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THE ELECTRODE REACTION OF HEXAAMMINECHROMIUM(III) IN THE PRESENCE OF ETHYLENEDIAMINETETRAACETATE AND NITRATE IONS

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It has been confirmed experimentally that $Cr(NH_3)_6^{3+}$ gives a catalytic wave on its polarogram in the presence of EDTA and NO_3^- ions according to the $EC(C'E')^n$ type mechanism; $Cr(NH_3)_6^{2+}$ which is produced on the electrode surface by the electrochemical reaction reacts with EDTA rapidly to form Cr(II)-EDTA (denoted as EC), which in turn gives a catalytic wave in the presence of NO_3^- ions (denoted as $(C'E')^n$). In addition, it was suggested that the reduction intermediates of nitrate ion oxidize $Cr(H_2O)_p(NH_3)_{6-p}^{2+}$ at an appreciable rate, which nitrate ion itself does not.

It was reported in previous papers[1,2] that the reduction wave of hexaamminechromium(III) ($Cr(NH_3)_6^{3+}$) splitted into two waves upon the addition of ethylenediaminetetraacetate (EDTA), and that the first wave decreased in height with the increase in the concentration of EDTA and finally vanished completely, but the height of the second wave remained constant. The electrode reaction of the first wave was explained by the ECE (Electrochemical-Chemical-Electrochemical) mechanism. On the other hand, Cr(III)-EDTA complex was found to give a catalytic wave in the presence of nitrate ions[3]; the mechanism of this electrode reaction was denoted as $(EC)^nE$ mechanism, where n means the number of repetition of EC[4]. These two electrode reactions suggested to the authors the existence of $EC(C'E')^n$ type mechanism where C' and E' are a chemical and an electrochemical reaction different than C and E, respectively. This letter presents the experimental confirmation on that the electrode reaction of $Cr(NH_3)_6^{3+}$ in the presence of EDTA and nitrate ions proceeds by the $EC(C'E')^n$ type mechanism.

(1) Electrode reactions taking place when [EDTA] > $[Cr(NH_3)_6^{3+}]$ —— $Cr(NH_3)_6^{3+}$ gives a reduction wave of Cr(III)-EDTA complex in the presence of excess EDTA (curve 3 in Fig. 1). When nitrate ions were added to this solution, the height of the wave increassed depending on the

concentration of nitrate. (See curves 4 to 6 in Fig. 1). However, the original reduction wave of $Cr(NH_3)_6^{3+}$ was never recovered. The wave height depended also on the pH of the solution; it increased as the pH became smaller, as is shown in Fig. 2 (curves 1 and 2).

The electrode process of this wave is considered to be catalytic in nature and explained by the following processes:

$$Cr(NH_3)_6^{3+} + e \longrightarrow Cr(NH_3)_6^{2+} \qquad (1)$$

$$Cr(NH_3)_6^{2+} + H_2edta^{2-} + 4\,H^+ + H_2O \longrightarrow Cr(H_2O)edta^{2-} + 6\,NH_4^+ \qquad (2)$$

$$\left\{\begin{array}{c} Cr(H_2O)edta^{2-} \\ -H^+ \upharpoonleft\downharpoonright H^+ \\ Cr(H_2O)Hedta^- \end{array}\right\} + NO_3^- \longrightarrow Cr(H_2O)edta^- + (NO_3^-)_M \qquad (3)$$

$$\left\{\begin{array}{c} Cr(H_2O)edta^{2-} \\ -H^+ \upharpoonleft\downharpoonright H^+ \\ Cr(H_2O)Hedta^- \end{array}\right\} + (NO_3^-)_M \xrightarrow{fast} Cr(H_2O)edta^- \qquad (3')$$

$$Cr(H_2O)edta^- + e \longrightarrow Cr(H_2O)edta^{2-} \qquad (4)$$

where $(NO_3^-)_M$ represents various reduction intermediates of nitrate ion, which react much faster than nitrate ion itself. The mechanism given by Eqs. (1) to (4) may be denoted as $EC(C'E')^n$, although C' (Eqs. (3) and (3')) consists of $\sum C'_i$ and C (Eq. (2)) has a possibility to proceed by two steps:

$$Cr(NH_3)_6^{2+} + pH_2O + pH^+ \longrightarrow Cr(NH_3)_{6-p}(H_2O)_p^{2+} + pNH_4^+ \qquad (5)$$

$$Cr(NH_3)_{6-p}(H_2O)_p^{2+} + H_2edta^{2-} + (4 - p)H^+$$
$$\longrightarrow Cr(H_2O)edta^{2-} + (p - 1)H_2O + (6 - p)NH_4^+ \qquad (6)$$

The net reaction between $Cr(H_2O)edta^{2-}$ or $Cr(H_2O)Hedta^-$ and nitrate ions is given by the equation,

$$8\,Cr(H_2O)edta^{2-}\ (\text{or } 8\,Cr(H_2O)Hedta^-) + NO_3^- + 10\,H^+\ (\text{or } 2H^+)$$
$$\longrightarrow 8\,Cr(H_2O)edta^- + NH_4^+ + 3H_2O \qquad (7)$$

The dependency of the wave height on the pH indicates that the $Cr(H_2O)Hedta^-$ reacts with nitrate ions faster than the $Cr(H_2O)edta^{2-}$ does.

(2) Electrode reactions taking place when [EDTA] ≤ [$Cr(NH_3)_6^{3+}$] —— When [EDTA] ≤ [$Cr(NH_3)_6^{3+}$] in the absence of nitrate ions, two reduction waves were obtained as reported previously[1,2]. (See also curve (7) in Fig. 1). Upon the addition of nitrate both the waves increased in height depending on the concentration of nitrate. The first wave, however, approached to the limiting value with the increase in the concentration of nitrate. Curves 3 to 5 in Fig. 2 show that the pH dependency of the wave heights are somewhat complicated; the height of the first wave increases while that of the second decreases with the increase in pH.

The electrode reaction taking place under the conditions that [EDTA] is smaller than [$Cr(NH_3)_6^{3+}$] may be explained by assuming, in addition to Eqs. (1) to (6), the reactions,

$$Cr(NH_3)_{6-p}(H_2O)_p^{2+} + (NO_3^-)_M \longrightarrow Cr(NH_3)_{6-p}(H_2O)_p^{3+} \quad (8)$$

$$Cr(NH_3)_{6-p}(H_2O)_p^{3+} + e \longrightarrow Cr(NH_3)_{6-p}(H_2O)_p^{2+} \quad (9)$$

The reduction intermediates of nitrate $(NO_3^-)_M$ oxidize at an appreciable rate $Cr(NH_3)_{6-p}(H_2O)_p^{2+}$, which nitrate ion itself does not.

References

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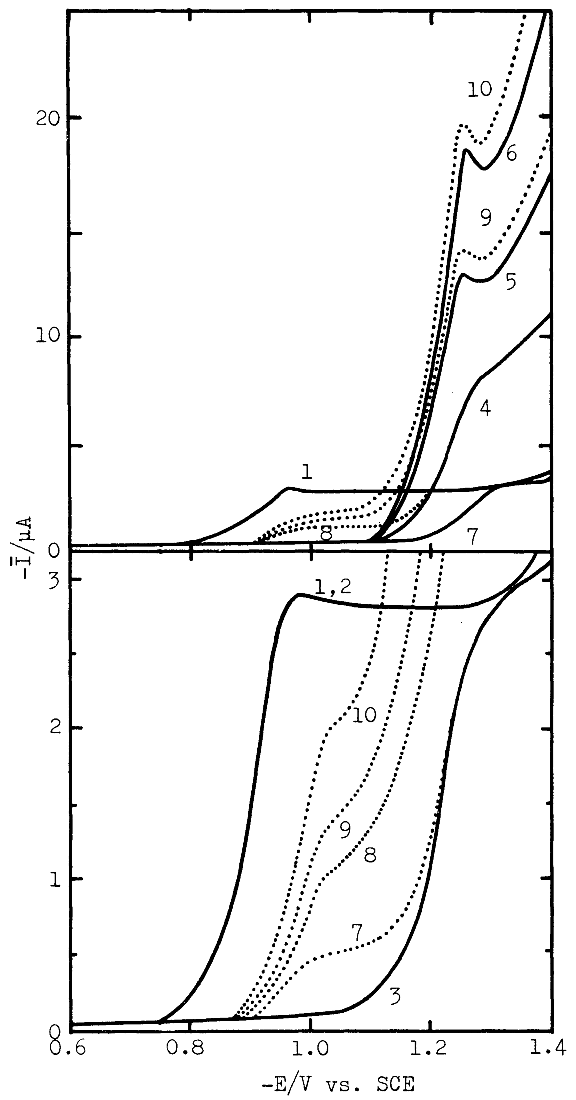

Fig. 1. Polarograms of 1 mM $Cr(NH_3)_6^{3+}$ in 0.1 M acetate buffer solutions (pH 4.4, μ = 0.5) containing EDTA and NO_3^-:

Polarogram	[EDTA]/mM	$[NO_3^-]$/mM
1	0	0
2	0	40
3	2.88	0
4	2.88	6
5	2.88	18
6	2.88	40
7	0.96	0
8	0.96	6
9	0.96	18
10	0.96	40

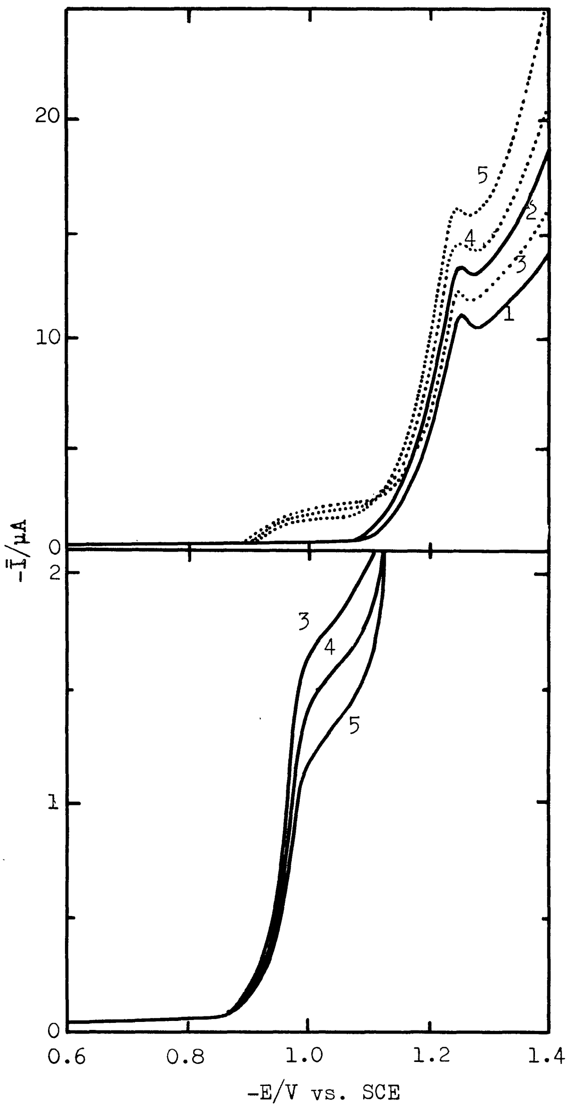

Fig. 2. Polarograms of 1 mM $Cr(NH_3)_6^{3+}$ in 0.1 M acetate buffer solutions of various pH's (μ = 0.5) containing 18 mM NO_3^- and EDTA:

Polarogram	pH	[EDTA]/mM
1	4.90	2.88
2	4.40	2.88
3	4.90	0.96
4	4.40	0.96
5	4.12	0.96

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