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The Behavior of Indium(III) Complexes in Several Liquid-Liquid Distribution System. I. A Solvent Extraction Study of Indium(III) Complexes in Aqueous Perchlorate Media Containing Several Anionic Ligands

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The stabilities of the indium(III) complexes in 4 M sodium perchlorate solutions with eight univalent anionic ligands have been studied at 25°C by using a TTA-chelate extraction method and a TBP adduct extraction method. The following conclusions have been reached. The stabilities of the indium(III) halide complexes are larger in this order; $Cl^- > Br^- > I^-$; on the other hand, those of indium(III) complexes with the halate anions increase in the order: $ClO_3^- < BrO_3^- < IO_3^-$. The former forms more stable complexes than the latter. Thiocyanate ions form the most stable indium(III) complexes (the first to the fifth complexes), while nitrate ions form the least stable one (only the first complex). The values obtained by the TTA method are almost identical with those obtained by the TBP method. It was also concluded that although the TTA method could be applied to all the systems studied, it is more suitable for the examination of the lower complexes; the TBP method, on the other hand, could be used only for the systems in which an extractable third complex is formed, but it could give more accurate constants for the higher complexes. Thus, only a combination of these two methods can give all the equilibria in a system where many complexes are formed.

Many kinds of indium(III) complexes in aqueous solutions have been reported. Among these, the halide complexes seem to have been most extensively studied and are known to be rather stable.[1]

The present author grew interested in the differences in stability among the indium(III) complexes with halide ions and among those with the other univalent ions. In order to determine stabilities of these different complexes, measurements over a wide ligand-concentration range were necessary; thus an ionic medium, 4 M Na(ClO_4), has been employed throughout the study for this purpose. Two different solvent extraction methods, a TTA (thenoyltrifluoroacetone) chelate extraction method and a TBP (tributylphosphate) adduct extraction method, were used for the determination of the stability constants. Indium(III) in aqueous solutions containing different concentrations of the ligand was extracted by using these extracting agents, and the stability constants were determined by a graphic treatment. Some discussion was made regarding the stabilities of these complexes and regarding the solvent extraction method as a technique for the determination of the stability constants.

Statistical

The complex formation of indium(III) in aqueous solutions containing a univalent ligand, L^-, may be described as follows:

$$In^{3+} + nL^- \rightleftharpoons InL_n{}^{3-n} \tag{1}$$

$$\beta_n = [InL_n{}^{3-n}]/[In^{3+}][L^-]^n \tag{2}$$

or:

$$K_n = [InL_n{}^{3-n}]/[InL_{n-1}^{4-n}][L^-] \tag{2'}$$

The total indium(III) concentration in the aqueous phase may be described as:

$$[In(III)]_{total} = [In^{3+}] + [InL^{2+}] + \cdots + [InL_n{}^{3-n}] \tag{3}$$

The distribution ratio of indium(III) in a solvent extraction system is defined as follows (it can be measured radiometrically):

$$D = [In(III)]_{org,\ total}/[In(III)]_{total} = \frac{\gamma\text{-count-rate per } ml \text{ of the org. phase}}{\gamma\text{-count-rate per } ml \text{ of the aq. phase}}$$

(i) Extraction with an Organophilic Chelating Acid. The tripositive indium ion could be extracted with an organophilic chelating acid HA, in an immiscible organic solvent as follows:

$$In^{3+} + 3HA(org) \rightleftharpoons InA_3(org) + 3H^+ \tag{4}$$

$$Kex_0 = [InA_3]_{org}[H^+]^3/[In^{3+}][HA]^3_{org} \tag{5}$$

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[1] L. G. Sillén and A. E. Martell, "Stability Constants", Spec. Pub. No. 17, The Chemical Society, London (1964).

When the aqueous phase contains only uncomplexed indium ions, the net distribution ratio may be described as follows:

$$D_0 = [\mathrm{InA_3}]_{org}/[\mathrm{In^{3+}}] \tag{6}$$

where the subscript "0" denotes no complex formation in the aqueous phase. The extraction constant can, then, be described as:

$$Kex_0 = D_0[\mathrm{H^+}]^3[\mathrm{HA}]_{org}^{-3} \tag{7}$$

When the indium ion undergoes complex formation with a uninegative ligand, L^-, and when only the InA_3 species is extractable, the net distribution ratio may be described as:

$$D = \frac{[\mathrm{InA_3}]_{org}}{[\mathrm{In^{3+}}] + [\mathrm{InL^{2+}}] + \cdots + [\mathrm{InL}_n{}^{3-n}]} = \frac{[\mathrm{InA_3}]_{org}}{[\mathrm{In^{3+}}](1 + \sum \beta_n [\mathrm{L^-}]^n)} \tag{8}$$

From Eqs. (7) and (8), we obtain:

$$D[\mathrm{H^+}]^3[\mathrm{HA}]_{org}^{-3}/Kex_0 = (1 + \sum \beta_n[\mathrm{L^-}]^n)^{-1} \tag{9}$$

(ii) Extraction as Adduct Neutral Complexes. The uncharged complex species in an aqueous phase, InL_3, could be extracted as an adduct with an organophilic neutral extractant, E, in the organic phase:

$$\mathrm{InL_3}(org) + e\mathrm{E}(org) \rightleftarrows \mathrm{InL_3E}_e(org) \tag{10}$$

$$\beta_e{}^{\circ} = \frac{[\mathrm{InL_3E}_e]_{org}}{[\mathrm{InL_3}]_{org}[\mathrm{E}]^e{}_{org}} \tag{11}$$

The net distribution ratio of indium(III) in such systems can be described as:

$$D = \frac{[\mathrm{InL_3}]_{org} + [\mathrm{InL_3E}]_{org} + [\mathrm{InL_3E_2}]_{org} + \cdots + [\mathrm{InL_3E}_e]_{org}}{[\mathrm{In^{3+}}] + [\mathrm{InL^{2+}}] + \cdots + [\mathrm{InL}_n{}^{3-n}]} = \frac{[\mathrm{InL_3}]_{org}(1 + \sum \beta_e{}^{\circ}[\mathrm{E}]^e{}_{org})}{[\mathrm{In^{3+}}](1 + \sum \beta_n[\mathrm{L^-}]^n)} \tag{12}$$

When the concentration of the extractant is kept at a constant value, c_1, we can define the following partition coefficient for this complex:

$$K_{DM} = \frac{[\mathrm{InL_3}]_{org}(1 + \sum \beta_e{}^{\circ} c_1{}^e{}_{,org})}{[\mathrm{InL_3}]} \quad (\text{at } [\mathrm{E}]_{org} = c_1) \tag{13}$$

From Eqs. (2), (12), and (13), the following equation is obtained:

$$D = \frac{K_{DM}\beta_3[\mathrm{L^-}]^3}{1 + \sum \beta_n[\mathrm{L^-}]^n} \quad (\text{at } [\mathrm{E}]_{org} = c_1) \tag{14}$$

On the other hand, when the ligand concentration, $[L^-]$, is kept at a constant value, c_2, the distribution ratio is dependent on the $[E]_{org}$, and from Eq. (12) the following is obtained:

$$D = D_0(1 + \sum \beta_e{}^{\circ}[\mathrm{E}]^e{}_{org}) \tag{15}$$

where D_0 stands for the $[InL_3]_{org}/[In^{3+}](1+\sum\beta_n c_2{}^n)$ term, that is, the distribution ratio when the $[E]_{org}$ is zero.

If the "eth" adduct, InL_3E_e, is dominant in the organic phase, Eq. (15) can be described as:

$$\log D = \log D_0\beta_e{}^{\circ} + e \log [E]_{org} \tag{16}$$

Therefore, the plot $\log D$ *vs.* $\log[E]_{org}$ should be a straight line with the slope of $+e$, and from the value of $+e$, we can determine the number of the extractant molecules in the organic complex species.

Experimental

Reagents. The indium-114 m tracer was obtained from the Radiochemical Center, Amersham, England, as a hydrochloric acid solution. This was diluted with a large amount of 0.1 M perchloric acid and used as the stock tracer solution. All of the reagents used were of a reagent grade. The TTA was obtained from Dojindo & Co. The TBP was obtained from the Tokyo Kasei Co. and was washed with 0.1 M perchloric acid, water, and 0.1 M sodium hydroxide, and then several times with water. The chloroform was washed three times with water; The sodium perchlorate was recrystallized twice from water. The other reagents were used without further purification.

Procedures. All of the procedures were carried out in a thermostatted room at 25±0.5°C. Stoppered glass tubes (volume 20 m*l*) were used to equilibrate the organic and aqueous phases. The tracer and various amounts of ligand solutions and the sodium perchlorate solution were placed in the tubes, and then the organic solution was added. The hydrogen-ion concentration was adjusted by the addition of perchloric acid. A small amount (0.01 M at initial) of sodium acetate was added as a buffer for the iodate (pK_a, *ca.* 0.7) and thiocyanate (pK_a, *ca.* 0.8) systems in order to prevent the association of the ligand with the portion. The initial volume of each phase was 5.0 m*l*. The aqueous phase was kept at a constant ionic medium, 4 M $Na(ClO_4)$. The two phases in the tubes were agitated mechanically for one hour and then centrifuged. A two-milliliter portion was pipetted from each phase and transferred into a small test tube. The γ-radioactivity of these sample solutions was measured with a well-type(NaI) scintillation counter. A small portion was also pipetted from the aqueous phase and transferred into a small glass vessel, and the hydrogen-ion concentration was measured potentiometrically by using a standard solution containing 0.0100 M perchloric acid and 3.99 M sodium perchlorate as a standard of $-\log[H^+]$ 2.00.

Results

TTA-Extraction. Figure 1 shows the $-\log[H^+]$ dependence of the indium(III) extraction into the chloroform phase containing 0.02 M TTA from a 4 M sodium perchlorate medium containing no ligand. It may be seen from the figure that the slope of the plot is +3. The extraction constant, K_{ex_0} in Eq. (7), was obtained as $\log K_{ex_0} = -3.62$. Figures 2 to 5 give the $\log D[H^+]^3 \cdot [HA]_{org}^{-3}/K_{ex_0}$ *vs.* $\log[L^-]$ plot. The $-\log[H^+]$ for these experiments was kept at 2.0, but it was kept around 3 for the experiments with iodate and thiocyanate ions. The stability constants of the

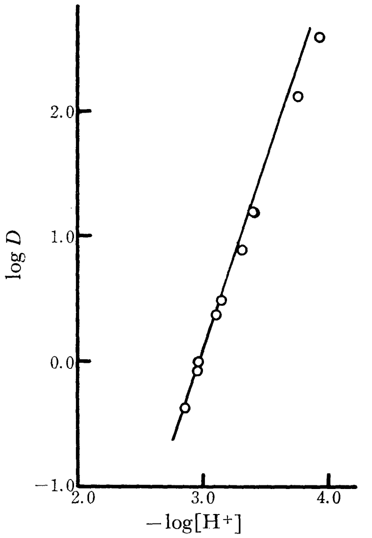

Fig. 1. Extraction of In(III) from aqueous phase containing no complexing ligands.
Organic phase: $CHCl_3$ containing 0.02 M TTA
Aqueous phase: 4 M $NaClO_4$
The straight line gives $\log D = -3\log[H^+] - 8.72$

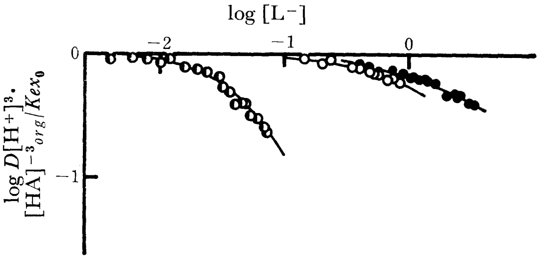

Fig. 2. Decrease in the extraction of indium(III) as a function of the ligand concentration.
● 0.2 M TTA-$CHCl_3$, 4 M Na(ClO_3, ClO_4)
○ 0.2 M TTA-$CHCl_3$, 4 M Na(BrO_3, ClO_4)
◐ 0.02 M TTA-$CHCl_3$, 4 M Na(IO_3, ClO_4)
The solid curves were calculated using the stability constants in Table 1.

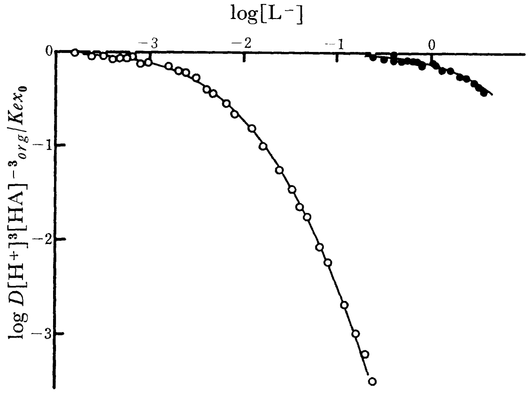

Fig. 3. Decrease in the extraction of indium(III) as a function of the ligand concentration.
● 0.2 M TTA-$CHCl_3$, 4 M Na(NO_3, ClO_4)
○ 0.02 M TTA-$CHCl_3$, 4 M Na(SCN, ClO_4)
The solid curves were calculated using the stability constants in Table 1.

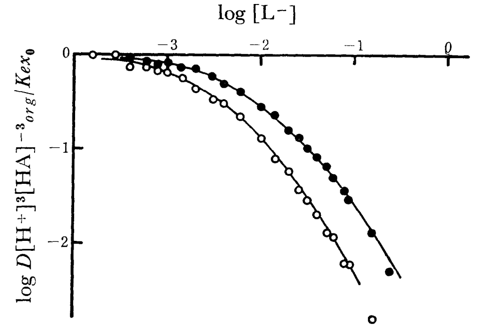

Fig. 4. Decrease in the extraction of indium(III) as a function of the ligand concentration
● 0.2 M TTA-$CHCl_3$, 4 M Na(Br, ClO_4)
○ 0.2 M TTA-$CHCl_3$, 4 M Na(Cl, ClO_4)
The solid curves were calculated using the stability constants in Table 1.

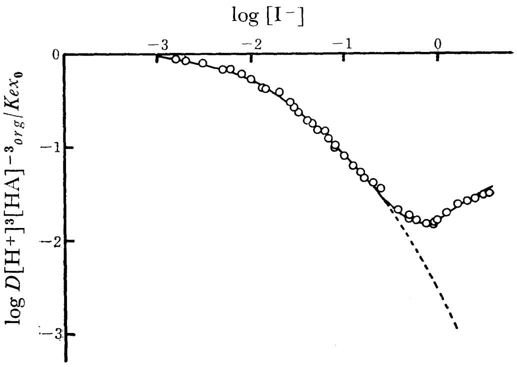

Fig. 5. Decrease in the extraction of indium(III) as a function of the iodide ion concentration (0.2 M TTA-$CHCl_3$, 4 M Na(I, ClO_4)).
The solid curve was drawn as:

$$y = \log(1+5[I^-]^3) - \log(1+93[I^-] + 190[I^-]^2 + 78[I^-]^3)$$

(The extraction of the InI_3 complex is taken into account for the calculation, *cf.* Eqs. (13) and (14)). The dotted curve was drawn as

$$y = -\log(1+93[I^-] + 190[I^-]^2 + 78[I^-]^3)$$

(A statistical curve assuming no InI_3 extraction, *cf.* Eq. (8))

complexes of indium(III) with these ligands were determined by a curve-fitting method.[2,3] They are summarized in Table 1-a.

As may be seen from Fig. 5, the slope for the plot obtained in the iodide system decreases in a manner to be expected from Eq. (9) in the lower ligand concentration region; however, the slope increases as the ligand concentration increases, and finally it becomes positive after a pronounced

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2) F. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York (1961).

3) T. Sekine, M. Sakairi and Y. Hasegawa, This Bulltin, **39**, 2141 (1966).

TABLE 1. EQUILIBRIUM CONSTANTS FOR In(III) COMPLEXES

a) Stablity constants determined by TTA chelate extraction method

Ligand	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	Ligand	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
Cl^-	2.61	4.18	—	NO_3^-	−0.43	—	—
Br^-	2.36	3.16	—	ClO_3^-	−0.37	—	—
I^-	1.97	(2.28)*	(1.89)*	BrO_3^-	−0.12	—	—
SCN^-	2.44	4.11	5.10	IO_3^-	1.02	2.64	—

* These stability constant for the iodide complexes were calculated by Eq. (14) in which $K_{DM}=[InI_3]_{org}/[InI_3]=10^{-1.2}$ (0.2 M TTA-$CHCl_3$) had been introduced, but the values in Table 1-b are recommended instead of these constants.

b) Distribution constants and stability constants by TBP-adduct extraction method.

Ligand	$[TBP]_{hexane}$	$\log K_{DM}$	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$	$\log\beta_5$
Br^-	0.1 M	0.11	~1.9*	3.32	3.24	2.18	—
I^-	0.01 M	1.63	~2.0*	2.18	2.20	—	—
SCN^-	0.01 M	0.70	~2.4*	4.11	5.10	4.57	5.45

* The values for the β_1 have not been determined accurately by this method.

minimum of D at about 0.7 M. From the statistical analysis of the data, it was concluded that the decrease in the distribution ratio in the lower iodide concentration region is caused by the iodide complex formation, but in the higher region the tris-iodide complex is assumed to be extracted into the chloroform phase. This may be the reason why the extraction curve deviates from that to be expected from Eq. (9).

The distribution ratio in this system may be described as:

$$D=\frac{[InA_3]_{org}+[InI_3]_{org}}{[In^{3+}]+[InI^{2+}]+[InI_2^+]+[InI_3]} \tag{13}$$

and from Eqs. (8) and (10), Eq. (13) can be described as:

$$D=\frac{Kex_0[HA]^3_{org}\times[H^+]^{-3}+K_{DM}\beta_3[I^-]^3}{1+\beta_1[I^-]+\beta_2[I^-]^2+\beta_3[I^-]^3} \tag{14}$$

At first, the values β_1 and β_2 were determined, by the curve-fitting of the plot in the lower iodide concentration region in Fig. 5, to be $\log\beta_1=1.97$ and $\log\beta_2=2.28$. However, after several trials the data in Fig. 5 were concluded to be too erroneous to determine the β_3 and K_{DM} in Eq. (14). The equilibrium constants, β_2, β_3, and K_{DM}, only tentatively determined from the data in Fig. 5, are given in Table 1-a.

TBP Extraction. It was found that some of the tris-indium(III) complexes in the aqueous phase were extracted with TBP in hexane. Figure 6 shows the extraction of indium(III) from solutions containing 3 M sodium perchlorate and 1 M sodium bromide, iodide, or thiocyanate as a function of the TBP concentration in hexane. In Fig. 6 we can see that the slope of the log D *vs.* log $[TBP]_{org}$ plot ("e" in Eq. (16)) is +2 for the bromide and iodide systems, but +3 for the thiocyanate system. The dominant species in the organic phase may, then, be regarded as $InL_3(TBP)_2$ for the former two systems and $InL_3(TBP)_3$ for the latter system. Figure 7 shows the log D *vs.* log $[L^-]$ plot when the ligand anion, L^-, is a bromide ion ($[TBP]_{org}=0.1$ M), an iodide ion ($[TBP]_{org}=0.01$ M), and a thiocyanate ion ($[TBP]_{org}=0.01$ M). The plot in Fig. 7 was explained in terms of the extraction of the neutral complex

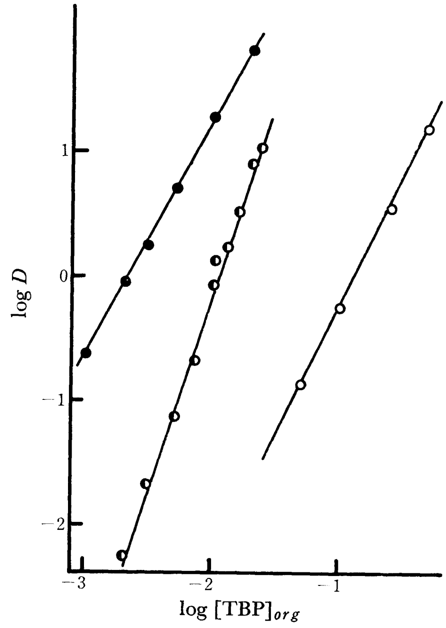

Fig. 6. TBP dependence of the distribution ratio.
Organic phase: hexane containing TBP.
Aqueous phase:
○ 1 M NaBr+3 M $NaClO_4$
● 1 M NaI+3 M $NaClO_4$
◐ 1 M NaSCN+3 M $NaClO_4$
The straight lines for the bromide and iodide plots show a slope of +2 and that for the thiocyanate plot shows a slope of +3.

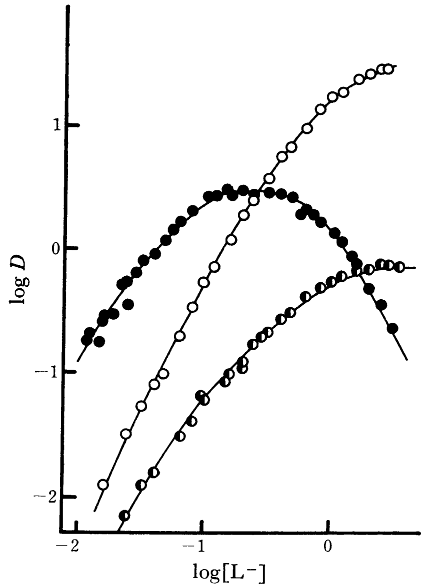

Fig. 7. TBP extraction of InL_3 complexes as a function of ligand concentrations.
○ 0.01 M TBP-hexane, 4 M Na(I, ClO_4)
◐ 0.1 M TBP-hexane, 4 M Na(Br, ClO_4)
● 0.01 M TBP-hexane, 4 M Na(SCN, ClO_4)
The solid curves were calculated using the stability constants in Table 1.

into the organic phase. The partition coefficient, K_{DM}, in Eq. (13) and the stability constants, β_n, were determined graphically by Eq. (14) as follows. In all cases, the slope of the $\log D$ *vs.* $\log [L^-]$ plot is smaller than $+3$ over the entire ligand concentration range studied; that is, even at the lowest concentration some of the indium ions are already complexed, and it is not possible to determine the β_1 accurately. For this reason, the values for β_1 determined by the TTA extraction method were introduced into Eq. (14); the rest of the stability constants and the partition coefficient, K_{DM}, were determined by a graphical method based on a successive approximation. The constants finally determined are listed in Table 1-b.

The extraction of indium(III) from 4 M Na(Cl, ClO_4) into hexane containing 0.1 M TBP was very poor over the entire chloride concentration range. When the TBP concentration was elevated, for example, to 1 M, a measurable extraction, one which was dependent on the chloride concentration, was observed. However, it was not possible to determine the stability constants of the chloride complexes from the analysis of these data by using Eq. (14), because those complexes which were extracted were assumed to be indium species containing perchlorate ions or both perchlorate and chloride ions.

Discussion

The Stabilities of the Complexes. It has previously reported[1)] that indium(III) forms stable complexes with halide ions. The present results also indicate this. The stabilities of the halide complexes increase in the decreasing order of the ionic radii. Table 2 summarizes some of the earlier data on indium(III) complexes. The present values of $\log \beta_1$ of chloride and bromide complexes seem to agree with the earlier data, but literature values of the stability constants of higher complexes are quite different from the present results. The literature constants for iodide complexes, especially, are not consistent.

It is remarkable that most of the earlier reports indicate the formation of such higher thiocyanate complexes as $In(SCN)_3$ and $In(SCN)_4^-$. The present results also indicate larger stabilities of the thiocyanate complexes.

The stabilities of indium(III) complexes with the halate and halide ions increase with the increase in the basicity of the ligands, as is usually to be expected. The nitrate ion, which has a

TABLE 2. SUMMARY OF THE REPRESENTATIVE EARLIER WORK ON THE INDIUM(III) HALIDE AND THIOCYANATE COMPLEXES

Ligand	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$	Medium	Ref.
Cl^-	2.26	2.50	3.55	—	4 M $Na(NO_3)$	4
	2.15	3.59	—	—	2 M $Na(ClO_4)$	5
Br^-	1.36	1.52	—	—	4 M $Na(NO_3)$	4
	2.08	3.36	3.96	4.81	4 M $Na(ClO_4)$	6
I^-	1.00	2.26	—	—	2 M $Na(ClO_4)$	7
SCN^-	2.58	3.60	4.63	—	2 M $Na(ClO_4)$	7
	2.08	3.20	4.24	4.23*	2 M $Na(ClO_4)$	8

* $\log\beta_5=4.81$, $\log\beta_6=4.84$ are also reported.

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4) Ya D. Fridman, R. I. Sorochan and N. V. Dolgashova, *Zhur. Neorg. Khim.*, **7,** 2127 (1962).

5) N. Sundén, *Svensk Kem. Tidskr.*, **66,** 20 (1954).

6) E. A. Burns and D. N. Hume, *J. Amer. Chem. Soc.*, **79,** 2704 (1957).

7) N. Sundén, *Svensk Kem. Tidskr.*, **66,** 50 (1954).

8) J. Selbin and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, **24,** 1111 (1962).

planar structure, forms the least stable indium complex among those studied; this may be explained in terms of the decrease in the polarity under steric conditions.

The Solvent Extractions for the Determination of the Stability Constants. As the distribution ratios in this study were always determined radiometrically, it was supposed that the distribution ratios would be accurate enough when they were between 10^{-2} and 10^{2}; thus, only the data in this range were used for the calculation and the discussion. The TTA extraction method may be applied to almost all complex formation systems, because it can determine the concentrations of the uncomplexed metal ion, which should decrease even upon the formation of a very weak complex. This method, however, is not appropriate for higher complexes with larger stability constants because, in such cases, the uncomplexed metal concentration is very low and, consequently, the distribution ratio is too low for an accurate determination ($D<10^{-2}$). Statistically, it would be possible to determine the distribution even under those conditions if the concentration of the chelating extractant is increased or if the hydration ion concentration is decreased ($[HA]_{org}/[H^+]$ is increased).

However, it is not always practically possible to carry out the above method practically because the aqueous chelate is very often formed in the higher $[HA]_{org}/[H^+]$ range, thus causing a systematic error in the stability constants.[4] Therefore, we should always confirm the constancy of K_{ex_0} value, $D_0[H^+]^3[HA]_{org}^{-3}$, in the absence of the ligand throughout the $[HA]_{org}/[H^+]$ region to be studied.

As may be seen from Fig. 1, the slope of the $\log D$ *vs.* $-\log [H^+]$ plot is $+3$ when the $\log D$ is smaller than $+1$. Thus, from Eq. (9) an accurate determination of the stability constants by the TTA method is possible when $10^3<(1+\sum\beta_n\cdot[L^-]^n)$. This fact and the results in Figs. 3 and 4 show that the TTA method can be applied only when the ligand concentration is lower than about 0.2 M.

When only the TTA method was used, no formation constants of the higher complexes could be determined, as may be seen in Table 1-a.

On the other hand, as may be seen from Fig. 7, the TBP method can cover the higher ligand-concentration region, where the TTA method can not be applied.

Statistically, it would be also possible to determine the complexes in the lower ligand-concentration range by the TBP method. Under such conditions, the distribution ratio should be very low if the TBP concentration is kept constant, as may be seen from Fig. 7. However, as may be seen in Fig. 6, the extraction of the TBP adduct increases when the TBP concentration is increased, and the distribution ratio becomes higher; consequently, a measurable distribution ratio should be obtained even in the ligand concentration range by the use of a high TBP concentration. However, when the TBP concentration is higher, the extraction of mixed complexes, such as $InX_n(ClO_4)_{3-n}$ or of such ion-pairs as $Na^+InX_4^-$ might be effected.

In the present paper, the ligand-concentration ranges studied have been too wide to allow for an accurate determination by using only one of these two methods. Only the combination of the two methods has made it possible to determine reasonable sets of stability constants for many such complexes. The agreement of the results obtained by these two different methods, shown in Tables 1-a and 1-b, is good.

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