-variable problem

The analysis of the mathematical problem when the diffusion coefficient of the oxidized and reduced species are different ($\gamma \neq 1$) points out that condition (5) does not apply in such case [7]. Nevertheless, in any electrochemical technique the following equivalent relationship holds for the surface concentrations ‘weighted’ by the square root of the diffusion coefficients:

$$\sqrt{D_1} c_1(0, t) + \sqrt{D_2} c_2(0, t) = \sqrt{D_1} c_1^* + \sqrt{D_2} c_2^* \quad (14)$$

as proven in Appendix B for the particular case of single pulse techniques. Taking into account Eq. (14) in the surface condition (13), the bvp (10)-(13) can be re-formulated as

a function of only one variable comprised by the differential equation (6), the condition (7) and the following surface condition,

$$t > 0, x = 0 \quad \left(\frac{\partial c_1(x, t)}{\partial x} \right)_{x=0} = \Lambda(A + \gamma B) [c_1(0, t) - c_1(0)_{\text{eq}}] \quad (15)$$

that reproduces Eq. (8) for $\gamma = 1$. The definitions of Λ , A , B and $c_1(0)_{\text{eq}}$ are given in Table 1.

The general and formally identical problem given by Eqs. (6), (7) and (15) covers all the reaction mechanisms in Scheme (I) in any voltammetric technique and regardless of the γ -value by just specifying the corresponding potential perturbation $E(t)$ in Eq. (9). For example, in the case of the linear sweep voltammetry, $E(t) = E_{\text{initial}} + vt$ is to be employed in Eq. (15) (with v being the scan rate) so that it can be solved at once for the E_{irrev} , CE, EC and CEC mechanisms by whatever suitable mathematical method, either analytical or numerical [8,9].

The current-potential-time response for all the mechanisms considered is given by:

$$I = FAD_1 \left(\frac{\partial c_1(x, t)}{\partial x} \right)_{x=0} \quad (16)$$

3. Discussion and Results

3.1. Normal pulse voltammetry

For the sake of example, in Appendix B the bvp above-discussed has been solved analytically for single pulse techniques, obtaining an explicit analytical solution for $c_1(x,t)$ (Eq. (B19)) and, together with Eq. (16), the following expression for the current-potential-time response is deduced for any of the mechanisms studied:

$$I = I_{\text{eq}} F(\chi) \quad (17)$$

where χ is a dimensionless parameter that accounts for the electrochemical and chemical kinetics and I_{eq} is the current corresponding to total electrochemical and chemical equilibrium conditions (see Table 1). Function $F(\chi)$ monotonously increases with χ up to 1 for $\chi \rightarrow \infty$ where it holds that $I = I_{\text{eq}}$.

From Eq. (17), the normal pulse voltammetry of the E_{irrev} , CE, EC and CEC mechanisms is studied in Figure 1 as a function of their electrochemical (k^0) or chemical (κ_1 and κ_2) kinetics. The behaviours expected are well described in all cases by the general analytical solution reported here. Thus, in the case of the E_{irrev} mechanism (Figure 1a), the increase of the electrode kinetics (indicated by the horizontal arrow in the figure) gives rise to steeper current-potential waves that shift towards less negative potential values when electro-reductions are considered. With regard to the CE mechanism (Figure 1b), the most apparent effect of the homogeneous chemical kinetics is the increase of the wave magnitude with κ_1 given the more rapid interconversion between the electroinactive species B and the electroactive species C. The NPV curves of the irreversible EC mechanism studied in Figure 1c ($K_1 \rightarrow 0$) shift towards less negative potentials when the chemical kinetics is faster as a response to the quick disappearance of the electrogenerated species B. The $\text{CEC}_{\text{irrev}}$ mechanism in Figure 1d ($K_1 = 1, K_2 = 0$

and $\kappa_1 = \kappa_2$) shows a ‘mixed’ CE-EC behavior such that the magnitude of the wave increases (CE-like) while it shifts to less negative potential values (EC-like) as κ_1 and κ_2 increase.

3.2. Cyclic voltammetry

In general, the species surface concentrations in the mechanisms considered are time-dependent such that the superposition principle does not apply [10] and the derivation of analytical solutions for multipulse techniques is prohibitively complicated. Alternatively, simple numerical approaches can be considered for the simultaneous simulation of the cyclic voltammetry (CV) response of the four mechanisms, taking advantage of the simplicity of the one-variable bvp with a single differential equation (Eqs. (6), (7) and (15)). In particular, the results included in this section have been obtained via a finite-difference method with backward implicit time integration and central three-point approximation of the spatial derivative, which leads to a tridiagonal equation system that can be solved very efficiently by the simple Thomas algorithm [8,9] (see Appendix C).

The results reproduce satisfactorily the behaviour expected [1–3] for the CV response of the four reaction mechanisms as shown in Figure 2. Thus, the main effects on the shape of the cyclic voltammograms when increasing the electrochemical or chemical kinetics are: (Figure 2a) the decrease of the peak-to-peak separation in the E_{irrev} mechanism and also... , (Figure 2b) the increase of the peak magnitudes in the CE mechanism as the conversion B-to-C is faster and so more electroactive species is available for electrolysis, and (Figure 2c) the gradual disappearance of the reverse peak and the shift of the signal towards more positive potentials in the case of the EC_{irrev} mechanism. Similarly to the NPV response (Figure 1), the CEC_{irrev} case considered in

Figure 2d ($K_1 = 1, K_2 = 0$ and $\kappa_1 = \kappa_2$), shows both CE-like and EC like features: the faster the chemical kinetics, the larger the forward reductive peak and the smaller the reverse oxidative one.

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Table 1. Definitions for the different reaction mechanisms considered (see Scheme (I)).

Mechanism <i>Concentrations and diffusion coefficients</i>	Definitions	
<i>E</i>_{irrev} $c_1(x,t) = c_A(x,t); D_1 = D_A$ $c_2(x,t) = c_B(x,t); D_2 = D_B$	$\Lambda = \frac{k_f}{D_1}$ $A = 1$ $B = e^{\eta(t)}$	$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2} \quad (i \equiv 1, 2)$ $\gamma = \sqrt{\frac{D_1}{D_2}}$
<i>CE</i> $c_1(x,t) = c_B(x,t) + c_C(x,t); D_1 = D_B = D_C$ $c_2(x,t) = c_D(x,t); D_2 = D_D$	$\Lambda = \frac{1}{K_1} \sqrt{\frac{\kappa_1}{D_1}}$ $A = 1$ $B = (1 + K_1)e^{\eta(t)}$	$c_1(0)_{\text{eq}} = (\gamma c_1^* + c_2^*) \frac{B}{A + \gamma B}$
<i>EC</i> $c_1(x,t) = c_A(x,t); D_1 = D_A$ $c_2(x,t) = c_B(x,t) + c_C(x,t); D_2 = D_B = D_C$	$\Lambda = \frac{1}{\gamma e^{\eta(t)}} \sqrt{\frac{\kappa_1}{D_1}}$ $A = 1 + K_1$ $B = K_1 e^{\eta(t)}$	$\chi = 2\sqrt{D_1 t} \Lambda (A + \gamma B)$ $F(\chi) = \sqrt{\pi} \frac{\chi}{2} e^{(\chi/2)^2} \text{erfc}(\chi/2)$
<i>CEC</i> $c_1(x,t) = c_B(x,t) + c_C(x,t); D_1 = D_B = D_C$ $c_2(x,t) = c_D(x,t) + c_E(x,t); D_2 = D_D = D_E$	$\Lambda = \frac{1}{K_1(1 + K_2) + \gamma e^{\eta(t)}(1 + K_1)\sqrt{\kappa_1/\kappa_2}} \sqrt{\frac{\kappa_1}{D_1}}$ $A = 1 + K_2$ $B = (1 + K_1)K_2 e^{\eta(t)}$	$I_{\text{eq}} = FA \sqrt{\frac{D_1}{\pi t}} (c_1^* - c_1(0)_{\text{eq}})$

Figure 1. Influence of the electrochemical (E_{irrev}) or chemical (CE, EC and CEC) kinetics on the normalized normal pulse voltammograms obtained from the general analytical solution (17) with $D_1 = D_2 (=10^{-5} \text{ cm}^2/\text{s})$ for the different mechanisms considered. $t = 1 \text{ s}$, (a) $\alpha = 0.5$, $k^0 = 10^{-4} (\dots)$, $10^{-3} (- -)$ and $10^{-2} (—)$ cm/s (b, c, d) $\kappa = 5 (\dots)$, $5 \times 10^2 (- -)$ and $5 \times 10^4 (—)$ s^{-1}

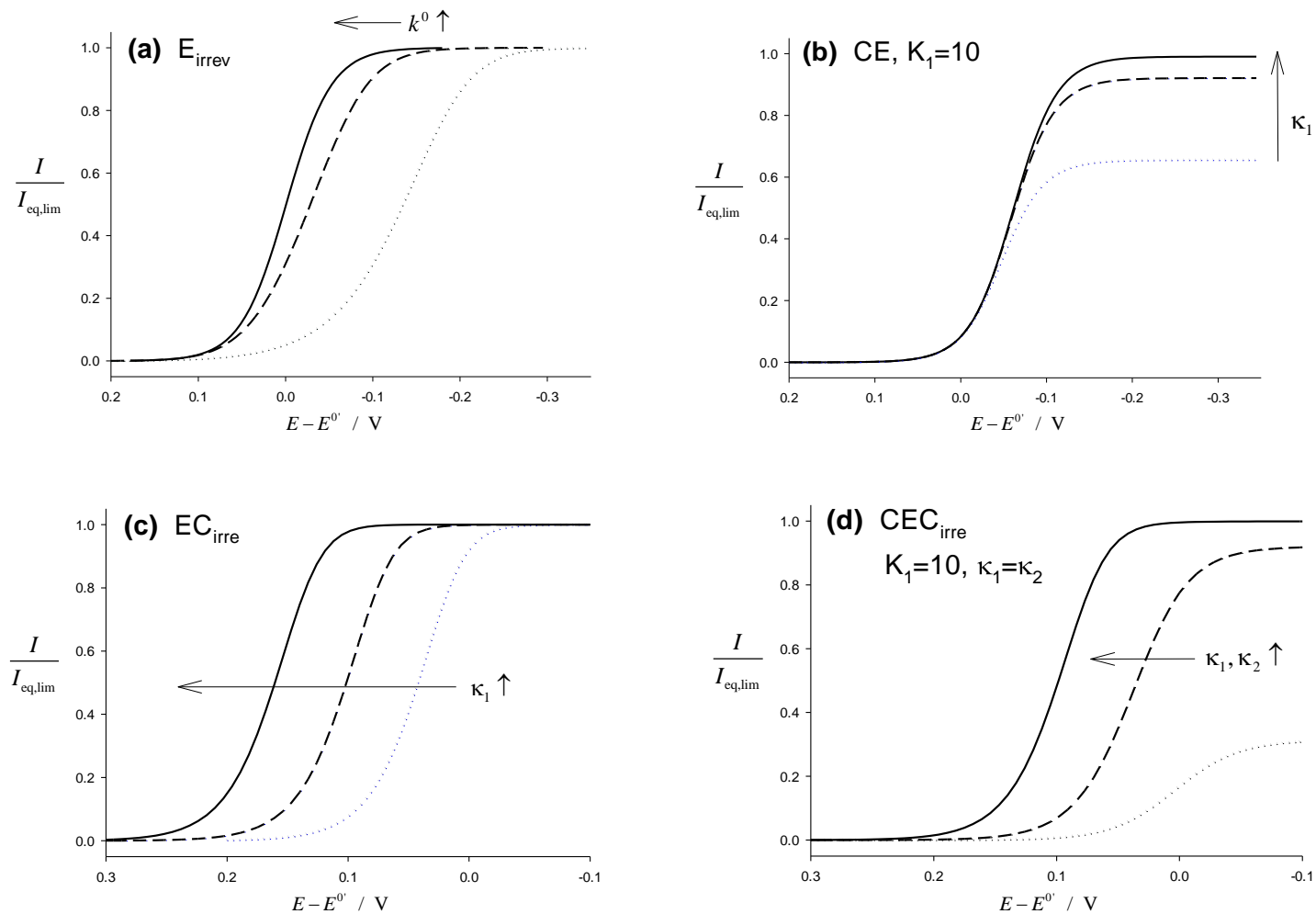
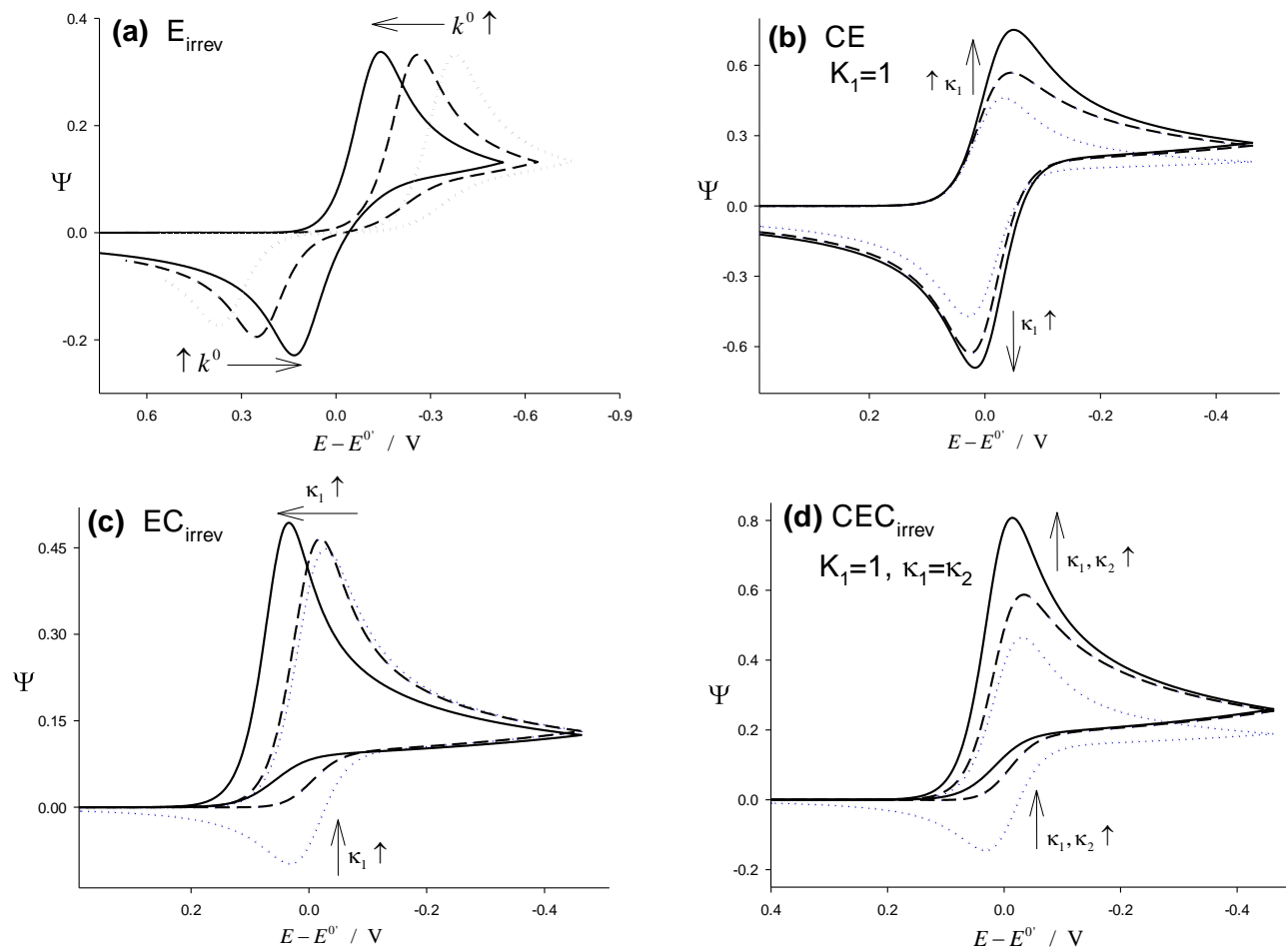


Figure 2. Influence of the electrochemical (E_{irrev}) or chemical (CE, EC and CEC) kinetics on the cyclic voltammetry of the four mechanisms considered as obtained numerically by solving the bvp with $D_1 = D_2$ (Eqs. (6)-(8)) as discussed in Section 3.2 and in Appendix C. $\Psi = \frac{I}{FAD_1c_1^*} \sqrt{\frac{RT}{Fv}}$. Other conditions as in Figure 1.



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Appendix A. Specific boundary value problem of the four mechanisms considered when the diffusion coefficients are different

a) For the **E_{irrev} mechanism** (see Scheme (I)), the differential equation system and boundary conditions are given by,

$$\hat{\delta}_A c_A(x,t) = \hat{\delta}_B c_B(x,t) = 0 \quad (\text{A1})$$

$$\left. \begin{array}{l} t = 0, \quad x \geq 0 \\ t \geq 0, \quad x \rightarrow \infty \end{array} \right\} c_A(x,t) = c_A^*; \quad c_B(x,t) = c_B^* \quad (\text{A2})$$

$t > 0, x = 0,$

$$D_A \left(\frac{\partial c_A(x,t)}{\partial x} \right)_{x=0} = -D_B \left(\frac{\partial c_B(x,t)}{\partial x} \right)_{x=0} \quad (\text{A3})$$

$$\left(\frac{\partial c_A(x,t)}{\partial x} \right)_{x=0} = \frac{k_f}{D_A} \left[c_A(0,t) - e^{\eta(t)} c_B(0,t) \right] \quad (\text{A4})$$

where (see Eq. (9)),

$$e^{\eta(t)} = \frac{k_b}{k_f} \quad (\text{A5})$$

whatever the electrode kinetic model.

b) For a **CE mechanism** as given in Scheme (I), the differential equation system and *bvp* are,

$$\begin{aligned} \hat{\delta}_B c_B(x,t) &= -\hat{\delta}_C c_C(x,t) = -k_1 c_B(x,t) + k_2 c_C(x,t) \\ \hat{\delta}_D c_D(x,t) &= 0 \end{aligned} \quad (\text{A6})$$

$$\left. \begin{array}{l} t = 0, \quad x \geq 0 \\ t \geq 0, \quad x \rightarrow \infty \end{array} \right\} c_B(x,t) = c_B^*; \quad c_C(x,t) = c_C^*; \quad c_D(x,t) = c_D^* \quad (\text{A7})$$

$t > 0, x = 0,$

$$D_C \left(\frac{\partial c_C(x,t)}{\partial x} \right)_{x=0} = -D_D \left(\frac{\partial c_D(x,t)}{\partial x} \right)_{x=0} \quad (\text{A8})$$

$$\left(\frac{\partial c_B(x,t)}{\partial x} \right)_{x=0} = 0 \quad (\text{A9})$$

$$\frac{c_C(0,t)}{c_D(0,t)} = e^{\eta(t)} \quad (\text{A10})$$

where Nernstian behaviour has been assumed for the CT reaction (Eq. (A10)).

Introducing the variables,

$$\zeta(x,t) = c_B(x,t) + c_C(x,t) \quad (\text{A11})$$

$$\phi(x,t) = c_B(x,t) - K_1 c_C(x,t) \quad (\text{A12})$$

and assuming the kinetic steady state (kss) approximation [4,5],

$$\frac{\partial \phi(x,t)}{\partial t} = 0 \quad (\text{A13})$$

which implies that,

$$\phi(x) = \phi(0) e^{-\sqrt{\kappa_1/D_C} x} \quad (\text{A14})$$

and then,

$$\phi(0) = K_1 \sqrt{\frac{D_C}{\kappa_1}} \left(\frac{\partial \zeta(x,t)}{\partial x} \right)_{x=0} \quad (\text{A15})$$

Eqs. (A6)-(A10) assuming $D_B = D_C$ become into,

$$\hat{\delta}_C \zeta(x,t) = \hat{\delta}_D c_D(x,t) = 0 \quad (\text{A16})$$

$$\left. \begin{array}{l} t = 0, \quad x \geq 0 \\ t \geq 0, \quad x \rightarrow \infty \end{array} \right\} \zeta(x,t) = \zeta^* = c_B^* + c_C^*; \quad c_D(x,t) = c_D^* \quad (\text{A17})$$

$t > 0, x = 0,$

$$D_C \left(\frac{\partial \zeta(x,t)}{\partial x} \right)_{x=0} = -D_D \left(\frac{\partial c_D(x,t)}{\partial x} \right)_{x=0} \quad (\text{A18})$$

$$\left(\frac{\partial \zeta(x,t)}{\partial x} \right)_{x=0} = \frac{1}{K_1} \sqrt{\frac{\kappa_1}{D_C}} \left[\zeta(0,t) - (1 + K_1) e^{\eta(t)} c_D(0,t) \right] \quad (\text{A19})$$

c) The case of the **EC mechanism** (see Scheme (I)) assuming kss conditions for the chemical reaction is equivalent to that of the **CE** one, by substituting in Eqs. (A16)-(A19)

$$\begin{aligned} \zeta_{\text{CE}} &\rightarrow \zeta_{\text{EC}}; \quad (c_{\text{D}})_{\text{CE}} \rightarrow (c_{\text{A}})_{\text{EC}}; \quad (D_{\text{D}})_{\text{CE}} \rightarrow (D_{\text{A}})_{\text{EC}}; \\ (K_1)_{\text{CE}} &\rightarrow \frac{1}{(K_1)_{\text{EC}}}; \quad (e^{\eta(t)})_{\text{CE}} \rightarrow \frac{1}{(e^{\eta(t)})_{\text{EC}}} \end{aligned} \quad (\text{A20})$$

in such a way that, from Eqs. (A18) and (A19), it is obtained that

$$\left(\frac{\partial c_{\text{A}}(x,t)}{\partial x} \right)_{x=0} = \frac{1}{D_{\text{A}} e^{\eta(t)}} \sqrt{D_{\text{C}} \kappa_1} \left[(1 + K_1) c_{\text{A}}(0,t) - K_1 e^{\eta(t)} \zeta(0,t) \right] \quad (\text{A21})$$

d) For the **CEC mechanism** (see Scheme (I)), by using the variables,

$$\zeta_1(x,t) = c_{\text{B}}(x,t) + c_{\text{C}}(x,t) \quad (\text{A22})$$

$$\phi_1(x,t) = c_{\text{B}}(x,t) - K_1 c_{\text{C}}(x,t) \quad (\text{A23})$$

$$\zeta_2(x,t) = c_{\text{D}}(x,t) + c_{\text{E}}(x,t) \quad (\text{A24})$$

$$\phi_2(x,t) = c_{\text{D}}(x,t) - K_2 c_{\text{E}}(x,t) \quad (\text{A25})$$

and considering that both equilibrium perturbation functions, ϕ_1 and ϕ_2 , are time-independent, the bvp can be written in the following way,

$$\left. \begin{array}{l} t = 0, \quad x \geq 0 \\ t \geq 0, \quad x \rightarrow \infty \end{array} \right\} \zeta_1(x,t) = \zeta_1^* = c_{\text{B}}^* + c_{\text{C}}^*; \quad \zeta_2(x,t) = \zeta_2^* = c_{\text{D}}^* + c_{\text{E}}^* \quad (\text{A26})$$

$$t > 0, \quad x = 0,$$

$$D_{\text{C}} \left(\frac{\partial \zeta_1(x,t)}{\partial x} \right)_{x=0} = -D_{\text{D}} \left(\frac{\partial \zeta_2(x,t)}{\partial x} \right)_{x=0} \quad (\text{A27})$$

$$\left(\frac{\partial \zeta_1(x,t)}{\partial x} \right)_{x=0} = \frac{1}{K_1(1 + K_2) + \gamma e^{\eta(t)}(1 + K_1) \sqrt{\kappa_1/\kappa_2}} \sqrt{\frac{\kappa_1}{D_{\text{C}}}} \left[(1 + K_2) \zeta_1(0,t) - (1 + K_1) K_2 e^{\eta(t)} \zeta_2(0,t) \right] \quad (\text{A28})$$

Note that the above points out that, for all the mechanisms considered, the bvp can be expressed at first as a function of two variables in the general form given by Eqs. (10)-(13) so that, taking into account Eq. (14) (see Eq. (B23) in Appendix B) in Eqs. (A4), (A19), (A21) and (A28), the general bvp with only one variable (Eq. (15)) is obtained.

Appendix B : General unified solution of the problem of the four mechanisms in single pulse techniques when the diffusion coefficients are different

In this appendix the case corresponding to different diffusion coefficients $\gamma \neq 1$ will be treated since, under these conditions, the problem is slightly more complex than in the case $\gamma = 1$ where the application of Eq. (5) enables us to reduce directly the problem to the one-variable bvp given by (6)-(8).

Thus, the boundary conditions in Eqs. (11)-(13) become into:

$$s_i \rightarrow \infty, \quad c_i(s_i \rightarrow \infty) = c_i^* \quad (i \equiv 1, 2) \quad (\text{B1})$$

$$s_i = 0$$

$$\left(\frac{\partial c_1(s_1)}{\partial s_1} \right)_{s_1=0} = -\frac{1}{\gamma} \left(\frac{\partial c_2(s_2)}{\partial s_2} \right)_{s_2=0} \quad (\text{B2})$$

$$\left(\frac{\partial c_1(s_1)}{\partial s_1} \right)_{s_1=0} = \chi \left[\frac{A c_1(0, t) - B c_2(0, t)}{A + \gamma B} \right] \quad (\text{B3})$$

where

$$s_i = \frac{x}{2\sqrt{D_i t}} \quad (i \equiv 1, 2) \quad (\text{B4})$$

and γ and χ are given in Table 1.

Thus, with the variables s_i and χ the equation system (10) becomes:

$$\begin{aligned} \frac{\partial^2 c_1(s_1, \chi)}{\partial s_1^2} + 2s_1 \frac{\partial c_1(s_1, \chi)}{\partial s_1} - 2\chi \frac{\partial c_1(s_1, \chi)}{\partial \chi} &= 0 \\ \frac{\partial^2 c_2(s_2, \chi)}{\partial s_2^2} + 2s_2 \frac{\partial c_2(s_2, \chi)}{\partial s_2} - 2\chi \frac{\partial c_2(s_2, \chi)}{\partial \chi} &= 0 \end{aligned} \quad (\text{B5})$$

The solutions of the differential equations system (B5) with the boundary conditions given by Eqs. (B1)-(B3) can be written as follows [3,11],

$$\begin{aligned}
c_1(x,t) &= c_1(s_1, \chi) = \sum_{j=0}^{\infty} \sigma_j(s_1) \chi^j \\
c_2(x,t) &= c_2(s_2, \chi) = \sum_{j=0}^{\infty} \rho_j(s_2) \chi^j
\end{aligned} \tag{B6}$$

By introducing Eq. (B6) in Eq. (B5) the following equation's system is obtained,

$$\begin{aligned}
\sigma_j''(s_1) + 2s_1 \sigma_j'(s_1) - 2j \sigma_j(s_1) &= 0 \\
\rho_j''(s_2) + 2s_2 \rho_j'(s_2) - 2j \rho_j(s_2) &= 0
\end{aligned} \tag{B7}$$

with the boundary conditions,

$$\begin{aligned}
s_i \rightarrow \infty, \quad \sigma_0(s_1 \rightarrow \infty) &= c_1^*; \quad \rho_0(s_2 \rightarrow \infty) = c_2^* \\
\sigma_j(s_1 \rightarrow \infty) &= 0; \quad \rho_j(s_2 \rightarrow \infty) = 0 \quad j \geq 1
\end{aligned} \tag{B8}$$

$$s_i = 0,$$

$$\sigma_j'(0) = -\frac{1}{\gamma} \rho_j'(0) \quad j \geq 0 \tag{B9}$$

$$\begin{aligned}
\sigma_0'(0) &= 0 \\
\sigma_j'(0) &= \frac{A \sigma_{j-1}(0) - B \rho_{j-1}(0)}{A + \gamma B} \quad j \geq 1
\end{aligned} \tag{B10}$$

with [3]

$$\begin{aligned}
\sigma_0(s_1) &= h_0 \Psi_0(s_1) + c_1^* \operatorname{erf}(s_1) \\
\sigma_j(s_1) &= h_j \Psi_j(s_1) \quad j \geq 1
\end{aligned} \tag{B11}$$

$$\begin{aligned}
\rho_0(s_2) &= g_0 \Psi_0(s_2) + c_2^* \operatorname{erf}(s_2) \\
\rho_j(s_2) &= g_j \Psi_j(s_2) \quad j \geq 1
\end{aligned} \tag{B12}$$

where $\Psi_j(s_i)$ ($i \equiv 1, 2$) are the Koutecký functions, which fulfill

$$\begin{aligned}
\lim_{s_i \rightarrow 0} \Psi_j(s_i) &= 1 \\
\lim_{s_i \rightarrow \infty} \Psi_j(s_i) &= 0 \\
\Psi_j'(s_i) &= -p_j \Psi_{j-1}(s_i) \\
\Psi_0(s_i) &= 1 - \operatorname{erf}(s_i)
\end{aligned} \tag{B13}$$

with p_j being

$$p_j = \frac{2\Gamma\left(1 + \frac{j}{2}\right)}{\Gamma\left(\frac{1}{2} + \frac{j}{2}\right)} \quad (\text{B14})$$

and Γ is the gamma function. From the above,

$$\begin{aligned} \sigma_j(0) &= h_j ; \rho_j(0) = g_j \quad j \geq 0 \\ \sigma_0'(0) &= -p_0(h_0 - c_1^*) ; \rho_0'(0) = -p_0(g_0 - c_2^*) \\ \sigma_j'(0) &= -h_j p_j ; \rho_j'(0) = -g_j p_j \quad j \geq 1 \end{aligned} \quad (\text{B15})$$

and introducing Eqs. (B15) into Eqs. (B9) and (B10), it is obtained that,

$$\begin{aligned} h_0 &= c_1^* \\ g_0 &= c_2^* \\ h_j &= \frac{(-1)^j}{\prod_{l=1}^j p_l} \frac{Ac_1^* - Bc_2^*}{A + \gamma B} \quad j \geq 1 \\ g_j &= -\gamma h_j \quad j \geq 1 \end{aligned} \quad (\text{B16})$$

with,

$$\frac{Ac_1^* - Bc_2^*}{A + \gamma B} = c_1^* - c_1(0)_{\text{eq}} \quad (\text{B17})$$

Thus, from (B11)-(B13) and (B16),

$$\begin{aligned} \sigma_0(s_1) &= c_1^* \\ \rho_0(s_2) &= c_2^* \\ \sigma_j(s_1) &= (c_1^* - c_1(0)_{\text{eq}}) \frac{(-1)^j}{\prod_{l=1}^j p_l} \Psi_j(s_1) \quad j \geq 1 \\ \rho_j(s_2) &= -\gamma (c_1^* - c_1(0)_{\text{eq}}) \frac{(-1)^j}{\prod_{l=1}^j p_l} \Psi_j(s_2) \quad j \geq 1 \end{aligned} \quad (\text{B18})$$

and the concentration profiles (Eq. (B6)) are:

$$\begin{aligned}
c_1(x,t) &= c_1(x,t)_{\text{eq}} + \frac{2}{\sqrt{\pi}} \frac{(c_1^* - c_1(0)_{\text{eq}})}{\chi} \sum_{j=0}^{\infty} \frac{(-1)^j}{\prod_{l=0}^j p_l} \Psi_j(s_1) \chi^{j+1} \\
c_2(x,t) &= c_2(x,t)_{\text{eq}} - \frac{2}{\sqrt{\pi}} \frac{\gamma(c_1^* - c_1(0)_{\text{eq}})}{\chi} \sum_{j=0}^{\infty} \frac{(-1)^j}{\prod_{l=0}^j p_l} \Psi_j(s_2) \chi^{j+1}
\end{aligned} \tag{B19}$$

and $c_1(x,t)_{\text{eq}}$ and $c_2(x,t)_{\text{eq}}$ are the concentration profiles for a total electrochemical and chemical equilibrium process, given by [1–3],

$$\begin{aligned}
c_1(x,t)_{\text{eq}} &= c_1^* + (c_1(0)_{\text{eq}} - c_1^*) \operatorname{erfc}(s_1) \\
c_2(x,t)_{\text{eq}} &= c_2^* - \gamma(c_1(0)_{\text{eq}} - c_1^*) \operatorname{erfc}(s_2)
\end{aligned} \tag{B20}$$

and $c_1(0)_{\text{eq}}$ is given in Table 1. From Eqs. (B19), the surface concentrations ($x = 0$) are immediately obtained,

$$\begin{aligned}
c_1(0,t) &= c_1(0)_{\text{eq}} + \frac{2}{\sqrt{\pi}} \frac{(c_1^* - c_1(0)_{\text{eq}})}{\chi} F(\chi) \\
c_2(0,t) &= c_2(0)_{\text{eq}} - \frac{2}{\sqrt{\pi}} \frac{\gamma(c_1^* - c_1(0)_{\text{eq}})}{\chi} F(\chi)
\end{aligned} \tag{B21}$$

where $F(\chi)$ is given in Table 1, and $c_1(0)_{\text{eq}}$ and $c_2(0)_{\text{eq}}$ fulfil that,

$$\gamma c_1(0)_{\text{eq}} + c_2(0)_{\text{eq}} = \gamma c_1^* + c_2^* \tag{B22}$$

Thus, from Eqs. (B21) and (B22) one finally obtains that,

$$\gamma c_1(0,t) + c_2(0,t) = \gamma c_1(0)_{\text{eq}} + c_2(0)_{\text{eq}} = \gamma c_1^* + c_2^* \tag{B23}$$

such that taking into account the relationship (B23) in the surface condition (13), the latter can be reformulated as a function of a single variable (Eq. (15)).

Appendix C. Numerical simulation

For the discretization of the differential equation (6), a central three-point approximation for the spatial second derivative and the backward implicit time integration for each spatial point i and time-step k can be considered so that:

$$\alpha_{(i)} C_{1,i-1}^k + \beta_{(i)} C_{1,i}^k + \gamma_{(i)} C_{1,i}^k = \delta_i \quad (1 \leq i \leq n-2) \quad (\text{C1})$$

where $C_1 = c_1 / c_1^*$. The two-point forward difference approximation for the surface derivative in the surface condition (15) leads to:

$$\frac{C_{1,1}^k - C_{1,0}^k}{\Delta X} = \frac{\Lambda r_e}{D_1} (A + \gamma B) (C_{1,0}^k - C_{1,0}^{\text{eq}}) \quad (\text{C2})$$

with ΔX being the first interval of the spatial grid, where $X = x / r_e$ and r_e is the radius of the macroelectrode.

The above is a tridiagonal equation system equivalent to that of a single chemical species subject to diffusion, a Robin-type surface condition and a Dirichlet-type bulk condition at $i = n - 1$:

$$C_{1,n-1}^k = 1 \quad (\text{C3})$$

Hence, it can be solved very efficiently by means of the simple Thomas algorithm [8,9]. Thus, for example, the numerical solution and C++ code for a simple reversible charge transfer process given in Chapter 3 in [9] can be easily adapted to simulate the cyclic voltammetry of the four mechanisms considered by just replacing the Thomas algorithm coefficients for the surface point ($i = 0$) by:

$$\begin{aligned} \beta_0 &= 1 + \frac{\Lambda r_e}{D_1} (A + \gamma B) \Delta X \\ \gamma_0 &= -1 \\ \delta_0 &= \frac{\Lambda r_e}{D_1} (A + \gamma B) \Delta X C_{1,0}^{\text{eq}} \end{aligned} \quad (\text{C4})$$