

Researches on the Polarographic Diffusion Current. II. Distribution of the Depolarizer in the Vicinity of Dropping Mercury Electrode and Some Experimental Verifications of the Revised Equation

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In Part I⁽¹⁾ of this research, it was reported that the thickness of the diffusion layer around the dropping mercury electrode can be expressed by an integral equation and upon solving this equation the new equation for the polarographic diffusion current is obtained, which is capable of elucidating many oscillographic

recordings of the current-time curves during one drop-life. In this paper this problem will be treated in an orthodox way, *viz.*, it will be shown that the differential equation representing the concentration of depolarizing matter is integrated and also that as for the formula for the diffusion current, the same result is obtained as in Part I, which is shown by numerous data to be more fitted than the old Ilkovič equation.

(1) T. Kambara, M. Suzuki, and I. Tachi, *This Bulletin*, **23**, 219 (1950).

Distribution of Depolarizer and the Revised Equation for the Diffusion Current

It may be assumed that the mercury drop expands concentrically, and let r be the distance from the center of drop considered as a sphere, and t the time elapsed after the growth of the drop has begun. If C is the concentration of the depolarizing substance, it is obvious that C is a function of r and t ; thus

$$C = C(r, t). \quad (1)$$

Hence

$$\frac{dC}{dt} = \frac{\partial C}{\partial t} + \frac{\partial C}{\partial r} \frac{dr}{dt}, \quad (2)$$

where $\partial C/\partial r$ is the variation of concentration with time at a fixed position ($r = \text{const.}$), and so is governed not only by diffusion but also by convection, whereas dC/dr is the variation of concentration due to the diffusion only. The rate of flow of mercury out of the capillary may be regarded to have a constant value m_1 g. per sec., independent of time, as is postulated also in the Ilkovič theory.⁽²⁾ Then the volume of mercury drop being proportional to the time elapsed after the drop has begun to grow, it is evident that

$$r_1^3 = \gamma t = a^3 t, \quad (3)$$

where r_1 denotes the radius of mercury drop, and a is given by

$$\gamma = a^3 = \frac{3m_1}{4\pi d}, \quad (4)$$

where $d = 13.6$ is the density of mercury. A volume element considered in the solution is pushed away from the center by the expansion of drop; hence the movement of solution is governed by the relation

$$r^3 = a^3 t + \text{const.}, \quad (5)$$

because the condition of the incompressibility of the medium holds. Accordingly the velocities with which the drop surface and the solution move are given by

$$v_{r_1} = \frac{\partial r_1}{\partial t} = \frac{a^3}{3r_1^2} \text{ and } v_r = \frac{dr}{dt} = \frac{a^3}{3r^2} \quad (6)$$

respectively. On the other hand, according to the Fick's law in spherical coordinate, it is evident that

$$\frac{dC}{dt} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right), \quad (7)$$

where D is the diffusion constant of the depolarizer. Inserting Eqs. (6) and (7) into Eq. (2) gives

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right) - \frac{a^3}{3r^2} \cdot \frac{\partial C}{\partial r} \quad (8)$$

which is identical with the differential equation derived by MacGillavry and Rideal.⁽³⁾ This equation can not be integrated immediately, but a special solution is readily seen to be

$$C = R(\text{const.}). \quad (9)$$

Next let us introduce a new function φ defined by

$$\varphi \equiv rC = \varphi(r, t). \quad (10)$$

Moreover the origin of coordinate will be transferred from the center of the sphere to the surface of drop, then the position of a volume element considered in the solution can be represented by the new coordinate x given by

$$x = r - r_1. \quad (11)$$

There is no doubt that φ can be expressed perfectly by the two independent variables x and t ; thus

$$\varphi = \varphi(x, t), \quad (12)$$

$$\frac{d\varphi}{dt} = \frac{\partial \varphi}{\partial t} + \frac{\partial \varphi}{\partial x} \cdot \frac{dx}{dt}. \quad (13)$$

The above mentioned Fick's law can be written in the form:

$$\frac{d\varphi}{dt} = D \cdot \frac{\partial^2 \varphi}{\partial x^2}. \quad (14)$$

From Eqs. (6) and (11), the approach of solution to the drop surface is readily seen to be expressed by

$$v_x = \frac{dx}{dt} = \frac{a^3}{3} \left(\frac{1}{r^2} - \frac{1}{r_1^2} \right). \quad (15)$$

Accordingly we obtain the following equation

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} - \frac{a^3}{3} \left(\frac{1}{r^2} - \frac{1}{r_1^2} \right) \frac{\partial \varphi}{\partial x}. \quad (16)$$

Since in the vicinity of the surface of dropping electrode the condition $r_1 \gg x$ holds, it is approximately shown that

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

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

$$\frac{\alpha^3}{3} \left(\frac{1}{r^2} - \frac{1}{r_1^2} \right) = -\frac{r_1^3}{3t} \cdot \frac{x(x+2r_1)}{r^2 r_1^2} - \frac{2x}{3t}$$

Consequently

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} + \frac{2x}{3t} \cdot \frac{\partial \varphi}{\partial x}, \quad (17)$$

which is an equation of the identical form with that derived by Ilkovič.⁽²⁾ In order to integrate this equation, since the procedure given by Ilkovič is very difficult, a new variable S given by

$$S = x/2\sqrt{\frac{3}{t}} Dt \quad (18)$$

will be introduced. Thus Eq. (17) can be integrated and the result is

$$rC \equiv \varphi = P \cdot \int_0^S e^{-S^2} \cdot dS + Q.$$

Consequently the general solution for the Eq. (8) is approximately given by

$$C = \frac{P}{r} \int_0^{\frac{r-r_1}{2\sqrt{\frac{3}{t}} Dt}} e^{-S^2} \cdot dS + \frac{Q}{r} + R, \quad (19)$$

where P , Q , and R , are constants. The boundary conditions are shown by

$$\left. \begin{aligned} C &= {}^*C \dots \text{when } r \rightarrow \infty, \\ C &= {}^\circ C \dots \text{when } r = r_1, \quad t > 0. \\ C &= {}^*C \dots \text{when } r > r_1, \quad t = 0. \end{aligned} \right\} \quad (20)$$

where *C is the concentration of the depolarizer in the bulk of the solution, and ${}^\circ C$ is that at the surface of the dropping electrode. Thus the appropriate solution is found to be

$$C = {}^\circ C \frac{r_1}{r} + {}^*C \left(1 - \frac{r_1}{r} \right) + ({}^*C - {}^\circ C) \frac{r_1}{r} \cdot \frac{2}{\sqrt{\pi}} \int_0^{\frac{r-r_1}{2\sqrt{\frac{3}{t}} Dt}} e^{-S^2} \cdot dS. \quad (21)$$

The concentration gradient at the electrode surface can be derived from this equation, and it is shown that

$$\left(\frac{\partial C}{\partial r} \right)_{r=r_1} = ({}^*C - {}^\circ C) \left\{ \frac{1}{r_1} + \frac{1}{\sqrt{\frac{3}{t}} \pi Dt} \right\}. \quad (22)$$

If the electricity required by the electrode

reaction of one mol of the depolarizer is nF (F : Faraday), from the Fick's first law the instantaneous current intensity i is shown by

$$i = 0.732 nF ({}^*C - {}^\circ C) \cdot D^{1/2} \times (m_1^{2/3} \cdot t_1^{1/6} + 4.46 D^{1/2} \cdot m_1^{1/3} \cdot t_1^{1/3}). \quad (23)$$

The mean current \bar{i} is given by

$$\bar{i} = \frac{1}{t_1} \int_0^{t_1} i \cdot dt,$$

where t_1 is the drop time; thus it is evident that

$$\bar{i} = 0.627 nF ({}^*C - {}^\circ C) \cdot D^{1/2} \times (m_1^{2/3} \cdot t_1^{1/6} + 3.91 D^{1/2} \cdot m_1^{1/3} \cdot t_1^{1/3}). \quad (24)$$

When the mean value of limiting diffusion current is obtainable, ${}^\circ C$ approaches to zero; then if the following conventional units are employed, *i. e.*,

$$\bar{i}_a \text{ Amp.} = I_a \mu \text{ Amp.},$$

$${}^*C \text{ mol per cc.} = C \text{ millimol per liter},$$

$$m_1 \text{ g. per sec.} = m \text{ mg. per sec.},$$

it can be seen, as described in Part I⁽¹⁾, that

$$I_a = 605 nC \cdot D^{1/2} (m^{2/3} \cdot t_1^{1/6} + 39.1 D^{1/2} \cdot m^{1/3} \cdot t_1^{1/3}) \quad (24,a)$$

Comparison with the Experimental Results

As for the polarographic current-time curves, the old Ilkovič equation can not elucidate the experimentally obtained recordings, and the validity of the above derived equation was described in Part I of this research. In this article, our revised equation will be compared with some other experimental observations.

Empirical Modification by Lingane and Loveridge.—For the polarographic diffusion current of lead ion, Lingane and Loveridge⁽⁴⁾ examined the exponent of m in the Ilkovič equation. With

$$I_a \propto m^\beta, \quad (25)$$

they obtained the result

$$\beta = 0.64 \quad (26)$$

instead of $2/3$ as required by Ilkovič. This result will be considered as follows. Writing

(4) J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.*, **68**, 395 (1946).

Eq. (24, a) in the form

$$I_d = k_1(m^{2/3} + 39.1 D^{1/2} \cdot t_1^{1/6} \cdot m^{1/3}),$$

$$k_1 = 605 nC \cdot D^{1/2} \cdot t_1^{1/6},$$

and inserting the values:

$$D(\text{Pb}^{++}) = 9.8 \times 10^{-6} \text{ cm}^2 \text{ per sec. (at } 25^\circ),$$

$$t_1 = 3 \text{ sec.},$$

it is shown that

$$I_d = k_1(m^{2/3} + 0.147 m^{1/3})$$

$$\div k_1 \left[\left\{ 1 + \frac{2}{3} (\ln m) + \frac{2}{9} (\ln m)^2 + \dots \right\} \right.$$

$$\left. + 0.147 \left\{ 1 + \frac{1}{3} (\ln m) + \frac{1}{18} (\ln m)^2 + \dots \right\} \right]$$

$$= 1.147 k_1 \{ 1 + 0.624 (\ln m) + \dots \}$$

$$\div 1.147 k_1 \cdot m^{0.624}.$$

Thus it is obvious that in general

$$\frac{1}{3} < \beta < \frac{2}{3}. \quad (27)$$

Diffusion Current Constant.—From Eq. (24, a) it is found that

$$K = \frac{I_d}{C \cdot m^{2/3} \cdot t_1^{1/6}} = k_2 + k_3 \cdot t_1^{1/6} \quad (28)$$

where k_2 and k_3 are constants. This equation

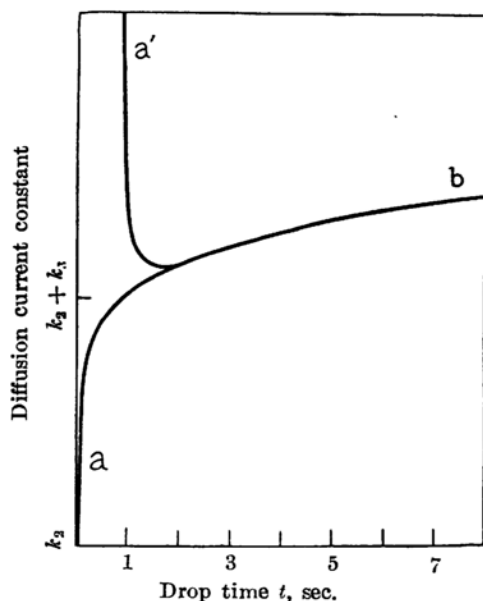


Fig. 1.—Relation between the diffusion current constant and the drop time: Curve ab, theoretical; Curve a'b, experimental.

indicates that the plot of diffusion current constant K against the drop time t_1 is not a horizontally straight line but a gradually increasing curve as illustrated by the curve ab in Fig. 1. The observed curve is reported by Lingane⁽⁵⁾ to be the one, the shape of which is demonstrated by a'b in Fig. 1. The exceedingly rapid increase in the value of K with the increasing shorter drop time, may be caused by the "stirring effect" due to the rapid alternation of drops, as already suggested by Lingane.

Dependence of the Current Intensity on the Height of Mercury Reservoir.—If P is the static pressure of mercury column, since the conditions

$$m \propto P \quad \text{and} \quad P \cdot t_1 = \text{const.} \quad (29)$$

holds,

$$I_d = k_4 \cdot P^{1/2} + k_5 \quad (30)$$

is followed, where k_4 and k_5 are constants. Although the plot of I_d against $P^{1/2}$ is a straight line, the line obtained does not pass the origin. Data by Ilkovič⁽⁶⁾ and O. H. Müller⁽⁷⁾ give the lines demonstrated in Fig. 2; thus it becomes clear that Eq. (30) is better than the equation

$$I_d = k_4 \cdot P^{1/2}, \quad (30, a)$$

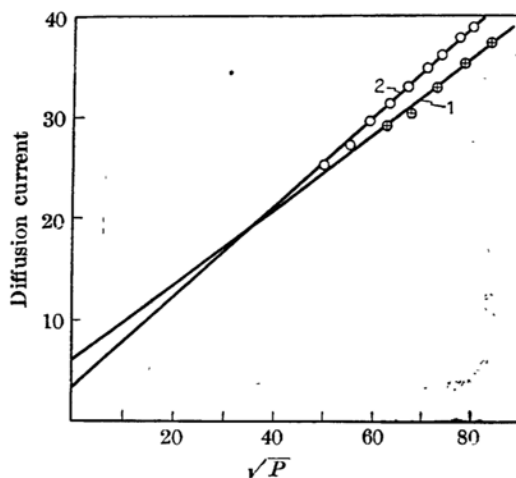


Fig. 2.—Relation between the diffusion current and the square root of the height of the mercury reservoir: Curve 1, data by Ilkovič; Curve 2, data by Müller; P means the height of the mercury reservoir.

(5) J. J. Lingane, *Anal. Chem.*, **21**, 45 (1949).

(6) D. Ilkovič, *Collect. Czech. Chem. Commun.*, **6**, 498 (1934).

(7) O. H. Müller, "Polarography" Chapt. XXIII in Weissberger's "Phys. Meth. of Organic Chemistry" Vol. II, 1946.

which results from the Ilkovič equation and Eq. (29). Thus it becomes clear that our equation is more fitted than the original Ilkovič's one.

The Ratio i_{max}/\bar{i} .—It can be readily seen. that

$$1.166 = \frac{7}{6} < \frac{i_{max}}{\bar{i}} < \frac{4}{3} = 1.33, \quad (31)$$

where i_{max} is the maximum current intensity which flows at the end of drop-life and \bar{i} is the mean current. This equation agrees very well with the results observed by McKenzie.⁽⁸⁾

Discrepancy between the Theory and the Experiment.—That the current increases remarkable slowly in the very infant age of drop-life, as experimented by McKenzie⁽⁸⁾ and also by us⁽¹⁾, is not comprehensible both from the Ilkovič theory and from the present considerations. It may be imagined that some retarding effects are operative in the beginning of each drop-life; if this problem was cleared up, the discontinuity in the current-time curve would be solved and a further progress towards the perfect elucidation would be made.

Note on the Procedure given by MacGillavry and Rideal

In order to integrate Eq. (8), MacGillavry and Rideal⁽³⁾ used the transformation of co-ordinate system given by

$$r^3 - \rho^3 = \gamma t$$

instead of Eq. (11), where ρ denotes the distance from the surface of the drop and is equal to x in our notations. Therefore

$$v_\rho = \frac{\partial \rho}{\partial t} = 0$$

which means that the solution does not approach to the surface of the drop during the expansion of mercury drop, whereas it is pushed away from the center of the drop; this is clearly erroneous. Thus they obtained the same result as attained by Ilkovič and Stackelberg who ignored the curvature of drop.

Summary

The differential equation representing the distribution of the depolarizer in the vicinity of dropping mercury electrode was integrated and the formula for the polarographic diffusion current was derived, which is identical with the equation obtained, as reported in our previous paper, in another way. Several experimental results were found to be in accordance with this equation; it may be said that our improved theory is not only the denial of the Ilkovič theory but also at the same time inclusive of the old theory.

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