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Theory of irreversible electrode reactions coupled to ion transfer across the liquid/liquid interface

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Abstract Kinetically controlled electro-oxidation of a redox probe dissolved in the organic solvent, which is interposed between an electrode surface and an aqueous solution as a thin layer, is analyzed theoretically. It is demonstrated that the electrode reaction rate constant can be measured by the variation of scan rate in linear scan voltammetry both in the absence and in the superfluity of the supporting electrolyte dissolved in the film.

Keywords Kinetics of electrode reaction · Liquid/liquid interface · Coupled electron and ion transfers

Introduction

A three-phase electrode consists of three different phases that are in intimate contact and contribute to the mechanism of electrochemical reaction [1, 2]. Some of the numerous examples of this type of electrodes are solid micro-particles of insoluble inorganic and organic electroactive compounds immobilized on the graphite and immersed into an aqueous electrolyte solution [3–6]. Another example is a solid electrode with attached droplets of water-immiscible electroactive liquid [7–9]. Standard Gibbs energies of transfer of ions across the interface of two

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immiscible liquids can be measured by the three-phase electrodes [10–15] and thin organic film modified electrodes [16–18]. These electrodes couple the electron transfer at the solid electrode/organic solvent interface with the ion transfer at the organic solvent/water interface [19–21]. Both charge transfers can be kinetically controlled [22–24]. The rate of the overall process depends on the slower step, which can be either the electron or the ion transfer. A general kinetic equation was developed and used for the measurement of the rate constants of transfer of various ions across the liquid/liquid interface [25–27]. In this short communication, an influence of experimental conditions on the linear scan voltammetric response of the oxidation of redox probe confined to the film on the working electrode surface is analyzed theoretically.

The model

It is assumed that a stationary, planar, graphite electrode is covered by a thin film of organic solvent, which is immiscible with water. In the film, an electroactive, neutral compound *Red* and a supporting electrolyte *CX* are dissolved. The electrode is immersed into an aqueous solution of the electrolyte *MX*. On anodic polarization of the electrode, the compound *Red* is oxidized while anions of the supporting electrolyte are transferred across the water/organic solvent interface:

$$Red_{(org)} + X^-_{(w)} \leftrightarrow Ox^+_{(org)} + X^-_{(org)} + e^- \qquad (1)$$
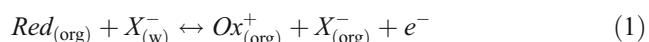
It is further assumed that there are no fluxes of *Red*, Ox^+, C^+ and M^+ across the liquid/liquid interface.

The potential difference between the working electrode and the reference electrode in water is a sum of the potential drop at the graphite/organic solvent interface and
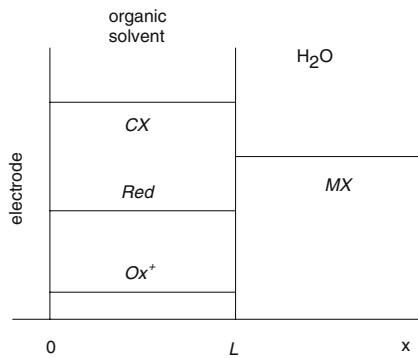
Scheme 1 An electrode covered by the film of organic solvent and immersed into an aqueous electrolyte solution

the total potential drop across the organic solvent/water interface [11]:

$$E = E_{C/org} + \Delta_w^{org}\phi \tag{2}$$

$$E_{C/org} = E_{Red/Ox^+}^0 + \frac{RT}{F}\ln\frac{[Ox^+]_{x=0}}{[Red]_{x=0}} \tag{3}$$

$$\Delta_w^{org}\phi = \Delta_w^{org}\phi_{X^-}^0 + \frac{RT}{F}\ln\frac{\left[X_{(org)}^-\right]_{x=L}}{\left[X_{(w)}^-\right]_{x=L}} \tag{4}$$

where L is the film thickness (see Scheme 1).

If the oxidation of the compound Red is kinetically controlled, the current depends on the potential drop at the graphite/organic solvent interface:

$$I = -FS\,k_s\,\exp\,(-\alpha\varphi_1)\big([Ox^+]_{x=0} - [Red]_{x=0}\exp\,(\varphi_1)\big) \tag{5}$$

$$\varphi_1 = \frac{F}{RT}\left(E_{C/org} - E_{Red/Ox^+}^0\right) \tag{6}$$

where I is a current, k_s is a standard rate constant of electrode reaction, α is a transfer coefficient, and S is the electrode surface area. Using Eqs. 2 and 4, the current can be calculated as a function of the electrode potential E [25, 26]:

$$E_{C/org} - E_{Red/Ox^+}^0 = E - E_{Red/Ox^+}^0 - \Delta_w^{org}\phi_{X^-}^0 \tag{7}$$

$$+ \frac{RT}{F}\ln\frac{\left[X_{(w)}^-\right]_{x=L}}{\left[X_{(org)}^-\right]_{x=L}}$$

$$I = -FS\,k_s\,\exp\,(-\alpha\varphi)\left[X_{(org)}^-\right]_{x=L}^{\alpha}\left[X_{(w)}^-\right]_{x=L}^{-\alpha}$$
$$\left([Ox^+]_{x=0} - [Red]_{x=0}\left[X_{(w)}^-\right]_{x=L}\left[X_{(org)}^-\right]_{x=L}^{-1}\exp(\varphi)\right) \tag{8}$$

$$\varphi = \frac{F}{RT}\left(E - E^0\right) \tag{9}$$

$$E^0 = E_{Red/Ox^+}^0 + \Delta_w^{org}\phi_{X^-}^0 \tag{10}$$

In this paper, Eq. 8 is solved for reversible and totally irreversible electrode reactions. Calculations are simplified by assuming that the transport of Red, Ox^+, and X^- in the film can be neglected:

$$[Red] = [Red]^* - \int\frac{I}{FSL}\,d\tau \tag{11}$$

$$[Ox^+] = \int\frac{I}{FSL}\,d\tau \tag{12}$$

$$\left[X_{(org)}^-\right] = \left[X_{(org)}^-\right]^* + \int\frac{I}{FSL}\,d\tau \tag{13}$$

where $[Red]^*$ and $\left[X_{(org)}^-\right]^*$ are initial concentrations of Red and X^- in the film. Furthermore, it is assumed that the initial concentration of anion X^- in water is much higher than the initial concentration of Red in the film, so that the diffusion of X^- in water can be also neglected:

$$\left[X_{(w)}^-\right] = \left[X_{(w)}^-\right]^* \tag{14}$$

Under these conditions, the voltammetric response of fast and reversible electrode reaction is calculated by solving a dimensionless recursive formula:

$$\Phi_k^2 + B\Phi_k + C = 0 \tag{15}$$

$$B = c_{X,org}^*\left(1 + \exp\left(\varphi_{f,k}^*\right)\right) + 2\sum_{j=1}^{k-1}\Phi_j \tag{16}$$

$$C = -c_{X,org}^*\exp\,(\varphi_{f,k}^*) + c_{X,org}^*\left(1 + \exp\left(\varphi_{f,k}^*\right)\right)\sum_{j=1}^{k-1}\Phi_j \tag{17}$$
$$+ \left(\sum_{j=1}^{k-1}\Phi_j\right)^2$$
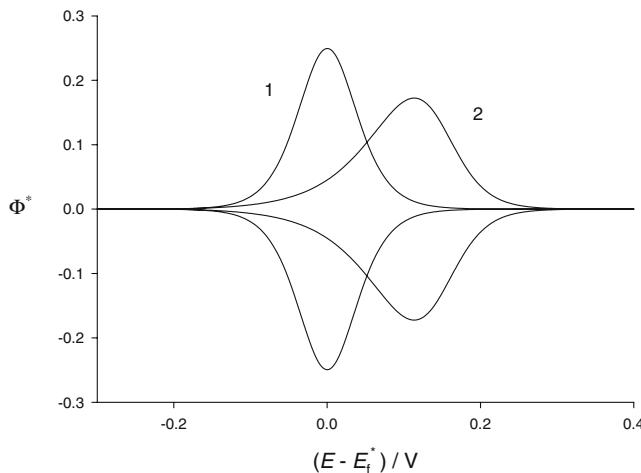
Fig. 1 Cyclic voltammetry of reversible electrode reaction (Eq. (1)) under the film conditions; $\Phi^* = I/FSL[Red]^*(F/RT)v$ and $c_{X,org}^* = 100$ (1) and 0.01 (2)
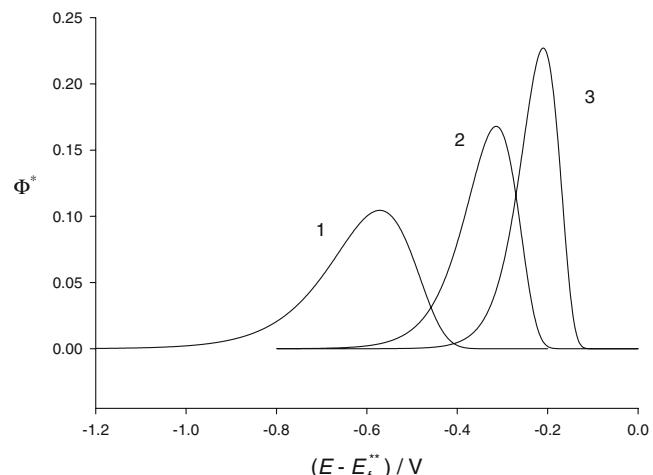

Fig. 3 Linear scan voltammetry of totally irreversible electrode reaction (1); $\beta = 0.3$ (1), 0.5 (2), and 0.7 (3)
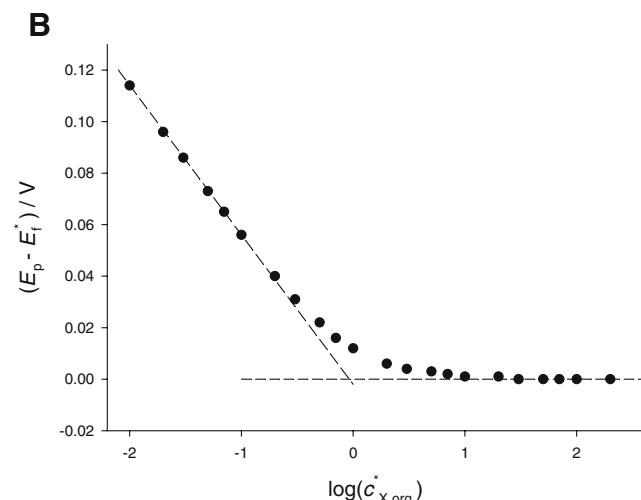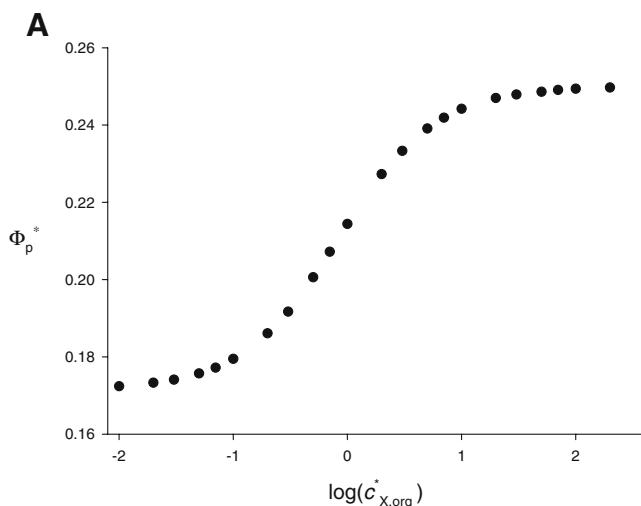

Fig. 2 Dependence of dimensionless peak currents (**a**) and peak potentials (**b**) of cyclic voltammograms of reversible reaction (1) on the logarithm of dimensionless initial concentration of anion X^- in the film
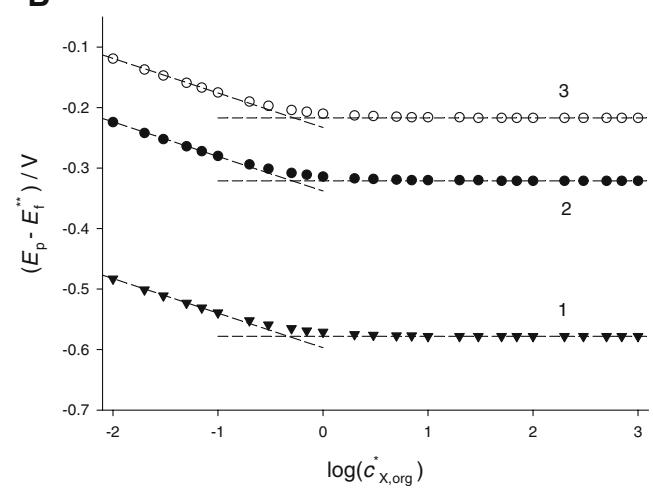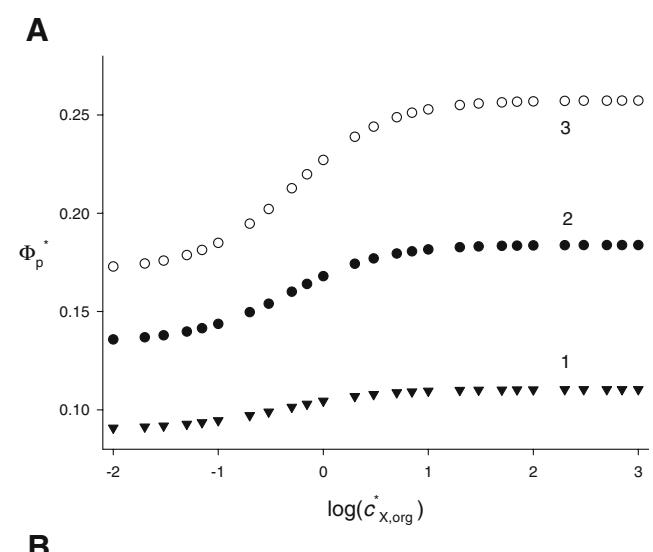

Fig. 4 Dependence of dimensionless peak currents (**a**) and peak potentials (**b**) of linear scan voltammograms of totally irreversible reaction (1) on the logarithm of dimensionless initial concentration of anion X^- in the film. $\beta = 0.3$ (1), 0.5 (2), and 0.7 (3)

$$\varphi_{\mathrm{f,k}}^* = \frac{F}{RT}\left(E_{\mathrm{k}} - E_{\mathrm{f}}^*\right) \tag{18}$$

$$E_{\mathrm{f}}^* = E^0 - \frac{RT}{F}\ln\left[X_{(\mathrm{w})}^-\right]^* + \frac{RT}{F}\ln\left[X_{(\mathrm{org})}^-\right]^*, \tag{19}$$

where $\Phi_k = I_k d/FSL[Red]^*$ is a dimensionless current, $c_{X,\mathrm{org}}^* = \left[X_{(\mathrm{org})}^-\right]^*/.[Red]^*$ is a dimensionless initial concentration of anion X^- in the film, d is a time increment and $k = 1, 2, 3 \ldots$ is the number of time increments in a certain moment t. In cyclic voltammetry the time increment depends on the scan rate: $d = \Delta E/v$, where $\Delta E = 0.0001$ V is a constant potential increment.

If the electrode reaction is totally irreversible, the following recursive formula applies:

$$\Phi_k\left(c_{X,\mathrm{org}}^* + \sum_{j=1}^{k}\Phi_j\right)^{1-\alpha}$$
$$= \left(c_{X,\mathrm{org}}^*\right)^{1-\alpha}\exp\left((1-\alpha)\varphi_{\mathrm{f,k}}^{**}\right)\left(1 - \sum_{j=1}^{k}\Phi_j\right) \tag{20}$$

$$\varphi_{f,k}^{**} = \frac{F}{RT}\left(E_{\mathrm{k}} - E_{f}^{**}\right) \tag{21}$$

$$E_{f}^{**} = E^0 - \frac{RT}{F}\ln\left[X_{(\mathrm{w})}^-\right]^* + \frac{RT}{F}\ln\left[X_{(\mathrm{org})}^-\right]^*$$
$$- \frac{RT}{(1-\alpha)F}\ln\frac{k_s \Delta E}{Lv} \tag{22}$$

Equation 20 is solved by the numerical search. The crossing of the curve $x(a+x)^\beta$ with the straight line $b-x$ was calculated for $x > 0$ by the method of trial and error. In a previous paper [25], the additional simplification $\left[X_{(\mathrm{org})}^-\right] = \left[X_{(\mathrm{org})}^-\right]^*$ was used instead of Eq. 13.

Results and discussion

Cyclic voltammograms of fast and reversible electrode reaction depend on the initial concentration of anion X^- in the film of organic solvent, as can be seen in Figs. 1 and 2. If $log\left(c_{X,\mathrm{org}}^*\right) > 1.3$, the peak potential is equal to the formal potential E_{f}^*, but if $log\left(c_{X,\mathrm{org}}^*\right) < -0.5$, the peak potential is a linear function of the logarithm of $c_{X,\mathrm{org}}^*$ (see Fig. 2b):

$$E_p - E_f^* = -(2.3 \times RT/F)\log\left(c_{X,\mathrm{org}}^*\right) - 0.002\ V \tag{23}$$

This is explained by the influence of the transfer of anion X^- from water into organic solvent on the total potential difference across the organic solvent/water interface. If $c_{X,\mathrm{org}}^* \gg 1$, this influence is negligible and the peak potential is defined by Eq. 19. However, if $c_{X,\mathrm{org}}^* \ll 1$, the concentration of anion X^- in the film is defined mainly by the concentration of cation Ox^+ and the peak potential depends on the initial concentration of the compound Red:

$$E_p = E^0 + \frac{RT}{F}\ln\ [Red]^* - \frac{RT}{F}\ln\ \left[X_{(\mathrm{w})}^-\right]^*$$
$$- \frac{RT}{F}\ln\ (1.081) \tag{24}$$

The dimensionless peak current $\Phi_p^* = I_p/FSL[Red]^*(F/RT)v$ changes from 0.1716, for $c_{X,\mathrm{org}}^* < 0.01$, to 0.25 for $c_{X,\mathrm{org}}^* > 100$ (see Fig. 2a).

The responses of totally irreversible electrode reaction depend on the transfer coefficient of oxidation $\beta = 1 - \alpha$, which is shown in Fig. 3. Figure 4 shows the dependence of dimensionless peak current Φ_p^* and peak potential on the logarithm of dimensionless initial concentration of anion X^- in the film. If $c_{X,\mathrm{org}}^* > 30$, the dimensionless peak current and the peak potential are defined by the equations:

$$\Phi_p^* = \beta \exp\left(\frac{\exp\left(\beta\varphi_{\mathrm{f,st}}^{**}\right)}{\beta(F/RT)\Delta E} - 1\right) \tag{25}$$

$$E_p = E_f^{**} + \frac{RT}{\beta F}\ln\frac{\beta F \Delta E}{RT} \tag{26}$$

where $\varphi_{f,st}^{**} = (F/RT)\left(E_{\mathrm{st}} - E_f^{**}\right)$ and E_{st} is a starting potential.

If $log\left(c_{X,\mathrm{org}}^*\right) < -1$, the peak potential depends linearly on the logarithm of $c_{X,\mathrm{org}}^*$, with the slope $-2.3 \times RT/F$. Under this condition, the peak potential is defined by the equation:

$$E_p = E^0 + \frac{RT}{F}\ln\ [Red]^* - \frac{RT}{F}\ln\ \left[X_{(\mathrm{w})}^-\right]^*$$
$$- \frac{RT}{\beta F}\ln\frac{k_s \Delta E}{Lv} + \frac{RT}{\beta F}\ln\frac{\beta F \Delta E}{RT}$$
$$- \frac{RT}{F}\ln\ (1.9381) \tag{27}$$

The standard rate constant of electrode reaction can be measured by the variation of scan rate if the reaction appears reversible at the lowest scan rate and totally irreversible at the highest scan rate. If $c_{X,\mathrm{org}}^* > 30$, the peak potential of reversible reaction is defined by Eq. 19, and the peak potential of totally irreversible reaction is defined by Eqs. 26 and 22. The intersection of the extrapolations of these two relationships is defined by the equation:

$$k_s = \beta FLv_0/RT, \tag{28}$$

where v_0 is the scan rate corresponding to the intersection. If $c^*_{X,org} < 0.1$, the peak potentials of reversible and totally irreversible electrode reactions are defined by Eqs. 24 and 27, respectively. The standard rate constant is defined by the relation:

$$k_s = \beta F L v_0 (0.5578)^\beta \big/ RT \qquad (29)$$

This shows that either the absence or the superfluity of anion X^- in the film is the necessary condition for the measurement of the rate constant, which is an addition to what was concluded in the previous paper [25]. However, the kinetic measurement should not be performed if $0.1 < c^*_{X,org} < 1$. Under this condition, the peak potentials are complex functions of initial concentrations of both anion X^- and compound Red in the film.

Equations 19, 22 and 26, as well as Eqs. 24 and 27, show that the slow electron transfer of the probe does not influence the determination of the energy of transfer of anion X^- if the rate constant k_s and the coefficient β are independent of the nature of the anion.

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