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Stability and Extractability of Zinc(II) Thiocyanate Complexes in Several Solvent Extraction Systems

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The formation and extraction equilibria of zinc(II) complexes with thiocyanate ions have been determined at 25°C. Zinc(II) ions in 1 M sodium perchlorate constant ionic media containing thiocyanate ions at various concentrations have been extracted into chloroform containing β-isopropyltropolone (IPT), into hexane containing trioctylphosphine oxide (TOPO), or into methyl isobutyl ketone (MIBK). The stability constants of the zinc(II) thiocyanate complexes in the aqueous phase were first determined from the decrease in the IPT chelate extraction, and then the distribution constants for the zinc(II) thiocyanate complexes into the latter two solvents were determined. The results were explained by saying that (i) zinc(II) forms the first ($\log \beta_1 = 0.56$), second($\log \beta_2 = 1.32$), and the third($\log \beta_3 = 1.18$) complexes in the above aqueous phase, (ii) TOPO in hexane extracts the second complex as an adduct in the $Zn(SCN)_2(TOPO)_2$ form, (iii) MIBK extracts both the second and the third complexes, and (iv) the addition of sodium perchlorate causes a salting-in effect in the lower-ligand-concentration region. Some discussion was made of the dissociation of ion-pairs in the organic phase.

Since Bock[1] reported a comprehensive study of the solvent extraction of metal ions as thiocyanate complexes, it has been recognized that thiocyanate extraction is an effective method for the separation of various metal ions. The solvent extraction of zinc(II) thiocyanate complexes has been studied both from the analytical and thermodynamical standpoints, and quantitative information about the chemical equilibria has been reported by several authors. Among them, Bock[1] first assumed that both the Zn-

1) R. Bock, *Z. anal. Chem.*, **133**, 110 (1951).

$(SCN)_2$ and $(NH_4)_2Zn(SCN)_4$ complexes are extracted into diethyl ether. Later on, Tribalat and Dutheil[2] determined the distribution of zinc(II) between methyl isobutyl ketone(MIBK) and aqueous 1 M sodium perchlorate constant ionic solutions containing various amounts of thiocyanate ions. They concluded, from an analysis of the distribution data, that all of the first, second, third, and fourth zinc(II) thiocyanate complexes are formed in the aqueous phase and that the $Zn(SCN)_2$ species is extracted into MIBK. The complex formation of zinc(II) in aqueous solutions with thiocyanate ions has been determined by various methods, and the stability constants have been reported.[3]

In the present investigation, the authors have also studied the complex formation of zinc(II) with thiocyanate ions and the extraction of them with trioctylphosphine oxide(TOPO) in hexane or with MIBK. They have determined the stability constants of the thiocyanate complexes in 1 M sodium perchlorate constant ionic media from the changes in the extraction of the divalent zinc ions with the chelating extractant, β-isopropyltropolone(IPT), in chloroform as a function of the thiocyanate concentration in the aqueous phase. Then they measured the extraction of zinc(II) thiocyanate complexes in these aqueous solutions into the two organic solvents, and the complex species in the organic phase were assigned from the distribution data. Some discussion was made of the extraction behavior in these systems and the extractability of each complex.

Experimental

Reagents. A radioactive tracer, zinc-65, was used in order to determine the distribution ratio of zinc(II). It was obtained from the New England Nuclear Co. as a hydrochloric acid solution. The tracer was diluted with a large amount of a 1 M sodium perchlorate solution and stored as the stock solution. The TOPO was obtained from the Dojindo Co. The IPT was obtained from the Takasago Koryo Co. The MIBK was obtained from the Tokyo Kasei Co.; it was washed with dilute perchloric acid, water, and a dilute sodium hydroxide solution respectively, and then several times with water. Sodium perchlorate was prepared from sodium carbonate and perchloric acid and recrystallized three times from water. The other reagents were of an analytical grade and were used without further purification. The concentration of the extractants in the organic solvents was calculated from the amount dissolved in the solvent, while that of the sodium perchlorate or thiocyanate solution was calculated from the weight of the residue left after a certain amount of the solution has been evaporated up in an air-bath at 120°C. The concentration of the thiocyanate solution was also determined by argentimetry.

Procedures. All of the procedures were carried out in a thermostated room at 25±0.5°C. Stoppered glass tubes (volume 20 m*l*) were used for the agitation of the two phases. A certain amount of the sodium thiocyanate solution, the tracer and an acetate buffer (the initial concentration in the aqueous phase was 0.01 M) and the sodium perchlorate solution were added to glass tubes, and then the organic solution was added. The initial concentration of zinc in the aqueous phase was 1×10^{-6} M. The hydrogen-ion concentration for the extraction with IPT was $10^{-3.3}$ to $10^{-5.3}$ M while for the extraction of the thiocyanate complexes, it was 10^{-4} to 10^{-5} M. The initial volume of the two phases was always 5.0 m*l*, and the ionic concentration in the aqueous phase was 1 M unless otherwise noted. The two phases in the tubes were agitated mechanically for about two hours and then centrifuged. A 2 m*l* portion was pipetted from each phase and transferred into small test tubes. The γ-radioactivity of the samples was measured with a well-type(NaI) scintillation counter. A small portion was also taken from the aqueous phase, and the hydrogen-ion concentration was measured potentiometrically by using a solution containing 1.00×10^{-2} M perchloric acid and 9.9×10^{-1} M sodium perchlorate as the standard of $-\log[H^+]$ 2.00 in the 1 M ionic medium.

Statistical

The formation and the stability constant for the "*n*th" zinc(II) complex with thiocyanate ions may be described as follows:

$$Zn^{2+} + nSCN^- \rightleftharpoons Zn(SCN)_n^{2-n}$$

$$\beta_n = \frac{[Zn(SCN)_n^{2-n}]}{[Zn^{2+}][SCN^-]^n} \quad (1)$$

The total concentration of zinc(II) in aqueous solutions containing thiocyanate ions can be described as;

$$[Zn(II)]_{total} = [Zn^{2+}] + [ZnSCN^+] + [Zn(SCN)_2] + [Zn(SCN)_3^-] + \cdots$$
$$= [Zn^{2+}](1 + \sum\beta_n[SCN^-]^n) \quad (2)$$

In the present paper, the subscript "*org*" denotes a chemical species in the organic phase, while the lack of any subscript denotes that in the aqueous phase.

(1) Extraction of Zinc(II) as Chelate Complexes. As was described in a previous paper,[4] the distribution ratios of zinc(II) from an aqueous phase containing no ligand, D_0, and that from an aqueous phase containing a ligand, L^-, can be described as follows if the concentration of the chelating extractant in the organic phase is the same;

$$D[H^+]^2/K_0 = (1+\sum\beta_n[SCN^-]^n)^{-1} \quad (3)$$

where $K_0=D_0[H^+]^2$.

As has been reported, the extracted zinc(II) complex with IPT in the organic phase is described as $ZnA_2(HA)$.[5] However, when the IPT concentration in the organic phase is kept constant, this K_0 should be constant as long as no IPT complexes are formed in the aqueous phase.[4,5] Thus, when the value of K_0 is determined in the absence of the ligand, the stability constants can be determined from this and the distribution ratio measured as a function of the ligand concentration by using Eq. 3.

2) S. Tribalat and C. Dutheil, *Bull. Soc. Chim. France*, **1960**, 160.

3) L. G. Sillén and A. E. Martell, "Stability Constants," Chem. Soc. Spec. Pub. **17**, (1964).

4) T. Sekine, M. Sakairi, F. Shimada, and Y. Hasegawa, This Bulletin, **38**, 847 (1965).

5) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1463 (1964).

(2) Extraction of Zinc(II) as Thiocyanate Complexes. (a) Extraction of Uncharged Thiocyanate Complex: When the uncharged complex in the aqueous phase is extracted with a neutral extractant, E, in the organic phase, it is described as;

$$Zn(SCN)_2 + eE(org)_2 \rightleftarrows Zn(SCN)_2E_e(org)$$

$$Kex_e' = \frac{[Zn(SCN)_2E_e]_{org}}{[Zn(SCN)_2][E]^e_{org}} \quad (4)$$

The distribution ratio of zinc(II) in such a system can be described as;

$$D = \frac{[Zn(SCN)_2]_{org} + [Zn(SCN)_2E]_{org} + [Zn(SCN)_2E_2]_{org} + \cdots}{[Zn^{2+}] + [ZnSCN^+] + [Zn(SCN)_2] + [Zn(SCN)_3^-] + \cdots} \quad (5)$$

By introducing Eqs. (2) and (4) into Eq. (5), we obtain;

$$D = \frac{(1 + \sum^{1+E} Kex_e'[E]^e_{org})\beta_2[SCN^-]^2}{1 + \sum\beta_n[SCN^-]^n} \quad (6)$$

When the concentration of the extractant, E, is kept at b M, the following constant can be defined;

$$K_{DM2} = 1 + \sum Kex_e'b^e = \frac{[Zn(SCN)_2]_{org.total}}{[Zn(SCN)_2]} \quad (7)$$

Then Eq. (6) can be described as;

$$D = \frac{K_{DM2}\beta_2[SCN^-]^2}{1 + \sum\beta_n[SCN^-]^n} \quad (8)$$

(b) Extraction of Both Uncharged Complex and Ion-pairs of Anionic Complexes with Sodium Ions: When the organic solvent is a solvating polar one and extracts the neutral complex, the extraction equilibrium can be described as;

$$Zn(SCN)_2 \rightleftharpoons Zn(SCN)_2(org) \quad (9)$$

The extraction constant for this may also be described by Eq. (7) except that the solvation number of the complex cannot be defined.

The extraction of anionic complexes with sodium ions may also occur. The extraction of the third complex may be described as;

$$Zn(SCN)_3^- + Na^+ \rightleftharpoons NaZn(SCN)_3(org)$$

$$Kex_3'' = \frac{[NaZn(SCN)_3]_{org}}{[Zn(SCN)_3^-][Na^+]} \quad (10)$$

The ion-pair could dissociate in the organic phase;

$$NaZn(SCN)_3(org) \rightleftharpoons Na^+(org) + Zn(SCN)_3^-(org)$$

$$Kdiss(org) = \frac{[Na^+]_{org}[Zn(SCN)_3^-]_{org}}{[NaZn(SCN)_3]_{org}} \quad (11)$$

The concentration ratio of the third complex in the two phases can be described from Eqs. (10) and (11) as;

$$\frac{[NaZn(SCN)_3]_{org} + [Zn(SCN)_3^-]_{org}}{[Zn(SCN)_3^-]} = Kex_3''[Na^+]\left(1 + \frac{Kdiss(org)}{[Na^+]_{org}}\right) \quad (12)$$

In the present study, however, the sodium-ion concentration is kept at 1 M; moreover, as will be described later, that in the organic phase could also be regarded as constant in the lower-ligand-concentration region. Thus, from Eq. (12), an extraction constant can be defined as;

$$K_{DM3} = \frac{[NaZn(SCN)_3]_{org} + [Zn(SCN)_3^-]_{org}}{[Zn(SCN)_3^-]} \quad (13)$$

When both the second and the third complexes are extracted, the distribution ratio may be described as;

$$D = \frac{[Zn(SCN)_2]_{org} + [NaZn(SCN)_3]_{org} + [Zn(SCN)_3^-]_{org}}{[Zn^{2+}] + [ZnSCN^+] + [Zn(SCN)_2] + [Zn(SCN)_3^-] + \cdots} \quad (14)$$

By introducing Eqs. (2), (7), and (13), Eq. (14) can be described as;

$$D = \frac{K_{DM2}\beta_2[SCN^-]^2 + K_{DM3}\beta_3[SCN^-]^3}{1 + \sum\beta_n[SCN^-]^n} \quad (15)$$

(3) Graphic Analysis of the Distribution Data. The zinc(II) IPT chelate distribution data obtained as a function of the thiocyanate concentration and given by a $\log D[H^+]^2K_0^{-1}$ *vs.* $\log[SCN^-]$ plot (*cf.* Eq. (3)) may be treated by a curve-fitting method.[6,7]

When the stability constants for the thiocyanate complexes in the aqueous phase are thus obtained, the extraction data of the zinc(II) thiocyanate complexes with TOPO or MIBK can be determined by using these stability constants as follows.

When only the $Zn(SCN)_2$ complex is extracted into the organic phase, (*cf.* Eq. (8)), the distribution constant can be determined from;

$$K_{DM2} = D(1 + \sum\beta_n[SCN^-]^n)/\beta_2[SCN^-]^2 \quad (16)$$

When both the $Zn(SCN)_2$ and $Zn(SCN)_3^-$ complexes are extracted (*cf.* Eq. (15)), the distribution data can be described as;

$$Y = \log \frac{D(1 + \sum\beta_n[SCN^-]^n)}{[SCN^-]^2} = \log(K_{DM2}\beta_2 + K_{DM3}\beta_3[SCN^-]) \quad (17)$$

When the data are plotted as Y *vs.* $\log[SCN^-]$, they may be fitted by the standard curve[5-7];

$$Y = \log(1 + v), \quad X = \log v \quad (18)$$

and the constants, K_{DM2} and K_{DM3}, can be determined from the curve-fitting and from the β_2 and β_3 values which have already been obtained from the IPT extraction.

Results

The extraction of zinc(II) in a 1 M sodium perchlorate solution into chloroform containing 0.1 M IPT was determined as a function of the hydrogen-ion concentration. The value of the constant, K_0, in Eq. (3) was obtained from the results as;

$$\log K_0 = -8.38$$

It was found that the K_0 value is independent of the hydrogen-ion concentration in the range of $-\log[H^+]$ 3.5 to 5.0 when the IPT concentration in the organic phase is 0.1 M.

Figure 1 shows the decrease in the zinc(II) extrac-

6) T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).
7) T. Sekine, M. Sakairi, and Y. Hasegawa, *ibid.*, **39**, 2141 (1966).

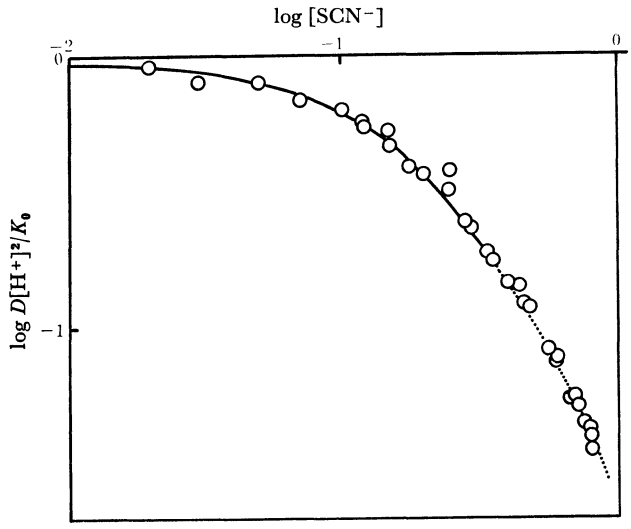

Fig. 1. Decrease in the Zn(II) extraction with IPT as a function of the aqueous thiocyanate concentration. Org. phase; chloroform containing 0.1 M IPT, Aq. phase; 1M Na(SCN, ClO_4). The solid curve is;
$\log D[H^+]^2K_0^{-1} = -\log(1+3.7[SCN^-]+21[SCN^-]^2+15[SCN^-]^3)$

Table 1. Stability and distribution constants of Zn(II) thiocyanate complexes in 1 M Na(SCN, ClO_4) at 25°C

(a) Stability constants in the aqueous phase.

$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$	Remarks
0.56	1.32	1.18	—	Present work
−0.3	0.5	0.8	1.7	Ref. 2

(b) Distribution constants.

Organic phase	$\log K_{DM2}$	$\log K_{DM3}$
Hexane containing 1.0×10^{-3} M TOPO	1.45	—
MIBK	1.39	3.63

tion with IPT as a function of the thiocyanate concentration in the aqueous phase. This plot was analyzed graphically by using Eq. (3), and the best-fit was obtained when the formation of the first, second, and third complexes was assumed. The stability constants obtained are given in Table 1. The solid curve in Fig. 1 was drawn by using these constants.

Figure 2 gives the distribution ratio of zinc(II) between 1 M Na(SCN, ClO_4) (−log[H⁺] was 4 to 5) and MIBK(closed circles) or hexane containing 1.0×10^{-3} M TOPO(open circles) as a function of the thiocyanate concentration. From these data and the stability constants of thiocyanate complexes in Table 1, the value of Y in Eq. (17) was determined for each plot, these values are given in Fig. 3. It may be seen from Fig. 3 that the values of Y for the TOPO extraction are almost constant in the thiocyanate concentration region from 8×10^{-3} M to 3×10^{-1} M; in other words, the values of K_{DM2} in Eq. (16) are not dependent on the thiocyanate concentration, and thus the only zinc(II) species in the organic phase should be the $Zn(SCN)_2$ complex. It was found that

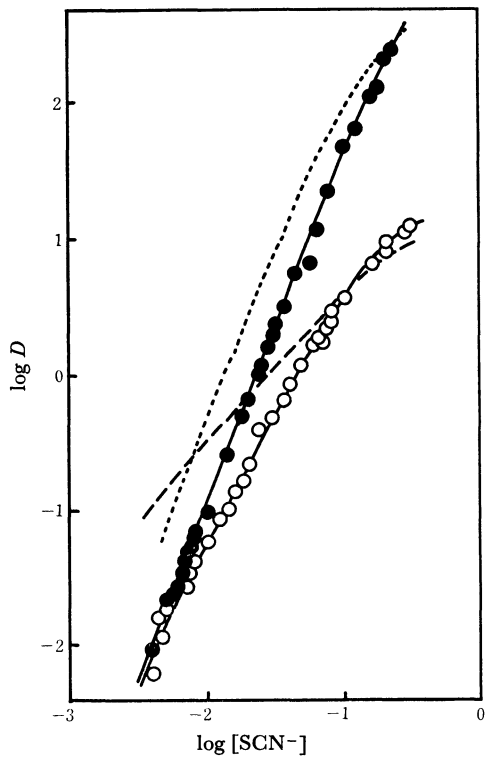

Fig. 2. Extraction of Zn(II) thiocyanate complexes as a function of the aqueous thiocyanate concentration. Org. phase; ○ hexane containing 1.0×10^{-3} M TOPO, ● MIBK, Aq. phase; 1M Na(SCN, ClO_4). The solid curves are;
$\log D=\log 5.8\times10^2[SCN^-]^2/(1+3.7[SCN^-]+21[SCN^-]^2+15[SCN^-]^3)$: ○
$\log D=\log(5.2\times10^2[SCN^-]^2+6.4\times10^4[SCN^-]^3)/(1+3.7[SCN^-]+21[SCN^-]^2+15[SCN^-]^3)$: ●
The broken line and the dotted line show the extraction into hexane containing 1.0×10^{-3} M TOPO or MIBK, respectively, when the aqueous phase is sodium thiocyanate solution containing no sodium perchlorate.

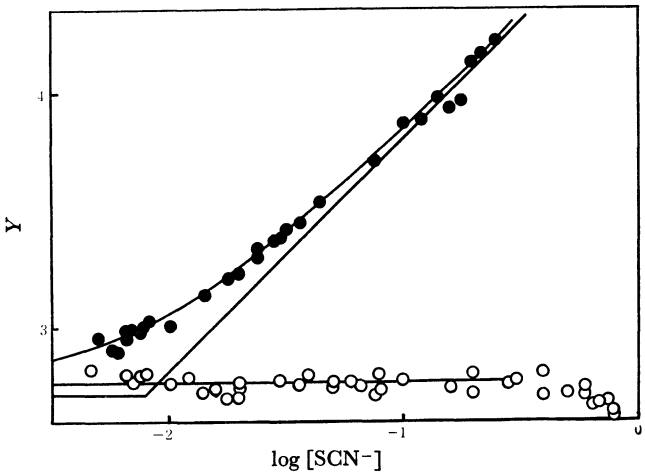

Fig. 3. Graphic analysis of the extraction data (○: TOPO, ●: MIBK).
The ordinate is; $Y=\log D(1+3.7[SCN^-]+21[SCN^-]^2+15[SCN^-]^3)/[SCN^-]^2$
The solid lines are; $Y=2.77$: ○, $Y=\log(5.2\times10^2+6.4\times10^4[SCN^-])$: ●

the distribution ratio between an aqueous phase containing 0.3 M thiocyanate ion and organic phases containing various amounts of TOPO is proportional to

the square of the TOPO concentration in the range of the TOPO concentrations from 2×10^{-4} M to 3×10^{-3} M; thus, the extraction equilibrium can be given by;

$$Zn(SCN)_2 + 2TOPO(org) \rightleftharpoons Zn(SCN)_2(TOPO)_2(org) \quad (19)$$

The distribution constant defined by Eq. (4) ($[Zn(SCN)_2(TOPO)_2]_{org}/[Zn(SCN)_2][TOPO]_{org}$) was obtained as $10^{7.45}$, and that defined by Eq. (7), was $10^{1.45}$ (at 1.0×10^{-3} M TOPO). The solid curve for the TOPO plot in Fig. 2 is a curve calculated by using Eq. (8) and the stability and the distribution constants obtained.

The slope of the extraction curve into MIBK in Fig. 2 is higher than that into hexane containing TOPO; this may be supposed to be due to the extraction of the higher thiocyanate complexes. The value of Y in Eq. (17) was calculated for each plot and plotted against log[SCN$^-$], as is shown in Fig. 3. The plot in Fig. 3 was fitted with the standard curve in Eq. (18). The best-fit curve is shown by the solid curve in Fig. 3. From the parameters of the best-fit curve, the distribution constants in Eqs. (7) and (13) were determined on the basis of Eq. (17). The solid curve for the MIBK plot in Fig. 2 is the curve calculated by using Eq. (15) and the stability and the distribution constants obtained.

Figure 4 shows the percentage distribution of the concentrations of zinc(II) species in the aqueous phase, and those in the hexane phase containing TOPO and in MIBK phase in an equilibrium with the aqueous phase.

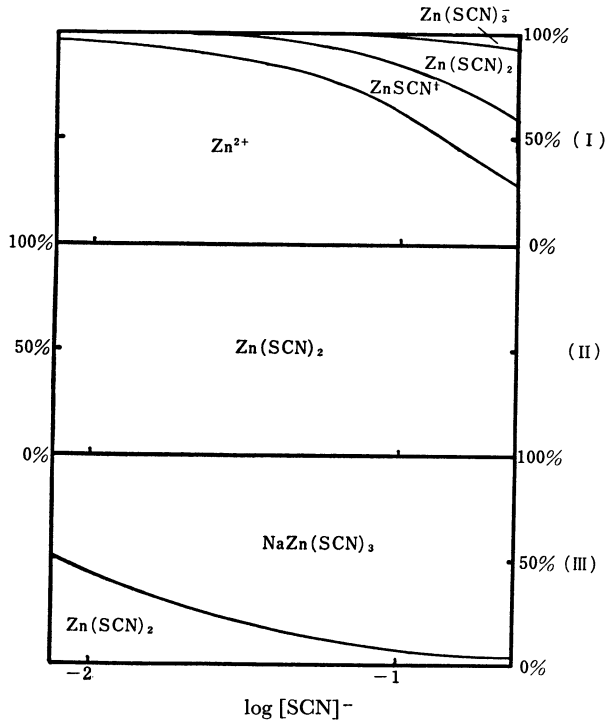

Fig. 4. Percentage distribution of Zn(II) species as a function of the thiocyanate concentration calculated from the constants in Table 1.
(I) 1 M Na(SCN, ClO_4). (II) hexane containing 1.0×10^{-3}M TOPO which is in an equilibrium with (I). (III) MIBK which is in an equilibrium with (I).

The above extractions were always made from the 1 M constant ionic medium. In order to ascertain the effect of the coexisting sodium perchlorate, extraction was also made from sodium thiocyanate solutions containing no sodium perchlorate.

The broken line and the dotted line in Fig. 2 give the extraction curve from these aqueous phases, in which the ionic concentration was not kept constant.

The results described above may be summarized as follows: (i) The extraction curve of zinc(II) in the 1 M Na(SCN, ClO_4) solutions with IPT was explained in terms of the formation of the first, second, and third complexes. The stability of the third complex is not high ($K_3=[Zn(SCN)_3^-]/[Zn(SCN)_2]$ [SCN$^-$] $=10^{-0.14}$). The stability constants given in Table 1 seem to be reasonable because they can explain the zinc(II) thiocyanate extraction with TOPO or MIBK. (ii) The extraction of zinc(II) into hexane containing TOPO was explained in terms of the extraction of the second complex species with two molecules of TOPO. (iii) The extraction of zinc(II) into MIBK was explained in terms of the extraction of the second and the third complexes. (iv) When the aqueous phase contains only sodium thiocyanate, the extraction becomes somewhat higher than that from the constant ionic medium in the region where the thiocyanate concentration is lower than 0.1 M.

Discussion

The extracted ion-pairs, $Na^+Zn(SCN)_3^-$, could dissociate in MIBK. When the dissociation occurs, the extraction of the third complex should be dependent on the sodium concentration in the organic phase, as may be seen from Eq. (12) (the sodium ion concentration in the aqueous phase is kept constant). When the other charged species, such as protons and hydroxide ions, are negligible, the following equation can be written on the basis of the electrical neutrality in the organic phase;

$$[Na^+]_{org} = [ClO_4^-]_{org} + [SCN^-]_{org} + [Zn(SCN)_3^-]_{org} \quad (20)$$

In the present study, the concentration of zinc(II) in the initial aqueous phase is 1×10^{-6} M; this is much lower than the concentration of sodium perchlorate in MIBK (that was estimated to be 1×10^{-2} M[8]). Although no information is availabe about the dissociation of sodium perchlorate and that of the extracted $NaZn(SCN)_3$ ion-pairs, it is most probable that the sodium-ion concentration in the organic phase is constant. Because the concentrations of zinc(II) and sodium thiocyanate in the aqueous phase are much smaller than that of sodium perchlorate under the experimental conditions used in the present study, Eq. (20) can be regarded as $[Na^+]_{org}\simeq[ClO_4^-]_{org}$. Thus the K_{DM3} defined by Eq. (13) could be regarded as a constant in this study.

The stability constants obtained in the present study indicate that they are not very stable. The

8) Y. Hasegawa, T. Ishii, and T. Sekine, This Bulletin, **44**, 275 (1971).

values of the stability constants in the literature[3] are rather scattered. The constants reported in the same ionic medium as in the present study by Tribalat and Dutheil[2] in Table 1 are also somewhat different from the present results; their constant for the first, second, and third complexes are lower than those in the present study, and they estimated a formation of a fourth complex in the same medium which was not found by the present authors.

The extraction curve of zinc(II) from the 1 M Na (SCN, ClO_4) solution into MIBK reported by Tribalat and Dutheil (Fig. 1 in Ref. 2) almost agrees with the results shown in Fig. 2. They analyzed the data by assuming that only the uncharged complex, $Zn(SCN)_2$, is extractable among the four complexes. In the present study, however, it was concluded that both the uncharged complex and the uninegative charged third complex are extracted into the MIBK phase. This assumption seems to be well supported by the extraction data with TOPO in hexane. It may be seen in Fig. 2 that the slope of the plot of the TOPO extraction becomes smaller in the highest-ligand concentration region than that of the MIBK extraction, and the calculated curves from the stability constants obtained by the IPT extraction, shown in Fig. 2 or in Fig. 3, fit the experimental results well.

This seems to agree with the results expected from the nature of the solvents. Hexane containing a small amount (1×10^{-3} M) of TOPO can be regarded as a nonpolar solvent to which the extraction of a polar species such as ion-pairs is unfavorable(although it is possible to extract ion-pairs into a hexane solution of TOPO, especially when the TOPO concentration is high[9]). On the other hand, as has been reported for many MIBK extraction systems,[9-12] the extraction of negatively-charged metal thiocyanate complexes as ion-pairs with cations in the background salt or that of pairs of the sodium ion and the perchlorate ion[8] seems to be very common into this polar and relatively high-dielectric-constant ($\varepsilon=12$) solvent, which also has a great ability of solvation on metal species.

It is remarkable that the $\log D$ *vs.* $\log[SCN^-]$ plot of the MIBK extraction in Fig. 2 is nearly a straight line with a slope of +2.5. As can be seen from the figures and Eq. (17), this apparent tendency for the $\log D$ *vs.* $\log[SCN^-]$ plot to be almost a straight line is probably due to the fact that, although the extraction of the uncharged complex does not increase any more in the highest concentration (this is the reason why the slope of the extraction curve with TOPO in Fig. 2 approaches zero), the extraction of the third complex, which increases in the highest region, will still enhance the distribution ratio. When the $\log D$ *vs.* $\log[SCN^-]$ plot is practically a straight line, in other words, when $\log D=n\log[SCN^-]=c$ where n or c is a constant, it seems to be usually difficult to determine the equilibrium constants, β_n and k_{DMn}, in Eq. (15) simultaneously from the extraction data due to the experimental errors. In the present study, the stability constants, β_n, had already been determined by separate experiments, and, as these constants were available, only the determination of K_{DMn} in Eq. (15) was necessary for the analysis of the equilibrium.

As may be seen in Fig. 2, the extraction curve is different when the aqueous phase is a constant ionic medium and when it contains only sodium thiocyanate. This is probably due in part to the changes in the activity coefficients of the chemical species by the change in the ligand concentration (and, consequently, by the change in the ionic strength); at the same time, it is probable also due to the lower concentration of sodium in the aqueous phase in the MIBK system, as can be seen from Eqs. (10) and (12).

The extraction in analytical work are usually carried out with no control of the activity or in the presence of various other electrolytes in the aqueous phase; in order to make a quantitative analysis of the extraction curves obtained under such conditions, a correction for these factors is indispensable. However, such a correction of the activity (not only of the ligand and metal ions, but also of all the other chemical species connected with the extraction, such as the complexes or the coexisting salts) is usually very difficult; thus, the information available from usual analytical data on the chemical equilibria involved in the systems is of limited use.

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10) T. Sekine and T. Ishii, This Bulletin, **43**, 2422 (1970).
11) S. Tribalat and C. Zeller, *Bull. Soc. Chim. France*, **1962**, 2041.
12) Y. Hasegawa, H. Takeuchi, and T. Sekine, This Bulletin, to be published.