Analytical Chemistry by Means of Organic Compounds XIV
Electrolytic Reduction of Organic Reagents at the Dropping Mercury Cathode and Its Application to Amperometric Titrations — 8-Hydroxyquinoline* (1)

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Many organic compounds are reducible at the dropping mercury electrode, so the organic reagents which precipitate metal ions are very useful in the amperometric titrations. Kolthoff and his coworkers have been greatly instrumental in developing these titrations.⁽¹⁾ In the meantime, we also introduced this titration method and described some examples of our works⁽²⁾ in which organic reagents were applied to it.

In the present paper, the behavior of electrolytic reduction of 8-hydroxyquinoline at the dropping mercury electrode is discussed and in the subsequent paper, the amperometric titration of magnesium, copper etc. with that reagent will be introduced.

Experimental

Chemicals and Apparatus Used Oxine (8-hydroxyquinoline) made by Takeda Chemicals Co. was twice steam-distilled and dissolved in pure dilute ethyl alcohol. Magnesium carbonate, ferric nitrate and zinc sulfate were Merk or Kahlbaum's "zur Analyse". The c. p. copper sulfate was twice recrystallized. They were all examined in their purity by the polarographic method. Buffer solutions from pH = 2.2 to 12.0 were Kolthoff, Vleeshhower's.⁽³⁾ pH = 1.0 and pH = 13.0 were 0.1 N hydrochloric acid and sodium hydroxide respectively. The polarograph used is a Heyrovsky-Shikata type made by Yanagimoto Co., Kyoto.

Polarographic Behavior of Oxine Polarograms of oxine in various pH solutions are shown

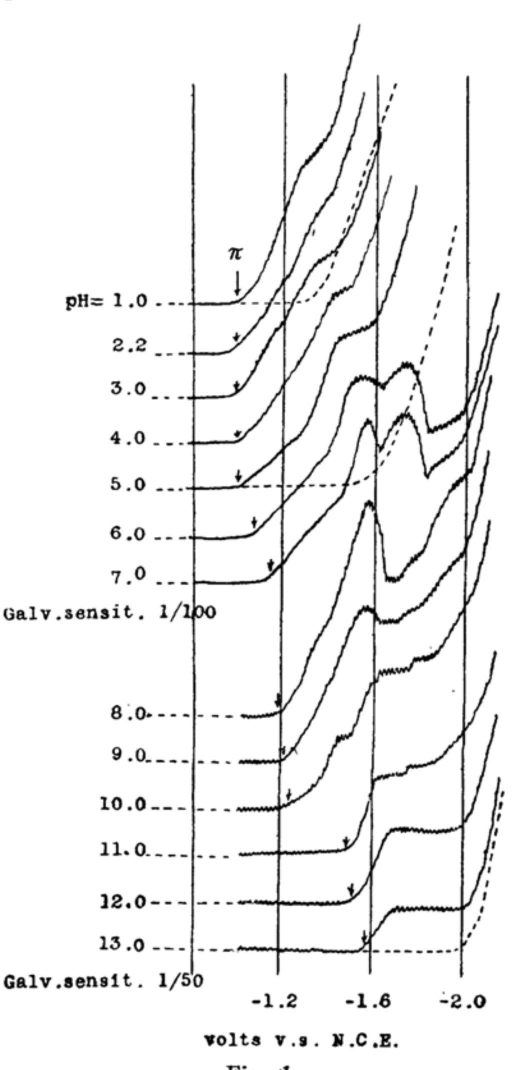

Fig. 1
Polarograms of oxine in various pH solutions

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* Presented at the annual meeting of the Chemical Society of Japan in 1948 and the annual meeting of the Research Institute of Chemistry, Kyoto University in 1947.

(1) I. M. Kolthoff *et al*, *J. Amer. Chem. Soc.*, **61**, 3402 (1939). ibid, **62**, 211, 3332, etc, (1940)

(2) M. Ishibashi and T. Fujinaga, "Polarography in Inorganic Analysis" in "The Review of Analytical Chemistry (in Japanese)" Vol. 2 Kyoritsusha publ. Co., Tokyo (1944)

(3) I. M. Kolthoff, "Acid-base Indicators", Macmillan Co. (1937)

in Fig. 1. These solutions have the composition of 10^{-3} M-oxine, 10^{-2} M-KCl and some tylose, except buffer agents. For the amperometric purpose, the polarograms of oxine in 1 N-NH_4OH, NH_4Cl and 1 N-CH_3COOH, CH_3COONa are researched (Fig. 2). Current-voltage curve of copper sulfate in 1 N-NH_4OH, NH_4Cl by using the platinium rotating electrode are also shown in Fig. 3.

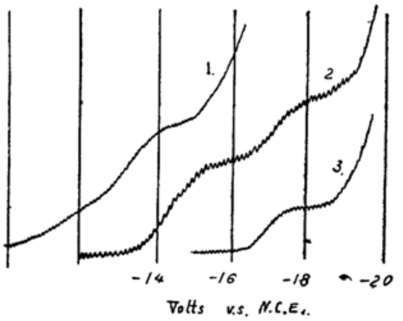

Fig. 2
Polarograms of oxine in some buffer solutions
Curve 1: 1 N- CH_3COOH, CH_3COONa
Curve 2: 1 N- NH_4OH, NH_4Cl
Curve 3: 0.1 N- NaOH

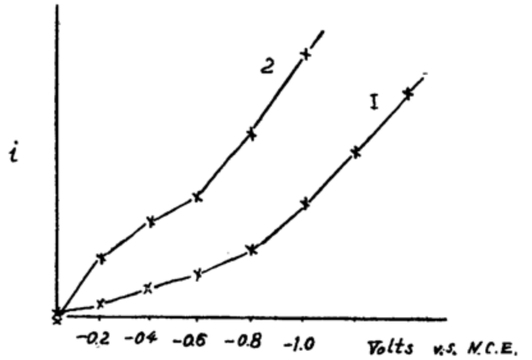

Fig. 3
Current-voltage curve using the rotating Pt electrode
Curve 1: 1 N- NH_4OH, NH_4Cl
Curve 2: 1 ml. of 0.001 N-$CuSO_4$ was added to the above solution.

Experimental Results

In the reversible polarographic wave, the equation is given as

$$E=E\,{}^1/_2-RT/nF\cdot\ln\, i/(i_d-i)$$

where E is the electrode potential of the dropping electrode, $E\,{}^1/_2$ is the half-wave potential of the wave, i is the reduction current at E volts and i_d is the diffusion current of the reducible ion. Then the plots of log $i/(i_d-i)$ against E will show the inclination of $0.058/n$ at 18°C. Fig. 4 shows the above analysis of the wave of oxine at pH=11.0 and it also shows that the reduction is reversible and that $n=1$, so oxine will be reduced in the alkaline medium as follows.

$$2\,R+2\,H=RH_2R \qquad (R:\ \text{oxine})$$

which is analogous to meriquinone formation.

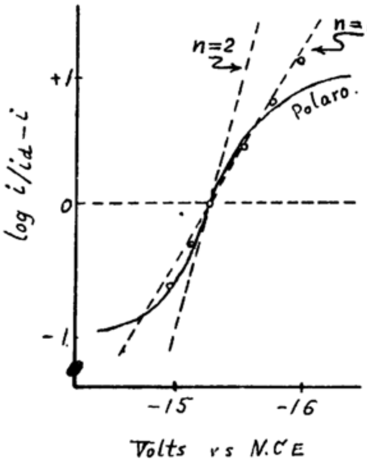

Fig. 4
Analysis of the polarographic wave of oxine at pH=11.0

With decreasing pH, the reduction becomes complicated and irreversible, so each polarogram becomes to produce characteristic maximum respectively whose behavior is analogous to quinoline(4) and so the reduction current of oxine is chiefly due to the quinoline nucleus. The addition of tylose suppresses the maximum but could not eliminate it even in its higher concentration.

In the acidic medium the reduction is also irreversible and the plots of log i/i_d-i against E does not give straight line and in these medium the deposition of hydrogen seems to be catalytically urged, comparing with the blank wave (the dotted curves in Fig. 1).

The relation of pH to the reduction potential of oxine π are shown in Fig. 5, where π is not the half-wave potential, but the potential at which 45° tangent touches the curve. Assuming

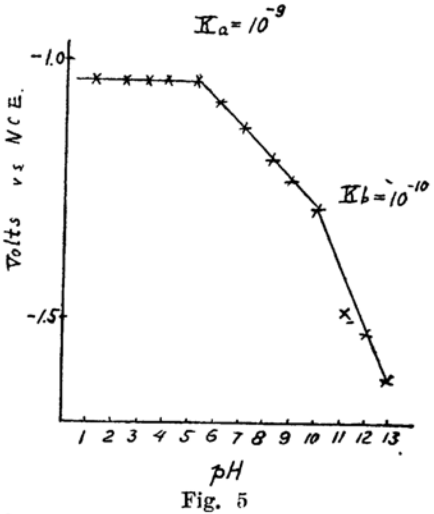

Fig. 5
Relation of the reduction potential π to pH

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(4) I. Tachi and H. Kabai, *J. Electrochem. Association Japan*, **3**, 1 (1935)

the π to be the parallel value to the standard reduction potential, the bending points will be the position of $pH=pK_a$ and $pH=pK_b$ respectively and it becomes $K_a=10^{-9}$ and $K_b=10^{-10}$. These dissociation constants coincide with Kolthoff's data.(5)

In ammoniacal solution, the diffusion current of the first wave of oxine is reached at $E_c=-1.60$ volts v. s. normal calomel electrode and at this potential the diffusion current of oxine is proportional to its concentration. In 0.1 N-NaOH, the same condition is found at $E_c=-1.80$ volts v.s. N.C.E. In acetic acid acetate medium, the short diffusion current range is found at $E_c=-1.40$ volts and the diffusion current of oxine is proportional to its concentration only in the limited concentration range.

These medium were used in the amperometric titration of magnesium, copper, etc. with oxine and it will be discussed in the subsequent paper.

Using the platinium rotating micro-electrode,(6) the oxine was not reduced before the hydrogen deposition even in the ammoniacal solution, but the copper was reduced (see Fig. 3).

Summary

The behavior of electrolytic reduction of oxine at the dropping mercury electrode was discussed. The reduction of oxine in alkaline medium is simple and reversible at the electrode and the possibilities of amperometric titrations with oxine in these mediums were researched.

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(5) I. M. Kolthoff, *Chem. Weekbl.*, **24**, 606 (1927)

(6) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem. Anl. Ed.*, **18**, 161 (1946)