POLARIZATION CURVE FOR QUASIEQUILIBRIUM PROCESS OF ELECTROCHEMICAL ANION REDUCTION

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In an earlier paper [1] a solution was found to the problem of the current in a 2−1−1 (1−2−1) solution of an electrolyte during a quasiequilibrium electrode reaction. The object of the present paper is to discuss the error in this solution and the derivation of current−voltage characteristics for the respective electrode process. As mentioned earlier, both these problems involve determination of the integration constant entering into the argument of the hyperbolic functions which describe the distributions of the particles in the field. Discussion of these questions must therefore commence with determination of this constant.

Normally continuity of the potential at the boundary between the Helmholtz and diffusion layers is used as the boundary condition which determines this constant in similar problems. If it is assumed that the dielectric constant at this boundary changes abruptly from ε_0 (in the compact layer) to ε (in the diffusion layer and in the whole solution), the condition for continuity of the potential can be described in the following form:

$$\varepsilon_0 E|_{0-0} = \varepsilon E|_{0+0}, \tag{1}$$

where $E|_{0-0}$ and $E|_{0+0}$ are the potential gradients which are realized on approaching the Helmholtz plane from the left (from the electrode side) and from the right (from the solution) respectively. Since the potential drop in the compact layer is assumed to be linear,

$$E|_{0-0} = (\psi_1 - \varphi)/d\varkappa, \tag{2}$$

where φ is the electrode potential, ψ_1 is the potential of the Helmholtz plane,* and $d\varkappa$ is the dimensionless thickness of the compact layer. After determination of the integration constant by means of Eq. (1) the current−voltage characteristics can be obtained by using an expression for the electrode reaction rate in accordance with the equations of electrochemical kinetics. It is difficult to perform these operations specifically owing to the impossibility of obtaining an analytic solution for Eq. (1) written in explicit form. It is found, however, that the problem is substantially simplified when the operations are performed in the reverse order (determination of the constant from an expression for j and derivation of the polarization curve from the condition of Eq. (1)).

The expression for the rate of the electrode process (irreversible cathode reaction) in dimensionless form can be written as follows:

$$j = \frac{k_1}{z_1 D_{1.1} \varkappa} n_1(0) \exp[\alpha z_S(\varphi - \psi_1)].$$

If for the sake of definiteness it is assumed that $z_S = 2$ and $\alpha = 0.5$,† the latter equation takes the following form:

*φ and ψ_1 are dimensionless potentials which differ by the factor e/kT = F/RT from those normally used in practice.

† The case where $\alpha \neq 0.5$ does not introduce any fundamental difficulties but only complicates the specific form of the final results.

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$$j = k_1 \frac{n_1(0)}{n_3(0)} e^{\varphi}, \qquad k_1 = \frac{k_1}{2D_{11}\varkappa}. \tag{3}$$

Substitution of the ratio of the surface dimensionless concentrations $n_1(0)/n_3(0)$, calculated from the results of the earlier paper, in Eq. (3) leads to the following equation with respect to the integration constant C_3:

$$\mathrm{sh}^2\left[\frac{(6-2C_0)^{3/2}}{3\beta j} + C_3\right] = \frac{2 + n_1(l)\,(1 + j/j_d)}{2\{(j_T/j)^{1/3} - 1\}}, \tag{4}$$

where $n_1(l)$ is the dimensionless depth concentration of the discharging substance, $j_d = n_1(l)/\beta l$ is the limiting diffusion current, and $j_T = k_1 n_1(l)(1 + j/j_d)e^{\varphi}$, where $j < 0$.

As will be seen from the following analysis there is no need to solve Eq. (4), i.e., to determine C_3 in explicit form, although this is a simple task. It is therefore possible to turn now to discussion of the error in the previously obtained solution, with a view to establishing the applicability region of results based on this solution.

In our case determination of the accuracy of the solution must comprise two stages. Firstly, it is necessary to determine the possibility of reducing the equation for the relative concentration of "nonconducting" ions (n_3) to the Painlevé equation and, secondly, it is necessary to determine the error in the asymptotic solution of the latter. Here both questions will be examined in a fair amount of detail since, apart from their importance for determining the region of electrode process parameters where the results are formally capable of being used, they are of additional interest. Here it is necessary to turn to the original equation with respect to the function $n = n_3 - 1$. We will write it for the case where $\alpha z_1 = \beta z_2$ with $z_1 = 2z_2 = 2z_3 = 2$:

$$n''' - 6nn' - [6 - 2C_0 - \beta j y]\, n' = 0. \tag{5}$$

It is easy to confirm that the substitutions

$$n = 2[6 - 2C_0 - \beta j y]\, W \quad \text{and} \quad S = -\frac{2[6 - 2C_0 - \beta j y]^{3/2}}{3\beta j}$$

bring it to the following form:

$$W''' = \frac{8W^2}{S} + \frac{2W}{3S} + 12WW' + W' - \frac{3W''}{S} - \frac{5}{9S^3} W'. \tag{6}$$

If in this equation we reject all the terms which contain the new independent variable S in the denominator, we obtain the following expression for W:

$$W = -\frac{1}{4\,\mathrm{Sh}^2\,\gamma}, \quad \text{where} \quad \gamma = \frac{[6 - 2C_0 - \beta j y]^{3/2}}{3\beta j} + C_3. \tag{7}$$

On changing to n_3 the last expression gives the same result as the result obtained in [1] by replacement of Eq. (5) by the corresponding Painlevé equation followed by asymptotic solution. It should be noted that when the conditions $\alpha z_1 \neq \beta z_2$ and $z_1 = 2z_2 = 2z_3 = 2 (z_2 = 2zI = 2z_3 = 2)$ are satisfied the equation with respect to the analogous function W_1 has the following form:

$$W_1''' = \frac{aW_1^2}{S} + \frac{bW_1}{S} + 12W_1W_1' + W_1' + \frac{C}{S^2} W_1' + \frac{d}{S} W_1'',$$

where the coefficients a, b, c, and d are determined by the ratio between α and β. If it is found that retention only of terms 12WW' and W' in the right hand side of Eq. (6) with $\alpha z_1 = \beta z_2$ is sufficient to obtain a solution which is valid over a wide range of electrode reaction parameters, it is possible that under certain conditions a similar method would also be legitimate with $\alpha z \neq \beta z_2$. It is proposed subsequently to determine the conditions for realization of this possibility.

To return now to an evaluation of the solution obtained in [1], it can be said that the latter will be clearly valid if the above-mentioned method for solving Eq. (5) is legitimate. In order to determine the

accuracy of the proposed solution it is necessary to analyze Eq. (6). As already mentioned, with the asymptotic solution only the terms 12WW' and W' are retained in the right hand side of Eq. (6). By using Eq. (7) to write these terms it can be seen that they have identical sign; consequently the right hand side of the retained equation only becomes zero at the end of the diffusion layer (of the capillary [1]), and the condition $12|WW'| > |W'|$ can be satisfied near the electrode, whereas this inequality is reversed at a distance from the electrode. Hence, for the solution to be correct it is sufficient that the rejected terms should always remain much less than $|W'|$ in absolute value. For the terms $2W/3S$ and $5/9S^2W'$ this is fulfilled when $|S| \gg 1$. On the other hand, the term $|8W^3/S| \ll 12|WW'|$ under the same condition $|S| \gg 1$. Finally, the term $3W'/S$ is commensurate with 12WW' only in the region where $Sh\ 2\gamma \simeq |S|$, but there $12|WW'| \ll |W'|$ if $|S| \gg 1$. To summarize the foregoing it can be stated that the proposed asymptotic solution of Eq. (6) is legitimate if the condition $|S| \gg 1$ is satisfied. However,

$$|S| = \frac{2}{3}\frac{[6 - 2C_0 - \beta j y]^{3/2}}{|\beta j|} \geqslant \frac{2}{3}\frac{[6 - 2C_0 - \beta j y]^{3/2} L\varkappa}{n_1(l)} \gg 1$$

at reasonable values for the electrolyte concentration ($\varkappa^2 = 4\pi e^2 N_{30}/\varepsilon kT$, where L is the length of the capillary), and the solution is therefore certainly valid. Thus, Eq. (4) can be used formally for the constant C_3 in a practically limitless range of electrode process parameters. After establishing this fact it is possible to pass on to derivation of the current–voltage characteristics.

It is easy to show by means of Eq. (1) and the results of the earlier paper that the polarization curve is determined by the following equation:

$$\frac{1}{3}\ln\frac{j_T}{j} = \varphi + \frac{\varepsilon\, d\varkappa}{\varepsilon_0}\{(j/j_T)^{1/3} - 1\}\{2(j_T/j)^{1/3} + n_1(l)(1 + j/j_d)\}^{1/2}. \tag{7}$$

From the definition of j_T and, moreover, it follows formally from Eq. (4) that $j \leq j_T$ and $j \leq j_d$. By analyzing Eq. (7) at special points it can be found that the condition for a maximum (or two if j almost coincides with j_d when $\varphi = 0$) is $j = j_d$, and the condition for a minimum has the following form:

$$[2(j_T/j)^{1/3} + n_1(l)(1 + j/j_d)]^{1/2} = \frac{\varepsilon\, d\varkappa}{2\varepsilon_0}\left[1 + \left(\frac{j_T}{j}\right)^{1/3} + \left(\frac{j}{j_T}\right)^{1/3} n_1(l)(1 + j/j_d)\right]. \tag{8}$$

It can be shown that Eq. (8) practically coincides with

$$(j_T/j)^{1/6} = \frac{\varepsilon\, d\varkappa}{2^{3/2}\varepsilon_0}[1 + (j_T/j)^{1/3}],$$

from which we obtain the following values for $(j_T/j)^{1/6}$ at the minimum $(j_T/j)^{1/6} \simeq 2^{1/2}\varepsilon_0/\varepsilon\, d\varkappa \mp [2\varepsilon_0^2/(\varepsilon\, d\varkappa)^2 - 1]^{1/2}$. If it is assumed that $d \sim 10^{-8}$ cm, the discriminant $2\varepsilon_0^2/(\varepsilon\, d\varkappa)^2 - 1$ is greater than zero with not too large N_{30} values, and moreover $2\varepsilon_0^2/(\varepsilon\, d\varkappa)^2 \gg 1$, so that for $(j_T/j)^{1/6}_{min}$ we obtain:*

$$(j_T/j)^{1/6}_{min} = 2^{3/2}\varepsilon_0/\varepsilon\, d\varkappa. \tag{9}$$

By substituting the value for j_T in this expression we obtain for the potential corresponding to the minimum:

$$\varphi_m = A - 5\ln\varkappa + \ln N_{30} + \ln j_m - \ln(1 + j_m/j_d), \tag{10}$$

where $A = 9\ln 2 + 6\ln(\varepsilon_0/\varepsilon d) - \ln(k_1/D_{11}) + \ln N_{10}$; N_{10} and N_{30} are the volume concentrations of the reacting "nonconducting" ions respectively. Substitution of Eqs. (9) and (10) in Eq. (7) leads after rearrangement† to the following relationship:

$$\ln\frac{j_m}{1 + j_m/j_d} = 4 + 3\ln 2 - A + 2\ln(\varepsilon_0/\varepsilon d\varkappa) + 3\ln\varkappa - \ln N_{30} \tag{11}$$

*The second route is not suitable since $j \ll j_T$.

†Here the terms $(j_m/j_T)^{1/3}$ and $n_1(l)(1 + j/j_d)$ in Eq. (7) are rejected.

and Eq. (10) then takes the following form:

$$\varphi_m = 4 + 3\ln 2 + 2\ln(\varepsilon_0/\varepsilon d) - \ln(4\pi e^2/\varepsilon kT) - \ln N_{30}. \quad (12)$$

The following expression for the current at the minimum follows from Eq. (11):

$$j_m = -\frac{aj_d}{a + j_d}, \quad (13)$$

where

$$a = -\exp[4]\cdot 2^{-3}\left(\frac{\varepsilon d}{\varepsilon_0}\right)^4 \frac{k_1 N_{30}^{1/2}}{D_{1.1}}\left(\frac{\pi e^3}{\varepsilon kT}\right)^{3/2} N_{10}.$$

Thus, with increase in N_{30} the current should tend towards a limiting value. In the region with low concentrations of indifferent electrolyte $j_m \simeq a$, and therefore for the measured current at the minimum we obtain:

$$J_m = -\frac{\exp[4]}{4} k_1 N_{10} N_{30}^2 \varepsilon^2 \left[\frac{d}{\varepsilon_0}\right]^4 \left[\frac{\pi e^2}{kT}\right]^2.$$

Finally we should discuss the possibility of making practical use of the results. The first limitation to their use is the requirement for quasiequilibrium in the process ($\alpha z_1 = \beta z_2$), i.e., $2 - 2mD_{11}/D_{12} = pD_{11}/D_2$, where (according to [1]) m and p are the numbers of doubly and singly charged anions formed in the elementary discharge event from one particle of the reacting anion,* and D_{12}, D_2, and D_{11} are the respective diffusion coefficients of the same ions. According to data on the diffusion coefficients [2, 3], the process $[PtCl_6]^{2-} + 4e^- \rightarrow Pt^0 + 6Cl^-$ ($D_{PtCl_6^{-2}} \simeq 0.6\text{-}0.7 \times 10^{-5}$ cm^2/sec, $D_{Cl^-} \simeq 2.0 \times 10^{-5}$ cm^2/sec) can evidently be considered to be quasiequilibrium. It is likely that other examples of reactions in a similar class may be found, but the author did not attach fundamental significance to this question.

The second limitation arises from the imperfection of the electrolyte model, to the ions of which no finite size has been attributed. At the same time the idea of a compact layer, the existence of which arises partially from the very existence of an effective ionic radius, has been introduced. Evidently this internal inconsistency of the theory will not lead to any substantial distortion of results until the radius of the ionic atmosphere, calculated directly for the Helmholtz plane, is much greater than the thickness of the compact layer. If we consider the case of large negative charges on the electrode surface, there will be mainly cations of the indifferent electrolyte in the Helmholtz plane, and then for the Debye parameter $1/\varkappa_0$ we obtain:

$$\frac{1}{\varkappa_0} \simeq \frac{(\varepsilon kT)^{1/2}}{2\pi^{1/2} e n_3^{1/2}(0) N_{30}^{1/2}} = \frac{1}{\varkappa} n_3^{-1/2}(0).$$

Substitution of the surface concentration $n_3(0)$ gives $1/\varkappa_0 = (1/\varkappa)(j/j_T)^{1/6}$. Hence, the above-mentioned limitation will have the following form:

$$(j/j_T)^{1/6} \gg |\varkappa d|. \quad (14)$$

Although the condition (14) considerably narrows the region of applicability for the relationships obtained, it should merely be regarded as a necessary but by no means satisfactory limitation. This is due to the fact that the value of the potential gradient in the compact layer including its end ($E|_{0-0}$) is here assumed to be constant. † In accordance with the ideas of a discrete double layer [4, 5], the value of $E|_{0-0}$ should differ appreciably from the potential gradient within the compact layer, although the potential drop remains practically linear on the greater part of it. In fact the existence of this deviation results from the discreteness of the double layer and cannot be taken into the calculation in the region where the effect of the ionic radius is insignificant. The Debye theory of strong electrolytes, the analog of which is the theory of the diffuse

*The discharge of an anion is considered as the most frequently encountered case where the signs of the charges on the electrode and the reacting particle coincide.

† The assumption about the stepwise nature of the change in ε is less rigid.

double layer, is known to be applicable to the concentrations of electrolyte in the order of 10^{-6}-10^{-5} mole/cc, and Eq. (14) therefore certainly becomes adequate with the imposition of an additional limitation on N_{30}. Thus, for regions on the polarization curves where the results obtained are applicable the condition $j/j_T \gg |\varkappa d|^6$ is satisfied, and values up to 10^{18}-10^{19} particles/cm^3 are permissible for N_{30}. It is possible that this region can be widened somewhat by using some more flexible model of the compact layer. However, construction of such a model will only be expedient in the absence of bridging nature in the discharge of the anions [6]. Unfortunately the author does not have the appropriate experimental data at his disposal, and further discussion cannot as yet be continued here. It is possible that relationships analogous to those obtained in the present work can be obtained for processes of the type $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ and also in certain other cases.

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