61. **Takashi Isshiki and Keizo Tada** : Nonaqueous Polarography of Quinones. I. Polarography of Anthraquinone in Glacial Acetic Acid.

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Although a remarkable progress has been seen in recent polarography of organic compounds, only a few papers have been found on anthraquinone itself, except some of its derivatives. However, much have been studied on simplest quinones such as benzoquinone or naphthoquinones.

These seem, at least partly, to depend upon the fact that anthraquinone without any snbstituents is so sparingly soluble in usual polarographic mediums such as buffer solution alone, buffered alcohols, or others that the experiment on it often encounters many difficulties.

Most recently, nonaqueous solvents such as benzene, glacial acetic acid[1], various kinds of alcohols, liquid ammonia, or dimethylformamide[2] are considered in the polarographic field, because they have a noticeable dissolving ability for less soluble substances, but, except the last one, no papers have been published using these solvents as medium for the polarography of anthraquinone.

Edsberg *et al.*[2] have reported a polarographic method for quantitative determination of this quinone in presence of other related compounds using dimethylformamide as a solvent. This study seems to be of significance because it may be the first nonaqueous polarography for this substance. The results obtained here are not always coincident with those obtained from our tracing experiments in our laboratory. We shall discuss on our findings on another occasion.

On the other hand, we have once studied the polarographic reduction of this quinone together with some of polycyclic quinones in buffered isopropanol. Although no sufficient results to report have yet been obtained it has been found that only nonaqueous solvent would permit carrying out experiments quantitatively or more precisely.

We selected, therefore, glacial acetic acid as the nonaqueous solvent for quinones because of its strong dissolving ability, probable indifference to them, and easiness of purification. Ammonium acetate was used as the supporting electrolyte, which has the concentration of 0.25 *N*. All measurements were carried out at 25° ± 0.2°.

The recorded polarogram of anthraquinone in the above medium showed different

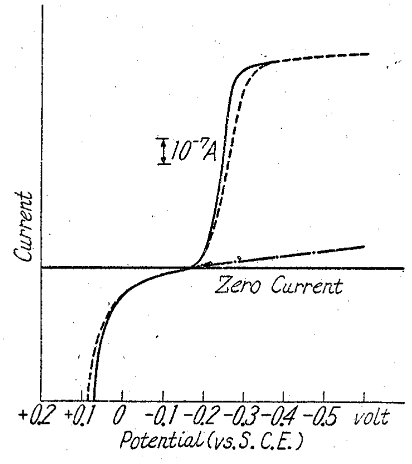

Fig. 1.

Current-Potential Curves (25° ± 0.2°)

Broken line : Recorded wave

(Cell resistance = $3.6\times10^{4}\Omega$)

Solid line : Corrected wave for IR drop

Chain line : Residual current

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* Hongo, Tokyo (一色　孝, 多田敬三).

[1] e. g. Eduard Hila : Chem. Obsor., **23**, 145 (1948) (C. A., 2874 (1949)).

[2] Edsberg, Eichli : Anal. Chem., **25**, 798 (1953).

slope at its reduction wave in each run, because the voltage drop caused by the internal resistance through the cell circuit (namely IR drop) differed widely in each case.

In Fig. 1, the recorded current–voltage curve is shown in broken line, and the corrected one for IR drop in solid line, together with blank polarogram in chain line. It was found that, anthraquinone, like simplest quinones, also produced a single wave which defined and exhibited a half-wave potential at −0.240 volt vs. S.C.E.

Determination of diffusion currents for various concentrations gave values shown in Table I. Plotting these against concentrations gave a linear relationship shown in Fig. 2, and the diffusion current constant, I_D, 3.186 was obtained as the mean value of those given in Table I.

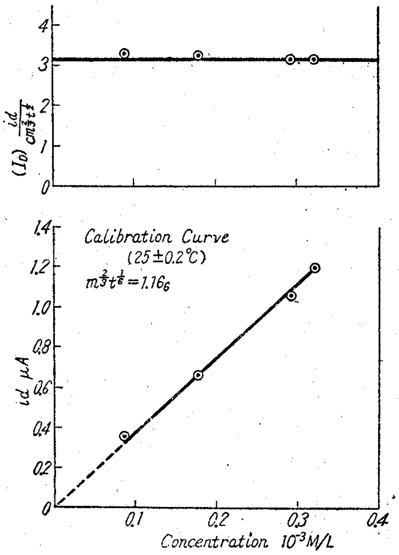

Fig. 2.

TABLE I.

C $\times 10^{-4}\,M$	i_d $\times 10^{-7}$A	$i_d/\mathrm{cm}^{2/3}\mathrm{t}^{1/6}$
3.20_9	11.9_6	3.19_6
2.92_2	10.6_4	13.11_1
1.79_1	6.81_0	3.25_8
0.89_5	3.43_2	3.27_9
	mean value	3.18_6

It has been found now that simplest quinones exhibit a single wave composed of a typical reversible oxidation–reduction system involving two–electron change per molecule in a usual polarographic medium.

In case of anthraquinone, there have been a few papers published regarding the number of electrons contributing to the polarographic reduction. One of them is Edsberg's work[2], which was already referred to and another is Stone's suggestion[3] of probable semiquinone formation in some pH medium, but Stone's work was on anthraquinone derivatives.

By plotting the $\log i/i_d-i$ against various potentials over the corrected wave, a linear relationship was obtained as shown in Fig. 3, whose slope indicated the number of electron change to be 1.66, which was a bit low for a clear cut result, but it may be reasonable to decide that the reduction is a reversible reduction involving two–electron change as those of simplest quinones. These results were different from those obtained from Edsberg's experiment.

On the other hand, the number of electrons could not be determined by the calculation from Gilbert–Rideal's equation, because the wave–height was being maintained practically constant during prolonged electrolysis. This was probable because hydroanthraquinone thus formed

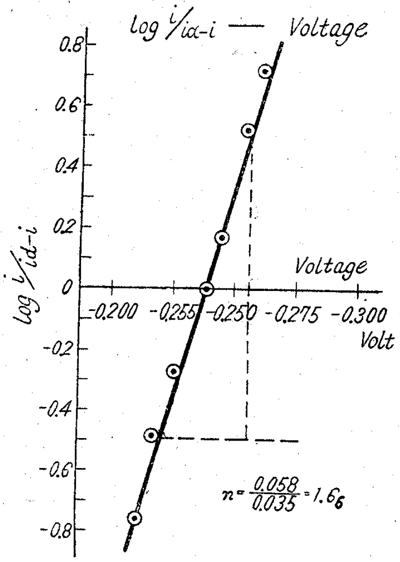

Fig. 3.

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[3] N. Furman, K. G. Stone: J. Am. Chem. Soc., 70, 3055 (1948).

was very unstable and extremely sensitive to oxidation.

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Experimental

Reagents—Anthraquinone : Anthraquinone (C. P.) was purified by sublimation and recrystallized from abs. MeOH, m.p. 286°.

Ammonium acetate : Neutral substance. Special grade substance supplied by Kanto Reag. Co. was used without any purifications after drying in conc. H_2SO_4-desiccator sufficiently. m.p. 112~112.5°.

Glacial acetic acid : Purified by distillation after standing with $KMnO_4$ for three days and the distillate was collected at 118.0~118.1°.

Apparatus—Instruments : Yanagimoto Co.'s polarograph was improved in our laboratory, and thermostat used was made in our laboratory also.

Electrolysis cell : Improved H-type[4] cells as shown in Fig. 4 were used. Ordinary cell having mercury-pool anode was occasionally used for the confirmation of wave height obtained by the H-type cell.

Capillary constants : Measured in each run at mercury pressure of 469 mm. Hg and at the applied voltage of -0.4 volt when connected with S.C.E. and at -0.6 V when used without S.C.E., respectively; $m=0.922_7$ mg./sec. (whose value was measured in glacial acetic acid and identical with that in distilled water); $t=3.50\sim3.70$ sec.

Galvanometer sensibility : Calibrated according to the method of Kolthoff-Lingane ($3.42_6\times10^{-9}$ A/mm. at full sensitivity).

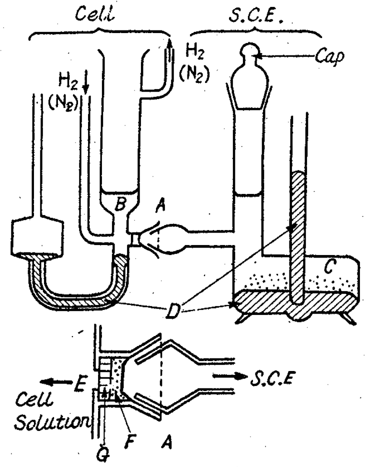

Fig. 4.
Electrolysis Cell of H-Type

A : Ground universal joint
B : Cell solution
C : Satd. solution with KCl, Hg_2Cl_2
D : Mercury
E : Small hole (diameter : more than 2 mm.)
F : Agar gel satd. with KCl (thickness : about 5 mm.)
G : Round slice of pith of Yamabuki (*Kerria japonica* DC. var. *typica* Makino) (satd. with KCl); thickness : about 2mm.; diameter : sufficient for packing.

Procedure—Preparation of the solvent was as follows : 4.818 g. of ammonium acetate was dissolved in glacial acetic acid in graduated flask (250 cc.) and the total volume of the solution was adjusted to 250 cc. at 25.0°. The concentration of ammonium acetate in this solution was then equivalent to 0.25 *N*.

Preparation of cell solution : A sample (1.000~1.010 mg.) was weighed accurately with microbalance and it was dissolved in 15.0~16.0 cc. of the solvent at 25.0° accurately, using special cylinder of 20.0 cc. This solution was employed as a stem cell solution for measuring half-wave potential, and it was diluted to suitable concentrations in other cases. Keeping the temperature at 25.0° was necessary to prevent errors from expansion of the solvent which was unexpectedly large.

Concentrations : They were within the range of $1.0\sim3.0\times10^{-4}$ *M*/L.

Correction for IR drop : The voltage drop caused by the internal resistance[5] through the cell circuit, that is IR drop, was measured, immediately after each run, by plotting the current against the voltage applied step by step to the cell up to 15 volts and extrapolating the curve to the infinite value of voltage. Each half-wave potential exhibited was corrected for the IR drop thus obtained. The internal resistance measured in various runs widely varied from maximum of $5\times10^4\,\Omega$ to mininum

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4) Isshiki, *et al.*; J. Japan. Chem., 8, 116 (1954).
5) Various methods were reported, regarding this, e.g., M. R. Pesce, *et al.*; Anal. Chem., 25, 979 (1953).

of $1\times10^4\,\Omega$ probably owing to the difference between the cell conditions such as the position of capillary in the cell solution.

Removing of dissolved oxygen: Hydrogen free from oxygen and saturated with solvent-vapor was bubbled through the cell solution for about 40~50 mins. before the first recording and for about 15~20 mins. at the interval of each recording in order to remove oxygen perfectly from the cell solution.

Drawing method: $E_{1/2}$ and i_d were determined according to the drawing method reported in this journal[6].

Blank polarogram: As Hila reported[7], the blank polarogram of this medium showed ascending step of the curve with higher negative potentials than about −1.2 volt and it was probably caused by hydrogen.

Summary

Polarography of anthraquinone was carried out favorably in glacial acetic acid containing ammonium acetate. Although it was necessary to correct for IR drop through the cell in each run, it was found that anthraquinone produced a single wave and exhibited a half-wave potential of −0.240 volt vs. S.C.E. Diffusion current was also measured for various concentrations and the diffusion current constant, 3.18_6, was obtained. The reduction was found to be reversible involving two-electron change as those of simplest quinones.

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[6] cf. Isshiki, *et al.*: This Bulletin, **2**, 256 (1954).

[7] E. Hila: Chem. Obzor., **23**, 145 (1948).