Studies on A.C. Polarography. I. Theoretical Treatment

By Isamu TACHI and Tomihito KAMBARA

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Introduction

Application of the square wave voltage in the polarographic electrolysis originates from Kemula¹⁾, who employed the rotating switch for the abrupt change of electrode potential. Recently, the polarographic electrolysis, in which the conventional sine wave a.c. voltage is superimposed upon the ordinary d.c. voltage has been elaborated by Breyer and his co-workers²⁾, and also by Randles³⁾ and Fournier⁴⁾, and their works teem with many interesting findings. Therefore the present authors will discuss this problem mathematically from the general viewpoint.

General Aspects of the Problem

The diffusion processes of the oxidised form (suffix O) and the reduced from (suffix R) are given by Fick's second law of diffusion; i.e.

$$\frac{\partial C_o}{\partial t}=D_o\frac{\partial^2 C_o}{\partial x^2}\ ;\ \frac{\partial C_R}{\partial t}=D_R\frac{\partial^2 C_R}{\partial x^2}. \tag{1}$$

Here C represents the concentration, D the diffusion coefficient, x the distance from the electrode surface, and t the time. Let $^*C_o$ and $^*C_R$, respectively, be the uniform initial concentrations of the oxidised and reduced forms, then the initial condition is given by

$$t=0,\ 0\leq x\leq\infty,\ C_o={}^*C_o,\ C_R={}^*C_R. \tag{2}$$

Upon employing the Laplace-transformation defined by

$$\mathfrak{L}C=p\int_0^\infty e^{-pt}\cdot C(x,t)\cdot dt=u(x,p)$$

we obtain from Eqs. (1) and (2)

$$p(u-{}^*C)=D\cdot\partial^2u/\partial x^2,$$

which yields the following general integral.

$$u={}^*C+B\cdot\exp\left[-\sqrt{\frac{p}{D}}\,x\right]$$

It follows further that

$$D(\partial u/\partial x)_{x=0}=-\sqrt{pD}\,B.$$

The integral constants B_o and B_R are functions of p, and are determined by the boundary condition. Next, it is quite clear that

$$t>0,\ x=0,\ \phi(t)=\frac{I}{nFq}=D_o\frac{\partial C_o}{\partial x}=-D_R\frac{\partial C_R}{\partial x} \tag{3}$$

where I, q, F and n represent current intensity, area of the electrode surface, Faraday's constant and the number of electrons associated with the reaction of one molecule of oxidant. Writing

$$\mathfrak{L}\phi(t)=\Phi(t)\ ;\ \mathfrak{L}Z_o(\mathrm{t})=B_o(p)\ ;\ \mathfrak{L}Z_R(t)=B_R(p),$$

it is seen that

$$-\sqrt{D_o}B_o=\sqrt{D_R}B_R=\frac{\sqrt{p}\,\Phi(p)}{p},$$

which is inversely transformed into

$$-\sqrt{D_o}Z_o=\sqrt{D_R}Z_R=\int_0^t\frac{\phi(\xi)}{\sqrt{\pi(t-\xi)}}d\xi.$$

Thus it follows that the interfacial concentrations of both forms are shown by

$$\left.\begin{aligned}{}^\circ C_O&={}^*C_O-\frac{1}{\sqrt{\pi D_O}}\int_0^t\frac{\phi(\xi)}{\sqrt{t-\xi}}\cdot d\xi\ ;\\ {}^\circ C_R&={}^*C_R+\frac{1}{\sqrt{\pi D_R}}\int_0^t\frac{\phi(\xi)}{\sqrt{t-\xi}}\cdot d\xi.\end{aligned}\right\} \tag{4}$$

On the other hand, the current intensity is also governed by the rate constants of the electrode processes; thus

$$\phi(t)=\frac{I}{nFq}=\overrightarrow{k}f_o{}^\circ C_o-\overleftarrow{k}f_R{}^\circ C_R, \tag{5}$$

where $\overrightarrow{k}$ and $\overleftarrow{k}$ are the rate constants of the cathodic reduction and anodic oxidation, respectively, and f_o and f_R are the respective activity coefficients at the electrode surface.

According to the theory of absolute reaction rate, $\overrightarrow{k}$ and $\overleftarrow{k}$ are given by

$$\left.\begin{aligned}\overrightarrow{k}&=\overrightarrow{k_S}\exp\frac{-\alpha nFV}{RT}\ ;\\ \overleftarrow{k}&=\overleftarrow{k_S}\exp\frac{(1-\alpha)nFV}{RT}.\end{aligned}\right\} \tag{6}$$

where V denotes the potential of the observation electrode, $\overrightarrow{k_S}$ and $\overleftarrow{k_S}$ are the respective rate constants at $V=0$, and other symbols α, R and T are employed in their usual significances. In a.c. polarography, to the dropping mercury electrode is applied the usual constant voltage E and further a sine-

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1) W. Kemula, *Collection Czech. Chem. Communs.*, 2, 502 (1930).

2) B. Breyer and F. Gutman, *Discuss. Faraday Soc.*, 1, 19 (1947); B. Breyer, F. Gutman and S. Hacobian, *Austral. J. Sci. Research*, **A3**, 558, 567 (1950), **A4**, 595 (1951); B. Breyer and S. Hacobian, ibid., **A4**, 604, 610 (1951).

3) J. E. B. Randles, *Discuss. Faraday Soc.*, 1, 11 (1947).

4) M. Fournier, *Compt. rend.*, 232, 1673 (1951).

wave a.c. voltage is superimposed thereupon. Thus it is seen that

$$V=E-A\sin\omega t. \tag{7}$$

Namely, both rate constants are also functions of time. The combination of Eqs. (3)…(7) gives the following relationship:

$$\phi(t)=g_1(t)+g_2(t)\int_0^t\frac{\phi(\xi)}{\sqrt{\pi(t-\xi)}}d\xi. \tag{8}$$

In this equation the functions $g_1(t)$ and $g_2(t)$ are shown by

$$\left.\begin{aligned}
&g_1(t)=k_f{}^*C_Of_1(t)-k_b{}^*C_Rf_2(t)\,;\\
&g_2(t)=-\frac{k_f}{\sqrt{D_O}}\cdot f_1(t)-\frac{k_b}{\sqrt{D_R}}f_2(t)\,;\\
&k_f=\overrightarrow{k_S}f_O\cdot\exp\frac{-\alpha nFE}{RT}\,;\\
&k_b=\overrightarrow{k_S}f_R\cdot\exp\frac{(1-\alpha)nFE}{RT}\,;\\
&f_1(t)=\exp\frac{\alpha nFA\cdot\sin\omega t}{RT}\,;\\
&f_2(t)=\exp\frac{-(1-\alpha)nFA\cdot\sin\omega t}{RT}\,;
\end{aligned}\right\} \tag{9}$$

Thus it is seen that in the case that the electrode potential is a function of time, the resulting diffusion current I is, as shown by Eq. (8), in general demonstrated by Volterra's integral equation of the second kind; this has been already shown in the mathematical treatment of oscillographic polarography of Sevcik-Randles type by Matsuda[5], who has taken the rates of forward and backward reactions into account. The equation of the same form has been discussed also by Delahay[6] dealing with the perfectly irreversible process. Although the solution of Eq. (8) has been mathematically known, the result thereof is too complicated for any practical application.

We will next consider the problem with assumption that both the rate constants $\overrightarrow{k_S}$ and $\overleftarrow{k_S}$ are extraordinarily great. Under such a condition, we can legitimately apply the Nernst formula, since the interfacial concentrations of both forms may be then regarded to be always at equilibrium. Therefore we have the following boundary condition.

$t>0,\ x=0,\ K={}^\circ C_R/{}^\circ C_O=({}^*C_R+Z_R)/({}^*C_O-Z_O)$

$$\begin{aligned}
&=\exp\frac{-nF(V-E_o)}{RT}\\
&=\exp\frac{-nF(E-E_o-A\cdot\sin\omega t)}{RT}.
\end{aligned} \tag{10}$$

In this equation E_O denotes the normal potential of the concerned redox system. Then, upon utilizing the relationship:

$$-\sqrt{D_O}Z_O=\sqrt{D_R}Z_R$$

we can easily obtain the following expression.

$$Z_O=\frac{{}^*C_R-K{}^*C_O}{K+\sqrt{\dfrac{D_O}{D_R}}}=\mathfrak{L}^{-1}B_O(p).$$

Then it is seen that

$$\begin{aligned}
\phi(t)&=\mathfrak{L}^{-1}[-\sqrt{pD_O}\cdot B_O(p)]=\\
&=-\sqrt{D_O}\frac{d}{dt}\int_0^t\frac{Z_O(\xi)}{\sqrt{\pi(t-\xi)}}\cdot d\xi.
\end{aligned}$$

Namely, we have

$$\left.\begin{aligned}
&\phi(t)=-\frac{d}{dt}\int_0^t\sqrt{\frac{D_O}{\pi\xi}}X\\
&\times\left\{{}^*C_R-{}^*C_O\beta\exp\frac{nFA\cdot\sin\omega(t-\xi)}{RT}\right\}\times\\
&\times\left\{\sqrt{\frac{D_O}{D_R}}+\beta\exp\frac{nFA\cdot\sin\omega(t-\xi)}{RT}\right\}^{-1}\cdot d\xi\,;\\
&\beta=\exp\frac{-nF(E-E_o)}{RT},
\end{aligned}\right\} \tag{11}$$

which is the fundamental equation for the instantaneous current intensity due to the a.c. voltage polarization of a reversible electrode.

The above stated theoretical treatment is based on the sound basis, and although the conclusion is mathematically complicated, it may be noteworthy to compare the present theory with the earlier works performed by Randles[3], Breyer with colleagues[2] and others.

Let us at first call to mind the Helmholz theory of electric double layer. For a long time, the electrode surface has been regarded as behaving like an electrostatic condenser. As is well known, the electrolysis with an a.c. voltage is intimately connected with the experimental measurement of the conductivity of electrolytic solution; and in the course of development of the investigations, the terms "polarization resistance" and "polarization capacitance" have been introduced, which indicate the essential rôle of the electrode-solution interface in the electrolysis with a.c. voltage. On the other hand, the electrochemists, who have been studying the "ideal polarized electrode", i.e. the electrode, across the surface of which no charged particle moves, have recently begun to treat the present problem; and especially the works performed by Grahame[7] are decidedly of importance. His opinion may be summarised qualitatively from the a.c. polarographic viewpoint as follows. At a reversible electrode, at which

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[5] H. Matsuda, Reported at the Discussion Meeting at Nagoya held in November 1952 by the Electrochemical Society of Japan.

[6] P. Delahay, *J. Am. Chem. Soc.*, **75**, 1190 (1953).

[7] D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

the two rate constants of the electrode processes in forward and reverse directions, i.e. the rate constants of reduction and oxidation, are sufficiently great, by the superposition of an a.c. voltage, the electrode potential is made more negative in a half-period resulting in the predominance of the reduction process of oxidised form at the interface, and thus the reduction product is accumulated considerably at the surface, although some portion of the product may diffuse away. And in the next half-period, the electrode potential becomes so positive that the reductant accumulated at the surface is readily to be oxidised. Hence, corresponding to the periodic change of the electrode potential, the cathodic reduction and anodic oxidation happen alternatively at the electrode surface. Therefore in such a case, a prominant alternating current flows through the surface, so that the electrode surface behaves like a condenser of great capacity. Grahame called such an apparent capacity of electrolytic nature at first " pseudo-capacity "(7) and later introduced a more adequate term " faradayic admittance "(8) in which not only the pseudo-capacity but also the polarization resistance of the electrode surface are taken into consideration.

The above quoted conceptions are to be rationally elucidated by the aid of the integral equation (8) and the Duhamel's integral shown by Eq. (11). Unfortunately these expressions are too complicated to be employed without further modifications; however, the oscillatory character of the electrolytic current is easily to be predicted, since we can legitimately judge that the function $\phi(t)$ may be composed of the periodic functions from the forms of the above equations. This has been really performed in our laboratory by Senda and Tachi(9); they have transformed the Eq. (8) and (11) into more convenient forms, and thus it is found that the resulting a.c. current is composed of non-alternating d.c. component and a.c. component consisting of many higher harmonic waves.

It must next be mentioned here that Randles' theory(3) concerning such a phenomenon gives a prominent result; i.e. upon assuming the periodic changes of interfacial concentrations, he has derived the equations, by which the rate constant of the electrode reaction can be calculated from the experimental data of a.c. voltage electrolysis. It must however, be pointed out that a weak a.c. voltage of the amplitude of a few millivolts should be employed, owing to the approximate mathematical treatment. Breyer and others(2) have also elaborated the same problem, but is seems that they have not considered the structural change of the diffusion layer with time and regarded the instantaneous current intensity as governed by the value corresponding to the mean diffusion current in the classical polarogram. It may be safe to say that the ordinary polarogram does not show behaviour similar to the characteristic curve of the triode vacuum tube. Nevertheless, their works provide us much experimental information most lavishly and the term " a.c. polarography " has actually originated from them. On the other hand, the articles of Fournier(4) and Kalousek(10) are of special interest, and a more advanced systematic theory for the a.c. polarography will be fully discussed in the succeeding chapter.

Simplified Theory for the A.C. and D.C. Components of Electrolytic Current

(1) **Reversible Electrode.**—The electrode potential in the a.c. polarographic electrolysis is composed of the d.c. voltage E and the sine-wave a.c. voltage $A \sin wt$, as illustrated in Fig. 1(a). Now, let us suppose that the sine-wave a.c. voltage is equivalent to a square-wave voltage, then the electrode potential V shows a change with time as shown in Fig. 1(b); namely,

$$\left.\begin{array}{l} E=\begin{cases} E_1 & \text{for } 0<t<T \\ E_2 & \text{for } T<t<2T\,; \end{cases} \\ V(t)=V(t+2T)\,; \\ 2T=1/f=2\pi/\omega. \end{array}\right\} \qquad (12)$$

In this case, the suitable amplitude of the hypothetical squarewave voltage may be equal to the effective value of amplitude of the original sinusoidal voltage; i.e.

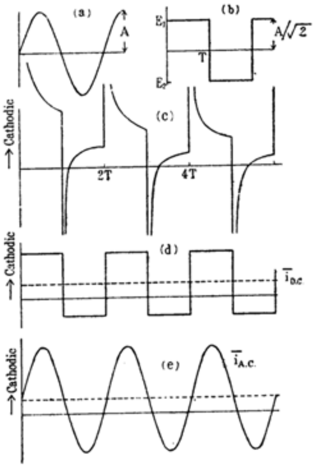

Fig. 1.

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[8] D. C. Grahame, *J. Electrochem. Soc.*, **99**, 370C (1952).

[9] M. Senda and I. Tachi, Reported at the 7th Annual Meeting of the Chemical Society of Japan, held on the 3rd April 1954 in Tokyo.

[10] M. Kalousek, *Collection Czech. Chem. Communs.*, **13**, 105 (1948).

$$\frac{1}{2}(E_2-E_1)=\frac{A}{\sqrt{2}} \qquad (13)$$

The course of the current-time curve due to the application of a rectangular voltage has been elaborated theoretically by Kambara[11], and an example thereof is given in Fig. 1(c). Further it has been manifested that upon evaluating the respective mean current flowing in each half-period shown by $V=E_1$ and $V=E_2$, we may approximately regard the whole electrolytic current to be the algebraic sum of the constant current $\bar{i}_{D.C.}$, and the square-wave-current $\bar{i}_{A.C.}$, as illustrated in Fig. 1(d); and the current is possessed of the same period $2T$ as the applied square-wave voltage. Let $\bar{i}_1$ be the mean current, that is to be observed when the constant potential E_1 is applied, and let $\bar{i}_2$ be that observed with the constant voltage E_2. Then it can be demonstrated from Kambara's theoretical treatment that

$$\bar{i}_{D.C.}=(\bar{i}_1+\bar{i}_2); \qquad (14)$$

$$\bar{i}_{A.C.}=2\left(s\sqrt{f}-\frac{1}{4}\right)(\bar{i}_1-\bar{i}_2)\cdot M(t,\ T) \qquad (15)$$

where $S=1.195$ and the meander function $M(t,\ T)$ is defined by

$$M(t,\ T)=\left\{\begin{matrix}+1 \text{ for } 0<t<T \\ -1 \text{ for } T<t<2T;\end{matrix}\right\} \qquad (16)$$

$$M(t,\ T)=M(t+2T,\ T)$$

Next, we will regard the square wave current, that is shown by Eq. (15) and in Fig. 1(d), as equivalent to a sine-wave alternating current; in order to keep the integrated amount of electricity flowing in each half-period constant, upon employing the familiar factor $\pi/2$, we may be able to describe

$$\bar{i}_{A.C.}=\pi\left(s\sqrt{f}-\frac{1}{4}\right)\cdot(\bar{i}_1-\bar{i}_2)\cdot\sin\omega t. \qquad (17)$$

From the above cited somewhat conventional consideration, it may be concluded that when the polarographic electrolysis is carried out under the superposition of sine-wave voltage, the resulting electrolytic current, which is to be represented by a complicated function of time, may be regarded as the sum of two components, i.e. the d.c. component given by Eq. (14) and the a.c. component given by Eq. (17). It follows immediately therefrom that Fournier's polarogram[4] is the register of the d.c. component, and Breyer's current-voltage curve[2] is the recording of the a.c. component. The essential validity of the above conclusion concerning the Fournier's polarogram, has been already reported[11] (see Fig. 2); and further it is expected from the above theory that when we register $\bar{i}_{A.C.}$ against the usual d.c. voltage E, the derivative curve of the reversible polarogram is to be obtained according to Eq. (17), provided that the amplitude of the superimposed a.c. voltage remains constant. This conclusion is quite in harmony with the observations of Breyer's school as well as with the experimental results obtained with the I-F apparatus[12]. It must be, however, pointed out that Breyer and others, although their experimental work is prominent, have shown an irrational consideration in regard to the a.c. component of the irreversible wave; the fast that the irreversible system shows no peak in a.c. polarogram is not due to the less steep inclination at the half-wave point, but it should be essentially ascribed to the irreversible character of the system concerned.

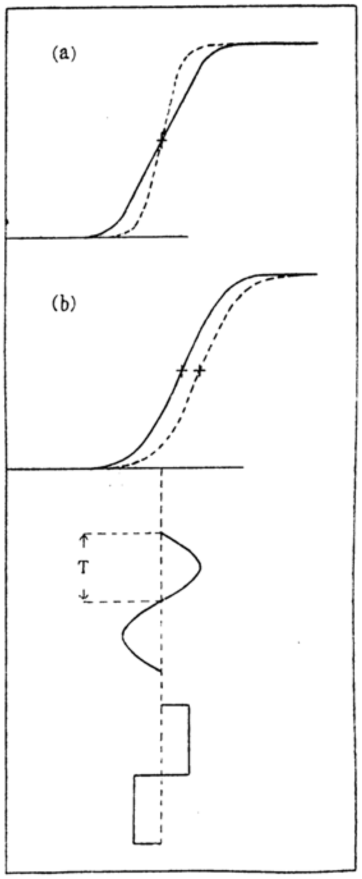

Fig. 2. Fournier's polarogram (a, reversible; b, irreversible).

(2) **Fournier's Polarogram in the Case of Irreversible Wave.**—It has been pointed out that what governs the whole course of polarogram of irreversible redox system is not the interfacial equilibrium concentration of the

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[11] T. Kambara, This Bulletin, 27, 527, 529 (1954).

[12] M. Ishibashi and T. Fujinaga, This Bulletin, 23, 261 (1950), 25, 68, 238 (1952).

depolarizer, but the rate constant at that electrode potential[13]. Now, let us again suppose that the superimposed sine-wave voltage $A \sin wt$ is equivalent to the square-wave voltage of the same frequency, the amplitude of which is shown by $\Delta E = A/\sqrt{2}$ (Fig. 3). Then the rate constant of the cathodic reduction is given by

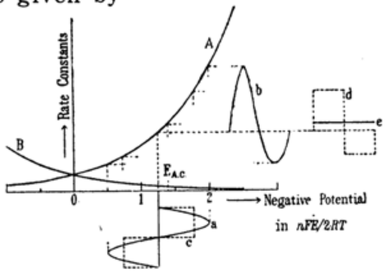

Fig. 3.

$$\overrightarrow{k}_{A\cdot C\cdot} = \left\{ \begin{array}{l} \overrightarrow{k}_E \exp\dfrac{\alpha nF\Delta E}{RT} \\ \quad \text{for } 2nT < t < (2n+1)T\,; \\ \overrightarrow{k}_E \exp\dfrac{-\alpha nF\Delta E}{RT} \\ \quad \text{for } (2n+1)T < t < (2n+2)T\,; \end{array} \right\} \quad (18)$$

where n denotes the integer, and $\overrightarrow{k}_E$ is shown by

$$\overrightarrow{k}_E = \overrightarrow{k}_S \exp\frac{-\alpha nFE}{RT} \quad (19)$$

where $\overrightarrow{k}_S$ shows the rate constant for $E=0$ [cf. Eq. (6)]. Next writing

$$\Delta\xi = \frac{\alpha nF}{RT}\cdot\Delta E, \quad (20)$$

we can find that

$$\text{Mean value of } \overrightarrow{k}_{A\cdot C\cdot} = \overrightarrow{k}_E\cdot\frac{1}{2}\left(e^{+\Delta\xi}+e^{-\Delta\xi}\right)$$

$$= \overrightarrow{k}_E \cosh\Delta\xi =$$

$$= \overrightarrow{k}_S \exp\left\{\frac{-\alpha nF}{RT}\left(E - \frac{RT}{\alpha nF}\ln\cosh\Delta\xi\right)\right\} (21)$$

It has been derived[14] that when a constant potential E is applied to a stationary plane electrode, at which the cathodic reduction proceeds irreversibly, then the resulting rate constant $\overrightarrow{k}_E$ determines the instantaneous current intensity i; viz.

$$i = nFq\overrightarrow{k}_E{}^{*}C_O \exp\left(\frac{\overrightarrow{k}_E{}^2 t}{D_O}\right)\operatorname{erfc}\left(\frac{\overrightarrow{k}_E\sqrt{t}}{\sqrt{D_O}}\right) \quad (22)$$

Further it is known that the polarogram, in which the mean current I is plotted against E, is shown by

$$I = \frac{I_a}{2}\left\{1+\tanh\frac{-\alpha nF(E-E_{1/2})}{2RT}\right\},$$

which is transformed into

$$E = E_{1/2} + \frac{RT}{\alpha nF}\ln\frac{I_a - I}{I} \quad (23)$$

where I_a denotes, as usual, the mean value of the limiting cathodic diffusion current, and $E_{1/2}$ the half-wave potential of the irreversible wave[13]. It follows from Eq. (21) that the superposition of the a.c. voltage on the constant voltage E is effectively equivalent to the application of the constant voltage $E_{A\cdot C\cdot}$, which is more negative than E as shown in Fig. 3 and is given by

$$E_{A\cdot C\cdot} = E - \frac{RT}{\alpha nF}\ln\cosh\Delta\xi. \quad (24)$$

Therefore, the Fournier's polarogram is the case of irreversible wave is represented by

$$E = E_{1/2} + \frac{RT}{\alpha nF}\ln\cosh\frac{\alpha nF\Delta E}{RT}$$

$$+ \frac{RT}{\alpha nF}\ln\frac{I_a - I}{I}. \quad (25)$$

Namely, by the superposition, the resulting polarogram should be shifted positively (see Fig. 2 and 3); and the half-wave potential of Fournier's polarogram $E_{1/2\text{-Fournier}}$ is more positive than that of the classical polarogram. And the difference between the two half-wave potential is shown by

$$(\Delta E_{1/2})_{A\cdot C\cdot} = E_{1/2\text{-Fournier}} - E_{1/2} =$$

$$\frac{RT}{\alpha nF}\ln\cosh\frac{\alpha nF\Delta E}{RT}. \quad (26)$$

In a case when the amplitude of the superimposed a.c. voltage is of the order of hundred millivolts or more, i.e., $\alpha nF\Delta E/RT \gg 1$, it can be derived approximately that

$$(\Delta E_{1/2})_{A\cdot C\cdot} \simeq \Delta E + \frac{RT}{\alpha nF}\ln\frac{1}{2}. \quad (27)$$

Thus at the room temperature, the shift of half-wave potential is given by

$$(\Delta E_{1/2})_{A\cdot C\cdot} \simeq \Delta E - \frac{0.301}{\alpha n}\times 58\,mV.$$

Hence it is found that there is a linear relationship between the shift of half-wave potential and the amplitude of the superimposed a.c. voltage. On the other hand, for the smaller value of ΔE, it can be readily seen that

$$\ln\cosh\Delta\xi \simeq \ln\left(1+\frac{1}{2}\Delta\xi^2\right) \simeq \frac{1}{2}\Delta\xi^2\,;$$

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[13] H. Eyring, L. Marker and T. C. Kwoh, *J. Phys. Coll. Chem.*, **53**, 1453 (1949); N. Tanaka and R. Tamamushi, This Bulletin, **22**, 187 (1949); R. Tamamushi and N. Tanaka, ibid., **227**, **23**, 110 (1950); R. Goto and I. Tachi, *Proc. I. Inter. Polarogr. Congr. in Prague*, Part 1, 69 (1951); N. Tanaka and R. Tamamushi, ibid., 486; M. Kalousek and A. Tockstein, ibid., 563.

[14] T. Kambara and I. Tachi, This Bulletin, **25**, 135 (1952).

therefore it is found that

$$(\Delta E_{1/2})_{A.C.} \simeq \frac{\alpha n F}{RT}\cdot \Delta E^2.$$

There is no doubt that $(\Delta E_{1/2})_{A.C.}$ becomes zero for $\Delta E=0$, which is a quite rational conclusion. The above developed theoretical consideration has been amply confirmed experimentally and will be reported in our succeeding paper.

Fundamental Theory of A.C. Polarography

It may be concluded from the above stated theory that the essential principle of a.c. polarography is as follows. I.e., when we superimpose an a.c. voltage, the wave form of which may be sinusoidal or rectangular, on the usual polarographic d.c. voltage, then the resulting electrolytic current is an extraordinarily complicated function of time; it is, however, possible to separate the current into the a.c. component and the d.c. component and to observe and record both the components individually. The former is to be called Breyer's polarogram and the latter Fournier's current-voltage curve, and the essential features of Breyer's and Fournier's polarograms are easily comprehensible from the present theory. Thus, from the practical standpoint of polarographic application, the methodology of a.c. polarography is expected to be very important. In the case of the irreversible redox system the a.c. component will show no appreciable peak, which would be advantageous for the elimination of disturbing irreversible waves; and as for the d.c. component, the superposition of the a.c. voltage will surely shift the anodic wave negatively as well as shifting the cathodic one positively, so that at last the separated two waves of the irreversible redox system would unite together, as illustrated in Fig. 4 Although such an example has not yet been reported, it may be safe to say that the superposition of a.c. voltage shows the behaviour of catalyst, since in a half-period it accelerates the cathodic reduction and in another half-period it promotes the anodic oxidation. Next, in the case of the reversible wave, the a.c. component shows a peak, which is to be regarded as the derivative polarogram; and in the case of decreased reversibility, the peak height depends on the degree of reversibility concerned as well as the concentration of the depolarizer; it is well known that the peak height is remarkably dependent of the nature of supporting electrolyte, as reported by Breyer and others.[2] If we record the d.c. component together with the a.c. component and the classical polarogram, then the half-wave potential is to be indicated by the summit potential of the peak and also by the intersection of Fournier's polarogram with the classical one.

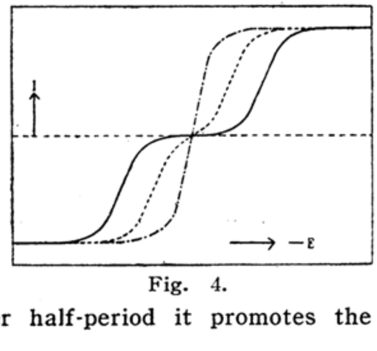

Fig. 4.

So far the a.c. polarography with the a.c. voltage of the constant amplitude has been discussed. It is further possible to make the amplitude vary with time as the d.c. voltage in the ordinary polarography. Then it may be possible with the sine-wave voltage to attain the polarogram of increased sensitivity, which has been shown by I-F apparatus[12] with the aid of rotating switch and current alternator. Further some attractive and characteristic findings obtained with Kalousek's apparatus,[8] which have been cleared up theoretically by Kambara[11], may also be developed by the a.c. polarography, in which the amplitude of a.c. voltage is made to change linearly with time as well as the d.c. voltage.

Addendum[15]

Recently Breyer and Hacobian[16] have published a new theoretical treatment of the present problem, in which the essential role of diffusion in a.c. polarography is legitimately taken into account. The theory deals with the complete reversible electrode reaction. The present authors wish to publish our opinion on the paper later.

Summary

At first the rigorous and orthodox treatment of the polarographic electrolytic current due to the superposition of an alternating voltage upon a constant voltage is shown and the earlier polarographic studies, in which an alternating voltage is employed, are discussed. Next it is shown that in order to treat the a.c. polarography theoretically, we can profitably assume that the superimposed sinusoidal a.c. voltage is equivalent

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[15] At the request of the editor the present paper was rewritten in a new form. Consequently the new paper by Breyer and Hacobian can be cited here.

[16] B. Breyer and S. Hacobian, *Austral. J. Chem.*, 7, 225 (1954).

to the square-wave voltage of the same frequency. In a case when an a.c. voltage, is superimposed upon the usual d.c. voltage, the resulting current becomes a very complicated function of time. It can be shown, however, that the current is the algebraic sum of a.c. component and d.c. component, the latter of which is Fournier's polarogram and the former Breyer's polarogram. Some outstanding characteristics of both components are satisfactorily cleared up, and it demonstrated that in such a manner a rational and systematic explanation of a.c. polarography is given.

The authors wish to express their hearty thanks to Prof. B. Breyer, who has communicated to them the progress of studies carried out in the University of Sydney.

Department of Agricultural Chemistry,
Faculty of Agriculture, Kyoto
University, Kyoto