Analytical Theory for Ion Transfer-Electron Transfer Coupled Reactions at Redox Layer/Thick Film-Modified Electrodes

E. Laborda, J. González, A. Molina*

Departamento de Química Física, Facultad de Química, Regional Campus of International Excellence "Campus Mare Nostrum", Universidad de Murcia, 30100 Murcia, Spain

Abstract

Electrodes modified by liquid films or plasticized polymeric membranes containing a redox species offer valuable alternatives for the study of ion transfers and bimolecular electron transfers at liquid|liquid interfaces with conventional electrode arrangements and stable interfaces. The ion-to-electron (or electron-to-electron) transducer affects the electrochemical signal, complicating the accurate analysis of experimental data. This can be reduced through the use of an electrode surface-attached redox species of well-defined electrochemical behaviour. As will be demonstrated, the voltammetry of these systems show significant deviations with respect to individual charge transfers, which must be considered for appropriate diagnosis and quantitative analysis. For this, a simple analytical theory is presented here, deducing mathematical expressions for the current-potential response, as well as for the potential difference at the two polarized interfaces, the surface excess of the redox species and the ion interfacial concentrations.

Keywords: Coupled ion transfer-electron transfer; Thick film-modified electrodes; Redox layers; Analytical theory; Cyclic voltammetry

1. Introduction

Heterogeneous charge transfers at 'soft' interfaces underpin many environmental, biological and industrial systems, and it enables us to expand electroanalytical applications. Such processes can be investigated and monitored electrochemically by polarizing the biomimetic interface between two immiscible liquid phases. This was initially achieved with a four-electrode arrangement (two pairs of reference and counter electrodes) and electrolyte solutions of conventional solvents [1,2], the use of ionic liquids and polymeric membranes being later employed [3]. Alternatively, more conventional three-electrode arrangements have been proposed where one of the immiscible phases modifies the surface of the working electrode, either in the form of a liquid film [4], a plasticized polymeric membrane [5–8], immobilized (micro)droplets [9–14] or impacting nanodroplets [15–17].

In the above systems, two coupled heterogeneous charge transfer processes underlie the voltammetric signal. Thus, at film and membrane-modified electrodes (see Scheme 1), the charge transfer at the polarized liquid liquid interface is compensated by the electron transfer reaction at the electrode solution interface that, most frequently, is also polarized. The process at the liquid liquid interface is primarily the one of interest, corresponding either to a simple [18] or facilitated [19,20] ion transfer (IT) or to a bimolecular electron transfer (ET). Both cases are very relevant in biological terms in order to understand and predict the uptake/release of ionic species through lipophilic barriers [3,21,22] and the nature of electron transfers where the participating species are located in media of different polarity [23]. Regarding the electron transfer (ET) process at the electrode solution interface, different systems have been considered, including freely-diffusing redox molecules [4,7,19,20,23–30], redox polymers [5,31– 33] and redox monolayers [34–36]. Although their role is to act as a mediator of the charge transfer at the liquid liquid interface, they must be carefully considered since they highly affect the system's overall behaviour and electrochemical signal. Thus, as discussed below, the intrinsic characteristics of the ET have an effect on the position, magnitude and shape of the voltammetric response. Also, the redox species can participate in 'secondary' charge transfers at the liquid-liquid interface and/or they can interact with the transferred ion via, for example, ion pairing [37]. In order to minimize such detrimental effects, different strategies have been proposed, including the modification of the working electrode with films of sufficient thickness (thick film-modified electrodes) [19] and the immobilization of the redox species at the electrode surface [35,36].

The theoretical treatment of the voltammetry of thick film modified-electrodes has been well-developed in the literature for the case of soluble, freely-diffusing redox species with both simple and facilitated ion transfers [38–40]; also, the theory available for systems with two polarized liquid|liquid interfaces can be adapted by identifying one of the interfacial charge transfers as the electrode reaction [41–44]. In this work, the theoretical modelling of ET-IT systems where the molecular redox species is bound to the electrode surface (Scheme 1) is carried out for the first time to the best of our knowledge. Theoretical expressions are deduced for the dynamic electrochemical response of such IT-ET systems whatever the initial concentration of the ion in each phase and the fraction of reduced:oxidized forms in the redox layer, assuming reversible IT and ET processes and semi-infinite linear diffusion for the ion. Mathematical solutions for the interfacial potentials, surfaces excesses and interfacial ion concentrations are also included. These are applied to investigate the cyclic voltammetry (CV) response, finding striking peculiarities that must be considered in order to analyse correctly the CV signal, as well as to extract accurate data of transfer formal potentials.

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2. Theory

In the system outlined in Scheme 1, two heterogeneous charge transfer processes of very different nature take place in a concomitant way so that charge is compensated in the organic phase: an electron transfer of a redox monolayer at a polarized electrode|solution interface (hereafter, *inner interface*), and the transfer of a freely-diffusing ion at a polarized liquid|liquid interface (*outer interface*). The potential difference between the redox monolayer-modified electrode (ϕ_M) and the water solution (ϕ_W) can be controlled externally ($E = \phi_M - \phi_W$), and the current (I) due to the electron flux (inner interface) and to the ion flux (outer interface) must be obviously the same.





Considering that both charge transfers are reversible and that the mass transport of species R⁺ takes place under semi-infinite linear diffusion (*i.e.*, migration and convection are suppressed, the liquid liquid interface is of macrometric size and the organic film is thick compared to the diffusion layer), when a potential $E(=E_{inn} - E_{out})$ is applied, the response of the system is described by the following boundary value problem (bvp):

$$\frac{\partial c_{\mathbf{R}^{+}}^{\mathrm{o}}(x,t)}{\partial t} = D_{\mathbf{R}^{+}}^{\mathrm{o}} \frac{\partial^{2} c_{\mathbf{R}^{+}}^{\mathrm{o}}(x,t)}{\partial x^{2}} \left\{ \frac{\partial c_{\mathbf{R}^{+}}^{\mathrm{w}}(x,t)}{\partial t} = D_{\mathbf{R}^{+}}^{\mathrm{w}} \frac{\partial^{2} c_{\mathbf{R}^{+}}^{\mathrm{w}}(x,t)}{\partial x^{2}} \right\}$$
(1)

$$\begin{cases} 0 < x < d, t = 0 \\ x \to 0, t \ge 0 \end{cases} c_{R^+}^0 = c_{R^+}^{0^*}$$
(2)

$$x = 0, t = 0: \qquad \Gamma_{\text{Ox}} = \Gamma_{\text{Ox}}^* \quad ; \quad \Gamma_{\text{Red}} = \Gamma_{\text{Red}}^*$$
(4)

$$x = 0, t > 0: \qquad \Gamma_{\text{Ox}} = \Gamma_{\text{Red}} e^{\eta_{\text{inn}}}$$
(5)

$$x = d, t > 0: \qquad D_{\mathbb{R}^{+}}^{\mathrm{O}} \left(\frac{\partial c_{\mathbb{R}^{+}}^{\mathrm{O}}}{\partial x} \right)_{x=d} = D_{\mathbb{R}^{+}}^{\mathrm{W}} \left(\frac{\partial c_{\mathbb{R}^{+}}^{\mathrm{W}}}{\partial x} \right)_{x=d}$$
(6)

$$c_{\rm R^{+}}^{\rm O}(d) = c_{\rm R^{+}}^{\rm W}(d) e^{\eta_{\rm out}}$$
 (7)

with:

$$\eta_{\text{inn}} = \frac{F}{RT} \left(E_{\text{inn}} - E_{\text{Ox/Red}}^{0'} \right)$$

$$\eta_{\text{out}} = \frac{F}{RT} \left(E_{\text{out}} - \Delta_{\text{O}}^{\text{W}} \phi_{\text{R}^{+}}^{0'} \right)$$
(8)

where Γ_{Ox} and Γ_{Red} are the surface excess of the oxidized and reduced species, respectively, Γ_{Ox}^{*} and Γ_{Red}^{*} their initial values, Γ_{T} the total surface excess of the monolayer ($=\Gamma_{Ox}^{*}+\Gamma_{Red}^{*}=\Gamma_{Ox}+\Gamma_{Red}$), $c_{R^{+}}^{O^{*}}$ and $c_{R^{+}}^{W^{*}}$ the bulk concentration of the ion R⁺ in the organic and water solutions, respectively, and $D_{R^{+}}^{O}$ and $D_{R^{+}}^{W}$ the corresponding diffusion coefficients. Additionally, the applied potential E relates the *unknown* potential differences at the outer ($E_{out} = \phi_{W} - \phi_{O}$) and inner ($E_{inn} = \phi_{M} - \phi_{O}$) interfaces in the following way:

$$E = E_{\rm inn} - E_{\rm out} \left(= \phi_{\rm M} - \phi_{\rm W}\right) \tag{9}$$

and the current across the two interfaces must be equal at any time of the experiment: $I_{inn} = I_{out} = I$. For this ET-IT system where the redox component is surface-bound and reversible, it is mathematically more convenient to impose the equivalent condition of equal charge transferred across the interfaces for any period of time considered: $Q_{inn} = Q_{out} = Q$ (see the Supplementary Material).

Following the procedure detailed in the Supplementary Material, the following expressions are obtained for the current-potential response upon the application of an arbitrary sequence of potential pulses E_1 , E_2 , ... E_m ... E_p of the same duration τ :

$$I^{(p)} = \frac{FAD_{R^{+}}^{W}}{\sqrt{\pi D_{R^{+}}^{W}\tau}} \sum_{m=1}^{p} \frac{c_{R^{+}}^{W(m-1)}(d) - c_{R^{+}}^{W(m)}(d)}{\sqrt{p - m + 1}}$$
(10)

as well as for the accumulated charge ($Q_{
m accum}^{
m (p)}$), surface excesses and ion interfacial concentrations:

$$Q_{\rm accum}^{(p)} = \frac{Q_{\rm T}}{1 + e^{\eta_{\rm inn}^{(p)}}}$$
(11)

$$\Gamma_{\rm Ox}^{(p)} = \Gamma_{\rm T} \frac{e^{\eta_{\rm inn}^{(p)}}}{1 + e^{\eta_{\rm inn}^{(p)}}} \quad ; \ \Gamma_{\rm Red}^{(p)} = \Gamma_{\rm T} - \Gamma_{\rm Ox}^{(p)}$$
(12)

$$c_{\rm R^+}^{\rm W(p)}(d) = \frac{c_{\rm R^+}^{\rm O^*} \gamma + c_{\rm R^+}^{\rm W^*}}{1 + \gamma e^{\eta_{\rm out}^{\rm (p)}}} \quad ; \quad c_{\rm R^+}^{\rm O(p)}(d) = \frac{e^{\eta_{\rm out}^{\rm (p)}} \left(c_{\rm R^+}^{\rm O^*} \gamma + c_{\rm R^+}^{\rm W^*} e^{\eta_{\rm out}^{\rm (p)}}\right)}{1 + \gamma e^{\eta_{\rm out}^{\rm (p)}}} \tag{13}$$

where
$$c_{\mathrm{R}^{+}}^{\mathrm{W}\!(0)}\!\left(d
ight)\!=\!c_{\mathrm{R}^{+}}^{\mathrm{W}\!*}$$
 and:

$$e^{\eta_{out}^{(1)}} = \frac{\zeta(\tau) - 1 - \sqrt{[\zeta(\tau) - 1]^{2} + 4e^{\eta_{t}}\zeta(\tau) / \gamma}}{2e^{\eta_{t}}}$$

$$e^{\eta_{out}^{(p)}} = \frac{e^{\eta_{inn}^{(p)}}}{e^{\eta_{p}}} = \frac{e^{\eta_{p}} + \gamma\zeta(\tau) - \omega_{p}(\tau)\gamma(1 + e^{\eta_{p}}) + \sqrt{[\omega_{p}(\tau)\gamma(1 + e^{\eta_{p}}) - e^{\eta_{p}} - \gamma\zeta(\tau)]^{2} + 4\omega_{p}(\tau)\gamma^{2}e^{\eta_{p}}(\zeta(\tau) + 1 - \omega_{p}(\tau))}}{2\omega_{p}(\tau)\gamma^{2}e^{\eta_{p}}} \quad (p > 1)$$

 $e^{\eta_{inn}^{(p)}} = e^{\eta_p} e^{\eta_{out}^{(p)}} \quad (\forall p)$

(14)

with:

$$\eta_{\rm p} = \frac{F}{RT} \left(E_{\rm p} - \Delta E^{0^{\circ}} \right) \tag{15}$$

$$\Delta E^{0'} = E^{0'}_{\text{Ox/Red}} - \Delta^{\text{W}}_{\text{O}} \phi^{0'}_{\text{R}^{Z^+}}$$
(16)

$$\gamma = \sqrt{\frac{D_{R^+}^0}{D_{R^+}^W}}$$
(17)

$$\zeta(\tau) = \frac{\Gamma_{\rm T}}{2\sqrt{\frac{D_{\rm R^+}^{\rm W}\tau}{\pi}}c_{\rm R^+}^{\rm W^*}}$$
(18)

$$\begin{split} \omega_{\rm p}(\tau) &= \frac{\zeta(\tau)}{1 + e^{\eta_{\rm inn}^{(p-1)}}} + \left(\sqrt{p} - \sqrt{p-1}\right) \frac{\gamma e^{\eta_{\rm out}^{(1)}}}{1 + \gamma e^{\eta_{\rm out}^{(1)}}} + \left(\sqrt{p-1} - \sqrt{p-2}\right) \frac{1}{1 + \gamma e^{\eta_{\rm out}^{(1)}}} \\ &+ \sum_{n=2}^{p-2} \left(2\sqrt{p-n} - \sqrt{p-n+1} - \sqrt{p-n-1}\right) \frac{1}{1 + \gamma e^{\eta_{\rm out}^{(n)}}} \\ &+ \left(2 - \sqrt{2}\right) \frac{1}{1 + \gamma e^{\eta_{\rm out}^{(p-1)}}} \end{split}$$
(19)

3. Results and Discussion

Cyclic voltammetry (CV) calculated considering a cyclic staircase perturbation of very small potential step ($\Delta E = 0.1 \text{ mV}$) to obtain the current-potential response from the analytical solution here deduced (Eq. (10) with $\tau = \Delta E / v$ where v is the scan rate.

The chief parameter $\zeta(\tau)$ (Eq. (18)) establishes whether the extent of the voltammetric response of the ET-IT system is predominantly controlled by the availability of reactant for the redox process, by the ion transfer or by both, mainly as a function of the surface excess of redox species and the ion concentration. In Figure 1 the theoretical cyclic voltammetry is studied for an ET-IT system where the surface-bound species is initially in the oxidized state and the cation R⁺ is only present in the water solution. As can be observed, for large values of the surface excess (black line in Figure 1), the CV curve is predicted to show a shape very similar to that expected when the current is controlled by diffusion. The potential dependence and position of the signal is influenced by both interfacial charge transfers since the potential difference at the outer interface is linked to the redox process at the inner interface (Eq. (9)). Thus, on a closer inspection, the voltammogram reveals differences with respect to the case of a simple reversible IT in a one-polarizable interface system [45–47] in terms of the peak-to-peak separation ($\Delta E_{pp} \approx$

29 mV instead of *ca*. 58 mV for T=298K) and the peak current ($\Psi_{dif,peak} = \frac{I_{peak}}{FA c_{R^+}^{W^*}} \sqrt{\frac{RT}{DFv}} = 0.369$

instead of 0.446 for the forward peak current).

As the amount of surface-bound redox species is decreased, the diffusion tail of the CV response is distorted in the forward scan and it vanishes gradually in the backward one (blue line in Figure 1). For a very small surface excess relative to the bulk concentration of R⁺ (red line in Figure 1), the forward CV curve is practically controlled by the reduction reaction at the redox monolayer. A Gaussian-like peak is observed in the forward scan, which resembles that of an electrochemically reversible redox monolayer though the peak current is *ca*. 25% smaller (*i.e.*,

 $\Psi_{ads, peak} = \frac{I4RT}{F^2 A \Gamma_T v} \approx 0.75$ instead of 1.0) and the half-peak width is slightly larger (*ca*. 118 mV

instead of *ca*. 90 mV for T=298K). More importantly, there is a remarkable asymmetry between the signals in the forward and backward scans, in contrast with the fully symmetric cyclic voltammograms predicted for reversible redox monolayers [45,46]; thus, the backward peak in the ET-IT system is considerably smaller than the forward one (see below) and the former is situated at more positive potentials ($\Delta E_{no} \approx 24$ mV for T=298K).



Figure 1. Normalized cyclic voltammograms $(I/I_{p,f} \text{ vs } E - \Delta E^{0'})$, where $I_{p,f}$ is the peak current of the forward scan) of the ET-IT system for different $\zeta(\tau)$ -values when the ion is only initially present in the aqueous phase $(c_{p^*}^{0^*} = 0)$. v = 100 mV/s, $\Delta E = 0.1$ mV, $\gamma = 1$, T = 298K.

In order to get full insight into the voltammetric behaviour of the ET-IT system, the evolution of Γ_{ox} / Γ_{T} and $c_{R^{+}}^{W}(d)$ throughout the forward and backward scans is examined in Figure 2 for the three situations considered in Figure 1. For the largest $\Gamma_{T} / c_{R^{+}}^{W^{*}}$ -value (Figure 2A), the surface excess of the oxidized species remains almost unaltered given that only a small fraction is transformed in balancing the charge transferred across the liquid-liquid interface. Hence, as anticipated above, the extent of the electrochemical signal is controlled by the

diffusional charge transfer, as reflected in the value of $c_{R'}^{W}(d)$ that becomes null at most negative potentials.

In the opposite limit case where the surface excess of the surface-attached species is very small (Figure 2C), it is the interfacial concentration of R⁺ that remains almost constant and equal to the bulk value ($C_{R^+}^{W^+}$) given that a very small portion of the ion is transferred to the organic phase in the forward scan. Interestingly, the surface coverage of the oxidized species (Γ_{Ox}) is not restored completely in the backward scan, which is directly related with the fact that the backward peak of the voltammogram is smaller than the forward peak (red line in Figure 1). This is explained by the lack of enough concentration of R⁺ at the organic side of the interface that can compensate the re-oxidation of the adsorbed species (Red) due to its diffusion into the organic phase away from the liquid-liquid interface as can be deduced from the inset of Figure 2C (note that it has been considered that the ions of the supporting electrolytes cannot compensate the electron transfer due to their very high affinity towards the organic or aqueous phase).

For intermediate $\Gamma_T / c_{R^+}^{W^*}$ -values (Figure 2B), both the surface and volumetric concentrations of Ox and R⁺, respectively, vary significantly with the applied potential in the forward and backward scans.

With respect to the evolution of the interfacial potential differences at the outer and inner interfaces (Figure 2'), it is worth highlighting that in the limits where the redox or ionic species is present in excess (surface or volumetric) concentration (Figures 2A' and 2C'), the interfacial potential at a certain interface remains almost constant in some intervals of the CV experiments. Thus, when the system is under 'ET-control' (Figure 2A'), it is the inner potential that remains almost constant in the reverse scan. Similarly, the outer potential takes an almost constant value in the second half of the forward scan and in the first half of the backward one when the system is 'IT-controlled' (Figure 2C').



Figure 2. Variation of the normalized surface excess of the oxidized species (Γ_{OX} / Γ_{T}), interfacial concentrations of R⁺ ($c_{R^{+}}^{w}(d) / c_{R^{+}}^{W^{*}}$) and interfacial potentials (E_{inn} and E_{out}) along the CV scans for the cases considered in Figure 1.



Figure 2'. Variation of the normalized surface excess of the oxidized species ($\Gamma_{\text{Ox}} / \Gamma_{\text{T}}$), interfacial concentrations of R⁺ ($c_{\text{R}^{+}}^{\text{W}}(d) / c_{\text{R}^{+}}^{\text{W}^{*}}$) and interfacial potentials (E_{inn} and E_{out}) along the CV scans for the cases considered in Figure 1. $E_{\text{Ox/Red}}^{\text{O'}} = \Delta_{\text{O}}^{\text{W}} \phi_{\text{R}^{2^{+}}}^{\text{O'}} = 0 \text{ mV}$

The above results point to the interest of investigating the effect of the presence of the ion R⁺ in the organic solution. This is performed in Figure 3A that shows the effect of the $c_{R^+}^{o^+}$ value under conditions where the surface excess is very small. When R⁺ is not present in the organic phase $(c_{R^+}^{o^+}/c_{R^+}^{o^+}=0)$, black line in Figure 3A; see also Figure 1) or it is present in a very small concentration $(c_{R^+}^{o^+}/c_{R^+}^{o^+}=10^{-3})$, pink line in Figure 3A) relative to the surface excess, the backward peak is significantly smaller than the forward one, as mentioned above. As $c_{R^+}^{o^+}$ is increased, the magnitude of the backward peak increases given that there is enough availability of charge-compensating species (R⁺) in the organic phase. Eventually, two symmetrical peaks are obtained and further increase of $c_{R^+}^{o^+}$ only leads to the shift of the signal towards more negative potentials. The features of the signal ($w_{1/2} = 90$ mV and $\Psi_{ads, peak} = 1$) are equivalent to those of a reversible redox monolayer given that under such conditions (excess of ion in both phases) the outer sphere acts as a non-polarizable interface so that only the position of the voltammogram is affected.

The influence of the presence of both the oxidized and reduced forms in the redox layer is considered in Figure 3B where the ion is assumed to be present in both phases in a relatively small concentration (i.e., large $\zeta(\tau)$ -value) with $c_{\kappa^*}^{o^*} / c_{\kappa^*}^{w^*} = 0.1$. When the reduced form is not present in the surface-bound layer ($f_{\text{Red}} = 0$, Figure 3A and black line in Figure 3B), the current at the beginning of the voltammogram is null in spite of the presence of R⁺ in the organic phase due to that the egress of R⁺ to the water solution cannot be compensated by any oxidation process at the electrode in this region of the scan. On the other hand, when $f_{\text{Red}} \neq 0$, the voltammograms do show a negative current at the beginning of the scan corresponding to the egress of the ion due to that this is now compensated by the conversion of species Red into Ox at the electrode, the voltammogram shifting towards more negative potentials as f_{Red} is increased.



Figure 3. (A) Effect of the presence of the ion in both liquid phases in the limit of very large surface coverage of the redox species and (B) of the presence of both redox forms in the layer in the limit of very

small surface coverage. Other conditions as in Figure 1.
$$\Psi_{ads} = I \frac{4RT}{F^2 A \Gamma_T v}$$
, $\Psi_{dif} = \frac{I}{FA c_{R^+}^{W^*}} \sqrt{\frac{RT}{DFv}}$

The chief parameter $\zeta(\tau)$ also points out the dependence on the time-scale of the experiment, which is studied in Figure 4 for cyclic voltammetry. A remarkable influence of the scan rate on the ET-IT CV curves is found and illustrated for the two limit cases of very small and large surface coverage. Thus, the CV shows some deviations from the signal of 'pure' reversible surface-attached ETs or diffusional ITs in terms of peak height and peak-to-peak separation, as mentioned above. Most remarkably, the value of the scan rate affects the position of the wave so that is shifts towards more negative potential as v is increased, the shift being of the same magnitude (*ca.* 29 mV/dec) in the two limit cases considered in the figure (i.e., very large and very small $\zeta(\tau)$ -values). On the other hand, the peak current of the forward scan scales with the square root of v under diffusional IT control (large Γ_{τ}) and with v under monolayer ET control (small Γ_{τ}), as in the case of simple individual charge transfers.



Figure 4. Effect of the scan rate on the normalized CV response in the limits of very small (A) and very large (B) surface coverage of the redox species. Other conditions as in Figure 1. $\Psi_{ads} = I \frac{4RT}{F^2 A \Gamma_T v}$,

$$\Psi_{\rm dif} = \frac{I}{FA \, c_{\rm R^+}^{\rm W^*}} \sqrt{\frac{RT}{DFv}}$$

4. Conclusions

Redox layer/film-modified electrodes offer advantageous experimental approaches for the electrochemical study of ion and electron transfers at liquid liquid interfaces. Depending on the experimental conditions, the shape of the voltammogram can be analogous to that of redox monolayers or that of solution-phase systems. Nevertheless, as demonstrated here, the correct understanding of these systems requires us to recognize the interplay between two concomitant heterogeneous charge transfers of very different nature: a surface electron transfer at a solid electrode modified with exhaustible redox species, and a charge transfer at a soft interface where the reactant is continuously supplied by diffusion.

In this work a novel analytical theory has been developed for coupled reversible ion transfer-electron transfer reactions (IT-ET) at thick film-modified electrodes when the ET involves a surface-attached redox system. From the analysis of the charge transferred across the two polarizable interfaces interfaces, it has been possible to solve the problem and obtain simple mathematical expressions. These have been applied to inspect the variation of the redox surface excess, interfacial ion concentrations, interfacial potential differences and current-potential response as a function of the surface coverage (Γ), the bulk concentrations of the ion ($c_{R^+}^*$) and the experiment time scale (τ). The theoretical treatment reveals that $\zeta(\tau) = \frac{\Gamma_{T}}{2\sqrt{\frac{D_{W}\tau}{\pi}}c_{R^+}^{W^*}}$ is

a chief parameter that accounts for whether the shape, magnitude and time-scale dependence of the voltammetric response is controlled by the redox process (small $\zeta(\tau)$ -values), the ion transfer (large $\zeta(\tau)$ -values) or both (intermediate $\zeta(\tau)$ -values).

It is worth noting that the position of the IT-ET signal is affected by a number of variables, which must be considered in the experimental study of the ion lipophilicity, specifically: (1) The formal potentials of the *two* charge transfers, (2) the surface excess and the volumetric concentrations of the ion in each phase, (3) the time scale of the measurement (that is, the pulse length in pulse techniques and the scan rate in sweep methods), and (4) the ratio between the

diffusion coefficient of the ion in the two phases. The first three factors, particularly the ion concentration and the time scale (scan rate) of the measurements, can be easily modified for experimental diagnosis and quantitative study of the system.

If the electron transfer showed kinetic limitations, this would obviously affect the voltammetric response, together with the ET-IT coupling. The combined effect on the voltammograms is not trivial and to be studied in the future.

Acknowledgements

The authors greatly appreciate the financial support provided by the Fundacion Séneca de la Región de Murcia (Project 19887/GERM/15).

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