DIFFUSION KINETICS OF THE ANODIC DISSOLUTION OF A METAL WITH THE FORMATION OF AN ANIONIC COMPLEX WITH THE ANION OF THE SOLUTION

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Theoretical calculations of the rate of transfer of material in the anodic dissolution of a metal under conditions in which a cationic complex of the dissolving metal with the anion of the dissolved electrolyte is formed were carried out earlier [1] for the simple case in which the number of charges of the anion and the two cations is the same. It was found that the establishment of the limiting current with respect to the anions of the solution taking part in the reaction can take place only when the diffusion current of this anion is less than the diffusion coefficient of the complex formed in the reaction.

The present paper deals with the steady-state anodic dissolution of a metal $M_{(2)}$ (not complicated by passivation) in a solution containing $M_{(1)}^{z+}$ cations and A^{z-} anions, with the formation of an anionic complex according to the reaction

$$M_{(2)} + nA^{z-} \rightarrow M_{(2)}A_n^{z-} + z(n-1)e^-. \quad (1)$$

The diffusion coefficients of the ions $M_{(1)}^{z+}$, A^{z-}, $M_{(2)}A_n^{z-}$, which are assumed to be independent of concentration, are denoted by the symbols D_1, D_2, and D_3 respectively, and the charges are expressed in units of the charge on the proton.

For the steady-state process, the fluxes of the anions j_2 and the complexes j_3 are related by the following expression

$$j_2 = -nj_3. \quad (2)$$

If a constant current density I is passed through the system, it can be expressed in terms of the ion fluxes as follows

$$I = zF(j_2 + j_3).$$

Thus in the electrical-neutrality approximation we can write

$$\begin{aligned}
D_1Fz\frac{dc_1}{dx} &= \frac{D_1F}{RT}Fz^2\mathcal{E}c_1,\\
D_2Fz\frac{dc_2}{dx} &= -\frac{D_2F}{RT}Fz^2\mathcal{E}c_2 + \frac{Inz}{z(n-1)},\\
D_3Fz\frac{dc_3}{dx} &= -\frac{D_3F}{RT}Fz^2\mathcal{E}c_3 - \frac{Iz}{z(n-1)},\\
c_1 - c_2 - c_3 &= 0,
\end{aligned} \quad (4)$$

where c_1, c_2, and c_3 are the concentrations of the ions $M_{(1)}^{z+}$, A^{z-}, $M_{(2)}A_n^{z-}$ respectively, and $\mathcal{E}$ is the electric field intensity. The origin of the axis of abscissae is situated in the solution at a distance d, which is of the order of magnitude of the thickness of the Helmholtz layer, from the surface of the electrode (Fig. 1).

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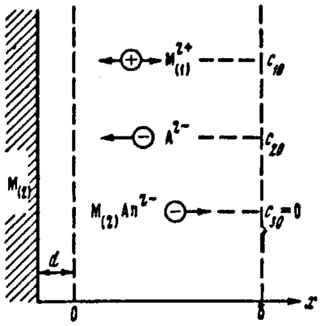

Fig. 1. Diagram of the layer next to the electrode.

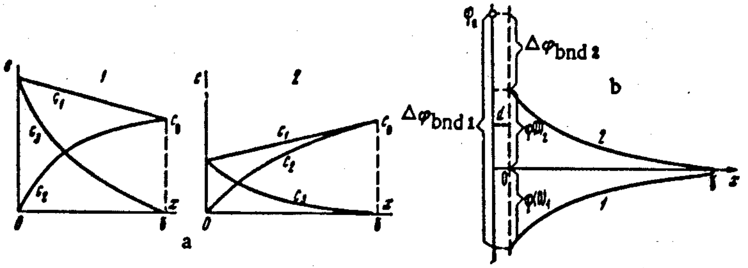

Fig. 2. Distribution of the concentrations of the ions (a) and the potential (b) in the diffusion layer for the cases: 1) $D_2 > nD_3$; 2) $D_2 < nD_3$.

The system (4) has the following boundary conditions:

$$c_1(\delta) = c_{10}; \quad c_2(\delta) = c_{20}; \quad c_3(\delta) = 0, \tag{5}$$

where δ is the thickness of the diffusion boundary layer, and

$$c_{10} = c_{20} = c_0. \tag{6}$$

In Eqs. (4) and (5) we can change to dimensionless quantities, as in [1]:

$$x = s\delta; \quad c_k = m_k c_0 \quad (k = 1, 2, 3); \quad I = \frac{2D_2Fc_0}{\delta} i; \quad \mathcal{E} = E\frac{RT}{F\delta}; \quad \gamma = \frac{D_2}{D_3} \tag{7}$$

and introduce the new variables

$$\rho = m_1 - m_2 - m_3; \quad \sigma = m_1 + m_2 + m_3. \tag{8}$$

The system (4) will have the form

$$\frac{d\sigma}{ds} = zE\rho + \frac{2i}{z(n-1)}(n-\gamma),$$

$$\frac{d\rho}{ds} = zE\sigma - \frac{2i}{z(n-1)}(n-\gamma),$$

$$\frac{dm_2}{ds} = -zEm^2 + \frac{2n}{z(n-1)}i,$$

$$\rho = 0,$$

with boundary conditions

$$\sigma(1) = 2; \quad m_2(1) = 1.$$

Solution of the last system leads to the following relationships:

$$m_1 = \frac{i(n-\gamma)(s-1) + z(n-1)}{z(n-1)}, \tag{9}$$

$$m_2 = \frac{n[i(n-\gamma)(s-1) + z(n-1)]}{z(n-1)(n-\gamma)} - \frac{\gamma z(n-1)}{(n-\gamma)[i(n-\gamma)(s-1) + z(n-1)]}, \tag{10}$$

$$m_3 = \frac{\gamma z(n-1)}{(n-\gamma)[i(n-\gamma)(s-1) + z(n-1)]} - \frac{\gamma[i(n-\gamma)(s-1) + z(n-1)]}{z(n-1)(n-\gamma)}, \tag{11}$$

$$E = \frac{i(n-\gamma)}{z[i(n-\gamma)(s-1) + z(n-1)]}. \tag{12}$$

By integrating E(s) with respect to the thickness of the diffusion layer, we find the drop in potential in the layer ($\psi = \varphi F/RT$ is the dimensionless potential):

$$\psi(s) = \int_s^1 E\,ds = \frac{1}{z}\ln\frac{z(n-1)}{i(n-\gamma)(s-1)+z(n-1)}. \tag{13}$$

The potential is measured from the right-hand boundary ($x=\delta$) of the diffusion layer (Fig. 1), that is $\psi(1) = 0$. The relationship between the current and the potential drop in the diffusion layer will have the form

$$\psi(0) = \frac{1}{z}\ln\frac{z(n-1)}{z(n-1)-i(n-\gamma)}. \tag{14}$$

We shall assume that an equation of the Volmer type is applicable for reaction (1), and we shall write the corresponding relationship between the current density I and the potential jump at the electrode/solution boundary $\Delta\varphi_{\text{bound}}$:

$$I = Fk_1 z(n-1)c_2^n(0)\exp\left[\alpha z(n-1)\frac{F\Delta\varphi_{\text{bnd}}}{RT}\right], \tag{15}$$

where k_1 is the reaction rate constant. In Eq. (15) we can change to dimensionless quantities

$$2i = K_1 z(n-1)m_2^n(0)\exp\left[\alpha z(n-1)\Delta\psi_{\text{bnd}}\right] \tag{16}$$

or

$$\Delta\psi_{\text{bnd}} = \frac{1}{\alpha z(n-1)}\ln\frac{2i}{K_1 z(n-1)m_2^n(0)}, \tag{17}$$

where $K_1 = k_1(\delta c_0^{n-1}/D_2)$.

The volt-ampere characteristic of the process then has the form

$$\left[\frac{z(n-1)}{z(n-1)-i(n-\gamma)}\right]^{1/z}\cdot\left[\frac{2i}{K_1 z(n-1)m_2^n(0)}\right]^{1/\alpha z(n-1)} = e^{\Delta\psi}, \tag{18}$$

where $\Delta\psi = \psi(0) + \Delta\psi_{\text{bound}}$.

It can be seen from expressions (10), (14), (16), and (18) that in contrast to the case examined in [1], a limiting current exists at all diffusion coefficient ratios and is equal to

$$i_{\text{lim}} = \frac{z(n-1)}{n\left(1+\sqrt{\frac{\gamma}{n}}\right)}$$

or, in dimensionless quantities

$$I_{\text{lim}} = \frac{2z(n-1)D_2c_0F}{\delta n\left[1+\sqrt{\frac{D_2}{nD_3}}\right]}. \tag{19}$$

The existence of a limiting current is attributed to a deficit of the anions of the electrolyte, taking part in reaction (1), at the electrode surface. When D_2 and D_3 are equal, the equation obtained for the limiting current differs formally, by a numerical coefficient, from the familiar equation $I_{\text{lim}} = zD_2c_0F/\delta$, applicable for the case where the electrochemical reaction takes place in the presence of an excess of an indifferent electrolyte [2]. In the range of values of n from 2 to 10, the numerical coefficient takes values from 0.58 to 1.37, and for $n=4$ it is equal to unity. If $D_2 = 4D_3$ (this may be the case, for example, when the anion A^{z-} is OH^-), the corresponding coefficient $[2(n-1)/n-4](1-\sqrt{4/n})$ varies from 0.41 to 1.1 in the range of values of n from 2 to 10.

These results are illustrated in Fig. 2, a and b, which shows the distribution of the concentrations of the ions and the potential in the diffusion layer. The concentrations of the ions in this case change monotonically with change in the distance from the electrode for any ratio of the coefficients D_2 and D_3.

It may be noted that analogous calculations can be carried out for the cathodic deposition of a metal from complex ions. This also applies to our previous calculations [1].

LITERATURE CITED

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