# ANALYSIS OF POLARIZATION CURVES FOR ELECTROREDUCTION OF ANIONS

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It is well known that the magnitude of charge on a species being discharged and the value of the transfer coefficient are of prime importance when the corresponding corrections are introduced in the $\Psi_1$ effect. In the application to anion electroreductions the problem is usually solved by determining the value of the derivative $(\partial \ln[I_d/(1 + I/I_d)]/\partial \ln N_{30})N_{110}$ on the secants $\Phi + (RT/Fz_3)nN_{30} = \text{const}$* according to the method of Frumkin and Petri [1] and by constructing corrected Tafel plots (CTP) with the aid of Gierst's graphic method [2].

In the present communication an expression will be obtained on the basis of the results in [4] for the partial derivative referred to above; certain additional properties of the secants $\Phi + (RT/Fz_3)\ln N_{30} = \text{const}$ will be cited; and a method will be proposed for determining the transfer coefficient (with an accuracy even to the number of electrons transferred in the slow step of the electrode reaction) which, in contrast to the CTP method, does not require knowledge of the dependence of double-layer capacity on electrode potential.

It had been shown earlier [4] that in the case of irreversible electroreduction of anions on a sufficiently negatively charged electrode surface,† the polarization is defined by the equation

$$\frac{1}{z_3}\ln n_3(\rho) + a\ln(j_T/j) + \frac{\varepsilon\, d\varkappa}{\varepsilon_0}\left[\frac{2n_3(\rho)}{z_3}\right]^{1/2}(j_T/j)^{\alpha z_3/2} = \varphi, \qquad (1)$$

where $n_3(\rho) = N_3(\rho)/N_{30}$ is the dimensionless concentration of a cation of charge $z_3$ at the boundary between diffuse layer and diffusion layer; the quantity

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

is understood as the dimensionless rate of electroreduction of the discharging anion (of charge $z_1$) under the condition where the dimensionless concentration $n_{11}(\rho)$ has been established at the boundary between diffuse layer and diffusion layer at a rate $j = I/D_{11}\varkappa z_3 N_{30}$ and at a potential $\varphi = F\Phi/RT$ in the absence of the $\Psi_1$ effect; $k_1$ and $D_{11}$ are the rate constants of the electrode reaction and of diffusion, respectively; $d\varepsilon/\varepsilon_0$ is the ratio between the thickness and dielectric constant of the Helmholtz layer, multiplied by the dielectric constant of the solvent; $\varkappa^2 = 4\pi e^2 z_3 N_{30}/\varepsilon kT$, $a = [z_1 + \alpha_1 z_S]^{-1}$, and $\alpha_1 \cdot z_S$ is the apparent transfer coefficient. The terms on the left-hand side of (1) correspond to the potential drops across the diffusion layer, diffuse layer, and compact layer.

In order to simplify the subsequent calculations we shall assume that the concentration of the base electrolyte is large enough so that the change in electrolyte concentration in the diffusion layer can be

*The notation of [3, 4] is preserved here; especially, the potential in the region of negative charges on the electrode surface is taken as positive.

†The condition for sufficiently large negative surface charge is written in the form $(j_T/j)^a \gg 1$ and corresponds to a condition in the double layer where the concentration of anions in the Helmholtz plane can be neglected in comparison to that of the cations.

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neglected in comparison with its bulk value. From this assumption it follows that $n_3(\rho) \simeq 1$, and $n_{11}(\rho) \simeq n_{110}(1 + j/j_d)$, when $j < 0$, $j_d > 0$, where $j_d$ is the limiting diffusion current. The assumption formulated above is not one of principle, and leads only to the absence of a migrational correction in the current. In the electroreduction of anions this is usually small and can, at least to a first approximation, be calculated [5].

Consider the variation in the reaction rate when the potential drop across the compact layer is constant, i.e., when

$$\frac{\varepsilon\, d\varkappa}{\varepsilon_0}\left[\frac{2}{z_3}\right]^{1/2}(j_T/j)^{\alpha z_3/2} = \text{const}'. \tag{2}$$

Taking logarithms in (2) and considering that $\psi_1 = a \ln (j_T/j)$, we have at constant $\varphi - \psi_1$ and constant bulk concentration of the discharging species:

$$\varphi + \frac{1}{z_3}\ln N_{30} = \text{const}. \tag{3}$$

Thus, constancy of the potential drop across the compact layer corresponds to the invariability of the quantity $\varphi + (1/z_3)\ln N_{30}$, as had to be expected. By differentiating (1) with respect to $\ln N_{30}$ it is not difficult to obtain the well-known expression for $\partial \ln[I/(1 + I/I_d)]/\partial \ln N_{30}|_{N_{110}}$ on the secants $\varphi + (1/z_3)\ln N_{30} = \text{const}$.

$$\left.\frac{\partial \ln [I/(1+I/I_d)]}{\partial \ln N_{30}}\right|_{N_{110},\ \varphi+\frac{1}{z_3}\ln N_{30}} = z_1/z_3. \tag{4}$$

We shall discuss certain properties of current and potential on the secants mentioned. We note, first of all, that the potentials of the minima also belong to the family of curves $\varphi + (1/z_3)\ln N_{30} = \text{const}$; this follows from the expression for the potential at the minimum of the I–Φ curve

$$\Phi_{\min} = A - \frac{RT}{z_3 F}\ln N_{30},$$

which in general form was obtained in [4]. Once this fact has been established experimentally, then the other secants can be constructed from the condition $\Phi - \Phi_{\min} = \text{const}''$. From the identity

$$j_T/j = [j_T/j]_{\min}[(j + j_d)/(j_d + j_{\min})]\left[\frac{j_{\min}}{j}\right]\exp[\alpha_1 z_S(\varphi - \varphi_{\min})],$$

where the index "min" is attached to the values of the variables in the minimum, it follows further—when the expression*

$$[j_T/j]_{\min}^{\frac{\alpha z_3}{2}} = \frac{2z_1}{\alpha_1 z_S z_3}\cdot\frac{\varepsilon_0}{\varepsilon d\varkappa}\left(\frac{z_3}{2}\right)^{1/2}$$

is inserted, first into this identity and then into (2)—that along the secant $\varphi + (1/z_3)\ln = \text{const}$. The ratio $[(j_d + j)j_{\min}/(j_d + j_{\min})j]$ must be constant, where j and $j_{\min}$ correspond to the same values of $N_{30}$. One more point must be made, viz., that for $\psi_1$ at the minimum one must have

$$\psi_{1,\min} = \Phi_{\min} - \frac{2z_1 RT}{\alpha_1 z_S z_3 F} \tag{5}$$

* This is obtained from (1) as condition for the minimum.

and one, therefore, has for the current in the minimum the expression

$$I_{\min} = k_1 N_{110} \left(1 + \frac{I_{\min}}{I_d}\right) \exp\left[\frac{2z_1^2 + 2z_1\alpha_1 z_S}{\alpha_1 z_S z_3}\right] \exp\left[-z_1\varphi_{\min}\right]. \tag{6}$$

We shall now dwell on the possibility of determining the apparent transfer coefficient directly from the I–Φ curves without using data on the double layer capacity. We shall first point out certain general properties of the polarization curves which are readily obtained from relation (1) upon differentiating it with respect to the corresponding parameters:

$$\begin{aligned}
&\text{I } ap = \frac{1}{2}\gamma[1 - az_3 p] && \text{V } z_1(t-2) = \frac{z_3}{2}\gamma[z_1 - \alpha_1 z_S - z_1 t]\\
&\text{II } az_1 q = \frac{1}{2}\gamma[1 + az_3\alpha_1 z_S q] && \text{VI } z_1 a + z_3 a\omega = \frac{z_3}{2}\gamma[1 + a\alpha_1 z_S - az_3\omega]\\
&\text{III } \dot{r}z_1 - 1 = \frac{z_3}{2}\gamma[1 + \alpha z_S r] && \text{VII } \tau = 1\\
&\text{IV } az_1 S = \frac{z_3}{2}\gamma[1 - az_3 S] && \text{VIII } d\nu = -\frac{1}{2}\gamma[1 + az_3\nu]
\end{aligned} \tag{7}$$

The following notation was introduced into (7):

$$p = \left.\frac{\partial \ln I_n}{\partial \ln N_{30}}\right|_{N_{110},\varphi}; \quad q = \left.\frac{\partial\varphi}{\partial \ln N_{30}}\right|_{N_{110}, I_n};$$

$$r = \left.\frac{\partial\varphi}{\partial \ln N_{110}}\right|_{N_{30}, I_n}; \quad S = \left.\frac{\partial \ln I_n}{\partial \ln N_{110}}\right|_{N_{30},\, \varphi - \frac{1}{z_1}\ln N_{110}};$$

$$t = \left.\frac{\partial \ln I_n}{\partial \ln N_{110}}\right|_{N_{30},\, \varphi + \frac{1}{z_1}\ln N_{110}}; \quad \omega = \left.\frac{\partial \ln I_n}{\partial \ln N_{110}}\right|_{N_{110},\, \varphi - \frac{1}{z_3}\ln N_{30}};$$

$$\tau = \left.\frac{\partial \ln I_n}{\partial \ln N_{110}}\right|_{N_{30},\varphi} = \left.\frac{\partial \ln I}{\partial \ln N_{110}}\right|_{N_{30},\varphi};$$

$$\nu = \left.\frac{\partial \ln N_{110}}{\partial \ln N_{30}}\right|_{\varphi, I}; \quad I_n = \frac{I}{1 + I/I_d}; \quad \gamma = \frac{\varepsilon\, dx}{\varepsilon_0}\left[\frac{2}{z_3}\right]^{1/2} [j_T/j]^{az_3/2}.$$

The relations (7) seem to allow us, at first glance, to calculate the transfer coefficient $\alpha_1 z_S$; it can be shown, however, that these relations establish only the correlation between the corresponding partial derivatives and the charges on the discharging anion and the base electrolyte cation. One can readily see from (7), moreover, that all partial derivatives along secants $\varphi + (1/z_3) \ln N_{30} = \text{const}$ must be constant because on these secants, the potential drop across the compact layer, $\gamma$, is constant.*

According to (7), the potential drop across the compact layer can be expressed through any partial derivative, e.g.,

$$\gamma = 2ap / (1 - az_3 p). \tag{8}$$

This way of writing down the above potential drop is convenient because in the experimental determination of the partial derivative used in writing the expression of $\gamma$, one can always work in a sufficiently narrow range of currents and potentials, while assuming a constant ratio $d/\varepsilon_0$. Writing now the volt–ampere characteristic (1), with (8), in the form

$$\varphi - a \ln (j_T / j) - (2ap / 1 - az_3 p) = 0,$$

*With an accuracy defined by the variation in the compact-layer parameters $(d/\varepsilon_0)$.

we have after simple transformations

$$z_1\varphi + \ln I_n - \frac{2(z_1+\alpha_1 z_S)^2}{z_3^2\left(\frac{z_1+\alpha_1 z_S}{z_3}-p\right)} = \ln(k_1 N_{110}) - \frac{2(z_1+\alpha_1 z_S)}{z_3}. \quad (9)$$

If we write in this equation, instead of the constant $k_1$, the expression following for it from Eq. (6) we obtain a result which gives the theoretical solution to the problem of determining $\alpha_1 z_S$ solely on the basis of data from polarization curves. In practice it may turn out, however, that the results concerning the minima are distorted for some reason or other. The following way of determining $\alpha_1 z_S$, also based on the application of (9), can, therefore, be recommended. If on a plot of $\varphi$ against $\ln I_n$ one draws a secant $b\varphi + \ln I_n = \text{const}^m$ (or, better, a number of secants with different values of b which, however, should not equal $z_1$) then it follows from (9) that the difference $(z_1-b)\varphi - 2(z_1+\alpha_1 z_S)^2/z_3^2[(z_1+\alpha_1 z_S)/z_3 - p]$ must remain constant along this secant when $N_{110}$ is fixed. If, then, the value of p is known (the quantities $\partial \ln I_n/\partial \ln N_{30}|_N$ at the points of intersection between the experimental $\varphi - \ln I_n$ curves and the secants $b\varphi + \ln I_n = \text{const}^m$) it will in principle not be difficult to select the correct value for $\alpha_1 z_S$, the more so because the slope of the plot of $\varphi$ against $[(z_1+\alpha_1 z_S)/z_3 - p]^{-1}$ is also determined by the transfer coefficient. Together with this, Eq. (9) gives the possibility of simultaneously determining also the rate constant of the cathodic reaction.

It is possible to find other, analogous approaches for the determination of $\alpha_1 z_S$ but, in the author's opinion, the approach outlined here is the simplest in the analysis of the experiment, even though it does require good experimental accuracy. But the CTP method involves, basically, the same requirement. The author was unable to use the method indicated for determining the transfer coefficient because there are no data in the literature sufficient to do so.

In conclusion it must once again be stressed that the accuracy of the results in determining the parameters of the electrode reaction ($\alpha_1 z_S$ and $k_1$) is limited only by the experimental uncertainties, in spite of the fact that the volt–ampere characteristic is obtained with the premise that the ratio $d/\varepsilon_0$ is independent of the position on the I–Φ curve. Of course, it is here assumed that the common conceptual models of the theory of slow discharge are valid.

## LITERATURE CITED


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