The Solvent Extraction of Zinc(II) in Sodium Perchlorate-halide Solutions with Trioctylphosphine Oxide

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The solvent extraction of zinc(II) in 1 M sodium perchlorate ionic media containing chloride, bromide, or iodide ions at 25°C was determined as a function of the halide-ion (X^-) concentration by using the zinc-65 tracer. From the extraction data with isopropyltropolone (IPT) in chloroform, the formation of the ZnX^+ complex was observed, but the stability constants of these complexes were not large ($ZnCl^+$: β_1 is $10^{0.00}$, $ZnBr^+$: β_1 is less than $10^{-0.5}$ and the formation of ZnI^+ is negligible), and the higher complexes were negligible in all cases. The extraction of zinc(II) from these media with methylisobutylketone (MIBK) was not effective, although the extracted species could be identified as ZnX_2. The extraction with trioctylphosphine oxide (TOPO) in hexane, on the other hand, was much better than that with MIBK. From the distribution ratio determined as a function of the halide and TOPO concentrations, the extracted species were concluded to be $Zn(ClO_4)_2(TOPO)_4$, $ZnX(ClO_4)(TOPO)_3$, and $ZnX_2(TOPO)_2$. The extraction constants for these species were determined by a graphic analysis of the data, and it was concluded that the extractabilities are larger in the order: iodide>bromide>chloride. From these data, it is clear that, if a suitable and effective neutral extractant is employed, the extractions of the above complexes are possible, even from aqueous solutions in which practically no complex is formed.

In a previous paper,[1] the present authors studied the solvent extraction of zinc(II) in 1 M sodium perchlorate media containing various amounts of thiocyanate ions with trioctylphosphine oxide (TOPO) in hexane or methylisobutylketone (MIBK). They have reported, on the basis of these results, that zinc(II) in the aqueous phase forms the first, the second, and the third thiocyanate complexes, and that only the second one was extractable with TOPO in hexane, whereas both the second and the third complexes were extracted with MIBK.

After the above had been concluded, the authors desired to know further about the extraction of zinc(II) with the same extractants from aqueous solutions containing halide ions, which often form complexes somewhat similar to thiocyanate ions. The present paper will describe measurements of the stabilities and extractabilities of zinc(II) halide complexes from this standpoint. The results will be analyzed statistically, and some discussion will be made of the extraction of zinc(II) complexes, which are less stable in aqueous solutions than in organic solutions.

Experimental

The experiments were carried out in the same way described in the previous paper.[1] Zinc-65 was used for the determination of the distribution ratio of zinc(II). The organic solutions of the extractants and the aqueous solutions of the sodium salt were prepared in the manner described in the previous paper except that sodium chloride, bromide, or iodide solutions were prepared by dissolving an analytical-grade reagent and were added to the aqueous phase instead of sodium thiocyanate, as in the previous work. The concentrations of these ligand solutions were determined by gravimetry. The initial concentration of zinc(II) in the aqueous phase was 1×10^{-6} M, and the hydrogen-ion concentration at equilibrium was 10^{-4} to 10^{-5} M.

Statistical

As was also described,[1] the stability constants of zinc(II) complexes with an anionic ligand, X^-, in the aqueous phase can be determined from the decrease in the extraction of zinc(II) with a chelating extractant, HA, if the concentration of the extractant is kept constant:

$$D[H^+]^2/K = (1+\beta_1[X^-]+\beta_2[X^-]^2+\cdots) \tag{1}$$

where K is equal to $D_0[H^+]^2$ (D_0 is the distribution ratio in the absence of the ligand anions in the aqueous phase).

When the uncharged zinc(II) complex, ZnX_2, is extracted into the organic phase with e molecules of an organophilic extractant, E, the extraction equilibrium can be described as;

$$Zn^{2+} + 2X^- + eE(org) \rightleftarrows ZnX_2E_e(org)$$

$$K_{ex2,e} = \frac{[ZnX_2E_e]_{org}}{[Zn^{2+}][X^-]^2[E]^e_{org}} \tag{2}$$

However, if the concentration of the extractant, $[E]_{org}$, is kept constant over a series of experiments, this term can be eliminated, then;

$$K_{ex2} = \frac{[ZnX_2]_{org}}{[Zn^{2+}][X^-]^2} = K_{ex2,0} + K_{ex2,1}[E]_{org} + \cdots + K_{ex2,e}[E]^e_{org} \tag{3}$$

Furthermore, when zinc(II) species combining with perchlorate ions are extracted, the equilibrium can be described in the same manner as in Eqs. (2) and (3);

$$Zn^{2+} + X^- + ClO_4^- + eE(org) \rightleftarrows ZnX(ClO_4)E_e(org)$$

$$K_{ex1,e} = \frac{[ZnX(ClO_4)E_e]_{org}}{[Zn^{2+}][X^-][ClO_4^-][E]^e_{org}} \tag{4}$$

$$K_{ex1} = \frac{[ZnX(ClO_4)]_{org}}{[Zn^{2+}][X^-][ClO_4^-]} \tag{5}$$

$$Zn^{2+} + 2ClO_4^- + eE(org) \rightleftarrows Zn(ClO_4)_2E_e(org)$$

$$K_{ex0,e} = \frac{[Zn(ClO_4)_2E_e]_{org}}{[Zn^{2+}][ClO_4^-]^2[E]^e_{org}} \tag{6}$$

$$K_{ex0} = \frac{[Zn(ClO_4)_2]_{org}}{[Zn^{2+}][ClO_4^-]} \tag{7}$$

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[1] H. Moriya and T. Sekine, This Bulletin, **44**, 3347 (1971).

It should be possible to evolve a general expression for the distribution ratios in such systems. However, in this study, the following equations are introduced, assuming that each zinc(II) species in the organic phase forms only one kind of solvate with the extractant and that it can be described as $Zn(ClO_4)_2E_{e0}$, $ZnX(ClO_4)E_{e1}$, or ZnX_2E_{e2}. The distribution ratio can then be described as;

$$D = \frac{[Zn(ClO_4)_2E_{e0}]_{org} + [ZnX(ClO_4)E_{e1}]_{org} + [ZnX_2E_{e2}]_{org}}{[Zn^{2+}] + [ZnX^{+}] + \cdots} \tag{8}$$

$$= \frac{K_{ex0,e0}[ClO_4^-][E]_{org}^{e0} + K_{ex1,e1}[X^-][ClO_4^-][E]_{org}^{e1} + K_{ex2,e2}[X^-]^2[E]_{org}^{e2}}{1+\sum\beta_n[X^-]^n} \tag{9}$$

$$= \frac{K_{ex0}[ClO_4^-]^2 + K_{ex1}[X^-][ClO_4^-] + K_{ex2}[X^-]^2}{1+\sum\beta_n[X^-]^n} \tag{10}$$

When a series of extractions are carried out at a certain concentration of the extractant, it is clear from Eq. (10) that;

$$Y = \left(\frac{D(1+\sum\beta_1[X^-]+\cdots)}{[ClO_4^-]^2} - K_{ex0}\right) \times \frac{[ClO_4^-]}{[X^-]}$$

$$= K_{ex1} + K_{ex2}\frac{[X^-]}{[ClO_4^-]} \tag{11}$$

The extraction constant, K_{ex0} or $K_{ex0,e0}$, can be determined from the extraction data in the absence of the ligand, and the other constants in Eq. (11) can be determined from the $\log Y$ *vs.* $\log[X^-]/[ClO_4^-]$ plot, by a curve-fitting method with the following standard curve, as has been described;[2-4]

$$Y = \log(1+v);\ X = \log v \tag{12}$$

When the extraction constants, K_{ex0}, K_{ex1}, and K_{ex2}, are determined at various concentrations of the extractant, the solvation number, $e0$, $e1$, and $e2$, can be determined from the slope of the $\log K_{exe}$ *vs.* $\log[E]_{org}$ plot, because, for example, as the above assumption, Eq. (3) can be rewritten as;

$$\log K_{ex2} = \log K_{ex2,e} + e\log[E]_{org} \tag{13}$$

and K_{exe} can be obtained by a calculation based on Eq. (13).

Results

The results were reproducible, and the recovery of the zinc(II) tracer from the two phases was quantitative within the limit of experimental accuracy.

Extraction with IPT. As has been described,[1] the extraction of zinc(II) in 1 M sodium perchlorate with IPT is proportional to the square of the hydrogen-ion concentration, and the value of K in Eq. (1) is $10^{-8.38}$ when the IPT concentration is 0.1 M in chloroform. When the perchlorate ions in the aqueous phase were replaced with chloride ions, a decrease in the extraction of zinc(II) was observed. On the other hand, when they were replaced with bromide ions, the decrease was much smaller, and with iodide ions, the decrease was practically negligible in the ligand concentration range below 0.5 M. The results in the chloride and the bromide systems are given in Fig. 1. From these results, the stability constants were determined by the curve-fitting method and were found to be;

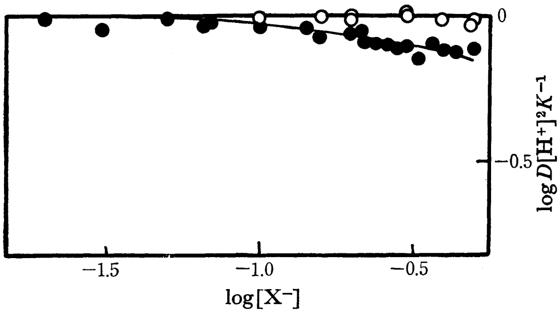

Fig. 1. Decrease in the IPT extraction of Zn(II) as a function of the ligand concentration.
Org. phase. $CHCl_3$ containing 0.1 M TPT
Aq. phase. 1 M $Na(X, ClO_4)$ ●: Cl^- ○: Br^-
The solid curve indicates (K is defined by Eq. (1) $\log D[H^+]^2K^{-1} = \log(1+1.0\times[Cl^-])$)

$ZnCl^+$: $\log\beta_1 = 0.00$

$ZnBr^+$: $\log\beta_1 < -0.5$

ZnI^+: very small

The higher complexes were concluded to be negligible.

Extraction with MIBK. The extraction of zinc(II) in 1 M sodium perchlorate solutions containing no ligand or in 1 M $Na(Cl,ClO_4)$ with MIBK was found to be very low. The distribution ratio was, in both cases, less than 10^{-3}. The extraction of zinc(II) from 1 M $Na(Br,ClO_4)$ or in 1 M $Na(I,ClO_4)$ was also poor. The distribution ratio was $10^{-2.3}$ and $10^{-1.6}$ when the aqueous phase contained 0.5 M bromide and 0.5 M iodide ions, respectively, (and consequently, in both cases, 0.5 M perchlorate was also present). The extraction was proportional to the square of the ligand concentration. The following extraction constants in Eq. (3) were determined from these results;

Extraction of $ZnCl_2$: $\log K_{ex2} < -2.5$

Extraction of $ZnBr_2$: $\log K_{ex2} = -1.7$

Extraction of ZnI_2: $\log K_{ex2} = -1.0$

Extraction with TOPO in Hexane. Zinc(II) in 1 M sodium perchlorate containing no ligand is extractable with TOPO in hexane, and the extraction is proportional to the fourth power of the TOPO concentration, as is given in Table 1.

The extraction of zinc(II) from 1 M $Na(X,ClO_4)$ with TOPO in hexane was determined as a function of the ligand concentration at certain TOPO concentrations.

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[2] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," Mcgraw-Hill (1961).

[3] T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

[4] T. Sekine, M. Sakairi, and Y. Hasegawa, *ibid.*, **39**, 2141 (1966).

TABLE 1. EXTRACTION OF ZINC(II) IN 1M $NaClO_4$ WITH TOPO IN HEXANE (for K_{ex0} and $K_{ex0,4}$ see Eqs. 6,7)

$[TOPO]_{org}$	D	$\log K_{ex0}$	$\log K_{ex0,4}$
5×10^{-2}	1.36	0.17	5.37
5×10^{-2}	1.25	0.13	5.34
3×10^{-2}	2.22×10^{-1}	−0.62	5.47
3×10^{-2}	1.74×10^{-1}	−0.72	5.37
2.4×10^{-2}	7.60×10^{-2}	−1.08	5.40
2×10^{-2}	4.70×10^{-2}	−1.29	5.50
2×10^{-2}	4.18×10^{-2}	−1.34	5.45
1.98×10^{-2}	3.52×10^{-2}	−1.42	5.42
1×10^{-2}	2.42×10^{-2}	−2.58	5.42
		av.	5.42

The slopes of the curves obtained at the same ligand concentration are larger in this order; iodide>bromide>chloride. Figure 2 gives the extraction with 1×10^{-2}M TOPO as an example of these experiments.

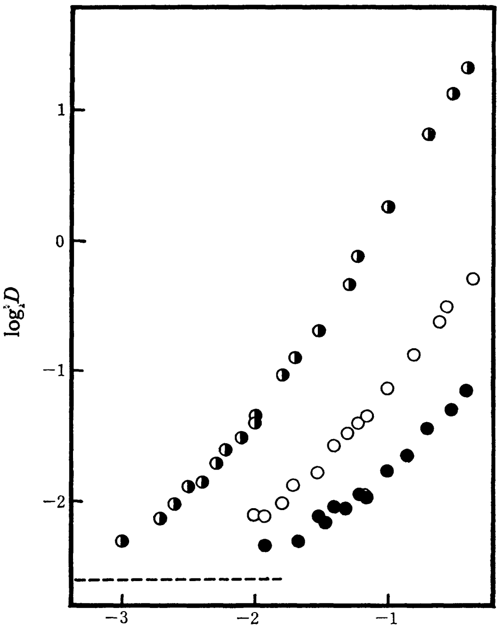

Fig. 2. Extraction of zinc(II) in 1M Na(X, ClO_4) with 1.0×10^{-2}M TOPO in hexane determined as a function of the ligand concentration.
(●: Cl^- ○: Br^- ◑: I^-)
The broken line indicates the extraction in the absence of halide ion ($\log D=-2.60$)

In order to determine the extraction constants in Eqs. (3), (5), and (7), the distribution ratio, the ligand concentration, the perchlorate concentration (that is, $1-[X^-]$M), and the K_{ex0} value in Table 1 were introduced into Eq. (11), and on the basis of the values thus calculated, the $\log Y$ vs. $\log[X^-]/[ClO_4^-]$ plot was made. It is given in Figs. 3, 4, or 5. The extraction constants were determined from these figures by the curve-fitting method. The solid curves in these figures show the best-fit curves. When a large part of the background perchlorate ions are replaced by the ligand anions, changes in the activity coefficients of solutes could occur. Thus, the extraction constants were determined by using the data in the ligand-concentration range below 0.5M. Thus, the fitted standard curves above this concentration, that is, at $\log[X^-]/[ClO_4^-]$ ratios higher than zero, are given by broken lines. The extraction constants thus obtained are given in Table 2. It was found that the slopes of the $\log k_{exe}$ vs. $\log[TOPO]_{org}$ plots were +4, +3, and +2 for K_{ex0}, K_{ex1}, and K_{ex2}, respectively, for all of the extractable complexes containing one of these three ligands. The extraction constants defined by Eqs. (2), (4), and (6) were determined from these data; they are also listed in Tables 1 and 2.

Discussion

The stability constants of zinc(II) halide complexes have been determined by many authors by using various

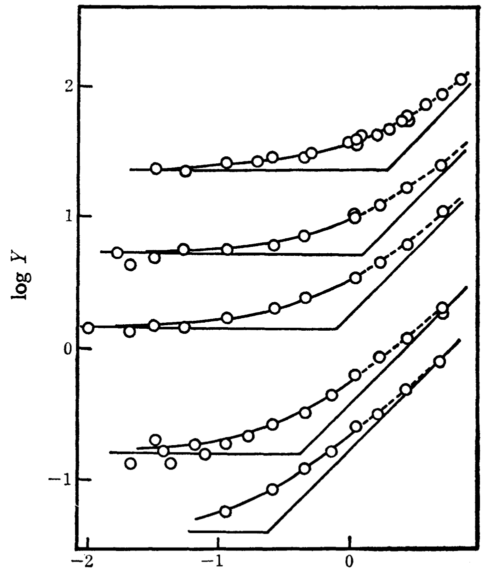

Fig. 3.

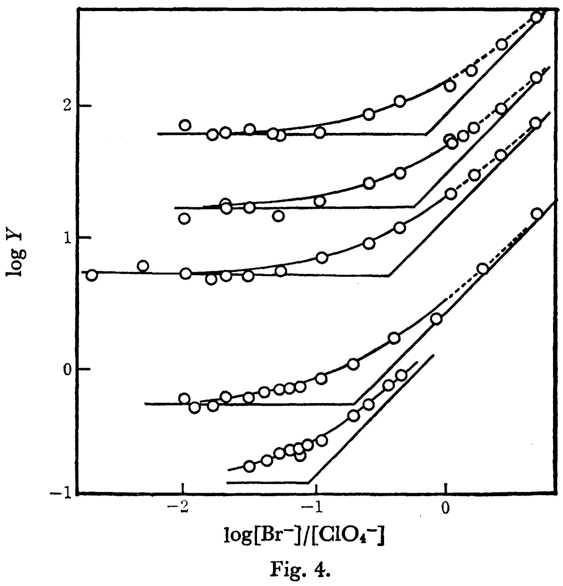

Fig. 4.

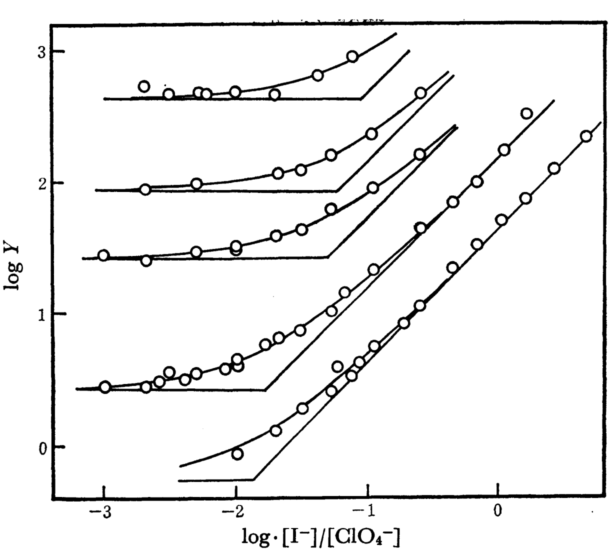

Fig. 5.

Fig. 3 to 5. Extraction of zinc(II) in 1M Na(X, ClO_4) with TOPO in hexane at various concentrations.
The data are plotted according to Eq. (11). The solid curves are $\log Y = \log(K_{ex1} + K_{ex2}[X^-]/[ClO_4])$ were K_{ex1} and K_{ex2} are taken from Table 2.
The aqueous phase contains chloride (Fig. 3), bromide (Fig. 4) or iodide ions (Fig. 5).
The concentration of TOPO in hexane is 5×10^{-2}M, 3×10^{-2}M, 2×10^{-2}M, 1×10^{-2}M or 6×10^{-3}M (top to bottom).

Table 2. Extraction constants of zinc(II) from 1M Na(X,ClO) with TOPO in hexane
(cf. Eqs. (11), (13))

(a) Chloride system

$[TOPO]_{org}$	$\log K_{ex1}$	$\log K_{ex2}$	$\log K_{ex1,3}$	$\log K_{ex2,2}$
6×10^{-3}	−1.40	−0.78	5.27	3.66
1×10^{-2}	−0.80	−0.42	5.20	3.58
2×10^{-2}	0.16	0.26	5.26	3.66
3×10^{-2}	0.72	0.60	5.29	3.65
5×10^{-2}	1.36	1.07	5.26	3.67
		av.	5.26	3.64

(b) Bromide system

$[TOPO]_{org}$	$\log K_{ex1}$	$\log K_{ex2}$	$\log K_{ex1,3}$	$\log K_{ex2,2}$
6×10^{-3}	−0.87	0.16	5.80	4.60
1×10^{-2}	−0.27	0.41	5.73	4.41
2×10^{-2}	0.71	1.13	5.81	4.53
3×10^{-2}	1.22	1.46	5.77	4.51
5×10^{-2}	1.78	1.91	5.68	4.51
		av.	5.76	4.51

(c) Iodide system

$[TOPO]_{org}$	$\log K_{ex1}$	$\log K_{ex2}$	$\log K_{xe1,3}$	$\log K_{xe2,2}$
6×10^{-3}	−0.26	1.60	6.41	6.04
1×10^{-2}	0.43	2.19	6.43	6.19
2×10^{-2}	1.43	2.69	6.53	6.09
3×10^{-2}	1.94	3.12	6.51	6.17
5×10^{-2}	2.64	3.63	6.54	6.13
		av.	6.48	6.12

experiments methods.[5] The values determined in different ionic media are rather scattered. However, it is the general tendency for the stability constants for the first chloride complex at higher ionic concentrations to be around one ($\log\beta_1$ is −0.19 in 3M $NaClO_4$,[6] 0.30 in 4M $NaClO_4$,[7] and 0.2 in 1M $NaClO_4$[8]), and for those of the first bromide complex to be smaller than those of the chloride complex ($\log\beta_1$ is −0.60 in 3M $NaClO_4$[6]). These values practically agree with the present results. Some authors have also reported higher chloride or bromide complexes which are generally less stable than the first complex. However, the present authors could not determine any complexes higher than ZnX^+ from the results in Fig. 1. The stability constants determined by Morris and his coworkers in a 0.69M ionic medium by an ion-exchange method,[9] and in a 1M perchloric acid medium by a solvent extraction method with dinonylnaphthalene sulfonic acid[10] ($\log\beta_1=0.83$, $\log\beta_2=0.56$, $\log\beta_3=0.66$ for the chloride complexes and $\log\beta_1=0.10$, $\log\beta_2=-0.12$ for the bromide complexes), are obviously larger than the present results.

The extracted zinc(II) species with MIBK in the organic phase is assumed to be ZnX_2, and those with TOPO in hexane are assumed to be $Zn(ClO_4)_2$, $ZnX(ClO_4)$, and ZnX_2. Practically the only zinc(II) species in the aqueous phase, on the other hand, is the Zn^{2+} species in the bromide or iodide system, while the zinc(II) species are the Zn^{2+} and $ZnCl^+$ species in the chloride system. This indicates that the interaction between the metal ion and the ligand anions, or those between the metal ion and the perchlorate ions, are much stronger in the organic phase than in the aqueous phase, in which all the cations and anions are in a hydrated and uncomplexed form except for the $ZnCl^+$ species.

The dissociation of the extracted species in the organic phase should not be important in hexane, which is a low dielectric solvent, and it may be negligible in MIBK, which extracts only the $ZnBr_2$ or ZnI_2 complex.

No direct information is available on the nature of the bond in the extracted species from only the distribution data. However, the results in Table 2 indicate rather clearly the four coordination of znic(II) in the organic phase, although it is not possible to know if one or two molecules of water are coextracted with the metal species. Since the solvation numbers for the $Zn(ClO_4)_2$, $ZnX(ClO_4)$, and ZnX_2 species are four, three, and two, respectively, it can be assumed that the interaction between metal ion and the perchlorate ions are electrostatic and that those between the metal ion and the halide ions are coordinative. This also suggests that, among the four coordination positions of zinc(II), those unoccupied by the ligand anions are solvated with TOPO in the organic phase. The

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[5] A. E. Martell and L. G. Sillén "Stability Constants," The Chemical Society, London, spec, pub. **17**, (1964).

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[9] E. L. Short and D. F. C. Morris, *J. Inorg. Nucl. Chem.*, **18**, 192 (1961).

[10] D. F. C. Morris, D. T. Anderson, S. L. Waters, and G. L. Reed, *Electrochim. Acta*, **14**, 643 (1969).

extraction of the thiocyanate complex in the previous study was also estimated to be $Zn(SCN)_2(TOPO)_2$.[1)]

Thus, it can reasonably be concluded that, for example, the extracted zinc(II) iodide is not an ion-pair of Zn^{2+} and the large iodide ions, but is a coordination complex which is stable only in these organic solvents and is completely dissociated in the aqueous phase.

In the previous paper,[1)] the distribution ratio of zinc(II) between hexane containing TOPO and aqueous thiocyanate solutions was described in terms of the formation of zinc(II) complexes in the aqueous phase and the extraction of the uncharged complex species. This extraction was represented by the distribution constant;

$$K_{DM} = [ZnX_2]_{org,tot}/[ZnX_2] \tag{14}$$

As can be seen from Eqs. (3) and (14), the extraction constant of the second complex is the product of the stability constant of the ZnX_2 species in the aqueous phase and the distribution constant of this species, that is, $K_{ex2}=K_{DM}\beta_2$. The extraction constant of the zinc(II) thiocyanate complex with TOPO, $K_{ex2,2}$ in Eq. (2), can be calculated from the constants in the previous paper[1)] to be $10^{8.76}$. In the present study, however, the determination of the β_2 and K_{DM} was not possible. Thus, the extraction constant, K_{ex2}, is used in order to describe the distribution equilibrium.

It is remarkable that the extractabilities of the complexes given in Figs. 2 to 5 or in Table 2 and in the previous paper[1)] are larger in the order of; chloride< bromide<iodide<thiocyanate. The most stable thiocyanate complex ($\log\beta_1=0.57$, $\log\beta_2=1.32$, and $\log\beta_3=1.18$) shows the highest extractability, but among the three halide complexes, the magnitude of the extractabilities shows an inverse order to the stability of the complexes in the aqueous phase.

Without any further information about these constants, it seems to be impossible to make a more detailed discussion of the extractability of these complexes. However, the fact that iodide, which forms the least stable complex (most probably the value of β_2 is also larger in the same order as β_1), is extracted better than bromide or chloride is probably due to the larger molecular size or the larger aquophobic tendency of the ZnI_2 species. The much higher extractability of the thiocyanate complex is probably mainly due to the greater stability of the $Zn(SCN)_2$ species than those of these bis-halide complexes.

It is remarkable that the extraction with the neutral extractant takes place even when no measurable amount of the extracted metal complexes are present in the aqueous phase. Such extractions, however, are very commonly observed when chelating extractants are employed for the metal extraction. Actually, in many metal extractions with chelating agents, HA, the distribution ratio can be denoted by $D=[MA_m]_{org}/[M^{m+}]$.

When the stability of the extractable species in the aqueous phase is low, the extraction of the species is obviously low. As has been pointed out,[11)] the K_{DM} in Eq. (14) is the product of the distribution constant of the uncharged species between the diluent and the aqueous phase and the terms of the adduct formation constants between the metal complex and the extractant. From this point of view, the use of a strongly basic extractant such as TOPO is always suitable. However, the effect on its extractablilty of the stability and the molecular size of the complex is complicated. It seems to be common that the extractability of the larger halide complexes is higher than the smaller halide complexes if the stability constants of the former is larger. However, we have not found any general principle for the order of the extractability of halide complexes when the stabilities of the complexes of a smaller molecular size are higher than those of a larger molecular size.

Part of this study was carried out at the Laboratory of Nuclear and Analytical Chemistry, Institute of Physical and Chemical Research. The authors are grateful to Professor Nobufusa Saito, the head of the Laboratory.

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11) T. Sekine and T. Ishii, This Bulletin, **43**, 2422 (1970).