An approximate theoretical treatment of ion transfer processes at asymmetric microscopic and nanoscopic liquid–liquid interfaces: Single and double potential pulse techniques

A. Molina a,⇑, E. Laborda a, R.G. Compton b,⇑

a Departamento de Química Física, Facultad de Química, Regional Campus of International Excellence ‘Campus Mare Nostrum’, Universidad de Murcia, 30100 Murcia, Spain
b Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

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Abstract
Simple theory for the electrochemical study of reversible ion transfer processes at micro- and nano-liquid|liquid interfaces supported on a capillary is presented. Closed-form expressions are obtained for the response in normal pulse and differential double pulse voltammetries, which describe adequately the particular behaviour of these systems due to the ‘asymmetric’ ion diffusion inside and outside the capillary.

The use of different potential pulse techniques for the determination of the formal potential and diffusion coefficients of the ion is examined. For this, very simple analytical expressions are presented for the half-wave potential in NPV and the peak potential in DDPV.

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1. Introduction
The investigation of ion transfer through liquid|liquid interfaces by means of electrochemical techniques has been greatly developed given their value in the detection of ionic species (regardless of their electroactivity) and the study of their affinity to different media [1–4]. This includes important compounds such as drugs [5–8] and species of biological [9–13], environmental [14] and industrial [15] interest, and it assists the understanding of molecular interactions in facilitated extraction processes and the transport of compounds through biological membranes.

As in conventional electrode|electrolyte systems, the reduction of the size of the interface offers valuable advantages for quantitative analysis and therefore it has received a notable interest [4] since the pioneering work by Girault et al. [16]. Thus, distorting effects (mainly Ohmic drop) are reduced [17,18] and the characterization of very fast ion transfers and the miniaturization of electrochemical sensors are possible. Among the different approaches to these systems, pores, pipets and capillaries (cylindrical pipets) have been considered to support such small liquid|liquid interfaces, as well as arrays of them in order to amplify the electrochemical signal while retaining the benefits mentioned above.

In spite of the above advantages, the theoretical treatment and analysis of the results of these interfaces is not straightforward given the asymmetry of the diffusion fields inside and outside the pore or pipet. Thus, as can be seen in Figure 1, whereas diffusion can be approximated as linear in the inner phase, radial diffusion is significant in the outer phase, especially when the size of the capillary is decreased. As a result, the voltammograms show characteristics of the behaviour at macrointerfaces with respect to the egress of the ion, and features of radial diffusion for the ingress process, reaching a time-independent response [19]. A similar voltammetric behaviour has been reported for electron transfer processes at electrode|solution interfaces where the diffusion coefficients of the reactant and product species differ very markedly [20].

In this Letter, we develop and assess an approximate mathematical treatment of reversible ion transfers at liquid|liquid interfaces supported on micro- and nano-capillaries in normal pulse (NPV) and differential double pulse (DDPV) voltammetries. This approach enables the derivation of very simple, closed-form expressions for the half-wave potential in NPV and for the peak potential in DDPV. These describe adequately the influence of the duration of the potential pulses, the capillary size and the diffusivity of the target ion in the two phases, taking into account the special features that arise as a consequence of the different diffusion fields either side of the interface. These equations also allow for the determination of the ion transfer formal potential (with an error of at most 8 mV) in a much faster and easier way than numerical methods. This is of particular interest in the case of potential...
pulse techniques where numerical solutions can require very short time-steps (and so long calculation times) in order to deal conveniently with the time singularity after each potential jump [21].

2. Theory

We consider the case of a liquid–liquid interface supported at a small capillary such that a target ion \( X^+ \) can be transferred between the outer and inner phases under external polarization giving rise to an electrochemical potential gradient next to the interface (Figure 1). In the presence of an excess of supporting electrolyte in both solutions, the mass transport of the target ion takes place mainly by diffusion and it can be described by Fick’s second law that in cylindrical coordinates is given by:

\[
\frac{\partial c_{\text{out}}^{X^+}}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( D_{\text{out}}^{X^+} \frac{\partial c_{\text{out}}^{X^+}}{\partial r} \right) + \frac{\partial}{\partial z} \left( D_{\text{out}}^{X^+} \frac{\partial c_{\text{out}}^{X^+}}{\partial z} \right) \tag{1}
\]

The superscript \( x \) refers to the phase (inner, \( \alpha = \text{in} \), and outer, \( \alpha = \text{out} \)) where the ion \( X^+ \) diffuses and \( D_{\alpha}^{X^+} \) the diffusion coefficient of the target ion. Considering that the ion transfer is reversible and a constant potential pulse is applied, the boundary value problem is given by:

\[
\begin{align*}
    & \text{at } t = 0, z \geq 0, \quad z \rightarrow +\infty \quad c_{\text{out}}^{X^+} = c_{\text{in}}^{X^+} \\
    & \text{at } t > 0, z \leq 0, \quad 0 \leq r \leq a \quad c_{\text{in}}^{X^+} = c_{\text{out}}^{X^+} \\
    & \text{at } t > 0, z \rightarrow -\infty, \quad 0 \leq r \leq a \quad c_{\text{in}}^{X^+} = c_{\text{out}}^{X^+} \\
    & \text{at } t > 0, z = 0, \quad 0 \leq r \leq a \quad D_{\text{in}}^{X^+} \frac{\partial c_{\text{in}}^{X^+}}{\partial z} \bigg|_{z=0} = D_{\text{out}}^{X^+} \frac{\partial c_{\text{out}}^{X^+}}{\partial z} \bigg|_{z=0} \\
    & \text{with } a \text{ being the radius of the pore, } c_{\text{in}}^{X^+} \text{ the bulk concentration of species } X^+ \text{ in the inner/outer phase, } c_{\text{in}}^{X^+} \text{ the concentrations at the interface (} z = 0 \text{)} \text{ and:}
\end{align*}
\]

\[
\eta = \frac{2F}{RT} (\Delta_{\text{in}}^{X^+} - \Delta_{\text{out}}^{X^+}) \tag{3}
\]

with \( z \) being the charge of the target ion, \( \Delta_{\text{in}}^{X^+} \phi \) the electric potential difference across the interface, \( \Delta_{\text{out}}^{X^+} \phi \) the formal potential of the ion transfer and other symbols having their usual meanings.

Note that the above problem includes many important experimental systems such as capillaries (cylindrical pipets) [19,22] and pores where their length is longer than the inner diffusion layer (hundreds of micrometers for typical conditions).

2.1. Approximate analytical treatment

2.1.1. Single potential pulse

First, we consider the application of a potential pulse \( \Delta_{\text{in}}^{X^+} \phi \) during the time \( 0 \leq t_1 \leq t_2 \) such that the target ion is transferred. Analyzing the system shown in Figure 1, one can conclude that, provided that the diffusion layer in the inner solution is thinner than the length of the capillary/pore, the diffusive mass transport inside the capillary can be approximated as linear [23]:

\[
\frac{\partial c_{\text{in}}^{X^+}}{\partial t} = \frac{D_{\text{in}}^{X^+}}{\partial z^2} \tag{4}
\]

On the other hand, diffusion outside the capillary will have an important radial contribution and will be analogous to the case of microholes and microdisc electrodes, where, if the radius of the capillary is small enough and/or the time scale of the experiment long enough, a steady state response is obtained:

\[
\frac{\partial c_{\text{out}}^{X^+}}{\partial t} = 0 = \frac{D_{\text{out}}^{X^+}}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_{\text{out}}^{X^+}}{\partial r} \right) \tag{5}
\]

Attending to the differential Eq. (5), we can propose in an approximate way that the total flux at the interface in the inner solution will follow the mathematical form predicted for linear diffusion [24,25]:

\[
\text{total surfaceflux}_{\text{in}} = -\pi \alpha^2 D_{\text{in}}^{X^+} \left( \frac{\partial c_{\text{in}}^{X^+}}{\partial z} \right)_{z=0} = -\pi \alpha^2 \left( c_{\text{in}}^{X^+} - c_{\text{out}}^{X^+} \right) \left( \frac{\partial c_{\text{in}}^{X^+}}{\partial z} \right)_{z=0} \tag{6}
\]

and that at the outer side of the interface can be expressed as the steady state solution for microdisc interfaces [26,27]:

\[
\text{total surfaceflux}_{\text{out}} = 2\pi D_{\text{out}}^{X^+} \left( \int_0^{r_{\text{in}}} \frac{\partial c_{\text{in}}^{X^+}}{\partial z} r dr \right)_{r_{\text{in}}}^{r_{\text{out}}} = 4D_{\text{out}}^{X^+} a (c_{\text{in}}^{X^+} - c_{\text{out}}^{X^+}) \left( \text{mol} \cdot \text{s}^{-1} \right) \tag{7}
\]

and mass conservation establishes that:

\[
\pi \alpha^2 D_{\text{in}}^{X^+} (c_{\text{in}}^{X^+} - c_{\text{out}}^{X^+}) = -4D_{\text{out}}^{X^+} a (c_{\text{in}}^{X^+} - c_{\text{out}}^{X^+}) \tag{8}
\]

The above treatment enables us to obtain simple analytical solutions for liquid–liquid interfaces supported at micro- and nano-capillaries in single and double potential pulse techniques. These solutions offer simple and fast procedures for the characterization of the ion transfer potentials and the diffusivities of the target ion in the two phases.

By combining the relationship Eq. (8) with the Nernstian condition, \( c_{\text{in}}^{X^+} = e^{\phi} c_{\text{out}}^{X^+} \), expressions for the interfacial concentrations can be obtained immediately:

\[
c_{\text{in}}^{X^+} = c_{\text{in}}^{X^+} + \frac{c_{\text{in}}^{X^+} - c_{\text{out}}^{X^+}}{1 + e^{\phi}} \tag{9}
\]

where:
where \( \delta_p \) is the thickness of the linear diffusion layer in the inner phase where linear diffusion applies \( (\delta_p = \sqrt{\pi D_c^0/t_1}) \) and \( \delta_o^q \) the thickness of the linear diffusion layer in the outer phase where steady state conditions have been assumed: \( \delta_o^q = \frac{2}{a}t_2 \).

The current is given by:

\[
I = zFD_X^{in} \frac{a}{\pi a^2} \left( \frac{c_{X}^{in} - c_{X}^{out}}{\sqrt{\pi D_X^0 t_1}} \right) = -zFD_X^{out} a_c (c_{X}^{out} - c_{X}^{in})
\]

where a positive sign has been assigned to the egress of a cation from the inner solution (water) to the outer one (organic solvent) and a negative sign to the opposite process.

Eq. (11) enables us to obtain the response of the system in single step chronoamperometry and normal pulse voltammetry (NPV). The limiting currents and the half-wave potential \( \Delta \phi_{vol}^{0,1/2} \) are essential parameters for the characterization of the ion transfer. Under mass transport limiting conditions, the current is determined by the diffusion of the target ion to the interface in the phase from which this is transferred. Accordingly, the egress limiting current (i.e., \( c_{X}^{out} = 0 \)) is given by the Cottrell equation for linear, semi-infinite diffusion:

\[
I_{\text{lim ingress}} = -zFD_X^{out} a_c c_{X}^{in} = \frac{zFD_X^{out}}{\sqrt{\pi D_X^0 t_1}}
\]

whereas the ingress limiting current (i.e., \( c_{X}^{in} = 0 \)) corresponds to the Saito equation for steady state conditions:

\[
I_{\text{lim ingress, ss}} = -zFD_X^{out} a_c c_{X}^{out}
\]

Attending to the form of Eq. (11) and to Eqs. 12 and 13, the current–potential relationship can also be written in the following way:

\[
\Delta \phi_{vol}^{0} = \Delta \phi_{1/2}^{0} + \frac{RT}{zF} \ln \left( \frac{I_{\text{lim ingress, ss}} - I}{I_{\text{lim egress}}} \right)
\]

where \( \Delta \phi_{vol}^{0,1/2} \) is the half-wave potential for which a simple analytical expression can be derived:

\[
\Delta \phi_{1/2}^{0} = \Delta \phi_{vol}^{0,1/2} - \frac{RT}{zF} \ln \zeta
\]

Note that the above equation is of great interest since it allows for determination of the ion transfer potential from measurements of \( \Delta \phi_{1/2} \) in a very simple way. Given the asymmetry of the diffusion fields in the inner (linear) and outer (radial) solutions, not only does \( \Delta \phi_{1/2} \) depend on the ratio between the diffusion coefficients but also on the size of the capillary and the time scale of the experiments through the dimensionless parameter \( \zeta \).

### 2.1.2. Double pulse voltammetry

Let us now consider the application of a second potential pulse \( \Delta \phi_{vol}^{0,1/2} \) during the time \( 0 \leq t_2 \leq t_2 \), where \( t_2 \) is the total duration of the second pulse. Since the diffusion operator (4) is linear, one can assume that the solution of the problem, \( c_{X}^{out}(z,t) \), can be expressed as a linear combination:

\[
c_{X}^{out}(z,t) = c_{X}^{in}(z,t) + c_{X}^{in}(z,t_2)
\]

where \( c_{X}^{in}(z,t) \) corresponds to the concentration profile of the first pulse at the total time \( t = t_1 + t_2 \).

The bulk and initial conditions in this second pulse are given by:

\[
\begin{align*}
  z \geq 0 & \quad \text{in} & \quad \text{in} & \quad z \to \infty & \quad c_{X}^{out}(z_0) = c_{X}^{out} \\
  & \quad \text{out} & \quad \text{out} & \quad z \to -\infty & \quad c_{X}^{in}(z_0) = 0
\end{align*}
\]

Moreover, conservation of interfacial total flux establishes that:

\[
\pi a^2 D_X^{in} \left\{ \left( \frac{\partial c_{X}^{in}}{\partial z} \right)_{z=0} + \left( \frac{\partial c_{X}^{in}}{\partial z} \right)_{z=-0} \right\} = -2 \pi D_X^{out} a_c \left( \frac{\partial c_{X}^{out}}{\partial z} \right)_{z=0} dr
\]

and the Nernstian condition that:

\[
c_{X}^{out} = e^{\Delta \phi_{vol}^{0,1/2}} c_{X}^{in} \quad \text{in} \quad \text{out}
\]

In rigorous terms, as the first pulse component \( c_{X}^{in} \) in conditions (18) and (19) is time dependent, its analytical expression changes with the application of the second pulse. However, in order to simplify the resolution of the problem, we will assume that the mathematical expression of \( c_{X}^{out}(z,t) \) does not vary during the second step and then we can write that:

\[
\pi a^2 D_X^{in} \left( \frac{\partial c_{X}^{in}}{\partial z} \right)_{z=0} = - \pi a^2 D_X^{in} \left( \frac{c_{X}^{in} - c_{X}^{in}(z)}{\sqrt{\pi D_X^0 (t_1 + t_2)}} \right)
\]

Thus, taking into account the above expressions, the mass conservation in the second pulse establishes that:

\[
\pi a^2 D_X^{in} \left( \frac{\partial c_{X}^{out}}{\partial z} \right)_{z=0} = \pi a^2 D_X^{in} \frac{c_{X}^{out}}{\sqrt{\pi D_X^0 (t_1 + t_2)}}
\]

that, together with the Nernstian conditions (19), enable us to obtain the following expressions for the interfacial concentrations of the target ion during the second pulse:

\[
\begin{align*}
  c_{X}^{in} & = \left( c_{X}^{in} + \frac{c_{X}^{in}(z_0) - c_{X}^{in}(z_0)_{z=0}}{e^{\Delta \phi_{vol}^{0,1/2}}} \right) \left( 1 + \frac{e^{\Delta \phi_{vol}^{0,1/2}}}{e^{\Delta \phi_{vol}^{0,1/2}}} \right) \\
  c_{X}^{out} & = e^{\Delta \phi_{vol}^{0,1/2}} \left( c_{X}^{in}(z_0) - c_{X}^{in}(z_0)_{z=0} \right) \frac{1 + e^{\Delta \phi_{vol}^{0,1/2}}}{e^{2 \Delta \phi_{vol}^{0,1/2}}}
\end{align*}
\]

with:

\[
\zeta_2 = \frac{4}{\pi} \sqrt{\frac{\Delta \phi_{vol}^{0,1/2}}{a}} \sqrt{a \frac{\pi D_X^{in} t_2}{a}}
\]

\[
\zeta_1 = \frac{4}{\pi} \sqrt{\frac{\Delta \phi_{vol}^{0,1/2}}{a}} \sqrt{a \frac{\pi D_X^{in} (t_1 + t_2)}{a}}
\]

and:

\[
\eta_2 = \frac{2}{RT} (\Delta \phi_{vol}^{0,1/2} - \Delta \phi_{vol}^{0,1/2}(0))
\]

\[
\eta_1 = \frac{2}{RT} (\Delta \phi_{vol}^{0,1/2} - \Delta \phi_{vol}^{0,1/2}(0))
\]
Once $c_{x}^{3/2}$ are known (Eq. (23)), the current response can be immediately calculated from Eq. (21):

$$I_2 = zFD_{X}^{\text{in}} \pmb{\pi a} \left\{ \frac{(c_{x}^{\text{in}} - c_{x}^{\text{in}(1)})}{\pmb{\pi D}_{X}^{\text{in}} (t_1 + t_2)} - \frac{c_{x}^{\text{in}(2)}}{\sqrt{\pmb{\pi D}_{X}^{\text{in}} t_2}} \right\}$$

$$= -zFD_{X}^{\text{out}} a(c_{x}^{\text{out}} - c_{x}^{\text{out}(2)}) \quad (26)$$

2.2. Finite difference simulations

To check the validity of the approximate analytical solutions, the problem given by Eqs. 1, 2 has been solved by means of finite difference method. For this, the alternating direction implicit (ADI) method has been employed with 3-point approximations of the spatial derivatives and an unequally spaced grid in the $(r,z)$ space as described in [28]. The duration of the time-steps and the spatial mesh were refined based on convergence studies and comparison with the available analytical solutions (that is, the Cottrell and the Shoup and Szabo equations [24,25] for the egress and ingress limiting currents, respectively).

3. Results and discussion

3.1. Normal pulse voltammetry (NPV)

First, the validity of the approximate solutions was assessed by comparison with the voltammograms obtained numerically. Figure 2 shows the results for different values of the dimensionless size of the capillary, $\sigma = a^2/D_{X}^{\text{out}} t_1$, when the ion is initially present in both solutions. Given that steady state conditions have been assumed for the outer phase Eq. (5), it is expected that the analytical solutions will yield more accurate results as the radius of the capillary becomes smaller and/or the duration of the potential pulse is longer, that is, as $\sigma$ decreases. Indeed, this is the behaviour observed in Figure 2 such that for $\sigma < 0.02$ the error in the ingress limiting current is smaller than 5%, that is, a time-independent ingress flux is reached when the capillary radius and the pulse durations correspond to such a $\sigma$-range are employed. Regarding the half-wave potential, under these conditions the deviations observed are at most 8 mV over a wide range of $D_{X}^{\text{in}}/D_{X}^{\text{out}}$ values investigated (from 10 to 0.01). Note that the description of the egress limiting current by Eq. (12) is rigorous in all cases given that the response is not affected by the behaviour of the ion in the outer solution and then the current is given by the Cottrell equation.

The better accuracy of the analytical solutions as $\sigma$ decreases may also be related to the assumption that the concentration profile in the inner solution is not dependent on the coordinate $r$ (Eq. (4)). This is true in the case of macrointerfaces where edge effects are negligible but it does not necessarily hold true at microcapillaries. Figure 3 shows the variation of the concentration obtained with numerical simulations for a given $z$ value ($z/a = -0.1$) and different $\sigma$ values. It is observed that the larger ingress flux at the capillary edge gives rise to higher concentrations as $r \rightarrow a$ and therefore $r$-dependent concentration profiles. However, this dependence is found to be less significant as $\sigma$ is decreased, that is, as smaller capillaries and/or longer pulse times are employed. Under such conditions, homogenization of the ion concentration in the inner solution in the $r$-direction (where the diffusion domain is finite) is easier and the use of Eq. (4) is better.

Figure 4 considers the effect of the duration of the potential pulse on the NPVgrams when the target ion is initially present in both solutions. According to Eqs. 12 and 13, the egress limiting current decreases with $t$ in a Cottrellian way whereas the ingress limiting current is time-independent. Obviously, all the curves coincide at the equilibrium potential:

$$\Delta \phi_{\text{eq}} = \Delta \phi_{\text{eq}}^0 + \frac{R T}{2 F} \ln \left( \frac{c_{x}^{\text{out}}}{c_{x}^{\text{in}}} \right) \quad (27)$$
that is equal to the formal potential of the ion transfer under the conditions of the figure \( c_{\text{in}}^+/C_{3}\text{out}^+ \). Regarding the position of the wave, the half-wave potential follows the behaviour established by Eq. (15) (see the inset in Figure 4) in such a way that, as the duration of the pulses is longer, the voltammogram shifts to more negative values.

Figures 2 and 4 show that both the size of the capillary and the time scale of the experiments have an effect on the position of the voltammograms, which must be taken into account for accurate determination of the ion transfer formal potential. The influences observed can be understood noting the ‘asymmetry’ of the diffusion fields in the inner and outer solutions. Thus, as the duration of the pulse is longer and/or the radius of the capillary is decreased (i.e., more efficient mass transport towards the interface from the outer phase), the low efficiency of the mass transport in the inner solution gives rise to high concentrations of the target ion next to the interface (see Figure 4B). Consequently, further ion ingress is unfavoured, which is consistent with the variation of the half-wave potential observed in Figures 2 and 4.

The influence of the different diffusivities of the ion inside and outside the capillary is studied in Figure 5. As expected from Eq. (15), for a given \( r_\text{a} \)-value the position of the wave varies with the ratio \( D_\text{in}^+/D_\text{out}^+ \) such that the voltammograms appear at more negative values as the diffusion coefficient in the inner solution is smaller. Thus, the ingress of the ion into the capillary is more difficult (takes place at more negative potentials) as the diffusivity of the ion in the inner phase is slower and then its concentration next to the interface is higher. On the other hand, when the ion diffuses faster in the inner solution, its interfacial concentration decreases and the ingress of the ion takes place at less negative potentials.

**Figure 3.** Variation of the concentration of the target ion in the inner solution with the \( r \)-coordinate at \( z/a = 0.1 \) obtained with numerical simulations (Section 2.2) for different \( \sigma = a^2/D_\text{in}^+ r_1 \) values from macro- \((\sigma = 10^5)\) to ultramicro- \((\sigma = 10^{-3})\) capillaries. \( c_{\text{in}}^++c_0^+=0, D_\text{in}^+/D_\text{out}^+ \).

**Figure 4.** Normal pulse voltammetry: influence of the pulse duration, \( r_\text{in} \), on the voltammograms (A) and the interface concentrations under ingress limiting current conditions (B). \( a = 1 \mu m, D_\text{in}^+ = 10^{-5} \text{ cm}^2 \text{s}^{-1}, D_\text{out}^+ = 10 \times D_\text{in}^+, c_{\text{in}}^+=c_0^+ \).
The above results show that the characterization of the ion transfer can be achieved through NPV from the value of the half-wave potential, provided that the diffusion coefficients of the ion and the capillary diameter are available. $\Delta \phi_{1/2}$ can be determined accurately by smoothing and differentiation of the experimental NPV gram (so-called derivative voltammetry), and the consistency of the values obtained can be easily tested by varying the duration of the potential pulses. If the $D_X$ values are not known, these can be obtained from the mass transport limiting currents (Eqs. 12 and 13), which obviously requires the presence of the target ion in both liquid phases at known concentrations (common ion voltammetry). Under such conditions, the formal potential of the ion transfer can also be determined easily from the null current or equilibrium potential, $\Delta \phi_{eq}$ (Eq. (27)) [18].

3.2. Double potential pulse techniques

3.2.1. Double potential step chronoamperometry

Double potential step chronoamperometry under limiting current conditions can be envisaged as a suitable technique for the simultaneous determination of the diffusion coefficients of the ion in both phases, without requiring the addition of the ion to both solutions. Thus, considering the situation where $X^*$ is only present in the outer phase ($c_{Xout} = 0$, $c_{Xin} = 0$), a first potential pulse at a very negative overpotential ($\eta_1 \rightarrow -\infty$) enables the determination of $D_{X}^{in}$ from Eq. (13). Then, if a second pulse is applied under egress limiting current conditions ($\eta_2 \rightarrow +\infty$), the current predicted by Eq. (26) by making $\eta_1 \rightarrow -\infty$ and $\eta_2 \rightarrow +\infty$ is:

$$I_{2,lim} = -zF4D_{X}^{out} a_{X}^{out}$$

$$= zF4D_{X}^{out} a_{X}^{out}$$

Provided that $c_{Xin} = 0$, the above expression establishes that the current at the second pulse does not depend on the diffusion coefficient of the ion in the inner solution and it is determined by the duration of the potential pulses. This is also found at liquid/liquid macrointerfaces where the current at the second pulse is 'blind' to the diffusivity of the ion in the phase where it is absent at the beginning of the experiment [29].

If we consider the alternative situation where $c_{Xin} = 0$ and $c_{Xout} = 0$ such that the ion egresses in the first pulse and ingresses in the second one under limiting current conditions (i.e., $\eta_1 \rightarrow +\infty$ and $\eta_2 \rightarrow -\infty$), the current in the second pulse predicted by Eq. (26) is:

$$I_{2,lim} = -zF4D_{X}^{out} a_{X}^{out}$$

such that $I_{2,lim}$ is null for $c_{Xout} = 0$ as a consequence of the very fast diffusion of the ion in the outer solution, which is also observed at symmetric ultramicrointerfaces [29].

The above behaviours have been verified with numerical simulations, confirming that double potential step chronoamperometry is not suitable for simultaneous determination of diffusion coefficients at micro-/nano-capillaries unless the ion is initially present in both solutions. Note that under such conditions the obtaining of $D_{X}^{in}$ and $D_{X}^{out}$ can be achieved more easily with single step chronoamperometry as can be inferred from Eqs. 12 and 13.

3.2.2. Differential double pulse voltammetry (DDPV)

From Eqs. 26 and 11 the response of the system in differential double pulse voltammetry (DDPV) can be calculated. In this technique, a series of double potential steps with $\tau_1 > 50 \tau_2$ are applied and the signal corresponds to the difference between the currents at the end of the pulses:

$$\Delta I = I_2 - I_1 = -zF4D_{X}^{out} a_{X}^{out}$$

$$\left( \frac{c_{Xin}^{in} + \xi_1 c_{Xout}^{out}}{\sqrt{\frac{\tau_1}{\tau_2}} - 1} \right) \left( \frac{\tau_1}{\tau_2} + \xi_2 \right) - \frac{e^{\xi_2} - e^{\xi_1}}{\left( \frac{1}{\tau_1} + \xi_1 \right) \left( \frac{1}{\tau_2} + \xi_2 \right)}$$

As shown in Figure 6, the subtractive nature of this technique gives rise to peaked signals and the minimization of distorting background currents, which is very convenient for quantitative analysis. Note that for the potential-axis the average value of the applied potentials in each double pulse is chosen: $\Delta \phi_{out} = (\pm \omega_{in} + \phi_{out} + \Delta \phi_{2})/2$. At macrointerfaces this choice gives the advantage that the peak potential coincides with the half-wave potential [30]. With respect to derivative voltammetry, DDPV may be preferred given that the differentiation of the experimental NPV voltammogram can degrade the signal-to-noise ratio. In addition, higher sensitivity can be obtained by increasing the pulse amplitude: $\Delta \phi = \omega_{out} - \omega_{in}$. Comparison with numerical results shows that the peak potential obtained from Eq. (30) differs from the numerical one in less than 8 mV. Regarding the peak current, the analytical results are accurate to within 5% error when $\xi_2 > 30$.

As discussed for NPV, the DDPV peak shifts to more negative potentials as the ratio $D_{X}^{in}/D_{X}^{out}$ decreases due to the reasons above discussed. Quantitatively speaking, the variation of the peak
Differential double pulse voltammetry: influence of the potential pulses. It also includes the effect of the different diffusivities of the ion in both phases, which is of great interest in this context where significant differences can be found.

The analytical solutions obtained show the unsuitability of double potential step chronoamperometry for the determination of the ion diffusion coefficients in each phase ($D^0_{in}$ and $D^0_{out}$) unless the species is initially present in both solutions. This strongly limits the use of this technique given that under such conditions the determination of $D^0_{in}$ is easier through single step chronoamperometry.

Once the diffusion coefficients are known, the ion transfer formal potential can be determined from the NPV null-current potential (Eq. (27)) if the target ion is present in both phases or, otherwise, from the NPV half-wave potential (Eq. (15)) and the peak potential in double differential pulse voltammetry (DDPV). For the latter, a simple analytical solution (Eq. (31)) has also been derived for micro- and nano-interfaces that yields satisfactory values of the peak potential (with deviations smaller than 8 mV).

4. Conclusions

An approximate theoretical treatment of micro- and nano-liquid/liquid interfaces at capillaries has been developed, which enables the description of the ion transfer in single pulse and double potential pulse techniques. This approach leads to closed-form expressions which are much faster and easier to implement than numerical simulations.

A very simple equation has been obtained that describes adequately the variation of the response in normal pulse voltammetry (NPV) with the size of the capillary and the duration of the potential pulses. It also includes the effect of the different diffusivities of the ion in both phases, which is of great interest in this context where significant differences can be found.

As can be inferred from Eqs. 15 and 31, the peak potential does not coincide with the half-wave potential as it does in derivative voltammetry (see Figure 7). Therefore, unlike at macrointerfaces, the DDPV peak potential cannot be identified as the half-wave potential (Eq. (27)) if the target ion is present in both phases or, otherwise, from the NPV half-wave potential (Eq. (15)) and the peak potential in double differential pulse voltammetry (DDPV). For the latter, a simple analytical solution (Eq. (31)) has also been derived for micro- and nano-interfaces that yields satisfactory values of the peak potential (with deviations smaller than 8 mV).

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References