POSSIBLE USE OF CHRONOPOTENTIOMETRY AT THE INTERFACE BETWEEN TWO IMMISCIBLE LIQUID PHASES TO THE STUDIES OF HOMOGENEOUS CHEMICAL REACTIONS

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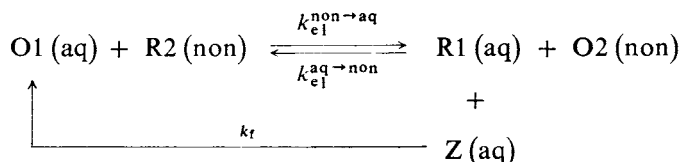
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The theoretical potential–time dependence corresponding to the electron transfer reaction proceeding at the interface between two immiscible liquid phases with the redox pairs O1/R1 in the aqueous (aq) phase and O2/R2 in the non-aqueous (non) phase, that is complicated by the reaction R1(aq) + Z(aq) $\xrightarrow{k_f}$ O1(aq) in the aqueous phase, has been derived under the galvanostatic conditions. Moreover, a method for the determination of the formal rate constant k_f for the given homogeneous chemical reaction is proposed.

The fundamental principles and ideas and, first of all, the general relations that describe the charge transfer through the interface of two immiscible electrolyte solutions followed by several electroanalytical methods (polarography with the electrolyte dropping electrode, cyclic voltammetry, chronopotentiometry) together with the demands made on the measurement procedure, equipment, and application possibilities are summarized in previous papers[1,2]. Papers[3-11] deal with the detail studies of the electron transfer across the interface mentioned above.

The aim of this paper is to demonstrate the possibility of the chronopotentiometric detection of the electron transfer across the interface between two immiscible liquid phases complicated by a homogeneous chemical reaction for a quantitative study of this reaction.

RESULTS AND DISCUSSION

Let us assume that the following electron transfer reaction

$$\text{O1 (aq)} + \text{R2 (non)} \underset{k_{el}^{aq \to non}}{\overset{k_{el}^{non \to aq}}{\rightleftarrows}} \text{R1 (aq)} + \text{O2 (non)}$$

$$+$$

$$\text{Z (aq)}$$

with k_f connecting Z(aq) back to O1(aq)

proceeding at the interface between the aqueous (aq) and non-aqueous (non) phases

of the two-phase system with the redox pair O1/R1, present only in the aqueous phase, and with the redox pair O2/R2 in the non-aqueous phase, is complicated by the inserted (catalytic) homogeneous reaction R1 (aq) + Z (aq) → O1 (aq) in the aqueous phase that proceeds with the formal rate constant k_f. The potential-dependent rate constants for the electron transfer from the aqueous phase into the non-aqueous one and *vice versa*, denoted by the symbols $k_{el}^{aq \rightarrow non}$ and $k_{el}^{non \rightarrow aq}$, respectively, are interconnected by the Eq. (*1*) (ref.[8]):

$$k_{el}^{non \rightarrow aq} = k_{el}^{aq \rightarrow non} \exp \left[nF(E - E^0)/RT \right] , \qquad (1)$$

where n is the number of electrons transferred between the pairs O1/R1 and O2/R2, E is the abbreviated symbol for the Galvani potential difference $\Delta_{non}^{aq}\varphi = \varphi \, (aq) - \varphi \, (non)$ between the two phases under study related to the constant potential differences involved in the reference electrodes[12]. The formal potential for the electron transfer reaction, E^0, is given by the formal redox potentials $E_{O1/R1} \, (aq)$ and $E_{O2/R2} \, (non)$ of the pairs O1/R1 and O2/R2 in the respective phases as defined by the Eq. (*2*) (ref.[8]):

$$E^0 = E_{O2/R2} \, (non) - E_{O1/R1} \, (aq) . \qquad (2)$$

Further, let us suppose that an indifferent base electrolyte is present in excess in each phase of the two-phase system so that the migration contributions to the material fluxes of the reactants may be neglected. The adsorption of all reactants at the interface is neglected, too.

The transport of the species O1 and R1 in the aqueous phase and the species O2 and R2 in the non-aqueous phase to or from the interface is assumed to be controlled by the linear and semi-infinite diffusion along the x-axis which is taken to be perpendicular to the interface $(x = 0)$ and oriented towards the bulk of the non-aqueous phase. Let the component Z, present only in the aqueous phase, be in such an excess that its volume concentration, $c_Z(x, t)$, is for any value of $x \leq 0$ and time $t \geq 0$ practically equal to the respective initial analytical volume concentration, c_Z^0, so that the diffusion of the species Z in the aqueous phase may be reasonably neglected.

If a constant current of the density $i_0 > 0$ (in this study, the current and hence also the current density are regarded as positive when a positive charge is transferred from the aqueous phase into the non-aqueous one) is forced in the direction perpendicular to the interface of the given two-phase system, then — with respect to the previous papers[3,5,8,10,15] — the problem stated above may be mathematically formulated by the following system of partial differential equations (using the simplified assumption that $D_{O1} = D_{R1} = D_1$ and $D_{O2} = D_{R2} = D_2$) with the respective initial and boundary conditions:

$$\partial c_{O1}(x, t)/\partial t = D_1 \, \partial^2 c_{O1}(x, t)/\partial x^2 + k_f c_Z^0 c_{R1}(x, t) \qquad (3)$$

$$\partial c_{R1}(x, t)/\partial t = D_1 \, \partial^2 c_{R1}(x, t)/\partial x^2 - k_f c_Z^0 c_{R1}(x, t) \tag{4}$$

$$\partial c_{O2}(x, t)/\partial t = D_2 \, \partial^2 c_{O2}(x, t)/\partial x^2 \tag{5}$$

$$\partial c_{R2}(x, t)/\partial t = D_2 \, \partial^2 c_{R2}(x, t)/\partial x^2 \tag{6}$$

$$t = 0, \quad x > 0: \quad c_{O2}(x, 0) = c_{O2}^0, \quad c_{R2}(x, 0) = c_{R2}^0 \tag{7}$$

$$t = 0, \quad x < 0: \quad c_{O1}(x, 0) = c_{O1}^0 \ll c_{R2}^0, \quad c_{R1}(x, 0) = 0 \tag{8}$$

$$t > 0, \quad x = 0: \quad D_1[\partial c_{R1}(x, t)/\partial x]_{x=0} = D_2[\partial c_{R2}(x, t)/\partial x]_{x=0} =$$
$$= -D_1[\partial c_{O1}(x, t)/\partial x]_{x=0} = -D_2[\partial c_{O2}(x, t)/\partial x]_{x=0} =$$
$$= i_0/nF, \tag{9}$$

$$-i_0/nF = k_{el}^{aq \to non} c_{R1}(0, t) \, c_{O2}(0, t) -$$
$$- k_{el}^{non \to aq} c_{O1}(0, t) \, c_{R2}(0, t) \tag{10}$$

$$t > 0, \quad x \to +\infty: \quad c_{O2}(x, t) = c_{O2}^0, \quad c_{R2}(x, t) = c_{R2}^0 \tag{11}$$

$$t > 0, \quad x \to -\infty: \quad c_{O1}(x, t) = c_{O1}^0 \ll c_{R2}^0, \quad c_{R1}(x, t) = 0. \tag{12}$$

If we denote

$$m_i = 2i_0/nFD_i^{1/2}\pi^{1/2}, \quad (i = 1, 2) \tag{13}$$

then, with regard to the results of the papers[13-15], the concentrations $c_j(0, t)$ (j = O1, R1, O2, R2) at the interface, that represent the solution of the above system of partial differential equations $(3)-(6)$ for $x = 0$, can be explicitly expressed by the Eqs $(14)-(17)$:

$$c_{O1}(0, t) = c_{O1}^0 - \frac{m_1 \pi^{1/2} \, \text{erf} \, [(k_f c_Z^0 t)^{1/2}]}{2(k_f c_Z^0)^{1/2}} \tag{14}$$

$$c_{R1}(0, t) = \frac{m_1 \pi^{1/2} \, \text{erf} \, [(k_f c_Z^0 t)^{1/2}]}{2(k_f c_Z^0)^{1/2}} \tag{15}$$

$$c_{O2}(0, t) = c_{O2}^0 + m_2 t^{1/2} \tag{16}$$

$$c_{R2}(0, t) = c_{R2}^0 - m_2 t^{1/2}. \tag{17}$$

Using (1) and $(14)-(17)$ and substituting for $k_{el}^{aq \to non}$ and $c_j(0, t)$ in the boundary condition (10) we get — after a simple arithmetics — the required potential–time dependence in the form

$$\left\{c_{O1}^0 - \frac{m_1 \pi^{1/2} \operatorname{erf}\left[(k_f c_Z^0 t)^{1/2}\right]}{2(k_f c_Z^0)^{1/2}}\right\} (c_{R2}^0 - m_2 t^{1/2}) =$$

$$= \frac{i_0}{nFk_{el}^{non \to aq}} + \frac{m_1 \pi^{1/2} \operatorname{erf}\left[(k_f c_Z^0 t)^{1/2}\right]}{2(k_f c_Z^0)^{1/2}} (c_{O2}^0 + m_2 t^{1/2}).$$

$$. \exp\left[-nF(E - E^0)/RT\right]. \tag{18}$$

In order to calculate the rate constant k_f according to the procedure given below the transition time, corresponding to the potential–time curve given by Eq. (18), must be determined by the equation

$$c_{O1}(0, \tau_c) = c_{O1}^0 - \frac{m_1 \pi^{1/2} \operatorname{erf}\left[(k_f c_Z^0 \tau_c)^{1/2}\right]}{2(k_f c_Z^0)^{1/2}} = 0 \tag{19}*$$

and not by the equation $c_{R2}(0, \tau_d') = c_{R2}^0 - m_2 \tau_d'^{1/2} = 0$. This requirement will be evidently fulfilled by the inequality

$$\tau_c^{1/2} \leqq \tau_d'^{1/2} = c_{R2}^0/m_2, \tag{20}$$

which can be easily shown — using the identity $c_{O1}^0 = m_1 \pi^{1/2} \operatorname{erf}\left[(k_f c_Z^0 \tau_c)^{1/2}\right]/2$. $.(k_f c_Z^0)^{1/2}$ following from Eq. (19) and from the fact that the $\operatorname{erf}(y) = (2/\pi^{1/2})$. $.\int_0^y \exp(-\xi^2)\,d\xi$ is a monotonously increasing function — to be equivalent with the following inequality

$$c_{O1}^0 \leqq \frac{m_1 \pi^{1/2} \operatorname{erf}\left[(k_f c_Z^0)^{1/2} c_{R2}^0/m_2\right]}{2(k_f c_Z^0)^{1/2}}. \tag{21}$$

In the absence of the component Z in the two-phase system under study but otherwise under the same initial and boundary conditions given by the Eqs $(7)-(12)$

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* Considering that $\operatorname{erf}(y) = (2/\pi^{1/2})\int_0^y \exp(-\xi^2)\,d\xi < 1$ for every $y \geqq 0$, from equation (19) we obtain the condition $\operatorname{erf}\left[(k_f c_Z^0 \tau_c)^{1/2}\right] = [2(k_f c_Z^0)^{1/2} c_{O1}^0/m_1 \pi^{1/2}] < 1$ from which it follows that the transition time τ_c defined by equation (19) exists only if $c_{O1}^0 < [m_1 \pi^{1/2}/2(k_f c_Z^0)^{1/2}]$. However, this requirement made on the concentration c_{O1}^0 is obviously fulfilled by the inequality (21) because

$$c_{O1}^0 \leqq \frac{m_1 \pi^{1/2} \operatorname{erf}\left[(k_f c_Z^0)^{1/2} c_{R2}^0/m_2\right]}{2(k_f c_Z^0)^{1/2}} < \frac{m_1 \pi^{1/2}}{2(k_f c_Z^0)^{1/2}}.$$

the potential-time dependence — with regard to the results of the previous paper[10] — can be directly rewritten in the form

$$\frac{(c_{O1}^0 - m_1 t^{1/2})(c_{R2}^0 - m_2 t^{1/2})}{m_1 t^{1/2}(c_{O2}^0 + m_2 t^{1/2})} = \frac{i_0}{nFk_{el}^{non \to aq} m_1 t^{1/2}(c_{O2}^0 + m_2 t^{1/2})} +$$

$$+ \exp\left[-nF(E - E^0)/RT\right] \qquad (22)$$

for which the transition time is generally given by $\tau_d^{1/2} = \min\{c_{O1}^0/m_1, \ c_{R2}^0/m_2\}$. Assuming that

$$c_{O1}^0/m_1 \leqq c_{R2}^0/m_2 \qquad (23)$$

(in most cases this assumption will be obviously fulfilled by the condition $c_{O1}^0 \ll c_{R2}^0$ mentioned above), the transition time τ_d will be given by the relation

$$\tau_d^{1/2} = c_{O1}^0/m_1 . \qquad (24)$$

Combining (19) and (24) we get Eq. (25) that is formally identical with the relation derived in the paper by Delahay, Mattax, and Berzins[15]:

$$(\tau_c/\tau_d)^{1/2} = 2\gamma/\pi^{1/2} \operatorname{erf}(\gamma), \qquad (25)$$

where

$$\gamma = (k_f c_Z^0 \tau_c)^{1/2} . \qquad (26)$$

The Eqs (25) and (26) can be easily used for the determination of the rate constant k_f from the experimentally determined transition times τ_c and τ_d. The value of the function on the right hand side of Eq. (25) is known and the argument γ can be determined from the tabulated values of the function $F(\gamma) = 2\gamma/\pi^{1/2} \operatorname{erf}(\gamma)$. Then, the value of the rate constant k_f can be evaluated from the respective values of γ, c_Z^0, and τ_c, using the Eq. (26).

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