163. *The Polarography of Quinoline Derivatives. Part III. The Reduction of Quinoline-8-carboxylic Acid at the Dropping-mercury Cathode.*

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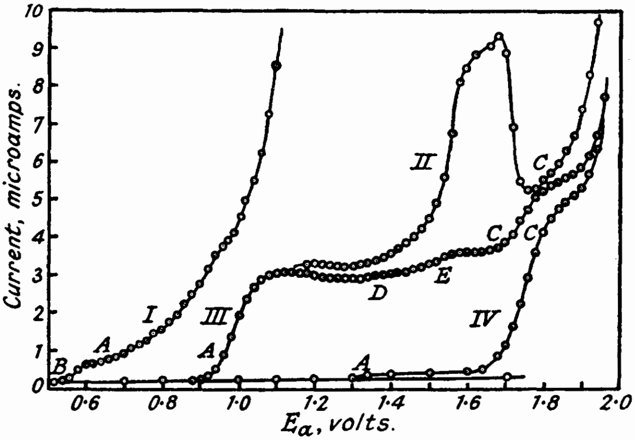
Current–voltage curves of quinoline-8-carboxylic acid in well-buffered solutions covering the pH range 1—12 have been constructed, reduction occurring over the entire pH range. The two principal waves appear to correspond respectively to a reversible one-electron reduction involving one hydrogen ion per molecule and a two-electron reduction not directly involving hydrogen ions. The height of the former wave in approximately neutral or alkaline buffer solutions is directly proportional to concentration and its measurement is suitable for the polarographic determination of quinoline-8-carboxylic acid. A small preceding wave, the height of which is almost independent both of concentration and of pH, is observed in acid solutions.

QUINOLINE-8-CARBOXYLIC acid has been used by Majumdar (*J. Indian Chem. Soc.*, 1941, **18**, 419) and by Gilbreath and Haendler (*Ind. Eng. Chem. Anal.*, 1942, **14**, 866) as a selective precipitant for copper. Since organic reagents for metals have proved generally useful in amperometric titration (cf. Kolthoff and Lingane, " Polarography ", New York, 1941, pp. 447—478; Stock, *Analyst*, 1947, **72**, 291), the polarography of quinoline-8-carboxylic acid was studied with a view to its use in this method of titration. Well-buffered solutions at 25° covering a pH range of about 1—12 were used. Potentials are referred to the saturated calomel electrode at the same temperature and, unless otherwise specified, solutions were 0·001M with respect to quinoline-8-carboxylic acid.

FIG. 1.



Curve I : pH 1·13; *II, pH* 7·00 (*in part : remainder almost coincident with III*) ; *III, pH* 7·53 ; *IV*, 0·1N-NaOH.

Cathodic waves were obtained over the entire pH range examined. In the acid part of the range the considerable diminution in hydrogen overvoltage usually occasioned by quinoline derivatives occurs (cf. Stock, Part I, *J.*, 1944, 427; Part II, *J.*, 1949, 586). Up to about pH 5·5, wave *A* (Fig. 1, Curve I) is with difficulty distinguishable, but in solutions of higher pH definition improves markedly. A small preceding wave *B* is visible up to about pH 6; in the voltage range covered by this wave the galvanometer spot oscillates jerkily.

Between pH 6 and 7·5, the polarogram becomes more complex. At pH 6·5, the region of almost constant current succeeding wave *A* merges into a large double maximum. The latter is single at pH 7 and is followed by indications of another wave *C* (Fig. 1, Curve II). In faintly alkaline solution (Fig. 1, Curve III) the maximum vanishes, wave *C* becomes much more distinct, and small indistinct waves *D* and *E* appear (cf. Part I). In solutions more alkaline than pH 8, the only waves visible are *A* and *C*, the former diminishing, the latter increasing with pH (Fig. 1, Curve IV).

The relationships between the half-wave potentials ($E_{1/2}$) of the persistent waves and pH are shown in Fig. 2. For wave *A*, the equation $E_{1/2} = -(0{\cdot}78 + 0{\cdot}060\text{pH})$ holds up to pH 4, but between pH 7·5 and 10·5 the relationship is $E_{1/2} = -(0{\cdot}40 + 0{\cdot}079\text{pH})$. The behaviour between pH 5 and 7, where the half-wave potential *decreases* with increasing pH and passes through a minimum, is peculiar. Although incomplete, the $E_{1/2}$–pH curve of the corresponding wave given by 8-hydroxyquinoline (Part II) appears to be of the same general form. Fields and Blout (*J. Amer. Chem. Soc.*, 1948, **70**, 930) report that the $E_{1/2}$–pH curve of the second wave of certain aliphatic polyene aldehydes likewise shows a minimum, in this case at about pH 8. Their tentative explanation that this unusual behaviour might be caused by low buffer capacity of the supporting electrolytes is unlikely to apply to the present work in almost alcohol-free buffers of usual concentration.

FIG. 2.

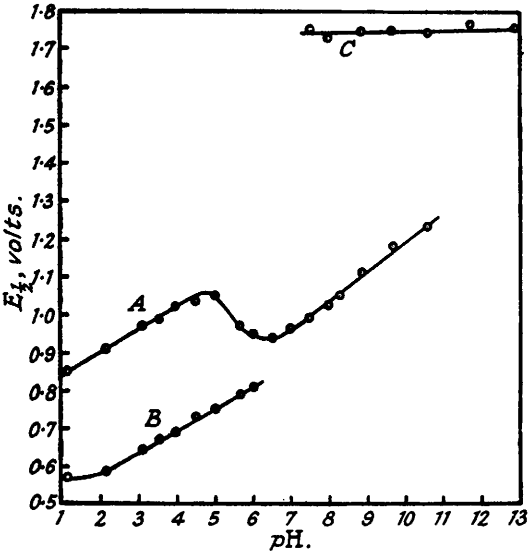
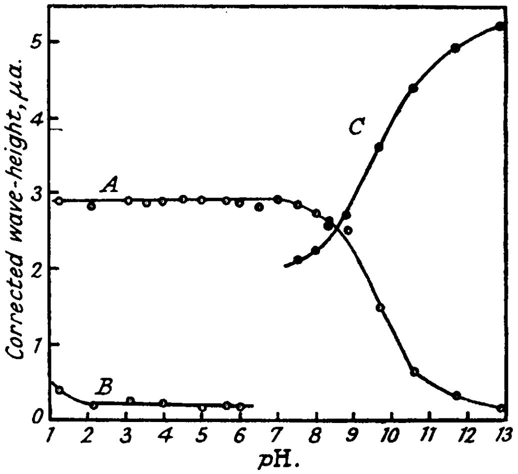


FIG. 3.



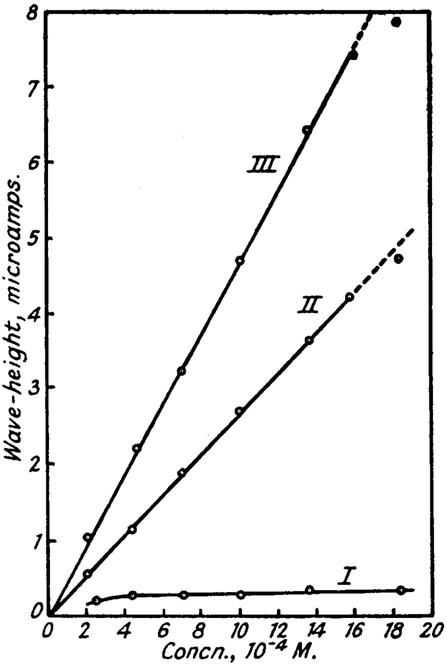
Except in strongly acid solutions, the relationship $E_{1/2} = -(0{\cdot}46 + 0{\cdot}58\text{pH})$ holds for wave *B*. In contrast to the behaviour of 8-hydroxyquinoline (Part II), there is no distinct region in which the half-wave potential is independent of pH. The half-wave potential of wave *C* is almost unaffected by pH change.

The effect of pH change on the heights of the persistent waves (here corrected both for the residual current and for the differing drop-times due to measurement of the waves at different potentials) is shown in Fig. 3. The heights of wave *B*, and of wave *A* up to the appearance of wave *C*, are practically constant. As with the corresponding wave of 8-hydroxyquinoline (Part II), the height of wave *B*, except at concentrations $<4 \times 10^{-4}$ M, is almost independent of concentration (Fig. 4, Curve I; wave heights are here corrected for residual current only). The height of wave *A*, however, increases linearly with concentration (*e.g.*, Fig. 4, Curve II), and measurement of the height of this wave in neutral or alkaline buffer solutions permits the polarographic determination of quinoline-8-carboxylic acid. The height of wave *C* also increases with concentration, but, owing to the absence of a region of almost constant diffusion current, measurement is less easy. Nevertheless, by measuring the *total* wave height (*i.e.*, of *A* plus *C*) at a selected fixed potential, a linear calibration curve (*e.g.*, Fig. 4, Curve III), also useful for quantitative work, may be obtained. The total wave height in alkaline solution is practically independent of pH.

With the same dropping-mercury electrode, the constant height of wave *A* up to pH 7 is almost exactly half that of the corresponding wave, indicative of a two-electron change, of 8-hydroxyquinoline between pH 2·7 and 5·2 (Part II). Accordingly, wave *A* at its maximum height almost certainly corresponds with a one-electron reduction. By application to this wave of the Ilkovic equation, $I_d = 605nD^{1/2}Cm^{2/3}t^{1/6}$, where the symbols have their usual significance (Kolthoff and Lingane, *op. cit.*, p. 55), the diffusion coefficient, D, of quinoline-8-carboxylic acid was calculated to be $0{\cdot}92 \times 10^{-5}$ cm.^{2} sec.$^{-1}$.

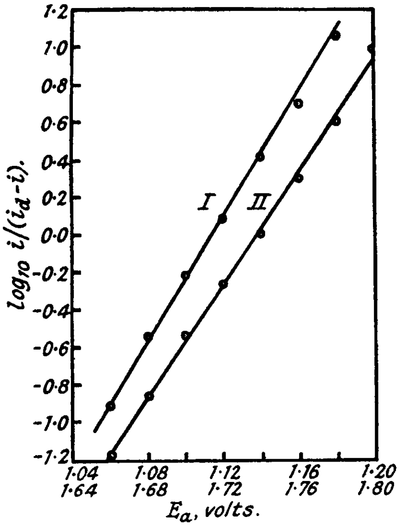
Discussion.—Apart from the small wave *B*, wave *A* is the only one visible in acid solutions. The pH coefficient in the equation holding up to pH 4 of the latter wave agrees well with the theoretical 0·0591 required for a reaction involving a single hydrogen ion per molecule. The very poor definition of the wave under these conditions prevents logarithmic analysis (Kolthoff and Lingane, *op. cit.*, p. 144), but in alkaline solutions such analysis yields a linear curve (Fig. 5, Curve I), the reciprocal slope of which is 0·062. Hence it is probable that, as with quinaldinic acid and with 8-hydroxyquinoline between certain pH limits (Parts I and II, respectively), wave *A* corresponds to a reversible one-electron reduction involving one hydrogen ion per molecule, to give a free radical which may then undergo dimerisation. Onset of the hydrogen wave prevents observation of any further reduction.

FIG. 4.



Curve I; wave B, *pH* 4·53; *II, wave* A, *pH* 6·51; *III, total wave height, pH* 8·34, *measured at* —1·85 *volts.*

FIG. 5.



Analysis of waves at pH 8·84. *Curve I (upper voltage scale), wave* A; *II (lower voltage scale), wave* C.

The equation of wave *B* indicates that here too one hydrogen ion per molecule is involved. As, however, the height of this wave is, except at high dilution, almost independent of the concentration of quinoline-8-carboxylic acid, adsorption or similar phenomena not subject to diffusion control are probably involved. This point is being further studied with the similar effect shown by 8-hydroxyquinoline.

Even in 0·1N-sodium hydroxide solution (pH ~13) wave *C* does not appear to have reached its maximum height; inspection of Fig. 3, however, indicates that the maximum height is about twice that of wave *A*. Accordingly, wave *C* corresponds with a two-electron reduction and the probable formation of a dihydro-derivative. The growth with increasing pH of the (two-electron) wave *C* at the expense of the (one-electron) wave *A* might be expected to occur with an increase in the total wave height, whereas the latter is almost constant. A possible explanation is that wave *C* really represents two almost coincident one-electron waves, and that the height of one of these increases as that of wave *A* diminishes. In this connection, logarithmic analysis of wave *C* (Fig. 5, Curve II) yields a linear curve, the reciprocal slope of which is 0·068 (instead of 0·0295 required for a reversible two-electron reduction and approximating to that required for a reversible one-electron reduction). Since the half-wave potential of wave *C* is independent of pH, the electrode reaction does not directly involve hydrogen ions.

Although 1 : 2 : 3 : 4-tetrahydroquinoline-8-carboxylic acid is quite stable (cf. Heilbron and Bunbury, " Dictionary of Organic Chemistry ", London, 1943, III, 704), and can be obtained by reducing quinoline-8-carboxylic acid with tin and hydrochloric acid (Chakravarti and Ganapati, *J. Annamalai Univ.*, 1934, **3**, 223; cf. Chakravarti and Venkatasubban, *ibid.*, 1933, **2**, 227), no wave corresponding to the definite formation of a tetrahydro-derivative was observed. Quinaldinic acid (Part I) is similar in this respect.

EXPERIMENTAL.

Quinoline-8-carboxylic Acid.—8-Methylquinoline (B.D.H.) was fractionally distilled and oxidised by the method of Glenn and Bailey (*J. Amer. Chem. Soc.*, 1941, **63**, 641). The product was recrystallised three times from water (m. p. 187°) and used to prepare a 0·02M-stock solution in 50% aldehyde-free alcohol. This solution was diluted 20 times or 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° ± 0·2°. The characteristics of the dropping-mercury electrode (the same one as in Part II) were : $m = 1{\cdot}511$ mg. sec.$^{-1}$, $t = 3{\cdot}08$ secs., $m^{2/3}t^{1/6} = 1{\cdot}588$ (determined on open circuit in 0·1N-potassium chloride at 25°).

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