

1047. *The Polarographic Reduction of Some Heterocyclic Molecules.*
Part III. Quinoline Ethiodide.*

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Quinoline ethiodide is reduced at the dropping mercury electrode over the pH range 2—10, giving a well-defined wave at pH >5 with $E_{\frac{1}{2}} - \sim 0.8$ v (vs. S.C.E.) for concentrations 2—200 $\times 10^{-5}$ M. This wave corresponds to the addition of one electron to the 1-ethylquinolinium ion. At pH <8 this reduction is followed by a hydrogen discharge which appears as a "peak" on the diffusion current plateau, but at pH <5 tends to merge with the 1-ethylquinolinium ion reduction. Evidence is obtained that the reduction product is adsorbed on the mercury drop and that the final product is a mixture of polymers of the 1-ethylquinolinium radical.

A PRELIMINARY polarographic investigation of quinoline showed that the reduction in a buffered supporting electrolyte of low pH, where the quinoline molecule exists predominantly in the protonated form, was difficult to distinguish from the overlying hydrogen discharge. This problem is commonly encountered in the polarographic examination of heterocyclic nitrogen compounds. Quinoline ethiodide was chosen to avoid this difficulty and to allow the reduction mechanism of quinolinium-type ions to be studied over a wide pH range.

Shchennikova and Korshunov¹ investigated the polarography of pyridine, quinoline, and related compounds, including quinoline ethiodide. They studied the reduction of quinoline ethiodide over the pH range 3—10 and observed four reduction waves with pH-independent $E_{\frac{1}{2}}$'s at -0.25 , -0.8 , -1.2 , and -1.7 v. (All potentials are referred to the saturated calomel electrode.) The solutions contained a maximum of 5% of ethanol by volume and buffers contained, appropriately, borax and boric acid, phosphoric, boric, and acetic acids, and sodium hydroxide. No reduction mechanisms were postulated except that for the wave with $E_{\frac{1}{2}} - 0.8$ v which is stated to be possibly due to reduction of the nitrogen-carbon double bond and the formation of a dihydro-compound. The only pH-dependent diffusion current was found in the wave with $E_{\frac{1}{2}}$ at -0.8 v over the pH range 5—7.

The present authors did not observe any reduction wave in the region of -0.25 v and consider the wave at -0.8 v, the diffusion current of which showed little pH-dependence, to be due to the reduction of the 1-ethylquinolinium ion. The two most negative waves reported by the previous workers are similar to a series of anomalous "peaks" observed by us on the diffusion-current plateau when using an aqueous buffered supporting electrolyte. Addition of a relatively large proportion of ethanol has been shown² to suppress anomalies in polarographic reduction waves caused by certain types of adsorption at the electrode surface; it was found by the present authors that a 43% concentration of ethanol by weight eliminated all but one of those "peaks" more negative than the quinolinium ion discharge. Thus the polarograms were simplified and it is evident that the remaining peak is not of the type readily removed by the presence of ethanol. All polarographic solutions which were examined contained ethanol at this concentration unless otherwise indicated.

First Wave.—Polarographic plots are shown in Figs. 1 and 2. A clear first wave is obtained over the pH range 5—10. In addition, a catalytic hydrogen discharge is obtained at pH <8. At pH <5 this discharge becomes sufficiently positive to prevent study of the first wave.

Fig. 2 indicates that the second part of the first wave is irregular. This irregularity

* Part II, *J.*, 1950, 1575.

¹ Shchennikova and Korshunov, *Zhur. f.z. Khim.*, 1948, **22**, 503.

² Kaye and Stonehill, *J.*, 1951, **27**, 2638.

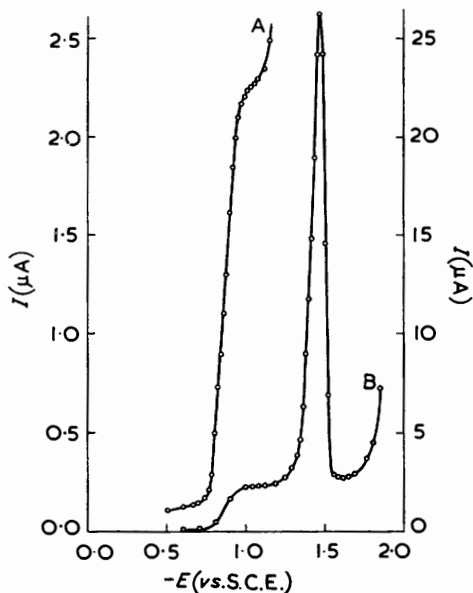


FIG. 1. Typical normal (A, left-hand ordinates) and catalytic (B, right-hand ordinates) polarographic waves of the 1-ethylquinolinium ion. $[Q^+] = 8 \times 10^{-4}M$; pH = 7.54; EtOH concn. = 43%; temp. = 25.0°.

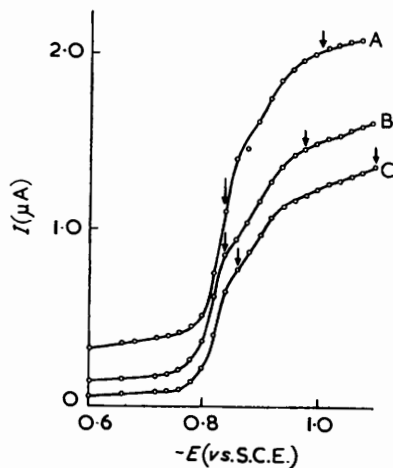


FIG. 2. Influence of ethanol concentration upon first wave. A, 0%; B, 22%; C, 43% of EtOH. Arrows indicate potential range corresponding to abnormal galvanometer oscillations. $[Q^+] = 4 \times 10^{-4}M$; pH = 6.98; temp. = 25.0°.

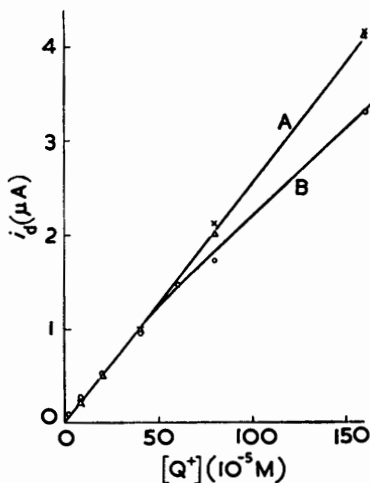


FIG. 3. Dependence of diffusion current, i_d , on $[Q^+]$. A, pH = 7.52, 6.98; B, pH = 5.70. EtOH concn. = 43%; temp. = 25.0°.

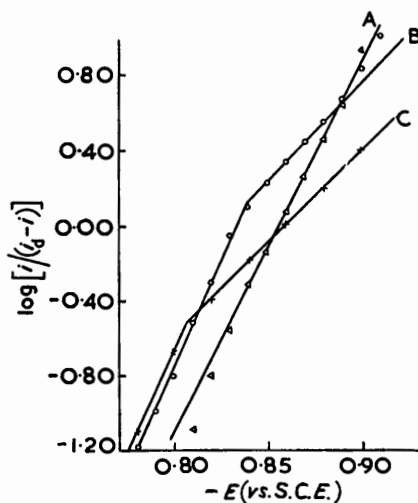


FIG. 4. Effect of $[Q^+]$ upon logarithmic plots. A, $[Q^+] = 8 \times 10^{-5}M$; B, $[Q^+] = 4 \times 10^{-4}M$; C, $[Q^+] = 8 \times 10^{-4}M$. pH = 6.98; EtOH concn. = 43%; temp. = 25.0°.

decreases with increasing pH and at pH 9.5 is difficult to discern. With lower concentrations of the 1-ethylquinolinium ion $[Q^+]$, e.g., $8 \times 10^{-5}M$, the irregularity is not present within the pH range examined. We associate the irregularity with adsorption of the reduction product. This is confirmed by the fact that adsorption phenomena were indicated by abnormal galvanometer oscillations during drop growth over the potential ranges shown by arrows in Fig. 2. Abnormalities took the form of a sudden increase in current after drop fall, the current sometimes remaining steady or even decreasing during the remainder of the drop life. Several maxima in the current-drop time relation were sometimes observed. Kaye and Stonehill² have reported similar current-time relations with acridines.

Dependence of diffusion current i_d on $[Q^+]$ is shown in Fig. 3. The proportionality indicates a diffusion-controlled electrode reaction. A direct relation is observed with $[Q^+]$ up to $\sim 5 \times 10^{-4}M$, and with higher $[Q^+]$ at pH 7 and above. If the Ilkovic equation holds, the apparent diffusion coefficient at pH 5.7 is reduced by some 40% at high $[Q^+]$. The rate of diffusion of reducible ions to the electrode surface is possibly hindered by electrostatic repulsion arising from an adsorbed product of reduction which is protonated.

The facts that i_d increases 1.8% per °C rise in temperature between 25° and 50° and that i_d is proportional to the square root of the height of the mercury column confirm³ the view that the wave is diffusion-controlled.

The influence of ethanol concentration is shown in Fig. 2. The decrease in i_d is 30% when the ethanol concentration is increased from 0% to 43%. Similar decreases have been reported with other substances.^{2,4} Consequently, by analogy with the diffusion coefficient of quinoline-2- and -4-carboxylic acids,⁵ the value of $D^{\frac{1}{2}}$ for the 1-ethylquinolinium ion in 43% ethanol is 2.0×10^{-3} cm. sec.^{-1/2}.

When the value of $D^{\frac{1}{2}}$ so obtained is substituted in the Ilkovic equation, n is found to lie between 0.90 and 1.19 for the conditions studied, indicating the addition of one electron to each cation discharged.

Typical log plots showing variation in slope with $[Q^+]$ are given in Fig. 4, revealing a single straight-line log plot only for very low concentrations. When $[Q^+] \geq 4 \times 10^{-4}M$, the log plot consists of two intersecting straight lines; the plot relating to the first part of the wave is similar in slope to that obtained for the complete wave at low concentrations. The Table gives values for n in the usual expression for a reversible polarographic wave,

$$E = E_{\frac{1}{2}} - (0.059/n) \log [i/(i_d - i)],$$

as determined from the slopes of the log plots. These are not integral but have values n_1 equal to 1.25 ± 0.12 for the initial section of the wave, and values n_2 equal to 0.65 ± 0.19 for the part of the wave at more negative potentials where two distinct log-plot slopes are given.

The best correlation for n values as determined from the Ilkovic equation and log plots occurs, as expected, under conditions where $n = n_1$. For $[Q^+] = 8 \times 10^{-5}M$, n (Ilkovic) = 1.19, and $n_1 = 1.18 \pm 0.06$, indicating the addition of 1 electron per 1-ethylquinolinium ion in the electrode reaction.

Where two slopes are obtained for the log plots, the currents are listed in the Table for the points at which the log plots intersect. The current i_i at the intersection point is constant at a value of $0.49 \pm 0.05 \mu A$ and is approximately independent of pH, temperature, and ethanol concentration when $[Q^+] \geq 4 \times 10^{-4}M$. This may be explained by a dependence of the current on the surface area of the electrode. With $m = 0.002672$ g. sec.⁻¹, $t = 3.05$ sec., the maximum surface area attained by the mercury drop is 3.44 mm.². The number of ions discharged with an average current flow of $0.49 \mu A$ over the drop life is 9.2×10^{12} . If all the ions discharged are assumed to remain at the electrode interface,

³ Gardner and Lyons, *Rev. Pure Appl. Chem. (Australia)*, 1953, **3**, 137.

⁴ Shreve and Markham, *J. Amer. Chem. Soc.*, 1949, **71**, 2993.

⁵ Casimir and Lyons, *J.*, 1950, 783.

Data for logarithmic plots.

[Q ⁺] (10 ⁻⁵ M)	Temp.	pH	[EtOH] (%)	Positive end of wave		Negative end of wave		<i>i</i> ₁ (μA) intersection
				Slope	<i>n</i> ₁	Slope	<i>n</i> ₂	
8	25°	5.70	43	0.047	1.25	—	—	—
8	25	6.98	43	0.051	1.16	—	—	—
8	25	7.51	43	0.052	1.13	—	—	—
40	25	5.70	43	0.051	1.16	0.11	0.536	0.54
40	25	6.98	43	0.044	1.34	0.088	0.625	0.52
40	50	6.98	43	0.044	1.34	0.088	0.625	0.45
40	25	7.51	43	0.041	1.44	0.082	0.720	0.54
40	25	7.8(?)	43	0.05	1.18	0.07	0.84	0.47
40	25	6.98	0	0.032	1.90	0.088	0.625	0.53
40	25	6.98	22	0.044	1.34	0.088	0.625	0.40
80	25	5.70	43	0.047	1.25	0.15(?)	—	0.50
80	25	6.98	43	0.051	1.16	0.10	0.59	0.42
80	25	7.51	43	0.042	1.40	0.066	0.90	—

Mean 0.49

the surface area occupied per reduced ion (if present in a monolayer) can be calculated as 37 sq. Å. This agrees closely with a value of 34 sq. Å obtained for the cross-section of the ion by projection of a scale model with the plane of the aromatic rings perpendicular to the surface, it being reasonable to assume that 1-ethylquinolinium approaches the cathode oriented with the positive centre localized on the nitrogen atom towards the electrode.

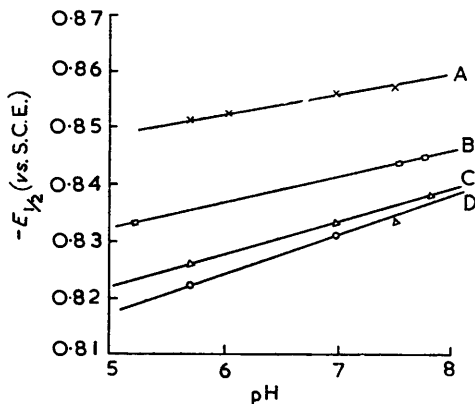
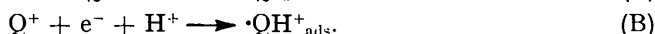


FIG. 5. Dependence of $E_{1/2}$ upon pH. A, $[Q^+] = 8 \times 10^{-5}M$; B, $[Q^+] = 2 \times 10^{-4}M$; C, $[Q^+] = 4 \times 10^{-4}M$; D, $[Q^+] = 8 \times 10^{-4}M$. EtOH concn. = 43%; temp. = 25.0°.

Determination of $E_{1/2}$ by conventional graphical methods, or from log plots, *i.e.*, when $\log i/(i_d - i) = 0$, leads to values which vary over a range of some 40 mv. However, by considering the slope of the log plot for the initial portion of the wave, projected where necessary, values of $E_{1/2}$ are obtained for electrode conditions existing before complete coverage by a monolayer of the reduction product. Fig. 5 shows that $E_{1/2}$ determined graphically depends linearly on pH at any $[Q^+]$. For a given pH, $E_{1/2}$ becomes less negative with increasing $[Q^+]$.

The slopes of the $E_{1/2}$ -pH plots are considerably less than those expected for usual participation of hydrogen ion in the electrode reaction. The observed variation is 3.5—6.9 mv/pH unit for $[Q^+]$ between 8 and $80 \times 10^{-5}M$. Conditions when the reduction is relatively uncomplicated by adsorption occur at high pH and low $[Q^+]$: then $E_{1/2}$ is more negative than -0.86 v (see Table and Fig. 4).

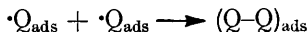
The electrode reaction (A) rather than (B) can therefore be considered to take place in the pH range studied:



Here $\cdot Q_{ads}$ denotes a free radical adsorbed on the mercury surface.

For the electrode reaction taking place at current densities higher than those producing a monolayer at the electrode interface, $E_{1/2}$, determined from the log plots of the more negative section of the wave as indicated previously, becomes more negative with increased $[Q^+]$. It follows that, to discharge the ethylquinolinium ion, more energy is required to transfer an electron through a monolayer (double layer, etc.) of the reduction product at the electrode surface than otherwise. Some irreversibility of the electrode reaction is indicated because $E_{1/2}$ becomes ~ 0.5 mv more positive per 1°C for all $[Q^+]$ over the temperature range $25-50^\circ$.

All the evidence supports electrode mechanism (A), the reduction product being adsorbed in a mono- or multi-layer. However, subsequent dimerization of the reduced cation could occur in the adsorbed layer:



The large-scale reduction of the 1-ethylquinolinium ion by use of a potentiostat similar to that of Lingane and Jones⁶ was attempted.⁷ An unstable brown-grey amorphous product was obtained from which no single substance could be isolated. Chromatographic investigations indicated the presence of at least ten substances. A variety of substances, corresponding to different degrees of polymerization, was possible from the interaction of the free radicals which were considered to be the initial reduction product.

Second Discharge.—Fig. 1 also shows the second discharge which appears, not as a smooth continuation of the initial wave, but as a maximum on the diffusion-current plateau. The addition of maximum-suppressors, *e.g.*, methylcellulose, had little influence, indicating that this is not a maximum of the type normally encountered.

This maximum was observed in the pH range 5—8 and was affected mainly by pH, $[Q^+]$, and buffer capacity. No maximum is present at $\text{pH} > 8.0$, and for $\text{pH} < 5.0$ the first wave and the buffer discharge merge.

This maximum is due to lowering of hydrogen overvoltage similar to that observed with other heterocyclic nitrogen compounds.⁸

EXPERIMENTAL

A three-electrode circuit similar to that of Lingane⁹ was used with a reproducible liquid junction of negligible potential¹⁰ between cell and saturated calomel reference electrode. Cell and reference electrode were kept (thermostat) at $25.0^\circ \pm 0.05^\circ$ unless otherwise indicated. The polarographic solutions were freed from oxygen by passage of purified hydrogen. Buffer solutions were prepared from "AnalaR" chemicals by addition of the required quantity of concentrated ammonia solution to a solution 0.2M with respect to orthophosphoric acid, acetic acid, and potassium chloride.¹¹ The pH was recorded by a Doran universal pH-meter.

A Cambridge galvanometer with a curved scale of one metre radius was calibrated by measuring the potential developed across a standard resistance.

Quinoline ethiodide was recrystallised from aqueous ethanol and had m. p. $158-159^\circ$.

Capillary characteristics in solutions prepared as above with an applied potential of -1.0 v were $m^{2/3}t^{1/6} = 2.57, 2.325, \text{ and } 2.06$ mg.^{2/3} sec.^{1/6} at mercury heads of 56.3, 46.5, and 36.2 cm. respectively.

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⁶ Lingane and Jones, *Analyt. Chem.*, 1950, **22**, 1169.

⁷ Harle, M.Sc. Thesis, University of Sydney, 1957.

⁸ Knobloch, *Coll. Czech. Chem. Comm.*, 1947, **12**, 407; Tompkins and Schmidt, *Univ. California Pub. Physiol.*, 1944, **8**, 229; Stock, *J.*, 1949, 586.

⁹ Lingane, *J. Amer. Chem. Soc.*, 1939, **61**, 2099.

¹⁰ Gardner and Diamantis, *Austral. J. Sci.*, 1951, **14**, 23.

¹¹ Coulson and Cromwell, *J. Amer. Chem. Soc.*, 1952, **74**, 1290.