Studies on the Irreversible Polarographic Wave of Nickel-thiocyante Complex

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The polarographic reduction wave of nickel-thiocyanate complex is one of the problems studied by several researchers from the standpoint of chemical analysis.(1) However, its theoretical treatment has not been carried out and its reduction mechanism has not been clarified, because it is considered to be of irreversible character. For these several years the theoretical treatment for the irreversible wave has been proposed by the author and other researchers, and it has appeared possible theoretically to analyse the irreversible wave of the complex. In this situation the present study was taken up. One of the purposes was to clarify the reduction mechanism of the complex using the theoretical consequence reported in the previous paper(2) and the other was to show that the theoretical consequence is applicable to the analysis of such an irreversible wave.

After some preliminary experiments, however, it was found out that the dissociation of nickel-thiocyanate complex in the solution is not simple and the reduction wave of the complex has most complicated behaviors. In spite of these facts it was possible to explain the result

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(1) J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **13**, 77 (1941); etc.

(2) R. Tamamushi and N. Tanaka, this Bulletin, **23**, 110 (1950).

obtained by the experiment, though partly, with the result derived from the theoretical treatment. In addition of the fact, the reduction wave of this complex is characteristic in several points of view. In the present paper the experimental results of the reduction wave of this complex and the reduction mechanism estimated from them have been presented.

Experiments and Experimental Results

Apparatus. — A manually operating polarograph and a photo-recording polarograph were employed, of which the former was employed for the accurate measurements. A dropping mercury electrode was used for the cathode and a normal calomel electrode, for the anode. Four capillaries were used for the dropping mercury electrode, which have the capillary constants, $m^{2/3}\ t^{1/6}$, of (a) 1.795, (b) 2.082, (c) 1.203 and (d) 1.336 (mg.$^{2/3}$ sec.$^{-1/2}$), measured in distilled water free from oxygen without the applied potential. Of these capillaries, (c) and (d) were used for measuring the limiting currents at various heights of mercury reservoir. The value of 1.203 for (c) and 1.336 for (d) were the values measured at a 82 cm. of mercury height. All polarographic measurements were made in a thermostat of 25.0° with a normal calomel electrode as a reference electrode.

Standard Solution of Nickel and Supporting Electrolyte. — The nickel standard solution was prepared by dissolving Kahlbaum's nickel chloride (free from cobalt) in distilled water. The concentration of the stock solution was 1.640 milli *M*, which was determined by the gravimetric method.

For the supporting electrolyte the mixtures of potassium thiocyanate and potassium chloride and of potassium thiocyanate and potassium nitrate were used. When the medium of KSCN-KNO_3 was used, gelatine was added by 0.005% in concentration.

Polarograms of Nickel-thiocyanate Complex in the Supporting Electrolyte of Various Concentrations of Potassium Thiocyanate. — (a) In the Medium of KSCN-KCl. The current-voltage curves were measured with the solutions containing 0.328 milli *M* of nickel and various concentrations of potassium thiocyanate. Potassium chloride was added to all the solutions by 1 *M* in concentration to eliminate the effect of migration current appearing when the quantity of potassium thiocyanate was insufficient. Some of the polarograms obtained are shown in Fig. 1.

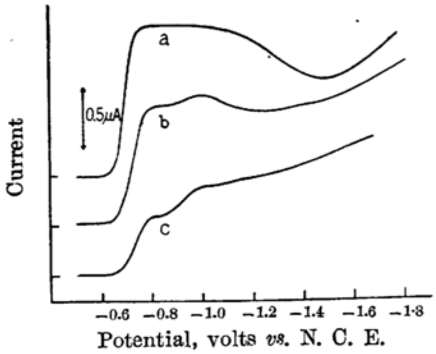

Fig. 1.—Polarograms of nickel-thiocyanate complex: the concentration of nickel, 0.328 milli *M*; supporting electrolyte, 1 *M* KCl +, (a) 0.5 *M* KSCN, (b) 0.02 *M* KSCN, (c) 0.01 *M* KSCN.

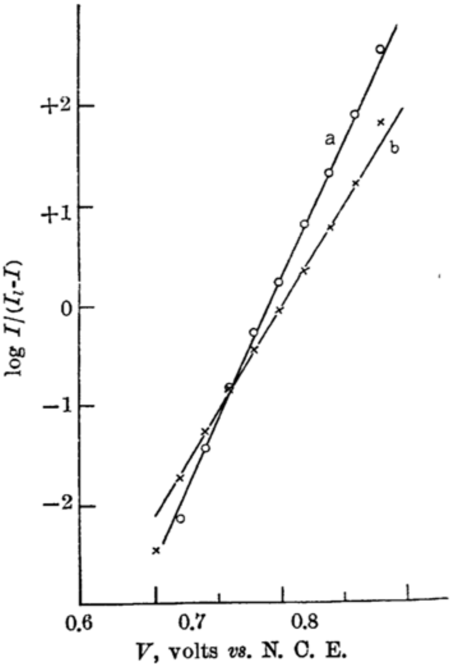

Fig. 2.—Relation of log $I/(I_l\text{-}I)$ and V of polarograms of nickel-thiocyanate complex: supporting electrolyte, 1 *M* KCl +, (a) 0.5 *M* KSCN, (b) 0.04 *M* KSCN.

For all the polarograms log $I/(I_l\text{-}I)$ was plotted against V, the plots holding a straight lines, some of which are shown in Fig. 2. From these log plots their inclinations and the half-wave potentials were obtained, which are shown in Table 1.

Some of the results obtained from these experiments are as follows: (1) The reduction waves of the nickel-thiocyanate complex have the center of symmetry at the half-wave potential, but their inclinations are not in accord with those expected from the reversible reduction wave. (2) Their half-wave potential

Table 1

The Half-wave Potential and the Inclination of Log Plot of the Polarograms Obtained in the Supporting Electrolyte Containing Various Concentsations of Potassium Thiocyanate and 1 *M* of Potassium Chloride

	First wave		Second wave	
Concentration of KSCN, *M*	Half-wave potential,* V.	Inclination of log plot, mV.	Half-wave potential,* V.	Inclination of log plot, mV.
2.00	−0.720	35		
1.00	−0.704	35		
0.50	−0.691	36		
0.20	−0.687	41		
0.10	−0.689	43		
0.04	−0.704	49		
0.02	−0.716	52	−0.925	48
0.01	−0.725	51	−0.916	79
0.005	−0.725	52	−0.912	82

* The half-wave potential is referred to a normal calomel electrode.

is the most positive when the supporting electrolyte contains about 0.2 *M* of potassium thiocyanate and shifts to negative potential with the increase or the decrease of concentration of potassium thiocyanate in the supporting electrolyte. (3) The second wave appears when the concentration of potassium thiocyanate is less than 0.04 *M*. (4) A minimum of current appears in the part of the limiting current's plateau of the current-voltage curve in the supporting electrolyte containing potassium thiocyanate more than 0.02 *M*, and it disappears when the concentration of potassium thiocyanate decreases down to 0.01 *M*. This is one of the most characteristic features of the polarograms of the complex. Some experiments were carried out on it, but the reason why it appears on the current-voltage curve could not be clarified in the present study.

(b) In the Medium of KSCN-KNO$_3$. The current-voltage curves were measured with the solutious containing 0.328 milli *M* of nickel, various concentration of potassium thiocyanate and potassium nitrate and 0.005% of gelatine; the total concentration of potassium thiocyanate and potassium nitrate in the solution being adjusted to be 2 *M* to keep the ionic strength in the solution constant. They were also measured with the solutions containing various concentrations of nickel, 0.2 *M* of potassium thiocyanate, 1.8 *M* of potassium nitrate and 0.005% of gelatine to know whether the half-wave potential varies with the change of the concentration of nickel. The polarograms obtained showed similar behaviors to those obtained in the medium of potassium thiocyanate and potassium chloride, so far as the appearance, the shift of half-wave potential with the concentration change of potassium thiocyanate and the less reversibility were concerned. The half-wave potentials, the inclination of the log plots and the diffusion current constants obtained in the supporting electrolytes containing various concentrations of potassium thiocyanate are shown in Table 2 and the half-wave potentials and the diffusion current constants obtained with the changing of the concentration of nickel, in Table 3. In this case the log plots were somewhat less linear when the concentration of potassium thiocyanate in the supporting electrolyte is considerably large.

Table 2

The Half-wave Potential, the Inclination of Log Plot and the Diffusion Current Constant of the Polarograms Obtained in the Supporting Electrolytes Containing Various Concentrations of Potassium Thiocyanate and Potassium Nitrate

Concentration of KSCN, *M*	Concentration of KNO$_3$, *M*	Half-wave potential *vs.* N.C.E., V.	Inclination of log plot, mV.	Diffusion current constant, μA(milli *M*)$^{-1}$ (mg.$^{2/3}$sec.$^{-1/2}$)$^{-1}$
2.00	0	−0.745	39	3.23
1.50	0.50	−0.732	36	3.15
1.00	1.00	−0.726	43	3.25
0.50	1.50	−0.715	42	3.24
0.20	1.80	−0.708	47	3.03
0.10	1.90	−0.713	48	2.91
0.05	1.95	−0.727	49	2.48
0.03	1.97	−0.737	53	2.27
0.01	1.99	−0.764	63	(1.14)

Table 3

The Half-wave Potential and the Diffusion Current Constant of the Polarograms Obtained with Various Concentrations of Nickel in the Supporting Electrolyte Containing 0.20 *M* of KSCN and 1.80 *M* of KNO$_3$

Concentration of nickel, $\times 10^{-3}$*M*	Half-wave potential *vs.* N.C.E., V.	Diffusion current constant, μA(milli *M*)$^{-1}$ (mg.$^{2/3}$sec.$^{-1/2}$)$^{-1}$
0.0656	−0.706	2.92
0.164	−0.704	3.04
0.328	−0.708	3.03
0.656	−0.701	3.22
1.640	−0.700	3.12

Limiting Current Measured at Various Heights of Mercury. — (a) In the Medium of KSCN-KCl. The limiting currents were measured at various heights of mercury. If the limiting current is determined only by the diffusion process, it should be proportional to the square root of mercury height. The experimental results indicated that when the supporting electrolyte contains less than 0.2 M of potassium thiocyanate the ratio of limiting current to the square root of mercury height, $I_l/\sqrt{H}$, increases with the decrease of mercury height, H, which means clearly that the limiting current involves the kinetic current besides the diffusion current. Some of the experimental results are shown in Table 4. In the supporting electrolyte containing 0.005 M of potassium thiocyanate the limiting current of the first wave is completely determined by the rate of the association but not by the diffusion because it is independent of the height of mercury as indicated in Table 4.

Table 4

The Limiting Current Obtained at Various Heights of Mercury

H, cm.	$\sqrt{H}$	$I_{l(1)}$, μA	$I_{l(2)}$, μA	$\frac{I_{l(1)}}{\sqrt{H}}$	$\frac{I_{l(2)}}{\sqrt{H}}$
Supporting electrolyte, 1 M KCl−2 M KSCN					
81	9.00	1.291	……	0.143	……
61	7.81	1.114	……	0.143	……
46	6.78	0.977	……	0.144	……
Supporting electrolyte, 1 M KCl−0.2 M KSCN					
81	9.00	1.341	……	0.149	……
61	7.81	1.174	……	0.150	……
46	6.78	1.033	……	0.152	……
Supporting electrolyte, 1 M KCl−0.005 M KSCN					
82	9.06	0.219	0.308	0.0242	0.0340
62	7.87	0.219	0.292	0.0278	0.0371
47	6.86	0.221	0.270	0.0322	0.0393

(b) In the Medium of KSCN-KNO$_3$. It was found out that in this medium the limiting current is completely determined by the diffusion process even in the case of low concentration of potassium thiocyanate. Since this medium contains 0.005% of gelatine, the disappearance of kinetic current is possibly considered to be due to the existence of gelatine.

Polarograms obtained by the Kalousek's Method.—It has been already reported that the reduction wave of nickel-thiocyanate complex has an irreversible character, and it has been also expected from the ordinary polarographic measurements of the present study: the log plot of the wave does not give the slope expected from the reversible wave, as described above. The result obtained by P. Delahay(3) with a technique of oscillographic polarography shows the reduction of this complex to be irreversible in the supporting electrolyte containing 0.5 M of potassium thiocyanate. To these verifications of the irreversibility of the reduction of this complex, the confirmation of the fact has been added by the author using the Kalousek's method.(4) The polarograms of this complex obtained with the method are shown in Figs. 3 and 4, compared with the polarograms of the reduction wave of lead which is considered to be reversible. When the polarograms are obtained with the circuit I-a of the Kalousek's method, they should give a well-defined minimum of current if the reduction of the substance concerned is reversible, as shown in polarogram (a) of Fig. 3. No minimum of current is clearly seen in the polarograms (b) and (c) of Fig. 3. The polarograms (b) and (c) of Fig. 4 are also quite different from the polarogram (a) in the same figure, although they were all obtained with the same circuit. From these facts it can be concluded that the reduction of this complex is irreversible as already recognized from the other informations.

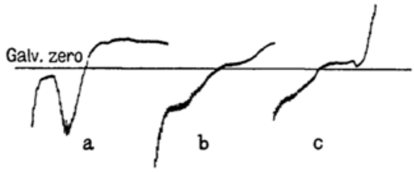

Fig. 3.—Polarograms obtained with the circuit I-a of the Kalousek's method, polarograms of, (a) Pb^{++} in the KOH solution, (b) nickel-thiocyanate complex in the KNO$_3$-KSCN medium, and (c) nickel-thiocyanate complex in the KCl-KSCN medium. Voltage difference = 0.3 volt.

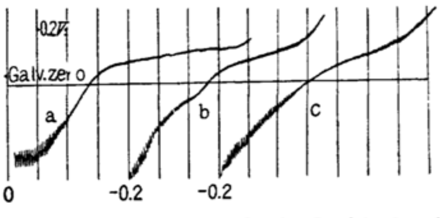

Fig. 4.—Polarograms obtained with the circuit II of the Kalousek's method, polarograms of, (a) Pb^{++} in the KOH solution, (b) nickel-thiocyanate complex in the KNO$_3$-KSCN medium, and (c) nickel-thiocyanate complex in the KCl-KSCN medium.

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(3) P. Delahay, *Jour. Phys. Coll. Chem.*, **54**, 630 (1950).

(4) M. Kalousek, *Collection Czechoslov. Chem. Communs.*, **13**, 105 (1948).

Discussion

Since the reduction wave of nickel-thiocyanate complex has most complicated behaviors, the reduction mechanism of the complex has been explained incompletely only with the present experiment. However, if the following mechanisms are assumed for the reduction of the complex, the experimental results can be explained at least qualitatively.

(1) In the solution containing an extremely high concentration of potassium thiocyanate, nickel exists mainly in the form of $\mathrm{Ni(SCN)}_u{}^{(2-u)+}$; in the solution containing a moderate concentration of potassium thiocyanate, mainly in the form of $\mathrm{Ni(SCN)}_v{}^{(2-v)+} (u>v)$; and in the solution containing a low concentration of potassium thiocyanate, mainly in the form of $\mathrm{Ni(SCN)}_w{}^{(2-w)+} (v>w)$.

(2) The polarographic wave appearing at the potential of about -0.7 volt *vs.* N.C.E. is due to the reduction of $\mathrm{Ni(SCN)}_v{}^{(2-v)+}$ ion without the dissociation, which proceeds according to Eq. (1).

$$\mathrm{Ni(SCN)}_v^{(2-v)+} + 2\varepsilon \rightleftharpoons \mathrm{Ni(Hg)} + v\,\mathrm{SCN}^- \qquad (1)$$

(3) $\mathrm{Ni(SCN)}_u{}^{(2-u)+}$ is reduced according to Eq. (1), after it dissociates into $\mathrm{Ni(SCN)}_v$ according to Eq. (2).

$$\mathrm{Ni(SCN)}_u^{(2-u)+} \rightleftharpoons \mathrm{Ni(SCN)}_v + (u-v)\,\mathrm{SCN}^- \qquad (2)$$

The rate of the dissociation of $\mathrm{Ni(SCN)}_u{}^{(2-u)+}$ into $\mathrm{Ni(SCN)}_v{}^{(2-v)+}$ is considered to be extremely large compared with the diffusion rate of $\mathrm{Ni(SCN)}_u{}^{(2-u)+}$ or $\mathrm{Ni(SCN)}_v{}^{(2-v)+}$.

(4) $\mathrm{Ni(SCN)}_w{}^{(2-w)+}$ is reduced according to Eq. (1), after it associates with SCN^- ion to form $\mathrm{Ni(SCN)}_v{}^{(2-v)+}$ according to Eq. (3).

$$\mathrm{Ni(SCN)}_w^{(2-w)+} + (v-w)\mathrm{SCN}^- \rightleftharpoons \mathrm{Ni(SCN)}_v^{(2-v)+} \qquad (3)$$

The rate of the association of $\mathrm{Ni(SCN)}_w{}^{(2-w)+}$ with SCN^- ion appears to be comparable in magnitude with the rate of the diffusion in the medium containing potassium thiocyanate and potassium chloride, but it appears to be extremely large in the medium containing potassium thiocyanate and potassium nitrate. This consideration makes it possible to explain the phenomenon that the limiting current of the wave contains the kinetic current in the medium of KSCN-KCl, but it does not in the medium of $\mathrm{KSCN\text{-}KNO_3}$.

(5) The reduction of $\mathrm{Ni(SCN)}_v{}^{(2-v)+}$ to Ni(Hg) is of the activation-controlled one.

In the above description any complex-forming substance except thiocyanate ion is not represented. It does not mean necessarily that nickel ion takes only thiocyanate as a complex-forming ion. On the contrary it is considered with a great possibility that nickel ion takes other ions than thiocyanate ion as a complex-forming ion. In the above description they are omitted for simplicity.

If the reduction mechanisms mentioned above are assumed for the reduction of the complex, the polarographic wave of the complex should be explained with the formulas which are obtained by the modification of the formulas described in the previous papers[2]. The half-wave potential should be independent of the activities of the $\mathrm{Ni(SCN)}_v{}^{(2-v)+}$ and the relation of $\log I/(I_l-I)$ *vs.* V, a straight line, whether the limiting current is governed by the diffusion process only or not. Moreover, the assumption that the activation-controlled process is rate-determining requires the inclination of the log plot being more than 0.029 volt at 25.0° if the number of electron concerning the reduction equals two.

The experimental results shown in Table 4 indicate clearly that the half-wave potential is independent of the activity of nickel-thiocyanate ion, and these shown in Fig. 2 indicate the relation of $\log I/(I_l-I)$ *vs.* V holding straight lines. From the inclinations of the log plot shown in Tables 1 and 3 and the polarograms obtained by the Kalousek's method the activation-controlled process can be expected for the rate-determining step.

In order to confirm the above assumptions it should be examined whether the shift of the half-wave potential with the change of the concentration of complex-forming substance is in accord with the theoretical consequence. If the complex ion is reduced according to Eqs. (2) and (1) and if the rate of dissociation is extremely rapid compared with the diffusion, the shift of the half-wave potential with the change of the concentration of potassium thiocyanate is represented with the following equation:

$$\varDelta V_{1/2} = -(u-v)\frac{0.059}{2\alpha}\varDelta \log[\mathrm{SCN}], \ \text{(volt)} \qquad (4)$$

where [SCN] represents the activity of thiocyanate ion and α has the meaning described in the previous papers(2), (5). The half-wave potential should be shifted more to negative

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(5) N. Tanaka and R. Tamamushi, this Bulletin, **22**, 187 (1949); R. Tamamushi and N. Tanaka, this Bulletin, **22**, 227 (1949).

with the increase of the concentration of potassium thiocyanate. The experimental results obtained in the supporting electrolyte containing more than about 0.2 *M* of potassium thiocyanate is in accord with the fact. Being treated quantitatively, it was found out that the value of (u-v) approaches to 2 as potassium thiocyanate increases, as shown in Fig. 5.(6) It means that (u-v) is 2 and that $\mathrm{Ni(SCN)}_w^{(2-w)+}$ still remains in the concentration region of more than 0.2 *M* where the experiments are made.

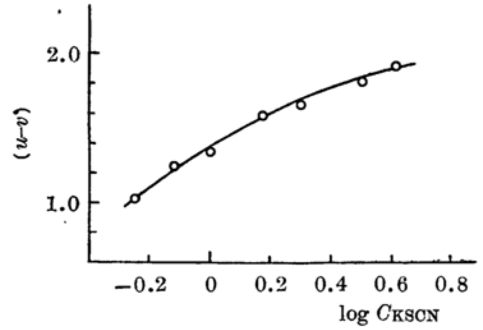

Fig. 5.—Relation of (u–v) calculated with Eq. (4) and the logarithm of the concentration of potassium thiocyanate.

As for the concentration region where the reduction proceeds according to Eqs. (3) and (1), the following equation is derived if the kinetic current is not concerned.

$$\Delta V_{1/2} = (v - w)\frac{0.059}{2\alpha}\Delta \log[\mathrm{SCN}], \ \text{(volt)} \qquad (5)$$

The theoretical consequence that the half-wave potential shifts more to positive as the concentration of potassium thiocyanate increases explains the experimental results obtained in the supporting electrolyte containing potassium thiocyanate of less than 0.2 *M*. Taking up the case of medium containing potassium thiocyanate and potassium nitrate because of the absence of kientic current, (v-w) will be calculated according to Eq. (5) using the value of α and the shift of the half-wave potential both obtained experimentally. Since over the range from 0.05 *M* to 0.01 *M* of potassium thiocyanate the relation of log $I/(I_l\text{-}I)$ holds a straight line, this range was taken for the calculation. The shift of the half-wave potential, $\Delta V_{1/2}$, corresponding to 0.699 of $\Delta\log[\mathrm{SCN}]$ is 0.037 volt and the mean value of α over the range is 0.54.(6)

$$v - w = \frac{0.037}{\dfrac{0.059}{2\times 0.54}\times 0.699} = 0.97$$

The result indicates that the value of (v-w) equals approximately 1.

From these discussions it is concluded that the nickel-thiocyanate complex is reduced according to the mechanisms mentioned above. As for the value of u, v and w, 4, 2 and 1 are the most reasonable to be applied to them from the above discussions and the spectroscopic data.(7)

Summary

The polarographic reduction wave of nickel-thiocyanate complex has been studied for the purpose of clarifying the reduction mechanism of the complex. The current-voltage curves of the complex were measured in media of KSCN-KCl and KSCN-$\mathrm{KNO_3}$. In the medium of KSCN-KCl, the reduction wave involved the kinetic current as well as the diffusion current, when the concentration of potassium thiocyanate was less than 0.2 *M*. The relation of log $I/(I_l\text{-}I)$ and V held a straight line, but its slope was not in accord with the value expected from the reversible reduction. From these experimental results and the polarograms obtained with the Kalousek's method, the reduction of the complex was confirmed to proceed irreversibly at the dropping mercury electrode.

The reduction mechanism of the complex and the number of thiocyanate ions coordinated to the centered metal ion in the supporting electrolytes containing various concentrations of potassium thiocyanate were estimated from these experimental results, when the theoretical consequence for the activation-controlled reduction of the complex ion reported in the previous paper was applied.

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(6) In this calculation the concentration was used instead of activity, and ΔF_1 and the ionic strength were assumed to be constant.

(7) Pal Csokan, *Chem. Abstract*, **33**, 1594 (1939).