THE POSSIBILITY OF USING CHRONOPOTENTIOMETRY IN STUDIES OF IONIC ASSOCIATION OR COMPLEXATION AT THE INTERFACE BETWEEN TWO IMMISCIBLE ELECTROLYTE SOLUTIONS

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Theoretical potential–time curves were derived in the form $\Delta_\alpha^\beta \varphi = f(t)$ ($\Delta_\alpha^\beta \varphi$ denotes Galvani potential difference between phases β and α), expressing mathematically a reversible transfer of a cation across the interface between two immiscible electrolyte solutions under galvanostatic conditions. The formation of ion pairs or complexes was taken into account, and the influence of certain components of two-phase systems on the form of potential–time curves is discussed.

Ion transfer across the interface between two immiscible electrolyte solutions has been investigated, e.g., by steady-state polarization measurements[1], chronopotentiometry[2-5], polarography with an electrolyte dropping electrode[6,7], and cyclic voltammetry[8,9]. The transfer of electrons, representing another possibility of the charge transfer across the liquid/liquid interface, was also detected by cyclic voltammetry in water–nitrobenzene system[10-12].

In contradistinction to cyclic voltammetry[5,13], chronopotentiometric studies of complexation or ionic association at the interface between two immiscible electrolyte solutions have not been described in the literature. The present paper deals with the derivation of potential–time curves for model two-phase systems where the reversible transfer of cations across the interface between two immiscible liquids is complicated by the formation of ion-pairs or complexes. Further, the influence of some two-phase system components on the potential–time curves is discussed.

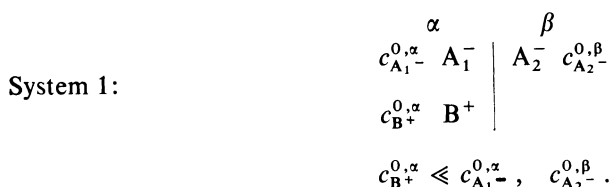## RESULTS AND DISCUSSION

Basic Assumptions

We assume that both phases of the two-phase systems 1−4 described in the text below contain sufficiently concentrated base electrolytes. Their ions fulfil certain conditions[13,14] expressed mainly by the changes of the standard Gibbs energies of transfer of the ions, $\Delta G_{tr,i}^{0,\alpha \rightarrow \beta}$, from phase α into phase β. The presence of the base electrolytes in both phases in conjunction with the assumptions that the transfer of B^+ or B^{n+} ions across the interface of systems 1−4 is reversible and the rate

of attainment of all chemical equilibria is "infinitely" high ensure that the transport of the cations B^+ or B^{n+} or other particles (ion-pairs, complex cations, ligands, anions) from the bulk phase to the interface or *vice versa* can be considered as diffusion--controlled process.

For the sake of simplification, we assume that the molar activity coefficients of all species in both phases are equal to 1.

Transfer of Cation B^+ *across the Interface between Two Immiscible Electrolyte Solutions Influenced by Ion-Pair Formation*

The considered two-phase system can be written schematically as follows (the base electrolytes are omitted for simplicity although the ions indicated can be, of course, also base electrolyte ions)

$$\begin{array}{cc|cc} & \alpha & \beta & \\ c_{A_1^-}^{0,\alpha} & A_1^- & A_2^- & c_{A_2^-}^{0,\beta} \\ & & & \\ c_{B^+}^{0,\alpha} & B^+ & & \\ \end{array}$$

System 1:

$$c_{B^+}^{0,\alpha} \ll c_{A_1^-}^{0,\alpha} , \quad c_{A_2^-}^{0,\beta} .$$

Here, the ions B^+ and A_1^- are present only in the phase α and the anion A_2^- only in the phase β, further, the volume concentrations of the anions, $c_{A_1^-}^{0,\alpha}$ and $c_{A_2^-}^{0,\beta}$, in the respective phases are much higher than the initial concentration of the cation B^+, $c_{B^+}^{0,\alpha}$, in the phase α.

Let us assume that the cation B^+ forms an ion-pair $B^+A_1^-$ in the α phase and $B^+A_2^-$ in the β phase (after its transfer) with the association constants $K_{BA_1}^{\alpha}$, $K_{BA_2}^{\beta}$, corresponding to the equilibria $B^+(\alpha) + A_1^-(\alpha) \rightleftharpoons B^+A_1^-(\alpha)$, $B^+(\beta) + A_2^-(\beta) \rightleftharpoons B^+A_2^-$. (β).

The transport of the particles B^+, $B^+A_1^-$ in the α phase and B^+, $B^+A_2^-$ in the β phase to the interface or *vice versa* is assumed to be controlled by linear diffusion along the x axis perpendicular to the interface and oriented into the bulk of the β phase.

We denote the analytical concentration of B^+ at a point $x \leq 0$ and time $t \geq 0$ as $c_1^{\alpha}(x, t)$ and similarly for $x \geq 0$ (in the β phase) $c_2^{\beta}(x, t)$. Then

$$x \leq 0: \quad c_1^{\alpha}(x, t) = c_{B^+}^{\alpha}(x, t) + c_{BA_1}^{\alpha}(x, t) , \tag{1}$$

$$x \geq 0: \quad c_2^{\beta}(x, t) = c_{B^+}^{\beta}(x, t) + c_{BA_2}^{\beta}(x, t) , \tag{2}$$

where $c_{B^+}^{\beta}(x, t)$, $c_{BA_1}^{\alpha}(x, t)$, $c_{B^+}^{\alpha}(x, t)$, and $c_{BA_2}^{\beta}(x, t)$ are the concentrations of the cation B^+ and the ion-pairs in the respective phases.

The association constants are defined as

$$x \leqq 0: \; K_{BA_1}^{\alpha} = c_{BA_1}^{\alpha}(x, t) / c_{B^+}^{\alpha}(x, t) \, c_{A_1^-}^{\alpha}(x, t) \,, \tag{3}$$

$$x \geqq 0: \; K_{BA_2}^{\beta} = c_{BA_2}^{\beta}(x, t) / c_{B^+}^{\beta}(x, t) \, c_{A_2^-}^{\beta}(x, t) \,. \tag{4}$$

Further $c_{A_1^-}^{\alpha}(x, t) \approx c_{A_1^-}^{0,\alpha}$, $c_{A_2^-}^{\beta}(x, t) \approx c_{A_2^-}^{0,\beta}$, since $c_{B^+}^{0,\alpha} \ll c_{A_1^-}^{0,\alpha}$, $c_{A_2^-}^{0,\beta}$. By simple rearrangements of Eqs $(1)-(4)$ it follows that

$$x \leqq 0: \; c_{B^+}^{\alpha}(x, t) = c_1^{\alpha}(x, t) / (1 + K_{BA_1}^{\alpha} c_{A_1^-}^{0,\alpha}) \,, \tag{5}$$

$$x \geqq 0: \; c_{B^+}^{\beta}(x, t) = c_2^{\beta}(x, t) / (1 + K_{BA_2}^{\beta} c_{A_2^-}^{0,\beta}) \,. \tag{6}$$

If a constant imposed current density $i_0 > 0$ passes in the direction normal to the interface of System 1 (the current is positive if the positive charge is transferred from the phase α into the phase β), then the problem described above may be mathematically formulated by the following system of partial differential equations expressing Fick's second law

$$\frac{\partial c_1^{\alpha}(x, t)}{\partial t} = \bar{D}_{B^+, BA_1}^{\alpha} \frac{\partial^2 c_1^{\alpha}(x, t)}{\partial x^2} \,, \quad \frac{\partial c_2^{\beta}(x, t)}{\partial t} = \bar{D}_{B^+, BA_2}^{\beta} \frac{\partial^2 c_2^{\beta}(x, t)}{\partial x^2} \tag{7}$$

with the initial and boundary conditions

$$t = 0, \; x < 0: \; c_1^{\alpha}(x, 0) = c_{B^+}^{0,\alpha} \,, \quad t = 0, \; x > 0: \; c_2^{\beta}(x, 0) = 0 \,, \tag{8}$$

$$t > 0, \; x = 0: \; \Delta_{\alpha}^{\beta}\varphi(t) = \Delta_{\alpha}^{\beta}\varphi_{B^+}^0 + (RT/F) \ln \left[(1 + K_{BA_2}^{\beta} c_{A_2^-}^{0,\beta}) / (1 + K_{BA_1}^{\alpha} c_{A_1^-}^{0,\alpha}) \right] +$$

$$+ (RT/F) \ln \left[c_1^{\alpha}(0, t) / c_2^{\beta}(0, t) \right] \,, \tag{9}*$$

$$\bar{D}_{B^+, BA_1}^{\alpha} \left[\frac{\partial c_1^{\alpha}(x, t)}{\partial x} \right]_{x=0} = \bar{D}_{B^+, BA_2}^{\beta} \left[\frac{\partial c_2^{\beta}(x, t)}{\partial x} \right]_{x=0} = -\frac{i_0}{F} \,, \tag{10}$$

$$t > 0, \; x \rightarrow -\infty: \; c_1^{\alpha}(x, t) = c_{B^+}^{0,\alpha} \,, \quad t > 0, \; x \rightarrow \infty: \; c_2^{\beta}(x, t) = 0 \,, \tag{11}$$

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*   The boundary condition (9) can be derived by substituting Eqs (5) and (6) for the concentrations into the Nernst–Donnan equation for reversible transfer of cation B^+ across ideally polarizable interface[13] written in the form $\Delta_{\alpha}^{\beta}\varphi(t) = \Delta_{\alpha}^{\beta}\varphi_{B^+}^0 + (RT/F) \ln \left[c_{B^+}^{\alpha}(0, t) / c_{B^+}^{\beta}(0, t) \right]$.

where

$$\bar{D}^{\alpha}_{B^+,BA_1} = \left(D^{\alpha}_{B^+} + D^{\alpha}_{BA_1}K^{\alpha}_{BA_1}c^{0,\alpha}_{A_1^-}\right)\big/\left(1 + K^{\alpha}_{BA_1}c^{0,\alpha}_{A_1^-}\right),$$

$$\bar{D}^{\beta}_{B^+,BA_2} = \left(D^{\beta}_{B^+} + D^{\beta}_{BA_2}K^{\beta}_{BA_2}c^{0,\beta}_{A_2^-}\right)\big/\left(1 + K^{\beta}_{BA_2}c^{0,\beta}_{A_2^-}\right) \qquad (12)$$

are mean diffusion coefficients for "dependent" diffusion of species B^+ and $B^+A_1^-$ in phase α, or species B^+ and $B^+A_2^-$ in phase β. These species do not diffuse independently, since at any point x and time t in System 1, in accord with the above assumptions, the association equilibria must be obeyed (Eqs (12) for the mean diffusion coefficients are formally identical to the equation for the mean diffusion coefficient for "dependent" diffusion[15] of species B^+ and BX^+). The term $\Delta^{\beta}_{\alpha}\varphi = \varphi(\beta) - \varphi(\alpha)$ is the Galvani potential difference between phases β and α, and $\Delta^{\beta}_{\alpha}\varphi^0_{B^-}$ is the standard Galvani potential difference for the cation B^+ between phases β and α (ref.[13]).

The following equation can be derived for System 1 in an analogous way as in refs[16,17]

$$\Delta^{\beta}_{\alpha}\varphi(t) = \Delta^{\beta}_{\alpha}\varphi^0_{B^+} + \frac{RT}{F}\ln\frac{\left(D^{\beta}_{B^+} + D^{\beta}_{BA_2}K^{\beta}_{BA_2}c^{0,\beta}_{A_2^-}\right)\left(1 + K^{\beta}_{BA_2}c^{0,\beta}_{A_2^-}\right)}{\left(D^{\alpha}_{B^+} + D^{\alpha}_{BA_1}K^{\alpha}_{BA_1}c^{0,\alpha}_{A_1^-}\right)\left(1 + K^{\alpha}_{BA_1}c^{0,\alpha}_{A_1^-}\right)} +$$

$$+ \frac{RT}{F}\ln\left[(\tau^{1/2} - t^{1/2})/t^{1/2}\right] \qquad (13)$$

for the time interval $0 < t < \tau$, where the transition time τ (ref.[18]) is given in the form

$$\tau^{1/2} = \left(\pi^{1/2}Fc^{0,\alpha}_{B^+}/2i_0\right)\left[\left(D^{\alpha}_{B^+} + D^{\alpha}_{BA_1}K^{\alpha}_{BA_1}c^{0,\alpha}_{A_1^-}\right)\big/\left(1 + K^{\alpha}_{BA_1}c^{0,\alpha}_{A_1^-}\right)\right]^{1/2}. \qquad (14)$$

If $t = \tau/4$, Eq. (13) gives

$$\Delta^{\beta}_{\alpha}\varphi_{\tau/4} = \Delta^{\beta}_{\alpha}\varphi_{B^+} + \frac{RT}{2F}\ln\frac{\left(D^{\beta}_{B^+} + D^{\beta}_{BA_2}K^{\beta}_{BA_2}c^{0,\beta}_{A_2^-}\right)\left(1 + K^{\beta}_{BA_2}c^{0,\beta}_{A_2^-}\right)}{\left(D^{\alpha}_{B^+} + D^{\alpha}_{BA_1}K^{\alpha}_{BA_1}c^{0,\alpha}_{A_1^-}\right)\left(1 + K^{\alpha}_{AB_1}c^{0,\alpha}_{A_1^-}\right)}. \qquad (15)$$

It can be easily shown[19] that the polarographic half-wave potential for the same system on the electrolyte dropping electrode[6,7] is equal to the value of $\Delta^{\beta}_{\alpha}\varphi_{\tau/4}$ defined by Eq. (15).

By combining Eqs (13) and (15) we obtain the sought dependence for System 1 in the form

$$\Delta^{\beta}_{\alpha}\varphi(t) = \Delta^{\beta}_{\alpha}\varphi_{\tau/4} + \frac{RT}{F}\ln\left[(\tau^{1/2} - t^{1/2})/t^{1/2}\right] \qquad (16)$$

for $0 < t < \tau$.

As in ref.[17], we assume that the current is reversed at a time $t = \tau$, so that for $t > \tau$ the cations B^+ are transported from the phase β into α. In an analogous way as in the cited work[17], we obtain the equation

$$\Delta_\alpha^\beta \varphi(t') = \Delta_\alpha^\beta \varphi_{\tau/4} + \frac{RT}{F} \ln \frac{\tau^{1/2} - [(\tau + t')^{1/2} - 2t'^{1/2}]}{(\tau + t')^{1/2} - 2t'^{1/2}}, \qquad (17)$$

where $0 < t' < \tau' = \tau/3$ and $t' = t - \tau$.

Since the derivation of the equations for systems given in the text below is analogous, we restrict ourselves only to a schematic description of the problems; the resulting equations are given in Table I.
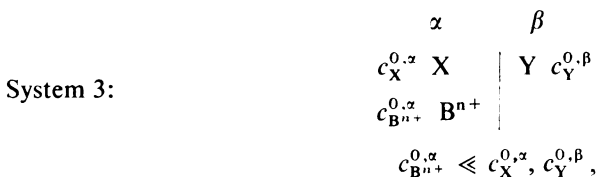
We assume that in System 2

$$\begin{array}{cc} \alpha & \beta \end{array}$$

System 2:
$$c_{B^+}^{0,\alpha} \ B^+ \ \Big| \ A^- \ c_{A^-}^{0,\beta}$$
$$c_{B^+}^{0,\alpha} \gg c_{A^-}^{0,\beta}$$

the transfer of the cation B^+ from phase α into β results in the formation of the ion-pair B^+A^- only in phase β; the association constant is denoted as K_{BA}^β. In contrast to System 1, the concentration of cation B^+ in phase α is substantially higher than that of anion A^- in phase β. With respect to the condition $c_{B^+}^{0,\alpha} \gg c_{A^-}^{0,\beta}$, changes of the concentration of the cation B^+ and hence its diffusion in phase α are neglected. Thus, we may set $c_{B^+}^\alpha(x, t) \approx c_{B^+}^{0,\alpha}$. It should be noted that the equations valid for this case (Table I) were derived on the assumption that the constant K_{BA}^β is so high that the flux of B^+ cations in phase β can be neglected against that of B^+A^- ion pairs.

Transfer of B^{n+} Cations across the Interface between Two Immiscible Electrolyte Solutions Influenced by Complex Formation

To simplify the notation, we disregard the charge of the ligands. Let us consider the following system:

$$\begin{array}{cc} \alpha & \beta \end{array}$$

System 3:
$$c_X^{0,\alpha} \ X \ \Big| \ Y \ c_Y^{0,\beta}$$
$$c_{B^{n+}}^{0,\alpha} \ B^{n+} \ \Big|$$
$$c_{B^{n+}}^{0,\alpha} \ll c_X^{0,\alpha}, c_Y^{0,\beta},$$

where the B^{n+} cations, originally present only in phase α, where they form complexes with the ligand X, $BX^{n+}, BX_2^{n+}, \ldots, BX_l^{n+}$, can be transferred into phase β to form complexes with the ligand Y, $BY^{n+}, BY_2^{n+}, \ldots, BY_m^{n+}$. The corresponding stability

TABLE I

Theoretical potential–time curves for systems 1—4

System 1

$$\tau^{1/2} = \left(\pi^{1/2} F c_B^{0,\alpha}/2i_0\right) \left[\left(D_{B^+}^{\alpha} + D_{BA_1}^{\alpha} K_{BA_1}^{\alpha} c_{A_1^-}^{0,\alpha}\right)/\left(1 + K_{BA_1}^{\alpha} c_{A_1^-}^{0,\alpha}\right)\right]^{1/2}$$

$0 < t < \tau$:

$$\Delta_\alpha^\beta \varphi(t) = \Delta_\alpha^\beta \varphi_{\tau/4} + \left(RT/F\right) \ln \left[\left(\tau^{1/2} - t^{1/2}\right)/t^{1/2}\right],$$

$$\Delta_\alpha^\beta \varphi_{\tau/4} = \Delta_\alpha^\beta \varphi_{B^+}^0 + \left(RT/2F\right) \ln \frac{\left(D_{B^+}^\beta + D_{BA_2}^\beta K_{BA_2}^\beta c_{A_2^-}^{0,\beta}\right)\left(1 + K_{BA_2}^\beta c_{A_2^-}^{0,\beta}\right)}{\left(D_{B^+}^\alpha + D_{BA_1}^\alpha K_{BA_1}^\alpha c_{A_1^-}^{0,\alpha}\right)\left(1 + K_{BA_1}^\alpha c_{A_1^-}^{0,\alpha}\right)}$$

$0 < t' < \tau' = \tau/3$:

$$\Delta_\alpha^\beta \varphi(t') = \Delta_\alpha^\beta \varphi_{\tau/4} + \left(RT/F\right) \ln \frac{\tau^{1/2} - \left[\left(\tau + t'\right)^{1/2} - 2t'^{1/2}\right]}{\left(\tau + t'\right)^{1/2} - 2t'^{1/2}}$$

System 2

$$\tau^{1/2} = \pi^{1/2} F \left(D_{A^-}^\beta\right)^{1/2} c_A^{0,\beta}/2i_0$$

$0 < t < \tau$:

$$\Delta_\alpha^\beta \varphi(t) = \Delta_\alpha^\beta \varphi_{\tau/4} + \left(RT/F\right) \ln \left[\left(\tau^{1/2} - t^{1/2}\right)/t^{1/2}\right],$$

$$\Delta_\alpha^\beta \varphi_{\tau/4} = \Delta_\alpha^\beta \varphi_{B^+}^0 + \left(RT/2F\right) \ln \left(D_{BA}^\beta/D_{A^-}^\beta\right) + \left(RT/F\right) \ln \left(K_{BA}^\beta c_{B^+}^{0,\alpha}\right)$$

$0 < t' < \tau' = \tau/3$:

$$\Delta_\alpha^\beta \varphi(t') = \Delta_\alpha^\beta \varphi_{\tau/4} + \left(RT/F\right) \ln \frac{\tau^{1/2} - \left[\left(\tau + t'\right)^{1/2} - 2t'^{1/2}\right]}{\left(\tau + t'\right)^{1/2} - 2t'^{1/2}}$$

System 3

$$\tau^{1/2} = \left(\pi^{1/2} n F c_{B^{n+}}^{0,\alpha}/2i_0\right) \left\{\left[D_{E^{n+}}^\alpha + \sum_{j=1}^l D_{BX_j}^\alpha K_{BX_j}^\alpha \left(c_X^{0,\alpha}\right)^j\right]/\left[1 + \sum_{j=1}^l K_{BX_j}^\alpha \left(c_X^{0,\alpha}\right)^j\right]\right\}^{1/2}$$

$0 < t < \tau$:

$$\Delta_\alpha^\beta \varphi(t) = \Delta_\alpha^\beta \varphi_{\tau/4} + \left(RT/nF\right) \ln \left[\left(\tau^{1/2} - t^{1/2}\right)/t^{1/2}\right],$$

$$\Delta_\alpha^\beta \varphi_{\tau/4} = \Delta_\alpha^\beta \varphi_{B^{n+}}^0 + \left(RT/2nF\right) \ln \frac{\left[D_{B^{n+}}^\beta + \sum_{j=1}^m D_{BY_j}^\beta K_{BY_j}^\beta \left(c_Y^{0,\beta}\right)^j\right]\left[1 + \sum_{j=1}^m K_{BY_j}^\beta \left(c_Y^{0,\beta}\right)^j\right]}{\left[D_{B^{n+}}^\alpha + \sum_{j=1}^l D_{BX_j}^\alpha K_{BX_j}^\alpha \left(c_X^{0,\alpha}\right)^j\right]\left[1 + \sum_{j=1}^l K_{BX_j}^\alpha \left(c_X^{0,\alpha}\right)^j\right]}$$

$0 < t' < \tau' = \tau/3$:

$$\Delta_\alpha^\beta \varphi(t') = \Delta_\alpha^\beta \varphi_{\tau/4} + \left(RT/nF\right) \ln \frac{\tau^{1/2} - \left[\left(\tau + t'\right)^{1/2} - 2t'^{1/2}\right]}{\left(\tau + t'\right)^{1/2} - 2t'^{1/2}}$$

TABLE I
(*Continued*)

System 4

$$\tau^{1/2} = \pi^{1/2} nFc_X^{0,\beta}(D_X^\beta)^{1/2}/2mi_0$$

$0 < t < \tau$:

$$\Delta_\alpha^\beta\varphi(t) = \Delta_\alpha^\beta\varphi_{B^{n+}}^0 + (RT/nF)\ln\left(K_{BX_m}^\beta c_{B^{n+}}^{0,\alpha}\right) +$$

$$+ (RT/nF)\ln \frac{2^{m-1}m^m i_0^{m-1}(D_{BX_m}^\beta)^{1/2}(\tau^{1/2} - t^{1/2})^m}{(\pi^{1/2})^{m-1} n^{m-1}F^{m-1}(D_X^\beta)^{m/2} t^{1/2}}$$

$t = \tau/4$:

$$\Delta_\alpha^\beta\varphi_{\tau/4} = \Delta_\alpha^\beta\varphi_{B^{n+}}^0 + (RT/2nF)\ln\left(D_{BX_m}^\beta/D_X^\beta\right) +$$

$$+ (RT/nF)\ln\left(K_{BX_m}^\beta c_{B^{n+}}^{0,\alpha}\right) + (RT/nF)\ln\left[(c_X^{0,\beta})^{m-1} m/2^{m-1}\right]$$

$0 < t' < \tau' = \tau/3$:

$$\Delta_\alpha^\beta\varphi(t') = \Delta_\alpha^\beta\varphi_{B^{n+}}^0 + (RT/nF)\ln\left(K_{BX_m}^\beta c_{B^{n+}}^{0,\alpha}\right) +$$

$$+ (RT/nF)\ln \frac{2^{m-1}m^m i_0^{m-1}(D_{BX_m}^\beta)^{1/2}\{\tau^{1/2} - [(\tau + t')^{1/2} - 2t'^{1/2}]\}^m}{(\pi^{1/2})^{m-1} n^{m-1}F^{m-1}(D_X^\beta)^{m/2}[(\tau + t')^{1/2} - 2t'^{1/2}]}$$

constants are denoted as $K_{BX_i}^\alpha$ $(i = 1, 2, ..., l)$ and $K_{BY_j}^\beta$ $(j = 1, 2, ..., m)$. We assume that $c_{B^{n+}}^{0,\alpha} \ll c_X^{0,\alpha}, c_Y^{0,\beta}$. System 3 can be considered as generalized System 1 for the case where the ion pair plays the role of a complex.

Finally, consider the system

$$\begin{array}{ccc} & \alpha & \beta \\ \text{System 4:} & c_{B^{n+}}^{0,\alpha}\ B^{n+} \mid X\ c_X^{0,\beta} \\ & c_{B^{n+}}^{0,\alpha} \gg c_X^{0,\beta} \end{array}$$

in which B^{n+} cations are transferred from phase α into phase β with the formation of a complex BX_m^{n+} with a stability constant $K_{BX_m}^\beta$ $(m, n \geq 1$, ligand X is present only in phase β and its concentration satisfies the condition $c_X^{0,\beta} \ll c_{B^{n+}}^{0,\alpha})$. This constant is assumed to be so high that the flux of the cations in phase β is negligible against that of the complex. Here, similarly to System 2, for analogous reasons $c_{B^{n+}}^\alpha(x, t) \approx c_{B^{n+}}^{0,\alpha}$.

The potential–time curves characterizing all the four systems under galvanostatic conditions are expressed by equations given in Table I.

If we set $K_{BX_i}^{\alpha} = K_{BY_j}^{\beta} = 0$ for each value of i and j (System 3, Table I), we obtain the equation of a reversible potential–time curve for a "simple" transfer (not complicated by association, complexation, or any other chemical reaction) of B^{n+} cations from phase α into phase β in the form

$$\Delta_{\alpha}^{\beta}\varphi(t) = \Delta_{\alpha}^{\beta}\varphi_{\tau/4} + \frac{RT}{nF}\ln\left[(\tau^{1/2} - t^{1/2})/t^{1/2}\right] \qquad (18)$$

for $0 < t < \tau$, and for the reverse transfer from phase β into α, if the direction of current is reversed at $t = \tau$,

$$\Delta_{\alpha}^{\beta}\varphi(t') = \Delta_{\alpha}^{\beta}\varphi_{\tau/4} + \frac{RT}{nF}\ln\frac{\tau^{1/2} - \left[(\tau + t')^{1/2} - 2t'^{1/2}\right]}{(\tau + t')^{1/2} - 2t'^{1/2}}, \qquad (19)$$

where $0 < t' < \tau' = \tau/3$. In addition, we have

$$\Delta_{\alpha}^{\beta}\varphi_{\tau/4} = \Delta_{\alpha}^{\beta}\varphi_{B^{n+}}^{0} + \frac{RT}{2nF}\ln\left(D_{B^{n+}}^{\beta}/D_{B^{n+}}^{\alpha}\right), \qquad (20)$$

$$\tau^{1/2} = nFc_{B^{n+}}^{0,\alpha}(\pi D_{B^{n+}}^{\alpha})^{1/2}/2i_0. \qquad (21)$$

It is seen from Table I that the equations of potential–time curves for Systems 1 − 3 in both time intervals limited by the transition times τ and τ' are formally similar (for Systems 1 and 2, $n = 1$); the differences are in the definition of the quantities $\Delta_{\alpha}^{\beta}\varphi_{\tau/4}$ and $\tau^{1/2}$. For System 4 with $m \geq 2$, however, there is a change due to the term $(\tau^{1/2} - t^{1/2})^m$ for $0 < t < \tau$, or to the term $\left[\tau^{1/2} - (\tau + t')^{1/2} + 2t'^{1/2}\right]^m$ for $0 < t' < \tau'$. In this system, the values of $\tau^{1/2}$ (or $\tau'^{1/2}$) decrease with increasing number of X ligands bound to the transported cation B^{n+} in phase β. If $m = n = 1$, the dependences for System 4 are, of course, formally identical with the corresponding ones for System 2 (where the anion A^- stands for the ligand X).

Generally, the formation of ion pairs B^+A^- only in phase β (System 1, $K_{BA_i}^{\alpha} = = 0$) or complexes only in phase β (System 3, $K_{BX_j}^{\alpha} = 0$ for $j = 1, 2, ..., l$) "facilitates" the transfer of the cations B^+ or B^{n+} from phase α to β. The reason for this is that the transport connected with the formation of ion pairs or complexes in phase β proceeds at more positive values of $\Delta_{\alpha}^{\beta}\varphi$ compared to the "simple" transport, described by Eqs (18), (20), and (21) for $0 < t < \tau$.

The stimulation or hindrance of the transport of cations B^+ or B^{n+} from phase α into β in Systems 1 and 3 depends on the values of the association or stability constants, concentration of anions or ligands, and on the values of the corresponding diffusion coefficients.

In Systems 1 and 3, measurable changes of the values of τ with changing concentration of the anion $(c_{A_i}^{0,\alpha}$, System 1) or ligand $(c_X^{0,\alpha}$, System 3) may occur. This effect

will depend on the values of the association or stability constants, $K_{BA_i}^{\alpha}$ or $K_{BX_j}^{z}$ ($j = 1, 2, ..., l$), concentrations $c_{A_i^-}^{0,\alpha}$ or $c_X^{0,\alpha}$, eventually the corresponding diffusion coefficients, as follows from the expressions for $\tau^{1/2}$ (Table I).

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