

62. Keizo Tada : Nonaqueous Polarography of Quinones. II*. Polarography of 1,2-Benzanthraquinone(9,10) in Glacial Acetic Acid.

(Pharmaceutical Institute, Medical Faculty, University of Tokyo**)

This experiment was carried out, as one of a series of studies on the nonaqueous polarography of quinones, in relation to researches for carcinogens.

1,2-Benzanthracene, the original hydrocarbon corresponding to the subject quinone (I), has been believed to have more or less relationships with carcinogens and much have been investigated for this hydrocarbon and even for more complicated aromatic hydrocarbons in many fields.

Recently, using tetralkylammonium salts as supporting electrolyte, polarographic studies of these polycyclic aromatic hydrocarbons have been reported by Wawzonek, *et al.*¹⁾, but no papers regarding their quinones have been found except pentacene quinones²⁾.

By the previous study on the polarography of (I), anthraquinone (II), and 1,2,5,6-dibenzanthraquinone in the medium of buffered isopropanol, as referred in the previous paper³⁾, it was already found that, with increasing number of rings involved in their structures, their solubilities in usual polarographic solvents and even in other organic solvents decreased.

From the results as previously reported, however, it was expected that glacial acetic acid would also be favorable for the polarography of such less soluble quinone as (I).

All the measurements could, in fact, be carried out in strictly the same conditions as in the previous case which permitted comparison of these results with those obtained previously.

The polarogram of (I) in glacial acetic acid containing ammonium acetate was satisfactorily obtained although the slope of wave recorded in each run differed far from that of real wave, owing to the IR drop, and it was necessary to correct in each run as described in the previous paper.

It was found that (I), giving a single, well-defined wave, exhibited a half-wave potential at -0.168 volt vs. S.C.E., which was 0.072 volt positive than that of (II).

In Fig. 1, the recorded polarogram of (I) is shown in broken line, the corresponding corrected polarogram in solid line, and blank polarogram in chain line.

All of diffusion currents were also easily measured under various concentrations and

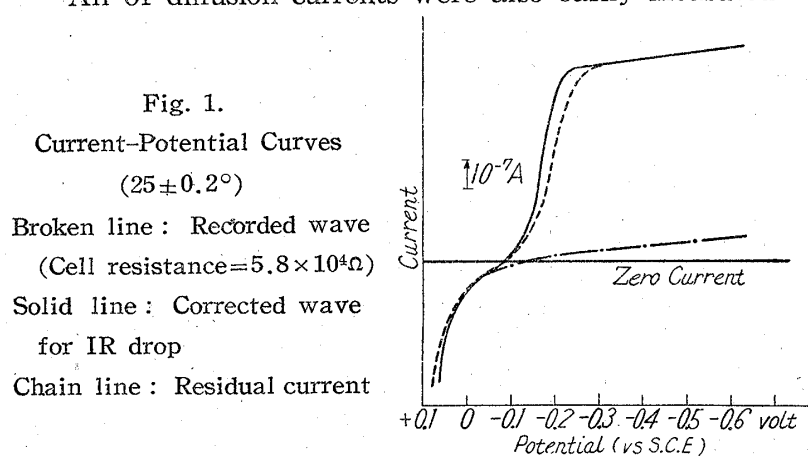


TABLE I.

C $10^{-4} M$	i_d $10^{-7} A$	I ($i_d/cm^{2/3} t^{1/6}$)
2.46 ₉	7.42 ₇	2.54 ₅
1.23 ₁	3.65 ₈	2.52 ₇
0.61 ₅	1.76 ₀	2.44 ₈
	mean value	2.50 ₇

* Takashi Isshiki : Nonaqueous Polarography. II.

** Hongo, Tokyo (多田敬三).

1) e.g. S. Wawzonek, J. W. Fan : J. Am. Chem. Soc., **68**, 2541 (1946).

2) I. Ya. Postovskii : Zhur. Obschei Khim., **20**, 522 (1950).

3) Takashi Isshiki, Keizo Tada : This Bulletin, **2**, 266 (1954).

these results are given in Table I.

The plotting of the diffusion currents against the concentrations indicated a linear relationship as shown in Fig. 2. The diffusion current constant 2.50_7 , was obtained as the mean value of those given in Table I, which were well coincident with the one shown in Fig. 2.

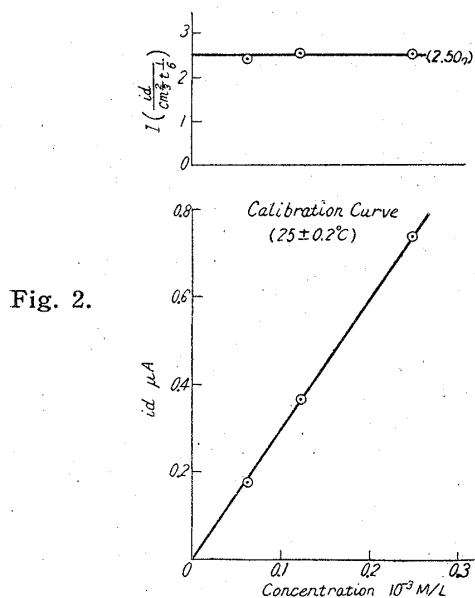


Fig. 2.

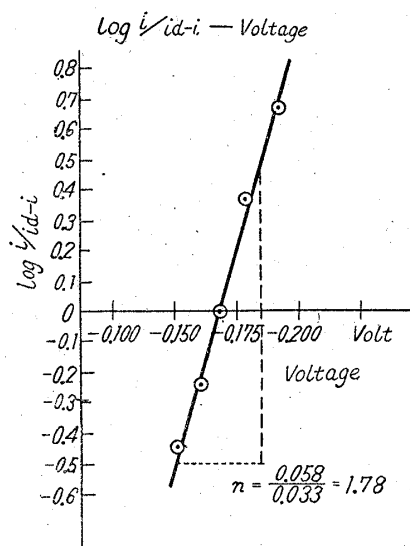


Fig. 3.

By plotting the $\log i/i_a - i$ against various voltages over the corrected wave, a linear relationship was obtained as shown in Fig. 3, whose slope was 1.78, showing that the polarographic reduction of (I) in this medium was a typical reversible one involving two-electron change per molecule like that in (II).

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Experimental

Reagents—1,2-Benzanthraquinone: Synthesized by ring-closure of *o*-(α -naphthoyl)-benzoic acid (m.p. 173–175°), which was obtained from naphthalene and phthalic anhydride after the original procedure of Helle⁴⁾ with some modification made by Fieser⁵⁾.

Purified by passing its benzene solution through an activated alumina column and finally recrystallized from toluene, m.p. 168°. Other reagents, apparatus, and procedures were all same as those described in the previous paper and all experiments were carried out at $25^\circ \pm 0.2^\circ$. Only difference was that (I) was less soluble than (II) in this medium though no difficulties were encountered during this experiment.

Summary

Glacial acetic acid containing ammonium acetate was found to be also favorable medium for such less soluble quinone as 1,2-benzanthraquinone. Using this medium, the polarogram was satisfactorily obtained together with a well-defined single wave and a half-wave potential (-0.168 volt vs. S.C.E.), though the correction for IR drop was necessary in each run as in the case of anthraquinone. The diffusion current constant (2.50_7) was obtained with minimum errors and the number of electrons participating in the reduction was found to be two.

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4) G. Heller, *et al.*: *Ber.*, **41**, 3633 (1908).

5) L. F. Fieser: *J. Am. Chem. Soc.*, **6**, 1032 (1937).