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Simulation of ion mass transfer processes with allowance for the concentration dependence of diffusion coefficients

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The system of equations describing ion transport in a binary electrolyte z_a—z_c with allowance for the linear dependence of the diffusion coefficients on the concentration was analyzed in the framework of the phenomenological Nernst—Planck approach. The expressions are obtained that define concentration profiles of ions and conditions favorable for the limiting current caused by the achievement of the concentration of a saturated solution (in the case of the anodic reaction) and depletion of the near-electrode region in electroactive cations (in the case of the cathodic reaction). The revealed theoretical dependence of the limiting current on the volume concentration of the salt agrees with published experimental data. The voltammetric characteristics of the corresponding systems were calculated. The role of the migrational component of the ion flow is discussed.

Key words: diffusion coefficient, ion transport, limiting current, migration, voltammetric curve, concentration distribution.

Physicochemical and transport characteristics of electrolyte solutions (diffusion coefficients of ions, viscosity, density) depend substantially on the concentrations of the components. In particular, measurements of the diffusion coefficients (D) of the Ni^{2+} and Cl^- ions in aqueous solutions of sodium chloride by the radioactive isotope method showed[1] that the $D_{Ni^{2+}}$ value changed by 2.9 times and D_{Cl^-} changed by 3.3 times with a change in the concentration of the $NiCl_2$ salt from 1.5 to 4.0 mol L^{-1}.

In heterogeneous systems where chemical reactions occur not in the whole solution volume, a change in the concentrations of the reactants and products can have a local character. For instance, for electrochemical oxidation or reduction, the composition of a solution in the near-electrode layers differs from the bulk composition. Especially pronounced changes occur in the cases of high-performance anodic dissolution and cathodic deposition of metals, which are controlled by mass transfer in solution.[2] During the anodic process, the concentration of the products in the near-electrode layer increases and can achieve the solubility limit (saturation effect). In turn, during electrodeposition the near-cathodic layer is depleted in electroactive cations.

Local changes in concentrations appeared during the reaction affect the diffusion coefficients of ions and thus complicate the physical pattern of the processes that occur in solution. Therefore, concentration dependences of the transport properties of solution should be taken into account for the adequate description of mass transfer.

To solve a similar problem, an assumption was used[3,4] that the concentration dependences of the viscosity, density, and diffusion coefficients are well described by an exponential law. It is shown that the difference between the expression for the current density and that calculated in the framework of the traditional Levich theory[5] lies in additional terms, which take into account the variable character of the physical and transport properties of solution. The concentration dependence of the diffusion coefficient makes the main contribution to the correction value.[6]

In the present work, based on the phenomenological Nernst—Planck approach,[7,8] we performed the theoretical study of ion mass transfer processes in a binary solution z_a—z_c assuming a linear change in the diffusion coefficients with concentration (C). The linear character of the $D(C)$ dependence can be substantiated by earlier published data.[1] The processing of these experimental results (Fig. 1) showed that for solutions of $NiCl_2$ with salt concentrations (C_0) of 1.5—4.0 mol L^{-1} the decrease in the diffusion coefficients of the cations ($D_{Ni^{2+}}$/cm^2 s^{-1}) and anions (D_{Cl^-}/cm^2 s^{-1}) is described by the correlations

$$D_{Ni^{2+}} = [(0.634\pm0.012) - (0.122\pm0.004)C_0]\cdot10^{-5} \quad (R = 0.998), \qquad (1)$$

$$D_{Cl^-} = [(1.538\pm0.037) - (0.309\pm0.013)C_0]\cdot10^{-5} \quad (R = 0.997). \qquad (2)$$

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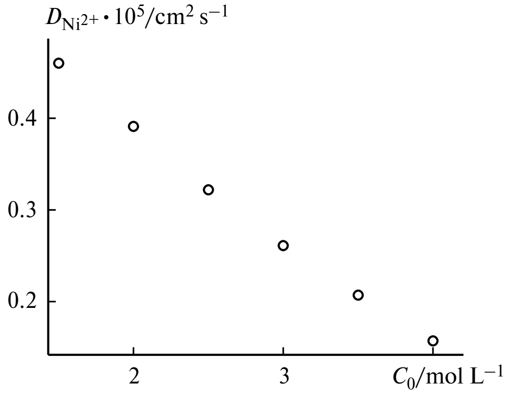

Fig. 1. Concentration dependence of the diffusion coefficients of Ni^{2+} ions in aqueous solutions of $NiCl_2$ (experimental data**[1]**).

According to the Nernst—Planck model, we assume that flows of the M^{z_c+} and A^{z_a-} anions in a solution are caused by the concentration and electric field gradients. In the whole diffusional layer (except for the narrow near-electrode region about the Debye radius in size), electroneutral is retained, the electrode—solution boundary is permeable only for cations, and the behavior of anions is indifferent. Then the system of phenomenological equations describing ion transport in the binary solution z_a—z_c takes the form

$$i_c = -z_c F D_c \frac{dC_c}{dX} - \frac{z_c^2 F^2}{RT} D_c C_c \frac{d\Phi}{dX}, \tag{3}$$

$$i_a = -z_a F D_a \frac{dC_a}{dX} + \frac{z_a^2 F^2}{RT} D_a C_a \frac{d\Phi}{dX} = 0, \tag{4}$$

$$z_c C_c = z_a C_a. \tag{5}$$

Here C_c and C_a are the concentrations of cations and anions, respectively; z_c and z_a are the charges of cations and anions (in terms of the absolute value), respectively; D_c and D_a are the diffusion coefficients of particles related to the mobilities through the Nernst—Einstein equation; X is the coordinate counted from the electrode; i_c and i_a are the cationic and anionic currents, respectively; Φ is the electric potential; R is the gas constant; T is absolute temperature; F is the Faraday number. The sign of the i_c value that characterizes the direction of the cation flow is determined by the type of the electrode process. The current is negative if the metal cations are the reactants (electrodeposition) and positive if the cations are the reaction products (electrodissolution).

For the integration of the initial system of equations (3)—(5), it is convenient to introduce the C value (salt concentration)

$$C = C_c/z_a = C_a/z_c. \tag{6}$$

In this case, the boundary conditions at the external boundary of the diffusional layer ($X = \mathrm{L}$) take the following form:

$$C_c(X = \mathrm{L})/z_a = C_a(X = \mathrm{L})/z_c = C_0,$$

$$\Phi(X = \mathrm{L}) = 0, \tag{7}$$

where C_0 is the salt concentration in the solution bulk.

Let us introduce dimensionless variables

$$x = X/\mathrm{L}, \qquad c = C/C_0 \qquad \gamma = D_c/D_0,$$

$$\phi = F\Phi/(RT), \qquad j = i_c\mathrm{L}/(z_c F D_0 C_0),$$

where D_0 is the diffusion coefficient of the cations for infinite dilution.

Taking into account these designations, we have

$$\gamma[z_a(dc/dx) + z_a z_c c(d\phi/dx)] = j, \tag{8}$$

$$(dc/dx) - z_a c(d\phi/dx) = 0, \tag{9}$$

$$c(1) = 1, \qquad \phi(1) = 0. \tag{10}$$

Let us assume that the diffusion coefficient of the cations depends linearly on the concentration

$$D_c = D_0 + \alpha_1 C_c \tag{11}$$

or in the dimensionless variables

$$\gamma = 1 + \gamma_1 c, \tag{12}$$

where $\gamma_1 = (\alpha_1 z_a C_0)/D_0$.

The solution of the system of Eqs (8) and (9) taking into account formulas (10) and (12) results in the expression

$$2(1 - c) + \gamma_1(1 - c^2) = -\frac{2j}{z_a + z_c}(1 - x). \tag{13}$$

Equation (13) describes the concentration profile of ions in the diffusional layer for the current flowing through the binary electrolyte z_a—z_c. Unlike the described**[5,7,8]** cases when the diffusion coefficient is independent of the concentration, formula (13) contains the nonlinear term in the left part.

Taking into account Eq. (6), the solution of the quadratic equation (13) gives the distribution of the cation concentration in the explicit form

$$c_c(x) = \frac{z_a}{\gamma_1}\left[-1 + \sqrt{(1 + \gamma_1)^2 + \frac{2j\gamma_1}{z_a + z_c}(1 - x)}\right]. \tag{14}$$

The choice of the sign "+" in front of the root depends on the boundary conditions (10). As follows from Eq. (14), the near-electrode value of the cation concentration $c_c(0)$

is a function of the flowing current and parameters of the problem according to the law

$$c_c(0) = \frac{z_a}{\gamma_1}\left[-1 + \sqrt{(1+\gamma_1)^2 + \frac{2j\gamma_1}{z_a + z_c}}\right]. \tag{15}$$

By integrating Eq. (9) one can show that the ion concentration and potential are related to each other similarly to the Boltzmann equation and the electric potential distribution in the diffusional layer $\phi(x)$ has the form

$$\phi(x) = \frac{1}{z_a}\ln\left\{\frac{1}{\gamma_1}\left[-1 + \sqrt{(1+\gamma_1)^2 + \frac{2j\gamma_1}{z_a + z_c}(1-x)}\right]\right\}. \tag{16}$$

An analysis of formulas (14) and (16) suggests that for the linear dependence of the diffusion coefficient on the concentration the migration component of the ionic current ($j^{\mathrm{migr}} \propto c(\mathrm{d}\phi/\mathrm{d}x)$) has a local character and depends on the coordinate x. This dependence is not observed if the D_c and D_a values are constant.[5,7,8] At the same time, the ratio of contributions of the diffusional and migrational components remains unchanged.

Substituting $x = 0$, $\phi = \phi(0)$ into Eq. (16) and using the boundary conditions (10) give the expression for the potential drop in the diffusional layer $\phi_0 = \phi(0) - \phi(1)$:

$$\phi_0 = \frac{1}{z_a}\ln\left\{\frac{1}{\gamma_1}\left[-1 + \sqrt{(1+\gamma_1)^2 + \frac{2j\gamma_1}{z_a + z_c}}\right]\right\}. \tag{17}$$

The sign of the electric potential drop is determined by the current sign: $\phi_0 > 0$ for the oxidation process and $\phi_0 < 0$ for the reduction process.

Particular cases corresponding to different directions of the electrochemical reaction are considered below.

Case of the anodic reaction ($i_c > 0$)

During metal oxidation, the M^{z_c+} cations are generated in the near-electrode region according to the reaction

$$M^0 \rightarrow M^{z_c+} + z_c e^-. \tag{18}$$

The concentration distributions corresponding to this case and calculated by formula (14) are presented in Fig. 2, *a*. As can be seen, when approaching to the electrode surface, the ion concentration increases monotonically.

However, this increase cannot be infinite. As shown by the study[4,9] of anodic dissolution of the iron group metals in chloride media, at rather high currents the concentration of the reaction products in the near-electrode region reaches the concentration of a saturated solution ($c(x = 0) = c_{sat}$). Inserting these conditions into formula (15), one can obtain the expression for the limiting current $j^{l(1)}$ caused by the achievement of the saturation concentration

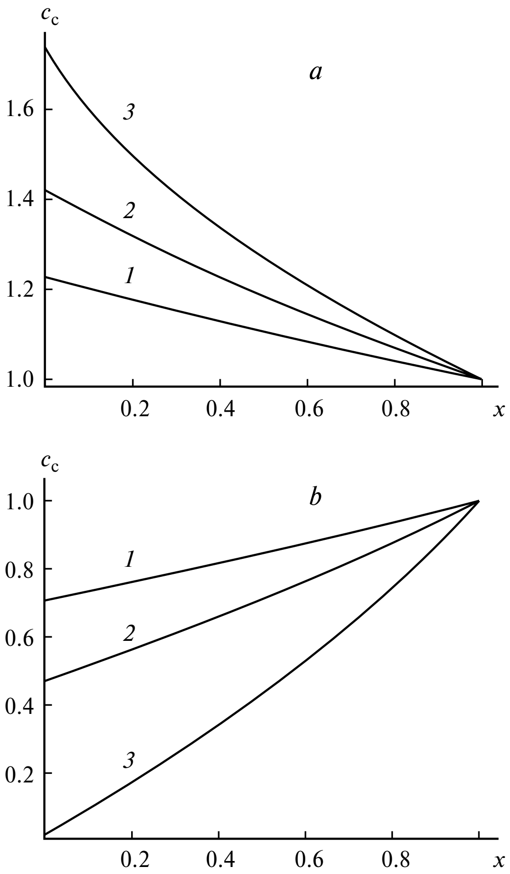

Fig. 2. Distributions of the cation concentrations $c_c(x)$ in the diffusional layer calculated by Eq. (14) at $z_a = 1$, $z_c = 2$, $\gamma_1 = -0.5$: *a* is the anodic reaction, $j = 0.3$ (*1*), 0.5 (*2*), and 0.7 (*3*); *b* is the cathodic reaction, $j = -0.5$ (*1*), -1 (*2*), and -2.2 (*3*).

$$j^{l(1)} = \frac{z_a + z_c}{2}\left[2(c_{sat} - 1) + \gamma_1(c_{sat}^2 - 1)\right]. \tag{19}$$

The second term in the right part of Eq. (19) quantitatively describes the effect of decreasing limiting current due to a decrease in the diffusion coefficient with an increase in the concentration.

Another sequence of the variable character of the diffusion coefficient is a change in the analytical form of the dependence of the limiting current on the volume concentration of the salt. Going to dimensional variables in formula (19), we have

$$i_c^{l(1)} = (z_a + z_c)z_c\frac{FD_0}{\mathrm{L}}\left[C_{sat} - C_0 + \frac{\alpha_1 z_a}{2D_0}\gamma_1\left(C_{sat}^2 - C_0^2\right)\right]. \tag{20}$$

As can be seen from Eq. (20), deviations from linearity of the $i_c^{l(1)}(C_0)$ function take place at rather high concentrations.

The dependence of the limiting current on the salt concentration (see formula (20)) agrees qualitatively with the experimental data obtained in the study[9] of anodic dissolution of iron in binary solutions of $FeCl_2$. At the same time, unlike our results, the earlier[9] published analytical expressions for the $i_c^{l(1)}(C_0)$ dependence are linear and, hence, contradict the experimental data.

The achievement of the limiting value by the current should manifest itself in the character of the voltammetric curve of the system under study, *i.e.*, in the character of the $j(\Delta\varphi)$ dependence ($\Delta\varphi = \varphi_0 + \Delta\varphi_b$, where $\Delta\varphi_b$ is the dimensionless jump at the electrode—solution boundary).

Let us assume that for reaction (18) the $j(\Delta\varphi_b)$ dependence obeys the Butler—Volmer equation

$$j = k_0^a \exp(z_c \beta^a \Delta\varphi_b), \tag{21}$$

where the dimensionless jump ($\Delta\varphi_b$) and the dimensionless kinetic constant of the anodic reaction (k_0^a) are related to the corresponding dimensional values ($\Delta\Phi_b$ and K_0^a) through the correlations

$$\Delta\varphi_b = F\Delta\Phi_b/(RT), \qquad k_0^a = K_0^a L/(D_0 C_0)$$

(β^a is the transfer coefficient).

Based on formulas (17) and (21), one can determine the voltammetric characteristic of the oxidation process, which has the following form in the considered case of the linear concentration dependence of the diffusion coefficient:

$$\Delta\varphi = \frac{1}{z_c\beta^a}\ln\frac{j}{k_0^a} + \frac{1}{z_a}\ln\left\{\frac{1}{\gamma_1}\left[-1 + \sqrt{(1+\gamma_1)^2 + \frac{2j\gamma_1}{z_a + z_c}}\right]\right\}. \tag{22}$$

As can be seen from the data in Fig. 3, *a*, in the region of low currents when the process rate is limited by the intrinsic electrode reaction, the course of the voltammetric curve is virtually independent of the γ_1 parameter, which characterizes the $D(C)$ dependence. When the intensity of dissolution increases, the concentration of the products in the near-electrode layer increases, diffusional restrictions begin to appear, and the role of γ_1 increases: the stronger is the decrease in the diffusion coefficient with an increase in the concentration, the lower is the current (at the same potential values).

Case of the cathodic reaction ($i_c < 0$)

In the case of diffusional restrictions in a solution during the electroreduction of cations on the electrode *via* the reaction

$$M^{z_c+} \rightarrow M^0 - z_c e^- \tag{23}$$

the concentration of particles in the diffusional layer is decreased compared to the volume value (see Fig. 2, *b*). For the current equal to the limiting value ($j = j^{l(2)}$), the near-electrode concentration value approach zero. Taking into account this fact, it is easy to obtain that the limiting current value depends on the γ_1 parameter

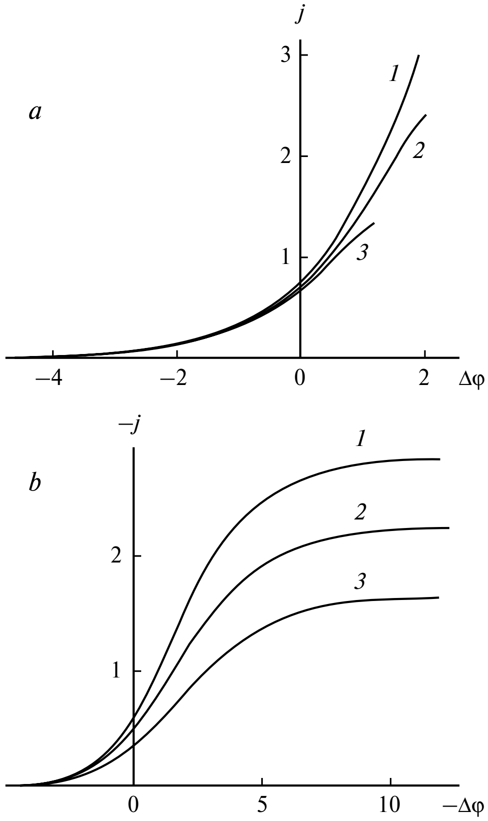

Fig. 3. Voltammetric characteristics of the system for the anodic (*a*) and cathodic (*b*) processes calculated by Eqs (22) and (28), respectively, at $z_a = 1$ and $z_c = 2$: *a* — $\beta^a = 0.5$, $k_0^a = 1$; $\gamma_1 = -0.1$ (*1*), -0.3 (*2*), and -0.4 (*3*); *b* — $\beta^c = 0.5$, $k_0^c = 1$; $\gamma_1 = -0.1$ (*1*), -0.5 (*2*), and -0.9 (*3*).

$$j^{l(2)} = [(z_a + z_c)/2](-2 - \gamma_1). \tag{24}$$

It can be concluded from formula (24) that the intensity of mass transfer decreases substantially due to a decrease in the diffusion coefficient with an increase in the concentration.

It is necessary to mention that in an excess of indifferent ions, when the influence of the electric field on the mass transfer in solution can be neglected, the expression for the limiting current has the form

$$j^{l(2)} = (z_c/2)(-2 - \gamma_1). \tag{25}$$

Thus, ion migration in the electric field increases the limiting current by $1 + z_a/z_c$ times. This result is valid in the case of constant diffusion coefficients.[5,8]

After going to dimensional variables in formula (24)

$$i_c^{l(2)} = \left(1 + \frac{z_c}{z_a}\right)\left[-\frac{z_c F D_0 C_c^0}{L} - \frac{z_c \alpha_1 F (C_c^0)^2}{2L}\right] \qquad (26)$$

one can analyze the dependence of the limiting current on the volume cation concentration. As can be seen, this dependence is close to linear only at low C_c^0 values.

An increase in the diffusion coefficients in the near-electrode region due to a decrease in the cation concentration affects the voltammetric curve of the system under study. Let us assume that reduction process (23) is the first-order reaction with respect to cations, so that the kinetic equation (in dimensionless variables) has the form

$$j = -k_0^c c_c(0)\exp(-z_c\beta^c\Delta\phi_b), \qquad (27)$$

where the dimensionless rate constant of the cathodic process (k_0^c) is related to the dimensional constant (K_0^c) through the equation

$$k_0^c = K_0^c L/D_0.$$

Taking into account Eqs (17) and (27), which describe the potential drop in the diffusional layer and the potential jump at the electrode—solution boundary, the voltammetric characteristics of the reduction process can be written in the form

$$\Delta\phi = \frac{1}{z_c\beta^c}\ln\frac{z_a k_0^c}{-j} + \left(\frac{1}{z_c\beta^c} + \frac{1}{z_a}\right)\ln\left\{\frac{1}{\gamma_1}\left[-1 + \sqrt{(1+\gamma_1)^2 + \frac{2j\gamma_1}{z_a + z_c}}\right]\right\}. \qquad (28)$$

An analysis of Eq. (28) and the data in Fig. 3, *b* show that with an increase in the potential drop the cationic current increases and reaches the limiting value determined by formula (24). The limiting current value decreases with an increase (by modulus) in the γ_1 parameter.

Thus, the theoretical studies demonstrated that the concentration dependences of the diffusion coefficients of ions should necessarily be taken into account. Ignoring this fact in the description of mass transfer processes in electrochemical systems can result in invalid values of the kinetic parameters and incorrect treatment of the obtained experimental data.

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