ESTABLISHMENT OF ADSORPTION EQUILIBRIUM ON FLAT AND DROPPING ELECTRODES AND IRREVERSIBLE ELECTROCHEMICAL CONVERSION OF ADSORBED SUBSTANCES

(UDC 541.13)

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Translated from Élektrokhimiya, Vol. 1, No. 10,
pp. 1273-1279, October, 1965
Original article submitted June 10, 1965

An approximate method is proposed for solving the problems of diffusion kinetics, and has been used to solve the following problems: (1) for the adsorption of a surface-active substance on flat and dropping electrodes with an arbitrary adsorption isotherm under conditions of diffusion control, the dependence of the surface coverage by the adsorbed substance on the time has been found; (2) for irreversible electrochemical conversion of a substance adsorbed according to the Henry isotherm on a dropping electrode, the electric current has been calculated.

The adsorption of a depolarizer and electrochemically in active substances exerts a substantial influence on the kinetics of electrode processes [1]. Hence, for an understanding of many observed phenomena, one must know the principles of the adsorption of substances on the electrode.

The solution of the problems of diffusion kinetics pertaining to these questions in the case of a flat electrode is complex in the mathematical respect for nonlinear isotherms, while in the case of a dropping electrode, it is complex even for linear isotherms. Suffice it to indicate that there are solutions in the literature only for particular cases [2], mainly obtained through the use of computers. In view of this, it seems advisable to seek approximate methods of obtaining analytical solutions, the accuracy of which is sufficient for many practical applications.

In this work, an approximate method is proposed for the solution of these problems and is applied below to a number of concrete questions pertaining to adsorption.

ESTABLISHMENT OF ADSORPTION EQUILIBRIUM ON FLAT AND DROPPING ELECTRODES FOR ARBITRARY ADSORPTION ISOTHERMS

Let an electrode be placed in a solution containing a substance capable of being adsorbed at a moment of time $t = 0$. Let us denote the concentration of this substance as c_0. If the rate of adsorption is sufficiently great, then the surface concentration $\Gamma = \Gamma_m \theta$ (Γ_m is the maximum surface concentration), and the concentration near the electrode $(c)_{x=0}$ (x is the distance from the surface of the electrode to the depth of the solution) are related by the adsorption isotherm

$$\beta(c)_{x=0} = f(0). \tag{1}$$

The function $f(\theta)$ is determined by the concrete type of isotherm: for the Henry isotherm $f(\theta) = \theta$; for the Langmuir isotherm $f(\theta) = \theta/(1-\theta)$; for the Frumkin isotherm $f(\theta) = [\theta/(1-\theta) \exp(-\gamma\theta)$, etc. The value of β in (1) is a function of the electrode potential E. The equilibrium coverage θ_e is determined by the formula $\beta c_0 = f(\theta_e)$.

TABLE 1. Linear Isotherm (Arbitrary θ_e, $\xi = Dt/(\Gamma^2_m\ \beta)$)

	0,01	0,04	0,16	0,36	0,81	1,69	3,24	9
(θ/θ_e) Exact	0,10	0,19	0,33	0,43	0,54	0,64	0,72	0,82
(θ/θ_e) Approxi.	0,10	0,18	0,31	0,40	0,50	0,60	0,67	0,77
Discrepancy, %	—	5,3	6,0	6,7	7,4	6,2	6,9	6,1

TABLE 2. Langmuir Isotherm ($\xi = De^2_0t/\Gamma^2_m$)

	$\theta_e=0,3$			$\theta_e=0,6$			$\theta_e=0,9$		
	(θ/θ_e)Exact	(θ/θ_e)Approximate	Discrepancy %	(θ/θ_e)Exact	(θ/θ_e) Approximate	Discrepancy %	(θ/θ_e) Exact	(θ/θ_e) Approxi.	Discrepancy %
0,01	0,32	0,30	6,2	0,18	0,17	5,6	0,12	0,12	—
0,02	0,40	0,37	7,5	0,23	0,22	4,3	0,17	0,17	—
0,04	0,50	0,47	6,0	0,33	0,32	3,0	0,24	0,24	—
0,06	0,56	0,52	7,1	0,38	0,37	3,9	0,30	0,29	3,3
0,12	0,66	0,62	6,1	0,50	0,48	4,0	0,41	0,40	2,4
0,18	0,71	0,67	5,6	0,58	0,54	6,0	0,50	0,48	4,0
0,24	0,75	0,70	6,7	0,62	0,59	5,1	0,56	0,55	1,8
0,32	0,78	0,73	6,4	0,68	0,64	5,9	0,64	0,61	4,7
0,40	0,81	0,76	6,2	0,71	0,67	5,6	0,69	0,66	4,4

The solution of the corresponding diffusion problem for a flat electrode with the aid of the Duhamel equation is reduced to the following integral equation:

$$\Gamma = \int\limits_0^t dt' D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \left(\frac{D}{\pi}\right)^{1/2} \int\limits_0^t \frac{c_0 - (c)_{x=0}}{(t-t')^{1/2}} dt'. \tag{2}$$

For a dropping electrode, the analogous integral equation takes the form

$$\Gamma = t^{-2/3} \int\limits_0^t dt' (t')^{2/3} D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \left(\frac{3D}{7\eta}\right)^{2/7} \frac{1}{\pi^{1/2}} \int\limits_0^\eta \frac{c_0 - (c)_{z=0}}{(\eta-\eta')^{1/2}} d\eta'. \tag{3}$$

In the derivation of (3), we used the following transformation of the variables

$$z = xt^{2/3}, \qquad \eta = (3D/7)t^{7/3} \tag{4}$$

which reduces the diffusion equation for an expanding drop to the diffusion equation for a flat electrode.

In the expression beneath the integral sign in (2), the denominator for t' close to t is small; hence, if $(c)_{x=0}$ is a function that varies slightly with time, it can be brought out of the integral sign when t' = t. Analogously, in (3), $(c_{z=0}$ can be brought out of the integral sign when n' = n. After this, it is easy to obtain

$$\tau^{1/2} = \theta \frac{f(\theta_e)}{f(\theta_e) - f(\theta)} \tag{5}$$

where $\tau = t/t_0$ is the dimensionless time; t_0 is determined by the function

$$t_0 = \frac{\pi}{4} \frac{\Gamma_m{}^2}{Dc_0{}^2} \tag{6}$$

for a flat electrode and by the function

$$t_0 = \frac{7\pi}{12}\frac{\Gamma_m^2}{Dc_0^2} \tag{7}$$

for a dropping electrode. From (6) and (7) it is easy to see that the time of achievement of a definite coverage on a dropping electrode is $^{7}/_{3}$ times greater than the corresponding time for a flat electrode.

For short times, when $f(\theta) \simeq \theta$ and $\theta < f(\theta_e)$

$$\theta = \tau^{1/2} - \tau / f(\theta_e) \tag{8}$$

for long times, when $\theta \simeq \theta_e$

$$\frac{\theta}{\theta_e} = 1 - \frac{f(\theta_e)}{(df/d\theta)_{\theta=\theta_e}}\tau^{-1/2} \tag{9}$$

From the asymptotic expression (9) we can evaluate the time of establishment of adsorption equilibrium τ_0. If we consider that adsorption equilibrium is achieved when $\theta/\theta_e = 1-\gamma(\gamma < 1)$, then

$$\tau_0 = \left[\frac{1}{\gamma}\frac{f(\theta_e)}{(df/d\theta)_{\theta=\theta_e}}\right]^2. \tag{10}$$

In order to evaluate the accuracy of our approximation, let us compare the approximate solution obtained here with the exact analytical solution for the linear isotherm and the numerical solution for the Langmuir isothern (see Tables 1 and 2).

From the Table it is evident that the accuracy of the approximate solution in the case of a flat electrode is of the order of 8%. In view of the fact that the concentration near the electrode varies even somewhat more slowly for a dropping electrode than for a flat electrode, we should expect that the accuracy of the approximate solution will be no worse in this case.

IRREVERSIBLE ELECTROCHEMICAL CONVERSION OF ADSORBED SUBSTANCES ON A DROPPING ELECTRODE

Let us consider the process in which a substance from within the solution ($x \to \infty$), where it possesses a concentration c_0, diffuses to the surface of a dropping electrode ($x = 0$), is adsorbed upon it, and then enters into an irreversible electrochemical reaction:

$$\mathrm{A} \overset{\mathrm{el}}{\rightleftarrows} \mathrm{A}^{\mathrm{ads}} \qquad \mathrm{A}^{\mathrm{ads}} + ne^- \overset{\mathrm{el}}{\rightarrow} \text{product.}$$

The rate of adsorption, just as in the preceding case, will be considered sufficiently great that the surface concentration Γ and the concentration near the electrode $(c)_{x=0}$ are related by the adsorption isotherm. We shall consider the isotherm to be linear, i. e., $\beta\Gamma_m(c)_{x=0} = \Gamma$.

The mathematical problem is formulated in the following way:

$$\begin{gathered}\frac{\partial c}{\partial t} - \frac{2}{3}\frac{x}{t}\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} \\ t = 0,\ x > 0: c = c_0 \\ t > 0,\ x \to \infty: c \to c_0 \\ x = 0: \beta\Gamma_m(c)_{x=0} = t^{-2/3}\int_0 dt'(t')^{2/3} D\left(\frac{\partial c}{\partial x}\right)_{x=0} - \beta\Gamma_m k t^{-2/3}\int_0 dt'(t')^{2/3}(c)_{x=0}\end{gathered} \tag{11}$$

Here it is assumed that the current density $i = nFk\Gamma$, where k is the rate constant of the electrochemical reaction of the adsorbed substance.

Introducing new variables according to (4) in place of x, t, let us transform Eq. (11) into an equation of diffusion to a flat electrode, for which we shall subsequently use the Duhamel integral. The final problem reduces to a solution of the integral equation

$$\Gamma_m(c)_{x=0} = \left(\frac{7\eta}{3D}\right)^{-3/7} \frac{1}{\pi^{1/2}} \int_0^{\eta} d\eta' \frac{c_0 - (c)_{z=0}}{(\eta - \eta')^{1/2}} - \frac{\beta\Gamma_m k}{D}\left(\frac{7}{3D}\right)^{-4/7} \eta^{-2/7} \int_0^{\eta} d\eta' (\eta')^{-2/7} (c)_{z=0} \tag{12}$$

From physical considerations it is clear that in the case under consideration, the concentration near the electrode $(c)_{z=0}$ varies no more rapidly than in the cases outlined above. Hence, in the calculation of the integral

$$\int_0^{\eta} \frac{(c)_{z=0}}{(\eta - \eta')^{1/2}} d\eta'$$

just as in the preceding case, we can bring $(c)_{z=0}$ out from under the integral sign when $\eta' = \eta$. As a result, the integral Eq. (12) is reduced to the usual first-order linear differential equation

$$\zeta \frac{du}{d\zeta} + \frac{\frac{2}{3} + \frac{7}{6}\zeta^{1/2} + \frac{1}{2}\varepsilon\zeta}{1 + \zeta^{1/2}} u = \frac{7}{6} \frac{\zeta^{1/2}}{1 + \zeta^{1/2}} \tag{13}$$

here $u = (c)_{z=0}/c_0 = \theta/\theta_e$, $\zeta = t/t_0$,

$$(c)_{z=0}/c_0 = \theta/\theta_e, \quad \zeta = t/t_0,$$
$$t_0 = \frac{7\pi}{12}\frac{(\beta\Gamma_m)^2}{D}, \quad \varepsilon = \frac{7\pi}{6}\frac{k(\beta\Gamma_m)^2}{D}. \tag{14}$$

The solution of this equation takes the form

$$u = \frac{7}{3}\zeta^{-2/3}(1 + \zeta^{1/2})^{\varepsilon - 1}\exp(-\varepsilon\zeta^{1/2}) \int_0^{\zeta^{1/2}} dv\, v^{4/3}(1 + v)^{-\varepsilon}\exp(\varepsilon v). \tag{15}$$

Expression (15) is the solution of the problem posed. Its accuracy evidently is no lower than the accuracy of the solutions obtained in the first section of this work.

From (15) in the case of short times ($\zeta^{1/2} < 1, 1/\varepsilon$), we can obtain the following expressions for the function of u, the instantaneous current $I = nFk\Gamma S$ (S is the surface area of the dropping electrode), and the average current $\bar{I} = \frac{1}{t}\int_0^t I\,dt$:

$$u = \zeta^{1/2} - \zeta + \left(1 - \frac{3}{13}\varepsilon\right)\zeta^{3/2}\ldots$$
$$I = I_0\left[\zeta^{7/6} - \zeta^{5/3} + \left(1 - \frac{3}{13}\varepsilon\right)\zeta^{13/6}\ldots\right]$$
$$\bar{I} = I_0\left[\frac{6}{13}\zeta^{7/6} - \frac{3}{8}\zeta^{5/3} + \frac{6}{19}\left(1 - \frac{3}{13}\varepsilon\right)\zeta^{13/6}\ldots \tag{16}$$

For long times ($\zeta^{1/2} > 1, 1/\varepsilon$), the same quantities take the following form

$$
\begin{aligned}
u &= \frac{7}{3\varepsilon}\frac{1}{\zeta^{1/2}} - \frac{28}{9\varepsilon^2}\frac{1}{\zeta} + \left(\frac{28}{27\varepsilon^3} - \frac{7}{9\varepsilon^2}\right)\frac{1}{\zeta^{3/2}}\cdots \\
I &= I_0\left[\frac{7}{3\varepsilon}\zeta^{1/6} - \frac{28}{9\varepsilon^2}\frac{1}{\zeta^{1/3}} + \left(\frac{28}{27\varepsilon^3} - \frac{7}{9\varepsilon^2}\right)\frac{1}{\zeta^{5/6}}\cdots\right] \\
\bar{I} &= I_0\left[\frac{2}{\varepsilon}\zeta^{1/6} - \frac{14}{3\varepsilon^2}\frac{1}{\zeta^{1/3}} + 6\left(\frac{28}{27\varepsilon^3} - \frac{7}{9\varepsilon^2}\right)\frac{1}{\zeta^{5/6}}\cdots\right]
\end{aligned}
\tag{17}
$$

here

$$
I_0 = nFk\Gamma_m\theta_e 4\pi\left(\frac{3}{4\pi}\frac{m}{\rho}t_0\right)^{2/3}
\tag{18}
$$

m is the mass of mercury flowing out in 1 sec, ρ is the density of mercury.

From the results obtained it follows that the current density i ~ θ at the initial moments of time increases in proportion to $t^{1/2}$, while for sufficiently long times, it falls in proportion to $t^{-1/2}$, so that the current density i as a function of the time has a maximum. Physically, this result can be understood from the following considerations. At the initial moment of time, the diffusion flux is great, while the rate of the electrochemical reaction is small; hence θ increases. However, as θ increases, the rate of the electrochemical reaction increases, at the same time, the diffusion flux falls as a result of an increase in the thickness of the diffusion layer. As a result, θ, reaching some maximum value, begins to decrease. The time t_m at which θ is a maximum can be evaluated from (16), (17)

$$
kt_m \simeq 1.
\tag{19}
$$

t_m can be determined exactly by solving the equation

$$
\int_0^{\zeta_m^{1/2}} dv\, v^{4/3}(1+v)^{-\varepsilon}\exp(\varepsilon v) = \frac{\zeta_m^{2/3}(1+\zeta_m^{1/2})^{-\varepsilon}\exp(\varepsilon\zeta_m^{1/2})}{(4/3)\zeta_m^{-1/2} + (\varepsilon-1)(1+\zeta_m^{1/2})^{-1} - \varepsilon}.
\tag{20}
$$

The problem of irreversible electrochemical conversion of the substance in the adsorbed state, under consideration, when the limiting transition

$$
\beta\Gamma_m \to 0 \qquad \beta\Gamma_m k \to K
\tag{21}
$$

is fulfilled, turns into the problem of irreversible electrochemical conversion of a depolarizer without preliminary adsorption, with rate constant K ($i = nFK(c)_{x=0}$). When the limiting transition (21) is fulfilled, the time t_m at which the current density is a maximum approaches zero, so that in the limit the current density i as a function of the time decreases monotonically. In this limiting case, we obtain the following expression for i from (15):

$$
i = \frac{7}{3}\eta^{-7/6}\exp\left(-\frac{7}{3}\eta^{1/2}\right)\int_0^{1/2} dv\, v^{4/3}\exp\left(\frac{7}{3}v\right)
\tag{22}
$$

here

$$
\eta = \frac{3\pi}{7}\frac{K^2}{D}t.
$$

Expression (22) is the approximate equation of an irreversible polarographic wave. It is of interest to compare (22) with the exact solution of the corresponding problem [4]

For short times ($\eta^{1/2} < 1$)

$$
\begin{aligned}
i &= 1 - 0.70\eta^{1/2} + 0.38\eta\ldots \\
i &= 1 - 0.79\eta^{1/2} + 0.52\eta\ldots
\end{aligned}
$$

according to formula (2) according to [4]

For long times ($\eta^{1/2} > 1$)

$$i = \eta^{-1/2} - 0.57\eta^{-1} + 0.08\eta^{-3/2} \ldots$$

$$i = \eta^{1/2} - 0.66\eta^{-1} + 0.14\eta^{-3/2} \ldots$$

according to formula (22) according to [4]

When the limiting transition

$$k \to 0 \tag{23}$$

is fulfilled, the problem that we are considering is reduced to the problem of establishment of adsorption equilibrium for a linear isotherm. In this case, the time t_m for which the coverage θ is a maximum approaches infinity, so that in the limit the coverage θ as a function of the time monotonically increases. In this limiting case, we obtain formula (5) with $f(\theta) = \theta$ from (15).

Formulas (15), (16), and (17), which give sufficiently accurate approximate solution of the problem under consideration, are not very convenient for practical calculations. Hence, in those cases when great requirements for the accuracy of the calculations are not set, the following interpolation formulas can be used

$$u = \frac{\zeta^{1/6}}{1 + \zeta^{1/2} + \frac{3\varepsilon}{7}\zeta} \tag{24}$$

$$I = I_0 \frac{\zeta^{7/6}}{1 + \zeta^{1/2} + \frac{3\varepsilon}{7}\zeta} \tag{25}$$

$$\bar{I} = I_0 \frac{\frac{6}{13}\zeta^{7/6}}{1 + \frac{39}{48}\zeta^{1/2} + \frac{3}{13}\varepsilon\zeta} \tag{26}$$

These interpolation formulas have been selected in such a way that at short times they coincide with the first two members of formula (16), while for long times they coincide with the first member of formula (17).

From (24), we obtain the following expression for t_m

$$kt_m = 7/6 . \tag{27}$$

The maximum coverage θ_m in this case takes the form

$$\theta_m = \theta_e \frac{\left(\frac{7}{3\varepsilon}\right)^{1/6}}{2 + \left(\frac{7}{3\varepsilon}\right)^{1/2}} . \tag{28}$$

It is easy to find the formula of the wave from (26). From the condition $I = \frac{1}{2} I_d$, where the average limiting diffusion current I_d is equal to $I_0(2/\varepsilon)\,\zeta^{1/6}$, we obtain the following equation for the half-wave potential $E_{1/2}$

$$\zeta = \left[\frac{\frac{39}{48} + \left(\left(\frac{39}{48}\right)^2 + \frac{12}{13}\varepsilon\right)^{1/2}}{\frac{6}{13}\varepsilon} \right]^2 . \tag{29}$$

If $\varepsilon < 13/12(39/48)^2$, then (29) is converted to

$$\zeta^{1/2}\varepsilon = \frac{(13)^2}{48}. \tag{30}$$

If $k = k_0 \exp(-\alpha n F/RT\text{-}E)$ while β does not depend on the potential, then (30) can be represented as follows

$$E_{1/2} = \frac{RT}{\alpha nF}\left[\ln\left(\frac{7\pi}{3}\right)^{1/2}\frac{48}{(13)^2} + \ln\frac{k_0\beta\Gamma_m}{D^{1/2}} + \frac{1}{2}\ln t\right]. \tag{31}$$

If we consider the fact that $(-\alpha nF/RT\text{-}E)$, while $\beta = \beta_0 \exp[-a(E-E_m)^2]$ [5], then (30) takes the form

$$E_{1/2} = E_m - \frac{\alpha nF}{2RTa} \pm \left[\left(E_m - \frac{\alpha nF}{2RTa}\right)^2 - E_m^2 - \frac{1}{a}\left(\ln\left(\frac{3}{7\pi}\right)^{1/2}\frac{(13)^2}{48} - \ln\frac{k_0\beta_0\Gamma_m}{D^{1/2}} - \frac{1}{2}\ln t\right)\right]^{1/2}. \tag{32}$$

In this case there are two values of the half-wave potential, i. e., the wave possesses a maximum. Similar phenomena have been considered earlier [6]. If $\varepsilon > 13/12(39/48)^2$, then (29) is converted to the expression

$$\zeta\varepsilon = \frac{13}{3} \tag{33}$$

to which the following form may be imparted

$$E_{1/2} = \frac{RT}{\alpha nF}\left(\ln\frac{6}{13} + \ln k_0 + \ln t\right). \tag{34}$$

The authors are grateful to S. G. Mairanovskii for his useful discussion of this work.

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