PHYSICAL CHEMISTRY

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1962

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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

(Presented by Academician A. N. Frumkin, 12 IV 1962)

It is of fundamental interest to carry out a sufficiently complete quantitative study of the properties of the simplest electrochemical system—an immobile solution of a binary electrolyte. Up to the present time no unified expressions have been obtained that describe equally well the distribution of concentrations and of the electric field throughout the solution when a direct current passes through it. Usually, at low solution concentration and relatively small polarization, the whole solution is divided into two regions—the region of electroneutral solution and the region of the Gouy diffuse double layer. Such a division is, strictly speaking, unjustified. Moreover, it is not clear how the effective thickness of the diffuse layer changes with the magnitude of the current. Below, the field and concentration distributions in a symmetric 1-1 electrolyte will be found without first dividing the solution into regions. Usually ions of only one kind are discharged at the electrode. We shall take them to be positive.

In order to exclude the influence of natural convection, let us assume 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 ([1]). The passage through the region of the diffuse layer of ions discharging at the electrode of the same sign is determined by an effective diffusion length exceeding the Gouy length ([2]). Here the length of the capillary will be assumed sufficiently large that, even in the case of a positively charged electrode surface, the limiting current is the usual diffusion limiting current. The equations of diffusion kinetics have the form:

$$I_+ = D_+\left(-\frac{dN_+}{dX} + \frac{e}{kT}\,\mathcal{E}N_+\right); \qquad I_- = D_-\left(\frac{dN_-}{dX} - \frac{e}{kT}\,\mathcal{E}N_-\right) = 0; \qquad (1)$$

$$\frac{d\mathcal{E}}{dX} = \frac{4\pi e}{\varepsilon}(N_+ - N_-),$$

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 intensity;

e is the electron charge ($e > 0$); ε is the dielectric constant of the solution; T is the absolute temperature; k is Boltzmann' s constant. It is convenient to pass to dimensionless variables

$$n_+ = N_+/N_0; \qquad n_- = N_-/N_0; \qquad E = e\mathcal{E}/kT\varkappa;$$

$$\varkappa^2 = 4\pi e^2 N_0/\varepsilon kT; \qquad x = \varkappa X; \qquad j_+ = I_+/D_+N_0\varkappa.$$

Then we have

$$j_+ = -dn_+/dx + En_+; \qquad 0 = -dn_-/dx - En_-; \qquad dE/dx = n_+ - n_-; \tag{2}$$

$$n_+(l) = n_-(l) = 1 \qquad (l = \varkappa L). \tag{3}$$

First of all, note that (2) has the first integral

$$n_+ + n_- = E^2/2 + C_0 - j_+x, \tag{4}$$

where C_0 is an arbitrary constant. Using (4), one can show that $n_-(x)$ satisfies the equation

$$n_-\frac{d^2n_-}{dx^2} - 2n_-^3 - \frac{1}{2}\left(\frac{dn_-}{dx}\right)^2 + (C_0 - j_+x)n_-^2 = 0. \tag{5}$$

Making the substitution

$$n_- = 2^{1/3}j_+^{2/3}\eta^2(\xi); \qquad \xi = -2^{-1/3}j_+^{-2/3}(C_0 - j_+x), \tag{6}$$

we obtain an equation for determining $\eta(\xi)$,

$$d^2\eta/d\xi^2 = 2\eta^3 + \xi\eta, \tag{7}$$

which is the canonical form of the second Painlevé equation [3]. Thus, all three unknown functions $n_-(x)$, $n_+(x)$, and $E(x)$ turn out to be connected with solutions of equation (7), the so-called Painlevé transcendents. The latter possess a number of interesting analytic properties, but have not been tabulated, since they have not been studied in connection with questions of an applied character. Therefore the problem arises of approximately integrating system (2). To solve it we shall use a method based on the asymptotic properties of the Painlevé transcendents [4].

Introduce new variables $\widetilde{W}, s$ according to the formulas

$$\eta = \xi^{1/2}\widetilde{W}(s), \qquad s = \frac{2}{3}\xi^{3/2}. \tag{8}$$

In the new variables equation (7) takes the form

$$\frac{d^2\widetilde{W}}{ds^2} = 2\widetilde{W}^3 + \widetilde{W} - \frac{1}{s}\frac{d\widetilde{W}}{ds} + \frac{1}{9s^2}\widetilde{W}. \tag{9}$$

Equation (9) may be compared with the equation

$$d^2W/ds^2 = 2W^3 + W. \tag{10}$$

It follows from this comparison that, for large values of $|s|$, $\widetilde{W}(s) \sim W(s)$, i.e., the solutions of equation (7) are asymptotically related to the solutions of equation (10). Let us now note that, according to (3) and (4), for sufficiently small $|j_+|$ one has $C_0 \approx 2$. Therefore, as is seen from (6), (8), for any x in $[0, l]$ the inequality $|s| \gg 1$ will hold. This means that the asymptotic solution of system (2) will be a good approximation to its exact solution over the entire range of variation of x that is of interest to us, provided only that $|j_+|$ is sufficiently small.

It is not difficult to show that the solution of equation (10) is expressed in terms of the $\wp$-function of Weierstrass [5]:

$$W^2(s) = -\frac{1}{3} + \wp(s + C_2;\ g_2, g_3), \tag{11}$$

where $g_2 = C_1;\ g_3 = \frac{1}{3}\left(\frac{4}{9} - C_1\right);$ C_1 and C_2 are arbitrary constants. According to (6), (8), (11),

$$n_-(x) = (C_0 - j_+x)\left\{\frac{1}{3} + \wp\left[\frac{\sqrt{2}}{3}(-j_+)^{-1}(C_0 - j_+x)^{3/2} + (-1)^{3/2}C_2;\ g_2, -g_3\right]\right\}. \tag{12}$$

Near the open end of the capillary the electric field is small and $n_+(x) \approx n_-(x)$. Therefore, as follows from (4), expression (12) in this region must have the form *

$$n_-(x) \approx (C_0 - j_+x)/2.$$

If this condition is required to be satisfied, the $\wp$-function is expressed in terms of a hyperbolic function, and instead of (12) we have

$$n_-(x) = \frac{C_0 - j_+ x}{2}\,\mathrm{cth}^2\left[\frac{1}{3}(-j_+)^{-1}(C_0 - j_+ x)^{3/2} + C\right],$$

$$C = (-1)^{1/2}\frac{\sqrt{2}}{2}C_2. \tag{13}$$

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* This expression coincides with the usual expression for the concentration distribution in the diffusion region [(6)].

It is interesting to note that $n_-(x)$, as defined by formula (12), satisfies the equation

$$n_-\frac{d^2 n_-}{dx^2} - 2n_-^3 - \frac{1}{2}\left(\frac{dn_-}{dx}\right)^2 + (C_0 - j_+ x)n_-^2 + \frac{3}{2}\,\frac{j_+}{(C_0 - j_+ x)}\,n_-\frac{dn_-}{dx} + \frac{2j_+^2}{(C_0 - j_+ x)^2} = 0.$$

If this equation is compared with equation (5), it turns out that the latter is solved in elliptic functions if certain small terms (for small j_+) are added to it. However, it would have been very difficult to guess the form of these terms in advance.

Using expression (13) for $n_-(x)$, from equations (2) we find, neglecting small terms,

$$E(x) = \frac{j_+}{C_0 - j_+ x} + \frac{2(C_0 - j_+ x)^{1/2}}{\mathrm{sh}\left[\frac{2}{3}(-j_+)^{-1}(C_0 - j_+ x)^{3/2} + 2C\right]}; \tag{14}$$

$$n_+(x) = \frac{C_0 - j_+ x}{2}\,\mathrm{th}^2\left[\frac{1}{3}(-j_+)^{-1}(C_0 - j_+ x)^{3/2} + C\right]. \tag{15}$$

From (4), neglecting the electric field small at the end of the capillary, we obtain

$$C_0 = 2 + j_+ l. \tag{16}$$

Since the ion concentration is a positive quantity, it follows from the form of (13) that $C_0 \geq 0$. Therefore, for $|j_+|$ with $j_+ < 0$, not all values are admissible, but only values smaller than $2/l$. The value $j_+ = -2/l$ corresponds to the usual limiting current $I_+^{\lim} = 2D_+ N_0 / L$. Using (16), one can clarify the meaning of the applicability condition for the asymptotics ($|s| \gg 1$). This condition is fulfilled in any case if the inequality

$$\left|\left(I_+^{\lim} + I_+\right)/I_+^{\lim}\right| \gg (\varkappa L)^{-2/3}. \tag{17}$$

is satisfied.

Since the length of the capillary considerably exceeds the Gouy length, the asymptotics is applicable almost up to the limiting currents.

In writing (13)–(15) we assumed that the positive ions are discharged at the electrode of the same sign. By an appropriate choice of the arbitrary constant C, one can write the corresponding expressions for the opposite case. Formally, they are obtained from (13)–(15) if in (13) the cotangent is replaced by the tangent, in (15) the tangent by the cotangent, and in (14) the sign before the second term is changed.

Far from the point of zero charge, because of the rapid variation of the hyperbolic functions, it is indeed possible to divide the entire volume of the solution into two regions: the region of the diffuse layer, where there is a volume electric charge ($0 \leq X \leq L_d$), and the region of the diffusion layer ($L_d \leq X \leq L$), in which the condition of electroneutrality is satisfied. In this case the thickness of the diffuse part of the double layer does not remain constant, but changes when the current changes. For positive current ($I_+ > 0$) the diffuse layer is somewhat pressed toward the electrode. From (13)–(16) it follows that, for the thickness of the diffuse layer, in order of magnitude one may write

$$L_d \sim \varkappa^{-1} \frac{1}{\sqrt{1 + I_+/I_+^{\lim}}}. \tag{18}$$

For negative current ($I_+ < 0$) the thickness of the diffuse layer expands according to law (18), provided only that $|I_+| \ll I_+^{\lim}$. As the current approaches the limiting value ($I_+ \to -I_+^{\lim}$), the thickness of the diffuse layer tends to a finite value $L_d^{\max}$, of order of magnitude equal to

$$L_d^{\max} \sim \varkappa^{-1}(L\varkappa)^{1/3}. \tag{19}$$

It follows from (19) that the maximum thickness of the diffusion layer considerably exceeds the Gouy length, since the length of the capillary is much greater than the Gouy length. The presence of volume charges at distances exceeding the Gouy length, as the current approaches the limiting value, was first qualitatively investigated in ([7]).

It follows from (19) that even the most extended diffusion layer occupies only a small part of the capillary, since

$$L_d^{\max}/L \sim (L\chi)^{-2/3} \ll 1.$$

We express our gratitude to Corresponding Member of the Academy of Sciences of the USSR V. G. Levich for formulating the problem and for his constant interest in the work, and also to Yu. A. Chizmadzhev for useful discussions.

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Received
12 IV 1962

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