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Differential double pulse voltammetry at spherical microelectrodes for the characterization of the square mechanism

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ABSTRACT

A rigorous analytical solution is presented for the study of chemical equilibria coupled to reversible electron transfers by means of differential double pulse voltammetry (DDPV) at (hemi)spherical electrodes. Special attention is paid to situations where the chemical processes in solution involve a significant change in the diffusivity of one of the electroactive species. This leads to a more complex behaviour of the DDPV response at microelectrodes with respect to the case of equal effective diffusion coefficients. The impact of such behaviour on the variation of the DDPV peak with the technique parameters (double pulse duration and pulse amplitude) and with the electrode size is discussed. Also, experimental conditions and methodology for the determination of the diffusion coefficients, formal potential and equilibrium constants are proposed.

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1. Introduction

Differential Double Pulse Voltammetry (DDPV) is an electrochemical technique suitable for quantitative analysis of electrochemical systems due to its high sensitivity and minimization of double layer and background effects [1–4]. Moreover, the peak-shaped response offers high resolution of the signal and accurate determination of its position. Therefore, this technique can be used for quantitative determination of trace elements and for the study and identification of homogeneous and heterogeneous kinetics [1–6].

The waveform in DDPV consists of the application of successive double potential pulses, the duration of the first pulse being much longer than the second one and the initial conditions being restored after each double pulse. The current is measured at the end of the two consecutive potential pulses and the DDPV response is obtained from the difference between them (see Fig. 1). This technique is different from Differential Multi Pulse Voltammetry (DMPV), where a train of pulses is applied without restoring the initial conditions before each double pulse such that the experiments are shorter though the interpretation of results is more complicated as well as the theoretical modeling.

In this paper a rigorous analytical expression for the DDPV response at a spherical electrode is presented for the square mechanism, where both the oxidized and reduced species may take part in homogeneous chemical equilibria (see Scheme 1). The electron transfers are considered to be reversible and the analytical solution is valid without any limitation in the values of the diffusion coefficients of the participating species. The spherical geometry of the electrode enables us to look into the behaviour of the electrochemical response when microelectrodes are employed and so convergent diffusion can be very significant. The findings discussed in the manuscript can be extended qualitatively to other microelectrode geometries such as microdiscs, though this case is theoretically more complex and numerical simulations are required for quantitative analysis.

The interest of the results reported is justified by the number of electrochemical systems where the charge transfer is coupled to chemical reactions that lead to significant changes in the diffusivity of the species. For example, this is the case of the formation of supramolecular adducts [7] and of the complexation of metal ions in natural media [8]. Thus, a ratio of 0.41 has been reported between the diffusion coefficient of the anion of ferrocenecarboxylic acid and the corresponding complex with β-ciclodextrin in pH 9.2 aqueous solution [9]. Also, variations of 2–3 orders of magnitude in the diffusion coefficients can be expected upon the association of metal species with nanoparticles or humic substances [10]. When room-temperature ionic liquids are employed as solvents, significant differences between the diffusion coefficients of the oxidized and reduced species have also been reported [11,12]. For example, a ratio $D_{ox}/D_{red} = 5.3$ has been found for the mono-electron reduction of 2-methyl-2-nitropropane in $[Et_3BuN][TFSI]$

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[13] and this relationship is 33.3 in the electro-reduction of oxygen to superoxide in $[N_{6222}][N(Tf)_2]$ [14].

From the theoretical results obtained, the effect of the divergence between the species diffusivities is analysed for a wide range of electrode radii, from macro- to ultramicroelectrodes. It is observed that for spherical microelectrodes under transient conditions the peak potential in DDPV depends on the duration of the potential pulses and the electrode size when the effective diffusion coefficients of oxidized and reduced species are different. The use of such electrodes allows us to obtain simultaneously the ratio between the effective diffusion coefficients (D_{eff}/D'_{eff}) and the apparent formal potential ($E^{0'}_{app}$) from two DDPV experiments performed with a positive and a negative pulse amplitude, which is not possible with macro- and ultramicro-electrodes.

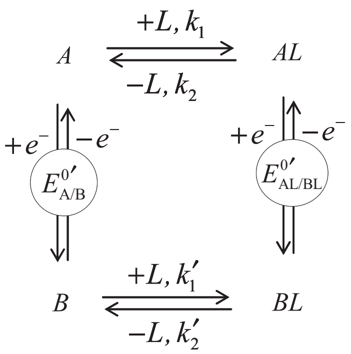
A remarkable difference between the peak potential in DDPV (E_{peak}) and the half wave potential ($E_{1/2}$) is observed for medium-size microelectrodes and $D_{eff}/D'_{eff} \neq 1$. Thus, the identification of the E_{peak} -value as $E_{1/2}$ can lead to notable errors when these microelectrodes are employed and the diffusion coefficients are quite different.

2. Theory

Let us consider a reversible one electron transfer coupled to homogeneous chemical processes, according to Scheme 1 where k_1, k'_1 and k_2, k'_2 are the forward and backward rate constants of the chemical reactions and $E^{0'}_{\mathrm{AL_i/BL_i}}(i = 0{,}1)$ is the formal potential of the redox pair AL_i/BL_i (AL_0 = A, BL_0 = B). Moreover, the chemical reactions are assumed to be at equilibrium and the species L to be in large excess such that the effective equilibrium constants can be defined as

$$K = \frac{c^*_{AL}}{c^*_A} \quad ; \quad K' = \frac{c^*_{BL}}{c^*_B} \tag{1}$$

with c^*_k being the equilibrium concentration of species k (≡A, AL, B, BL).



Scheme 1.

We will consider the application of a double potential pulse perturbation on the above system by using a spherical electrode. First, the applied potential is set at a value E_1 in the interval $0 \leqslant t \leqslant \tau_1$, with the current response (under total equilibrium conditions) being given by [15]

$$I_1 = FAD_{\mathrm{eff}}\left(\frac{c^*_{\mathrm{AT}}}{1+\gamma e^{\eta'_1}}\right)\left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_{\mathrm{eff}} t}} - \frac{\gamma(\gamma-1)e^{\eta'_1}}{(1+\gamma^2 e^{\eta'_1})r_0} + \frac{2(\gamma-1)^2 e^{\eta'_1} F(\xi_1)}{\xi_1\sqrt{\pi}(1+\gamma^2 e^{\eta'_1})^2\sqrt{\pi D'_{\mathrm{eff}} t}}\right] \tag{2}$$

where

$$e^{\eta'_1} = \omega e^{\eta_1} \tag{3}$$

with ω being

$$\omega = \frac{1+K}{1+K'} \tag{4}$$

and η_1 the dimensionless overpotential corresponding to the electroreduction of species A

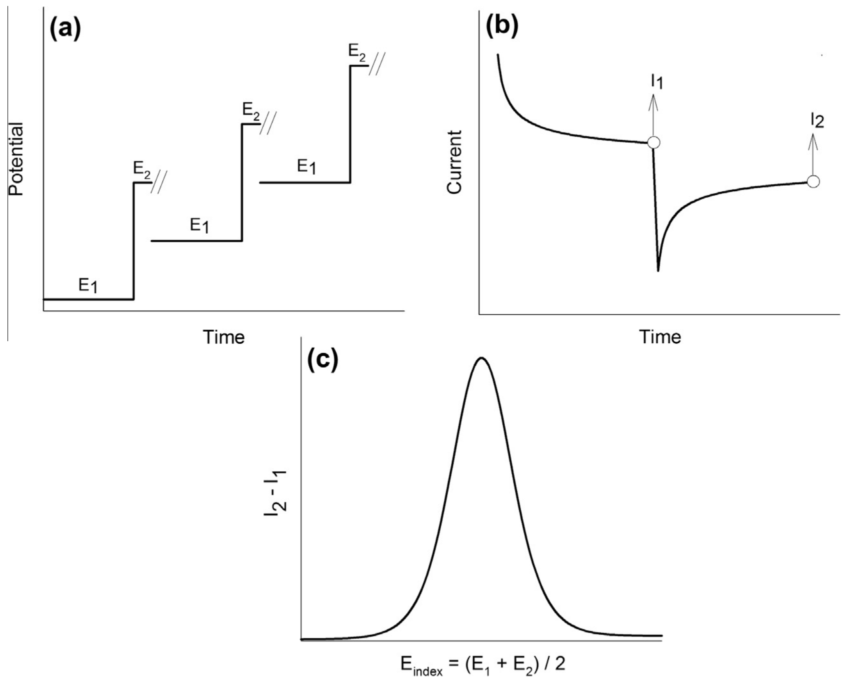


Fig. 1. Differential Double Pulse Voltammetry (DDPV). (a) Potential-time waveform, with double slash indicating that the initial conditions are restored. (b) Current sampling points. (c) DDPV response.

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