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The Polarographic Investigation on the Reaction between Chromium(II)-ethylenediaminetetraacetate and Nitrate Ions

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The effect of nitrate ions on the polarographic waves of ethylenediaminetetraacetatoaquochromate(III) ions has been studied in acetate buffer solutions and acid potassium chloride solutions. Nitrate ions are chemically reduced in the vicinity of the mercury drop of the electrode by chromium(II)-EDTA complexes which are formed by the electroreduction of chromium(III)-EDTA complexes. The chromium(III)-EDTA complexes thus formed are reduced again at the DME and the intermediate products of nitrate ions are reduced further chemically with chromium(II)-EDTA complexes or electrochemically, resulting in the enhancement of the current. The nature of the limiting current is investigated and compared with that predicted from the theoretical treatment. The reaction between chromium(II)-EDTA and nitrate ions has also been investigated in acetate buffer solutions and its rate constant, 35 l. mol^{-1} sec^{-1} at nearly 0°C, $\mu=0.1$, has been compared with 30 l. mol^{-1} sec^{-1}, the value obtained from the polarographic catalytic current under almost the same condition.

Catalytic poloargraphic currents due to the presence of nitrate have been observed in several electrolytic reductions. The effect of nitrate ions on the reduction waves of uranyl ions,[1-5] molybdate ions[6-8] and chromium complexes[9-11] has been reported. In the last case, it has been known that the reduction of chromium complexes with glycine,[9] alanine[10] thiourea[11] and oxalate give peculiar maximum waves in the presence of nitrate ions. This was attributed to the induced reaction of nitrate ions.

In addition, another kind of polarographic catalytic wave due to nitrate ions was found in the course of a systematic investigation of the chromium complexes in this laboratory. It was considered as due to the reaction between nitrate ions and chromium(II)-EDTA complexes taking place at the electrode surface, the latter being formed by the electroreduction of ethylenediaminetetraacetatoaquochromate(III) ions at the electrode.

In this communication the polarographic investigation on this reaction taking place in the solution and at the electrode surface is presented; the stoichiometry and the rate constant of the reaction are determined and the reaction mechanisms are discussed.

Experimental

Hydrogen ethylenediaminetetraacetatoaquochromate(III), H[Cr(H_2O)edta], was prepared according to the procedure of Hamm.[12] It was identified by the measurement of the absorption spectra and by the determination of hydrogen, nitrogen and carbon contents.

Found: C, 33.05; N, 7.82; H, 4.26. Calcd. for H[Cr(H_2O)edta]: C, 33.40; N, 7.80; H, 4.21%.

All the chemicals used were of a guaranteed reagent grade.

Current-potential curves were obtained with a pen-recording polarograph, Yanagimoto Galvarecorder Model GR-103, with an automatic potential scanner. The same polarograph but without an automatic potential scanner was used for the automatic recording of limiting current-time curves of the reactions in the solution. The dropping mercury electrode (DME) used had a rate of mercury flow, m, of 1.65_7 mg./sec. and a drop time, t_d, of 5.22 sec., when measured in an air-free solution containing 0.1 M acetate buffer (pH 4.9) at −0.5 V. vs. SCE and at 50 cm. of height of a mercury reservoir. The potential of the DME was referred to the saturated calomel electrode (SCE). The temperature of the electrolytic solution was maintained by means of a water thermostat at 25°C, unless otherwise stated. The dissolved oxygen in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution. No maximum suppressor was used.

The measurements were made in 0.1 M acetate buffer

1) I. M. Kolthoff, W. E. Harris and C. Matsuyama, *J. Am. Chem. Soc.*, **66**, 1782 (1944).
2) J. Koryta, *Collection Czech. Chem. Commun.*, **20**, 667 (1955).
3) B. Kelin and J. W. Otvos, *J. Am. Chem. Soc.*, **68**, 2665 (1946).
4) T. Murata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **81**, 1240 (1960).
5) J. Collat and J. J. Lingane, *J. Am. Chem. Soc.*, **76**, 4214 (1954).
6) M. Johnson and R. Robinson, *Anal. Chem.*, **24**, 366 (1952).
7) D. Chow and R. Robinson, ibid., **25**, 1493 (1953).
8) I. M. Kolthoff and I. Hodara, *J. Electroanal. Chem.*, **5**, 2 (1963).
9) R. E. Hamm and C. D. Withrow, *Anal. Chem.*, **27**, 1913 (1955).
10) H. Hamaguchi, J. Hashimoto and N. Fukushi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **79**, 1482 (1958).
11) K. Nakano, K. Morinaga and Y. Narusawa, Presented at the 8th Annual Symposium on polarography, the Chemical Society of Japan Fukuoka (1961), Abstracts, p. 95.
12) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 6570 (1953).

solutions (pH 4.9), unless otherwise stated. The experimental conditions were in most cases such as those postulated in the theoretical treatment so that it was possible to compare the experimental results with the theoretical ones.

The controlled potential electrolysis was carried out with a Yanagimoto automatic potentiostat, Model VE-3. The working electrode was a mercury pool and the auxiliary electrode was platinum wire which was connected to the electrolytic solution through a potassium chloride agar bridge. The potential of the working electrode was controlled against the saturated calomel electrode (SCE). The solution was stirred by means of a magnetic stirrer. Nitrogen gas was bubbled through the solution continuously to provide stirring and to remove atmospheric oxygen.

Results

Polarographic Characteristics of Ethylenediaminetetraacetatoaquochromate(III) Ions in the Presence of Nitrate.—Ethylenediaminetetraacetatoaquochromate(III) ions, $[Cr(H_2O)edta]^-$, gave a well-defined polarographic reduction wave in a 0.1 M acetate buffer solution. This wave was found to correspond to the one-electron reduction of chromium(III) to chromium(II). The half-wave potential, $E_{1/2}$, was -1.24 V. vs. SCE and the diffusion current constant, I, was 1.48 μamp. $sec^{1/2}$ mM^{-1} $mg^{-2/3}$, both of which were in accord with the values obtained by Pecsok, Shields and Schaeffer.[13]

The addition of nitrate caused the exaltation of the limiting current, although the solutions with or without nitrate ion gave the identical current-potential curves in the absence of $[Cr(H_2O)edta]^-$ (Fig. 1). The exaltation phenomenon was so sensitive that the effect of nitrate ion on the d. c. polarograms could be observed at the concentration as low as 10^{-6} M of $[Cr(H_2O)edta]^-$.

The effect of nitrate ions on the polarograms of $[Cr(H_2O)edta]^-$ was found to be of the catalytic nature, as will be proved later. The polarographic characteristics of the solution containing $[Cr(H_2O)edta]^-$ and nitrate ions were examined and compared with those predicted from the theoretical studies on the catalytic polarographic current.[14,15]

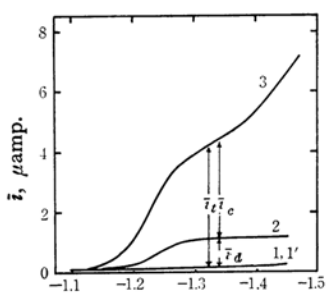

Fig. 1. Polarograms obtained with the solutions containing (1) 0.1 M acetate buffer, (1′) (1)+19.6 mM KNO_3, (2) (1)+0.36$_4$ mM $H[Cr(H_2O)edta]$, and (3), (2)+19.6 mM KNO_3.

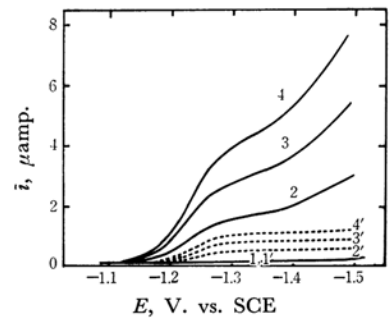

Fig. 2. Polarograms of 0 (1, 1′), 0.12$_2$ (2, 2′), 0.25$_3$ (3, 3′), and 0.36$_4$ (4, 4′) mM of $H[Cr(H_2O)edta]$ in the solutions containing 0.1 M acetate buffer in the presence (1, 2, 3, 4) and the absence (1′, 2′, 3′, 4′) of 19.6 mM KNO_3.

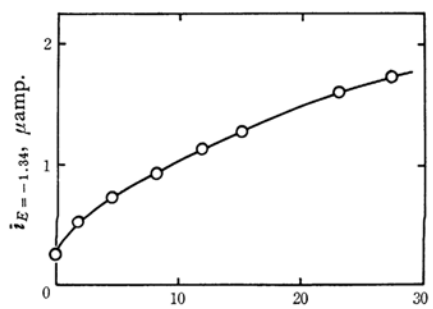

Fig. 3. The limiting currents (at -1.34 V.) obtained with 0.1 mM $H[Cr(H_2O)edta]$ in 0.1 M acetate buffer solutions containing varied concentrations of nitrate.

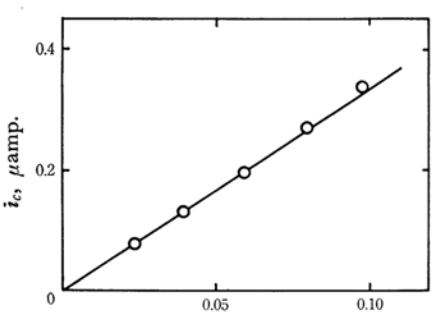

Fig. 4. The relation between the catalytic current and the concentration of nitrate, obtained with 1.2$_4$ mM $H[Cr(H_2O)edta]$ in 0.1 M acetate buffer solutions containing varied concentrations of nitrate.

13) R. L. Pecsok, L. D. Shields and W. P. Schaeffer, *Inorg. Chem.*, **3**, 114 (1964).

14) P. Delahay and G. L. Stiehl, *J. Am. Chem. Soc.*, **74**, 350 (1952).

15) J. Koutecký, *Collection Czech. Chem. Commun.*, **18**, 311 (1953).

The polarograms obtained at various concentrations of $[Cr(H_2O)edta]^-$ and at the given concentration of nitrate are shown in Fig. 2. The limiting current at -1.34 V. was found to be almost proportional to the concentration of $[Cr(H_2O)edta]^-$.

Figure 3 indicates a relation between the limiting current and the concentration of nitrate, which was obtained at the given concentration of $[Cr(H_2O)edta]^-$. When the concentration of nitrate was relatively small, in other words, when the experimental condition was not that postulated in the theoretical study on the catalytic current, the catalytic current, $\bar{i}_c$, (the additional portion on the limiting current caused by the presence of nitrate, cf. Fig. 1) was almost proportional to the concentration of nitrate (Fig. 4). The presence of nitrate did not bring about the plateau but the rather inclined limiting current, even after the residual current was corrected. The inclination of the limiting current became larger with increasing concentrations of nitrate.

The catalytic currents obtained at various heights of the mercury reservoir are given in Table I. The total limiting currents are almost proportional to the square root of the height of the mercury reservoir under the conditions where $\bar{i}_c$ is proportional to the concentration of nitrate.

Table I. Limiting currents of $[Cr(H_2O)edta]^-$ obtained in the presence of nitrate ions at various heights of the mercury reservoir (h) in acetate buffer solutions

h cm.	Solution 1*		Solution 2**	
	$\bar{i}_t$, μamp.	$\bar{i}_c$, μamp.	$\bar{i}_t$, μamp.	$\bar{i}_t/h$
65	3.1	2.4	5.1	1.6
60	3.0	2.3	4.9	1.6
55	2.9	2.3	4.8	1.5
50	2.8	2.2	4.6	1.5
45	2.7	2.1	4.5	1.5
40	2.6	2.1	4.3	1.5

* Solution 1 contains 0.2 mM $[Cr(H_2O)edta]^-$ and 19.6 mM KNO_3.

** Solution 2 contains 1.0_3 mM $[Cr(H_2O)edta]^-$ and 0.8_3 mM KNO_3.

The measurements were also made at various pH's of the solution (Fig. 5). The lower the pH value was, the larger the catalytic waves were obtained in acetate buffer solutions. However, the further increase in hydrogen ion concentration with hydrochloric acid decreased the height of the catalytic waves. At lower pH of the solution, chromium(II) ion is no longer Cr(II)-EDTA, but some other aquated species which are considered less or least effective in the catalytic process.*

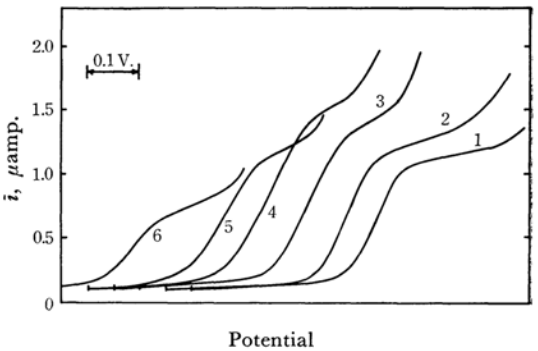

Fig. 5. Polarograms of 0.2 mM $[Cr(H_2O)edta]^-$, obtained in the presence of 2.0 mM KNO_3 in 0.1 M acetate buffer solutions of pH 5.5_0 (1), 4.8_8 (2) and 3.4_0 (3) and in 0.1 M potassium chloride solutions of pH 2.9_5 (4), 2.6_8 (5) and 2.0_2 (6). Each curve starts at -0.90 V. vs. SCE. Residual currents are not corrected.

The Reaction between Cr(II)-EDTA and Nitrate Ions in Solutions.—The presence of nitrate has no effect unless the potential is negative enough so that the reduction of $[Cr(H_2O)edta]^-$ occurs (Fig. 1). The fact strongly suggests that Cr(II)-EDTA formed at the electrode surface reacts with nitrate ion. In order to find the mechanism of the reaction taking place at the electrode surface, the characteristics of the reaction between Cr(II)-EDTA and nitrate ions in solutions were studied.

Cr(II)-EDTA was prepared by reducing the corresponding chromium(III) complex, $[Cr(H_2O)edta]^-$, at a mercury pool cathode, whose potential was controlled at -1.3 V. vs. SCE using an automatic potentiostat. The electrolysis cell used was shown in Fig. 6. Polarograms obtained after the electrolysis are of the typical reversible oxidation-reduction wave of chromium(II)- and chromium-

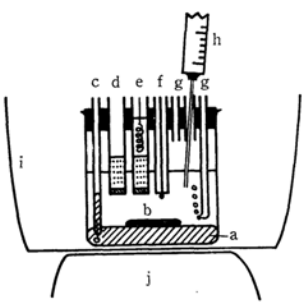

Fig. 6. Electrolysis cell: a, Hg-pool served as working electrode; b, stirrer; c, contact of working electrode; d, KCl-agar bridge connected to SCE; e, Pt-wire electrode; f, DME; g, N_2 gas disperser; h, syringe used for adding reagent after electrolysis; i, water thermostat; j, magnetic stirrer.

* According to Pecsok et al., the Cr(II)-EDTA complex has 13.61 of logarithmic stability constant and -3.00 of logarithmic acidity constant.[13] From these values, the percentage of the species Cr(II)edta, Cr(II)edtaH and Cr^{2+} which are in equilibrium in the solution are calculated to be 0, 0, ~100% at pH 2, 19, 19, 62% at pH 3, 82, 8, 10% at pH 4 and 98, 1, 1% at pH 5, respectively.

Table II. Stoichiometry of the reaction between Cr(II)-EDTA and nitrate ions, obtained in acetate buffer solutions at room temperature

Run	Initial concn. of Cr(II)-EDTA mM	Concn. of KNO_3 mM	Cr(II)-EDTA reacted with nitrate, mM	Reaction ratio, Cr(II)-EDTA/KNO_3	Temp. °C
1	0.68_9	0.049_5	0.39_1	7.9_2	27.0
2	0.69_6	0.049_5	0.39_4	7.9_6	27.0
3	0.57_6	0.049_5	0.39_8	8.0_4	26.5
4	0.70_9	0.049_5	0.39_2	7.9_4	26.5
5	0.74_5	0.049_5	0.39_9	8.0_4	25.5
6	0.64_4	0.049_5	0.39_4	7.9_6	25.5

(III)-EDTA complexes.* The concentration of Cr(II)-EDTA formed was determined by the measurement of the decrease in the reduction wave of $[Cr(H_2O)edta]^-$ at -1.4 V. vs. SCE or by the measurement of the height of the oxidation wave of Cr(II)-EDTA at -0.55 V. vs. SCE. In all experiments at pH 4.9 the sum of the height of the reduction wave at -1.4 V. and that of the oxidation wave at -0.55 V. after the electrolysis was approximately equal to the height of the reduction wave at -1.4 V. before the electrolysis. However this did not hold at lower pH, because the dissociation of Cr(II)-EDTA complex takes place. The anodic current observed at -0.55 V. results from the oxidation of Cr(II)-EDTA, but not from the oxidation of the aquated species.

When nitrate ions were added to this solution, the oxidation wave was decreased or sometimes completely obliterated according to the quantities of nitrate added. The formation of $[Cr(H_2O)edta]^-$ was at first confirmed spectrophotometrically. The stoichiometry was then ascertained at room temperature (ca. 25—27°C). The consumption of Cr(II)-EDTA by the addition of a known quantity of nitrate ions showed that one mole of nitrate reacted with eight moles of Cr(II)-EDTA (Table II).

This stoichiometry seems to show that the reaction proceeds as,

$$8\,\text{Cr(II)-EDTA} + NO_3^- + 10H^+ + 5H_2O = 8[Cr(H_2O)edta]^- + NH_4^+ \quad (1)$$

and that the final product in the reduction of a nitrate ion is an ammonium ion. The fact well accords with the results which were obtained by Lingane and Pecsok[16,17] on the reaction between chromium(II) and nitrate ions in sulfuric acid solutions.

In order to clarify the kinetics of the reaction, the decrease in the concentration of Cr(II)-EDTA by the addition of nitrate was pursued at approximately 0°C; the change in height of the oxidation wave of Cr(II)-EDTA at -0.55 V. was followed with time. Figure 7 shows an example of the wave height-time relationship. The rate constant was calculated with the assumption that the reaction is of second order. This assumption was not proved strictly but seemed to be most probable. Let a and b represent the initial concentrations of Cr(II)-EDTA and nitrate, respectively. At a given time t, x moles of nitrate react with $8x$ moles of Cr(II)-EDTA, and then we have

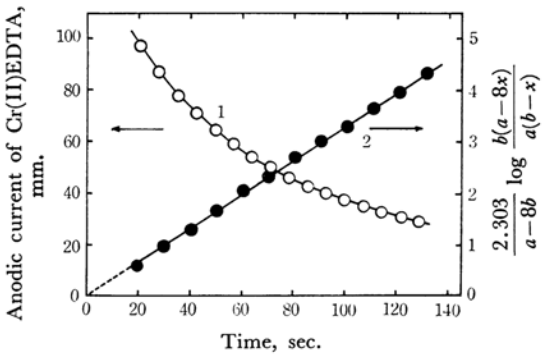

Fig. 7. The relation of the anodic limiting current with time (1) and that of the right-hand side of Eq. 4 with time (2), of the Cr(II)EDTA-nitrate reaction, obtained in a 0.1 M acetate buffer solution at nearly 0°C. The current was measured at -0.55 V. vs. SCE. The initial concentrations of Cr(II)-EDTA and KNO_3 were 0.24_6 and 0.06_1 mM, respectively.

$$-\frac{1}{8}\frac{d(a-8x)}{dt} = -\frac{d(b-x)}{dt} = k(a-8x)(b-x) \quad (2)$$

$$\frac{dx}{dt} = k(a-8x)(b-x) \quad (3)$$

Integrating and using the boundary values, the following relation is obtained:

$$kt = \frac{1}{a-8b}\ln\frac{b(a-8x)}{a(b-x)} \quad (4)$$

The rate constant can be determined from the slope of the straight line which is obtained from the plot of t against the right-hand side of Eq. 4. The value of $(a-8x)$ can be found by the measurement of the polarogram. As an example, the

* It was impossible to reduce completely, even though the dissolved and the atmospheric oxygen was sufficiently removed. Therefore, the sample solution of Cr(II)-EDTA always contained Cr(III) species, $[Cr(H_2O)edta]^-$.

16) J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **21**, 622 (1949).

17) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Company, New York (1960), p. 449.

Table III. The rate constant of the reaction between Cr(II)-EDTA and nitrate ions, obtained in 0.1M acetate buffer solutions of various pH's at nearly 0°C

pH	Initial concentration Cr(II)-EDTA mM	Initial concentration KNO_3 mM	Rate constant l.mol^{-1}sec^{-1}
5.0_4	0.27_0	0.060_5	35
4.9_0	0.33_3	0.024_8	37
4.8_8	0.28_1	0.024_8	35
4.7_7	0.37_0	0.060_5	34
4.0_2	0.26_9	0.060_5	38
3.4_1	0.21_6	0.060_5	35

relation mentioned above is also given in Fig. 7. The rate constants thus obtained at various pH's are given in Table III.

According to the stability constant obtained by Pecsok et al., the acid complex Cr(II)edtaH is formed at lower pH.[13] Nevertheless, the kinetic studies at various pH's yielded approximately the same rate constant. This seems to indicate that Cr(II)edtaH reacts with nitrate ion as fast as Cr(II)edta dose.

Discussion

The experimental results clearly show that the effect of nitrate ions on the polarographic reduction waves of $[Cr(H_2O)edta]^-$ is of a catalytic nature and that the initiation of the catalytic process is the reaction of Cr(II)-EDTA with nitrate ions. The reoxidized $[Cr(H_2O)edta]^-$ is reduced again at the DME, resulting in an exaltation of the current. The reaction product of nitrate is again reduced by Cr(II)-EDTA or it may be reduced electrochemically, until it is reduced to the final product.

The reaction between Cr(II)-EDTA and nitrate ions at the vicinity of the electrode surface proceeds regardless of the electrode potential. The presence of EDTA causes the decrease of the limiting current of $[Cr(NCS)_6]^{3-}$ over some potential range to split a one-electron reduction wave into two steps. This is caused by the electro-oxidation of Cr(II)-EDTA wich is formed at the electrode surface through the chemical reaction following the electron transfer.[18-20] When nitrate is added to this solution, the decrease of the limiting current of $[Cr(NCS)_6]^{3-}$ becomes smaller, because some of the Cr(II)-EDTA formed were not oxidized electrochemically but chemically by the reaction with nitrate ions (Fig. 8). This indicates that the exaltation phenomena described in this paper are entirely different from those obtained in the reduction of nitrate ions in the presence of multi-

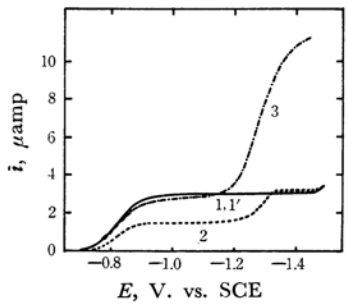

Fig. 8. Polarograms of 1.0 mM $K_3[Cr(NCS)_6]$, obtained in the solutions containing 0.9 M KSCN, 0.1 M acetate buffer and 0.005% gelatin without (1) and with (1′) 5.0 mM KNO_3 and also after the addition of 0.5 mM EDTA without (2) and with (3) 5.0 mM KNO_3.

valent cations.[21]

In the case of catalytic currents, substance O is reduced to substance R, and the latter is oxidized again to substance O by the reaction with substance Z:

$$O + ne \rightarrow R \quad (5)$$

$$R + Z \xrightarrow{k} O \quad (6)$$

In the following discussion, the currents denoted by $\bar{i}_d$, $\bar{i}_c$ and $\bar{i}_t$ represent the diffusion current of substance O, the catalytic current due to the presence of substance Z and the total limiting current, respectively (Fig. 1.). The symbol k means the rate constant of the reaction 6.

The polarographic characteristics of the catalytic currents and the relation between k and $\bar{i}_c$ were reported by Delahay and Stiehl[14] and Koutecký[15]. The experimental results concerned with the dependency of the current on the concentration of $[Cr(H_2O)edta]^-$ (Fig. 2) and nitrate ion (Fig. 3) and the height of the mercury reservoir (Table I) are consistent, although not satisfactorily, with the theoretical prediction.

The results given in Fig. 4 and the last two columns of Table I were obtained under the condition where the concentration of nitrate is relatively small. Under this condition, it seems that the rate of the catalytic process is determined by the rate of the diffusion of nitrate ions, as was observed by Kolthoff et al. in the study of the catalytic current of the uranyl ions.[1]

The effect of pH on the catalytic waves was observed as given in Fig. 5. The decrease of the limiting current at pH 2 is explained, as mentioned before, by considering the dissociation of Cr(II)-EDTA complexes.

Collat and Lingane[5] studied by means of the controlled potential coulometric analysis the

18) N. Tanaka, T. Ito and R. Tamamushi, This Bulletin, **37**, 1430 (1964).
19) N. Tanaka, K. Ebata, *J. Electroanal. Chem.*, **8**, 120 (1964).
20) K. Ebata, *Sci. Repts. Tohoku Univ. Ser.*, I, **47**, 191 (1964).
21) I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Publishers, New York (1952), p. 533.

reduction product of nitrate which was formed in the electrode reaction of uranyl ions taking place in the presence of nitrate. From the consumption of electricity and that of hydrogen ion and the chemical analysis, they concluded that nitrate ions were primarily reduced to hydroxylamine. They also reported that the reduction of nitrate ion was accompanied by the reduction of hydrogen ion and that a considerable fraction of the electricity was evidently consumed for the reduction of hydrogen ions.

In the present case, similar reactions may take place. The phenomenon that the limiting current increased with decreasing pH in acetate buffer solutions may be attributed to the change in the quantity of the reduction of hydrogen ions. The formation of acid complex, $[CredtaH]^-$, does not seem to bring about the larger limiting current, because the $[CredtaH]^-$ was found to react with nitrate ion at almost the same rate as $[Credta]^{2-}$.

From the above discussions, the catalytic reduction of nitrate ion in the electrode reaction of $[Cr(H_2O)edta]^-$ is considered as follows. The reduction of nitrate ion is initiated by the reaction with Cr(II)-EDTA, which is followed by a series of rapid consecutive reactions, presumably both electrochemical and chemical. That the electrochemical and the chemical reactions are both involved might be the cause for the inconsistency of the polarographic characteristics with the prediction of the theoretical study on the catalytic polarographic current. There may be some possibilities that a nitrate ion is reduced to a product different from that in the homogeneous reaction. Hydroxylamine, which is formed by the six-electron reduction of nitrate ion, can react with Cr(II)-EDTA in solution, but the rate is not so large as that of the reaction of nitrate. Hydroxylamine can be reduced also at the DME and gives the polarographic wave as shown in Fig. 9.

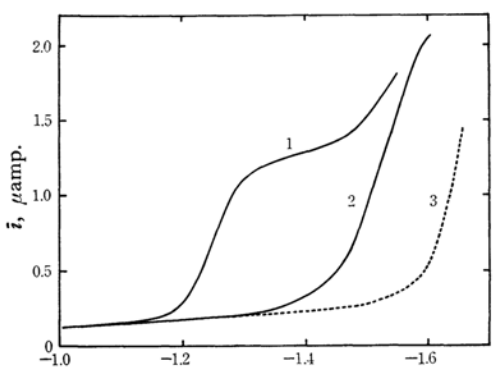

Fig. 9. Polarograms of (1) 0.2 mM $[Cr(H_2O)edta]^-$ with 2.0 mM KNO_3 and (2) 0.2 mM $NH_2OH \cdot HCl$, obtained in 0.1 M acetate buffer solutions of pH 4.8_8. Curve 3 represents the residual current.

The rate constant of the reaction between Cr(II)-EDTA and nitrate ion given by Eq. 1 or 6 was calculated from the catalytic polarographic current, using the Koutecký's equation with the assumption that the reaction occurring in the vicinity of the electrode surface proceeds in the same way as the homogeneous reaction does. In other words, nitrate ions were assumed to be reduced chemically, but not electrochemically. With a further assumption that the backward reaction is negligible, the ratio $\bar{i}_t/\bar{i}_d$ is written in the form,

$$\frac{\bar{i}_t}{\bar{i}_d} = 0.812\chi^{-1/2} + 1.92\chi^{-7/6} \quad (7)$$

with

$$\chi = \alpha k C_Z t_d \quad (8)$$

where t_d represents the drop time and α is the stoichiometry of the reaction 6($\alpha=8$ in the present case).[15,22] Using the numerical relation between χ and $\bar{i}_t/\bar{i}_d$ calculated by Koutecký,[15,23] the rate constant in the present case was determined, from the current at -1.34 V. vs. SCE to be approximately 30 $l.mol^{-1}sec^{-1}$ at 0°C and 70 $l.mol^{-1}sec^{-1}$ at 25°C, $\mu=0.1$, pH 4.9 (Table IV). It should be noted that only a small portion, if any, of the measured catalytic current is considered to be due to the reduction of hydrogen ions.

TABLE IV. THE RATE CONSTANT OBTAINED FROM THE CATALYTIC CURRENT AT -1.34 V. VS. SCE IN 0.1 mM $[Cr(H_2O)edta]^-$ SOLUTIONS CONTAINING 0.1M ACETATE BUFFER AND VARIOUS AMOUNTS OF KNO_3 AT NEARLY 0°C

Temp. °C	Concn. of KNO_3 mM	$\bar{i}_d$ μamp.	$\bar{i}_t$ μamp.	Rate constant $l.mol^{-1}sec^{-1}$
0	11.7_3	0.1_7	0.4_6	28
0	15.0	0.1_7	0.5_2	28
0	23.2_6	0.1_7	0.6_6	28
0	31.4	0.1_7	0.7_9	30
25	15.0	0.2_5	1.2_7	72
25	19.1_5	0.2_5	1.5_5	64
25	23.2_6	0.2_5	1.5_9	73
25	27.3_8	0.2_5	1.7_2	73

The rate constant obtained from the catalytic current is in good agreement with the one obtained in the homogeneous reaction. However this agreement seems to be rather fortuitous, if the complication of the reaction at the electrode surface is considered. A more precise comparison between the result from the homogeneous reaction and that from the electrode reaction seems less feasible, unless the reaction mechanisms are clarified on both kinds of the reactions.

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