The Reduction of Isothiocyanato-ammine Complexes of Chromium(III) at the Dropping Mercury Electrode

By Nobuyuki TANAKA, Tasuku ITO and Reita TAMAMUSHI

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The polarographic behavior of some isothiocyanato complexes of chromium(III) has been reported. Maki, Shimura and Tsuchida[1] investigated the polarographic behavior of several isothiocyanato chromium(III) complexes in neutral unbuffered solutions. The electrode process of hexaisothiocyanatochromate(III) was studied by Fischerová and Fischer,[2] and the polarographic behavior of some isothiocyanato-ammine chromium(III) complexes in Divers' liquid was reported by Ichniowski and Clifford.[3] Meanwhile, an extremely high adsorbability of isothiocyanato complexes on the mercury electrode has been demonstrated.[4] A systematic study of the electrode processes of a series of isothiocyanato chromium(III) complexes seems, therefore, to be worthwhile and desirable.

In this paper, the reduction of isothiocyanato-ammine chromium(III) complex ions, $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ ($p=0, 1, 2, 4$ and 6), at the dropping mercury electrode has been studied by the measurement of the direct current, the alternating current and the Kalousek polarograms. The electrode processes of these complexes have been discussed on the basis of other chromium(III) complexes which were previously studied.[5-8]

Experimental

Materials.—$[Cr(NH_3)_6]Cl_3$,[9] $[Cr(NCS)_2(NH_3)_4]Cl$,[10] $NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2/3H_2O$[11] and $K_3[Cr(NCS)_6]\cdot 4H_2O$[12] were prepared according to the procedures described in the literature. $[Cr(NCS)(NH_3)_5]Cl_2$ was prepared by a modification of the procedure of Werner and Halben.[13] The complexes were identified by the measurement of the absorption spectra and by the determination of the nitrogen and chromium contents. The nitrogen content was determined by the usual method, and the chromium content by a method which has previously been reported.[7] The analysis gave the following results:

$[Cr(NH_3)_6]Cl_3$
Calcd.: Cr, 19.9; N, 32.2%
Found: Cr, 19.0; N, 31.3%
$[Cr(NCS)(NH_3)_5]Cl_2$
Calcd.: Cr, 19.5; N, 31.6%
Found: Cr, 19.4; N, 31.8%
$[Cr(NCS)_2(NH_3)_4]Cl$
Calcd.: Cr, 19.1; N, 30.9%
Found: Cr, 18.5; N, 30.1%
$NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2/3H_2O$
Calcd.: Cr, 14.9; N, 28.2%
Found: Cr, 14.6; N, 27.6%
$K_3[Cr(NCS)_6]\cdot 4H_2O$
Calcd.: Cr, 8.82; N, 14.2%
Found: Cr, 8.55; N, 14.2%

All the chemicals used were of a guaranteed reagent grade.

Apparatus and Procedure.—Direct-current (d. c.) and alternating-current (a. c.) polarograms were recorded with a Yanagimoto Model PR-2 pen-recording polarograph and a Yanagimoto Galvarecorder Y-GR 2 respectively. The Kalousek circuit and the cell equipments used were the same as have been reported previously.[7] The dropping mercury electrode (DME) employed had an m value of 1.62_5 mg./sec. and a drop-time, t_d, of 5.21 sec. when measured in an air-free solution containing 0.9 M potassium chloride, 0.1 M acetate buffer and 0.005% gelatin at -0.5 V. vs. SCE and at 50 cm. of height of the mercury reservoir. The potential of DME was referred to the saturated calomel electrode (SCE). The cell temperature was maintained at 25°C by means of a water thermostat. The dissolved oxygen in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution.

All the measurements were carried out in the solution of ionic strength 1.0 containing 0.1 M acetate buffer (pH 4.7) and 0.005% gelatin or 2×10^{-5} M LEO (polyoxyethylene lauryl ether) unless otherwise stated. As the complexes are not stable in an aqueous solution, each solution for the electrolysis

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[1] N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **31**, 413 (1958).
[2] E. Fischerová and O. Fischer, *Collection Czechoslov. Chem. Commun.*, **26**, 2570 (1961).
[3] T. C. Ichniowski and A. F. Clifford, *J. Inorg. Nucl. Chem.*, **22**, 133 (1961).
[4] N. Tanaka, E. Kyuno, G. Satô and R. Tamamushi, *J. Phys. Chem.*, **66**, 2706 (1962).
[5] N. Tanaka and G. Satô *Nature*, **197**, 176 (1963).
[6] N. Tanaka, K. Ebata and G. Satô, This Bulletin, **36**, 912 (1963).
[7] N. Tanaka, Y. Sato, R, Tamamushi and G. Satô ibid., **36**, 1059 (1963).
[8] N. Tanaka, E. Itabashi and E. Kyuno, ibid., **36**, 917 (1963).
[9] M. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon kagaku Zassi*), **74**, 253 (1953).
[10] P. Pfeiffer and M. Tilgner, *Z. anorg. Chem.*, **55**, 361 (1907).
[11] H. D. Dakin, "Organic Syntheses," Vol. 15, John Wiley & Sons, New York (1935), p. 74.
[12] J. Rösler, *Ann.*, **141**, 185 (1867).
[13] A. Werner and J. von Halben, *Ber.*, **39**, 2668 (1906).

was made freshly from the dry crystalline chromium(III) complexes, and polarographic measurements were made as soon as possible after the removal of the dissolved oxygen.

Results

It has been shown in a previous study[6] that isothiocyanato-ammine complex ions of chromium(III), $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$, give no well-defined polarographic reduction wave in unbuffered neutral solutions, but do in acetate buffer or acid solutions. As typical examples of the current-potential curve, the polarograms of isothiocyanatopentamminechromium(III) ion, $[Cr(NCS)(NH_3)_5]^{2+}$, are given in Figs. 1 and 2. The maximum appears when the solution does not contain a sufficient amount of maximum suppressor and this can be attributed to the high adsorbability of the complex ions which have thiocyanate coordinated.[4] The addition of 0.005% gelatin or 2×10^{-5} M LEO suppresses this maximum.

The current-potential curves were obtained at various concentrations of the complex ions and at various heights of the mercury reservoir. The limiting current, $\bar{i}_l$, is proportional to the concentration of the complex ion in the range from 0.2 mM to 2.5 mM. Table I presents the linear relationship between the limiting current and the square root of the effective height of the mercury reservoir. These two relationships hold in every case and this indicates clearly that the limiting currents are diffusion-controlled.

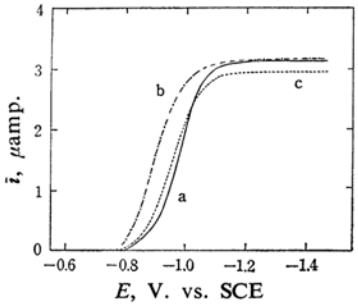

Fig. 1. Polarograms of 1.0 mM $[Cr(NCS)(NH_3)_5]Cl_2$ in 0.9 M KCl (a), 0.9 M KSCN (b) and 0.3 M Na_2SO_4 (c) solutions containing 0.1 M acetate buffer and 0.005% gelatin.

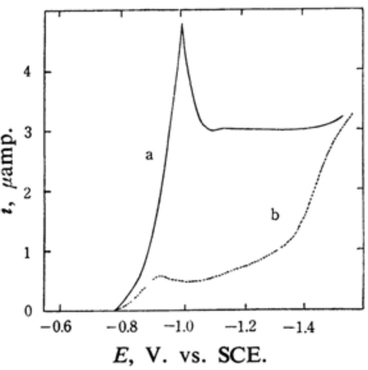

Fig. 2. Polarograms of 1.0 mM $[Cr(NCS)(NH_3)_5](NCS)_2$ in 0.9 M KCl + 0.1 M acetate buffer without maximum suppressor (a) and in 1 M KCl + 0.005% gelatin (b).

TABLE I. EFFECT OF THE HEIGHT OF MERCURY RESERVOIR ON THE LIMITING CURRENT OF 1.0 mM $[Cr(NCS)(NH_3)_5](NCS)_2$ IN THE SOLUTION CONTAINING 0.9 M KSCN, 0.1 M ACETATE BUFFER AND 0.005% GELATIN

$h_{\mathrm{corr.}}$, cm.*	$\bar{i}_l/\sqrt{h_{\mathrm{corr.}}}$, μamp. cm$^{-1/2}$
58.5	0.59_4
53.5	0.59_4
48.5	0.59_8
43.5	0.59_6
38.5	0.59_7

* Effective height of the mercury reservoir, corrected for the back pressure.

The half-wave potentials and the diffusion current constants, which were obtained in the solutions of ionic strength 1.0 containing various kinds of supporting electrolytes, are given in Table II. The reduction potentials of these complexes have been found to be affected to a great extent by the kind of supporting electrolyte.

Kalousek and a. c. polarograms were recorded to examine the polarographic reversibility of the electrode processes of the complexes. Typical Kalousek polarograms are reproduced in Fig. 3. The effect of the supporting electrolyte on Kalousek and a. c. polarograms is significant.. Nevertheless, all the

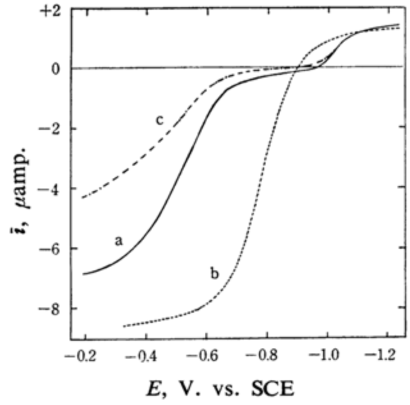

Fig. 3. Kalousek polarograms of 1.0 mM $[Cr(NH_3)_6]Cl_3$ in 0.9 M KCl(a), 0.9 M KSCN (b) and 0.3 M Na_2SO_4(c) solutions containing 0.1 M acetate buffer and 0.005% gelatin. The reduction potential is set up at −1.2 V. vs. SCE.

TABLE II. HALF-WAVE POTENTIALS (V. VS. SCE) AND DIFFUSION CURRENT CONSTANTS (μamp./mM mg$^{2/3}$ sec$^{-1/2}$) OF $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$

	In 0.9 M KCl, 0.1 M acetate buffer and 2×10⁻⁵ M LEO	In 0.3 M Na_2SO_4, 0.1 M acetate buffer and 0.005% gelatin	In 0.9 M KSCN, 0.1 M acetate buffer and 0.005% gelatin	In 0.9 M KI, 0.1 M acetate buffer and 0.005% gelatin
$[Cr(NH_3)_6]^{3+}$	$E_{1/2}=-1.01$ $I=1.7_3$	$E_{1/2}=-0.99$ $I=1.5_2$	$E_{1/2}=-0.85$ $I=1.7_3$	$E_{1/2}=-0.89$ $I=1.6_6$
$[Cr(NCS)(NH_3)_5]^{2+}$	$E_{1/2}=-0.98$ $I=1.6_1$	$E_{1/2}=-0.95$ $I=1.5_2$	$E_{1/2}=-0.89$ $I=1.6_4$	— —
$[Cr(NCS)_2(NH_3)_4]^+$	$E_{1/2}=-0.91$ $I=1.5_9$	$E_{1/2}=-0.88$ $I=1.5_1$	$E_{1/2}=-0.90$ $I=1.6_3$	$E_{1/2}=-0.90$ $I=1.6_6$
$[Cr(NCS)_4(NH_3)_2]^-$	$E_{1/2}=-0.80$ $I=1.5_0$	$E_{1/2}=-0.78$ —	$E_{1/2}=-0.83$ $I=1.5_7$	$E_{1/2}=-0.81$ $I=1.6_1$
$[Cr(NCS)_6]^{3-}$	$E_{1/2}=-0.62$ $I=1.5_0$	— —	$E_{1/2}=-0.80$ $I=1.5_3$	$E_{1/2}=-0.68$ $I=1.5_5$

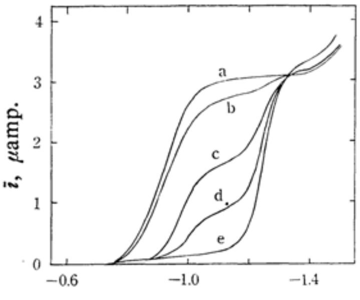

Fig. 4. D. c. polarograms of 1.0 mM $[Cr(NCS)_2(NH_3)_4]Cl_2$ in 0.9 M KSCN, 0.1 M acetate buffer and 0.005% gelatin without (a) and with 0.1 mM (b), 0.5 mM (c), 0.75 mM (d) and 5.0 mM (e) of EDTA.

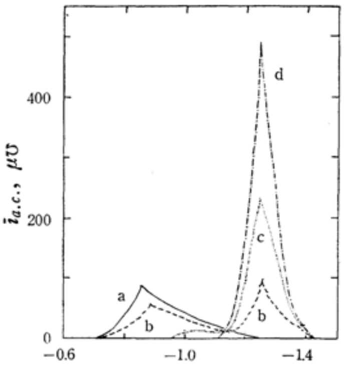

Fig. 5. A. c. polarograms of 1.0 mM $[Cr(NCS)_2(NH_3)_4]Cl_2$ in 0.9 M KSCN, 0.1 M acetate buffer and 0.005% gelatin without (a) and with 0.2 mM (b), 0.5 mM (c) and 5.0 mM (d) of EDTA.

complexes investigated gave similar Kalousek polarograms in a given supporting electrolyte solution.

The measurements of d. c. and a. c. polarograms of $[Cr(NCS)_2(NH_3)_4]^+$ were also made in the presence of EDTA (Figs. 4 and 5). The addition of EDTA causes a decrease in the limiting current over some potential range, as seen in Fig. 4. On a. c. polarograms, upon the addition of EDTA, the original wave decreases in height and a new wave appears at −1.25 V.; this wave increases in height with an increasing concentration of EDTA.[14] These phenomena were observed with all of the complexes investigated.

Discussion

One of the distinctive characteristics of the isothiocyanato-ammine complex ions, $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$, is their specific adsorption on the mercury electrode,[4] and this is well reflected in their polarographic behavior. The maximum wave shown in Fig. 2 seems to be due to the high adsorbability of the isothiocyanato complexes. The ligand NCS^- is coordinated with the central chromium atom through the nitrogen atom[4,15,16], and consequently the sulfur atom turns to the surface of the electrode.

As is shown in Table II, the supporting electrolyte has an important effect on the half-wave potential. The difference in the ease with which one electron enters in the reacting chromium(III) seems to be changed by some factors determined by the supporting electrolyte used. In potassium chloride or sodium sulfate solutions, the half-wave potential shifts to less negative potentials with an

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[14] N. Tanaka and H. Ogino, *J. Electroanal. Chem.*, **7**, 332 (1964).

[15] Y. Takeuchi and Y. Saito, This Bulletin, **30**, 319 (1957).

[16] J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3295 (1956).

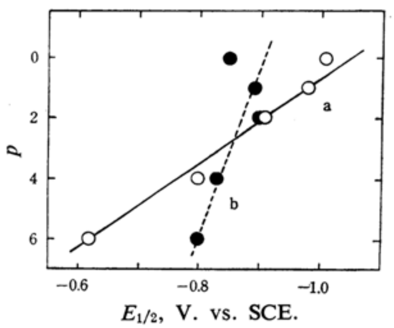

Fig. 6. Relation between p of $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ and the half-wave potential: Half-wave potentials were observed in 0.1 M acetate buffer solutions containing 0.9 M KCl and 2×10^{-5} M LEO (a), and those containing 0.9 M KSCN and 0.005% gelatin (b).

increase in the number of the thiocyanate group coordinated in $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$. On the other hand, no such tendency holds in potassium thiocyanate or potassium iodide solutions. Fig. 6 gives the relations between the p value of $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ and the half-wave potential in potassium chloride and potassium thiocyanate solutions. The linear relation in the potassium chloride solution (curve a in Fig. 6) may indicate that the number of the coordinating thiocyanate is one of the important factors in determining the reduction potential. In the potassium thiocyanate solution, the half-wave potentials of the complex cations are at less negative potentials than in the potassium chloride solution, whereas those of the complex anions are at more negative potentials (curve b in Fig. 6). Similar shifts of the half-wave potentials were also observed in potassium iodide solutions.

It seems that the above-mentioned observations can be explained by considering the specific adsorption of thiocyanate ions (or iodide ions) and that of the complex ions, and the electrostatic interaction between the electrode surface and the complex ions. At the concentration of the experimental conditions, a large amount of thiocyanate ions (or iodide ions) is specifically adsorbed at the surface of the DME at the potentials where the complex ions are reduced. The negative charge on the surface of the DME, therefore, is so large that $[Cr(NH_3)_6]^{3+}$, a tervalent cation, is attracted to the electrode surface, whereas $[Cr(NCS)_6]^{3-}$, a tervalent anion, is repelled. This causes the shifts of the reduction potential toward the opposite directions.

However, there is an alternative explanation of this potential shift. Isothiocyanato complexes are very adsorptive at the mercury electrode and seem to be reduced in the adsorbed state. The specific adsorption of the complexes with more NCS^- coordinated are partially disturbed when the adsorptive electrolyte is used. This results in the shift of the half-wave potential to more negative potentials. On the other hand, the reduction of the complex ions with less NCS^- coordinated, e. g., $[Cr(NH_3)_6]^{3+}$, is accelerated by the effect of the adsorbed supporting electrolyte SCN^-, as is the case in the polarographic reduction of Ni^{2+},[17] Zn^{2+} [18] and In^{3+}.[19] The acceleration effect caused by adsorbed SCN^- is seen in the Kalousek and the a. c. polarograms.

In most cases, the log-plot gave no straight line but two straight-line segments or curved lines, except in the case of $[Cr(NH_3)_6]^{3+}$ in a potassium chloride solution. Fig. 7 shows the plots of $\log \bar{i}/(\bar{i}_d-\bar{i})$ vs. E for the reduction waves of $[Cr(NCS)(NH_3)_5]^{2+}$ in the supporting electrolyte solutions indicated. It should be noted that the steeper portion of the slope comes at less negative potentials in a potassium thiocyanate solution, but at more negative potentials in a potassium chloride solution. This was observed with all of the complexes investigated.

As is seen in Fig. 3, the reversibility of the reduction of chromium(III) to chromium(II) at the dropping mercury electrode varies to some extent with the supporting

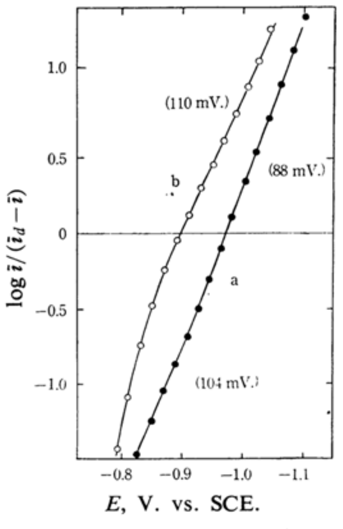

Fig. 7. Log-plots for the reduction waves of 1.0 mM $[Cr(NCS)(NH_3)_5]Cl_2$ in 0.9 M KCl (a) and 0.9 M KSCN (b) solutions containing 0.1 M acetate buffer and 0.005% gelatin.

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[17] J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **13**, 77 (1941).

[18] R. Tamamushi, K. Ishibashi and N. Tanaka, *Z. physik. Chem., N.F.*, **35**, 209 (1962); **39**, 117 (1963).

[19] R. Tamamushi, T. Takeuchi and N. Tanaka, 18th International Congress of Pure and Applied Chemistry, Montreal, Canada (August, 1961), No. B3-39.

electrolyte used. The Kalousek polarograms of $[Cr(NH_3)_6]^{3+}$ obtained in potassium chloride and sodium sulfate solutions (curves a and c in Fig. 3), where the anodic waves are clearly separated from the cathodic ones, indicates that the reduction proceeds irreversibly. The corresponding a. c. peaks are as small as that for Ni^{2+} ion, which is known to be of a typical irreversible nature.⁷⁾ In a potassium thiocyanate solution (curve b in Fig. 3), however, the polarographic reversibility increases.

The value of $i_p/(n\bar{i}_d\sqrt{t_d})$ represents the degree of the polarographic reversibility of the electrode reaction, where i_p is the peak current of the a. c. wave (in $\mu\mho$), $\bar{i}_d$, the average diffusion current of the corresponding d. c. polarograms (in μamp.), and n, the number of electrons involved in the electrode process²⁰⁾. Table III shows the $i_p/(n\bar{i}_d\sqrt{t_d})$ values for the reduction of the complex ions.

TABLE III. VALUES OF $i_p/(n\bar{i}_d\sqrt{t_d})$
($\mho$ amp^{-1} sec$^{-1/2}$)

	In 0.9 M KSCN, 0.1 M acetate buffer and 0.005% gelatin	In 0.9 M KCl, 0.1 M acetate buffer and 2×10^{-5} M LEO
$[Cr(NH_3)_6]^{3+}$	16.7	8.1
$[Cr(NCS)(NH_3)_5]^{2+}$	9.9	4.4
$[Cr(NCS)_2(NH_3)_4]^+$	14.1	2.6
$[Cr(NCS)_4(NH_3)_2]^-$	27.8	10.8
$[Cr(NCS)_6]^{3-}$	44.3	9.3

The a. c. wave height became higher with an increasing p value of $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ in a potassium thiocyanate solution. The reversibility revealed by the a. c. polarography accords well with that revealed by the measurement of the Kalousek polarograms.

All experimental results indicate that no preceding chemical reaction takes place prior to the electron transfer process, which is always followed by a rapid aquation of the divalent species, and that the aquation reaction may contribute to the polarographic reversibility.

From their detailed investigation of the polarographic reduction of $[Cr(NCS)_6]^{3-}$ in a potassium thiocyanate solution, Fischerová and Fischer concluded that the reversibility increased at higher concentrations of potassium thiocyanate.²⁾ Furthermore, Ichniowski and Clifford, who recently investigated the polarographic behavior of isothiocyanato-ammine complexes of chromium(III) in Divers' liquid, reported that the reduction proceeds reversibly.³⁾ These facts may suggest that the polarographic reduction proceeds reversibly under conditions where the following chemical reaction does not or hardly occurs.

The effect of EDTA on the reduction waves of $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ is interpreted in the same way as the effect of ethylenediammine on the polarograms of $[Co(NH_3)_6]^{3+}$ which was reported by Laitinen and Kivalo.²¹⁾

The complex ion $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ is reduced at the electrode to form $[Cr(NCS)_p(NH_3)_{6-p}]^{(2-p)+}$, which in turn reacts with EDTA:

$$[Cr(NCS)_p(NH_3)_{6-p}]^{(2-p)+}+\text{EDTA}$$
$$=\text{Cr(II)-EDTA}+p\text{NCS}^-+(6-p)\text{NH}_3$$

Because of the lability and the relative stability of these divalent chromium complexes, the reaction proceeds rapidly to the right. The Cr(II)-EDTA thus formed may or may not be oxidized at the electrode to the Cr(III)-EDTA complex, depending on the electrode potential. If the oxidation takes place, the oxidation current cancels the reduction current of $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ and the limiting current of the $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ wave decreases. The wave which appears at more negative potentials corresponds to the oxidation-reduction wave of the Cr(II)-EDTA and $[Cr(H_2O)(edta)]^-$ system. The effect of EDTA on the a. c. polarographic wave can be explained in the same way. A detailed study of the d. c. and the a. c. polarography of $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ in the presence of EDTA will be reported elsewhere.

Summary

The reduction of a series of isothiocyanatoammine chromium(III) complexes $[Cr(NCS)_p(NH_3)_{6-p}]^{(3-p)+}$ at the dropping mercury electrode has been studied. The direct current, the alternating current and the Kalousek polarograms of these complexes have been measured in various supporting electrolyte solutions. The nature of the reduction waves, corresponding to the one-electron reduction of chromium(III) to chromium(II), has been discussed.

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Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai

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20) M. Senda, M. Senda and I. Tachi, *J. Electrochem. Soc.* Japan (*Denki Kagaku*), **27**, 83 (1959).

21) H. A. Laitinen and P. Kivalo, *J. Am. Chem. Soc.*, **75**, 2198 (1953).