CURRENT-VOLTAGE CURVES FOR THE ELECTROREDUCTION OF ANIONS

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UDC 541.138.3 :546

In the analysis of polarization curves for anion electroreduction it is obviously necessary to calculate the so-called "ψ_1-effect". The equilibrium formula of Frumkin and Florianovich [1] reflects very well the basic features of the $J - \varphi$ curves for these types of electrode processes. At the same time, sufficient attention has not been paid to the question of the validity of its application. The answer to this question can be obtained only by comparing this equilibrium formula with the results obtained from examining the nonequilibrium double layer. In [2], on the basis of a solution of the corresponding problem [3], a polarization curve was obtained for a quasi-equilibrium electrode process which follows the scheme:

$$A_{1.1}^{2-} + [2(m-1)+p]\,e^- \rightarrow mA_{1.2}^{2-} + p\,A_2^-. \tag{1}$$

An examination was carried out for the case where the transfer coefficient α_1 is equal to 0.5 and the number of electrons taking part in the slow step of the electrode reaction z_S is equal to the charge on the ion being discharged, that is for $z_S = 2$. Generalization of these results to other values of α_1 and z_S do not present any difficulty; the corresponding equations will be derived below. In addition, current-voltage characteristics for processes of the following type:

$$A_{1.1}^{2-} + 2(m-1)\,e^- \rightarrow mA_{1.2}^{2-} \tag{2}$$

will be worked out in this paper for the presence of either a mono- or divalent base electrolyte cation in the solution.* And finally, a comparison of the results obtained with results from the equilibrium formula of Frumkin – Florianovich will be presented. Since the premises and deduction method for the polarization curves in the cited cases are analogous to those used in the previous paper [2], we can confine ourselves here to the final relationships. It is only necessary to stipulate that the results of the diffusion problem calculation considered in [5] for a 2-2-1 electrolyte, and the results of [4] (for a 1-1-1-electrolyte) generalized for a 2-2-2 electrolyte, are used in the derivation of $J - \varphi$ curves.

The polarization curve for electrode reaction (2) when the base electrolyte cation is monovalent (2-2-1 electrolyte) has the following form:

$$\ln\left[\frac{1}{2}+\frac{\alpha-\beta}{3}jl\right]+a\ln(j_\tau/j)+\frac{\varepsilon d\varkappa}{\varepsilon_0}\left\{2\left[\frac{3}{2}+(\alpha-\beta)jl\right]\right\}^{1/2}$$
$$\times\left\{\left(j_\tau/j\right)^a-\frac{2}{3}\right\}\left[\left(j_\tau/j\right)^a+\frac{1}{3}\right]^{1/2}\left(j/j_\tau\right)^a=\varphi. \tag{3}$$

In the case of a divalent cation (2-2-2 electrolyte), the polarization curve expression becomes:

$$\frac{1}{2}\ln[1+(\alpha-\beta)jl]+\frac{a}{2}\ln(j_\tau/j)+\frac{\varepsilon d\varkappa}{\varepsilon_0}[1+(\alpha-\beta)jl]^{1/2}$$
$$\times\{(j_\tau/j)^{a/2}-(j_\tau/j)^{-a/2}\}=\varphi. \tag{4}$$

*It is easily seen that Eq. (2) is obtained from (1) for p = 0. It turns out that the diffusion problem corresponding to this particular case (2-2-1-1 electrolyte) can be solved.

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Here j and φ are the dimensionless reaction rate and potential ($j = \frac{J}{D_{11} z_3 N_{30} \varkappa}$, $\varphi = e\Phi/kT$), $\alpha = 1$, $\beta = mD_{11}/D_{12}$, $l = \varkappa L$, the dimensionless diffusion layer thickness, $\varkappa^2 = \frac{4\pi e^2 z_3 N_{30}}{\varepsilon kT}$, ε, the dielectric constant of the solvent, d/ε_0, the ratio of the thickness of the Helmholtz layer to its dielectric constant,

$$a = \begin{cases} [2 + \alpha_1 z_S]^{-1} & \text{2-2-1- electrolyte} \quad (z_3 = 1) \\ 2[2 + \alpha_1 z_S]^{-1} & \text{2-2-2- electrolyte} \quad (z_3 = 2) \end{cases}$$

$$j_T = \frac{k_1}{D_{11}\varkappa} \frac{2 \cdot 3^{\alpha_1 z_S - 1} \alpha}{(\alpha - \beta)} \cdot \left\{ [3/2 + (\alpha - \beta) jl]^3 - [3/2]^3 + \frac{27(\alpha - \beta)}{4\alpha} n_{11}(l) \right\} \times [3/2/(\alpha - \beta) jl]^{-[2 + \alpha_1 z_S]} \exp [\alpha_1 \varkappa_S \varphi] \quad \text{2-2-1- electrolyte}$$

$$j_T = \frac{k_1}{D_{11}\varkappa} n_{11}(l) \left\{ 1 + \frac{\alpha jl}{n_{11}(l)} [2 + (\alpha - \beta) jl] \right\} \{1 + (\alpha - \beta) ji\}^{-\left(1 + \frac{\alpha_1 z_S}{2}\right)} \times \exp [\alpha_1 z_S \varphi] \text{ 2-2-2- electrolyte}$$

$n_{11}(l) = 2N_{10}/N_{30}$ for a 2-2-1 electrolyte and $n_{11}(l) = N_{110}/N_{30}$ for a 2-2-2 electrolyte, and k_1, the rate constant for the cathodic process calculated with respect to the point of zero charge (i.e., for $\varphi = 0$).

In addition, for electrode reaction (1) we have for any value of α_1 and z_S with quasi-equilibrium conditions [2, 3]:

$$a \ln j_T/j + \frac{\varepsilon d\varkappa}{\varepsilon_0} 2^{1/2} \{1 - (j_T/j)^\alpha\} \left\{ (j_T/j)^\alpha + \frac{n_{11}(l)}{2} (1 + j/j_d) \right\}^{1/2} = \varphi, \tag{5}$$

where

$$a = [2 + \alpha_1 z_S]^{-1}, \quad j_T = \frac{k_1 n_{11}(l)}{2D_{11}\varkappa} (1 + j/j_d) \exp[\alpha_1 z_S \varphi], \; n_{11}(l) = 2N_{110}/N_{30}.$$

According to the results obtained in Eqs. (3), (4), and (5), the electrode potential is divided into three terms, the first of which represents the potential fall caused by the presence of a variable cation concentration within the limits of the diffusion layer [6],* the second, the potential drop in the diffuse layer, and the third, the potential jump in the compact layer. The ohmic potential drop caused by the current flow through the solution does not enter the expression for the polarization curve, since small terms proportional to j were omitted in the derivation of $j - \varphi$ curves [2]. For potentials greatly removed from the point of zero charge $|j_T|$ must be much larger than $|j|$, if $|j|$ for $\varphi = 0$ is close to j_d. Indeed, if the bulk electrolyte concentration is low ($\varepsilon d\varkappa/\varepsilon_0$ significantly less than 1), then the magnitude of $(j_T/j)^a$ must be much greater than unity in order that the potential jump in the compact layer make up a noticeable part of the bulk drop. Then the current-voltage characteristics in the stated region can be written in the following form:

$$\ln \left[1/2 + \frac{\alpha - \beta}{3} jl \right] + a \ln \frac{j_T}{j} + \frac{\varepsilon d\varkappa}{\varepsilon_0} [3 + 2(\alpha - \beta) jl]^{1/2} (j_T/j)^{\alpha/2} = \varphi. \tag{3'}$$

$$\frac{1}{2} \ln [1 + (\alpha - \beta) jl] + \frac{a}{2} \ln (j_T/j) + \frac{\varepsilon d\varkappa}{\varepsilon_0} [1 + (\alpha - \beta) jl]^{1/2} (j_T/j)^{\alpha/2} = \varphi \tag{4'}$$

$$a \ln (j_T/j) + \frac{\varepsilon d\varkappa}{\varepsilon_0} 2^{1/2} (j_T/j)^{\alpha/2} = \varphi. \tag{5}$$

Far from the point of zero charge, the base electrolyte cations should be mainly found in the compact layer, and thus, it can be assumed that the corrected equilibrium expression can be used to determine the potential. We will now check this.

Dividing the pre-electrode layer into diffuse and diffusion regions we can write down the following expression for j†:

$$j = \frac{k_1 z_3}{z_1 D_{11}\varkappa} n_{11}(\rho) [n_3(\rho)]^{-\frac{[z_1 + \alpha_1 z_S]}{z_3}} \exp [-(z_1 + \alpha_1 z_S) \psi_1] \exp [\alpha_1 z_S \varphi], \tag{6}$$

* This component of the potential is absent in Eq. (5) because the base electrolyte cation concentration in the diffusion layer is constant for a quasi-equilibrium process [2].

† Here ψ_1 signifies the potential drop in the diffuse layer only. The potential drop in the diffusion layer is reckoned by the factor $[n_3(\rho)]^{\frac{-(z_1 + \alpha_1 z_S)}{z_3}}$.

where $n_{11}(\rho)$ and $n_3(\rho)$ are the values of the dimensionless concentrations of the anion being discharged and the base electrolyte cation, respectively, at the boundary between the diffuse and diffusion regions. If we assume that

$$j_T = \frac{k_1 z_3}{z_1 D_{11} \varkappa} n_{11}(\rho) [n_3(\rho)]^{-1/\alpha z_3} \exp[\alpha_1 z_S \varphi], \tag{6'}$$

we obtain from Eq. (6)

$$\psi_1 = a \ln (j_T / j), \text{where } a = [z_1 + \alpha_1 z_S]^{-1}. \tag{7}$$

On the other hand, one can write* from the equations for the equilibrium double layer for $(d\psi/dy)|_{y=0}$:

$$(d\psi/dy|_{y=0} = E|_{0+0} = -\left\{\frac{2n_1(\rho)}{z_1}(e^{-z_1\psi_1} - 1) + \frac{2n_2(\rho)}{z_2}(e^{-z_2\psi_1} - 1) + \frac{2n_3(\rho)}{z_3}(e^{z_3\psi_1} - 1)\right\}^{1/2}. \tag{8}$$

In the stated region of large cathodic polarization, the last expression can be replaced by

$$E|_{0+0} \cong -\left[\frac{2}{z_3}\right]^{1/2} [n_3(\rho)]^{1/2} \exp\left[\frac{z_3\psi_1}{2}\right]. \tag{9}$$

Now, using the same condition of continuity of the polarization vector as in [2] in the form

$$\psi_1 = \varphi - \frac{\varepsilon d\varkappa}{\varepsilon_0}[(2/z_3) n_3(\rho)]^{1/2} \exp\left[\frac{z_3\psi_1}{2}\right],$$

we have for substitution of ψ_1, from Eq. (7):

$$a \ln (j_T/j) = \varphi - \frac{\varepsilon d\varkappa}{\varepsilon_0} [(2/z_3) n_3(\rho)]^{1/2} (j_T/j)^{\alpha z_3/2}.$$

If the potential drop in the diffusion layer is now added to the left-hand side of this equation (it was not considered in Eq. (8), then we finally obtain:

$$\frac{1}{z_3} \ln n_3(\rho) + a \ln (j_T/j) + \frac{\varepsilon d\varkappa}{\varepsilon_0} [(^2/z_3) n_3(\rho)]^{1/2} (j_T/j)^{\alpha z_3/2} = \varphi. \tag{10}*$$

The magnitudes of the dimensionless concentrations of the cation $n_3(\rho)$ and the anion being discharged $n_{11}(\rho)$ at the boundary of the diffuse and diffusion layers can be found easily within the limits of the assumption that electroneutrality is maintained in the diffusion layer [1, 7]. It is not difficult to convince oneself of the fact that Eq. (10) for the conditions discussed above (2-2-1, 2-2-2, and 2-1-1 electrolytes) reduces to Eqs. (3'), (4'), and (5'), respectively. The following expression for the potential and the rate measured at the minimum of the J – φ curve is easily obtained from Eq. (10):

$$\Phi_{\min} = \frac{2z_1}{\alpha_1 z_S z_3}\frac{RT}{F} + \frac{2RT}{z_3 F} \ln \frac{2z_1}{\alpha_1 z_S z_3} + \frac{2RT}{z_3 F} \ln (\varepsilon_0/d) - \frac{RT}{z_3 F} \ln (4\pi e^2 \varepsilon / kT) - \frac{RT}{z_3 F} \ln 2 - \frac{RT}{z_3 F} \ln N_{30}. \tag{11}$$

* In writing Eq. (8) it is assumed that the conditions $l \gg \rho > \varkappa^{-1}$ are realized, although this may not be the case [4, 5].

†When j_T is written in the form $j_T = (k_1 Z_3)/(z_1 D_{11} \varkappa) n_{11}(\rho) \exp[\alpha_1 z_S \varphi]$, the term $1/z_3 \ln n_3(\rho)$ would be absent in Eq. (10). However, here we adhere to the stated sequence of operations, which are conducive to a fuller understanding of the physical picture.

$$J_{\min} = (z_3)^{\frac{z_1+z_3-\alpha_1 z_S}{z_3}} \left[\frac{\alpha_1 z_S}{z_1}\right]^{2z_1/z_3} \exp\left[\frac{2z_1}{z_3}\right] \times \left[\frac{d}{\varepsilon_0}\right]^{\frac{2z_1}{z_3}} \left[\frac{2\pi e^2 \varepsilon}{kT}\right]^{z_1/z_3}$$

$$\times k_1 N_{11}(\rho)\, N_{30}^{z_1/z_3}, \text{where } n_{11}(\rho) = \frac{z_1 N_{11}(\rho)}{z_3 N_{30}}. \qquad (12)$$

For $|j| \ll j_{d,m}$ (limiting current with correction for migration) $N_{11}(\rho) \simeq N_{110}$, and, therefore for solutions close to a binary electrolyte,

$$J_{\min} = k_2 N_{110} N_{30}^{z_1/z_3}$$

It is obvious from Eq. (11) that the shift in the potential of the minimum point with respect to the point of zero charge should be equal to the order of 10 RT/F for small N_{30}. Thus, the assumption made above that $(j_T/j)^a \gg 1$ is valid for this potential region. At the same time, this justifies the use of the process parameters of the equilibrium expressions in this region. The limitations concerning possible use of the results obtained in an experimental study of anionic electroreduction processes have the same character that was found in [2].

All of the discussion presented above was concerned with the case of an irreversible cathodic reaction. It is not difficult to carry out their generalization for a completely reversible cathodic wave. In this case it is shown that specific minima on the curves for anion electroreduction disappear, and thus it can be concluded that for the case of an imperfectly reversible wave the depth of the minimum should depend on the degree of reversibility of the process.

The author thanks Prof. Ya. V. Durdin, V. I. Kravtsov, and a series of other co-workers in the Electrochemistry Department of the A. A. Zhdanov Leningrad State University for discussing the results of this and previous studies.

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