Researches on the Polarographic Diffusion Current. I. Criticism of the Ilkoič Theory and Theoretical Revision of the Ilkovič Equation

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Introduction

The widely known Ilkovič equation representing the diffusion current at the dropping mercury electrode was first derived by D. Ilkovič(1) and later by MacGillavry and Rideal(2) and by Stackelberg(3); they obtained the same result, although each of them treated this problem in a different manner. Thus derived Ilkovič equation has been examined experimentally in several manners and it is proved that in many features this equation shows an excellent harmony with the observed facts. Recently, however, it has been pointed out by McKenzie(4) that the oscillographic investigation of the current-time curves during one drop-life gives a considerable deviation between the theoretical predictions and the experimental observations. Upon examining some fundamental postulates underlying the Ilkovič theory, we have reached to the conclusion that the ignorance of the curvature of mercury drop is not legitimate and that the Ilkovič theory should be revised to some extent.

In this paper the short derivation of Ilkovič equation will be shown in order to criticize

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(1) D. Ilkovič, *Collection Czech. Chem. Communs.*, **6**, 498 (1934).

(2) D. MacGillavry and E. K. Rideal, *Rec. trav. chim. Pays-Bas*, **56**, 1013 (1937).

(3) M. v. Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

(4) H. A. McKenzie, *J. Am. Chem. Soc.*, **70**, 3147 (1948).

the theory and then our revised theoretical treatment will be described comparing with the old one.

Derivation and Criticism of the Ilkovič Theory

Since in the ordinary polarographic electrolysis an excess amount of indifferent electrolyte is added to the solution to be electrolyzed, the depolarizer is obliged to reach to the dropping electrode surface only by diffusion. Thus the depolarizer is exhausted near the cathode surface and a diffusion layer surrounding the dropping electrode is established. Ilkovič has assumed that the thickness of the diffusion layer should be very small compared with the radius of the mercury drop, and that the movement of depolarizer is expressed by the first and the second laws of Fick; *i. e.*,

$$\mathrm{d}n = -D\cdot q\cdot \frac{\partial C}{\partial x}\cdot \mathrm{d}t \qquad (1)$$

and

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}, \qquad (2)$$

where C is concentration of the depolarizer in mol per cc., x, distance from the dropping electrode surface in cm., t, time in sec., D, diffusion constant of the depolarizer in cm.^{2} per sec. and $\mathrm{d}n$, the amount of the depolarizer which penetrates the cross-section q during the time $\mathrm{d}t$.
Then it is considered that the diffusion of the depolarizer is a unidimensional problem. The boundary conditions are as follows:

$$\left.\begin{array}{l} C = {}^*C\cdots\cdot\text{when } x>0,\quad t=0 \\ C = {}^\circ C\cdots\cdot\text{when } x=0,\quad t>0 \end{array}\right\} \qquad (3)$$

where $^*C$ and $^\circ C$ are the concentration in the bulk of the solution and at the electrode surface, respectively. Hence Eq. (2) can be integrated and the result is

$$C = {}^\circ C + ({}^*C - {}^\circ C)\cdot \mathrm{H}\left(\frac{x}{2\sqrt{Dt}}\right), \qquad (4)$$

where

$$\mathrm{H}(S) = \frac{2}{\sqrt{\pi}}\int_0^S e^{-\alpha^2}\cdot \mathrm{d}\alpha\ .$$

The concentration gradient at the cathode surface ($x=0$) can be expressed as follows:

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{{}^*C - {}^\circ C}{\sqrt{\pi D t}} = \frac{{}^*C - {}^\circ C}{\delta_1} \qquad (5)$$

$$\delta_1 = \sqrt{\pi D t}\ , \qquad (6)$$

where δ_1 is the differential thickness of the diffusion layer (see Fig. 1).

From Eqs. (1), (5) and (6), the total amount of the depolarizer transferred to the electrode surface by diffusion during the time interval from $t=0$ to $t=t$ is shown to be

$$\begin{aligned} -\int_{t=0}^{t=t}\mathrm{d}n &= \int_0^t D\cdot q\cdot \frac{{}^*C - {}^\circ C}{\delta_1}\cdot \mathrm{d}t \\ &= \int_0^t \frac{D\cdot q\cdot({}^*C - {}^\circ C)}{\sqrt{\pi D t}}\cdot \mathrm{d}t \\ &= \frac{1}{\pi}\left\{2q\,({}^*C - {}^\circ C)\sqrt{\pi D t}\right\} \end{aligned}$$

and accordingly

$$\frac{2}{\pi D}\cdot q\cdot \delta_1 = \int_0^t \frac{q}{\delta_1}\,\mathrm{d}t\ . \qquad (7)$$

This equation, which should be called the Stackelberg's intergral equation, represents that the differential thickness of the diffusion layer at the time t depends not only on the total amount which has reached the electrode surface in the whole time elapsed after the diffusion has begun, but also on the surface area. Stackelberg considered an integral thickness of the diffusion layer, Δ_1, which would exist if there were a linear fall of the concentration. The differential and integral thickness of the diffusion layer are related to each other, as shown in Fig. 1, by the equation

$$4\delta_1 = \pi\Delta_1\ . \qquad (8)$$

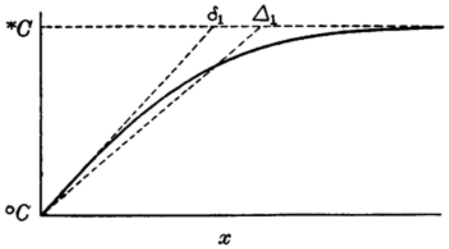

Fig. 1.—Schematic repesentation of the differential and integral thickness of the diffusion layer at a plane electrode.

Now at the dropping electrode, the volume and also the surface area of mercury drop increase with the time elapsed after the formation of the drop has commenced. Ilkovič has assumed a linear increase in the volume of the drop with time, *i. e.*,

$$\frac{4}{3}\pi\cdot r_1{}^3 = \frac{m_1}{d}\cdot t\,, \qquad (9)$$

where r_1 is the radius of the drop considered as a sphere at the time t, and m_1 is the rate of flow of mercury from the capillary in g. per sec., and $d=13.6$ is the specific gravity of mercury. Hence the surface area of mercury drop is given by

$$q=4\pi r_1^2=4\pi\left(\frac{3m_1}{4\pi d}\right)^{2/3}\cdot t^{2/3}. \qquad (10)$$

If this relation is inserted into Eq. (7), and the equation thus obtained is solved, ${}^d\delta_1$, the thickness of the diffusion layer around the dropping mercury electrode, is shown to be

$$^d\delta_1=\sqrt{\frac{3}{7}\pi D t}\,, \qquad (11)$$

which means that at the dropping electrode the diffusion layer is compressed by the expansion of the mercury drop and becomes much thinner compared with that at a stationary electrode. Consequently the concentration gradient at the dropping electrode surface is given by

$$^d\left(\frac{\partial C}{\partial x}\right)_{x=0}=\frac{{}^*C-{}^\circ C}{{}^d\delta_1}=\frac{{}^*C-{}^\circ C}{\sqrt{\frac{3}{7}\pi Dt}}\cdot \qquad (12)$$

If nF is the electricity equivalent to the electrode reaction of one mol of the depolarizer, it is shown from the Fick's first law that the instantaneous current intensity i is given by

$$i=\left(\frac{112\pi}{3}\right)^{1/2}\cdot\left(\frac{3}{4\pi d}\right)^{2/3} \cdot nF({}^*C-{}^\circ C)\cdot D^{1/2}\cdot m_1^{2/3}\cdot t^{1/6}. \qquad (13)$$

If t_1 is the drop time, the mean current $\bar{\imath}$ is shown to be

$$\bar{\imath}=\frac{1}{t_1}\int_0^{t_1} i\cdot \mathrm{d}t\,;$$

accordingly the following equation can be obtained :

$$\begin{aligned}\bar{\imath}&=\frac{6}{7}\cdot\left(\frac{112\pi}{3}\right)^{1/2}\cdot\left(\frac{3}{4\pi d}\right)^{2/3} \cdot nF\,({}^*C-{}^\circ C)\cdot D^{1/2}\cdot m_1^{2/3}\cdot t_1^{1/6}\\ &=0.627\,nF\,({}^*C-{}^\circ C)D^{1/2}\cdot m_1^{2/3}\cdot t_1^{1/6} \qquad (14,\mathrm{a})\end{aligned}$$

and also

$$\bar{\imath}=\frac{6}{7}i_{max}\,, \qquad (15)$$

where i_{max} is the maximum value of instantaneous current which flows at $t=t_1$. Under the condition where the mean value of the limiting diffusion current $\bar{\imath}_d$ is obtained,

$$\bar{\imath}_d=0.627\,nF\cdot{}^*C\cdot D^{1/2}\cdot m_1^{2/3}\cdot t_1^{1/6}, \qquad (14,\mathrm{b})$$

because in this case, $^\circ C$, the concentration of the depolarizer at the cathode surface can be regarded to be nearly zero. When $\bar{\imath}_d$ is measured in microampere (I_d), m_1 in mg. per sec. (m), and $^*C$ in millimol per liter (C), then the above equation is transformed to the form

$$I_d=605\,nCD^{1/2}m^{2/3}t_1^{1/6}. \qquad (14,\mathrm{c})$$

Note.— Ilkovič ⁽⁵⁾ has derived Eq. (12) by the following procedure. The movement of solution near the drop surface owing to the expansion of mercury drop can be represented by

$$qx=\text{const.}, \qquad (16)$$

and hence the diffusion layer is compressed to a much thinner layer, as already mentioned; Stackelberg ⁽³⁾ denoted this effect of the convection of solution by the word "Seifenblasenmodell."

Combination of Eqs. (10) and (16) gives v, the velocity of approach of solution to the drop surface; thus

$$v=\frac{\mathrm{d}x}{\mathrm{d}t}=-\frac{x}{q}\cdot\frac{\mathrm{d}q}{\mathrm{d}t}=-\frac{2x}{3t}\,. \qquad (17)$$

The concentration of the depolarizer C is completely determined by the two independent variables x and t; *i. e.*,

$$C=C\,(x,\,t)\,. \qquad (18)$$

Hence

$$\frac{\partial C}{\partial t}=\frac{\mathrm{d}C}{\mathrm{d}t}-\frac{\partial C}{\partial x}\cdot\frac{\mathrm{d}x}{\mathrm{d}t}. \qquad (19)$$

The Fick's second law states:

$$\frac{\mathrm{d}C}{\mathrm{d}t}=D\cdot\frac{\partial^2 C}{\partial x^2}\,. \qquad (20)$$

Consequently the following differential eqation is obtained from Eqs. (17), (19) and (20):

$$\frac{\partial C}{\partial t}=D\,\frac{\partial^2 C}{\partial x^2}+\frac{2x}{3t}\cdot\frac{\partial C}{\partial x} \qquad (21)$$

Ilkovič has derived Eq. (21) in such a manner. This equation, however, can be obtained in a different way, *i. e.*, the flux of the depolarizer, $\boldsymbol{f}$, is given by

$$\boldsymbol{f}=-D\cdot\frac{\partial C}{\partial x}+v\cdot C\,.$$

Accordingly it follows that

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(5) D. Ilkovič, *J. chim. phys.*, **35**, 129 (1938).

$$\operatorname{div} f = -\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial x^2} + v\frac{\partial C}{\partial x} + C \operatorname{div} v .$$

Since the medium is approximately incompressible it is seen that

$$\operatorname{div} v = 0 .$$

Consequently inserting Eq. (17) into the above equation gives Eq. (21).

Eq. (21) can be intergrated, as carried out by Ilkovič, but his procedure is rather difficult. The easiest way is as follows. Let us introduce a new quantity defined by

$$S = x \Big/ 2\sqrt{\frac{3}{7}Dt} \tag{22}$$

then the appropriate solution can be readily seen to be given by

$$C = {}^{\circ}C + ({}^{*}C - {}^{\circ}C)\cdot \mathrm{H}\left(\frac{x}{2\sqrt{(3/7)Dt}}\right). \tag{23}$$

From this equation the concentration gradient at the surface of dropping electrode, *i. e.*, Eq. (12) is obtained immediately.

It is quite curious that MacGillavry and Rideal⁽²⁾ obtained the same result although they treated this problem as a tri-dimensional diffusion, *i. e.*, they employed the spherical coordinate system. Upon examining their procedure it becomes evident that their theory is not legitimate because the velocity of approach of solution to the dropping electrode surface is considered to be zero, owing to the erroneous transformation of the coordinate system. This will be discussed again in the following article.

The Theoretical Revision of the Ilkovič Equation

Suppose that a diffusion process is occurring at a stationary spherical electrode. Let r be the distance from the center of the sphere, then in such a spherical coordinate the Fick's laws are written as follows:

$$\mathrm{d}n = -D\cdot q\cdot \operatorname{grad} C \cdot \mathrm{d}t, \tag{I}$$

$$\frac{1}{D}\cdot\frac{\partial C}{\partial t} \equiv \operatorname{div}\operatorname{grad} C = \frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial C}{\partial r}. \tag{II}$$

If r is the radius of the spherical electrode, the boundary conditions are given by

$$\left.\begin{aligned} C &= {}^{\circ}C \cdots\cdots \text{when} \quad r = r_1, \quad t > 0. \\ C &= {}^{*}C \cdots\cdots \text{when} \quad r > r_1, \quad t = 0. \\ C &= {}^{*}C \cdots\cdots \text{when} \quad r \to \infty . \end{aligned}\right\} \tag{III}$$

Thus the appropriate integral of the Eq. (II) is shown to be

$$C = {}^{\circ}C\frac{r_1}{r} + {}^{*}C\left(1 - \frac{r_1}{r}\right) + ({}^{*}C - {}^{\circ}C)\frac{r_1}{r}\cdot\frac{2}{\sqrt{\pi}}\int_0^{\frac{r-\,'1}{2\sqrt{Dt}}} e^{-S^2}\cdot \mathrm{d}S. \tag{IV}$$

Accordingly the concentration gradient at the electrode surface is given by

$$\left(\frac{\partial C}{\partial r}\right)_{r=r_1} = ({}^{*}C - {}^{\circ}C)\left(\frac{1}{r_1} + \frac{1}{\sqrt{\pi D t}}\right) = \frac{{}^{*}C - {}^{\circ}C}{\delta_r} \tag{V}$$

and δ_r, the differential thickness of the diffusion layer at the spherical electrode, is seen to be given by

$$\frac{1}{\delta_r} = \frac{1}{r_1} + \frac{1}{\sqrt{\pi D t}}. \tag{VI}$$

It can be shown from this formula that in this case the equation corresponding to the Stackelberg's integral equation is given by

$$\pi D \int_0^t \frac{r_1^2}{\delta_r}\cdot \mathrm{d}t = r_1^3\left\{\left(\frac{\delta_r}{r_1 - \delta_r}\right)^2 + 2\left(\frac{\delta_r}{r_1 - \delta_r}\right)\right\}. \tag{VII}$$

Furthermore, if we assume a linear fall of the concentration at the electrode surface, the integral thickness of the diffusion layer, $\varDelta_r$, is obtainable from the following integral

$$-\int_{t=0}^{t=t} \mathrm{d}n = \int_{r_1}^{r_1+\varDelta_r} {}^{*}C\cdot 4\pi r^2\cdot \mathrm{d}r - \int_{r_1}^{r_1+\varDelta_r}\left\{{}^{\circ}C + \frac{{}^{*}C - {}^{\circ}C}{\varDelta_r}(r - r_1)\right\}4\pi r^2\cdot \mathrm{d}r ,$$

and it is seen, as illustrated in Fig. 2, that $\varDelta_r$ is given by the following equation

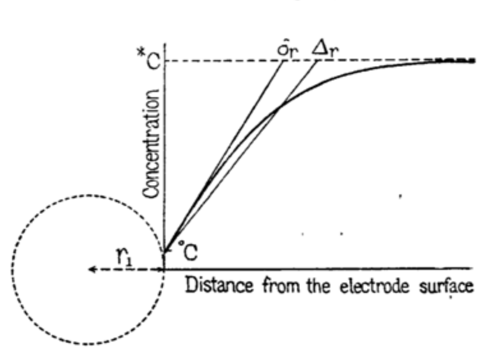

Fig. 2.—Schematic representation of the differential and integral thickness of the diffusion layer at a spherical electrode (dotted circle).

$$\pi\left\{\frac{1}{12}\left(\frac{\varDelta_r}{r_1}\right)^3+\frac{1}{3}\left(\frac{\varDelta_r}{r_1}\right)^2+\frac{1}{2}\left(\frac{\varDelta_r}{r_1}\right)\right\}=\left(\frac{\delta_r}{r_1-\delta_r}\right)^2+2\left(\frac{\delta_r}{r_1-\delta_r}\right) \quad \text{(VIII)}$$

If we assume a linear increase in the volume of mercury drop, it is evident that (cf. Eq. (9))

$$\left.\begin{aligned} r_1 &= a\cdot t^{1/3}, \\ a &= (3\,m_1/4\pi\,d)^{1/3}. \end{aligned}\right\} \quad \text{(i)}$$

If this relation is inserted into Eq. (VII), and the integral equation thus obtained is solved, the differential thickness of the diffusion layer around the dropping mercury electrode, denoted by ${}^d\delta_r$, can be derived as follows;

$$y=\frac{{}^d\delta_r}{r_1-{}^d\delta_r}$$

and

$$\mathrm{d}y/\mathrm{d}t=\dot{y}\,,$$

it can be readily seen that

$$\pi D\,a\int_0^t t^{1/3}\cdot\frac{y+1}{y}\cdot\mathrm{d}t=a^3t\,(y^2+2y).$$

Differentiation of this equation with respect to the time t gives

$$\begin{aligned}\pi Dat^{1/3}(y+1)&=a^3\{(y^3+2y^2)+2t(y+1)y\,\dot{y}\}\\ &\doteqdot a^3\{2(y^3+y^2)+2t(y+1)y\,\dot{y}\},\end{aligned}$$

where the condition $0<y<1$ is used. Thus it is found that the following relation holds approximately:

$$\pi Dt^{4/3}=a^2(2y^2t+2y\,\dot{y}t^2)=a^2\,\frac{\mathrm{d}}{\mathrm{d}t}\,(y^2t^2).$$

Upon integrating this equation, it is seen that

$$t^2\cdot a^2\cdot y^2=\frac{3}{7}\,\pi Dt^{7/3}$$

and

$$\frac{1}{y}=\frac{r_1}{{}^d\delta_r}-1\doteq\left(\frac{r_1^{\,2}}{\frac{3}{7}\,\pi\,D\,t}\right)^{1/2},$$

where it can be readily seen that the integral constant is zero.

Consequently the thickness of the diffusion layer at a dropping electrode is given by

$$\frac{1}{{}^d\delta_r}=\frac{1}{r_1}+\frac{1}{\sqrt{\frac{3}{7}\,\pi Dt}}\,. \quad \text{(XI)}$$

Therefore the concentration gradient at the surface of the dropping electrode is shown to be

$$\left(\frac{\partial C}{\partial\,r}\right)_{r=r_1}=({}^*C-{}^\circ C)\left(\frac{1}{\sqrt{\frac{3}{7}\,\pi Dt}}+\frac{1}{r_1}\right). \quad \text{(XII)}$$

The above developed theory, taking into account of the curvature of the mercury drop, is reduced to the Ilkovič-Stackelberg theory which ignores the curvature, when the following three conditions are used:

$$\left.\begin{aligned} q &= 4\pi\,r_1^{\,2}\,, \\ r-r_1 &= x\,, \\ r_1 &\to \infty\,. \end{aligned}\right\} \quad \text{(ii)}$$

There is no doubt that these conditions reduce the Eqs. (I)—(XII) to the Eqs. (1)—(12) respectively; accordingly it is obvious that the Ilkovič theory of the polarographic diffusion current is only a limiting law of our theory, obtained when the surface of mercury-drop is presumed to be plane. The instantaneous current intensity i can be derived from Eq. (XII); thus

$$\left.\begin{aligned} i&=nF\cdot 4\pi r_1^{\,2}\cdot D({}^*C-{}^\circ C)\left(\frac{1}{\sqrt{\frac{3}{7}\pi Dt}}+\frac{1}{r_1}\right),\\ i&=nF({}^*C-{}^\circ C)\cdot D^{1/2}\cdot 4\pi\left\{\left(\frac{3}{4\pi d}\right)^{2/3}\left(\frac{7}{3\pi}\right)^{1/2}\cdot\right.\\ &\qquad\left.\times\, m_1^{\,2/3}\cdot t^{1/6}+\left(\frac{3}{4\pi d}\right)^{1/3}\cdot D^{1/2}\cdot m_1^{\,1/3}\cdot t^{1/3}\right\},\\ i&=0.732\,nF\,({}^*C-{}^\circ C)D^{1/2}(m_1^{\,2/3}\cdot t^{1/6}\\ &\qquad+4.46\,D^{1/2}\cdot m_1^{\,1/3}\cdot t^{1/3}). \end{aligned}\right\} \quad \text{(XIII)}$$

The mean current $\bar{\imath}$ is further given by

$$\begin{aligned}\bar{\imath}&=0.627\,nF\,({}^*C-{}^\circ C)\,D^{1/2}(m_1^{\,2/3}\cdot t_1^{\,1/6}\\ &\qquad+3.91\,D^{1/2}\cdot m_1^{\,1/3}\cdot t_1^{\,1/3}),\end{aligned} \quad \text{(XIV)}$$

where t_1 denotes the drop time.

Current-Time Curves

It is required from Eq. (XIII) that the current-time curve at a constant applied voltage is not exactly a parabola of one-sixth order; writing

$$\begin{aligned} i&=k_1(t^{1/6}+4.46\,D^{1/2}\cdot m_1^{\,-1/3}\cdot t^{1/3})\\ k_1&=0.732\,nF({}^*C-{}^\circ C)\,D^{1/2}\cdot m_1^{\,2/3}\end{aligned}$$

and inserting some suitable values for D and m_1, *e. g.*, for simplicity assuming that

$$D = 16 \times 10^{-6} \text{ cm.}^2 \text{ per sec.,}$$
$$m_1 = 10^{-3} \text{ g. per sec.,}$$

it follows that

$$\begin{aligned} i &= k_1 (t^{1/6} + 0.178\, t^{1/3}) \\ &= k_1 \left[\left\{ 1 + \frac{1}{6}(\ln t) + \frac{1}{72}(\ln t)^2 + \cdots\cdots \right\} \right. \\ &\quad \left. + 0.178 \left\{ 1 + \frac{1}{3}(\ln t) + \frac{1}{18}(\ln t)^2 + \cdots\cdots \right\} \right] \\ &= 1.178\, k_1 \{1 + 0.192 \ln t + \cdots\cdots\} \\ &\fallingdotseq 1.178\, k_1 \cdot t^{0.192}. \end{aligned}$$

Thus it may be concluded that in the wide range of time, where $|\ln t|$ is not much greater than unity, the current-time curve is approximately parabolic; if we write

$$i \infty t^{\alpha}, \qquad \text{(iii)}$$

then α is given by

$$\frac{1}{6} < \alpha < \frac{1}{3}. \qquad \text{(iv)}$$

Not only the results obtained by McKenzie(4), but also that by Ilkovič(6) and by Antweiler(7) clearly show this relatianship.

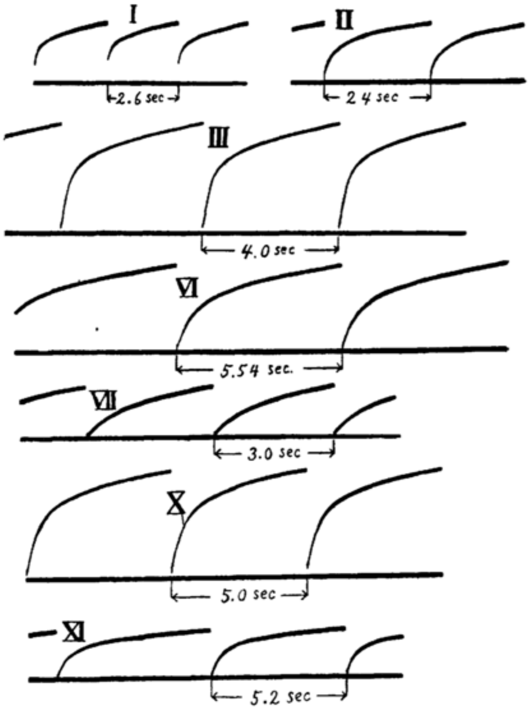

Fig. 3.—Oscillographic recordings of the polarographic current-time curves. Each number corresponds to the solution shown in Table 1.

We also investigated experimentally the change of current intensity during one drop-life; the apparatus employed were the polarographic equipment made by Yanagimoto Co. and the electro-magnetic oscillograph made by Yokogawa Co. Solutions shown in Table 1 were electrolyzed at the room temperature, each

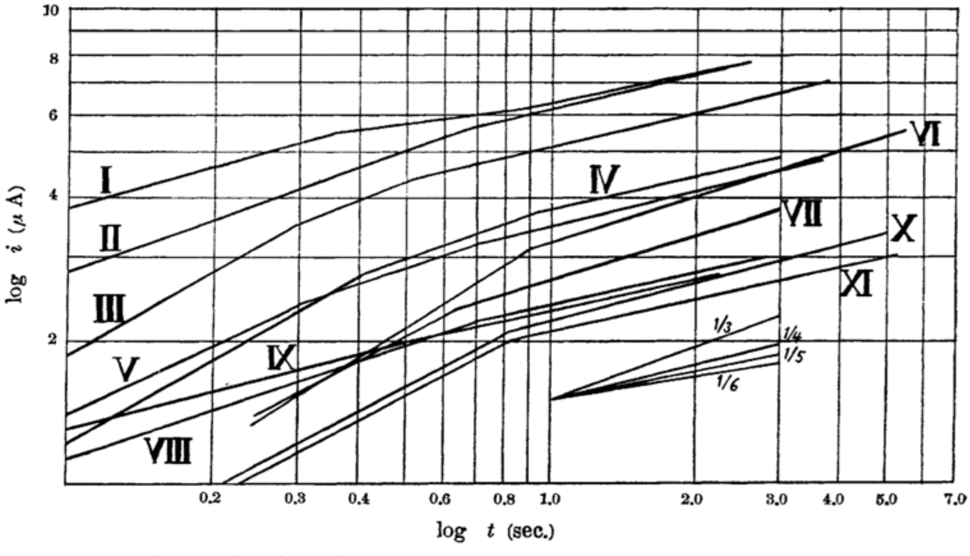

Fig. 4.—log i vs. log t curves. Each number corresponds to the solution shown in Table 1.

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(6) D. Ilkovič, *Collection Czech. Chem. Communs.*, **8**, 13 (1936).

(7) H. J. Antweiler, *Z. Elektrochem.*, **44**, 888 (1938).

with the suitably applied voltage determined from the current-voltage curve.

Table 1

Number	Depolarizer	Supporting electrolyte	Addition of gelatine
I	*ca.* 5×10^{-3} molar Nitrobenzene	sat. KNO_3*	+
II	〃	〃 *	−
III	*ca.* 10^{-2} molar $CoCl_2$	0.1 *N* KCl	+
IV	*ca.* 10^{-2} *N* $CdSO_4$	sat. KNO_3	−
V	〃	〃	+
VI	2×10^{-2} *N* $TlNO_3$	0.1 *N* KNO_3	+
VII	5×10^{-3} *N* HNO_3	〃	−
VIII	*ca.* 10^{-2} *N* $TlNO_3$	sat. KNO_3	−
IX	〃	〃	+
X	2×10^{-2} molar $CdSO_4$	0.1 *N* KCl	+
XI	1×10^{-2} molar $CdSO_4$	0.1 *N* KNO_3	+

* In buffer solution (pH = 7.0)

Oscillograms obtained are shown in Fig. 3; and Fig. 4 represents the plots of log i against log t, the slopes of which are obviously not 1/6 but are nearly 1/4 ∼ 1/5 (the mean value reported by McKenzie is 0.29). It is expected from our theory that the greater the diffusion constant, and the smaller the rate of flow of mercury, then the exponent α in Eq. (iii) will approach much nearer to 1/3, *i. e.*, α will increase. It is demonstrated in Fig. 3 that with the depolarizers, the diffusion constants of which are comparatively great, *e. g.*, hydrogen ion and thallous ion, the plot of log i against log t becomes much steeper in harmony with our theory. It may be concluded from our experiment that the discontinuity in the current-time curve exists at 0.3 ∼ 0.9 sec. (According to McKenzie it lies about at the first 0.3 sec.); and it may be noticed that an addition of gelatine causes a remarkable change in the current-time curve, especially in the very youth of drop-life, as shown in Figs. 2 and 3. Thus it may be said that the results obtained by McKenzie are confirmed by our experiment, although in some points complete coincidences are not found, probably owing to the difference in the experimental conditions; *i. e.*, in our experiment the concentration of depolarizer is appreciably greater than that used in the ordinary polarographic electrolysis and in the McKenzie's investigation.

Summary

The integral equation representing the thickness of the diffusion layer surrounding a spherical electrode is derived; upon solving this equation, the formula for the polarographic diffusion current is obtained. It becomes clear that the Ilkovič theory is not right because of its ignorance of the curvature of drop and that our revised equation can elucidate many oscillographic recordings of the polarographic current-time curves.

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