

### 125. *The Polarography of Quinoline Derivatives. Part II.\* The Reduction of 8-Hydroxyquinoline at the Dropping-mercury Cathode.*

By JOHN T. STOCK.

Current-voltage curves of 8-hydroxyquinoline in well-buffered aqueous solutions of pH 2—12 have been constructed, reduction occurring over the entire pH range. The waves correspond with the formation of dihydro- and tetrahydro-8-hydroxyquinoline. A small preceding wave, probably due to adsorption phenomena, is observed in acid solution. This wave is peculiar in that its height is almost independent both of concentration and of pH. The height of the single wave obtained at *ca.* pH 10 is directly proportional to the concentration and its measurement is suitable for the polarographic determination of 8-hydroxyquinoline.

THE reducibility of 8-hydroxyquinoline at the dropping-mercury cathode was used by Gillis, Eeckhout, and Standaert (*Meded. K. Vlaamsche Acad. Wetensch., Letteren Schoone Kunsten België, Klasse Wetensch.*, 1940, No. 7, 3; *Chem. Zentr.*, 1942, II, 202) and by Zan'ko (*Dopovidi Akad. Nauk U.S.S.R.*, 1940, 27, 31; *Chem. Zentr.*, 1942, II, 1606) for the amperometric titration respectively of bismuth and of zinc, copper, aluminium, and magnesium. Carruthers (*Ind. Eng. Chem. Anal.*, 1943, 15, 412) developed a method for the determination of magnesium by precipitation as oxine complex and polarographic determination of 8-hydroxyquinoline in the precipitate. He described the waves obtained in well-buffered solutions of pH 7.09—7.12 containing 0.02% of gelatin. Another method, based on the decrease in wave-height of a standard solution of 8-hydroxyquinoline by precipitation of magnesium-oxine complex, has been described by Stone and Furman (*ibid.*, 1944, 16, 596). These workers described the waves obtained at pH 10. The present work concerns the behaviour of 8-hydroxyquinoline in well-buffered solutions at 25° covering a pH range from 2 to *ca.* 12. Potentials are referred to the saturated calomel electrode at the same temperature. Unless otherwise specified, solutions are 0.001M with respect to 8-hydroxyquinoline.

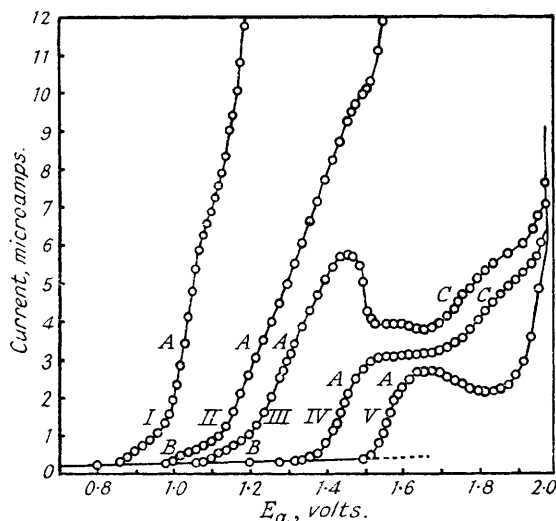
8-Hydroxyquinoline was found to be reducible over the entire pH range examined. As with other quinoline derivatives, the hydrogen overvoltage is considerably diminished in the acid part of the range (cf. Pech, *Coll. Czech. Chem. Comm.*, 1934, 6, 126; Tachi and Kabai, *J. Electrochem. Assoc. Japan*, 1935, 3, 250; Stock, *J.*, 1944, 427). In strongly acid solutions a single poorly-defined wave *A* (Fig. 1, curve I) is observed. The foot of this wave is of peculiar shape, suggesting the presence of a small ill-defined wave. Such a wave, *B* (Fig. 1, curves II and III), preceding wave *A* is visible in the pH range *ca.* 2.5 to *ca.* 7. In the voltage range covered by wave *B* the galvanometer spot oscillates jerkily and a kink occurs on the electrocapillary curve (cf. Brdička, *Z. Elektrochem.*, 1942, 48, 278).

In acid solutions there are signs of another wave immediately following wave *A*, but hydrogen

\* *J.*, 1944, 427 is regarded as being Part I of this work.

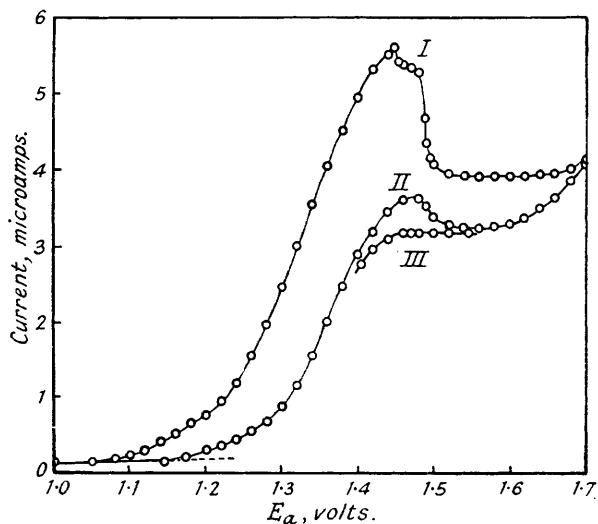
discharge interferes with the observations. Between pH 6.3 and 6.7, wave *A* appears to merge into this succeeding wave, producing a single wave about 80% greater in height and of half-wave potential ( $E_{1/2}$ ) about 0.1 volt more negative than expected of wave *A* alone (Fig. 1, curve II). In faintly alkaline solutions this larger wave is no longer visible; wave *A* is surmounted by a pronounced maximum (Fig. 1, curve III) and a drawn-out wave *C* appears at much more negative

FIG. 1.



Curve I, pH 1.97; II, pH 6.68; III, pH 7.90; IV, pH 9.67; V, pH 11.73.

FIG. 2.



Curve I, pH 8.32, no gelatin; II, 0.019% gelatin; III, 0.039% gelatin.

potentials. Wave *C* persists up to about pH 10.5, where it merges into the decomposition curve of the supporting solution. As the pH is increased, the height of the maximum decreases, vanishing at about pH 9. In strongly alkaline solutions, wave *A* diminishes in size, and the diffusion current decreases much more rapidly than is attributable to the diminution of the drop time with potential increase (Fig. 1, curve V).

The pronounced maximum may be suppressed with gelatin, but, as shown by Fig. 2 and as found with quinaldinic acid (Stock, *loc. cit.*), the wave is displaced laterally. The height of the

"flat" portion succeeding the maximum is also considerably diminished by small concentrations (<0.02%) of gelatin, but a comparison of curves II and III (Fig. 2) shows that further additions of gelatin required to suppress the maximum completely do not then greatly alter the wave height.

The relationships between the half-wave potentials of the various waves and pH are shown in Fig. 3. For wave *A* the relationship  $E_{\frac{1}{2}} = -(0.95 + 0.042\text{pH})$  holds up to about pH 5, and beyond pH 9.5 the equation is  $E_{\frac{1}{2}} = -(0.89 + 0.057\text{pH})$ . Up to about pH 5, the half-wave potential of wave *B* is almost constant, but between pH 5.7 and 7 it is considerably but linearly displaced by pH change according to  $E_{\frac{1}{2}} = -(0.45 + 0.083\text{pH})$ . This wave is also peculiar in that its height is almost independent of concentration; observed at pH 3.66 with concentrations of 8-hydroxyquinoline increasing from 0.5 to  $3.5 \times 10^{-3}$  M, the wave height decreased by 0.17 microamp. In a buffer of pH 6.36, similar results were obtained.

Wave height-pH relationships of the various waves are shown in Fig. 4 (the wave heights are here corrected both for the residual current and for varying drop time due to the occurrence of the waves at different potentials). Besides being almost independent of concentration, the height of wave *B* is but slightly affected by pH change. Curve *A*, with its two plateaux, is, except for the discontinuity due to impossibility of measurement between pH 5.3 and 6.9,

FIG. 3.

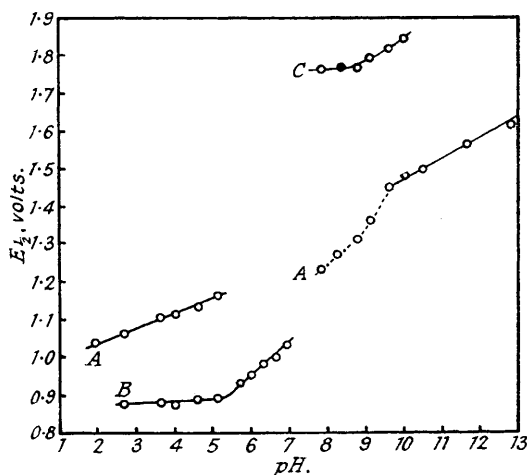
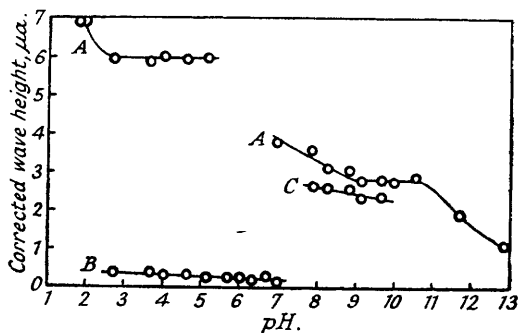


FIG. 4.



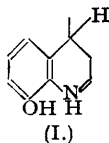
analogous to that obtained with quinaldonic acid. In the pH range 9.2–10.5, where wave *A* is well formed and without maxima (Fig. 1, curve IV), the wave height is directly proportional to concentration up to  $2.5 \times 10^{-3}$  M. Such conditions are well suited for the polarographic determination of 8-hydroxyquinoline (cf. Stone and Furman, *loc. cit.*).

If the diffusion coefficient (*D*) of 8-hydroxyquinoline be taken as being approximately equal to that of quinaldonic acid, *viz.*,  $0.80 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup> at 25° (Stock, *loc. cit.*; cf. Kolthoff and Lingane, "Polarography", New York, 1941, pp. 40, 51), then Ilkovič's equation,  $I_d = 605nD^{1/2}Cm^{1/2}t^{1/2}$  (*Coll. Czech. Chem. Comm.*, 1934, 6, 498) may be applied ( $I_d$  is the diffusion current or wave height, in microamps., *n* the number of electrons involved per mol., *C* the concentration in millimols./l., *m* the rate of flow of mercury from the capillary in mg./sec., and *t* the drop time in secs.). By its application to wave *A* in the pH range 9.2–10.6, *n* was found to be 1.03, corresponding with a one-electron change. In the other region of almost constant wave height, *viz.*, between pH 2.7 and 5.2, the value of *n* is 2.13.

*Discussion.*—The height of wave *A* between pH 2.7 and 5.2 indicates that two electrons are involved in the electrode reaction, and, since  $E_{\frac{1}{2}}$  increases with pH, that a dihydro-derivative (probably polymerised) is formed. This is in accordance with the polarographic behaviour of quinoline (Pech; Tachi and Kabai; *loc. cit.*) and of quinaldonic acid (Stock, *loc. cit.*). The height of the large wave observed between pH 6.3 and 6.7 corresponds roughly with that required for a four-electron change and the production of a tetrahydro-derivative—probably 1:2:3:4-tetrahydro-8-hydroxyquinoline (Bedall and Fischer, *Ber.*, 1881, 14, 1368; Cavallito and Haskell, *J. Amer. Chem. Soc.*, 1944, 66, 1166). Intermediate formation of a dihydro-derivative and its further reduction before polymerisation can occur appear likely here. In acid solution, the absence of a diffusion current region and the interference of wave *B* prevent

the logarithmic analysis (Kolthoff and Lingane, *op. cit.*, p. 144) of wave *A*, but the smooth, steep form suggests that the electrode reaction might be reversible.

Between pH 9.2 and 10.5, logarithmic analysis of wave *A* gives a linear curve of reciprocal slope 0.061. Since in this region *n* is unity and  $E_{\frac{1}{2}}$  obeys the Nernst equation, there is little doubt that wave *A* here corresponds to a reversible one-electron reaction involving one hydrogen ion. It is suggested that the product is a free radical such as (I). (Ionic dissociation is disregarded here.) In acid solution (I) may be formed as an intermediate, but is at once further reduced to a dihydro-derivative. By analogy with quinoline, the 1:4-isomer is expected (cf. Levchenko, *J. Gen. Chem. Russia*, 1941, 11, 686; Knowles and Watt, *J. Amer. Chem. Soc.*, 1943, 65, 410).



As the height of wave *A* falls, wave *C*, of height somewhat less than that required for a one-electron change, appears. The drawn-out form of *C* indicates a non-reversible change. Although in this region waves *A* and *C* together also correspond with the formation of a dihydro-derivative, the non-reversible nature of *C* and its much more negative half-wave potential indicate that the mechanism of acquisition of a second hydrogen atom is different from that in acid solution. Electron-capture, followed by abstraction of a proton from the solvent, is possible. Dimerisation of (I), instead of its further reduction, may prevent the full development of wave *C*.

The independence of the height of wave *B* of both pH and concentration, and the anomalous electrocapillary curve, are peculiar. Similar waves are given by riboflavin and by methylene-blue, and are attributed by Brdička (*Z. Elektrochem.*, 1942, 48, 278, 686; see also Brdička and Knobloch, *ibid.*, 1941, 47, 721) to adsorption of reduction products on the dropping-electrode surface. The energy of adsorption facilitates reduction, causing a wave, the height of which is limited by saturation of the electrode surface by adsorbed molecules, to occur before the main wave.

#### EXPERIMENTAL.

**8-Hydroxyquinoline.**—The B.D.H. "AnalaR" product was recrystallised twice from 50% alcohol and dried over sulphuric acid. A 0.02M-stock solution in 50% aldehyde-free alcohol was prepared and stored in the dark, being diluted as required with the appropriate buffer.

**Buffer Solutions.**—These were as in Part I, and were examined polarographically for reducible impurities.

**Apparatus.**—This was almost identical with that used in Part I. All measurements, including those of pH, were made at  $25^{\circ} \pm 0.2^{\circ}$ . The characteristics of the dropping electrode were:  $m = 1.511$  mg. sec.<sup>-1</sup>,  $t = 3.08$  sec.,  $m^{3/2}t = 1.588$  (determined on open circuit in 0.1N-potassium chloride at 25°).

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