General Theoretical Treatment of Ion Transfers in Two Polarisable Interface Systems when the Analyte has Access to Both Interfaces

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Abstract

A new theory is presented to tackle the study of transfer processes of hydrophilic ions in two polarisable interface systems when the analyte is initially present in both aqueous phases. The treatment is applied to macrointerfaces (linear diffusion) and microholes (highly convergent diffusion), obtaining analytical equations for the current response in any voltammetric technique. The novel equations predict two signals in the current-potential curves that are symmetric when the compositions of the aqueous phases are identical while asymmetries appear otherwise. The theoretical results show good agreement with the experimental behaviour of the "double transfer voltammograms" reported by Dryfe *et al.* in cyclic voltammetry (CV) (*Anal. Chem.* **2013**, *86*, 435-442) as well as with cyclic square wave voltammetry (cSWV) experiments here performed.

The theoretical treatment is also extended to the situation where the target ion is lipophylic and it is initially present in the organic phase. The theory predicts an opposite effect of the lipophilicity of the ion on the shape of the voltammograms, which is validated experimentally via both CV and cSWV.

For the above two cases, simple and manageable expressions and diagnosis criteria are derived for the qualitative and quantitative study of ions lipophilicity. The formal ion-transfer potentials can be easily quantified from the separation between the two signals making use of explicit analytical equations.

Keywords: Two polarisable interfaces; Ion-transfer voltammetry; Analytical theory; Standard Ion-Transfer Potential; Solvent polymeric membranes

INTRODUCTION

The transfer of ionic species between aqueous phases separated by a lipophilic barrier underpins many biological, technological and industrial processes, and liquid|liquid electrochemistry enables direct study and control of these systems. Thus, through the applied potential difference either side of the lipophilic layer, it is possible to examine and adjust the distribution of ions and electric potential. These will reflect the interplay between the coupled ion transfer processes at the two liquid|liquid interfaces [1], as a function of the lipophilicity of the different ions present, their concentration and the mass transport conditions.

In this work, a general analytical theory is developed to describe the ion fluxes and potential drop across each polarised interface as a function of the transmembrane potential and the factors above-mentioned. As it is common practice in dynamic electrochemical methods, fully supported conditions are assumed in order that the response is not affected by ohmic drop, migrational and electrical double layer effects. This makes the modelling and data analysis more accurate for the extraction of thermodynamic information of great relevance in fields such as liquid-liquid extraction [2], purification and separation of compounds [3], ion sensing [4], biological release-uptake processes [5], pharmacological tests [6], and energy conversion [3]. Among them, it is worth highlighting the contribution of these data to the understanding and optimization of ion-selective electrodes [7].

The equations obtained describe adequately the results previously obtained by several authors where the target ions were initially present in the two aqueous solutions and their transfer towards the liquid membrane was electrically modulated [1,8,9]. In addition, they are also applicable when there are two different analytes in the aqueous solutions, a situation that can be useful to study simultaneously two species that would overlap (similar $\Delta\phi^{0'}$) or react if they were present in the same solution (see Supporting Information).

Another situation of interest is that where the analyte is initially present in the organic phase. This can be helpful in the study of lipophilic compounds as well as for the reduction of

the amount of compound necessary for the assay. The theory here presented (which can also be easily adapted to cover other arrangements of immiscible phases) demonstrates that the voltammetric response when the lipophilic ion is released selectively either side of the membrane is similar to the first case, though it is affected in an opposite way by the lipohilicity of the ion under study.

The value of voltammetric techniques (specifically, cyclic voltammetry and cyclic square wave voltammetry) for the study of this kind of systems has been proven under very different diffusive transport conditions: linear diffusion (corresponding to macrointerfaces) and highly convergent diffusion (micro- and nano-holes [10]). The current-potential curve shows a centre of symmetry in CV or an axis of symmetry in SWV at the average of the half-wave potentials provided that the concentration of target ion is equal at both sides of the membrane. Qualitative and quantitative criteria are discussed, assisting the correct interpretation of experimental voltammograms and the prediction of effects that lead to asymmetries, that is: different concentrations of the aqueous electrolytes and different areas of the water|membrane interfaces.

Finally, the experimental study of the transfer of tetraalkylammonium cations of different lipophilicity (*i.e.*, of different chain length) is performed in the two operational modes above-mentioned and with two different experimental set-ups: a solvent polymeric membrane [11] and a water|1,2-dichloroethane|water system [12]. In all cases, the theory here developed describes satisfactorily the experimental responses obtained in cyclic voltammetry and cyclic square wave voltammetry. Thus, two ion-transfer signals ("double-transfer voltammograms" [8]) are observed that move closer or separate as the lipophilicity of the target ion increases, depending on whether this is initially present in the aqueous or organic phases, respectively. Moreover, values for the standard transfer potentials of the ions of the aqueous supporting electrolytes (Li^+ and Cl^-) are extracted, which are in good agreement with the data available in the literature.

THEORY

Two polarisable interfaces systems with a transferable ion present in the outer and inner aqueous phases

Macrointerfaces

Let us consider a system of two polarisable interfaces consisting in an organic solution (phase M) placed between two aqueous phases (phases $\mathrm{W}_{\mathrm{out}}$ and $\mathrm{W}_{\mathrm{inn}}$), according to Scheme 1a. The use of this kind of systems (where there is no common ions between the supporting electrolytes of two adjacent phases) offers advantages with respect to systems of one polarisable interface, the main one being that the polarisation window is significantly larger [13]. Also, within the cell scheme considered in this and previous [8] works (Scheme 1), it is possible to study simultaneously the transfer of an ionic species from/towards two different media or two analytes that would overlap or react if they were present in the same phase. Each aqueous phase in Scheme 1 contains a target cation X^+ that can be transferred to the organic solution under the application of a suitable potential difference ($E = E_{\mathrm{out}} - E_{\mathrm{inn}}$) between the two aqueous phases. Given that the same intensity of electrical current crosses both interfaces ($\mathrm{W}_{\mathrm{out}} \mid \mathrm{M}$ and $\mathrm{W}_{\mathrm{inn}} \mid \mathrm{M}$ in Scheme 1), the transfer of X^+ is necessarily coupled to the concomitant transfer of the anion R^- of the aqueous supporting electrolyte (the treatment would be similar in case that it was the cation of the organic supporting electrolyte that compensated the transfer of the target ions [11]). Species R^- is present in a high excess with respect to X^+, in such a way that c_R^{*W} in phase $\mathrm{W}_{\mathrm{out}}$ and $\mathrm{W}_{\mathrm{inn}}$ can be considered constant during the whole experiment. In addition, it is assumed that the thickness of the organic solution is large enough to assure that the diffusion layers associated to the mass transport of ionic species to interfaces $\mathrm{W}_{\mathrm{out}} \mid \mathrm{M}$ and $\mathrm{W}_{\mathrm{inn}} \mid \mathrm{M}$ do not overlap in the time scale of the experiment.

When the target ion X^+ in the aqueous phases is hydrophilic, it can be expected that the transfer of X^+ to the organic solution from phases $\mathrm{W}_{\mathrm{out}}$ and $\mathrm{W}_{\mathrm{inn}}$ occur at very different potentials of the polarisation window, leading to two well-separated waves in the voltammograms (see Results and Discussion). For example, the transfer of X^+ from $\mathrm{W}_{\mathrm{out}}$ will take place at quite positive E-values, the transfer of X^+ at the inner interface being negligible. This problem is solved according to the procedure described in Section S2[14], finding the following expressions for the currents of the two independent processes during the application of a constant potential pulse

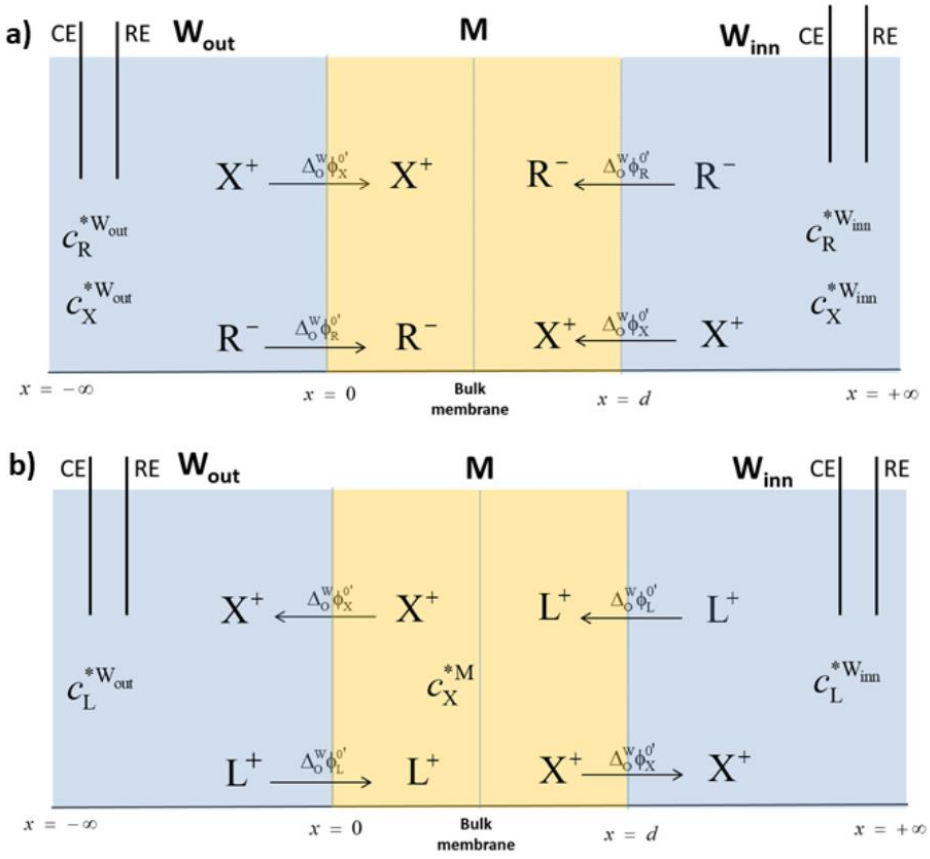
$$I^{(I)} = I_{d,W}^{out}\, g\left(\eta_{out}\right) \quad ; \quad I^{(II)} = I_{d,W}^{inn}\, g\left(\eta_{inn}\right) \tag{1}$$

where $I_{d,W}^{out}\left(= FA_{out} D_X^W c_X^{*W_{out}} / \delta_{d,X}^W\right)$ and $I_{d,W}^{inn}\left(= -FA_{inn} D_X^W c_X^{*W_{inn}} / \delta_{d,X}^W\right)$ are the limiting diffusion currents for the transfer of species X^+ from the water solution to the organic phase with $\delta_{d,i}^{\alpha}$ being the linear diffusion layer thickness of species i in phase α that under linear diffusion conditions is given by:

$$\delta_{d,i}^{\alpha} = \sqrt{\pi D_i^{\alpha} t} \tag{2}$$

and $g\left(\eta_i\right)$ is a function of the applied potential

$$g\left(\eta_{out}\right) = \frac{\sqrt{e^{2\eta_{out}} + 8e^{\eta_{out}}} - e^{\eta_{out}}}{4} \quad ; \quad g\left(\eta_{inn}\right) = \frac{\sqrt{1 + 8e^{\eta_{inn}}} - 1}{4e^{\eta_{inn}}} \tag{3}$$



Scheme 1. Ion transfers in a system of two polarisable interfaces when the target ion X^+ is initially present in a) both aqueous solutions $\mathrm{W}_{\mathrm{out}}$ and $\mathrm{W}_{\mathrm{inn}}$ and b) in the organic phase M. Species L^+ and R^- are ions of the aqueous supporting electrolytes. 'Bulk membrane' refers to distances far away from the interface (compared to the diffusion layer in phase M) where the concentration values are not perturbed. CE: counterelectrode; RE: reference electrode.

with $\eta_{out} = \frac{F}{RT}\left(E - E_{1/2,W}^{out}\right)$, $\eta_{inn} = \frac{F}{RT}\left(E - E_{1/2,W}^{inn}\right)$ and $E_{1/2,W}^{out}$ and $E_{1/2,W}^{inn}$ being the half-wave potential of the transfer of species X^+ from $\mathrm{W}_{\mathrm{out}}$ and $\mathrm{W}_{\mathrm{inn}}$ to phase M, respectively:

$$E_{1/2,W}^{out} = \left(\Delta\phi_X^{0'} - \Delta\phi_R^{0'}\right) + \frac{RT}{F}\ln\left(\frac{A_{out}\, c_X^{*W_{out}}\left(D_X^W\right)^2}{2A_{inn}\, c_R^{*W_{inn}} D_X^M D_R^M}\right) + \frac{RT}{F}\ln\left(\frac{\delta_{d,X}^M\, \delta_{d,R}^M}{\left(\delta_{d,X}^W\right)^2}\right) \tag{4}$$

$$E_{1/2,W}^{inn} = \left(\Delta\phi_R^{0'} - \Delta\phi_X^{0'}\right) - \frac{RT}{F}\ln\left(\frac{A_{inn}\, c_X^{*W_{inn}}\left(D_X^W\right)^2}{2A_{out}\, c_R^{*W_{out}} D_X^M D_R^M}\right) - \frac{RT}{F}\ln\left(\frac{\delta_{d,X}^M\, \delta_{d,R}^M}{\left(\delta_{d,X}^W\right)^2}\right) \tag{5}$$

Symbols in Eqs.(4) -(5) have their usual meaning (see Section S1). Finally, the net current is obtained from the sum of the currents associated to the two independent problems above-indicated:

$$I = I^{(I)} + I^{(II)} \tag{6}$$

Note that Eqs.(4) and (5) are applicable for any geometry of the interface, with the geometric features being included in $\delta_{d,i}^{\alpha}$.

Microholes

When the two polarisable interfaces have a micrometric size, as in the case of microholes, Eq. (1) remains valid by replacing the expression (2) of the linear diffusion layer thickness by

$$\delta_{d,microhole}^{\alpha} = \frac{\pi r_0}{4\left(0.7854 + 0.44315\left(r_0/\sqrt{D^{\alpha}t}\right) + 0.2146\exp\left(-0.39115\left(r_0/\sqrt{D^{\alpha}t}\right)\right)\right)} \tag{7}$$

where r_0 is the radius of the microhole. Under steady state conditions ($r_0/\sqrt{D^{\alpha}t} \ll 1$), Eq.(7) becomes into $\delta_{d,ss} = \pi r_0/4$. In this way, the current expression (1) at microholes is rigorous when equal diffusion coefficients ($D^W = D^M$) or steady state conditions hold. Also, excellent results are obtained under transient conditions with unequal diffusion coefficients, the error in the position of the I-E curve being lower than 3.5 mV for $0.001 \le D^W/D^M \le 1000$.

Multipulse techniques

When macrointerfaces and/or microholes under steady state conditions are used, the surface concentrations of the different species at both sides of each interface are only dependent on the applied potential whatever the values of the diffusion coefficients [14]. Hence,

the superposition principle is rigorously applicable [15], obtaining the following expressions for the currents associated with the transfer of species X^+ from $\mathrm{W}_{\mathrm{out}}$ and $\mathrm{W}_{\mathrm{inn}}$ during the application of the *n*-th pulse of any arbitrary sequence of potentials

$$I_n^{(I)} = FA_{out} D_X^W c_X^{*W_{out}} \sum_{m=1}^{n} \left(\frac{g\left(\eta_{out,m}\right) - g\left(\eta_{out,m-1}\right)}{\delta_{d,X}^W\left(t_{m,n}\right)} \right) \tag{8}$$

$$I_n^{(II)} = -FA_{inn} D_X^W c_X^{*W_{inn}} \sum_{m=1}^{n} \left(\frac{g\left(\eta_{inn,m}\right) - g\left(\eta_{inn,m-1}\right)}{\delta_{d,X}^W\left(t_{m,n}\right)} \right) \tag{9}$$

where $\delta_{d,X}^W\left(t_{m,n}\right)$ is given by Eqs.(2) and (7) for macrointerfaces and microholes, respectively, $t_{m,n} = \left(n-m+1\right)\tau$ (τ being the duration of the potential pulses), $g\left(\eta_{i,0}\right) = 0$ and $g\left(\eta_{i,m>0}\right)$ is given by Eqs.(3) with $\eta_{i,m} = F\left(E_m - E_{1/2,W}^i\right)/RT$. Finally, the net current during the *n*-th pulse of potential is given by:

$$I_n = I_n^{(I)} + I_n^{(II)} \tag{10}$$

Eqs.(8) and (9) are rigorous for microholes under transient conditions when equal diffusion coefficients are assumed ($D^W = D^M$), although it can also be used when they are different with the error in the position of the voltammograms being lower than 6mV for $0.001 \le D^W / D^M \le 1000$.

<u>Two polarisable interfaces systems with a transferable lipophilic ion only present in the organic phase: macrointerfaces and microholes</u>

Alternatively to the situation depicted in Scheme 1a, the target ion can be lipophilic and be added to the organic phase (M) such that it can be transferred towards the inner or outer aqueous solutions upon the application of a constant potential difference (see Scheme 1b). In this case, the ion transfer coupled to the egress of the analyte from the organic solution must involve the ingress of a cation L^+ from the aqueous supporting electrolyte (or the egress of an anion of the organic supporting electrolyte). Analogously to the case where the analyte is in the inner and outer aqueous phases, the global process depicted in Scheme 1b can also be divided into two independent processes when species X^+ contained in the organic solution is lipophilic (see Section S3). The net current is equal to the sum of the currents associated with them.

When species X^+ is transferred to phase $\mathrm{W}_{\mathrm{inn}}$ at positive potential differences between the outer and inner aqueous phases ($E_{\mathrm{out}} - E_{\mathrm{inn}} > 0$), the current response is given by

Eqs.(1) and (8) by replacing $I_{d,W}^{out}$ by $I_{d,M}^{inn}$, A_{out} by A_{inn}, D_X^W by D_X^M, $c_X^{*W_{out}}$ by c_X^{*M} and $\delta_{d,X}^W$ by $\delta_{d,X}^M$. Moreover, the half-wave potential of the transfer to phase $\mathrm{W_{inn}}$ is defined as follows

$$E_{1/2,M}^{inn} = \left(\Delta\phi_L^{0'} - \Delta\phi_X^{0'}\right) + \frac{RT}{F}\ln\left(\frac{A_{inn}c_X^{*M}\left(D_X^M\right)^2}{2A_{out}\,c_L^{*W_{out}}D_X^W D_L^M}\right) + \frac{RT}{F}\ln\left(\frac{\delta_{d,X}^W\,\delta_{d,L}^M}{\left(\delta_{d,X}^M\right)^2}\right) \qquad (11)$$

and for the transfer of species $\mathrm{X^+}$ to phase $\mathrm{W_{out}}$ as:

$$E_{1/2,M}^{out} = \left(\Delta\phi_X^{0'} - \Delta\phi_L^{0'}\right) - \frac{RT}{F}\ln\left(\frac{A_{out}c_X^{*M}\left(D_X^M\right)^2}{2A_{inn}c_L^{*W_{inn}}D_X^W D_L^M}\right) - \frac{RT}{F}\ln\left(\frac{\delta_{d,X}^W\,\delta_{d,L}^M}{\left(\delta_{d,X}^M\right)^2}\right) \qquad (12)$$

EXPERIMENTAL SECTION

a) Reagents and solutions

Poly (vinyl chloride) high molecular weight (PVC), 2-nitrophenyl octyl ether (NPOE) and tetrahydrofuran (THF) were Selectophore products from Fluka. Lithium chloride (LiCl, 8M solution), tetramethylammonium chloride (TMACl), tetraethylammonium chloride (TEACl), tetrapropylammonium chloride (TPACl), tetrabutylammonium chloride (TBACl), potassium tetrakis-(4-chloro-phenyl)borate (K-TClPB), tetradodecylammonium tetrakis-(4-chloro-phenyl)borate (TDDA-TClPB) and 1,2-dichloroetane (DCE) were purchased from Sigma. Nanopure water (18 MΩ) from a Milli-Q (Millipore) system was used throughout.

Tetraalkylammonium tetrakis-(4-chlorophenyl) borate salts (X-TClPB, with X = TMA, TEA and TPA) were obtained as precipitates by mixing water-ethanol solutions of tetraalkylammonium chloride and potassium tetrakis-(4-chloro-phenyl) borate in equimolar amounts, and twice recrystallized from a mixture ethanol/water to ensure high purity.

b) Membrane preparation

A membrane of *ca*. 300 μm of thickness was prepared as described elsewhere [11]. A 9 mm diameter piece of this membrane was cut out with a punch and incorporated into the electrochemical cell.

c) Electrochemical measurements

Two different electrochemical cells were employed for the voltammetric experiments, depending on whether the analytes are initially present in the aqueous phases:

$Ag|5x10^{-2}M\ LiCl,\ 2x10^{-4}M\ XCl\ (W_{out}) \parallel 5x10^{-2}M\ TDDA\text{-}TClPB\ (M) \parallel 5x10^{-2}M\ LiCl,\ 2x10^{-4}M\ XCl\ (W_{inn}) \mid 3M\ KCl \mid AgCl \mid Ag$ **Cell I**

or in the organic solution:

$Ag|5x10^{-2}M\ LiCl\ (W_{out}) \parallel 5x10^{-2}M\ TDDA\text{-}TClPB,\ yM\ XTClPB\ (M) \parallel 5x10^{-2}M\ LiCl\ (W_{inn}) \mid Ag$ **Cell II**

with X = TMA, TEA, TPA, TBA. Platinum wires were used as counter-electrodes both in Cell I and Cell I, whereas Ag-AgCl (Cell I) and a silver wire (Cell II) were used as (pseudo)reference electrodes.

A NPOE polymeric membrane was used as organic phase in studies with Cell I, whereas 1,2-dichloroethane was employed with Cell II. Description and photographies of these cells are included in the Supporting Information (Section S4).

RESULTS AND DISCUSSION

In conventional ion-transfer studies with systems of two polarisable interfaces, the target ion X^+ is added initially only to the outer aqueous solution[13]. Thus, a single signal is obtained in voltammetric experiments, corresponding to the transfer of X^+ to the organic solution through the interface $\mathrm{W}_{\mathrm{out}} \mid \mathrm{M}$. This response is highly affected by the addition of the analyte in the inner aqueous solution, which can give rise to the appearance of two voltammetric signals associated with the transfer of X^+ from each aqueous phase as shown in Figure 1 for different ratios $c_X^{*W_{inn}} / c_X^{*W_{out}}$, $c_R^{*W_{out}} / c_R^{*W_{inn}}$ and A_{out} / A_{inn} (see also Section S5). As can be observed, the position of the two signals for a fully symmetric cell (i.e., $c_X^{*W_{inn}} = c_X^{*W_{out}}$ and $A_{out} = A_{inn}$) are symmetric with respect to the average half-wave potential $\left\langle E_{1/2} \right\rangle_W = (E_{1/2,W}^{out} + E_{1/2,W}^{inn})/2$ that coincides with the centre of the polarisation windows ($E = 0$) when $c_X^{*W_{inn}} = c_X^{*W_{out}} = c_X^{*W}$, $c_R^{*W_{out}} = c_R^{*W_{inn}} = c_R^{*W}$ and $A_{out} = A_{inn}$. The separation between the two signals depends on the lipophilicity of species X^+ and R^- according to the following expression (see section S2)

$$\Delta E_{1/2}^{(W)} = 2\left(\Delta\phi_X^{0'} - \Delta\phi_R^{0'}\right) + \frac{RT}{F}\ln\left(\frac{\left(c_X^{*W}\right)^2\left(D_X^W\right)^4}{4\left(c_R^{*W}\right)^2\left(D_X^M\right)^2\left(D_R^M\right)^2}\right) \qquad (13)$$

Eq.(13) is applicable for $\Delta E_{1/2}^{(W)} > 200\,\mathrm{mV}$ and under such conditions the formal transfer potential of species X^+ or R^- can be extracted, provided that their initial concentrations and diffusivities are known, and with no influence of possible uncertainties on the ratio A_{out} / A_{inn}.

The average half-wave potential $\left\langle E_{1/2} \right\rangle$ shifts from the center of the polarisation windows when the concentrations of the supporting electrolytes in the outer and inner aqueous solutions are different ($c_R^{*W_{out}} \neq c_R^{*W_{inn}}$), always in excess with respect to species X^+ (see figure 1a). Thus, when $c_R^{*W_{inn}}$ is decreased, the transfer of X^+ from $\mathrm{W}_{\mathrm{out}}$ to the organic phase is hindered and the corresponding signal develops at more positive potentials. On the other hand, the signal appearing at negative potentials does not vary since the transfers of X^+ at the outer and inner interfaces are totally independent under the conditions of figure 1a.

The symetry of the current-potential response breaks down when species X^+ is present at different concentrations in the aqueous phases ($c_X^{*W_{out}} \neq c_X^{*W_{inn}}$, figure 1b) or when the interfacial areas are unequal ($A_{out} \neq A_{inn}$, figure 1c), as a consequence of the different

magnitude of the two signals. In addition, the decrease of A_{out} or the increment of $c_X^{*W_{inn}}$ leads to the shift of both waves to more negative potentials, which means that the transfer of X^+ at $\mathrm{W_{out}} \mid \mathrm{M}$ is favoured while it is hindered at the inner interface. This behaviour can be explained on the basis of that the coupled transfer of species R^- must be of the same extent as the transfer of the target ion, which is more 'demanding' when the concentration of X^+ increases and/or the interfacial area corresponding to the transfer of R^- decreases. The case where the analytes in the aqueous phases are different (see Section S2) also would lead to non symetric voltammograms (not shown). It is worth noting that the strategy of adding two different analytes can be useful to study two species that would overlap (similar $\Delta\phi^{0'}$) or react if they were present in the same solution, as well as to use one of them as inner reference.

The "double transfer voltammograms" obtained when the target ion is initially present in the outer and inner aqueous solutions were previously reported experimentally by Dryfe *et al.* [8]. These authors studied by cyclic voltammetry (CV) the transfer of several ionic species with a supported liquid membrane, observing the appearance of two reversible pair of peaks. The separation between the peaks was dependent on the lipophylic character of the ionic species: the higher the lipophilicity, the closer the voltammetric signals. These results are in agreement with the theory above-presented as shown in Figure 2a, where the theoretical reproduction of the results reported by Dryfe *et al.* for the transfer of tetramethylammonium (TMA^+), tetraethylammonium (TEA^+) and tetrabutylammonium (TBA^+) are displayed (see Figure 5 in [8]). The magnitude and position of the peaks in Figure 3a are consistent with those obtained experimentally.

The results are also in agreement with our own experimental results shown in Figure 2b, corresponding to cyclic square wave voltammograms (cSWV) for the transfer of TMA^+, TEA^+ and TBA^+ with a solvent polymeric membrane (cell I, see Section S4). Two pair of reversible peaks are obtained for each species, which separate following the same trend of lipophilicity as that reported in [8]. From the separation between the two cSWV signals, the value of the transfer potential of Cl^- was estimated from

$$\Delta E_{1/2}^{(W)} = 2\left(\Delta\phi_X^{0'} - \Delta\phi_R^{0'}\right) + \frac{RT}{F}\ln\left(\frac{\left(c_X^{*W}\right)^2\left(D_X^W\right)^2}{4\left(c_R^{*W}\right)^2 D_X^M D_R^M}\right) \qquad (14)$$

where $R \equiv Cl^-$ and $\Delta\phi_X^{0'}$ is the formal transfer potential of the alkylammonium cation. A value of $\Delta\phi_{Cl}^0 = -428 \pm 6$ mV is obtained, which is consistent with the data reported previously in the

literature (see Section S6). The use of cSWV has the advantage of offering peak-shaped signals, in a such way that the determination of the peak position is easier and more accurate . Also, the reversible character of the transfers can be readily evaluated from the degree of coincidence between the peak potentials in the forward and backward scans. Note that the response is not fully symetric in spite of that the concentrations of the analyte and of the supporting electrolytes are identical in both aqueous phases. This can be a consequence of differences between the areas of the inner and outer interfaces, as was also found in [8].

Including the target ion in the organic solution (Scheme 1b) can be convenient when the analyte solubility in aqueous media is low, or when its transfer to the organic phase takes place too close to the limits of the polarisation window. In this context, Figure 3 shows the experimental CV and cSWV-voltammograms recorded for the transfer of different alkylammoniums cations by placing them initially in the organic phase: 1,2-dichloroetane (cell II, see Section S4). As could be expected, the position of the voltammograms follows the opposite order to Figure 2: the more lipophylic the cation, the more distanced the waves. This behaviour is predicted by the following expression

$$\Delta E_{1/2}^{(M)} = 2\left(\Delta\phi_L^{0'} - \Delta\phi_X^{0'}\right) + \frac{RT}{F}\ln\left(\frac{\left(c_X^{*M}\right)^2\left(D_X^M\right)^2}{4D_X^W\, D_L^M\left(c_L^*\right)^2}\right) \qquad (15)$$

with $L \equiv Li^+$. The analysis of the experimental results with Eq. (15) yields a value of $\Delta\phi_{Li}^{0'} = 630 \pm 30$ mV, which is also in good agreement with the data previously reported (see Section S7).

CONCLUSIONS

A new theory has been developed for ion transfer processes between two aqueous phases separated by an organic solution when applying a potential difference between them. The theoretical expressions cover two general situations: i) a hydrophilic ion is initially present in the two aqueous solutions and ii) a lipophilic ion is in the organic phase. Analytical equations have been obtained that describe adequately the experimental 'double transfer voltammograms' reported as well as the flux of ions at each interface as a function of the transmembrane potential difference and of the lipophilicity, concentration and diffusivity of the ionic species. From the equations presented, it is possible to identify the charge transfer processes behind each signal and to extract information about the degree of lipophilicity of the species. Thus, the formal ion-transfer potentials can be determined from the corresponding values of the half-wave potentials for which simple expressions have been provided.

When the composition of the two aqueous phases is the same, the two voltammetric signals are identical and symmetric with respect to the centre of the polarisation window. On the other hand, the total signal symmetry breaks down when discrepancies arise owing to different: inner and outer solvents, target ions (see Supporting Information), concentrations of the target ion, supporting electrolytes and interfacial areas.

Experimental verification of the theoretical results has been achieved through the study of the transfer of tetraalkylammonium cations with solvent polymeric membranes and water|1,2-dichloroethane|water systems. The theoretical and experimental results in cyclic voltammetry and in cyclic square wave voltammetry are in total agreement, pointing out the opposite influence of the lipophilic character of the target ion on the separation of the two ion-transfer waves depending on whether the ion is initially present in the aqueous or in the organic phases.

Acknowledgements

The authors greatly appreciate the financial support provided by the Fundación Séneca de la Región de Murcia (Project 19887/GERM/15) and Ministerio de Economía y Competitividad (Projects CTQ-2015-65243-P and CTQ-2015-71955-REDT). E.L. and J.M.O. thank the Ministerio de Economía y Competitividad for the fellowship "Juan de la Cierva-Incorporacion 2015" and for the grant received under the Project CTQ-2012-36700 co-funded by the European Regional Development Fund, respectively.

Supporting Information

Notation; Two polarisable interfaces with two different transferable hydrophilic ions present in the outer and inner aqueous phases; Two polarisable interfaces with a transferable lipophilic ion present in the organic phase; Experimental details; Comparison between the responses obtained when the analyte is present in both aqueous phases or only in the outer aqueous phase; Determination of the standard transfer potential of Cl^-: membrane system; Determination of the standard transfer potentials of Li^+: water|DCE|water system; Variation of the outer and inner potential differences during CV experiments.

Figure 1. Effect of the ratios a) $c_R^{*W_{inn}} / c_R^{*W_{out}}$, b) $c_X^{*W_{inn}} / c_X^{*W_{out}}$ and c) A_{out} / A_{inn} on the CV-response (Eq.(10)) at a solvent polymeric membrane of macrometric size. $D_X^M / D_X^W = D_R^M / D_X^W = 0.001$, $\Delta\phi_X^{0'} = 0$ mV, $\Delta\phi_R^{0'} = -200$ mV, $c_X^{*W_{out}} = 1$ mM , $c_R^{*W_{out}} = 200$ mM, $A_{out} = 0.1$ cm², T = 298.15K. a) $c_X^{*W_{inn}} = c_X^{*W_{out}}$, $A_{inn} = A_{out}$. b) $c_R^{*W_{inn}} = c_R^{*W_{out}}$, $A_{inn} = A_{out}$. c) $c_R^{*W_{inn}} = c_R^{*W_{out}}$, $c_X^{*W_{inn}} = c_X^{*W_{out}}$. $\psi_{CV} = I_{CV} / FA_{out} c_X^{*W_{out}} \sqrt{\frac{FD_X^W \nu}{RT}}$, with ν being the scan rate.

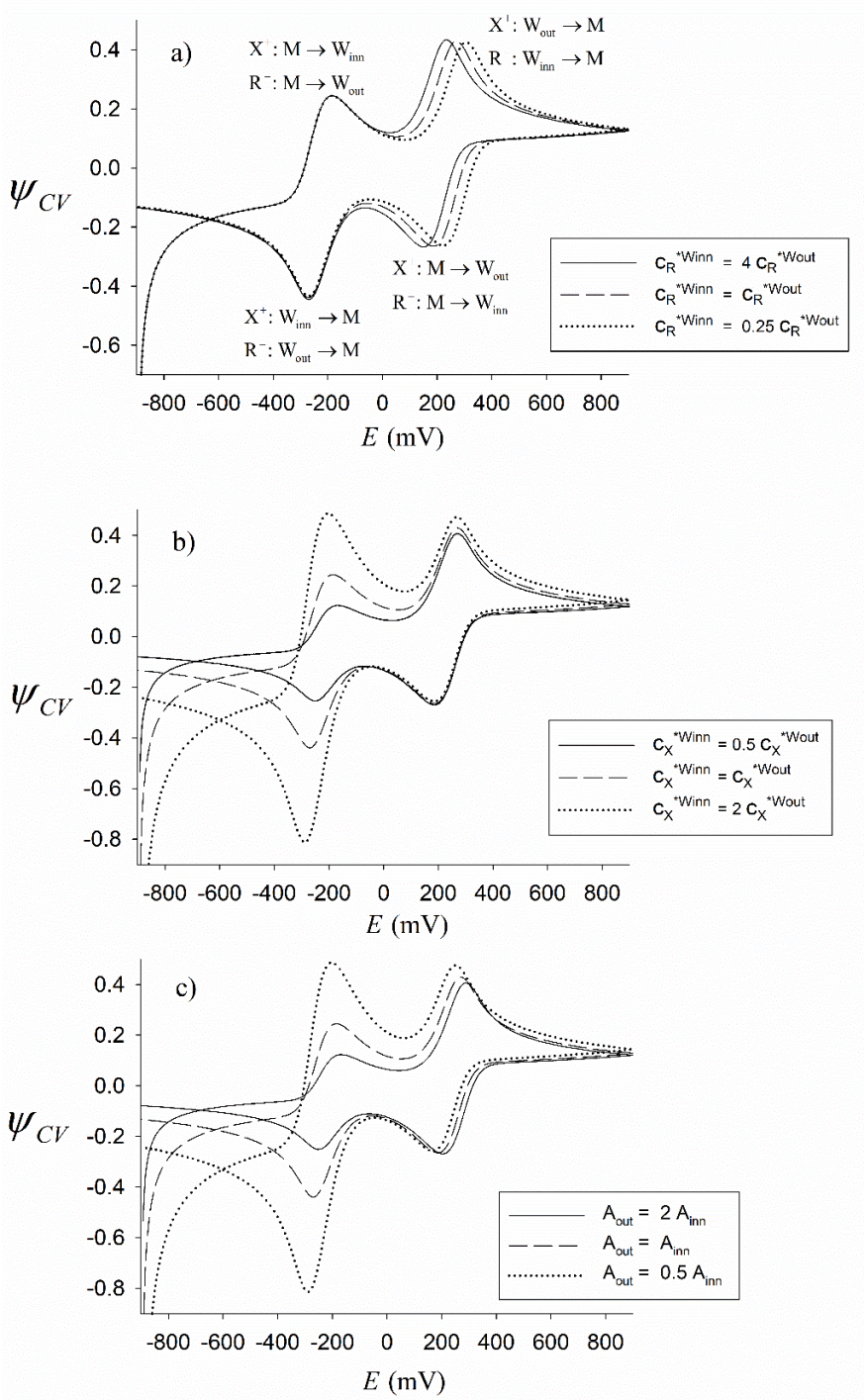


Figure 2. a) Theoretical and b) experimental reproduction of the results reported in[8], corresponding to the transfer of tetramethylammonium (TMA), tetraethylammonium (TEA), tetrapropilammonium (TPA) and tetrabutylammonium (TBA) at a NPOE supported liquid membrane system in CV [8] and at solvent polymeric membrane in cSWV (cell I, see section S4). The direction of the forward scan is towards positive potentials. T = 298.15K. a) Values of initial concentrations, scan rate, half-wave potentials and areas of each interface taken from Figure 5 of [8]. $D^{W}_{TMA} = 1.196\times10^{-5}$ cm^2 s^{-1}, $D^{W}_{TEA} = 8.68\times10^{-6}$ cm^2 s^{-1}, $D^{W}_{TBA} = 5.19\times10^{-6}$ cm^2 s^{-1} [16]. b) E_s = 10mV, E_{sw} = 50mV, f = 0.5 Hz. Values of initial concentrations of analytes and supporting electrolytes are given in the experimental section.

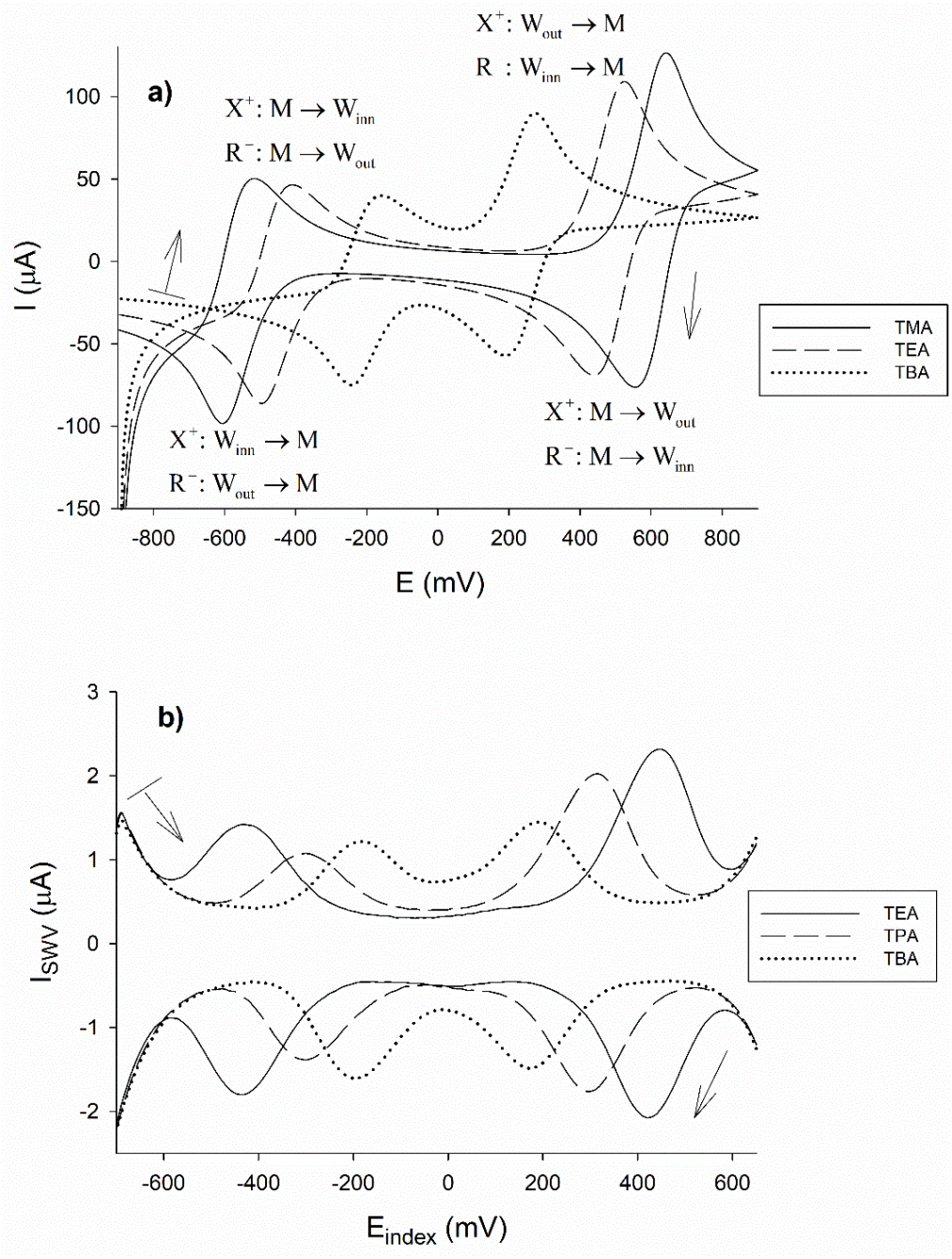
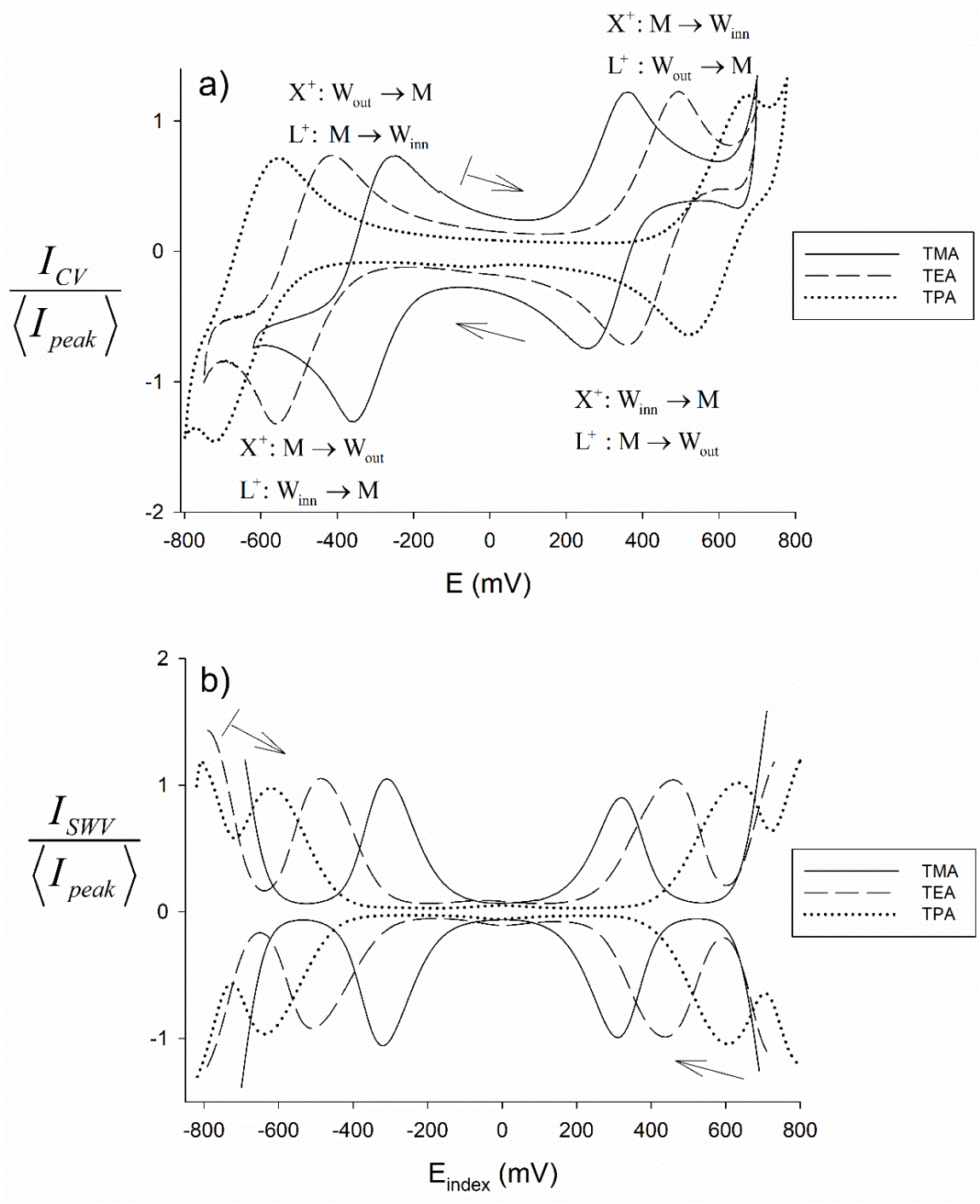


Figure 3. Experimental cyclic (a) and cyclic square wave (b) voltammograms when the target ion is only present in the organic phase. The transfer of tetramethylammonium (TMA), tetraethylammonium (TEA) and tetrapropilammonium (TPA) from 1,2-dichloroethane to aqueous solutions of LiCl 50 mM (cell II, see Section S4) are considered. The direction of the forward scan is towards positive potentials. $\langle I_{peak} \rangle$ refers to the average of the peaks currents obtained for each species. v = 20 mV s^{-1} , E_s = 10mV, E_{sw} = 50mV, f = 0.5 Hz. $c^{*M}_{TMA} = 9.1\times10^{-4}$M , $c^{*M}_{TEA} = 8.6\times10^{-4}$M, $c^{*M}_{TPA} = 7.8\times10^{-4}$M.



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