Studies on A. C. Polarography. III. Reversible Wave[*]

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Introduction

In Part I[1] and II[2] of this study the theoretical treatment of the Alternating Current-Polarography (a. c. polarography) was reported, and in Part III[3] the fundamental circuits together with the results of several basic experiments were communicated. In this article, the experiments concerning the d. c. and a. c. components of electrolytic current due to the reversible electrode reaction observed with the a. c. polarographic equipment, in which a sinusoidal alternating voltage of a constant amplitude is superimposed on the constant d. c. voltage used in the ordinary polarography, will be given and compared with the theoretical conclusion.

As is well known, the mean current $\bar{i}$, which is observed in the ordinary polarography using a dropping mercury electrode, is a function of the electrode potential V, and is given by

$$\bar{i}=\frac{\bar{i}_d}{2}\left\{1+\tanh\frac{nF\,(E_{1/2}-V)}{2RT}\right\}, \tag{1}$$

where $\bar{i}_d$ is the mean limiting diffusion current, n the number of electrons associated with the electrolytic reduction, $E_{1/2}$ the half-wave potential, and the other symbols have their usual significances. According to the theoretical treatment given in Part II of this study, in the case that the electrode reaction proceeds reversibly, the mean value, $\bar{i}_F$, of the d. c. component of the a. c. polarographic electrolytic current, i. e. Fournier's polarogram, is shown by

$$\bar{i}_F=\frac{1}{2}(\bar{i}_1+\bar{i}_2), \tag{2}$$

whereas the mean value of the amplitude of a. c. component, i. e. Breyer's polarogram, is given by

$$\bar{i}_{A.C.}=K(\bar{i}_1-\bar{i}_2). \tag{3}$$

Let E be the constant d. c. voltage applied to the dropping mercury electrode, and $\varDelta E$ the amplitude of the superimposed a. c. voltage, then $\bar{i}_1$ and $\bar{i}_2$, respectively, are given by

$$\left.\begin{aligned}\bar{i}_1&=(\bar{i})_{V=(E-\varDelta E)};\\ \bar{i}_2&=(\bar{i})_{V=(E+\varDelta E)}.\end{aligned}\right\} \tag{4}$$

K in Eq. (3) is given by $(s\sqrt{f}-1/4)$, in which f is the frequency of the a. c. voltage, and $S=1.192$ is a constant. Because we use a. c. voltage of 60 c/s, K is nearly equal to 9.04. The above theoretical treatment has been based on the assumption that the superimposed sinusoidal alternating voltage is equivalent to the square wave voltage of a suitable amplitude; we employ here the a. c. voltage of sinusoidal wave form. Thus, in the present experiment, the effective value of the superimposed a. c. voltage is regarded to be equivalent to the amplitude of the square wave voltage, and the results are discussed. As the depolarising cation, thallous ion in 0.1 N KCl solution is chiefly employed, since it is well known that the ion shows nearly a perfect reversible behaviour[4,5]; and further cadmium ion is often, according to the necessity, employed, which also shows a high degree of reversibility[4]. Circuit for a. c. polarography, as already reported in Part III of this study, is used. The superimposed a. c. voltage is obtained by lowering the 100 v., 60 cycle a. c. line by means of a transformer and a suitable rheostat divider; the electrolysis is carried out in room temperature at 25°C and the bottom mercury layer was used as the anode, against which the cathode potential is measured. The sensitivity of galvanometer used is 4×10^{-9} Amp./mm./m.

Experimental Results and the Theoretical Consideration

(1) Wave Form of the A. C. Polarogram.—Fig. 1 shows the theoretical a. c. polarograms together with the ordinary polaro-

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[*] Read at the monthly meeting of the Agric. Chemical Society of Japan held in Kyoto University on the 18th July 1953.

[1] I. Tachi and T. Kambara, This Bulletin, 28, 25 (1955).

[2] T. Kambara and I. Tachi, ibid., **28** 25 (1955).

[3] M. Senda, M. Okuda and I. Tachi, ibid., **28** 31 (1955)

[4] J. Heyrovský, *Discus. Farad. Society*, No. 1, 121 (1947).

[5] J.E. Randless, ibid., 11.

gram; and in Fig. 2 and 3 are illustrated the a. c. polarograms observed experimentally. In Fig. 1 curves d and e represent the

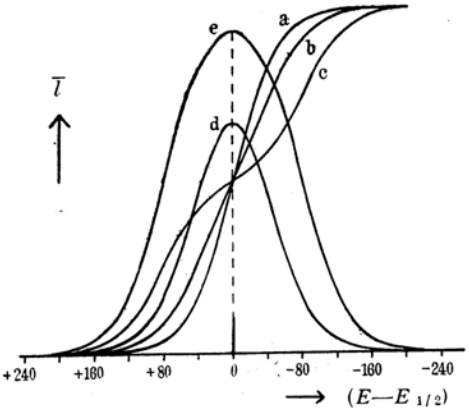

Fig. 1. Theoretical polarograms.
($n=1$, $t=25$°C)
a: ordinary polarogram, $\Delta E=0$mV
b: Fournier's polarogram, $\Delta E=40$mV
c: Fournier's polarogram, $\Delta E=80$mV
d: Breyer's polarogram, $\Delta E=40$mV
e: Breyer's polarogram, $\Delta E=80$mV

a. c. components, where the currents are plotted in $1/K$ unit of the calculated values. As required by the theoretical conclusion shown by the Eqs. (1) and (2), the d. c. component of a. c. polarogram (namely, the Fournier's polarogram) shows the less steep slope than the classical polarogram with the increasing amplitude of the superimposed a. c. voltage, until it begins to split into two steps; and the classical and Fournier's polarograms intersect with each other always at the half-wave point. The experimental results shown in Fig. 2 are in good harmony with the theoretical prediction. On the other hand, the a. c. component of the a. c. polarogram (namely, the Breyer's polarogram) is found to show a peak at the half-wave potential, as shown obviously by Eq. (3) and also in Fig. 3. In the case of the Breyer's polarogram, owing to the differential capacity[6] of the electric double layer at the electrode-solution interface, an alternating current governed by the product of the differential capacity and surface area flows, even when there is no depolarizer in the solution (Fig. 3 (a)); thus the recorded alternating current is the vector sum of the alternating current, $\bar{i}_B$, due to the differential capacity, which is to flow in the empty solution, and the electrolytic alternating current, $\bar{i}_{A.C.}$. It is clear that when we observe the Fournier's polarogram, the current due to the differential capacity is not observable by the galvanometer, since the mean value thereof is obviously zero.

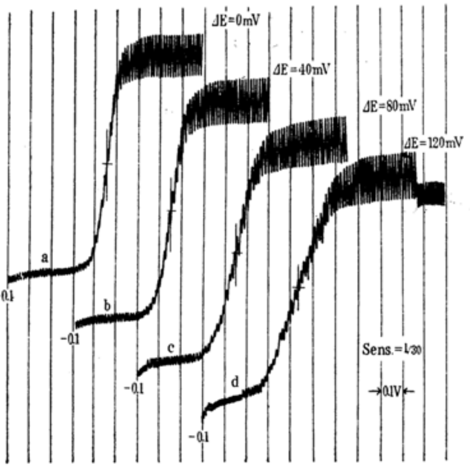

Fig. 2. Observed Fournier's polarogram due to the depolarization of Tl^+. Solution: 10^{-3} M $TlNO_3$ in 0.1 N KCl

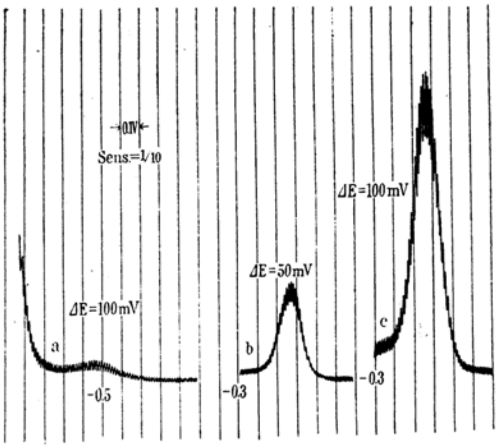

Fig. 3. Observed Breyer's polarogram due to the depolarization of Tl^+.
a: 0.1 N KCl solution
b and c: 2×10^{-3} M $TlNO_3$ in 0.1 N KCl solution

It must be mentioned here that the anodic dissolution of mercury affects the a. c. polarogram considerably. Namely, in Fig. 2 (d) the Fournier's polarogram due to the anodic reaction of mercury is observable in the more negative potential than in the case of classical polarogram. Also in Fig. 3 (a) the Breyer's polarogram increases suddenly at the positive potential, where the oscillatory current due to the reversible deposition and dissolution of mercury is of special importance.

It is seen further that the drop time often becomes abruptly short resulting in the sud-

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

den decrease in the current intensity; this is found in the ascending parts of the waves shown in Fig. 2 (c) and (d) and in the final part of the wave shown in Fig. 2 (d). This finding seems to be due to the effective decrease in the interfacial tension caused by the superposition of a. c. voltage. The critical potentials, at which such a sudden decrease occurs, lie in both sides of the potential corresponding to the electrocapillary maximum, and furthermore the two critical potentials shift nearly symmetrically with the varying amplitude of the superimposed a. c. voltage, as has been already reported by us[7].

According to the above cited theoretical equation, the half-wave potential of the Fournier's polarogram, denoted by E_F, and the peak potential of the Breyer's polarogram, denoted by E_p, are expected to be identical with the half-wave potential of the ordinary polarogram, independently of the concentration of depolarizer and the amplitude of the superimposed a. c. voltage. Table I gives the experimental results obtained with thallous ion. We can find a fairly good accordance thereof. However, it is found experimentally, that E_p is by ca. 20mV more negative than $E_{1/2}$ and E_F is shifted positively with the increasing amplitude. The reason of such phenomena will be perfectly clarified, when a more exact theoretical treatment, in which the velocity constants of the electrode processes and the transfer coefficient, usually denoted by α, are taken into consideration.

Also the limiting current in the Fournier's polarogram coincides with that of the classical polarogram at a *sufficiently* negative potential. The experimental results shown in Fig. 2 are in harmony with the theoretical prediction. On the other hand the observed peak height in Breyer's polarogram is far less than the theoretical value. This will be discussed in the succeeding section of this report.

TABLE I

COMPARISON OF THE HALF-WAVE POTENTIAL OF FOURNIER'S POLAROGRAM AND THE PEAK POTENTIAL OF BREYER'S POLAROGRAM

Solution: 10^{-3} M $TlNO_3$ in 0.1 N KCL

ΔE (mv.)	E_F (v.)	E_p (v.)
0	-0.55_0	
40	-0.54_8	-0.57_0
80	-0.54_5	-0.57_0
120	-0.54_0	-0.57_0

(2) Effects due to the Amplitude of the Superimposed A. C. Voltage.—Fournier has verified experimentally the influence of the frequency of the superimposed a. c. voltage on the d. c. component of the polarographic current, and found that in the case of the reversible electrode reaction the wave form remains nearly unchanged independently of the frequency, provided that the amplitude thereof is kept constant[8]. This is theoretically predicted by Eq. (2). Thus we have investigated the behaviour of d. c. component in the case that the amplitude is varied, while the frequency of 60 c/s is unchanged. As stated above, the d. c. component is at last splitted into two waves with the increasing amplitude employed, while the half-wave point lies unchanged at the original half-wave potential. This can be far more distinctly observed when the wave analysis is carried out concerning the Fournier's polarogram. Fig. 4 gives an example of thallous ion. A small deviation of the experimental observation from the theoretical equation is found, which may be due to the simplified supposition that the applied sinusoidal alternating potential is equivalent to a square wave voltage. The course of the observed current-potential curve, however, runs quite in the same manner to the theoretical curve, indicating the essential legitimacy of the theory.

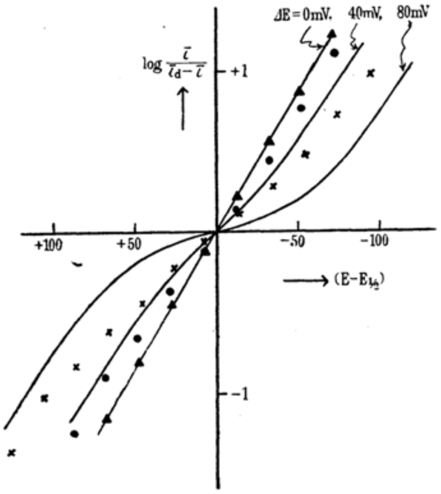

Fig. 4. Wave analysis of the Fournier's polarograms of Tl^+ (for a, b and c in Fig. 1 and 2) by means of the logarithmic plott.

——: theoretical curves

▲ (ΔE=0mV)
● (ΔE=40mV) : experimental values
× (ΔE=80mV)

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[7] I. Tachi and M. Okuda, This Bulletin, 27, 310 (1954).

[8] M. Fournier, *Comp. rend.*, 237, 1673 (1951).

In Fig. 5 is given the dependency of the peak current intensity of the Breyer's polarogram on the amplitude of the employed a. c. voltage. Ih this diagram each current intensity has been calibrated for the capacity current, which is also observable with the blank solution. From Eq. (3), it follows that

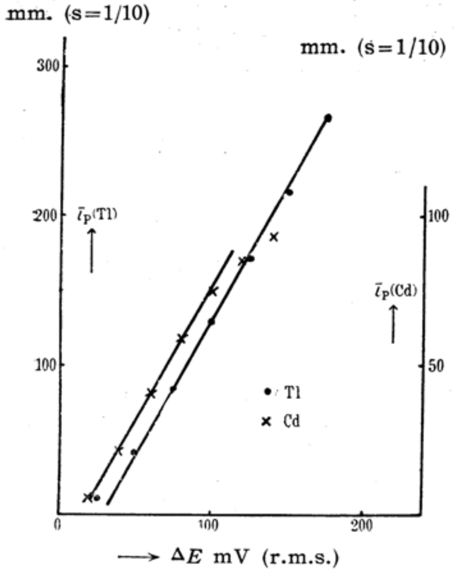

Fig. 5. Peak current vs. ΔE curve.
●: 2×10^{-3} M $TlNO_3$ in 0.1 N KCl
×: 5×10^{-4} M $Cd(SO_4)$ in 0.1 N KCl

$$\bar{i}_p=[\bar{i}_{A.C.}]_{V=E_p}=A\cdot K\cdot \bar{i}_a\cdot \tanh\frac{nF}{2RT}\cdot \Delta E \quad (5)$$

where A is a constant given experimentally and depends on some characteristic constants of circuit and equipment employed. In the present experiment this constant is about 1/40. This exhibits the relationship between the peak current and amplitude. It is expected therefrom that the slope of $\bar{i}_p$ vs. ΔE curve becomes gradually less steep with the increasing value of ΔE, until $\bar{i}_p$ approaches to a constant value given by $A\cdot K\cdot \bar{i}_a$. The experimentally obtained value with cadmium ion, shows such a tendency, however, not in such a remarkable manner as expected from Eq. (5), and a linear relationship between $\bar{i}_p$ and ΔE is observable in an appreciably wide range. In the case of thallous ion, such a linearity persists even with the amplitude greater than 170 mV. Such a difference between Cd^{++} and Tl^{+} seems to be ascribed to the difference of the reversibility as well as to the difference of number of electrons of the two redox-systems.

(3) **Effect due to the Height of Mercury Reservoir.**—Variations of the d. c. and a. c. component due to the change of the height of mercury reservoir are illustrated in Fig. 6.

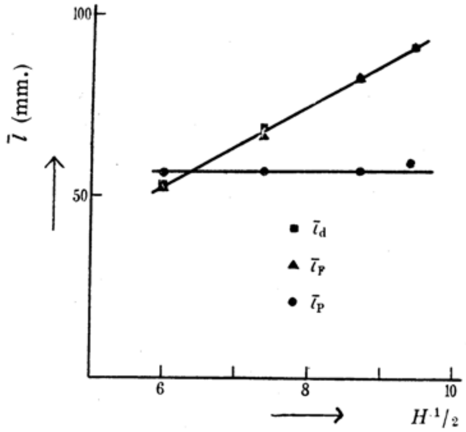

Fig. 6. Effect due to the height of mercury reservoir.
Solution: 10^{-3} M $TlNO_3$ in 0.1 N KCl
ΔE=100mV. Sensitivity of galvanometer is 1/30 for $\bar{i}_a$ and $\bar{i}_F$, and 1/10 for $\bar{i}_q$.

It is clear that the limiting diffusion current of the ordinary polarogram and also that of the Fournier's polarogram are nearly proportional to the square root of the reservoir height. That these two limiting currents must coincide at a sufficiently negative potential, is predicted theoretically by Eqs. (1) and (2). On the contrary, the peak current intensity of Breyer's polarogram remains *constant* independently of the reservoir height. This finding suggests that the a. c. component ought to be proportional to the mean value of the drop surface, as in the case of *kinetic current* investigated by Koutecky and Brdička[9]. This result seems to be comprehensible from the fact that the change of the a. c. component of the electrolytic current is much faster than that of the mercury drop surface.

(4) **Dependency of Current Intensity on the Concentration of Depolarizer.**—The limiting current in the Fournier's polarogram coincides with that of the classical polarogram at a sufficiently negative potential, provided that the drop time remains unchanged, so that it is proportional to the concentration of depolarizing matter. Also it can be derived from Eq. (5) that the peak current intensity of the Breyer's polarogram must be proportional to the concentration. Experimental results with thallous ion are shown

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[9] J. Koutecky and R. Brdička, *Collection Czech. Chem. Communs.*, **12**, 337 (1947).

in Fig. 7, and it is obvious that when the concentration lies in the concentration range varying from 10^{-4} to 10^{-3} mol. per liter, the satisfactory result is found. Quite the same results are also obtained with cadmium ion. Fig. 8 gives an experimental $\bar{i}_p$-$^*C$ curve, in which the bulk concentration $^*C$ of depolarizer is of the order of 10^{-3} molar, and it is found that the peak current approaches to a certain limiting value with the increasing concentration, the phenomenon of which will be discussed later elsewhere.

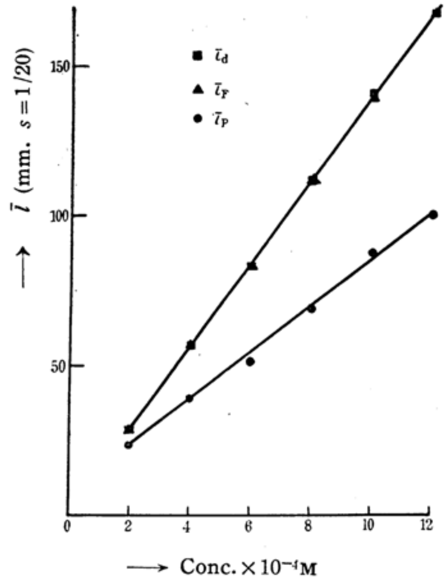

Fig. 7. Dependency of each current intensity on the concentration.
Solution: $TlNO_3$ in 0.1 N KCl. $\Delta E = 80$mV.

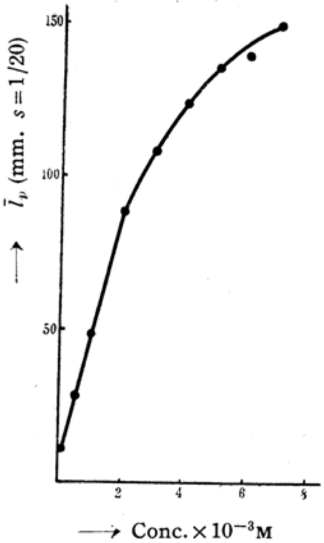

Fig. 8. Dependency of peak current on the concentration.
Solution: $Cd(SO_4)$ in 0.5 N KCl. $\Delta E = 100$mV.

Summary

The d. c. and a. c. components of the electrolytic current observed a. c. polarographically, i. e. the Fournier's and Breyer's polarograms, are investigated experimentally for the reversible electro- reductions of cadmium and thallous ions. The result of the experiment shows convincingly the essential legitimacy of our theoretical conclusion.

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