Linear Sweep and Cyclic Voltammetries of Reversible Ion Transfer Processes at Macro- and Microcapillaries under Transient Regime


Abstract: The voltammetry corresponding to the reversible transfer of an ionic species across a liquid|liquid interface supported at the tip of a capillary is modelled with an approximate analytical treatment. The solution obtained enables the calculation of the electrochemical response in any voltammetric technique when capillaries of any size are employed, including micro- and macro-liquid|liquid interfaces. The theory is applied to study the effect of the key system variables (capillary size, scan rate and ion diffusion coefficients) on the response obtained in cyclic voltammetry. In all cases, the explicit solution presented provides good description of the influence of the above variables and it allows for the accurate determination of the formal transfer potential.

Keywords: Ion transfer • Liquid|liquid interface • Microcapillary • Cyclic voltammetry • Analytical theoretical treatment

1 Introduction

The use of electrochemical methods for the study of ion transfer processes has been proven very powerful since the interface between two immiscible electrolyte solutions (for example, between water solution and organic solvents, ionic liquids or liquid membranes) can be polarized externally [1–6]. Within the potential window available, it is often possible to drive and study the transfer of ionic compounds by changing the potential difference between two reference electrodes placed at each side of the interface. The transfer potentials are directly related to the affinity of the target species towards the different phases, which gives very valuable information for example about the ability of charged compounds to go through lipophilic biological structures such as cell membranes [7,8]. Also, these interfaces are of interest in catalysis [9] and electroanalysis [8].

Analogous to the electrode|solution interface, much effort has been devoted to reduce the size of the liquid|liquid interface given the advantages that this offers in electrochemical studies [10–14]. The smaller currents recorded at micro- and nano-interfaces enable the minimisation of disturbing effects (mainly the Ohmic drop), the study of very fast (electro)chemical kinetics, the simplification of the instrumentation (moving from a four-electrode set-up for macro-interfaces to a two-electrode arrangement) and the reduction of the amount of supporting electrolyte employed, which can be a problem in the case of organic solvents. On the other hand, the modelling of the corresponding diffusion problem is more complicated since, in general, it cannot be reduced to a single spatial coordinate as for macro-interfaces and also certain effects cannot be assumed as negligible such as those associated with the double layer [13,15].

Within the above context, our group presented recently a simple and approximate analytical treatment [16,17] that yields simple explicit equations for the voltammetric response of reversible ion transfer processes at ultramicro-capillaries in any technique by assuming a steady-state flux in the outer solution. In this paper, this theoretical approach will be extended to capillaries of any radius including micro-capillaries where the advantages of small interfaces still hold whereas the fabrication, characterization and modelling are easier than for nano-interfaces. For the above purpose, the flux at the outer side of the liquid|liquid interface has been considered as transient. This enables us to cover a wider range of experimental situations including capillary radius of tens of microns up to macro-interfaces.

The theoretical results are applied to the study of cyclic voltammetry in the transition from the two-peak response obtained at large interfaces towards the characteristic voltammograms at (ultra)micro-interfaces [18–20]. The analytical expressions enable the simple calculation of the voltammetric curves of reversible ion transfer processes even when the diffusion coefficient of the ion changes significantly between the two immiscible phases, which is frequently the case when the ion is transferred from conventional solvents to ionic liquids [5,21–23] or to liquid
membranes [6,24]. The effects of the capillary size and experimental time-scale (i.e., scan rate) on the shape and position of the voltammograms are examined and quantified, providing tools for the determination of the formal transfer potential.

2 Theory

On the external polarization of a liquid|liquid interface between two immiscible electrolyte solutions, the transfer of a target ion $X^{Z}$ can be driven and monitored by making use of conventional electrochemical techniques. Considering that the interface is supported at a cylindrical pipet (capillary) (Figure 1) and that the ion transfer is reversible, the problem associated with the application of a potential pulse is defined by Fick’s second law in cylindrical coordinates where sufficient electrolyte is presumed in each phase such that transport via migration is negligible:

$$\frac{\partial c_{\text{in}}}{\partial t} = D_{\text{in}} \left( \frac{\partial^2 c_{\text{in}}}{\partial z^2} + \frac{\partial^2 c_{\text{in}}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{\text{in}}}{\partial r} \right)$$

$$\frac{\partial c_{\text{out}}}{\partial t} = D_{\text{out}} \left( \frac{\partial^2 c_{\text{out}}}{\partial z^2} + \frac{\partial^2 c_{\text{out}}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{\text{out}}}{\partial r} \right)$$

(1)

together with the corresponding boundary value problem:

$$c_{\text{out}} = c^*_{\text{out}} \quad t > 0, z = 0, 0 \leq r \leq a$$

$$c_{\text{in}} = c^*_{\text{in}} \quad t = 0, 0 \leq z \leq a$$

$$c_{\text{in}} = c^*_{\text{in}} \quad \text{subject to} \quad z > a$$

$$c_{\text{out}} = c^*_{\text{out}} \quad t > 0, z = 0, 0 \leq r \leq a$$

$$D_{\text{in}} \left( \frac{\partial c_{\text{in}}}{\partial r} \right)_{z=0} = D_{\text{out}} \left( \frac{\partial c_{\text{out}}}{\partial r} \right)_{z=0}$$

(2)

(3)

(4)

with $a$ being the radius of the capillary, $D_{\text{in/out}}$ the diffusion coefficient of the ion under study in each phase, $c^*_{\text{in/out}}$ its bulk concentration, $c_{\text{in/out}}$ the concentrations at the interface ($z=0$) and:

$$\eta = \frac{ZF}{RT} \left( \Delta_{\text{out}}^{\text{in}} \phi - \Delta_{\text{in}}^{\text{out}} \phi' \right)$$

(5)

where $Z$ is the charge of the target ion, $\Delta_{\text{out}}^{\text{in}} \phi$ the electric potential difference across the interface, $\Delta_{\text{in}}^{\text{out}} \phi'$ the
formal transfer potential and other symbols have their usual meanings.

2.1 Approximate Analytical Treatment

2.1.1 First Potential Pulse

First, we will consider the application of a first potential pulse $\Delta_{p1}^{in}$ during the time $0 \leq t_1 \leq t_f$ such that the target ion is transferred between the two electrolytes. From the analysis of the concentration profiles inside and outside the capillary during the application of the perturbation (Figure 1) one can propose that the diffusive mass transport inside the capillary can be approximated as [14,16,17]:

$$\frac{\partial c^{in(1)}(t_1)}{\partial t} \approx D^{in} \left( \frac{\partial^2 c^{in(1)}}{\partial z^2} \right)$$ (6)

such that the ion flux at the inner side of the interface can be assumed to have the mathematical form corresponding to planar diffusion [25,26]:

$$(total \ flux)_{in} = -\pi a^2 D^{in} \left( \frac{\partial c^{in(1)}(t_1)}{\partial z} \right)_{z=0}$$

$$= -\pi a^2 D^{in} \frac{c^{in(1)}(t_1)}{\sqrt{\pi D^{in} t_1}} \text{ (mol s}^{-1})$$ (7)

where the superscript (1) refers to the first potential pulse. Analogously, it is assumed that the interfacial flux at the outer side of the interface would follow a form analogous to the transient solution for microdisc interfaces [27]:

$$(total \ flux)_{out} = 2\pi D^{out} \int_0^a \left( \frac{\partial c^{out(1)}(t_1)}{\partial z} \right) \ r \ dr$$

$$= D^{out} \pi a^2 g_d(\sigma_1) (c^{out} - c^{out(1)}(t_1)) \text{ (mol s}^{-1})$$ (8)

where:

$$g_d(\sigma_1) = \frac{4}{\pi a} \left[ 0.7854 + 0.44315 \sqrt{\sigma_1} + 0.2146 \exp(-0.39115 \sqrt{\sigma_1}) \right]$$ (9)

and:

$$\sigma_1 = \sigma(t_1) = \frac{a^2}{D^{out} t_1}$$ (10)

Finally, the current response is given by:

$$I_1 = Z F D^{in} \pi a^2 \frac{c^{in} - c^{in(1)}(t_1)}{\sqrt{\pi D^{in} t_1}} = -Z F D^{out} \pi a^2 g_d(\sigma_1) (c^{out} - c^{out(1)}(t_1))$$ (16)

where a positive sign is assigned to the egress of a cation from the inner solution to the outer one.

2.1.2 Second Potential Pulse

We consider now the application of a second potential pulse $\Delta_{p2}^{in}$ during the time $0 \leq t_2 \leq t_f$. Given that the diffusion operators (Equation 1) are linear, the solutions of the problem, that is, the concentration profiles, can be expressed as linear combinations of solutions:

$$c^{in(2)}(r,z,t) = c^{in(1)}(r,z,t) + c^{in(2)}(r,z,t)$$ (17)

$$c^{out(2)}(r,z,t) = c^{out(1)}(r,z,t) + c^{out(2)}(r,z,t)$$ (18)

where $c^{in(1)}(r,z,t)$ and $c^{out(1)}(r,z,t)$ are the concentration profiles 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:

\[
t_2 = 0, \ z \geq 0, \ 0 \leq r \leq +\infty \quad z_{\text{in}}^{(2)}(t_2) = 0 
\]

\[
t_2 > 0, \ z \to +\infty, \ 0 \leq r \leq +\infty \quad z_{\text{out}}^{(2)}(t_2) = 0 
\]

and the mass conservation and Nernst relationships by:

\[
\pi a^2 D^m \left\{ \left( \frac{\partial c^{\text{in}}(t)}{\partial z} \right)_{z=0} + \left( \frac{\partial c^{\text{out}}(t_2)}{\partial z} \right)_{z=0} \right\} 
\]

\[
= -2\pi D^\text{out} \int_0^a \left\{ \left( \frac{\partial c^{\text{out}}_{\text{in}}(t)}{\partial z} \right)_{z=0} + \left( \frac{\partial c^{\text{out}}_{\text{out}}(t_2)}{\partial z} \right)_{z=0} \right\} r \, dr 
\]

\[
c^{\text{out}}(t) + c^{\text{out}}_{\text{out}}(t_2) = e^{\text{in}} \left( c^{\text{in}}(t) + c^{\text{out}}_{\text{in}}(t_2) \right) 
\]

To simplify the resolution of the problem, we will assume that the mathematical form of the surface gradient of the partial unknowns \( \tilde{z}_{\text{in}}^{(2)}(z,t_2) \) and \( \tilde{z}_{\text{out}}^{(2)}(r,z,t_2) \) is exactly as that in the first pulse. Thus, considering that Equation 11 holds for any value of \( t \), Equation 21 simplifies to:

\[
D^m \frac{\tilde{z}_{\text{in}}^{(2)}(t_2)}{\sqrt{\pi D^m t_2}} = -D^\text{out} g_d(\sigma_2) \frac{\tilde{z}_{\text{out}}^{(2)}(t_2)}{\sqrt{\pi D^m t_2}} 
\]

where:

\[
\sigma_2 = \alpha(t_2) = \frac{a^2}{D^\text{out} t_2} 
\]

From Equations 22 and 23, the values of the unknowns \( \tilde{z}_{\text{in}}^{(2)} \) and \( \tilde{z}_{\text{out}}^{(2)} \) are obtained and, attending to Equations 17 and 18, the interfacial concentrations of the ions during the second pulse are deduced:

\[
c^{\text{in}}(t_2) = \frac{c^{\text{in}} + \tilde{c}(t_2) c^{\text{out}}}{1 + \tilde{c}(t_2) c^{\text{out}}} 
\]

\[
c^{\text{out}}_{\text{out}}(t_2) = e^{\text{in}} \left( \frac{c^{\text{in}} + \tilde{c}(t_2) c^{\text{out}}}{1 + \tilde{c}(t_2) c^{\text{out}}} \right) 
\]

where:

\[
\tilde{c}(t_2) = \frac{D^\text{out} \delta(t_2)}{D^m \delta_z(t_2)} 
\]

\[
\delta(t_2) = \sqrt{\pi D^m t_2} 
\]

\[
\delta_z(t_2) = \frac{1}{g_d(\sigma_2)} 
\]

and as well as the expression for the current:

\[
I_2 = ZFD^m \pi a^2 \left\{ \frac{c^{\text{in}}_{\text{in}} - c^{\text{in}}_{\text{out}}(t_2)}{\sqrt{\pi D^m (t_1 + t_2)}} + \frac{c^{\text{in}}_{\text{out}}(t) - c^{\text{out}}_{\text{out}}(t)}{\sqrt{\pi D^m t_2}} \right\} 
\]

2.1.3 Multipulse Voltammetry

By extending the treatment presented in the previous sections to an arbitrary sequence of pulses, we can assume that the solutions of the \( n \)-th potential pulse \( \Delta_{\text{in}} \phi_n \) can be expressed as:

\[
c^{\text{in}}(n)(z,t) = e^{\text{in}}(n-1)(z,t) + \tilde{z}_{\text{in}}^{(n)}(z,t) 
\]

\[
c^{\text{out}}(n)(r,z,t) = e^{\text{out}}(n-1)(r,z,t) + \tilde{z}_{\text{out}}^{(n)}(r,z,t) 
\]

where \( t = t_1 + t_2 + t_3 + \ldots + t_n \) with \( 0 \leq t_n \leq t_n \) and \( c^{\text{in}}(n-1)(z,t) \) and \( c^{\text{out}}(n-1)(r,z,t) \) are the concentration profiles of the previous potential pulse. The bulk, initial and interface conditions in the \( n \)-th pulse are given by:

\[
t_n = 0, \ z \geq 0, \ 0 \leq r \leq +\infty \quad z_{\text{in}}^{(n)} = 0 
\]

\[
t_n > 0, \ z \to +\infty, \ 0 \leq r \leq +\infty \quad z_{\text{out}}^{(n)} = 0 
\]

\[
\pi a^2 D^m \left\{ \left( \frac{\partial c^{\text{in}}_{\text{in}}(t)}{\partial z} \right)_{z=0} + \left( \frac{\partial c^{\text{out}}_{\text{out}}(t_n)}{\partial z} \right)_{z=0} \right\} 
\]

\[
= -2\pi D^\text{out} \int_0^a \left\{ \left( \frac{\partial c^{\text{out}}_{\text{in}}(t)}{\partial z} \right)_{z=0} + \left( \frac{\partial c^{\text{out}}_{\text{out}}(t_n)}{\partial z} \right)_{z=0} \right\} r \, dr 
\]

\[
c^{\text{out}}(n-1)(t) + c^{\text{out}}_{\text{out}}(t_n) = e^{\text{in}} \left( c^{\text{in}}_{\text{out}}(t) + c^{\text{out}}_{\text{out}}(t_n) \right) 
\]

By following a reasoning analogous to that assumed in the derivation of Equation 23, Equation 31 turns into:

\[
D^m \frac{\tilde{z}_{\text{in}}^{(n)}(t_n)}{\sqrt{\pi D^m t_n}} = -D^\text{out} g_d(\sigma_n) \tilde{z}_{\text{out}}^{(n)}(t_n) 
\]

where:

\[
\sigma_n = \alpha(t_n) = \frac{a^2}{D^\text{out} t_n} 
\]

Equation 33 in combination with 32 leads to the following expressions for the interfacial concentrations of the target ion:
\[ c^{\text{in}(i)}(t) = \left( \frac{c^{\text{in}}_X + \xi(t)c^{\text{out}}_X}{1 + \xi(t) e^\eta} \right) \prod_{j=2}^{n} \left( \frac{1 + \xi(t) e^{\eta_{j-1}}}{1 + \xi(t) e^\eta} \right) \]

\[ c^{\text{out}(i)}(t) = e^\eta \left( \frac{c^{\text{in}}_X + \xi(t)c^{\text{out}}_X}{1 + \xi(t) e^\eta} \right) \prod_{j=2}^{n} \left( \frac{1 + \xi(t) e^{\eta_{j-1}}}{1 + \xi(t) e^\eta} \right) \]  

where:

\[ \xi(t) = \frac{D^{\text{out}} \delta_p(t)_{\text{in}}}{D^{\text{in}} \delta_p(t)_{\text{out}}} \]

\[ \delta_p(t)_{\text{in}} = \sqrt{\pi D^{\text{in}} t_{\text{in}}} \]

\[ \delta_p(t)_{\text{out}} = \frac{1}{8 a_\sigma(t)} \]

\[ \sigma(t)_{\text{in}} = \sigma(t)_{\text{out}} = \frac{a^2}{D^{\text{out}} t_{\text{in}}} \]

and for the current response:

\[ I_n = Z F D^{\text{in}} \pi a^2 \sum_{i=1}^{n} \frac{c^{\text{in}(i-1)} - c^{\text{in}(i)}}{\sqrt{\pi D^{\text{in}} t_{\text{in}}}} \]  

with \[ c^{\text{in}(0)} = c^{\text{in,in}} \] and:

\[ t_{\text{in}} = \sum_{i=1}^{n-1} \tau_i + t_n \]  

where the total time of the experiment corresponds to \[ t = t_{\text{in}} + t_m = t_r \].

### 2.2 Numerical Simulations

The problem defined by Equations 1–5 has been solved via numerical finite-difference methods [16,17]. For this, we have made use of the alternating direction implicit (ADI) approach with equal time-steps, unequal spatial grid in the \((r,z)\)-domain with high density of nodes at the electrode surface and edge, and 3-point difference approximations for the spatial derivatives. Throughout this paper, the numerical simulations have been employed to obtain the ion concentration profiles around the liquid|liquid interface (Figure 1) as well as to assess the accuracy of the voltammograms obtained from the analytical theoretical treatment (see Figure 2).

### 3 Results and Discussion

Figure 2 shows the response of the cyclic voltammetry of the reversible transfer of a monocation (as obtained from Equation 37) for different values of the dimensionless parameter \( \sigma_{CV} = a^2 v F D^{\text{out}} RT \), and of the ratio between the diffusion coefficients. In all the cases considered in Figure 2, the results obtained with the explicit solution (Equation 37) (solid line) are compared with those obtained via numerical finite-difference methods (dashed line, see Section 2.2). The analytical results are found to describe accurately the influence of the key variables of the system (that is, the capillary size, the scan rate and the ion diffusion coefficients) on the shape and position of the voltammograms (less than 5 mV difference with respect to the numerical ones for \( T = 298 \) K).

As can be observed in Figure 2, for large electrodes (i.e., large \( \sigma_{CV} \) values) the well-known response obtained at macro-interfaces shows a defined peak in both the forward and backward scans, separated by ca. 2.3RT/F (V) and the forward peak current following the Randles–Sevcik relation [25,26] that establishes that the peak current in the forward scan corresponding to the cation ingress in Figure 2 is given by:

\[ I_{p,F} = -0.4463 \pi F D^{\text{in}} a c^{\text{in,0}} \sqrt{\sigma_{CV}} \]  

When the size of the capillary is decreased and/or slower scan rates are employed, the peak in the forward scan deviates from Equation 39 and it gradually disappears as the diffusion in the outer solution is more convergent and so more efficient. Finally, a sigmoid response is obtained in the forward scan when \( \sigma_{CV} < 0.5 \) where the plateau current tends to the value predicted by the Saito equation [28] for the steady state current at a microdisc as described in our previous works on ultramicrocapillaries [16,17]:

\[ I_{\text{plateau ingress}} = -4 F D^{\text{in}} a c^{\text{in,0}} \]  

Values of \( \sigma_{CV} < 0.5 \) are associated with capillary radii \( a < 1–10 \) \( \mu \)m when the outer solution corresponds to conventional solvents (\( D^{\text{in}} = 10^{-9}–10^{-10} \) m²s⁻¹) and to \( a < 0.1–1 \) \( \mu \)m for ionic liquids and liquid membranes where \( D^{\text{out}} = 10^{-11}–10^{-12} \) m²s⁻¹. On the other hand, a peak is always observed in the reverse scan independently of the capillary size and the experimental time-scale since linear-like diffusion always applies for the ion diffusion inside the capillary.

Regarding the effect of the diffusion coefficients of the target ion in each phase, this is an important question in ion transfer studies given that, as mentioned above, significant differences between the ion diffusivities exist when this is transferred between water and ionic liquids [21,22] or liquid membranes [24]. In such systems, differences of even three orders of magnitude are found [22]. As can be seen in Figure 2, when the ion diffuses more slowly in the inner solution (\( D^{\text{in}} < D^{\text{out}} \)) there is a shift of the voltammograms towards more negative values such that the ingress requires higher overpotentials. The opposite behaviour is observed for \( D^{\text{in}} > D^{\text{out}} \). By comparing the different graphs in Figure 2 it is concluded that the magnitude of the shift with respect to the case where \( D^{\text{in}} = D^{\text{out}} \) is the same for any capillary size and it coincides with that expected for macro-interfaces, that is, \( \left( RT/2F \right) \ln \left( D^{\text{in}}/D^{\text{out}} \right) \) (V).

The effect of the value of the vertex potential (\( \Delta \phi_{\text{vertex}} \)) is studied in Figure 3. As \( \Delta \phi_{\text{vertex}} \) is more negative and so
the forward scan is longer, the reverse peak associated to the ion egress is larger as a result of its higher accumulation inside the capillary. This $D_f$ vertex-influence is more apparent as the capillary size decreases. However, and fortunately, the position of the peak in the reverse scan ($D_{p,r}$) is almost unaffected by $D_f$ vertex (as found at macro-interfaces [25]) such that $D_{p,r}$ provides a very general criterion for the characterization of the ion transfer Gibbs energy (see below).

For the above aim, the analytical theory presented in this paper enables us to establish procedures for the determination of $D_{in}/D_{out}$ without any restrictions on the capillary size and experiment time scale unlike our previous works focused on the use of ultramicrocapillaries [16,17]. The variation of the peak potential in the forward ($\Delta \phi_{p,f}$) and reverse ($\Delta \phi_{p,r}$) scans with $\sigma_{CV}$ are given for different $D_{in}/D_{out}$ values in Figure 4, where $\Delta \phi_{macro}$ is the peak potential of reversible transfer processes at macro-interfaces: $\Delta \phi_{p,t}^{macro} = \Delta \phi_{p,f}^{macro} + RT/2F \ln(D_{in}/D_{out}) - 1.109 RT/F$ [25]. In the case of the forward scan, a well-defined peak is only obtained for $\sigma_{CV} > 0.5$. For smaller $\sigma_{CV}$-values the corresponding sigmoid curve can be characterized by the midpoint potential ($\Delta \phi_{mid}$) for which a simple explicit expression was deduced in a previous work [17]:

$$\Delta \phi_{mid,f} = \Delta \phi_{out}^{\phi_{mid}} - \frac{RT}{T} \ln \left( \frac{2 \sqrt{D_{out} D_{in} RT}}{\sigma_{CV} F} \right)$$

The curves based on the position of the reverse peak can also be used when ultramicrocapillaries are employed given that this peak is obtained regardless of the size of
Indeed, a simple expression for $D_{fp,r}$ at ultramicrocapillaries (corresponding to the linear region in Figure 4) was given in [17]:

$$D_{in}/C_{30}^p = \Delta \phi_{peak} = \Delta \phi_{mid} + 1.44 \frac{RT}{F}$$

For both the forward and reverse peaks, the peak potential takes more negative values as $\sigma_{CV}$ decreases such that the more efficient diffusion outside the capillary leads to higher ion interface concentrations in the inner solution and so the ion ingress is unfavoured. Also, note that the peak-to-peak separation increases as $\sigma_{CV}$ is decreased (Inset in Figure 4) such that this is larger than the value expected for reversible processes at macro-interfaces, which is the limit value at large $\sigma_{CV}$ in Figure 4 (ca. 59 mV at 298 K).

Provided that the capillary size and ion diffusion coefficients are known (for example, by common-ion chronamperometry [16]) the curves given in Figure 4 enable...
the determination of the ion transfer formal potential from the $\Delta \phi_f$ values obtained at different scan rates (i.e., in a range of $\alpha_C$-values) when macro- and micro-capillaries are employed and so do Equations 41 and 42 for ultramicrocapillaries.

4 Conclusions

An approximate analytical treatment has been successfully applied to obtain an explicit solution for the voltammetric study of reversible ion transfers across a liquid|liquid interface supported at the tip of a capillary of any size.

The solution fully describes the influence of the capillary radius and scan rate on the cyclic voltammetry in their whole range of values, that is, the transition of the forward scan from a peak-shaped curve to a sigmoidal one together with the shift towards higher ion ingress overpotentials as the capillary size is reduced. With respect to the influence of the ion diffusion coefficients, this has been found to be equivalent to that observed at macro-surfaces regardless of the capillary size and the experimental time scale.

Based on the theoretical results, the formal transfer potential can be obtained from the position of the cyclic voltammograms provided that the capillary size and diffusion coefficients of the system are know. For this purpose, the new theory has enabled us to obtain working curves for quantitative analysis at macro- and microcapillaries, explicit equations being also available for ultramicro-surfaces.

Acknowledgements

AM, EL and JG greatly appreciate the financial support provided by the Ministerio de Economía y Competitividad (Project Number CTQ2012-36700, co-funded by European Regional Development Fund). EL also thanks the funding received from the European Union Seventh Framework Programme – Marie Curie Cofund (FP7/2007-2013) under UMU Incoming Mobility Programme ACTion (U-IMPACT) Grant Agreement 267143.

References


Received: August 2, 2014
Accepted: September 2, 2014
Published online: January 9, 2015