*Studies on A.C. Polarogroaphy. II. Fundamental Circuit and Some Experimental Results**)

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Introduction

A design of a.c. polarographic circuit, where a small alternating potential is superimposed on the usual direct potential applied to the dropping mercury electrode, has been proposed by Breyer and his coworkers1). In the circuit designed by them, the a.c. component of the electrolytic current flowing is measured by means of a vacum-tube voltmeter after amplifying the potential drop across a resistor inserted in the electrolytic circuit and the readings of the voltmeter are plotted against the direct potential, giving a.c. polarogram with peak currents at the potentials characteristic to the discharging depolarizers. Recently Ishidate and his coworkers2) have also showed a new design of a.c. polarograph, in which the amplifier circuit was mainly improved.

In another type of a.c. polarograph, which was first proposed by Kalousek3), a rectangular alternating potential is superimposed on the usual direct potential with the aid of a rotating switch and the electrolytic current is measured by means of a usual galvanometer by connecting the galvanometer circuit with the switch in a proper way. A similar circuit was also devised by Ishibashi and Fujinaga4) independently.

In the present paper a design of a.c. polarograph will be given, in which an alternating potential with not only constant but also varying amplitude is superimposed on the direct potential applied to the dropping mercury electrode and the a.c. component of the electrolytic current flowing is recorded against the direct potential automatically on photographic paper. The mean value of the total electrolytic current, which was first observed by Fournier5) and should be called Fournier's current, is easily obtained by inserting a galvanometer directly in the electrolytic circuit. A brief discussion on the experimental results is also given. All the experiments were carried out at room temperature.

Fundamental Circuit

A schematic diagram of a.c. polarograph designed is shown in Fig. 1. The circuit is composed of three main parts, i.e. an applied voltage source, A, a cell circuit, B, and a device for measuring the resulting current, C. In this figure, A_1B_1 is a potentiometric bridge wound upon an insulating drum, upon which a contact, P_1, slides from B_1 to A_1 with rotation of the drum as in the ordinary polarograph. A_2B_2 is a rheostat and L_1 is a transformer, through which a sinusoidal

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

1) B. Breyer and F. Gutmann, *Discussion Faraday Soc.* No. 1, 19 (1947). B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Research* A3 558, 567, 595 (1951). B. Breyer and S. Hacobian, Ibid. 604, 610 (1951). We are indebted to Prof. Dr. B. Breyer for sending us reprints of the papers on a.c. polarography.

2) M. Ishidate, T. Isshiki and Y. Masuko, *Japanese Patent*, Application No. 5561/1953.

3) M. Kalousek, *Collection Czech. Chem. Communs.*, 13, 105 (1948).

4) M. Ishibashi and T. Fujinaga. This Bulletin, 25, 68, (1952).

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

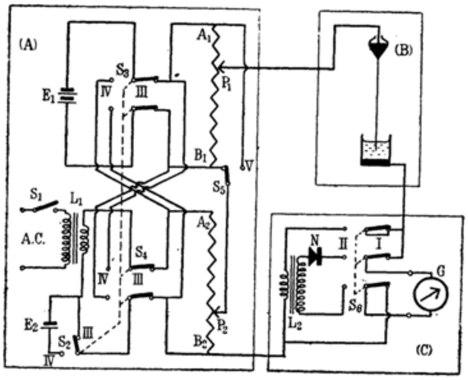

Fig. 1. A.C. Polarographic circuit.

alternating voltage of a definite amplitude is supplied from a 100 v., 60 cycle, A.C. line. Current supplied from a storage battery, E_2, is adjusted so that the direct potential drop across A_1B_1 is equal to the amplitude of the alternating potential drop across it. L_2 is a step-up transformer, N is a crystal rectifier, and G is a moving mirror galvanometer with a conventional shunt. The cell circuit is composed of a dropping mercury electrode inserted into an electrolytic solution and a mercury pool serving as a nonpolarizable reference electrode. Photographic recording of the polarogram is carried out by means of proper mechanical connection between photographic paper and rotation of the drum, as in the Heyrovský-Shikata polarograph.

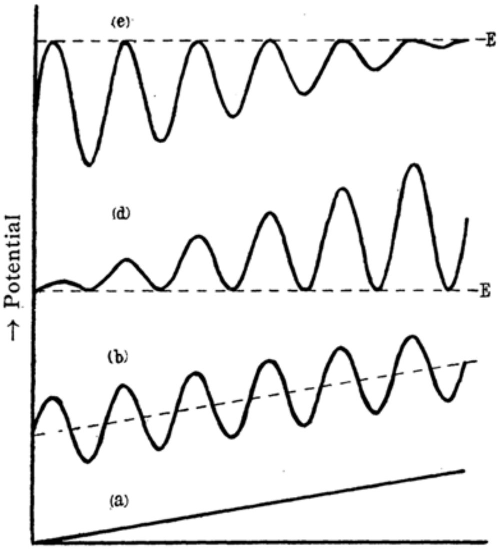

Fig. 2. The change of applied potential with time.
Curve (a): ordinary polarograph.
Curve (b): Fournier's and Breyer's polarograph.
Curve (d): Polarograph with increasing amplitude.
Curve (e): polarograph with decreasing amplitude.
E is the constant applied potential.

The circuit connection illustrated in Fig. 1 represents (a) a circuit operating as an ordinary polarograph. (b) When the switch S_1 is closed, the alternating potential drop of amplitude, ΔV, is produced across the rheostat, i.e.

$$\Delta E = \frac{P_2B_2}{A_2B_2}\Delta V$$

is superimposed upon the d.c. voltage, which, increasing gradually with time or rotation of the potentiometric drum, is applied to the electrolytic cell (Fig. 2-(b)) and the Fournier's polarogram is obtained. Furthermore, (c) connecting the switch S_6 to (II), the Breyer's polarogram, that is a.c. polarogram with constant amplitude, is registered. (d) Connecting the switches S_2, S_3 and S_4 to (IV) and the other switches as in (c), the amplitude of the applied alternating voltage increases gradually with time as is shown in Fig. 2-(d). The constant applied potential, E, is chosen to take the potential value, at which the residual current in ordinary polarogram is obtained, by adjusting the contact of the rheostat. In this case the a.c. component of the electrolytic current has the similar waveform as in the usual polarography⁶⁾ and should be called a.c. polarogram with increasing amplitude. (e) Connecting the switch S_5 to (V), the other switches as in (d), and adjusting P_2 so as to produce the applied direct potential at which the limiting current in ordinary polarography is obtained, the amplitude of the applied alternating voltage decreases gradually with time as is shown in Fig. 2-(e) and the a.c. polarogram with decreasing amplitude is obtained⁶⁾.

In the latter two cases the so-called base current, i.e. a.c. polarogram of empty solution changes considerably with the amplitude of the applied alternating potential but this change of the base current is easily compensated by connecting P_2 and B_2 to the galvanometer circuit by a resistor of large value, because the base current changes linearly with the amplitude, if the differential capacity of electrical double layer at the mercury-solution interface remains almost constant in the potential range, over which the polarograms are taken. All of the polarograms shown in Fig. 4 were taken using this method. Near the electrocapillary maximum potential, however, this condition is not

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6) I. Tachi and T. Kambara, This Bulletin, **28**, 25 (1955).

fulfilled (Fig. 4-(b) and (d)) and a current eliminator of differential type[7] will be necessary for getting well-defined waves. Polarograms recorded by the present circuit are shown in Fig. 3 and Fig. 4. The sudden change of current intensity in the polarograms (e) and (f) in Fig. 4 (marked by arrows) is due to the sudden decrease of drop time, which occurs at a certain potential governed by the amplitude of the applied alternating potential[8]. In such a case artificial control of drop time is needed.

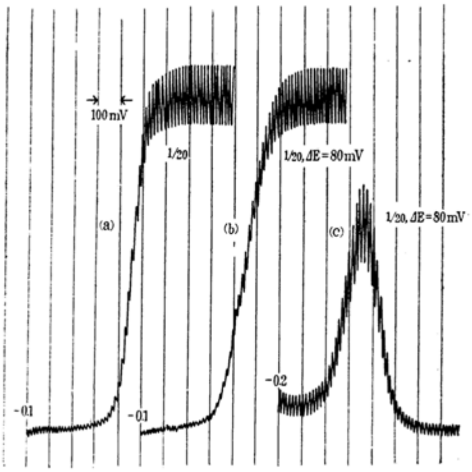

Fig. 3. Ordinary and a.c. polarograms of 10^{-3} M Tl^+ ion in 0.1 N. KCl solution.
Curve (a): ordinary polarogram.
Curve (b): Fournier's polarogram.
Curve (c): Breyer's polarogram.

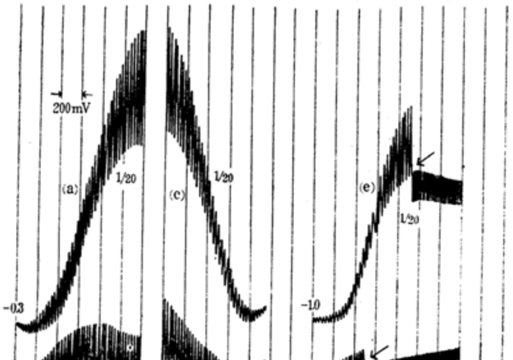

Fig. 4. A.C. Polarogram with varing amplitude.
Curve (a): 1.2×10^{-3} M Tl^+ ion in 0.1 N KCl soln., with increasing amplitude.
Curve (b): base current of 0.1 N KCl soln., with increasing amplitude.
Curve (c): 1.2×10^{-3} M Tl^+ ion in 0.1 N KCl soln., with decreasing amplitude.
Curve (d): base current of 0.1 N KCl soln., with decreasing amplitude.
Curve (e): 10^{-3} M Zn^{++} ion in N KCl soln., with increasing amplitude.
Curve (f): base current of N KCl soln., with increasing amplitude.

Effect of Circuit Characteristics on A.C. Polarogram

Because a.c. polarography is a sort of potential-conditioned electrolysis, the total impedance of the electrolytic circuit must be kept as small as possible, so that it is negligible compared with the equivalent impedance of the observed electrode interface. Though the latter is a function of the direct potential, the amplitude of alternating potential, concentration of depolarizer discharging and other factors concerning the electrode reaction, it is usually far less than it is in ordinary polarography. Accordingly this condition must be carefully fulfilled. In the present experiment the total impedance of the electrolytic circuit except the cell circuit was kept at about 500 ohms, which is not small enough when we carry out the experimental study of a.c. polarography, e.g. in a wide range of concentration of depolarizer. In a.c. polarography the resistance of the electrolytic solution can not be neglected, when the electrode impedance is vanishingly small, e.g. the concentration of depolarizer is high. Fig. 5 shows the effect of concentration of supporting electrolyte on the magnitude of a.c. polarographic current. This effect of supporting electrolyte might be partially due to the change of reversibility of electrode

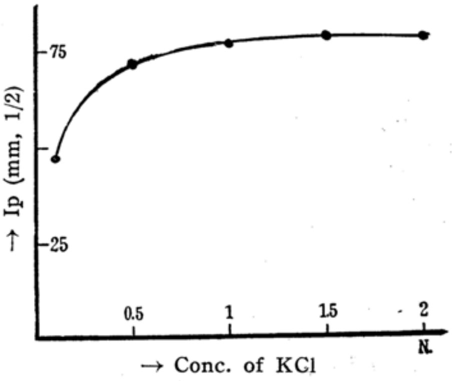

Fig. 5. Effect of concentration of supporting electrolyte on the peak height of a.c. polarographic current of 10^{-3} M Cd^{++} ion in KCl solution.

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[7] G. Semerano and L. Riccoboni, *Gazz. chim. ital.*, 72, 297 (1942).

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

reaction (see below) but, in a large part, due to the resistance of electrolytic solution.

The relation between galvanometer deflection and alternating current flowing across the primary coil of the transformer L_2, is shown in Fig. 6. When the alternating current flowing is negligibly small, the crystal rectifier loses its function. A high gain electronic amplifier is now being constructed in this laboratory.

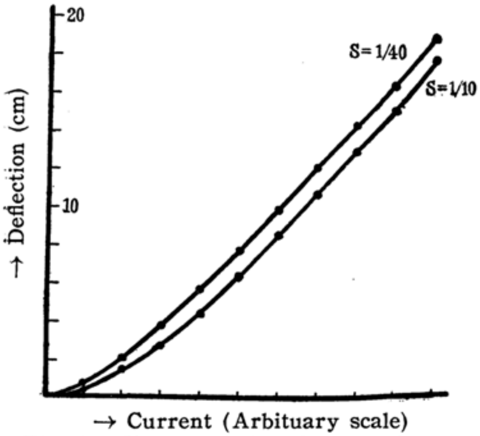

Fig. 6. Characteristics of alternating current detector.

Effect of Reversibility of Electrode Reaction

In a.c. polarography the reversibility of electrode reaction plays a far more important rôle than it does in the ordinary polarography. Detailed experimental study on the a.c. polarographic behaviour of sufficiently reversible electrode reaction will be reported in the succeeding paper of this series. In the present paper preliminary experimental study on the effect of reversibility will be given.

When the electrode reaction is irreversible, the half-wave potential of Fournier's polarogram is shifted to more positive potential with increasing amplitude of the applied alternating potential. According to the theory developed in the previous paper[6)], the difference $(\Delta E_{1/2})_{A\cdot C\cdot}$ of half-wave potentials between ordinary polarogram and Fournier's is given by the equation

$$(\Delta E_{1/2})_{A\cdot C\cdot}=\frac{RT}{\alpha nF}\ln\cosh\frac{\alpha nF}{RT}\Delta E$$

where ΔE is the amplitude of the alternating potential, n the number of electrons required for reduction of one molecule of depolarizer, α the transfer coefficient of reduction process at the electrode and F, R and T are Faraday constant, gas constant and absolute temperature, respectively. When ΔE is larger than a hundred millivolts, $(\Delta E_{1/2})_{A\cdot C\cdot}-\Delta E$ curve becomes a straight line and the tangent of the straight line must be unity. Moreover α could be calculated from the ordinate of the intersection of the straight line and $(\Delta E_{1/2})_{A\cdot C\cdot}$-axis. Experimental results with nickel ion in 0.1 N KCl solution, which is known to be reduced irreversibly at the dropping mercury electrode[9)], are given in Fig. 7, where ΔE is plotted in effective value.

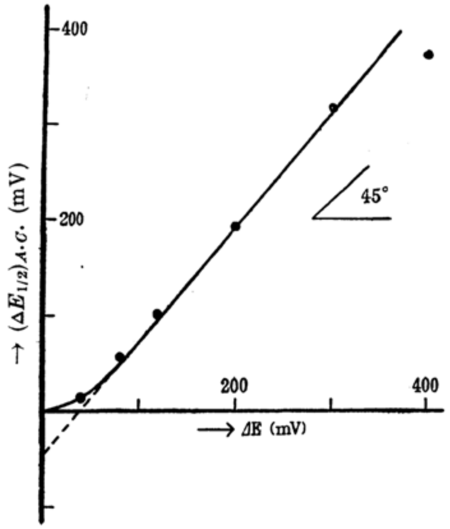

Fig. 7. Shift of the half-wave potential of Fournier's polarogarm with the amplitude of applied alternating potential.

By the graphical extrapolation of the experimental curve, the transfer coefficient was determined to be about 0.3. However, the slope of the experimental curve is slightly steeper than the slope of the theoretical one. This might be attributed to the assumption that the sinusoidal wave was supposed to be equivalent to the square wave.

Randles[10)] and others[11,12)] have shown that when the amplitude of the applied alternating potential is sufficiently small i.e.

$$\Delta E\frac{\alpha nF}{RT}\leqslant 1,$$

the electrode interface at equilibrium potential is at the stationary state electrically equivalent to the circuit shown in Fig. 8, where

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[9)] J. Heyrovský, *Discussion Faraday Soc.* No. 1, 121 (1947).

[10)] J.E.B. Randles, ibid., No. 1, 11 (1947).

[11)] H. Ershler, ibid., No. 1, 269 (1947).

[12)] H. Gerisher, *Z. physik. Chem.*, **198**, 286 (1951).

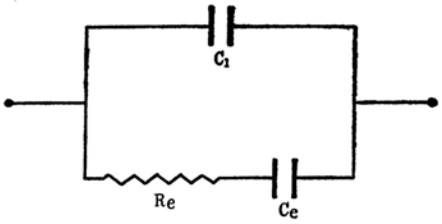

Fig. 8. Equivalent circuit of electrode surface at equilibrium potential at the stationary state.

C_l is the differential capacity of the electrical double layer and C_e and R_e are the capacity and resistance equivalent to the electrode reaction and given by

$$1/\omega C_e=\frac{RT}{n^2F^2}\cdot\frac{1}{qC}\cdot\sqrt{\frac{2}{\omega D}}$$

and

$$R_e=\frac{RT}{n^2F^2}\cdot\frac{1}{qC}\cdot\left(\sqrt{\frac{2}{\omega D}}+\frac{1}{k}\right)$$

respectively, where D is the diffusion coefficient of oxidized and reduced forms, assumed to have the same diffusion coefficient, ω is angular velocity of the alternating potential, k the rate constant of electrode reaction at the equilibrium potential, q surface area of electrode and C is concentration of the depolarizer. From this theory, it is easily recognised that the current intensity of the a.c. component is closely related to the reversibility of electrode reaction. Recently Grahame[13] has developed a more comprehensive theory of a.c. electrolysis and, assuming Ilkovič equation for the diffusion process of depolarizer, he showed that the current intensity at peak potential decreases with decreasing value of k. Fig. 9 shows the Breyer's polarogram and ordinary polarogram of Cd^{++} ion and Z_n^{++} ion in 0.1 N KCl solution; it is known that the reversibility of the former is higher than the latter. In Table I relative values of peak heights of a.c. polarograms of Zn^{++} ions in various supporting electrolytes are given. The experimental results confirm the above theoretical conclusion. Ni^{++} ion in 0.1 N KCl solution shows no appreciable a.c. polarographic wave, which corresponds to its characteristic behaviour in Fournier's polarogram.

TABLE I
CHANGE OF PEAK HEIGHT OF 10^{-3} M Z^{++} ION WITH THE REVERSIBILITY OF ELECTRODE REACTION

Supporting electrolyte (1 N.)	KNO_3	KCl	KBr	KI
k*) (cm/sec)	3.5×10^{-3}	4×10^{-3}	8×10^{-3}	7×10^{-3}
peak height (%)	71	100	201	570

*) B.E. Conway: Electrochemical data, Elsevier Pub. Co. (1952); see also reference (14).

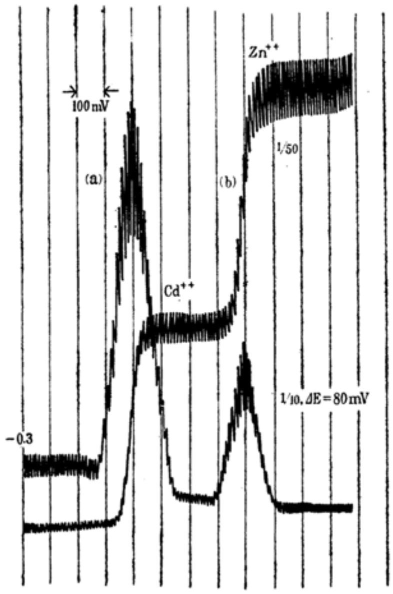

Fig. 9. Breyer's polarogram (Curve-(a)) and ordinary polarogram (curve-(b)) of 10^{-3} M $Cd(SO_4)+10^{-3}$ M $Zn(NO_3)_2$ in 0.2 N KCl solution.

Applications of A.C. Polarography

The high utility of a.c. polarography in analytical applications has been discussed by Breyer and his coworkers[1], i.e. (a) there is no need to remove dissolved oxygen from the electrolytic solution, (b) small amounts of less noble ions can be determined in the presence of a large excess of noble ions, (c) reduction potentials only 40 mV apart are separable using small alternating voltage, (d) the a.c. polarographic current is greater than the ordinary polarographic current, and the limit of sensitivity is at about 10^{-5} N.

The considerable effect of reversibility of electrode reaction on a.c. polarography leads to another interesting applicability of a.c. polarography as is shown in the following model experiment. In Fig. 10, a-I and II are

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

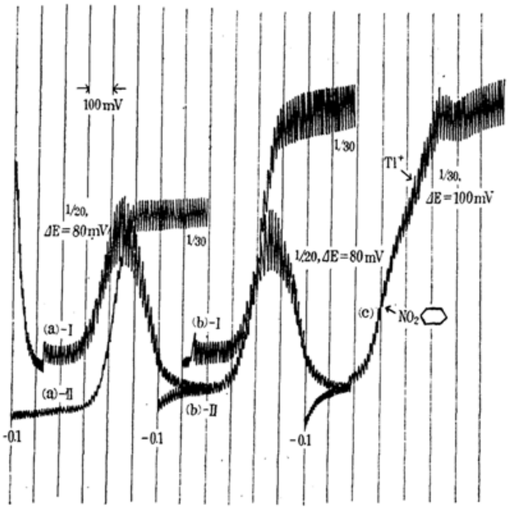

Fig. 10.

Curve (a)-I: Breyer's polarogram of 10^{-3} M $TlNO_3$ in 0.5 N KCl soln. pH=6.

Curve (a)-II: ordinary polarogram of the same solution as (a)-I.

Curve (b)-I: Breyer's polarogram of 10^{-3} M $TlNO_3$+nitrobenzen in 0.5 N KCl soln. pH=6.

Curve (b)-II: ordinary polarogram of the same solution as (b)-I.

Curve (c): Fournier's polarogram of the same solution as (b)-I.

a.c. polarogram and ordinary polarogram of Tl^+ ion, respectively, and b-I and II are the same polarograms, after addition of certain amounts of nitrobenzen to the same solution as (a). Curve (c) is Fournier's polarogram of the same solution as (b). Because the reversibility of electrode reaction of Tl^+ ion is sufficiently high but that of nitrobenzene is considerably low, the magnitude of a.c. polarographic current of the latter is negligible compared with that of the former. Also, because of the positive shift of Fournier's polarogram of nitrobenzene, the completely overlapped wave in b-II has a tendency to separate into two waves in (c). The above experimental results predicate that, when two depolarizers have half-wave potentials lying very close together, or lying even at the same potential, the separate determination is possible, if the degree of reversibility of them is considerably different. Using a.c. polarography for analytical purpose, the effect of the ionic species of supporting electrolytes on the reversibility must be also taken into account. The effect of change of reversibility caused by a minor contamination of surface active substances, which might come into electrolytic solution during sampling, could be avoided by addition of certain amounts of gelatine to the electrolytic solution. Reversibility of electrode reaction, though it decreases by the addition of gelatine, stays almost constant after the concentration of gelatine added attains to a certain range[14]. More detailed experimental as well as theoretical studies on a.c. polarography are now in progress in our laboratory.

Summary

Fundamental circuit for a.c. polarography, in which a.c. polarogram with varying as well as constant amplitude is automatically registered, was shown. And the close relation between reversibility of electrode reaction and a.c. polarographic behaviour of depolarizers was experimentally verified and another applicability of this method was pointed out.

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Kyoto

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[14] J. E. B. Randles and K. W. Somerton, *Trans. Faraday* Soc., **48**, 951 (1952).