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Theoretical model of ion transfer-electron transfer coupled reactions at the thick-film modified electrodes

Franco Martín Zanotto, Ricardo Ariel Fernández , Sergio Alberto Dassie*

Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), CONICET, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, X5000 HUA Ciudad Universitaria, Córdoba, Argentina

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ABSTRACT

The theory of cyclic voltammetry of ion transfer-electron transfer coupled reactions in a thick organic film modified electrode is developed. The model system consists of a planar electrode completely covered by an organic phase, which in turn is in contact with an aqueous phase, each containing a supporting electrolyte. It is shown that the coupling between the ion transfer-electron transfer processes at both, solid|liquid and liquid|liquid interfaces, has a marked effect on the shape of the voltammogram. The model allows the analysis of the system in different experimental conditions. In particular, the results for different concentration ratios of the redox probe and supporting electrolytes are presented. The variation of the potential of the solid|liquid and the liquid|liquid interfaces reflects changes in concentration of the species involved. This variation is presented as a descriptor of the shape of the voltammograms. The theoretical results are contrasted with experimental behaviour reported in literature.

1. Introduction

The transfer of charged species through a liquid|liquid interface has been studied extensively in recent years [1–9]. These heterogeneous charge transfer can be divided into ion transfer and electron transfer, while ion transfer can be either simple or assisted by a ligand dissolved in the system [5,10,11]

In general, the classic four-electrode system with a single polarized interface [12] has been widely used to study simple ion-transfer reactions, ion-transfer reactions assisted by a ligand or ionophore, and electron transfer-ion transfer (ET-IT) reactions between a hydrophilic and a hydrophobic redox couple [5,9]. In the last years, three-phase electrodes [13–22] and thin film-modified electrodes [20,23-32] emerged as a simple but powerful experimental tool for studying coupled ET-IT reactions [33–37]. In the case of three-phase electrodes, the electrode surface is not covered completely by the organic phase so an interface exists between the three adjacent phases. The electrode reaction starts at the three phase junction and then propagates towards the centre of the organic phase volume, which has no supporting electrolyte. On the other hand, in the case of thin organic-film-modified electrodes, the electrode surface is completely covered by the organic phase. For this reason, the organic phase must contain supporting electrolyte to ensure sufficiently high conductivity to perform electrochemical measurements. The working principle of both electrochemical configurations is based on the electroneutrality of each phase [37,38].

In the course of the electrochemical experiment the electrode reaction of the redox compound (neutral redox-active probe) is coupled with simultaneous charge compensating ion transfer reaction at the other side of the liquid phase. In voltammetric experiments, both the electron and ion transfer processes are recorded together [37]. Theoretical models have provided valuable contributions to thermodynamics, kinetics and ion transfer mechanism across the three-phase electrodes [39–44] and thin film-modified electrodes [45–48].

Recently, a new strategy based on a thick organic film modified electrode was developed and experimentally verified by Niu and coworkers [49]. This strategy is based on an electrode completely covered by an organic phase film of suitable thickness which ensures that the charged product of the redox reaction is kept away from the liquid|liquid interface. This experimental condition can be satisfied at high scan rates in cyclic voltammetry (i.e. greater than 0.1 V s^{-1}), where the electrochemical experiment time is very short. In this experimental condition, the electroneutrality of the organic phase is maintained by the simultaneous injection of ions through the liquid|liquid interface. The authors present a thermodynamic treatment of the coupled electron-ion transfer reactions that allows them to obtain the relationship between the potential of the global process and the concentration of the analyte ion [49].

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* Corresponding author.
E-mail address: sdassie@fcq.unc.edu.ar (S. Dassie).

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Herein, a model of thick organic film modified electrode that allows analysing the system in different experimental conditions is developed. In particular, the results for different concentration ratios of the redox probe and transferring ion are presented. The variation of the potential of the solid|liquid (S|L) and the liquid|liquid (L|L) interfaces reflects changes in concentration of the species involved. This variation is presented as a descriptor of the shape of the voltammograms. The theoretical results are contrasted with experimental behaviours reported in literature.

2. Theory

The coupled ET-IT process is considered in this model. This follows from the electroneutrality condition in each phase. Electron transfer (ET) is limited to a one electron process, between a solid electrode and an electrically neutral reduced species dissolved in the organic phase. Ion transfer (IT) can occur for any monovalent ion from the electrolytes involved in the electrolytic organic and aqueous phases. Thus, the possible equilibria can be written as:

$$\mathrm{Red}_{(o)} \rightleftharpoons \mathrm{Ox}^{+}_{(o)} + \mathrm{e}^{-} \tag{R.1}$$

$$\mathrm{Anion}^{-}_{(w)} \rightleftharpoons \mathrm{Anion}^{-}_{(o)} \tag{R.2}$$

$$\mathrm{Cation}^{+}_{(o)} \rightleftharpoons \mathrm{Cation}^{+}_{(w)} \tag{R.3}$$

The following assumptions for the calculation of the current-potential response are made:

1. The interfaces between the aqueous and the organic phase and between the electrode and organic phase are stationary and planar.
2. Both phases remain quiescent and contain enough inert electrolyte so that mass transport takes place only by diffusion. The potential drop due to solution resistance is neglected.
3. The presence of H^+ and HO^- ions from water autoprotolysis is neglected.
4. The partition of the redox species to the aqueous phase, either electrically charged (Ox^+) or neutral (Red), is neglected. Transfer of the other ions through the interface is reversible and diffusion controlled, dependent on the Nernst equation.
5. The redox reaction taking place at the electrode surface is reversible and diffusion controlled, dependent on the Nernst equation.
6. The thickness of the organic phase is large enough to avoid overlapping between the diffusion fronts of the species generated or consumed on the solid|liquid interface and the liquid|liquid interface.
7. Both interfaces present the same surface area, large enough for edge effects to be negligible. Therefore the semi-infinite linear condition is assumed.
8. Since the electron transfer and ion transfer processes are coupled, the current at both interfaces must be equal.
9. The activity coefficients for all species are assumed to be equal to one.
10. Neither double-layer effects, adsorption nor ion-pair formation are considered in the model.
11. The applied potential is distributed between the S|L interface and the L|L interface at any time. The potential difference on the former defines the concentration ratio of the redox species and on the latter the ion concentration ratios.

The model considers a solid electrode completely covered by a film of organic phase of thickness L containing a redox couple (Red and Ox^+) and an explicit supporting electrolyte, in contact with an aqueous phase containing completely dissociated electrolytes, as shown in Fig. 1 (the model is still valid if the organic and aqueous solutions are interchanged [32], or even for other solvent pairs, such as ionic liquid|aqueous solution and ionic liquid|organic solution interfaces[50]). Similar approaches combining coupled ion transfer-ion transfer were previously described for supported liquid membranes [51–54]

In this work, the following completely dissociated electrolytes are considered: MX, KA and NZ initially dissolved in the aqueous phase (NZ is the explicit supporting electrolyte), and OY, which is the organic explicit supporting electrolyte. In order to obtain the concentrations as a function of distance to the electrode and time, Fick's laws of diffusion were solved using explicit finite difference [55–60].

The determination of the initial equilibrium state involves the calculation of the distribution potential ($\Delta_o^w\phi_{eq}$) for this system, which in turn depends on the standard transfer potential of each ion i ($\Delta_o^w\phi_i^\circ$) and the initial concentration of ions in each phase, obtained by solving Eq. (8) from Ref. [38]:

$$\sum_i z_i \frac{c_i^w + rc_i^o}{1 + r(\theta_{eq}\theta_i)^{z_i}} = 0 \tag{1}$$

where z_i is the charge of ion i (in this model $z_i = +1$ or $z_i = -1$), $\theta_{eq} = \exp(\frac{F}{RT}\Delta_o^w\phi_{eq})$ and $\theta_i = \exp(-\frac{F}{RT}\Delta_o^w\phi_i^\circ)$. c_i^w and c_i^o are the equilibrium concentrations of the ion i in the aqueous and organic phases respectively, r is the volume ratio between the organic and aqueous phase. More details on the solution of this equation are presented in the appendix.

The initial applied potential difference ($t = 0$) was set in all cases as the sum of the potential difference at each interface: $E(0) = \Delta_o^s\phi(0) + [-\Delta_o^w\phi(0)]$. The Galvani potential difference between the electrode and the organic phase ($\Delta_o^s\phi(0)$) is calculated from the initial

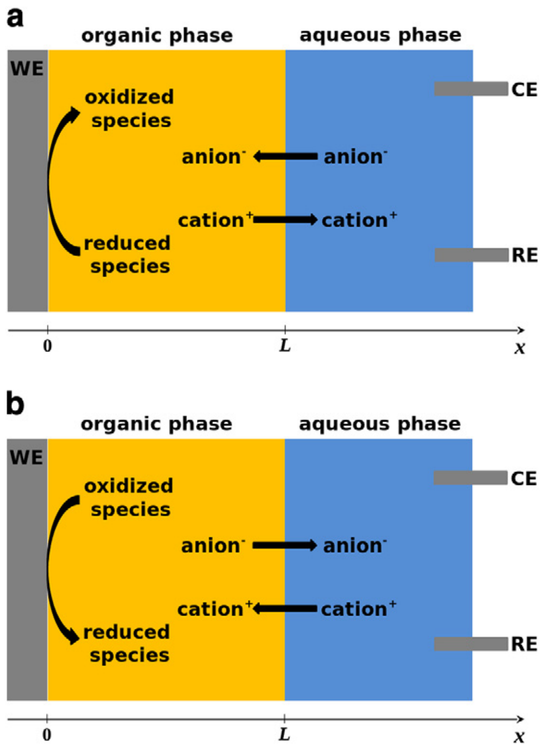

Fig. 1. Scheme of the electrochemical cell considered in the model showing coupled electron transfer and ion transfer processes resulting in positive current (top) and negative current (bottom). WE: working electrode. CE: counter electrode. RE: reference electrode.