Polarographic Studies of Some Metal(II)-Thiocyanate Complexes in Acetonitrile

Seizo Misumi, Makoto Aihara, and Setsuko Kinoshita
Inorganic Chemistry Laboratory, Faculty of Science, Kyushu University, Fukuoka 812

(Received April 14, 1973)

The formation of thiocyanate complexes of cadmium(II), copper(II), cobalt(II), and iron(II) has been studied in acetonitrile by polarographic, conductometric, and spectrophotometric methods. The values of overall stability constants were found to be; log β_4= 19.7 for $[Cd(SCN)_4]^{2-}$, log β_2=7.6 for $[Cu(SCN)_2]^-$ and log β_4= 15.5 for $[Co(NCS)_4]^{2-}$. The reaction between copper(II) species and mercury metal was investigated and the electrode reaction was estimated. Kinetic current for cobalt(II)-thiocyanate complex was observed and the rate constant for the dissociation of the complex was obtained. The rate constant of reduction in the iron(II)-thiocyanate system was determined to be 1.9×10^{-3} cm/s by cyclic voltammetry.

In the previous work,[1] cadmium(II), zinc(II), and manganese(II) iodide complexes were studied polarographically in acetonitrile and the overall formation constants of the complexes were evaluated. These values for other halide complexes of cadmium(II) and zinc(II) were determined by potentiometric titration using a saturated metal amalgam indicator electrode.[2]

In this work, the association constant of tetraethylammonium thiocyanate was determined by conductance measurements, and cadmium(II), copper(II), cobalt(II), and iron(II) thiocyanate complexes have been investigated in acetonitrile by polarography, conductometry and spectrophotometry.

Experimental

Materials. Tetraethylammonium thiocyanate (Et_4NSCN) was synthesized by the reaction of tetraethylammonium perchlorate and potassium thiocyanate in ethanol and fractionated by using acetone–ethyl ether mixture.

Found: C, 57.16; H, 10.65; N, 14.76%. Calcd for Et_4NSCN: C, 57.40; H, 10.71; N, 14.87%.

Et_4NClO_4 (TEAP) was used to keep the concentration of Et_4N^+ to be 0.1 M, and Triton X-100 as maximum suppressor. Other reagents were the same as described previously.[1]

Apparatus. Polarographic measurements have been described previously.[1] Conductance measurements were done by a Yokogawa universal bridge using a cathode ray tube as a detector. The cell, which was of the Pyrex cylinder type, had bright platinum electrodes. A Hitachi EPS-2 spectrophotometer was utilized in the spectral studies.

Procedure. A sample solution was prepared by dissolving 0.5 mM metal(II) perchlorate and an appropriate amount of Et_4NSCN in TEAP–acetonitrile and it was introduced into a polarographic or spectrophotometric cell. Conductance was measured at 1 kHz to 20 kHz at 25±0.01 °C and extrapolated to the infinite frequency (R *vs.* f^{-1}).[3] The cell constant was determined by using the Fuoss' equation[4] for the conductance of potassium chloride solution in water. The cell constant was found to be 0.09975 cm^{-1}.

Other procedures were the same as described previously.[1]

Results and Discussion

Determination of the Association Constant of Tetraethylammonium Thiocyanate. The data for Et_4NSCN were analyzed by the Fuoss-Onsager conductance theory.[5] The parameters obtained are as follows; $\Lambda_0=198.35$, $\mathring{a}=2.85$ and $K_A=0$. (refer to the values of $\lambda_0^+=85.05$[6] for Et_4N^+ and $\lambda_0^-=113.4$[7] for SCN^- in acetonitrile) Conductance data for Et_4NSCN in acetonitrile are shown in Table 1. The values of Λ_{calcd} in Table 1 were calculated by the Fuoss-Onsager conductance equation[5] for non-associated electrolyte. Therefore, tetraethylammonium thiocyanate used was assumed to be completely dissociated in the range from 0.5 to 50 mM in acetonitrile.

Table 1. Conductance data for tetraethylammonium thiocyanate in acetonitrile

10^4C M	Λ_{obsd} $cm^2/(\Omega\cdot equiv)$	Λ_{calcd} $cm^2/(\Omega\cdot equiv)$	$\Delta\Lambda$ $cm^2/(\Omega\cdot equiv)$
8.181	186.87	186.87	0.00
17.902	181.36	181.37	0.01
28.817	177.03	176.95	−0.08
28.232	173.99	173.88	−0.11
50.983	170.30	170.41	0.11
64.781	167.12	167.27	0.15

Cd(II)–SCN⁻ System. The electrode reaction of solvated cadmium(II) is reversible and of two-electron reduction and diffusion-controlled. The half-wave potential of the polarographic wave was −0.275 V *vs.* SCE. The wave due to the complexed species appeared by addition of thiocyanate ion. The electrode reaction was the same as that of solvated cadmium(II) and the plot of the difference of the half-wave potential, $\Delta E_{1/2}$ *vs.* log $[SCN^-]_0$ was found to be linear. The value of number p of ligands attached to Cd(II) was calculated to be $4._2$. The value of log β_4 was 19.7.

Cu(II)–SCN⁻ System. The Cu(II)–SCN^- system was investigated in acetonitrile by conductometric titration. When the conductance was plotted against mole ratio $[SCN^-]_t/[Cu(II)]_t$, the distinct inflection points were observed at 1.1 and 4.0, indicating the formation of $[CuSCN]^+$ and $[Cu(SCN)_4]^{2-}$ and other inflection points were ill-defined.

Polarograms of 0.5 mM Cu(II) in the presence of thiocyanate ions are shown in Fig. 1. Cu(II) perchlorate shows double wave. The half-wave potentials of the first and second waves are *ca.* +0.56 and −0.335 V *vs.* SCE. The first wave decreased and new waves (II and III) developed by addition of thiocyanate i n. The second wave was shifted to more negative potentials (Wave IV) with increasing concentration of thiocyanate ion. The electrode reactions of the first and third waves were found to be two-electron reduction and diffusion-controlled. The electrode reaction of the fourth wave was one electron and of reversible and diffusion-controlled.

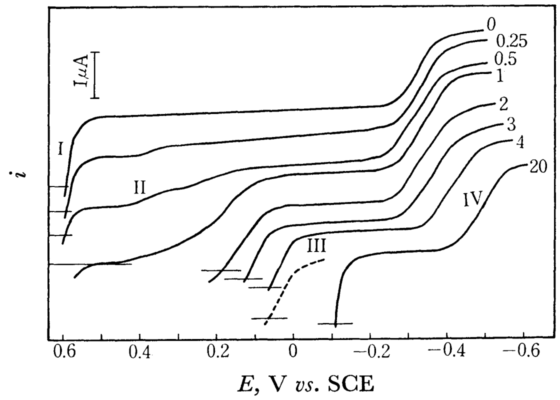

Fig. 1. DC polarograms of acetonitrile solutions containing copper(II)-thiocyanate complexes. Numbers on curves indicate mole ratio, $[SCN^-]_t/[Cu(II)]_t$.

Solvated Cu(II) reacts completely with mercury metal in acetonitrile as follows[8)]

$$Cu^{2+}_{solv} + \frac{1}{2}Hg \longrightarrow Cu^{+}_{solv} + \frac{1}{2}Hg^{2+}_{solv} \qquad (3)$$

A solution containing Cu(II) and thiocyanate ions was reddish brown in color in acetonitrile. It's color disappeared after a polarograms was recorded at $[SCN^-]_t/[Cu(II)]_t < 10$. Even at $[SCN^-]_t/[Cu(II)]_t = 50$, decolorization was complete when the solution containing metallic mercury was shaken. The polarograms did not give any changes for the solutions before and after decolorization. Therefore, the following chemical reaction must proceed at the electrode surface before the electrode reaction took place.

$$[Cu(SCN)_4]^{2-} + \frac{1}{2}Hg \longrightarrow$$
$$[Cu(SCN)_2]^- + \frac{1}{2}[Hg(SCN)_4]^{2-} \qquad (4)$$

The electrode reaction for each wave was presumed. The first wave corresponds to the reduction of Hg^{2+}_{solv}. formed in solution according to Eq. (3).

$$Hg^{2+}_{solv} + 2e \rightleftarrows Hg(0) \qquad (5)$$

This wave decreased with increasing concentration of thiocyanate ion and disappeared at mole ratio $[SCN^-]_t/[Cu(II)]_t = 1$. This is caused by complex formation of mercury ion with thiocyanate ion.

The second wave may correspond to the reduction of Hg(II)-SCN⁻ species, *e.g.* $[Hg(SCN)_3]^-$ *etc.*

The dashed line in Fig. 1 shows the reduction wave of tetrathiocyanato-mercurate(II) in acetonitrile. Therefore, the electrode reaction for the third wave is

$$[Hg(SCN)_4]^{2-} + 2e \rightleftarrows Hg(0) + 4SCN^- \qquad (6)$$

The fourth wave was always observed in the presence or the absence of thiocyanate ion. The half-wave potential was shifted to more negative potentials with increasing concentration of thiocyanate ion (Table 2). The electrode reactions of Cu(I) and Cu(I) complex are reversible, of one electron reduction and diffusion-controlled. The plot of $\Delta E_{1/2}$ *vs.* log $[SCN^-]_0$ was found to be linear and p was calculated to be $2._3$. The value of log β_2 was 7.6 for $[Cu(SCN)_2]^-$.

TABLE 2. POLAROGRAPHIC DATA FOR COPPER(II)-THIOCYANATE SYSTEM (The fourth wave)
$[Cu(II)] = 0.5$ mM

$[SCN^-]_t$ mM	i_d μA	$E_{1/2}$ V *vs.* SCE
0	1.58	−0.335
5	1.56	−0.465
10	1.56	−0.508
15	1.64	−0.531
20	1.57	−0.556
25	1.60	−0.559

The electrode reactions are expressed as Eqs. (7) and (8) in the absence or the presence of thiocyanate ion, respectively.

$$Cu^{+}_{solv} + e + Hg \rightleftarrows Cu^{\circ}(Hg) \qquad (7)$$

$$[Cu(SCN)_2]^- + e + Hg \rightleftarrows Cu^{c}(Hg) + 2SCN^- \qquad (8)$$

The stability (log β_2) of CuX_2^- (X^-: halide and thiocyanate ion) is in the order $Br^-(7.1) < SCN^-(7.6) < Cl^-(10.5)$[9)] in acetonitrile.

Co(II)-SCN⁻ System. Cobalt(II) and thiocyanate ion are known to form $[Co(NCS)]^+$, $[Co(NCS)_3]^-$, and $[Co(NCS)_4]^{2-}$[10)] but the formation constants for these complexes were not yet determined. The cobalt(II)-thiocyanate complex has an absorption spectrum characterized by maxima at 16000 and 31447 cm⁻¹. The intensity of these bands increases with increasing concentration of thiocyanate ion until $[SCN^-]_t/[Co(II)]_t$ attained to 4. The relation between absorbance for unit concentration of Co(II) at 16000 cm⁻¹ *vs.* mole ratio, $[SCN^-]_t/[Co(II)]_t$ is shown in Fig. 2. This indicates the formation of $[Co(NCS)_4]^{2-}$ in acetonitrile. The value of β_4 was calculated by the molar ratio method.[11)] From absorbance at 16000 and 31447 cm⁻¹, the values of log β_4 (15.6_4 and 15.5_3) were obtained, respectively. (The following spectral data were

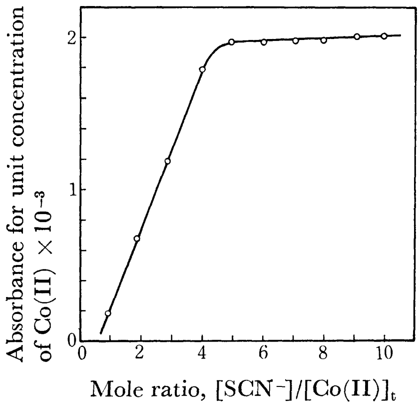

Fig. 2. Absorbance for unit concentration of Co(II) at 16000 cm⁻¹ *versus* mole ratio, $[SCN^-]_t/[Co(II)]_t$.

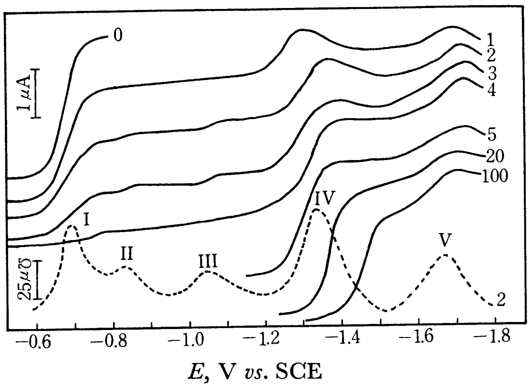

Fig. 3. DC and AC polarograms of cobalt(II)-thiocyanate complexes. Numbers on curves indicate mole ratio, $[SCN^-]_t/[Co(II)]_t$.

used for calculation. $E_m=0.994$ and $E_s=0.890$ at $16000\,cm^{-1}$. $E_m=0.762$ and $E_s=0.678$ at $31447\,cm^{-1}$.) The value of $\log K_4$, 5.2 for $[Co(NCS)_4]^{2-}$ was obtained by assuming that the concentration of $[Co(NCS)]^+$ and $[Co(NCS)_2]$ to be negligible at excess thiocyanate ion.

DC and AC polarograms of 0.5 mM cobalt(II) in the presence of thiocyanate ion are shown in Fig. 3. The electrode reaction of solvated cobalt(II) in acetonitrile is reversible, of two-electron reduction and diffusion-controlled. The original first wave decreased with increasing concentration of thiocyanate ion and the new waves appeared at more negative potentials. The waves in AC polarogram were termed as I, II, III, IV, and V. The waves II and III were ill-defined in DC polarogram. The wave IV had a maximum till $[SCN^-]_t/[Co(II)]_t=4$ but no maximum wave was observed at higher thiocyanate concentrations. The wave V appeared at low concentration of thiocyanate ion. The plots of limiting current and peak admittance *vs.* mole ratio, $[SCN^-]_t/[Co(II)]_t$ are shown in Fig. 4. The wave I which corresponds to the reduction of solvated cobalt(II) disappeared at $[SCN^-]_t/[Co(II)]_t=4$. The waves II and III may correspond to the reduction of Co(II)–SCN⁻ species, *e.g.*, $[Co(NCS)]^+$ *etc.*, but the heights of these waves are small because of large stability of $[Co(NCS)_4]^{2-}$. The wave IV increased till $[SCN^-]_t/[Co(II)]_t=6$ and decreased slightly at the above ratio. The wave V was almost constant. The wave IV did not diminish at high excess of thiocyanate ion ($[SCN^-]_t/[Co(II)]_t=100$) as shown in Fig. 3. Therefore, this wave must be due to the species of $[Co(NCS)_4]^{2-}$ and the current was found to be kinetic current. This kinetic current was treated by assumption of the following reaction layer.[12] Consider the reduction of $[Co(NCS)_3]^-$ according to the following reaction

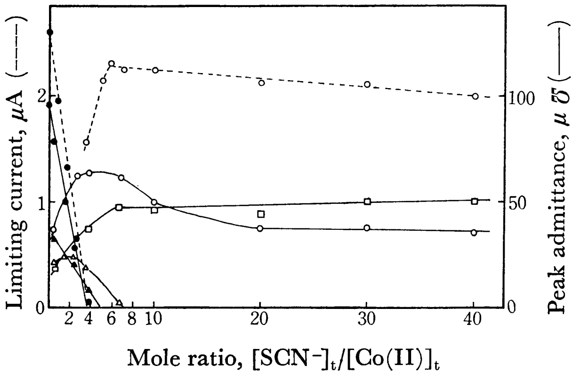

Fig. 4. Limiting current and peak admittance *versus* mole ratio, $[SCN^-]_t/[Co(II)]_t$ for cobalt(II)-thiocyanate system. ●, wave I; ▲, wave II; △, wave III; ○, wave IV; □, wave V.

$$Co^{2+}_{solv} + 4SCN^- \rightleftharpoons [Co(NCS)_4]^{2-} \qquad (9)$$

$$[Co(NCS)_4]^{2-} \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} [Co(NCS)_3]^- + SCN^- \qquad (10)$$

$$[Co(NCS)_3]^- + 2e \rightleftharpoons Co(0) + 3SCN^- \qquad (11)$$

The kinetic current, i_k is expressed as follows

$$\frac{i_k}{i_d-i_k} = 0.81\frac{\overrightarrow{k}^{1/2}t^{1/2}}{K_4^{1/2}[SCN^-]_0^{1/2}} \qquad (12)$$

where $[SCN^-]_0$ is the concentration of the thiocyanate ion at the electrode surface. $[SCN^-]_0$ was calculated by using $[SCN^-]_0=[SCN^-]_t-4\{(i_d-i_k)/i_d\}[Co(NCS)_4{}^{2-}]_{eq.}$. Equation 12 predicts a slope −0.5 for a plot of $\log i_k/(i_d-i_k)$ *vs.* $\log[SCN^-]_0$. The value of slope was found experimentally to be −0.44 as given in Fig. 5. $\overrightarrow{k}$ was calculated to be $1.2\times10^4\,s^{-1}$ using $\log K_4=5.2$ and $t=5.88$ sec. This indicates that kinetic current due to the fast dissociation of $[Co(NCS)_4]^{2-}$ occurs.

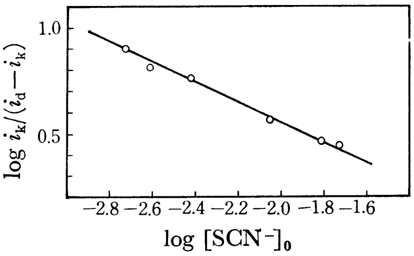

Fig. 5. Log $i_k/(i_d-i_k)$ *versus* log $[SCN^-]_0$ for cobalt(II)-thiocyanate system.

Fe(II)-SCN⁻ System. The formation of iron(II)-thiocyanate complexes was investigated by conductometric and spectrophotometric methods.

In conductometric titration curve for Fe(II)–SCN⁻ system, the inflection point was at $[SCN^-]_t/[Fe(II)]_t=1.0$ and other points were ill-defined. The thiocyanate complex of iron(II) has an absorption band at 20284 cm^{-1}. The intensity of this band increased until $[SCN^-]_t/[Fe(II)]_t=3$. Above this ratio, this band was shifted to $20619\,cm^{-1}$. The curves of absorbance for unit concentration of Fe(II) at 20284 and $20619\,cm^{-1}$ *vs.* mole ratio, $[SCN^-]_t/[Fe(II)]_t$ showed the inflection points at $[SCN^-]_t/[Fe(II)]_t=3$ and 4. These indicate the formation of $[Fe(NCS)]^+$, $[Fe(NCS)_3]^-$ and $[Fe(NCS)_4]^{2-}$.

The polarograms of Fe(II)–SCN⁻ system are shown in Fig. 6. Solvated Fe(II) perchlorate has a single reduction wave with the half-wave potential of −0.995 V *vs.* SCE. The electrode reaction was found to be two-electron reduction and diffusion-controlled. This

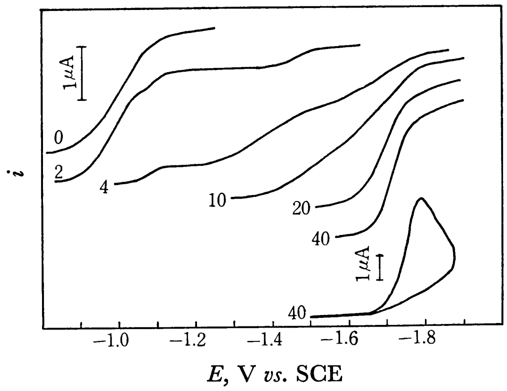

Fig. 6. DC polarograms and cyclic voltammogram of iron(II)-thiocyanate complexes. Number on curves indicate mole ratio, $[SCN^-]_t/[Fe(II)]_t$.

wave decreased with increasing concentration of thiocyanate ion and the new waves appeared at more negative potentials. The wave of complex ion appeared due to the reduction of $[Fe(NCS)_4]^{2-}$ at $[SCN^-]_t/[Fe(II)]_t \geq 20$. The electrode reaction was two-electron reduction and diffusion-controlled.

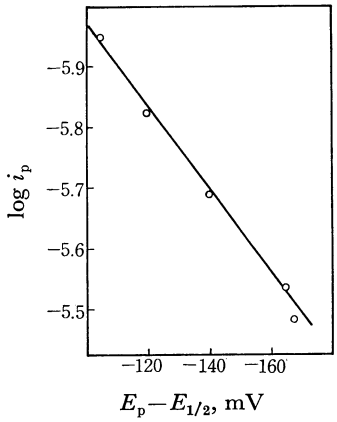

Fig. 7. Determination of the rate constant for solvated iron(II).

The rate constants of the electrode reaction were determined by cyclic voltammetry. Typical cyclic voltammogram (scan rate 0.2 V/s) is shown in Fig. 6. The determination of the rate constants was made by using the method proposed by Matsuda and Ayabe.[13)]

The plot of log i_p vs. $(E_p-E_{1/2})$ for solvated Fe(II) system is shown in Fig. 7 for example. The value of standard rate constant, k_s was calculated from the point of intersection on ordinate. Polarographic data for Fe(II)-SCN^- system are shown in Table 3. These data indicate that the electrode reactions for solvated Fe(II) and Fe(II)-thiocyanate complex are quasi-reversible.

Table 3. POLAROGRAPHIC DATA FOR IRON(II)-THIOCYANATE SYSTEM

[Fe(II)]=0.5 mM

$[SCN^-]$ mM	i_d μA	$E_{1/2}$ V vs. SCE	Slope mV	α	k_s cm/s
0	2.28	−0.995	75	0.39	6.6×10^{-4}
10	2.04	−1.672	59	0.50	9.8×10^{-4}
20	2.02	−1.691	35	0.84	1.9×10^{-3}

The authors are grateful for financial support given by the Ministry of Education for this work.

References

1) S. Misumi and M. Aihara, *Talanta*, **19**, 549 (1972).

2) S. Misumi and M. Aihara, This Bulletin, **46**, 1674 (1973).

3) J. E. Lind, Jr., and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961).

4) J. E. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Amer. Chem. Soc.*, **81**, 1557 (1959).

5) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, New York (1959).

6) D. S. Berns and R. M. Fuoss, *J. Amer. Chem. Soc.*, **82**, 5585 (1960).

7) H. L. Yeager and B. Kratochvil, *J. Phys. Chem.*, **74**, 963 (1970).

8) C. Furlani, L. Sestili, A. Ciana, and F. Garbassi, *Electrochim. Acta*, **12**, 1393 (1967).

9) L. Sestili, C. Furlani, A. Ciana, and F. Garbassi, *ibid.*, **15**, 225 (1970).

10) V. Gutmann and O. Bohunovsky, *Monatsh. Chem.*, **99**, 751 (1968).

11) A. E. Harvey, Jr., and D. L. Manning, *J. Amer. Chem. Soc.*, **72**, 4488 (1950).

12) R. Brdička, "Advances in Polarography," Vol. 2, Longmuir (1960), p. 655.

13) H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **59**, 494 (1955).