ON THE THEORY OF THE PASSAGE OF DIRECT CURRENT THROUGH A SOLUTION OF A BINARY ELECTROLYTE

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Abstract

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ON THE THEORY OF THE PASSAGE OF DIRECT CURRENT THROUGH A SOLUTION OF A BINARY ELECTROLYTE

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For the study of the kinetics of electrochemical reactions it is of interest to solve a number of problems connected with the passage of electric current through electrolyte solutions. In ([1]) it was shown that the problem of the distribution of the electric field and concentrations in a symmetric 1-1 electrolyte can be reduced to the study of a certain nonlinear differential equation whose solutions are the so-called Painlevé transcendents. The method proposed in ([1]) for approximating the solution of the problem, based on the asymptotic properties of the Painlevé transcendents, while logically justified, does not, however, possess sufficient flexibility, i.e., it proves applicable in fact only in the case of a 1-1 and 1-2 electrolyte ([2]). In this connection it is desirable to find a unified method for the approximate solution of a sufficiently broad class of problems of diffusion kinetics. For most of these problems the presence of small parameters at the highest derivatives in systems of differential equations describing the passage of currents, and a sharp change in their solutions near one of the boundaries (the electrode), which can be discerned from physical considerations, are characteristic. These two circumstances suggest applying to the solution of such problems methods of the type of the "boundary layer" method ([3]). Below, as an example, by the boundary-layer method the distribution of the field and concentrations in a symmetric 1-1 electrolyte far from the point of zero charge will be found.

Let us suppose that electrolysis is carried out in a capillary of length L, at the open end of which a constant ion concentration N_0 is maintained. For simplicity let us consider the case when only negative ions are discharged at the positively charged electrode. The equations of diffusion kinetics have the form

$$I_+ = D_+\left(-\frac{dN_+}{dx} + \frac{e}{kT}\mathcal{E}N_+\right) = 0, \qquad I_- = D_-\left(-\frac{dN_-}{dx} - \frac{e}{kT}\mathcal{E}N_-\right),$$

$$\frac{d\mathcal{E}}{dx} = \frac{4\pi e}{\varepsilon_0}(N_+ - N_-) \qquad (0 < x < L), \tag{1}$$

where I_+, I_-; D_+, D_-; N_+, N_- are respectively the fluxes, diffusion coefficients, and concentrations of positive and negative ions; $\mathcal{E}$ is the electric-field strength;

e is the electron charge ($e > 0$); ε_0 is the dielectric constant of the solution; T is the absolute temperature, and k is Boltzmann' s constant. The point $x = 0$ corresponds to the plane of closest approach of the ions.

To reveal the presence of a small parameter, it is necessary to pass to the dimensionless variables

$$n_+ = N_+/N_0, \qquad n_- = N_-/N_0, \qquad E = e\mathcal{E}L/kT; \qquad j = I_-L/D_-N_0, \quad s = x/L.$$

The system (1) in the variables ρ, n_-, E, s takes the form

$$d\rho/ds = E(\rho + 2n_-) + j, \qquad dn_-/ds = -En_- - j,$$
$$\varepsilon^2 dE/ds = \rho, \qquad n_-(1) = 1, \qquad \rho(1) = 0, \tag{2}$$

where $\varepsilon = L_d/L$ is a small parameter, $\rho = n_+ - n_-$, $L_d = \sqrt{\varepsilon_0 kT/4\pi e^2 N_0}$.

According to the boundary-layer method, the solution in the diffusion region is found by setting $\varepsilon = 0$ in (2):

$$\rho^{(0)}(s) = 0, \qquad n_-^{(0)}(s) = -\frac{j}{2}s + C_1, \qquad E^{(0)}(s) = -\frac{j}{2C_1 - js}, \tag{3}$$

where $C_1 = 1 + j/2$ is determined from the condition $n_-^{(0)}(1) = 1$.

We represent the solution of system (2) throughout the region $0 \le s \le 1$ in the form

$$\rho(s) = \rho^{(0)}(s) + \tilde{\rho}(s), \qquad n_-(s) = n_-^{(0)}(s) + \tilde{n}_-(s),$$

$$E(s) = E^{(0)}(s) + \varepsilon^{-1}\tilde{E}(s), \tag{4}$$

where $\tilde{\rho}, \tilde{n}_-, \tilde{E}$ are functions rapidly varying near the boundary $s = 0$.

Substituting (4) into (2), performing a "stretching" of the independent variable $s = \varepsilon\xi$, and letting ε tend to zero in the resulting equations, we arrive at the system of boundary-layer equations:

$$d\tilde{\rho}/d\xi = \tilde{E}\,(2\tilde{n}_- + \tilde{\rho} + 2 + j), \qquad d\tilde{n}_-/d\xi = -\tilde{E}\,(\tilde{n}_- + 1 + j/2), \qquad d\tilde{E}/d\xi = \tilde{\rho}. \tag{5}$$

The functions $\tilde{\rho}, \tilde{n}_-, \tilde{E}$ are subject to the condition*

$$\tilde{\rho}, \tilde{n}_-, \tilde{E} \to 0 \qquad \text{as } \xi \to \infty. \tag{6}$$

It can be shown that $\tilde{E}(\xi)$ satisfies the equation

$$\left(\frac{d\tilde{E}}{d\xi}\right)^2 = \frac{1}{4}\tilde{E}^4 + (2+j)\tilde{E}^2 + C_0, \tag{7}$$

where C_0 is an arbitrary constant.

Making the substitution

$$\tilde{E}^2(\xi) = -\frac{4}{3}(2+j) + 4W(\xi), \tag{8}$$

we find an equation for $W(\xi)$:

$$\left(\frac{dW}{d\xi}\right)^2 = 4W^3 - g_2 W - g_3, \tag{9}$$

where

$$g_3 = \frac{2+j}{3}\left[\frac{4}{9}(2+j) - g_2\right],$$

and g_2 is an arbitrary constant. As is known [4], the solution of (9) is the Weierstrass $\wp$-function. Consequently,

$$\tilde{E}^2(\xi) = -\frac{4}{3}(2+j) + 4\wp(\xi + C;\, g_2, g_3), \tag{10}$$

where C is a constant of integration.

From condition (6) we find that $g_2 = \frac{4}{3}(2+j)^2$. In this case the discriminant $g_2^3 - 27g_3^2 = 0$, and the elliptic function (10) degenerates into the hyperbolic one,

$$\tilde{E}(\xi) = \frac{2\sqrt{2+j}}{\operatorname{sh}\sqrt{2+j}\,(\xi + C)}. \tag{11}$$

In passing from (10) to (11), we took into account that $\tilde{E} > 0$, since the surface of the electrode is positively charged.

From (4), (5), and the relation $\rho = n_+ - n_-$, we obtain

$$n_-(s) = -\frac{j}{2}s + \frac{2+j}{2}\operatorname{cth}^2\frac{\sqrt{2}}{2}\left[\sqrt{\frac{2+j}{2}}\left(\frac{s}{\varepsilon}+C\right)\right], \tag{12}$$

$$n_+(s) = -\frac{j}{2}s + \frac{2+j}{2}\operatorname{th}^2\frac{\sqrt{2}}{2}\left[\sqrt{\frac{2+j}{2}}\left(\frac{s}{\varepsilon}+C\right)\right], \tag{13}$$

$$E(s) = -\frac{j}{2+j-js} + \frac{1}{\varepsilon}2\sqrt{2}\,\frac{\sqrt{\frac{2+j}{2}}}{\operatorname{sh}\sqrt{2}\left[\sqrt{\frac{2+j}{2}}\left(\frac{s}{\varepsilon}+C\right)\right]}. \tag{14}$$

* In this case solution (4) will satisfy the boundary conditions at $s = 1$ up to quantities of order ε. The calculations can be carried out in such a way that the boundary conditions are satisfied exactly; however, the solution, while in fact having the same accuracy, then has a more complicated structure.

It follows from formulas (12)–(14) that the effective thickness of the diffusion layer depends on the magnitude of the current passing through the system according to the law

$$S_d \sim \frac{\varepsilon}{\sqrt{\frac{2+j}{2}}},$$

which agrees exactly with the result obtained in (1). In our variables the dimensionless potential $\psi = e\varphi/kT$ is related to the electric-field strength $E(s)$ by the relation

$$\psi(s) = \int_s^1 E(s')\,ds'. \tag{15}$$

Substituting (14) into (15) and carrying out the integration, we find

$$\psi(s) = -\ln\left\{\left(-\frac{j}{2}s + \frac{2+j}{2}\right)\operatorname{th}^2\frac{\sqrt{z}}{2}\left[\sqrt{\frac{2+j}{2}}\left(\frac{s}{\varepsilon}+C\right)\right]\right\}. \tag{16}$$

From (12), (13), and (16) it follows that the expressions for the concentrations can be written in the form

$$n_-(s) = \left(1 + \frac{j}{2} - \frac{j}{2}s\right)^2 e^{\psi(s)}(1 + O(\varepsilon)), \tag{17}$$

$$n_+(s) = e^{-\psi(s)}(1 + O(\varepsilon)). \tag{18}$$

Thus, the distribution of ions that are not discharged is, to within terms of order ε, Boltzmann over the whole region $0 \leq s \leq 1$. The small deviations from the Boltzmann distribution in (18) have a nonphysical character and are due to the approximate method of calculation. Expression (17) shows that the passage of current disturbs the Boltzmann character of the distribution of the discharging ions in the diffusion region $\varepsilon/\sqrt{1 + j/2} \leq s \leq 1$, whereas in the diffusion region $0 \leq s \leq \varepsilon/\sqrt{1 + j/2}$ the Boltzmann distribution is preserved to within quantities of order ε. Indeed,

$$n_-(s) = \left(1 + \frac{j}{2}\right)^2 e^{\psi(s)}(1 + O(\varepsilon)) = n_-(s^*)e^{\psi(s)-\psi(s^*)}(1 + O(\varepsilon)) \tag{19}$$

for any points s and s^* from $[0, \varepsilon/\sqrt{1 + j/2}]$.

In deriving the boundary-layer equations (5) we formally made the limiting transition $\varepsilon \to 0$; however, in fact what was essential for us was the fulfillment of the inequality

$$\frac{2 + j}{2} \gg \varepsilon, \tag{20}$$

which also determines the range of applicability of expressions (12)–(14). Since in our case $j < 0$, the latter lose their meaning for values of j sufficiently close to -2. The value $j = -2$ corresponds to the generally accepted value of the limiting current in the system considered by us ([5]). Thus, the theoretically interesting question of the distribution of the field and concentrations at the limiting current remains open for the time being. The case in which negative ions are discharged at a negatively charged electrode requires a special approach and will be investigated in another paper.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.

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