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Abstract

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A. Ya. Gokhshtein

On the Theory of $I-t$ Curves in the Reduction of Anions at a Dropping Electrode in the Presence of an Adsorbing Catalyst

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A number of interesting results in the theory of polarographic currents with simultaneous adsorption of a surface-active substance, the rate of which is determined by diffusion, were obtained in the works of Weber, Koutecký, Koryta, and Kuta. These authors studied in detail the case of a linear dependence of the reaction rate on coverage (^{1}), and for an exponential dependence, without taking the influence of concentration polarization into account, gave a calculation of the initial segment of the $I-t$ curve (^{2}).

The direction of the present work was chosen in connection with the investigations of A. N. Frumkin, O. A. Petrii, and N. V. Nikolaeva-Fedorovich (^{3}), who obtained, in the reduction of multiply charged anions in the presence of adsorbing cations, $I-t$ curves with a well-pronounced maximum. The aim of the present work is to take concentration polarization into account and to derive relations between the characteristic points of the $I-t$ curve over its entire course and the quantities that determine the kinetics of ion discharge.

The current I, whose dependence on time t is to be determined, is caused by an irreversible reaction proceeding at a constant potential φ on the surface of an expanding spherical electrode. The volume of the sphere increases at a constant rate m/γ; m (in g/sec) is the rate of flow of mercury, γ (in g/cm^3) is the specific gravity of mercury. The initial concentrations of the anion and catalyst are C and C_0, and the diffusion coefficients are D and D_0. With the addition of a supporting electrolyte and for a diffusion-layer thickness small in comparison with the electrode radius, the equation of convective diffusion has the form (^{4})

$$\partial c/\partial t-(2x/3t)\partial C/\partial x=D\,\partial^2C/\partial x^2; \tag{1}$$

$C(x,t)$ is the concentration of the anion at a distance x from the electrode surface. The boundary condition follows from the equation of A. N. Frumkin (^{5})

$$\frac{I}{nFS} = D\,\frac{\partial C(0,t)}{\partial x} = C(0,t)\,k\exp\frac{(n+\alpha)F\psi_1}{RT}\exp\left[-\frac{\alpha F\varphi}{RT}\right], \tag{2}$$

where α is the barrier coefficient, n is the number of electrons, and k is the reaction-rate constant. The surface density of the adsorbed substance can be determined from the Ilkovič equation (^{1}).

$$Q(t) = 2(3/7\pi)^{1/2}D_0^{1/2}C_0t^{1/2} \quad (\text{mol/cm}^2). \tag{3}$$

Let us denote the ψ_1-potential in the absence of catalyst by ψ_{10}; then one may approximately take

$$\psi_1(t) = \psi_{10} + \sigma Q(t), \tag{4}$$

where the constant coefficient σ is determined by the kinetics of the process.

Combining (2), (3), and (4), we obtain

$$D\,\frac{\partial C}{\partial x}(0,t) = C(0,t)k\exp\left\{\frac{F}{RT}[(n+\alpha)\psi_{10}-\alpha\varphi]\right\}\exp\left[2\left(\frac{3}{7\pi}\right)^{1/2}\frac{F}{RT}\sigma(n+\alpha)D_0^{1/2}C_0t^{1/2}\right]. \tag{5}$$

In the new variables

$$y = t^{2/3}x, \qquad h = st^{7/3}, \qquad s = \left[2\left(\frac{3}{7\pi}\right)^{1/2}\frac{F}{RT}\sigma(n+\alpha)D_0^{1/2}C_0\right]^{14/3}. \tag{6}$$

(1) and (5) take the form

$$\frac{\partial C}{\partial h} = \frac{3D}{7s}\frac{\partial^2 C}{\partial y^2}, \qquad \frac{\partial C}{\partial y} = s^{2/7}\frac{k}{D}\exp\left\{\frac{F}{RT}[(n+\alpha)\psi_{10}-\alpha\varphi]\right\}h^{-2/7}e^{h^{3/14}}C(0,h). \tag{7}$$

The first of these equations, for $C(y,0) = C$, is equivalent to the following:

$$C(0,h) = C - \left(\frac{3D}{7\pi s}\right)^{1/2}\int\limits_0^h \frac{[\partial C(0,\xi)/\partial y]\,d\xi}{\sqrt{h-\xi}}. \tag{8}$$

Eliminating $C(0,h)$ from (7) and (8), introducing the new unknown function

$$f(h) = \frac{1}{C}\left(\frac{3D}{7\pi s}\right)^{1/2}\frac{\partial C(0,h)}{\partial y} \tag{9}$$

and, taking (6) into account, reducing the constants, we obtain for $f(h)$ the integral equation

$$f(h) = \frac{1}{p}h^{-2/7}e^{h^{3/14}}\left[1 - \int\limits_0^h \frac{f(\xi)\,d\xi}{\sqrt{h-\xi}}\right], \tag{10}$$

which contains the parameter

$$p = \frac{2F}{RT}\,\frac{\sigma(n+\alpha)D_0^{1/2}D^{1/2}C_0}{k\exp\frac{F}{RT}\left[(n+\alpha)\psi_{10}-\alpha\varphi\right]}; \tag{11}$$

f, h, and p are dimensionless. For what follows it is convenient to single out, from (11), groups of coefficients:

$$p = \frac{\nu C_0}{\omega}, \qquad \nu = \sigma(n+\alpha)D_0^{1/2}, \qquad \omega = \frac{RT}{2F}D^{-1/2}k\exp\frac{F}{RT}\left[(n+\alpha)\psi_{10}-\alpha\varphi\right]. \tag{12}$$

In a series of experiments in which ν and ω are constant, the parameter p varies with the catalyst concentration C_0. Estimation of the integral standing in the square brackets in (10) shows that for $h > 10^3$ and $p > 10^4$ (these limits do not constrain practical calculations) the singularity of the function f at $h = 0$ may be neglected without risk of making an error in the fourth digit.

Equation (10) was solved for various values of p by the numerical method described earlier (^{6}). Having determined the function $f(h)$ from (10), returning to the old variables and collecting the coefficients, we obtain for the current flowing from the entire surface $S(t)$ of the electrode at time t the expression

$$I = nFDS(t)\,\partial C(0,t)/\partial x = 6.458\,F(F/RT)^{2/3}(m/\gamma)^{2/3}nCD^{1/2}(\nu C_0)^{7/3}ft^{4/3}. \tag{13}$$

Owing to the relation (6) between t and h, the function f may be assigned to each of these variables, $f(h) = f(st^{7/3})$. The current is proportional to $ft^{4/3}$, and, consequently, to $fh^{4/7}$. It follows from this that I and f attain maxima at different values of h. We shall denote the values of f and h at which the current is maximal ($I_{\max}$) by f_m and h_m. To determine them it is sufficient to multiply the calculated function $f(h)$ by $h^{4/7}$. The position of its maximum will give h_m, after which $f_m = f(h_m)$. Using the relations obtained earlier for the

Figure 1

Figure 1: Figure 1

descending branches of polarograms (^{7}), the following representation of $f(h)$ at some distance from its maximum may be given:

$$f(h) = 0.318\,(h - h_a)^{-1/2}. \tag{14}$$

Here only h_a depends on p; thus, for $p = 10^6$, $h_a = 0.972 \cdot 10^5$. From (14) it is seen that after the current maximum on the $I - t$ curve there should follow a minimum ($I_{\min}$). The corresponding $h_{\min}$ is determined from the condition for the minimum of the function $fh^{4/7}$. According to (14),

$$h_{\min} = 8h_a, \qquad f_{\min} = 0.318(7h_a)^{-1/2}. \tag{15}$$

(14) makes it possible to continue $f(h)$ after the value of this function has been calculated at $h \approx 3h_a$. Following $f(h)$, $f(h)h^{4/7}$ and $f(st^{7/3})t^{4/3}$ are computed (Fig. 1); the latter, when substituted into (13), gives the current as a function of time. Figure 1 also shows the change in the near-electrode concentration of the vo

time. Multiplication of the right-hand side of (13) by $h^{1/2}s^{1/2}t^{1/6} = 1$ (see (6)) gives another expression for the $I - t$ curve:

$$I = 13.093\,F\,(m/\gamma)^{2/3} nCD^{1/2}h^{1/2}ft^{1/6} = 2.30\,Fm^{2/3}nCD^{1/2}h^{1/2}ft^{1/6}. \tag{16}$$

It follows from (14) that, as h increases, $\left(h^{1/2}f\right) \to 0.318$. Substituting this limit into (16), we obtain, as a special case, the well-known Ilkovič equation. Thus, at large h,

$$I/I_{\text{lim}} = \sqrt{h/(h - h_a)};$$

for $h \gg h_a$ the $I - t$ curve merges with the limiting-current curve. Nomograms for constructing $I - t$ curves at any value of p, $10^3 \leq p \leq 10^9$ cm, are shown in Fig. 2.

Fig. 1. 1 –theoretically calculated $I - t$ curve; 2 –limiting current $I_{\max}$; 3 – $C(0,t)/C$. $p = 10^6$

We now proceed to derive relations for the maximum on the $I - t$ curve. The corresponding values f_m, h_m, $C(0,t_m)/C$, calculated from (10) for different values of p, are shown in Fig. 3. The interval of values chosen there, $10^3 \leq p \leq 10^9$, over which the corresponding functions are defined, includes the values of

Figure 2

Figure 2: Figure 2

p encountered in practice. It is noteworthy that $h_m^{1/2} f_m$ depends almost linearly on $\lg p$,

$$h_m^{1/2} f_m = 0.290 + 0.0341 \lg p, \qquad 10^3 < p < 10^9. \tag{17}$$

Fig. 2. $I - t$ curves for values p: 10^3; 10^4; 10^5; 10^6; 10^7; 10^8; 10^9, and the limiting current. At right—interpolation nomogram

Substitution of (17) into (16) leads to the basic equation for the current at the maximum of the $I - t$ curve:

$$I_{\max} = (0.666 + 0.0782 \lg p)\, F m^{2/3} n C D^{1/2} t_m^{1/6}. \tag{18}$$

Dividing (18) by the value of the limiting current at the same instant gives a relation convenient for applications: $I_{\max}/I_{\lim} = 0.91 + 0.107 \lg p$. (19) From (19) one can determine p without knowing many experimental constants. The limiting current can be obtained experimentally either (more accurately) reproduced from a portion of the $I - t$ curve sufficiently far from the peak. At $p = 10^6$, $I_{\max}/I_{\lim} = 1.55$ (Fig. 1). For the time of appearance of the maximum, from (6) we obtain

$$t_m = \frac{7\pi}{12} \left(\frac{RT}{F}\right)^2 \frac{h_m^{3/7}}{v^2 C_0^2},$$

$$t_{m,(20^\circ)} = 1.169 \cdot 10^{-3} \frac{h_m^{3/7}}{v^2 C_0^2},$$

$$t_{m,(25^\circ)} = 1.209 \cdot 10^{-3} \frac{h_m^{3/7}}{v^2 C_0^2}. \tag{20}$$

Fig. 3. f_m (1), h_m (2), $h_m^{1/2} f_m$ (3), $C(0, t'_m)/C$ (4) as functions of the parameter p

The exact values of h_m are given in Fig. 3; for $10^4 < p < 10^9$ the representation $h_m^{8/7} = 4(\lg p)^{2.04} \simeq 4 \lg^2 p$ is admissible. For two $I - t$ curves with different catalyst concentrations C_{01} and C_{02}, from (20)

$$t_{m1}/t_{m2} = (C_{02}/C_{01})^2 (h_{m1}/h_{m2})^{3/7}. \tag{21}$$

When $(C_{02}/C_{01}) < 2$, $(h_{m1}/h_{m2})^{3/7}$ is close to 1 and $(t_{m1}/t_{m2}) \simeq (C_{02}/C_{01})^2$, i.e., the time of the maximum t_m is very sensitive to a change in C_0, which can be used for analytical determinations. Conversely, relation (19) changes slowly, as $\lg C_0$. To determine from experimental data the quantities v and ω, it is sufficient to find p from (19) and then use equations (20) and (12) successively. Since errors are possible in determining the limiting current (10%), the value of p found from (19) must be refined using the nomogram in Fig. 2, using points of the ascending branch. For the shift of the ψ_1-potential at the point of maximum, $\Delta\psi_{1m} = [RT/(n+\alpha)F]h_m^{3/14} \simeq 2[RT/(n+\alpha)F]\lg p$. Substitution of $C(0,t_m)/C$ (Fig. 3) into (2) gives a simple relation between the maximum current and the rate constant.

Fig. 4. Experimental points and the curve calculated at $p = 10^6$, on a relative scale

Figure 4 shows the results obtained by (3) in an experiment with a solution of $5{\cdot}10^{-4}\ M\ K_2S_2O_8{+}2.5{\cdot}10^{-3} M Na_2SO_4{+}3{\cdot}10^{-5} M(C_4H_9)_4NJ$ at 20°, compared with the curve calculated for $p = 10^6$. From formulas (20) and (12) for this case ($C_0 = 3\cdot10^{-8}$ mol/cm^3) $v = 0.75\cdot10^7$ cm mol^{-1}sec$^{-1/2}$; $\omega = 2.25\cdot10^{-7}$ sec$^{-1/2}$; $\sigma = 1.44\cdot10^9$ cm^{2}mol^{-1}; $\Delta\psi_{1m} = 0.14$ V.

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Institute of Electrochemistry
Academy of Sciences of the USSR

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