Kinetic Effects of the Complexation Reaction in the Facilitated Ion Transfer at Liquid Membrane Systems of One and Two Polarized Interfaces. Theoretical Insights

Ángela Molina,*† Encarnación Torralba,† Carmen Serna,† and Joaquín A. Ortúño‡

†Departamento de Química Física and ‡Departamento de Química Analítica Facultad de Química, Universidad de Murcia, 30100 Murcia, Spain

ABSTRACT: An in-depth study of the ion transfer facilitated by complexation in the organic phase (TOC mechanism) in liquid membrane systems of one and two polarized interfaces is carried out by taking into account the kinetic effects associated with the complexation reaction. Explicit analytical equations for the normal pulse voltammetric (I/E) and chronoamperometric (I/t) responses with an explicit dependence on the kinetic parameters of the chemical complexation are presented for both kinds of membrane system, which could be useful for modeling artificial and biological membranes. The equations are compared with those obtained by using the widely used approximation of total equilibrium conditions that leads to the transfer by interfacial complexation mechanism (TIC), which only depends on thermodynamic parameters. Simple methods are proposed that allow quantitative determination of the equilibrium and kinetic constants of the complexation reaction in the organic phase for both kinds of membrane system.

1. INTRODUCTION

Ion transfer across liquid–liquid interfaces is a fundamental physicochemical process with important implications in different areas, such as biology, chemistry, and technology. It has been the subject of both theoretical and experimental studies.1−5

In cases such as the transfer of highly hydrophilic ions from water to an organic phase, ion transfer can be facilitated by a complexing agent, which normally is present in the organic phase.6−11 This facilitated transfer is widely used in nature, for example, in the uptake of potassium ion in cell membranes by selective transport assisted by the natural antibiotic valynomicin,15 and also in artificial membranes for ion-selective sensors and metal ion separations.6−14

The electrochemical investigation of the facilitated ion transfer reaction at ITIES (interface between two immiscible electrolyte solutions) was pioneered in 1979 by Koryta, who studied the transfer of alkali metal ions facilitated by different natural and synthetic ionophores.15 Since the work of Koryta, extensive studies of facilitated ion transfer have been carried out, many of them focused on the elucidation of the mechanism that this process follows which, even today, is a matter of controversy. Currently, it is accepted that facilitated ion transfer can take place via three mechanisms: through a TOC (transfer followed by complexation in the organic phase) or EC mechanism, where the ion transfer is the electrochemical step and the subsequent complexation the chemical one; through an ACT (aqueous complexation followed by transfer) or CE mechanism, in which the ligand is partitioned from an organic to an aqueous phase, and the complexation occurs before the ion transfer; and through a TIC/TID (transfer by interfacial complexation/decomplexation), which involves a single ion transfer-ion complexation step occurring at the liquid/liquid interface.7,8 The active mechanism depends on many factors, such as the relative concentration of both the ion and the ligand in the two phases and the stability constant of the complex. In many references on facilitated ion transfer, the TIC mechanism is considered and the mathematical approaches used are based on pure thermodynamic principles, which implies that the kinetic effects of the chemical reaction are not considered. Moreover, in most of these references, the solution for the problem has been carried out with numerical methods in cyclic voltammetry, leading to complex integral solutions.

In this work we analyze the facilitated ion transfer followed by organic complexation (TOC or EC mechanism) by taking into account the kinetic of this complexation reaction. We have obtained simple explicit analytical expressions for the flux or current corresponding to a TOC mechanism as a function of the ratio of the interfacial concentrations of the target ion between the aqueous and organic phases or as a function of the applied potential. These equations can be applicable to the electrochemical techniques normal pulse voltammetry (I/E) and chronoamperometry (I/t) in liquid membrane systems of one of two polarized interfaces, be they artificial membrane systems such as supported liquid membranes, solvent polymeric membranes, and bilayers or biological membranes. Both one
and two polarized interfaces systems consist of an organic membrane that separates two aqueous solutions, but in the former, the polarization phenomena is only effective at one of the two liquid/liquid interfaces involved (the sample solution/membrane interface or outer interface), whereas in the latter, both interfaces are polarized.\textsuperscript{1,2,16–22} We have also solved this problem, by following the treatment proposed by Matsuda et al.\textsuperscript{8} (which does not consider the kinetic of the complexation reaction), in both kinds of membrane system, and a comparison between the responses obtained by following both methodologies has been made. The importance of taking into account the kinetic of the chemical complexation and the fact that the TIC mechanism can be obtained as a limiting case of the TOC or EC mechanism is shown.

Simple methods are proposed for the quantitative determination of the homogeneous equilibrium and kinetic constants of the complexation reaction in the membrane based on the evolution with time of the shift of the half-wave potential of the facilitated ion transfer.

2. THEORY

2.1. One Polarized Interface System. 2.1.1. Kinetic Effects of the Complexation Reaction (TOC or EC Mechanism). Let us consider the reversible ion transfer of a metal ion X\textsuperscript{+} from an aqueous solution (W\textsubscript{1}) to an organic one (M), which is facilitated by a highly lipophilic neutral ionophore, L\textsubscript{0} present only in the organic phase, according to

\[
M + X^+ \rightleftharpoons M X^+ + L^0 \]

Scheme 1. Schematic View of the Facilitated Ion Transfer via TOC or EC Mechanism (Solid Arrows), and via TIC or E Mechanism (Dashed Arrows) in a System of a Single Liquid/Liquid Polarized Interface

complexation is the rate determining step.\textsuperscript{8} Note that coupled to the transfer of the target cation X\textsuperscript{+} through the outer interface (W\textsubscript{1}/M interface), a common ion present in the supporting electrolyte of the membrane and inner aqueous phase (W\textsubscript{2}) is transferred through the inner interface (M/W\textsubscript{2} interface) to ensure electroneutrality, but as this ion is part of the supporting electrolytes of both phases, the inner interface is non-polarizable and the system constitutes a system of a single polarized interface.\textsuperscript{20}

For the sake of simplicity we assume that the bulk concentration of L in the membrane is large enough compared with that of X\textsuperscript{+} in the same phase for the condition of pseudo-first-order kinetic with respect to X\textsuperscript{+}(M) to be satisfied.

When a constant potential, \(E\), is applied to this system and the uptake process establishes a fixed ratio of concentrations of the species involved on both sides of the interfacial region, mass transport can be described by the following diffusive-kinetic equation system:

\[
\frac{\partial c_{M}(x,t)}{\partial t} = D_{X}^{M} \frac{\partial^{2} c_{M}(x,t)}{\partial x^{2}} - k_{i} c_{M}(x,t) + k_{-i} c_{XL}(x,t) \\
\frac{\partial c_{XL}(x,t)}{\partial t} = D_{XL}^{M} \frac{\partial^{2} c_{XL}(x,t)}{\partial x^{2}} + k_{i} c_{M}(x,t) - k_{-i} c_{XL}(x,t)
\]

with the boundary value problem

\[
t = 0, x \leq 0 \quad c_{W}^{M}(x,0) = c_{W}^{XL}(x,0) = c_{X}^{0} + \\
t \geq 0, x \rightarrow -\infty \quad c_{X}^{W}(x,\infty,t) = c_{X}^{W}(-\infty,t) = c_{X}^{0} +
\]

\[
t = 0, x \geq 0 \quad c_{M}(x,0) = c_{XL}(x,0) = 0 \\
t \geq 0, x \rightarrow \infty \quad c_{M}(x,\infty,t) = c_{XL}(x,\infty,t) = 0
\]

\[
x = 0, t > 0 \quad D_{W}^{M} \left( \frac{\partial c_{W}^{M}(x,t)}{\partial x} \right)_{x=0} = D_{X}^{M} \left( \frac{\partial c_{X}^{M}(x,t)}{\partial x} \right)_{x=0} = 0 \quad D_{XL}^{M} \left( \frac{\partial c_{XL}(x,t)}{\partial x} \right)_{x=0} = 0
\]

where \(c_{i}^{p}(x,t)\) and \(D_{p}^{i}\) are, respectively, the concentration of the species \(i\) in phase \(p \quad (i = X^+, XL^+; \quad p = W, M)\) and its diffusion coefficient, and \(c_{X}^{0}\) and \(\Delta M_{i}^{0}\) are the initial concentration of the ion \(X^+\) and its formal ion transfer potential. Other symbols have their usual meaning.

For simplicity, we assume that the diffusion coefficients of the free ion \(X^+\) and the complex \(XL^+\) in the organic phase are equal, i.e.

\[
D_{X}^{XL} = D_{XL}^{M}
\]
The current obtained is given by

\[ I = -FAD \frac{\partial W^X(x,t)}{\partial x} \bigg|_{x=0} \]  

To solve the problem given by eqs 1–7, we introduce two variables

\[ \zeta(x,t) = c^M_X(x,t) + c^M_{XL}(x,t) \]  
\[ \varphi(x,t) = Kc^M_X(x,t) - c^M_{XL}(x,t) \]

where \( \varphi(x,t) \) refers to the distortion of the chemical equilibrium, and \( K \) is the stability constant of the complex under the pseudo-first-order assumption

\[ K = K' c^*_L(M) = \frac{k_1^*}{k_2^*} = \frac{c^*_L (M)}{c^*_X (M)} \]

\( c^*_L(M) \), \( c^*_X(M) \), and \( c^*_M(M) \) being the equilibrium concentrations at phase \( M \).

Considering that the kinetic of the homogeneous chemical reaction are fast enough \( ((k_1 + k_2)t \geq 15) \), the kinetic steady state solution (kss) applies, which relies on the perturbation of the chemical equilibrium being independent of time \( (\partial \varphi(x,t)/\partial t) = 0^{23,24} \)

Under these conditions, we can derive the following expression for the current corresponding to the facilitated ion transfer in a system of a single polarized interface (Appendix A.1)

\[ \frac{I_{kss}}{I_d} = \frac{\gamma e^0(1 + K)}{1 + \gamma e^0(1 + K)} F(\chi^EC) \]

where

\[ \chi^EC = \frac{2\sqrt{\chi}}{K} (1 + \gamma e^0(1 + K)) \]

\[ = \frac{2\sqrt{D_Mt}}{K\delta_r} (1 + \gamma e^0(1 + K)) \]

with \( \chi \) being the dimensionless kinetic constant, given by

\[ \chi = \kappa \]  

\( \kappa \) is the sum of both kinetic constants involved in the chemical complexation, the forward pseudo-first-order kinetic constant \( (k_1) \) and the backward first-order kinetic one \( (k_2) \).

\[ \kappa = k_1 + k_2 \]

\( \delta_r \) is the reaction layer thickness, given by eqs A1.7 and A1.8

\[ \delta_r = \sqrt{D_M/k} \]

and

\[ \frac{I_{dss}}{I_d} = \frac{\gamma e^0(1 + K)}{1 + \gamma e^0(1 + K)} \]

with \( \delta_r \) being the reaction layer thickness, given by eq 17 and \( \delta \) the diffusion layer thickness, given by

\[ \delta = \sqrt{\pi D_M t} \]  

In this treatment, the kinetic effects of the complexation reaction are contained in the ratio \( \delta_r/\delta \) (=1/(\sigma\chi^{1/2})).

This response can be linearized in a formally identical way to that corresponding to a simple ion transfer process, such that we have the following linearized potential/current relation for the facilitated ion transfer

\[ E = E^{1/2} + \frac{RT}{F} \ln \left( \frac{I_{dss}/I_d}{1 - I_{dss}/I_d} \right) \]
with

\[ E^{1/2} = \Delta W^0_\Phi \phi + \frac{RT}{F} \ln \left( \frac{1}{\gamma} \right) \]

\[ + \frac{RT}{F} \ln \left( \frac{1 + K\delta/\delta}{1 + K} \right) \]

(25)

being the half-wave potential corresponding to the process.

In conditions of inert equilibrium (\( K \to 0 \)) and very slow kinetic (\( \delta \to \delta_i \)), eqs 21, 22, and 25 for the concentration profiles, current response, and half-wave potential corresponding to the facilitated ion transfer simplify to those corresponding to the simple ion transfer in this kind of membrane system

\[ \frac{c^{W}(x,t)}{c^*_X} = 1 - \frac{\gamma e^{\eta}}{1 + \gamma e^{\eta}} \text{erfc} \left( \frac{x}{2\sqrt{D^W t}} \right) \]

\[ \frac{c^{M}(x,t)}{c^*_X} = \frac{\gamma e^{\eta}}{1 + \gamma e^{\eta}} \text{erfc} \left( \frac{x}{2\sqrt{D^M t}} \right) \]

(26)

\[ I_{dss} = \frac{I_0}{1 + \gamma e^{\eta}} \]

(27)

\[ \frac{E^{1/2}}{2} = \Delta W^0_\Phi \phi + \frac{RT}{F} \ln \left( \frac{1}{\gamma} \right) \]

(28)

with \( \eta \) given by eq 7.

**2.1.2. Total Equilibrium Conditions (TIC Mechanism).**

Equations 22 and 24 are strongly simplified if we suppose that the rates of the complex formation and dissociation processes are sufficiently large in comparison with the diffusion rate, so it may be assumed that the complex formation and dissociation are at equilibrium even when current is flowing, i.e., \((k_1 + k_2) \delta_i \gg 1 \) or \( \delta_i \to 0 \). This situation, similar to that described by Matsuda et al. in ref 6, corresponds with that of the ion that is simultaneously transferred at the inner one (M/W2 interface) to the outer one (W1/M interface) and that of the ion that is involved, and half-wave potential have been given and experimentally verified by our research group.\(^{22,27-29}\)

When any constant potential, \( E \), is applied to study the facilitated ion transfer in this kind of membrane system, we need to solve two separate problems of mass transport: that corresponding to the facilitated ion transfer of the ion, \( X^+ \), at the outer interface (\( W_1/M \) interface) and that of the ion that is simultaneously transferred as the inner one (\( M/W_2 \) interface) to ensure electroneutrality.\(^{22}\) So, if we assume that coupled to the transfer of the metal ion through the outer interface, the ion of the supporting electrolyte of the membrane, \( R^+ \), is transferred through the inner one, by means of the procedure indicated in Appendix B, we can derive the following response for the concentration profiles and the current associated to the facilitated ion transfer at systems of two polarized interfaces (TPI)

\[ \frac{c^{W}(x,t)}{c^*_X} = 1 - h(\eta) \text{erfc} \left( \frac{x}{2\sqrt{D^W t}} \right) \]

\[ \frac{c^{M}(x,t)}{c^*_X} = \frac{h(\eta)}{\gamma(1 + K)} \left( \text{erfc} \left( \frac{x}{2\sqrt{D^M t}} \right) + \frac{K\delta}{\delta_i} e^{-x/\delta_i} \right) \]

\[ \frac{c^{M}(x,t)}{c^*_X} = \frac{kh(\eta)}{\gamma(1 + K)} \left( \text{erfc} \left( \frac{x}{2\sqrt{D^M t}} \right) - \frac{\delta_i}{\delta} e^{-x/\delta_i} \right) \]

\[ \frac{c^{W}(x,t)}{c^*_X} = \left[ \frac{D^{Wt}}{D^{W}} \right] h(\eta) \text{erfc} \left( \frac{x - d}{2\sqrt{D^W t}} \right) \]

(31)

Under total equilibrium conditions the expression for the current associated with the facilitated ion transfer takes the following form (Appendix A.3)

\[ I_{fe} = \frac{\gamma e^{\eta}(1 + K)}{1 + \gamma e^{\eta}(1 + K)} \]

(29)

which is an equivalent of the Deford–Hume equation deduced for planar diffusion.\(^{26}\)

**2.2. Two Polarized Interfaces System. 2.2.1. Kinetic Effects of the Complexation Reaction (TOC or EC Mechanism).** We consider now the facilitated ion transfer in a membrane system of two polarized interfaces (process described by the solid arrows in Scheme 2). The simple ion transfer process in this kind of membrane system has been quite widely studied.\(^{16,17,19}\) Recently, simple and manageable expressions for the concentration profiles, current response, membrane potential, potential differences at the two interfaces involved, and half-wave potential have been given and experimentally verified by our research group.\(^{22,27-29}\)

When any constant potential, \( E \), is applied to study the facilitated ion transfer in this kind of membrane system, we need to solve two separate problems of mass transport: that corresponding to the facilitated ion transfer of the ion, \( X^+ \), at the outer interface (\( W_1/M \) interface) and that of the ion that is simultaneously transferred as the inner one (\( M/W_2 \) interface) to ensure electroneutrality.\(^{22}\) So, if we assume that coupled to the transfer of the metal ion through the outer interface, the ion of the supporting electrolyte of the membrane, \( R^+ \), is transferred through the inner one, by means of the procedure indicated in Appendix B, we can derive the following response for the concentration profiles and the current associated to the facilitated ion transfer at systems of two polarized interfaces (TPI)

\[ \frac{c^{W}(x,t)}{c^*_X} = 1 - h(\eta) \text{erfc} \left( \frac{x}{2\sqrt{D^W t}} \right) \]

\[ \frac{c^{M}(x,t)}{c^*_X} = \frac{h(\eta)}{\gamma(1 + K)} \left( \text{erfc} \left( \frac{x}{2\sqrt{D^M t}} \right) + \frac{K\delta}{\delta_i} e^{-x/\delta_i} \right) \]

\[ \frac{c^{M}(x,t)}{c^*_X} = \frac{kh(\eta)}{\gamma(1 + K)} \left( \text{erfc} \left( \frac{x}{2\sqrt{D^M t}} \right) - \frac{\delta_i}{\delta} e^{-x/\delta_i} \right) \]

\[ \frac{c^{W}(x,t)}{c^*_X} = \left[ \frac{D^{Wt}}{D^{W}} \right] h(\eta) \text{erfc} \left( \frac{x - d}{2\sqrt{D^W t}} \right) \]

(31)
\( \frac{c_{x}^{w}(x, t)}{c_{x}^{+}} = 1 - g(\eta) \text{erfc} \left( \frac{x}{2\sqrt{D_{x}^{w}}t} \right) \) \( \frac{c_{x}^{\lambda}(x, t)}{c_{x}^{+}} = g(\eta) \text{erfc} \left( \frac{x}{2\sqrt{D_{x}^{\lambda}}} \right) \) \( \frac{c_{x}^{W}(x, t)}{c_{x}^{+}} = \frac{\sqrt{D_{x}^{W}}}{\sqrt{D_{x}^{W}}} g(\eta) \text{erfc} \left( \frac{x - d}{2\sqrt{D_{x}^{W}}t} \right) \) 

(39)

\( I_{\text{TPLE}} = I_{d} g(\eta) \) 

(40)

\[ E_{M}^{1/2} = E_{M}^{0'} + \frac{RT}{F} \ln \left( \frac{1}{\lambda} \right) \]

(41)

with \( g(\eta) \) given by

\[ g(\eta) = \frac{1}{4} \left( (\lambda e^{\eta})^{2} + 8\lambda e^{\eta} - \lambda e^{\eta} \right) \]

(42)

with \( \lambda \) given by eq 34 and \( \eta \) by eq 35.

2.2.2. Total Equilibrium Conditions (TIC Mechanism). If we assume the approximation of total equilibrium (see eq A3.1 and process described by dashed arrows in Scheme 2), by following the same methodology explained in Appendix B, but taking into account the solutions for the outer interface obtained under total equilibrium conditions (eqs 24 and 30), the following expression for the \( I/E \) curve and the potential difference in the system of two polarized interfaces are obtained

\[ I_{\text{TPLE}} = I_{d} h'(\eta) \]

(43)

with

\[ h'(\eta) = \frac{1}{4} \left( (\lambda(1 + K))^{2} e^{2\eta} + 8\lambda(1 + K)e^{\eta} \right)^{1/2} - \lambda(1 + K)e^{\eta} \]

(44)

and

\[ E = E_{M}^{1/2} + \frac{RT}{F} \ln \left( \frac{2(I_{\text{TPLE}}/I_{d})^{2}}{1 - I_{\text{TPLE}}/I_{d}} \right) \]

(45)

with

\[ E_{M}^{1/2} = E_{M}^{0'} + \frac{RT}{F} \ln \left( \frac{1}{\lambda} \right) + \frac{RT}{F} \ln \left( \frac{1}{1 + K} \right) \]

(46)

which, as can be seen, coincides with eqs 32, 33, 37, and 38 when \( \delta \) approaches to zero.

Equation 46 constitutes an equivalent of the Deford–Hume equation for planar diffusion in a system of two liquid/liquid polarized interfaces.

Concentration profiles and interfacial concentrations of the species involved under te conditions are given in Appendix B.

3. RESULTS AND DISCUSSION

Figure 1 shows the \( I/E \) curves corresponding to the facilitated ion transfer in a system of a single polarized interface obtained by using the kss solution (solid lines, eq 13), corresponding to a fixed value of the dimensionless kinetic constant \( \chi \) and different values of the stability constant of the complex \( K \) (Figure 1a), and to a fixed value of the stability constant and different values...
The Journal of Physical Chemistry A

Figure 1. Solid lines: $I/E$ curves corresponding to the ion transfer facilitated by organic complexation in a system of a single polarized interface obtained using the kss solution (eq 13) for a fixed value of $\chi$ and different values of $K$ (given on the curves, (a)), and for a fixed value of $K$ and different values of $\chi$ (b). Dotted lines: $I/E$ curves of the simple ion transfer (eq 27). $A_{\text{mix}}\phi_{\text{kss}}^0 = 0 \text{ mV}$, $c^0 = 1 \text{ mM}$, $D^0_X = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D^0_M = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $t = 1 \text{ s}$, $A = 0.081 \text{ cm}^2$, $T = 298.15 \text{ K}$.

Figure 2. $I/E$ curves of the ion transfer facilitated by complexation in the organic phase obtained by using the kss (solid lines, eq 13), dkss (dashed lines, eq 22), and te (dash-dotted lines, eq 29) solutions in a liquid membrane system of a single polarized interface, for a fixed value of $\chi$ and different values $K$ (a)–(c), and vice versa (d)–(f). $\Delta_{\text{mix}}\phi_{\text{kss}}^0 = 0 \text{ mV}$, $c^0 = 1 \text{ mM}$, $D^0_X = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D^0_M = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $t = 1 \text{ s}$, $A = 0.081 \text{ cm}^2$, $T = 298.15 \text{ K}$. $\chi$ and $K$ values are given in the graphs.

As can be seen from Figure 2a–c, as $K$ increases, the $I/E$ curves corresponding to the dkss and te approximations become less coincident with that corresponding to the more rigorous kss solution, with the dkss curves displaced toward more positive potential values and the te ones toward more negative potentials. This displacement is more important in the case of the te approximation, in which curves show a shift $\Delta E$ of $50 \text{ mV}$ with respect to the kss curves at potential values near the half-wave potential for a stability constant value of $K \geq 50$, whereas the shift shown by the dkss curves is around $8 \text{ mV}$. So, when the chemical equilibrium is displaced toward the complex, the dkss approximation is more suitable than the te one for characterizing the system. From Figure 2d–f it can be noted that, for a very high value of $\chi$ (Figure 2f), all the $I/E$ curves corresponding to the facilitated ion transfer overlap, and any of the approximations presented is suitable. However, as $\chi$ decreases, the dkss curves and the te ones differ from the kss curves. Thus, for $\chi = 15$ the dkss and te curves are displaced about $8$ and $30 \text{ mV}$, respectively, with respect to the kss curve at potential values closer to the half-wave potential of the system. So, from these drafts we can conclude that the dkss approximation can be confidently used for high stability constant values and relatively small values of the dimensionless kinetic constant, the te approximation not being acceptable under these conditions. For other conditions, the kss
system of a single polarized interface in limiting current conditions (Figure 3a), and for a potential applied of 50 mV (Figure 3b), for two different values of the stability constant (shown on the curves). The dotted lines correspond to the concentration profiles of a simple ion transfer (eq 26) in the same conditions. Figure 3c shows the I/E curves corresponding to the facilitated ion transfer at the two stability constants selected for Figure 3a,b obtained by the dks solution (solid lines, eq 22), together with those obtained with the te approximation (dashed lines, eq 29), and that corresponding to a simple ion transfer process (dotted lines, eq 27). A vertical dashed line shows the potential chosen for Figure 3b.

As can be seen from Figure 3a, when a very high positive potential is applied, the profile corresponding to the facilitated ion transfer of the metal X⁺ in the aqueous phase coincides with that corresponding to a simple ion transfer in the same conditions. So, the current flux of the facilitated ion transfer in this case is independent of the kinetic of the complexation reaction. This feature is not observed for the metal X⁺ in the membrane, because part of this ion is lost in its interconversion into the species X^L⁻. The more stable the complex, the less X⁺ remains free in the membrane.

For an intermediate applied potential, the concentration profile corresponding to the metal X⁺ in the aqueous phase is well differentiated from that corresponding to a simple ion transfer (Figure 3b). Therefore, the current does depend on the kinetic of the chemical complexation in these conditions, and hence, these conditions will be desirable for studying the kinetic of the chemical reaction following the ion transfer. Moreover, from an experimental point of view working at not very high potentials is also preferable, because the background currents of the experiment and the deterioration of the experimental membrane system are expected to be less, and to have a better selectivity. It is necessary to clarify that a slope for the concentration profile of the target ion in the organic phase is 1000 times steeper than in the aqueous phase, and a flat profile for the complex X^L⁻ near the interface is obtained in Figure 3a,b in agreement with that predicted by eqs 4 and 5; however, it cannot be evident at first sight due to the different scales used for the aqueous and organic phases.

From Figure 3c it can be observed that, under the conditions selected, the I/E curves corresponding to K = 0.7 obtained by taking into account the kinetic of the coupled chemical reaction overlap with that obtained with the hypotheses of total equilibrium. This is logical, because at these small complexation constants the complexation reaction scarcely takes place and the kinetic do not play an important role. However, as the stability constant increases, the kinetic effects gain importance, and the te curves differ from the dks ones, showing a displacement of approximately 8 mV for K = 20. The separation shown between the I/E curves of the facilitated ion transfer at the two stability constants selected for Figure 3a,b obtained by the dks solution responding to the facilitated ion transfer in conditions similar to those discussed in Figure 3, i.e., for an applied potential corresponding to limiting current I\text{lim}(x,t) (dash-dot lines) and to the half-wave potential \( \phi(x,t) \) (solid lines). In these conditions the expression for the function \( \phi(x,t) \) simplifies to the following

\[
\phi(x,t) = 2e^{\frac{x}{X}}K\delta_{i}/\delta_x e^{-x/\delta_i} \gamma (47)
\]

As can be observed from Figure 4 and also from eq 47, under limiting current conditions the function of the perturbation of the
chemical equilibrium takes values double those corresponding to the half-wave potential. For a given time value, \( \phi(x,t) \) decreases as the distance to the interface increases as a consequence of the inefficiency of the diffusion transport to supply ion \( X^+ \) to be complexed. The thickness of the linear reaction layer, which is given for the value in the abscissa axis of the cutoff point of the complexed, the diffusion coefficient and on the kinetic constants (eq 17). The plots given in Figure 5b are very useful to the complete characterization of the coupled chemical complexation. The representation of \( \exp(zF\Delta E^{1/2}/RT) \) with \( 1/\sqrt{t} \) is linear, and the values of the slope and the intercept can be used to obtain \( \kappa \) and \( K \) of the complexation reaction, as can be seen in Figure 5b and also in eq 49:

\[
\Delta E^{1/2} = E^{1/2}(\kappa\neq 0) - E^{1/2}(\kappa=0)
= \frac{RT}{F} \ln \left( \frac{1 + K/\sqrt{\pi\kappa}}{1 + K} \right)
\]
See eqs 25 and 28 for the dkss solution,

$$\exp\left(\frac{2zF\Delta E^{1/2}}{kT}\right) = \frac{1}{1 + K} + \frac{K}{(1 + K)^{\sqrt{2\pi K}}} \frac{1}{\sqrt{t}} \quad (49)$$

Note that eq 49 is also applicable to characterize the coupled chemical complexation in liquid membrane systems of two polarized interfaces because, according to our equations, the kinetic dependence of the half-wave potential is the same for both kinds of membrane system (eqs 25 and 38).

In Figure 6 we have plotted the $I/E$ curves corresponding to the facilitated ion transfer in systems of one (Figure 6a) and two (Figure 6b) polarized interfaces, obtained by using the dkss solution (solid lines, eqs 22 and 32) and that of total equilibrium (dashed-dotted lines, eqs 29 and 43). Dotted lines show the $I/E$ curves corresponding to the simple ion transfer process (eqs 27 and 40). $\Delta \phi^{c} = 0 \text{ mV}, \Delta \phi^{s} = -100 \text{ mV}, c_{i}^{c} = 1 \text{ mM}, c_{i}^{s} = 50 \text{ mM}, D_{i}^{c} = D_{i}^{s} = 10^{-5} \text{ cm}^{2} \text{ s}^{-1}, D_{M}^{c} = 10^{-8} \text{ cm}^{2} \text{ s}^{-1}, \chi = 500, t = 1 \text{ s, } A = 0.081 \text{ cm}^{2}, T = 298.15 \text{ K.}$

(Figure 6b) polarized interfaces, obtained by using the dkss approximation (solid lines, eqs 22 and 32) and the te one (dashed-dotted lines, eqs 29 and 43). In dotted lines, the $I/E$ curves corresponding to a simple ion transfer in both kinds of membrane system obtained for eqs 27 and 40, respectively, have been plotted.

Under the experimental conditions selected, the curves corresponding to the two polarized interfaces system are shifted to more positive potentials than that of the single polarized interface one. However, as we have pointed out in previous papers, by varying the concentration of the supporting electrolyte of the membrane in the two polarized interfaces system, displacements of the $I/E$ curve can be attained. This fact constitutes an additional advantage of the system of two polarized interfaces besides the well-known ones—such as the double wide of the potential window, or the huge separation between the signals of cations and anions with similar standard ion transfer potential—because it confers the signal of this system the possibility of being located in the potential window available. Moreover, as the equilibrium constant increases and the kinetic effects gain importance, the te curves start to differentiate from the dkss ones in both kinds of membrane system, and it is necessary to take into account the kinetic effects.

4. CONCLUSIONS

- Explicit analytical equations for the normal pulse voltammetric ($I/E$) and chronoamperometric ($I/t$) responses of the ion transfer facilitated by complexation in the organic phase (TOC mechanism) in liquid membrane systems of one and two polarized interfaces have been obtained by considering the kinetic effects of the chemical complexation. These expressions could be useful for modeling artificial and biological membranes.

- The dependence of the ion transfer process on the kinetic parameters of the complexation reaction have been analyzed in-depth for both kinds of membrane system, and the results have been compared with those obtained by using the widely used approximation of total equilibrium conditions, for which the results only depend on thermodynamic parameters.

- It is shown that, under certain conditions, the transfer by interfacial complexation mechanism (TIC), which involves a single ion transfer-ion complexation step can be obtained as a limiting case of the two steps comprising TOC or EC mechanism. The conditions under which the treatment of total equilibrium (TIC) is not acceptable and the importance of taking into account the kinetic effects of the complexation reaction have been shown.

- Simple methods are proposed for the quantitative determination of the equilibrium and kinetic constants of the complexation reaction in the membrane, based on the evolution with time of the shift of the half-wave potential of the facilitated ion transfer.

APPENDIX A. ANALYTICAL SOLUTION CORRESPONDING TO THE PROBLEM OF MASS TRANSPORT OF THE ION TRANSFER FACILITATED BY ORGANIC COMPLEXATION IN SYSTEMS OF ONE POLARIZED INTERFACE

Kinetic Steady State (kss)

In the following we consider that $X^{i}$ is only initially present in the sample aqueous solution because it is very hydrophilic (like the metal ions involved in facilitated ion transfer processes), and $L$ is only initially present in the membrane because it is very hydrophobic, and that all the phases, $W_{1}, W_{2}$, and $M$, contain sufficient concentrations of electrolytes such that the different ohmic drops can be neglected. It is worth clarifying that, although Scheme 1 shows a finite thickness...
for the membrane \(d\), we consider this thickness to be large enough in comparison with that of the diffusion layers of \(X^r\) and \(XL^r\) in this phase to consider semi-infinite diffusion into the membrane.

When the new variables \(\zeta(x,t)\) and \(\varphi(x,t)\) (given by eqs 10 and 11) were taken into account and \(D^M = D^M_{XL^r} = D^M_{XL^r}\) was assumed, the diffusive-kinetic equations and boundary value problem given by eqs 1–6 are transformed into the following

\[
\begin{align*}
\frac{\partial c^{W_i}(x,t)}{\partial t} &= D_i^{W_i} \frac{\partial^2 c^{W_i}(x,t)}{\partial x^2} \\
\frac{\partial \zeta(x,t)}{\partial t} &= D^M \frac{\partial^2 \zeta(x,t)}{\partial x^2} \\
\frac{\partial \varphi(x,t)}{\partial t} &= D^M \frac{\partial^2 \varphi(x,t)}{\partial x^2} - \kappa \varphi(x,t)
\end{align*}
\]

(A1.1)

\(t = 0, x \leq 0\)

\(t \geq 0, x \to -\infty\)

\(t = 0, x \geq 0\)

\(t \geq 0, x \to \infty\)

\(x = 0, t > 0\)

\(D_i^{W_i} \left( \frac{\partial c^{W_i}(x,t)}{\partial x} \right)_{x=0} = D^M \left( \frac{\partial \zeta(x,t)}{\partial x} \right)_{x=0} = \frac{\partial \varphi(x,t)}{\partial x} = 0\)

(A1.4)

\(\zeta(0,t) + \varphi(0,t) = (1 + K) c^{W_i}_{XL^r}(0,t)\)

(A1.6)

with \(\eta\) and \(\kappa\) being given by eqs 7 and eq 16.

If we consider the kinetic steady state approximation, which implies that the perturbation of the chemical equilibrium is independent of time, i.e., \(\partial \varphi(x,t)/\partial t = 0\), we can write

\[\varphi(x) = \varphi(0) \exp \left[ -\frac{K}{D^M x} \right]\]

(A1.7)

and thus,

\[\frac{d \varphi(x)}{dx} = \frac{\varphi(\infty) - \varphi(0)}{\delta_r} = \frac{-\varphi(0)}{\delta_r}\]

(A1.8)

with \(\delta_r\) being the reaction layer thickness, given in eq 17.

When eq A1.7 is taken into account, the diffusive-kinetic equations and boundary value problem eqs A1.1–A1.6 become

\[
\begin{align*}
\frac{\partial c^{W_i}(x,t)}{\partial t} &= D_i^{W_i} \frac{\partial^2 c^{W_i}(x,t)}{\partial x^2} \\
\frac{\partial \zeta(x,t)}{\partial t} &= D^M \frac{\partial^2 \zeta(x,t)}{\partial x^2} \\
\frac{\partial \varphi(x,t)}{\partial t} &= D^M \frac{\partial^2 \varphi(x,t)}{\partial x^2} - \kappa \varphi(x,t)
\end{align*}
\]

(A1.9)

\(t = 0, x \leq 0\)

\(t \geq 0, x \to -\infty\)

\(t = 0, x \geq 0\)

\(t \geq 0, x \to \infty\)

\(x = 0, t > 0\)

\[D_i^{W_i} \left( \frac{\partial c^{W_i}(x,t)}{\partial x} \right)_{x=0} = D^M \left( \frac{\partial \zeta(x,t)}{\partial x} \right)_{x=0} = \frac{\partial \varphi(x,t)}{\partial x} = 0\]

(A1.12)

\[
\begin{align*}
\zeta(0,t) &= (1 + K) c^{W_i}_{XL^r}(0,t) \\
\varphi(0,t) &= \varphi(\infty) - \varphi(0) = -\varphi(0) \exp \left[ -\frac{K}{D^M x} \right]
\end{align*}
\]

(A1.13)

Using a procedure based on Koutecký's dimensionless parameter method, the expression given by eqs 13–20 is deduced for the current.

**Diffusive-Kinetic Steady State (dkss)**

In this approximation the variable \(\varphi\) retains the form given by eq A1.7 for the kinetic steady state approximation \(\partial \varphi(x,t)/\partial t = 0\) and a purely diffusive behavior for the species \(c^{W_i}\) and the pseudo-species \(\zeta\) is assumed; i.e., it is assumed that the solution of equations for \(c^{W_i}\) and \(\zeta\) have the same form as that for species that would only suffer planar diffusion

\[
\zeta(x,t) = \zeta(0,t) \frac{x}{2 \sqrt{D^M t}}
\]

(A2.1)

\[
\varphi(0,t) = \varphi(\infty) - \varphi(0) = \frac{-\varphi(0)}{\delta_r} \frac{x}{2 \sqrt{D^M t}}
\]

(A2.2)

By inserting eqs A2.1 and A2.2 into eqs A1.12 and A1.13, we can derive the expressions for the interfacial concentrations and concentration profiles for the species involved in the facilitated ion transfer, given by eq A2.3 and 21

\[
\begin{align*}
c^{W_i}_{XL^r}(0,t) &= c^{W_i}_{XL^r}(0,0) + \frac{1 + K \delta_\eta}{1 + K \delta_\eta + \gamma \delta(1 + K)} \\
c^{M}_{XL^r}(0,t) &= c^{M}_{XL^r}(0,0) + \frac{\delta(1 + K \delta_\eta)}{1 + K \delta_\eta + \gamma \delta(1 + K)} \\
c^{M}_{XL^r}(0,t) &= c^{M}_{XL^r}(0,0) + \frac{K \delta(1 - \delta_\eta)}{1 + K \delta_\eta + \gamma \delta(1 + K)}
\end{align*}
\]

(A2.3)
and substituting eq 21a into eq 9, we deduce the expression for the current for the facilitated ion transfer given by eq 22.

**Total Equilibrium Conditions (te)**

If we assume that the complex formation and dissociation are at equilibrium even when current is flowing, i.e.

\[ K = \frac{c_{X1}^M(x,t)}{c_{X1}^*(x,t)} \quad \forall \ x, t > 0 \]  \hspace{1cm} (A3.1)

and we define the following variable

\[ c_{X1}^M(x,t) = c_{X1}^*(x,t) + c_{X1}^M(x,t) \]  \hspace{1cm} (A3.2)

Equations 1–5 corresponding to mass transport for the facilitated ion transfer at systems of a single polarized interface are transformed into

\[
\begin{align*}
\frac{\partial c_{X1}^W(x,t)}{\partial t} & = D_c \frac{\partial^2 c_{X1}^W(x,t)}{\partial x^2} \\
\frac{\partial c_{X1}^M(x,t)}{\partial t} & = D_c \frac{\partial^2 c_{X1}^M(x,t)}{\partial x^2}
\end{align*}
\]

\hspace{1cm} (A3.3)

\[
\begin{align*}
t = 0, \ s \leq 0 \quad & \quad c_{X1}^W(x,0) = c_{X1}^W(-\infty,t) = c_{X1}^* \\
t \geq 0, \ s = 0 \quad & \quad c_{X1}^M(x,0) = c_{X1}^M(\infty,t) = 0
\end{align*}
\]

\hspace{1cm} (A3.4)

\[
\begin{align*}
t = 0, \ s \geq 0 \quad & \quad c_{X1}^W(x,0) = c_{X1}^*(0) \quad c_{X1}^M(x,0) = c_{X1}^M(0)
\end{align*}
\]

\hspace{1cm} (A3.5)

\[
\begin{align*}
\frac{c_{X1}^W(x,t)}{c_{X1}^*} & = 1 - \frac{c_{X1}^W(0)}{c_{X1}^*} \left( \frac{x}{2 \sqrt{D_{X1}^W t}} \right) - \frac{c_{X1}^M(0)}{c_{X1}^*} \left( \frac{x}{2 \sqrt{D_{X1}^M t}} \right) \\
\frac{c_{X1}^M(x,t)}{c_{X1}^*} & = \frac{c_{X1}^M(0)}{c_{X1}^*} \left( \frac{x}{2 \sqrt{D_{X1}^M t}} \right)
\end{align*}
\]

\hspace{1cm} (A3.6)

Assuming that the interfacial concentrations for \( c_{X1}^W \) and \( c_{X1}^M \) are independent of time, the solution of eqs A3.3 is immediate

\[
\begin{align*}
c_{X1}^W(x,t) & = c_{X1}^*(0) + c_{X1}^W(0) - c_{X1}^*(0) \\
& \times \text{erfc} \left( \frac{x}{2 \sqrt{D_{X1}^W t}} \right) \\
c_{X1}^M(x,t) & = c_{X1}^M(0) \text{erfc} \left( \frac{x}{2 \sqrt{D_{X1}^M t}} \right)
\end{align*}
\]

\hspace{1cm} (A3.7)

\hspace{1cm} (A3.8)

and by substituting eqs A3.7 and A3.8 in the condition of the equality of fluxes (eq A3.6), taking into account eqs A3.1, A3.2, and 6, the following concentration profiles and interfacial concentrations for the species involved in the facilitated ion transfer are obtained

\[
\begin{align*}
\frac{c_{X1}^W(x,t)}{c_{X1}^*} & = 1 - \frac{\gamma e^0(1 + K)}{1 + \gamma e^0(1 + K)} \text{erfc} \left( \frac{x}{2 \sqrt{D_{X1}^W t}} \right) \\
\frac{c_{X1}^M(x,t)}{c_{X1}^*} & = \frac{e^0}{1 + \gamma e^0(1 + K)} \text{erfc} \left( \frac{x}{2 \sqrt{D_{X1}^M t}} \right)
\end{align*}
\]

\hspace{1cm} (A3.9)

As can be seen, these expressions coincide with those obtained by using the dks approximation when \( \delta_t \to 0 \).

The expression for the current corresponding to the facilitated ion transfer under these conditions is obtained by substituting eqs A3.7 and A3.10a into eq 9 and is given by eq 29.

**APPENDIX B. ANALYTICAL SOLUTION CORRESPONDING TO THE PROBLEM OF MASS TRANSPORT OF THE ION TRANSFER FACILITATED BY ORGANIC COMPLEXATION IN SYSTEMS OF TWO POLARIZED INTERFACES**

For simplicity, for the development of the analytical solution to this problem we will consider conditions of diffusive-kinetic steady state.

When a constant potential, \( E \), is applied to study the facilitated ion transfer given by Scheme 2 in a system of two polarized liquid–liquid interfaces, this applied potential is
distributed unequally between the outer and inner interfaces. Thus, the differential equations system and boundary value problem describing mass transport at phases $W_1$, $M$, and the outer interface are identical to those given by eqs 1–7 on changing $E$ for $E_{out}$ and $\eta$ for $\eta_{inn}$. The differential equations system and boundary value problem describing mass transport at phase $W_2$ and inner interface are given by

$$\frac{\partial c_{W_2}^{R_2}}{\partial t} = D_{W_2}^{R_2} \frac{\partial^2 c_{W_2}^{R_2}}{\partial x^2}$$ \hspace{1cm} (B.1)

$$c_{M}^{R_2}(x,t) = c_{R_2}^{*} \hspace{1cm} (B.2)$$

t $= 0$, $x > d$

t $\geq 0$, $x \rightarrow \infty$

t $> 0$, $x = d$

$$c_{M}^{R_2}(d,t) = e^{\eta_{inn}} c_{R_2}^{W_2}(d,t)$$ \hspace{1cm} (B.4)

with

$$\eta_{inn} = \frac{E}{RT} (E_{inn} - \Delta_{M}^{W_2} \Phi_{R_2}^{0'})$$ \hspace{1cm} (B.5)

where $E_{inn}$ is the potential difference at the inner interface (membrane/solution interface).

In this case, besides the considerations made in Appendix A, we assume that neither the diffusion layer nor the reaction layer corresponding to the facilitated ion transfer of $X^+$ overlap with the diffusion layer of $R^+$ and, moreover, that the concentration of $R^+$ is high enough to be considered constant in all the membrane, as this ion is part of the supporting electrolyte of the membrane and the transport is controlled by the diffusion of the ion $X^+$.

According to our model, the problem corresponding to the facilitated ion transfer of the ion $X^+$ at the outer interface is identical to that we have already solved for the same ion transfer at the system of a single polarized interface. Therefore, the expression for the current at this interface is equivalent to that given by eq 22 by changing $\eta$ for $\eta_{out}$ and $E$ for $E_{out}$.

With respect to the problem of mass transport of the ion $R^+$ at the inner interface (eqs B.1–B.5), its solution is relatively easy, because it consists of a simple reversible ion transfer, in such a way that by taking into account the condition of the equality of current fluxes at the outer and inner interfaces ($I(outer interface) = I(inner interface)$), it is easy to deduce the following expression for the potential difference at the inner interface, $E_{inn}$ (eq B.4)

$$E_{inn} = \Delta_{M}^{W_2} \Phi_{R_2}^{0'} + \frac{RT}{F} \ln \left( \frac{D_{W_2}^{R_2} c_{R_2}^{*}}{D_{W_2}^{R_2} c_{R_2}^{*}} \right) \hspace{1cm} (B.6)$$

and by subtracting the expressions for the potential differences of the outer and inner interfaces (eqs 24 and B.6, respectively), we can deduce the relations between the potential applied and the measured current in this kind of membrane system, given by eqs 33 and 37.

The interfacial concentrations of the ions involved in the facilitated ion transfer as a function of the membrane potential for the system of two polarized interfaces are given by

$$c_{X^+}^{W_2}(0,t) = 1 - h(\eta)$$

$$c_{X^+}^{M}(0,t) = \frac{h(\eta)}{(1 + K)\gamma} \left( 1 + \frac{K\delta_r}{\delta} \right)$$

$$c_{X^+}^{M}(0,t) = \frac{K h(\eta)}{(1 + K)\gamma} \left( 1 - \frac{\delta_r}{\delta} \right)$$

$$c_{R^2}^{W_2}(d,t) = \frac{D_{W_2}^{R_2} h(\eta)}{D_{W_2}^{R_2} h(\eta)}$$ \hspace{1cm} (B.7)

with $h(\eta)$ given by eq 33.

If we assume that the complex formation and dissociation are at equilibrium even when current is flowing (total equilibrium conditions), the expression for the concentration profiles and the interfacial concentrations of the species involved in the facilitated ion transfer take the following form

$$\frac{c_{X^+}^{W_2}(x,t)}{c_{X^+}^{*}} = 1 - h'(\eta) \operatorname{erfc} \left( \frac{x}{2\sqrt{D_{W_2}^{W_2} t}} \right)$$

$$\frac{c_{X^+}^{M}(x,t)}{c_{X^+}^{*}} = h'(\eta) \left( \frac{x}{(1 + K)\gamma} \operatorname{erfc} \left( \frac{x}{2\sqrt{D_{M}^{W_2} t}} \right) \right)$$

$$\frac{c_{X^+}^{M}(x,t)}{c_{X^+}^{*}} = \frac{K h'(\eta)}{(1 + K)\gamma} \left( \frac{x}{2\sqrt{D_{M}^{W_2} t}} \right)$$

$$\frac{c_{R^2}^{W_2}(x,t)}{c_{R^2}^{*}} = \sqrt{\frac{D_{W_2}^{R_2}}{D_{W_2}^{R_2} h'(\eta)}} \operatorname{erfc} \left( \frac{x - d}{2\sqrt{D_{W_2}^{W_2} t}} \right)$$ \hspace{1cm} (B.8)
and

\[
\frac{c_{W}(0,t)}{c_{X}} = 1 - h'(\eta) \\
\frac{c_{M}(0,t)}{c_{X}} = \frac{h'(\eta)}{(1 + K)\gamma} \\
\frac{c_{XL}(0,t)}{c_{X}} = \frac{K\eta'(\eta)}{(1 + K)\gamma} \\
\frac{c_{R}(d,t)}{c_{X}} = \sqrt{\frac{D_{W}W_{c}h'(\eta)}{D_{R}}} 
\]

with \( h'(\eta) \) being given by eq44.

**AUTHOR INFORMATION**

**Corresponding Author**

*Tel: +34 968 367524. Fax: +34 968 364148. E-mail: amolina@um.es.*

**ACKNOWLEDGMENTS**

We greatly appreciate the financial support provided by the Dirección General de Investigación Científica y Técnica (Project Numbers CTQ2011-27049/BQU and CTQ2009-13023/BQU), and the Fundación SENECA (Project Number 08813/PI/08). Also, E.T. thanks the Ministerio de Ciencia e Innovación for the grant received. In addition, we thank referees 1 and 2 for their valuable comments.

**REFERENCES**