Studies on the Polarographic Analysis. XVII.* Electrolytic Reduction of Cyclohexanedionedioxime and its Application to Amperometric Titrations

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In a previous paper[1], the behavior of electrolytic reduction of 8-hydroxy-quinoline at the dropping mercury electrode and the amperometric titration using it have been described. In the present paper, polarographic and amperometric investigations of cyclohexanedionedioxime are reported. Cyclohexanedionedioxime (nioxime) was first employed by Wallach[2] as a reagent for nickel. It is very similar to dimethylglyoxime in its reac-

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[1] M. Ishibashi, T. Fujinaga, This Bulletin, **23**, 25, 27 (1950).

[2] O. Wallach, *Ann.*, **437**, 148 (1924).

tion with nickel to form the red insoluble precipitate in an ammoniacal and weakly acid medium. However, nioxime has many advantages over dimethylglyoxime in the sensitivity of reaction, in the smaller percentage of nickel in the precipitate and in the solubility of the reagent in water (0.824 g./100 ml. at 25°C). Together with its stable property, nioxime is an ideal organic reagent for the amperometric titration of nickel.

Experimental

Chemicals Used. Nioxime.—This product was synthesized according to the method of Rauh, Smith, Banks and Diehl[3], which was modified in some respects. The crude nioxime was recrystallized several times from alcohol.

Other Reagents.—Such reagents as nickel sulfate and buffer agents were all of analytical grade. They were all examined as to their purity by the polarographic method. Buffer solutions were prepared according to Kolthoff and Vleeschhower[4].

Apparatus Used.—The potentiometric manual polarograph designed by the authors[5] is used for the polarographic study, for the amperometric titration and for the determination of pH.

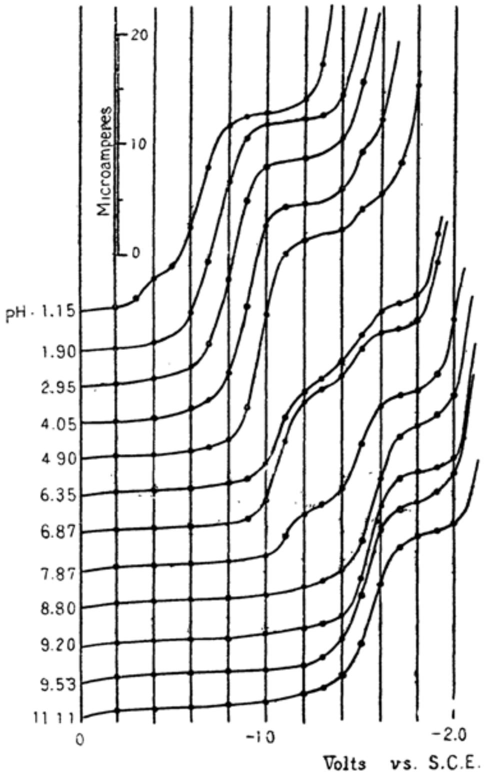

Fig. 1. Polarograms of nioxime at various pH

Polarographic Behavior of Nioxime.—Polarograms of nioxime at the dropping mercury cathode in various pH solutions are shown in Figure 1. These solutions have the composition of 10^{-3} M-nioxime, 10^{-2} M-KCl, and 0.01% gelatine except in the can of buffer agents. At a pH of 1.15, two waves appear at $E_{1/2}=-0.35$ and -0.65 volt vs. the saturated calomel electrode (S. C. E.) and in the pH range between 1.9 and 4.9, the first wave disappears and the second wave comes to predominate shifting to a more negative potential. At a pH of 4, the third wave appears at $E_{1/2}=-1.5$ volts vs. S. C. E. and above a pH of 8.8, the second wave disappears and the well-defined third wave predominates.

Amperometric Titration.—The general set-up was similar to that described in the previous paper[1]. For the performance of titration, a measured volume of the standard nickel solution in the proper medium was introduced into the cell, hydrogen was passed through for twenty minutes, the proper e.m.f. was applied to the cell and the current was measured. Successive amounts of nioxime standard solution were added from the burette. After each addition the contents of the cell were mixed by passing hydrogen through for half a minute and the current was recorded after it had become constant. In all cases the values of the current corrected for the volume change, were plotted against the amounts of reagent added.

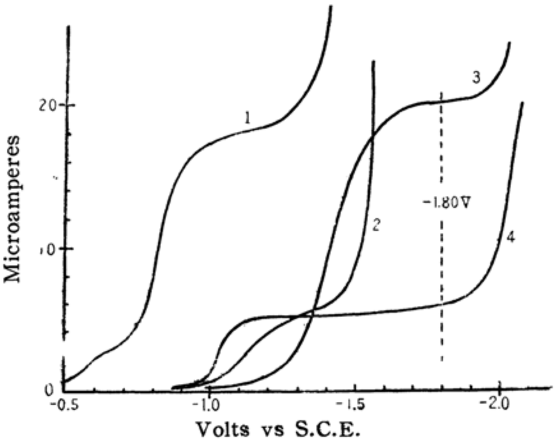

Fig. 2. Polarograms of nickel and nioxime in acetic acid medium and in ammoniacal medium

Curve 1. nioxime in 0.25M—CH_3CO_2Na, CH_3CO_2H
Curve 2. nickel in the same electrolyte
Curve 3. nioxime in 0.25M—NH_4Cl, NH_4OH
Curve 4. nickel in the same electrolyte
[nioxime]=1mM/l [Ni^{++}]=1mM/l

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[3] E. Rauh, G. F. Smith, C. V. Banks, H. Diehl, *J. Org. Chem.*, **10**, 197 (1945).

[4] I. M. Kolthoff, "Acid-base Indicators", Macmillian Co., p. 251 (1937).

[5] M. Ishibashi, T. Fujinaga, *J. Japanese Chem.* (in Japanese), 4, 554 (1950).

The most suitable titration medium for nickel was found to be an ammoniacal solution. Consequently, current voltage curves of nickel and nioxime were determined in order to find the most suitable condition for the titration. An applied e.m.f. of 1.80 volts was found to be the most suitable for the performance of the titration. See Figure 2.

In Figure 3 are given the data obtained in the titration of 0.000033M (1.955 mg.) nickel solution in 0.25M-ammonium chloride and ammonia with 0.0211M-nioxime at an applied e.m.f. of 1.8 v. The concentrations of ammonia and ammonium chloride could be changed within wide limits without affecting the results. In Table I is given a summary of some results obtained in the titration of nickel with nioxime and in the reverse titration. In an acetic acid medium, it is difficult to select a proper e.m.f. riding over good plateaux of the diffusion currents of both nickel and nioxime. So good reproducibility in the titration curve is not expected.

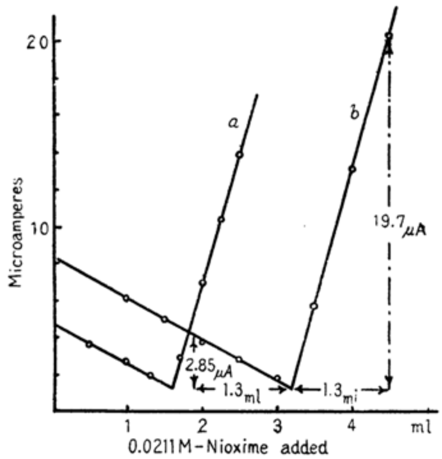


Fig. 3. Amperometric titration curves of nickel with nioxime
Curve a: 0.977 mg. of nickel in 20 ml. of 0.25M—NH_4Cl, NH_4OH.
Curve b: 1.955 mg. of nickel in the same solution

TABLE I　TITRATION OF NICKEL WITH NIOXIME

0.0667 N-Ni taken		0.211 N-nioxime used	Ni found	Error
0.50 ml.	(0.977 mg.)	1.59 ml.	0.987 mg.	+1.0 %
1.00	(1.955)	3.20	1.980	+1.2 %
2.00	(3.91)	6.35	3.92	+0.3 %
	"	6.36	3.93	+0.5 %
	"	6.37	3.94	+0.7 %
	"	6.39	3.96	+1.2 %
4.00	(7.82)	12.41	7.69	−1.7 %
Ni used		Nioxime taken	Ni found	Error
1.59 ml.	(3.12 mg.)	5.0 ml.	3.10 mg.	−0.7 %
3.17	(6.20)	10.0	6.19	−0.2 %
4.73	(9.27)	15.0	9.30	+0.3 %

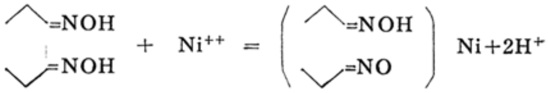
Discussion

Numbers of Electrons Transferred in the Reduction of Nioxime.—The theoretical equation, derived by Ilkovic, for the diffusion current at the dropping mercury electrode is

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/6} = KC$$

where i_d is the average current in microamperes, n is the number of Faraday's transferred per mole, D is the diffusion coefficient in cm.^{2} sec.$^{-1}$, C is the concentration of reduced ion in millimoles per litre, m is the rate of flow of mercury from the dropping mercury electrode in mg. sec.$^{-1}$, t is the drop time in seconds, and K is the proportionality constant. Although diffusion coefficient D of nioxime is not known, by means of the Stokes-Einstein diffusion equation, it is computed to be about 5×10^{-6} cm.^{2} sec.$^{-1}$ from its molecular weight ($C_6H_{10}O_2N_2 = 142.16$). Substitution of experimental values to the equation (1) yields a value for n of approximately 8; e.g. in one experiment, using the mercury electrode of characteristics of m = 0.641 and t = 2.10, 0.9 mM/1-nioxime showed the diffusion current of 8.25 microamperes. Then

$$n = i_d/605D^{1/2}Cm^{2/3}t^{1/6}$$
$$= 8.25/605 \cdot (5\times10^{-6})^{1/2} \cdot 0.9 \cdot (0.641)^{2/3} \cdot (2.1)^{1/6}$$
$$= 7.65$$



Again the number of electrons n was also calculated using the value of an amperometric titration curve of nickel with nioxime as they react according to the next formula.

At an applied e.m.f. of 1.8 volts, both nickel and nioxime are reduced at the dropping mercury electrode, thus the V shaped titration curves are obtained in the present titrations. In such a case, the normal concentration of nickel at one point before the end point of titration is equal to that of nioxime at the point symmetric for the end point, in other words, at the point where the corresponding volume of the reagent is further added after the end point of titration, provided that the volume change in titration is negligible. As the reduction current, which is proportional to its concentration, is corrected for the volume change, the ratio of two reduction currents at the two points should follow the following equation assuming that the capillary characteristics at the two points are unchanged.

$$\frac{i}{i'}=\frac{n\cdot D^{1/2}\cdot C}{n'\cdot D'^{1/2}\cdot C'}$$

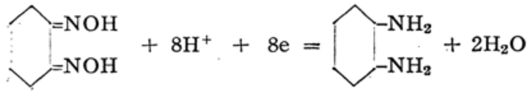
Here the numerators are of nickel and the denominators are of nioxime. As nickel ions are reduced to the metallic state at the applied e.m.f., $n=2$ and $C=C'/2$. Therefore,

$$n'=\frac{D^{1/2}\cdot i'}{D'^{1/2}\cdot i.}$$

From the experimental data shown in Figure 3, $i'/i=19.7/2.85=6.9$ and the diffusion coefficient of nickel calculated from its equivalent conductance at infinite dilution is 7.1×10^{-6} $\text{cm}^2\ \text{sec}^{-1}$. Using the above numerical value,

$$n'=\frac{(7.1\times10^{-6})^{1/2}}{(5\times10^{-6})^{1/2}}\times6.9=8.2$$

This value for n' is also very close to 8 and shows good coincidence with the value calculated according to the equation (1). This value for the number of electrons indicates that nioxime in an alkaline medium is reduced to 1,2-diaminocyclohexane at the dropping mercury cathode.



From the fact that oximes are generally reduced to the corresponding amines by metal reductants, the above inference is thought to be reasonable.

Summary

1. Cyclohexanedionedioxime (nioxime) was synthesized and its aqueous solution was used for the amperometric titration of nickel in ammoniacal medium, and the accurate results were obtained.

2. The polarographic behavior of nioxime was investigated and the reduction mechanism at the dropping mercury cathode was discussed.

Acknowledgement

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