Researches on the Polarographic Diffusion Current. III. Higher Order Approximation of the Ilkovič Equation

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(Received February 22, 1952)

Theoretical revision of the Ilkovič equation was carried out by Strehlow with Stackelberg,[1] Lingane with Loveridge,[2] and by us[3]; there is no doubt that the correction term of the form:

$$(D^{1/2}\cdot m^{2/3}\cdot t^{1/6}+A\cdot D\cdot m^{1/3}\cdot t^{1/3})$$

is required. As for the numerical value of the coefficient A, however, a further discussion is needed. In order to clear up this problem, our new treatment will be given below.

Derivation of the Equation

As reported in our preceding paper,[3] the thickness of diffusion layer, denoted by δ, surrounding any spherical electrode of radius r_e is given by the integral equation:

$$r_e^3(y^3+2y)\equiv\pi D\int_0^t \frac{r_e^2}{\delta}\cdot dt, \qquad (1)$$

where y is given by

(1) H. Strehlow und M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(2) J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.*, **72**, 438 (1950).

(3) T. Kambara, M. Suzuki, and I. Tachi, This Bulletin, **23**, 219 (1950); T. Kambara and I. Tachi, ibid., 225; *Proc. I. Intern. Polarographic Congress in Prague*, Part I, 126 (1951).

$$y=\delta/(r_e-\delta), \tag{2}$$

and D denotes the diffusion coefficient of the depolarizer. In the case of the dropping mercury electrode, it is seen that

$$\left.\begin{aligned} r_e &= a\cdot t^{1/3};\ a=\alpha\cdot m^{1/3}; \\ \alpha &= \frac{1}{10}\left(\frac{3}{4\pi d}\right)^{1/3}=2.602\times10^{-2}; \end{aligned}\right\} \tag{3}$$

where m is the rate of flow of mercury in mg./sec. and $d=13.55$ is the specific gravity of mercury at 20°C. Thus Eq. (1) can be transformed into the form :

$$\pi Dat^{1/3}(y+1)=a^3\left\{-y^3+2(y^3+y^2)+2t(y+1)y\frac{dy}{dt}\right\}. \tag{4}$$

Writing

$$a^3y^3/(y+1)=Y \tag{5}$$

and regarding this quantity of an infinitesimally small value as having a constant value during the time interval of interest, then it is seen that Eq. (4) is integratable; i. e.

$$\frac{3}{7}\pi Dat^{7/3}=-\frac{Y}{2}t^3+a^3y^2t^2. \tag{6}$$

Combination of the Eqs. (5) and (6) gives the following cubic equation :

$$F(y)=y^3+2y^2-2(\delta_1/r_e)^2y-2(\delta_1/r_e)^2=0, \tag{7}$$

where

$$\delta_1=\sqrt{\frac{3}{7}\pi Dt} \tag{8}$$

is the thickness of diffusion layer derived by Ilkovič.

Since y possesses a small positive value compared with unity, it is seen that one of the approximate solutions of Eq. (7) is given by

$$\eta=\delta_1/r_e\ ; \tag{9}$$

whence the Lingane-Loveridge equation:[2]

$$\frac{1}{\delta}=\frac{1}{r_e}+\frac{1}{\delta_1} \tag{10}$$

can be obtained, the procedure of which was already shown by us.[3] A more precise solution thereof is, according to the differential calculus, given by

$$y=\eta-\left[\frac{F(y)}{F'(y)}\right]_{y=\eta}\doteq\eta\cdot\frac{4+2\eta}{4+\eta}\ . \tag{11}$$

That Eq. (11) is more accurate than Eq. (10), is made out as follows; i. e., it can be readily seen that

$$F(\eta)=-\eta^3\ ;$$

$$F\left(\eta\frac{4+2\eta}{4+\eta}\right)=\frac{1}{8}\eta^4\left(1+\frac{7}{4}\eta+\frac{1}{2}\eta^2\right)\left(1+\frac{1}{4}\eta\right)^{-3}\ ;$$

accordingly it is seen that a more suitable value for y is found. It may be noticed here, however, that

$$F(\eta)=-\eta^3<0\ ;\quad F(2\eta)=4\eta^3+6\eta^2>0\ ;$$

and also that $F''(y)=6y+4$ and $F'(y)=3y^2+4y-2\eta^2$ are positive in the interval $[\eta,\ 2\eta]$.

Now it follows from the Eqs. (2), (9), and (11) that

$$\frac{1}{\delta}=\frac{1}{r_e}+\frac{1}{\delta_1}\cdot\frac{4+\eta}{4+2\eta}=\frac{1}{\sqrt{\frac{3}{7}\pi Dt}}\cdot f(\eta), \tag{12}$$

where $f(\eta)$ is, according to the Maclaurin's theorem, shown to be

$$\begin{aligned} f(\eta) &= \eta+\frac{4+\eta}{4+2\eta}=\eta+\frac{1}{2}+\frac{1}{2}\left(1+\frac{1}{2}\eta\right)^{-1} \\ &= 1+\frac{3}{4}\eta+\frac{1}{8}\eta^2-\frac{1}{16}\eta^3+\frac{1}{32}\eta^4-\frac{1}{64}\eta^5+\frac{1}{128}\eta^6-\cdots. \end{aligned} \tag{13}$$

Hence the instantaneous limiting diffusion current i_d in amp. is given by

$$i_d=nF\cdot4\pi r_e^2\cdot\frac{D\cdot{}^*C}{\sqrt{\frac{3}{7}\pi Dt}}\cdot f(\eta). \tag{14}$$

Further it is seen that

$$\eta=b\cdot D^{1/2}\cdot m^{-1/3}\cdot t^{1/6}\ ;\ b=44.593. \tag{15}$$

Adopting the usual conventional units, therefore, it is found that i_d in μ amp. is shown by

$$\begin{aligned} i_d=707.6\,nC[&D^{1/2}\cdot m^{2/3}\cdot t^{1/6}+33.45\,D\cdot m^{1/3}\cdot t^{1/3} \\ &+248.6\,D^{3/2}\cdot t^{1/2}-5543\,D^2\cdot m^{-1/3}\cdot t^{2/3}+123.6 \\ &\times10^3D^{5/2}\cdot m^{-2/3}\cdot t^{5/6}-2.755\times10^6\cdot D^3\cdot m^{-1}\cdot t \\ &+61.44\times10^6\cdot D^{7/2}\cdot m^{-4/3}\cdot t^{7/6}-\cdots\cdots]. \end{aligned} \tag{16}$$

Thus the mean current is shown by

$$\begin{aligned} \bar{i}_d=606.5\,nC[&D^{1/2}\cdot m^{2/3}\cdot t^{1/6}+29.27\,D\cdot m^{1/3}\cdot t^{1/3} \\ &+171.1\,D^{3/2}\cdot t^{1/2}-3880\,D^2\cdot m^{-1/3}\cdot t^{2/3}+81.38 \\ &\times10^3D^{5/2}\cdot m^{-2/3}\cdot t^{5/6}-1.607\times10^6D^3\cdot m^{-1}\cdot t \\ &+33.08\times10^6D^{7/2}\cdot m^{-4/3}\cdot t^{7/6}-\cdots\cdots]. \end{aligned} \tag{17}$$

In this equation t now represents the drop time.

Discussion of the Result

Since the above stated procedures are more exact than our former one, it can be concluded that as for the correction term of the Ilkovič equation, the coefficient 39 previously reported by us is too large. Then which is more adequate of the two coefficients, i. e. 17 given by Strehlow and Stackelberg or 29.27 given here? The answer to this question will become clear by the experimental work in future. It must be pointed out here, however, that the polarographic current-time curve, especially in the younger age of drop-life, considerably differs from that predicted by the formula of the form

$$i=(k_1\cdot t^{1/6}+k_2\cdot t^{1/3})\ ;$$

this is reasonably comprehensible from the considerations taking the rate of electrode reaction into account.(4) Thus it is expected that also the mean current would be effected for the same reason.

It was reported by Smith(5) that the current-time curve with a very slowly growing mercury drop shows a parabola of one-half order. This phenomenon was first clarified by Strehlow and Stackelberg(1) in a mathematically very simple way. The above theory can elucidate this finding very satisfactorily. It is further expected that with a capillary of small m-value and large t-value, the higher terms will become more and more important.

It must be pointed out here that the coefficient 606.5 in Eq. (16) is more adequate than the former reported value 605; this discrepancy arises from the fact that we used the value $d=13.6$ (0°C) for the density of mercury in the preceding papers.

We made a serious error when, in our preceding papers,(3) we wrote that the transformation of the coordinate system carried out by MacGillavry and Rideal(6) is erroneous. In order to elucidate the relation between the two theories proposed by MacGillavry with Rideal and by Ilkovič,(7) we will show the mathematical proof for the identity of these two theories. Because the quantity $(4\pi/3)\rho^3$ appearing in the MacGillavry theory, represents the volume of the spherical shell of incompressible medium surrounding the mercury drop, it is seen that

$$\frac{4\pi}{3}\rho^3 \doteq qx=a^2t^{2/3}\cdot x=a^2u, \qquad (18)$$

where u is the variable appearing in the Ilkovič theory. With the aid of this relationship, the solution given by MacGillavry becomes identical with that given by Ilkovič.

Next we will prove that the MacGillavry-Rideal theory, which starts from the differential equation taking the curvature of mercury drop into consideration, is neglecting the curvature effect in result. Their differential equation, i. e.

$$\frac{1}{D}\frac{\partial C}{\partial t}=\frac{\partial^2 C}{\partial r^2}+\frac{2}{r}\frac{\partial C}{\partial r}-\frac{1}{D}\frac{\gamma}{3r^2}\frac{\partial C}{\partial r} \qquad (19)$$

is converted into the form :

$$\frac{1}{D}\frac{\partial C}{\partial t}=\frac{(\rho^3+\gamma t)^{4/3}}{\rho^5}\left(\rho\frac{\partial^2 C}{\partial \rho^2}+2\frac{\rho^3-\gamma t}{\rho^3+\gamma t}\frac{\partial C}{\partial \rho}\right) \qquad (20)$$

by the transformation of the coordinate system shown by

$$r^3=\rho^3+\gamma t\ ;\quad \gamma=a^3. \qquad (21)$$

Since the condition $\gamma t \gg \rho^3$ holds, Eq. (20) is transformed into

$$\frac{1}{D}\frac{\partial C}{\partial t}=\frac{(\gamma t)^{4/3}}{\rho^5}\left(\rho\frac{\partial^2 C}{\partial \rho^2}-2\frac{\partial C}{\partial \rho}\right). \qquad (22)$$

Upon solving this equation, they derived the original Ilkovič equation.

If we ignore the curvature of drop, it is seen that Eq. (19) is written as

$$\frac{1}{D}\frac{\partial C}{\partial t}=\frac{\partial^2 C}{\partial r^2}-\frac{1}{D}\cdot\frac{\gamma}{3r^2}\cdot\frac{\partial C}{\partial r}. \qquad (23)$$

By the relation shown by Eq. (21), this equation is transformed into

$$\frac{1}{D}\frac{\partial C}{\partial t}=\frac{(\rho^3+\gamma t)^{4/3}}{\rho^5}\left(\rho\frac{\partial^2 C}{\partial \rho^2}-\frac{2\gamma t}{\rho^3+\gamma t}\frac{\partial C}{\partial \rho}\right). \qquad (24)$$

Also this equation can be simplified into Eq. (22), which leads to the same result; accordingly it can be demonstrated that the MacGillavry-Rideal theory ignores the curvature effect.

It is pointed out by Dr. H. Matsuda(8) that the mathematical procedure given in Part II of this research(3) is in some points incorrect, i. e. it holds only as the first order approximation. The procedure solving the MacGillavry-Rideal differential equation given by him, which will be published in the near future. is expected to contribute much to the study of polarographic diffusion current.

Summary

Starting from the integral equation for the thickness of diffusion layer at the spherical electrode, a new equation for the polarographic diffusion current is derived and discussed.

The authors wish to express their hearty thanks to Prof. M. v. Stackelberg and Dr. H. Strehlow for their kind communications of their opinions on this problem and for separate copies of their papers. The authors' thanks are also due to Dr. H. Matsuda for his kind and constructive criticism.

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