The Behavior of Indium(III) Complexes in Several Distribution Systems. II. The Extraction of Indium(III) Halide and Thiocyanate Complexes into 4-Methyl-2-Pentanone, 4-Methyl-2-Pentanol, or Nitrobenzene

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The solvent extraction of indium(III) from a bromide, iodide, or thiocyanate solution into 4-methyl-2-pentanone(MIBK), 4-methyl-2-pentanol(hexol), or nitrobenzene was determined by using a ^{114m}In tracer. The extraction was, in general, most effective with MIBK and poorest with nitrobenzene, except from iodide solutions. The extraction with a certain solvent was always better from iodide solutions than from bromide solutions. The extraction from thiocyanate solutions was better than that from iodide solutions in some cases, but it was poorer in other cases, and it was better than that from bromide solutions except with nitrobenzene. Furthermore, it was found that the distribution ratio, determined as a function of the ligand concentration, was always poorer when the aqueous phase contained only the sodium salt of these ligands than when it was 4M Na(X, ClO_4) (where X denotes the ligand anion). The extractions from 4M Na(X, ClO_4) were analyzed by using the stability constants for the indium complexes with these ligands in the aqueous phase, and the extraction equilibria were determined. From these results, it was concluded that these polar solvents extract not only the uncharged complex, InX_3, but also the cationic and/or anionic indium complexes as ion-pairs, with the oppositely charged ions in the background salt, and that, in some cases, the solvent extracts only charged indium species. Thus, the difference in the distribution ratio in the presence and in the absence of the background sodium perchlorate was concluded to be caused not only by the change in the activities due to the change in the total salt concentration, but also by the extraction of ion-pairs of charged indium(III) species, which should be very much enhanced by the presence of the bulk perchlorate.

In Part I of this series,[1] it was reported that indium (III) forms complexes with various uninegative ligands and that the bromide, iodide, and thiocyanate complexes are extractable into hexane containing tributylphosphate (TBP). These extraction curves were explained in terms of a successive complex formation and the extraction of the uncharged complex, InX_3 (where X^- is a uninegative ligand), into this non-polar organic solvent containing a small amount of the coordinating extractant.

In the lower ligand-concentration region in these systems, an increase in the amount of extractable uncharged complex is caused by an increase in the ligand-concentration; consequently, it enhances the distribution ratio.

In the higher ligand-concentration region, where higher anionic complexes are formed, on the other hand, the distribution ratio decreases upon an increase in the ligand-concentration, because these charged complexes are usually unextractable into non-polar organic solvents. However, if the solvent is a polar one, it is supposed that the anionic complexes may also be extracted as ion-pairs with other cations in the aqueous phase, and the distribution ratio in such systems might increase, even in the higher ligand-concentration region.

The present paper will describe the results of experiments carried out along with this line. Three polar organic solvents, 4-methyl-2-pentanone(MIBK), 4-methyl-2-pentanol (hexol), and nitrobenzene, were employed as the organic solvents. The aqueous phases equilibrated with these organic solvents were similar to that in the previous study.[1]

The equilibrium constants at 25°C were determined by a successive approximation analysis of the distribution data graphically.

Experimental

Most of the experimental procedures were the same as those described in the previous study.[1] The indium-114*m* tracer was obtained from the Radio Chemical Center, England. The 4-methyl-2-pentanone and hexol were obtained from Kanto Kagaku Co. and the Tokyo Kasei Co. respectively; they were washed with 0.1M perchloric acid, water, and 0.1M sodium hydroxide successively, and then several times with water. The nitrobenzene was also obtained from the Kanto Kagaku Co. The sodium perchlorate was prepared from perchloric acid and sodium carbonate and was recrystallized three times from water. The other reagents were of an analytical grade and were used without further purification.

Aqueous solutions containing indium(III) labelled with the indium-114*m* tracer, and various amounts of the ligand and sodium perchlorate solutions, together with one of these solvents, were placed in stoppered glass tubes (volume, 20 m*l*). The initial volume of each phase was 5 m*l*, and the aqueous phase was adjusted to be a constant ionic medium of 4M sodium perchlorate, unless otherwise mentioned. The hydrogen-ion concentration was 1×10^{-2}M for the experiments on the bromide and iodide complexes, but it was about 1×10^{-3}M for the thiocyanate complexes, and the initial concentration of indium in the aqueous phase was about 2.5×10^{-6}M. All of the procedures were carried out in a thermostatted room at 25°C. The two phases in the tubes were agitated mechanically for about two hours and then centrifuged. The γ-radioactivity of these samples was measured with a scintillation counter (NaI), and the distribution ratio was calculated as;

$$D=\frac{\gamma\text{-count-rate per m}l\text{ of the org. phase}}{\gamma\text{-count-rate per m}l\text{ of the aq. phase}}$$

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[1] Y. Hasegawa, This Bulletin, **43**, 2665 (1970).

Results

Figures 1 to 3 give the extraction of indium(III) into the three organic solvents as a function of the ligand concentration in the aqueous phase, together with the extraction into hexane-containing TBP which has been already given in Part I.[1] It will be seen from the figures that the distribution curves in the three polar organic solvent systems are rather different from that in the TBP-hexane system. As will be described later, this is due to the extraction of anionic complexes, such as InX_4^- and InX_5^{2-}, as well as to that of the uncharged complex; furthermore, that of cationic species is also assumed in some systems.

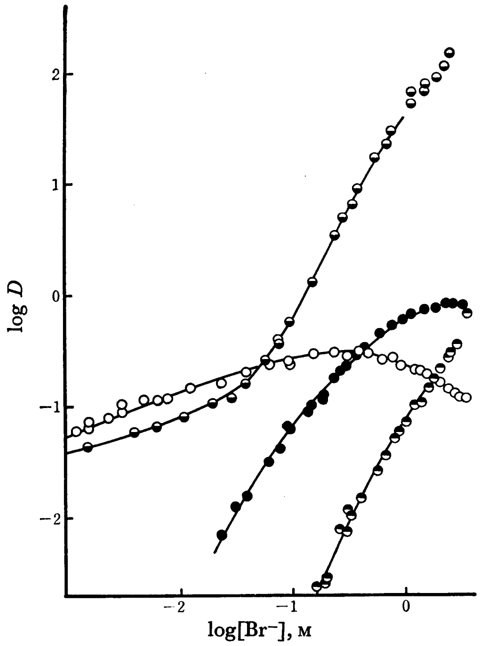

Fig. 1. The extraction of In(III) from 4M constant ionic medium containing bromide ions into various organic solvents.
◒: MIBK, ○: hexol, ●: 0.1M TBP-hexane taken from Ref. 1. ◓: nitrobenzene.

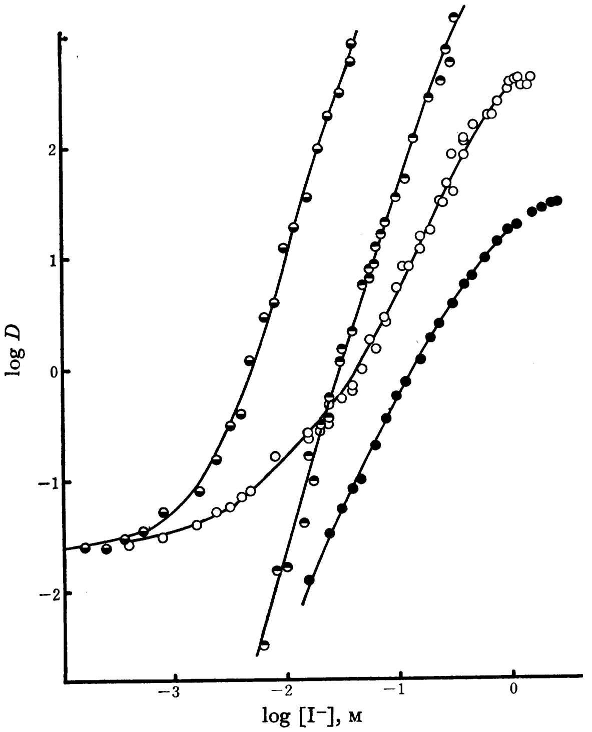

Fig. 2. The extraction of In(III) from 4M constant ionic medium containing iodide ions into various organic solvents.
◒: MIBK, ◓: nitrobenzene ○: hexol
●: 0.01M TBP-hexane taken from Ref. 1.

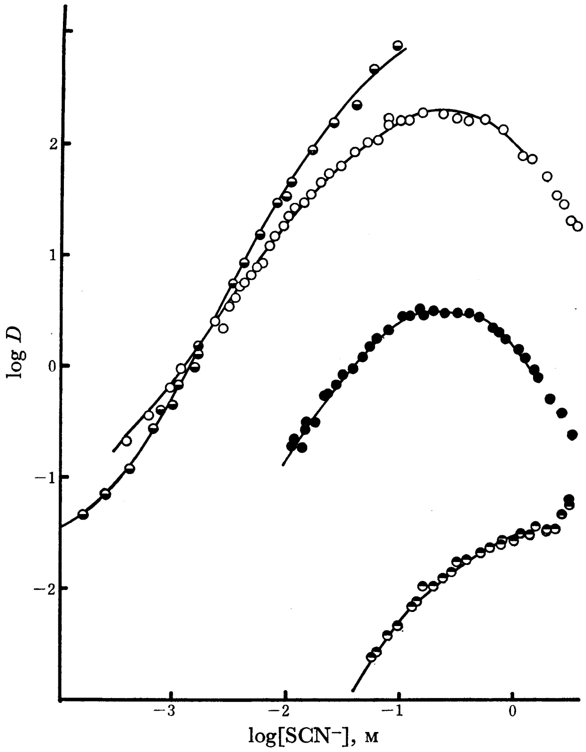

Fig. 3. The extraction of In(III) from 4M constant ionic medium containing thiocyanate ions into various organic solvents.
◒: MIBK, ○: hexol, ●: 0.01M TBP-hexane taken from Ref. 1. ◓: nitrobenzene

The following equilibrium was first assumed in order to explain the distribution ratio of the indium(III) measured experimentally (the complexes higher than the InX_5^{2-} were assumed to be very small, because they were found to be negligible under these conditions)[1]:

$$D = \frac{[\mathrm{In(III)}]_{org,t}}{[\mathrm{In(III)}]_{aq,t}} = \frac{[\mathrm{InX_3}]_{org}+[\mathrm{InX_4}]_{org,t}+[\mathrm{InX_5}]_{org,t}}{[\mathrm{In^{3+}}]+[\mathrm{InX^{2+}}]+[\mathrm{InX_2^{+}}]+[\mathrm{InX_3}]+[\mathrm{InX_4^{-}}]+[\mathrm{InX_5^{2-}}]} \tag{1}$$

The stability constant of the "*n*th" indium complex with a uninegative ligand, X^-, is defined as:

$$\beta_n = \frac{[\mathrm{InX}_n^{3-n}]}{[\mathrm{In^{3+}}][\mathrm{X^-}]^n} \tag{2}$$

The distribution constant for the uncharged complex is defined as:

$$K_{DM3} = \frac{[\mathrm{InX_3}]_{org}}{[\mathrm{InX_3}]} \tag{3}$$

The following constants were also defined for the extraction of the negatively-charged complexes:

$$K_{DM4} = \frac{[\mathrm{InX_4}]_{org,t}}{[\mathrm{InX_4}^-]} \tag{4}$$

$$K_{DM5} = \frac{[\mathrm{InX_5}]_{org,t}}{[\mathrm{InX_5}^{2-}]} \tag{5}$$

Here, the term $[\mathrm{InX}_n]_{org,t}$ denotes the total concentration of those chemical species in the organic phase containing negatively-charged indium(III) complexes (*cf.* Eq. (15) or (16)), such as $\mathrm{Na_2InX_5}$, $\mathrm{NaInX_5}^-$, and $\mathrm{InX_5^{2-}}$.

When the above-mentioned constants are introduced into Eq. (1), the following equation is obtained:

$$D = \frac{K_{DM3}\beta_3[\mathrm{X}^-]^3+K_{DM4}\beta_4[\mathrm{X}^-]^4+K_{DM5}\beta_5[\mathrm{X}^-]^5}{1+\beta_1[\mathrm{X}^-]+\beta_2[\mathrm{X}^-]^2+\beta_3[\mathrm{X}^-]^3+\beta_4[\mathrm{X}^-]^4+\beta_5[\mathrm{X}^-]^5} \tag{6}$$

An attempt was made to analyze the data in Figs. 1 to 3 graphically by using Eq. (6). However, it was not possible to explain by Eq. (6) the distribution behavior in the lowest ligand-concentration region because the distribution curves approach constant values in this region at these constant ionic medium solutions. This was assumed to be due to an extraction of positively-charged indium(III) species, InX_n^{3-n} (where $0 \leq n < 3$), most probably as ion-pairs with perchlorate ions. From this, the distribution ratio of indium(III) was assumed to be as follows:

$$D = \frac{[\mathrm{InX_0}]_{org,t}+[\mathrm{InX_1}]_{org,t}+[\mathrm{InX_2}]_{org,t}+[\mathrm{InX_3}]_{org}+[\mathrm{InX_4}]_{org,t}+[\mathrm{InX_5}]_{org,t}}{[\mathrm{In}^{3+}]+[\mathrm{InX}^{2+}]+[\mathrm{InX_2}^+]+[\mathrm{InX_3}]+[\mathrm{InX_4}^-]+[\mathrm{InX_5}^{2-}]} \tag{7}$$

Considering the extraction of these cationic indium(III) species, the following constants were also defined:

$$K_{DM0} = \frac{[\mathrm{InX_0}]_{org,t}}{[\mathrm{In}^{3+}]} \tag{8}$$

$$K_{DM1} = \frac{[\mathrm{InX_1}]_{org,t}}{[\mathrm{InX_1}^{2+}]} \tag{9}$$

$$K_{DM2} = \frac{[\mathrm{InX_2}]_{org,t}}{[\mathrm{InX_2}^+]} \tag{10}$$

A further detailed discussion of these constants will be given later. By introducing these constants and the constants in Eq. (6) into Eq. (7), the following equation could be obtained:

$$D = \frac{K_{DM0}+K_{DM1}\beta_1[\mathrm{X}^-]+\cdots+K_{DM5}\beta_5[\mathrm{X}^-]^5}{1+\beta_1[\mathrm{X}^-]+\cdots+\beta_5[\mathrm{X}^-]^5} \tag{11}$$

Equation (11) indicates that the distribution ratio in the lowest ligand-concentration or in the absence of the ligand ions can be denoted by K_{DM0} in Eq. (8). The value of K_{DM0} was very small in the extraction with nitrobenzene ($\log D = \sim -4$), but the values were rather larger in the other two solvents.

However, the constancy of the distribution constant, K_{DM1} or K_{DM2}, should not be kept when the perchlorate concentration in the aqueous phase can not be regarded as 4M. Consequently, the following expression would be more reasonable than Eq. (11):

$$D = \frac{Kex_{0,3}[\mathrm{ClO_4}^-]^3+Kex_{1,2}[\mathrm{ClO_4}^-]^2[\mathrm{X}^-]+Kex_{2,1}[\mathrm{ClO_4}^-][\mathrm{X}^-]^2+Kex_{3,0}[\mathrm{X}^-]^3+Kex_4[\mathrm{X}^-]^4[\mathrm{Na}^+]+Kex_5[\mathrm{X}^-]^5[\mathrm{Na}^+]^2}{1+\beta_1[\mathrm{X}^-]+\beta_2[\mathrm{X}^-]^2+\beta_3[\mathrm{X}^-]^3+\beta_4[\mathrm{X}^-]^4+\beta_5[\mathrm{X}^-]^5} \tag{12}$$

where $Kex_{a,(3-a)}$ and Kex_b are the extraction constants of cationic or neutral species and anionic species respectively and where they are expressed as follows:

$$\mathrm{In}^{3+} + a\mathrm{X}^- + (3-a)\mathrm{ClO_4}^- \rightleftarrows \mathrm{InX}_a(\mathrm{ClO_4})_{3-a}(org) \quad (0 \leq a \leq 3)$$

$$Kex_{a,(3-a)} = \frac{[\mathrm{InX}_a(\mathrm{ClO_4})_{3-a}]_{org}}{[\mathrm{In}^{3+}][\mathrm{X}^-]^a[\mathrm{ClO_4}^-]^{3-a}} \tag{13}$$

$$\mathrm{In}^{3+} + b\mathrm{X}^- + (b-3)\mathrm{Na}^+ \rightleftarrows \mathrm{Na}_{b-3}\mathrm{InX}_b(org) \quad (b \geq 3)$$

$$Kex_b = \frac{[\mathrm{Na}_{b-3}\mathrm{InX}_b]_{org}}{[\mathrm{In}^{3+}][\mathrm{X}^-]^b[\mathrm{Na}^+]^{b-3}} \tag{14}$$

The effect of the dissociation of the ion-pairs in the organic phase will be considered later.

The graphic analysis of the distribution data in Figs. 1 to 3 was carried out as follows. The stability constants already determined in Part I[1] and the extraction constants of uncharged species were introduced into Eq. (12). The distribution ratio was calculated as a function of the ligand concentration. When a deviation of the calculated curve from the experimental data was observed, the constants were improved. This successive approximation was continued until the best-fit curve was found. The final equilibrium constants were determined from the best-fit curve. The solid curves in the figures are the extraction curves calculated by the use of the constants.

The equilibrium constants obtained by such a graphic analysis of the data in Figs. 1 to 3 are shown in Tables 1(a) to (d).

Figures 4(A) to 4(C) show the percentage distribution of each species in the organic phase and the aqueous phase calculated from the values in Tables 1(a) to (d). The equilibrium constants were determined by using the experimental data obtained when the ligand concentration is less than 1M. Thus, the calculated extraction curves in Figs. 1 to 3 are drawn only for the experimental data obtained in the ligand-concentration region below 1M. In some systems, however, the distribution ratio was too large to determine accurately when the ligand-concentration was lower than 1M (the extraction of iodide into MIBK or nitrobenzene, or that of thiocyanate into MIBK). In such systems, the graphic analysis of the data were made by using those in the $10^{-3} < D < 10^3$ region. The percentage of the indium (III) species in the organic phase in these systems was calculated in these ligand-concentration regions which are given in Figs. 4(A) to 4(C). The figures show that the extraction of indium species containing perchlorate ions is remarkable, especially into hexol.

In the present study, the salt concentration was kept at 4M by the use of sodium perchlorate. In usual experimental work in analytical chemistry, however, the ionic concentration changes with a change in the ligand-concentration. In order to ascertain the effect of added sodium perchlorate on the distribution behavior of indium(III), some experiments were carried out in the

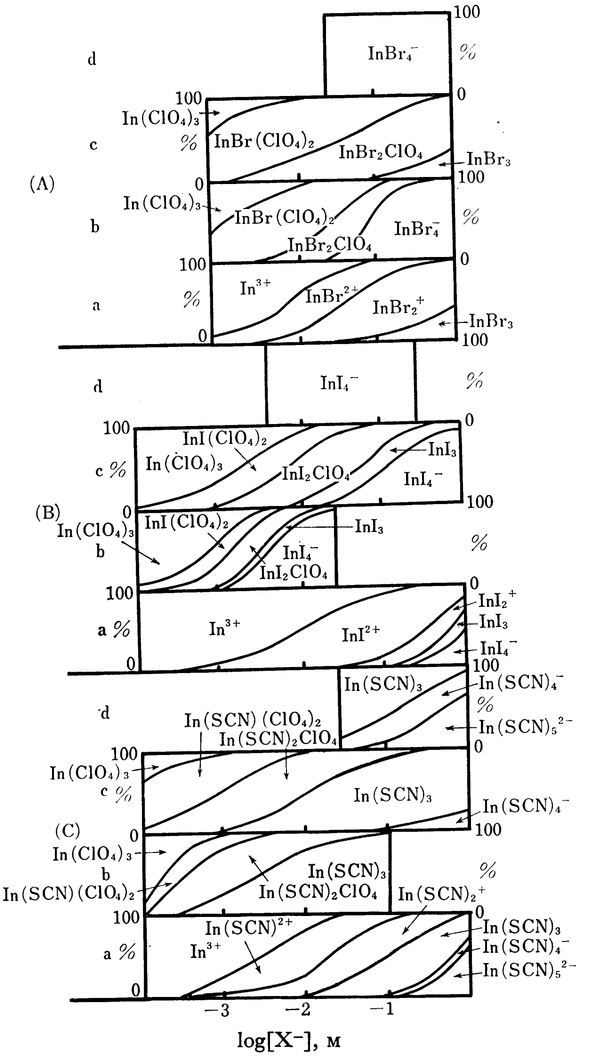

Fig. 4. The percentage distribution of In(III) species in 4M constant ionic medium containing bromide (A), iodide (B) or thiocyanate ions (C) and in the organic solvents equilibrated with the aqueous phase, within the ligand concentration range measured experimentally.

a: in aqueous phase, b: in MIBK, c: in hexol, d: in nitrobenzene

TABLE 1. EXTRACTION CONSTANTS OR DISTRIBUTION CONSTANTS OF INDIUM(III) COMPLEXES FROM 4M CONSTANT IONIC MEDIA INTO VARIOUS ORGANIC SOLVENTS

(a) Aqueous phase: 4M $NaClO_4$

Solvent	MIBK	Hexol	Nitrobenzene
$\log Kex_{0,3}$	−3.41	−3.40	<−3
$\log K_{DM0}$	−1.60	−1.59	—

(b) Aqueous phase: 4M Na(Br, ClO_4)

Solvent	MIBK	Hexol	Nitro-benzene	0.1M TBP-hexane[1)]
$\log Kex_{1,2}$	0.04	0.38	—	—
$(\log K_{DM1})$	(−1.12)	(−0.78)	—	—
$\log Kex_{2,1}$	2.17	2.26	—	—
$(\log K_{DM2})$	(−0.39)	(∼−0.3)	—	—
$\log Kex_{3,0}$	—	2.47	—	3.35
$(\log K_{DM3})$	—	(−0.77)	—	(0.11)
$\log Kex_4$	4.53	—	1.81	—
$(\log K_{DM4})$	(2.95)	—	(0.23)	—

The stability constants for the bromide complexes in the aqueous phase employed for the analysis are[1)] $\log\beta_1=2.36$, $\log\beta_2=3.16$, $\log\beta_3=3.24$, and $\log\beta_4=2.18$.

(c) Aqueous phase: 4M Na(I, ClO_4)

Solvent	MIBK	Hexol	Nitro-benzene	0.01M TBP-hexane[1)]
$\log Kex_{1,2}$	0.00	−0.22	—	—
$(\log K_{DM1})$	(−0.77)	(−0.99)	—	—
$\log Kex_{2,1}$	3.61	2.61	—	—
$(\log K_{DM2})$	(2.03)	(1.03)	—	—
$\log Kex_{3,0}$	6.20	4.20	—	3.83
$(\log K_{DM3})$	(4.00)	(2.00)	—	(1.63)
$\log Kex_4$	8.6	4.8	6.1	—
$(\log K_{DM4})$	(6.70)	(2.85)	(4.23)	—

The stability constants for the iodide complexes in the aqueous phase employed for the analysis are[1)] $\log\beta_1=1.97$, $\log\beta_2=2.18$, and $\log\beta_3=2.20$. The formation of the fourth complex $\log\beta_4=\sim 2.5$ is also assumed in this study in order to analyze the extraction data with hexol. However, this constant could be somewhat erroneous.

(d) Aqueous phase: 4M Na(SCN, ClO_4)

Solvent	MIBK	Hexol	Nitro-benzene	0.01M TBP-hexane[1)]
$\log Kex_{1,2}$	0.70	1.40	—	—
$(\log K_{DM1})$	(−0.54)	(0.16)	—	—
$\log Kex_{2,1}$	5.08	5.08	—	—
$(\log K_{DM2})$	(1.57)	(1.57)	—	—
$\log Kex_{3,0}$	8.25	7.59	2.90	5.80
$(\log K_{DM3})$	(3.15)	(2.49)	(−2.20)	(0.70)
$\log Kex_4$	—	6.51	3.00	—
$(\log K_{DM4})$	—	(2.54)	(−0.97)	—
$\log Kex_5$	—	—	2.70	—
$(\log K_{DM5})$	—	—	(−1.55)	—

The stability constants for the thiocyanate complexes in the aqueous phase employed for the analysis are[1)] $\log\beta_1=2.44$, $\log\beta_2=4.11$, $\log\beta_3=5.10$, $\log\beta_4=4.57$, and $\log\beta_5=5.45$.

absence of perchlorate ions. Figures 5 to 7 give the distribution ratios in bromide, iodide, and thiocyanate systems where sodium perchlorate is absent in the aqueous phase. The solid curves in these figures are the extraction curves obtained in the 4M constant ionic medium; they have been taken from Figs. 1 to 3 in order to make a comparison with these experimental data. The distribution ratio decreases abruptly with a decrease in the ligand concentration when the ionic concentration changes. In other words, the distribution ratio of indium(III) is very much enhanced by the presence of the sodium perchlorate in the aqueous phase.

The results given above may be summarized as follows: i) The extraction curves into these three polar solvents are quite different from that into hexane containing a small amount of TBP, which could be regarded as an essentially non-polar solvent. This can be explained by saying that the only extractable species into hexane solutions is the uncharged complex, InX_3, while those extractable into polar solvents include not only the uncharged complex but also the ion-pairs of

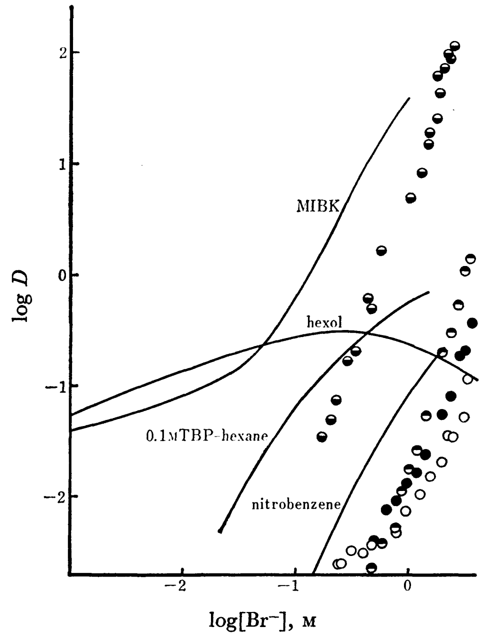

Fig. 5. The extraction of In(III) from aqueous solutions containing sodium bromide (ionic concentrations are varied) into various organic solvents. The solid curves indicate the extraction from 4 M Na(Br, ClO_4).

◒: MIBK, ◓: nitrobenzene ●: 0.1 M TBP-hexane, ○: hexol

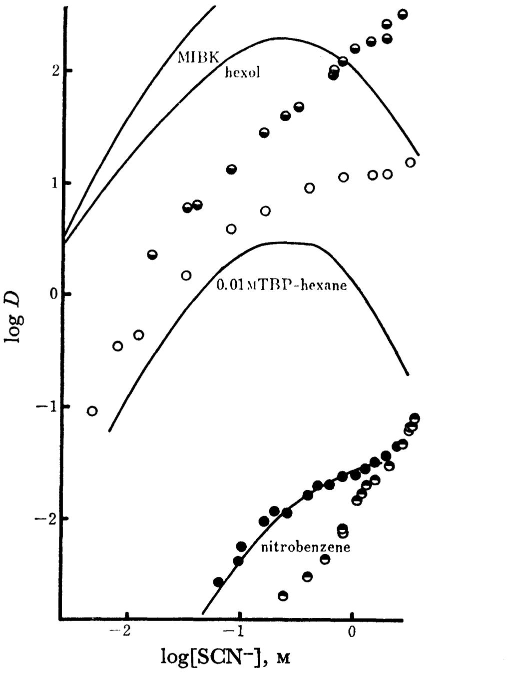

Fig. 7. The extraction of In(III) from aqueous solutions containing sodium thiocyanate into various organic solvents. The solid cruves indicate the extraction from 4 M Na(SCN, ClO_4).

◒: MIBK, ◓: nitrobenzene, ○: hexol, ●: 0.01 M TBP-hexane

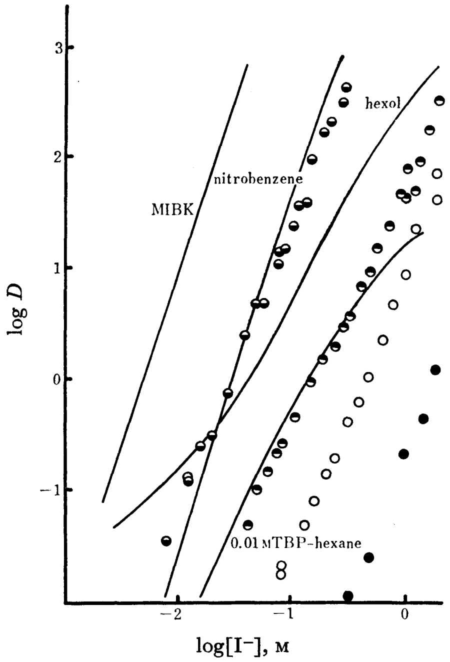

Fig. 6. The extraction of In(III) from aqueous solutions containing sodium iodide into various organic solvents. The solid curves indicate the extraction from 4 M Na(I, ClO_4).

◒: MIBK, ◓: nitrobenzene, ○: hexol, ● 0.01M TBP-hexane

the cationic species and/or the anionic ones. ii) MIBK extracts both anionic and cationic species. The extraction of anionic thiocyanate species into MIBK was not confirmed in the ligand-concentration region studied. However, it is possible that the extraction of the anionic species occurs when the ligand concentration is higher (above 5×10^{-2}M). The extraction of indium(III) complexes from the 4 M constant ionic media with MIBK is usually better than with the other two solvents. The extraction with MIBK is always the best when sodium perchlorate is absent in the aqueous phase. iii) Nitrobenzene, which has a much higher dielectric constant but a smaller solvation ability, extracts the ion-pairs of anionic complexes better than uncharged ones; furthermore, the extraction from the thiocyanate system is extremely inferior to that from other systems. iv) The distribution curves obatined by introducing the constants in Tables 1(a) to (d) as defined by Eqs. (2), (13), and (14), into Eq. (12) were found to fit with the data. Thus, it was concluded that the assumptions for the complex species in the two phases and the equilibrium constants for them listed in Tables 1(a) to (d) can explain the results within the limits of experimental accuracy.

Discussion

Not very much seems to know about the dissociation of ion-pairs in the organic phase of solvent extraction systems. However, the dissociation in the organic phase should be one of the most important factors to be taken into account in order to make a reasonable analysis of the experimental data. In the present study, this has been treated as follows.

As may be seen from Eqs. (4), (5), (8), (9), and (10), the concentration ratios of the charged species in the two phases are assumed to be constant, or it is assumed that Eq. (12) can be substituted for Eq. (7) only by using the extraction constant of the ion-pairs despite the possibility of the dissociation of the ion-pairs in the organic phase. However, this should not be true from a general standpoint.

As has been pointed out,[2] the total concentration of the fourth or the fifth anionic complexes in the organic phase can be described as follows if the ion-pairs are partially dissociated in the organic phase:

$$[\mathrm{InX_4}]_{org,t} = [\mathrm{NaInX_4}]_{org} + [\mathrm{InX_4}^-]_{org} \tag{15}$$

$$[\mathrm{InX_5}]_{org,t} = [\mathrm{Na_2InX_5}]_{org} + [\mathrm{NaInX_5}^-]_{org} + [\mathrm{InX_5}^{2-}]_{org} \tag{16}$$

The dissociation of the ion-pairs in the organic phase can be denoted as follows:

$$\mathrm{Na}_{b-3}\mathrm{InX}_b(org) \rightleftarrows (\mathrm{Na}_{b-3-n}\mathrm{InX}_b)^{n-}_{org} + n\mathrm{Na}^+(org)$$

$$Kdiss_{b,n} = \frac{[\mathrm{Na}_{b-3-n}\mathrm{InX}_b{}^{n-}]_{org}[\mathrm{Na}^+]^n_{org}}{[\mathrm{Na}_{b-3}\mathrm{InX}_b]_{org}} \tag{17}$$

where b is larger than 3.

By introducing Eqs. (14) and (17) into Eq. (15), the following equation is obtained:

$$[\mathrm{InX_4}]_{org,t} = Kex_4[\mathrm{In}^{3+}][\mathrm{X}^-]^4[\mathrm{Na}^+](1+Kdiss_{4,1}[\mathrm{Na}^+]^{-1}_{org}) \tag{18}$$

Equation (18) shows that the concentration of the anionic complex in the organic phase is proportional to that of sodium ions in the aqueous phase if no dissociation of the ion-pairs occurs. On the other hand, when the ion-pairs dissociate and charged species are formed in the organic phase, the concentration of the ion-pairs is also dependent on the sodium concentration in the organic phase. In the present study, the aqueous sodium ion concentration was kept as 4M and the extraction of hydrogen or hydroxide ions could be disregarded. Thus, the sodium concentration in the organic phase could be described from the point of view of electrical neutrality as:

$$[\mathrm{Na}^+]_{org} = [\mathrm{ClO_4}^-]_{org} + [\mathrm{X}^-]_{org} + [\mathrm{InX_4}^-]_{org} + [\mathrm{NaInX_5}^-]_{org} + 2[\mathrm{InX_5}^{2-}]_{org} \tag{19}$$

According to the previous papers, the sodium concentration in nitrobenzene, MIBK, and hexol in an equilibrium with 4M sodium perchlorate are 4×10^{-4}M,[3] 6×10^{-2}M, and 1×10^{-2}M[4] respectively. The organic phases studied in this work could contain sodium ions which are produced by the dissociation of the extracted ion-pairs of anionic indium(III) complexes other than those produced by the dissociation of the sodium perchlorate. However, since the indium(III) concentration is very low (the initial aqueous concentration is about 3×10^{-6}M), the contribution of the sodium ions from the ion-pairs of the complexes to the total sodium ion concentration in the organic phase should be very small when the aqueous phase can be regarded as nearly a 4M sodium perchlorate solution.

From this, the total sodium ion concentration in the organic phase given in Eq. (19) can be regarded as constant; consequently, the values in parentheses in Eq. (18) should also be constant in the present study. Thus, it should be reasonable to assume that the ratio of the total concentrations of the fourth complex in the two phases denoted by K_{DM4} in Eq. (4) is a constant under the conditions employed here. For a similar reason, the concentration ratio of the fifth complex may also be assumed to be a constant, K_{DM5}, as is given in Eq. (5).

As may be seen from Eq. (19), the above assumption is not valid when the extraction of the ligand salt is no longer negligible, because the extraction of sodium salts as ion-pairs and their dissociation in the organic phase can be generally assumed when the anion is different. Thus, the extraction data in the higher ligand-concentrations could not be treated by assuming the constancy of K_{DM4} and K_{DM5}.

A similar problem is also present in the analysis of the extraction of ion-apirs with perchlorate ions. The problem of the extracted ion-pairs of cationic species with perchlorate ions should also be considered like the dissociation of sodium ions. When they partially dissociate in the organic phase, the total concentration of indium(III) species may be denoted as follows:

$$[\mathrm{InX_0}]_{org,t} = [\mathrm{In(ClO_4)_3}]_{org} + [\mathrm{In(ClO_4)_2}^+]_{org} + [\mathrm{InClO_4}^{2+}]_{org} + [\mathrm{In}^{3+}]_{org} \tag{20}$$

$$[\mathrm{InX_1}]_{org,t} = [\mathrm{InX(ClO_4)_2}]_{org} + [\mathrm{InXClO_4}^+]_{org} + [\mathrm{InX}^{2+}]_{org} \tag{21}$$

$$[\mathrm{InX_2}]_{org,t} = [\mathrm{InX_2ClO_4}]_{org} + [\mathrm{InX_2}^+]_{org} \tag{22}$$

The dissociation of the second ion-pair in the organic phase may be described as:

$$\mathrm{InX_2ClO_4}(org) \rightleftarrows \mathrm{InX_2}^+(org) + \mathrm{ClO_4}^-(org)$$

$$Kdiss'_{2,1} = \frac{[\mathrm{InX_2}^+]_{org}[\mathrm{ClO_4}^-]_{org}}{[\mathrm{InX_2ClO_4}]_{org}} \tag{23}$$

From Eqs. (13) and (23), Eq. (22) may be described as:

$$[\mathrm{InX_2}]_{org,t} = Kex_{2,1}[\mathrm{In}^{3+}][\mathrm{X}^-]^2[\mathrm{ClO_4}^-] \times (1+Kdiss'_{2,1}[\mathrm{ClO_4}]^{-1}_{org}) \tag{24}$$

A similar but more complicated treatment is necessary for the term of $[\mathrm{InX_0}]_{org,t}$ or $[\mathrm{InX_1}]_{org,t}$.

Thus, like as the contribution of the sodium ions in the analysis of the extraction data of anionic complexes, the contribution of the perchlorate ions should be taken into account when the ion-pairs of cationic complexes with perchlorate ions dissociate in the organic phase. The concentration of perchlorate ions in the organic phase is dependent not only on the perchlorate concentration in the aqueous phase, but also on the total concentration of the dissociated ion-pairs of indium(III) species with perchlorate ions. However, for the same reason discussed in connection with the sodium concentration in the organic phase (that is, the concentration of indium(III) is much smaller than that of sodium perchlorate in the oragnic phase), it is possible to assume that the concentration ratio of cationic indium(III) species in the two phases denoted by Eq. (8), (9), or (10) is constant under the conditions employed in this study. Furthermore, the data obtained in solutions up to a ligand-concentration of 1M, where 25% of the perchlorate ions is replaced by the ligand anion, have been analyzed statistically. It seems to be very difficult to know if an aqueous solution containing 1M ligand salt in the 4M total salt can still be regarded practically as

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[3] T. Sekine and D. Dyrssen, *Anal. Chim. Acta*, **45**, 433 (1969).

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a 4M sodium perchlorate solution in the above statistical analysis. The present authors, however, consider that this is not very unreasonable because the constants which have been determined on the above assumption seem to explain the experimental data well, as can be seen from Figs. 1 to 3. Actually, the data fit the calculated curve well, even in the highest ligand concentration region studied, except for the extraction of the thiocyanate complexes in the highest ligand-concentration region into nitrobenzene.

As can be seen from Figs. 5 to 7, the extraction curves from sodium salt solutions of the ligand anions containing no sodium perchlorate (the total concentration is not kept constant) were quite different from the extraction curves in the 4M constant ionic media systems. As has been shown in Figs. 4(A) to 4(C), the majority of the extracted indium(III) species from the 4M sodium perchlorate media consist of charged indium(III) species in these polar solvents: moreover, as may be seen from Eq. (13) or (14), the extraction of these charged species is dependent not only on the concentration of ligand anions, but also on the concentration of sodium ions or of perchlorate ions. In the aqueous solutions containing no sodium perchlorate, the concentration of perchlorate ions is zero and that of sodium ions is always lower than 4M. Thus, no extraction of ion-pairs with cationic species and perchlorate ions, and much less extraction of ion-pairs with the anionic species and sodium ions, should occur from these aqueous solutions; this should be one of the reasons for the poorer extractions of indium(III) from these aqueous solutions than from 4M sodium perchlorate constant ionic media.

However, the above explanation may not cover all the reasons for these poorer extractions. As can be seen from Eq. (12), the distribution ratio is also dependent on the stability constants of the aqueous complexes, β_n, and the distribution constants, K_{DMn}. When the ionic concentration changes, the activity coefficients of each species may be changed, and then the constants defined by the stoichiometric concentration scale should also be changed. These influences of the background salt on the distribution behavior of the indium(III) complexes will be reported on in a more quantitative manner in the following papers of this series.

The aqueous phase in analytical work usually contains only the ligand anions and no perchlorate ions. The extraction from constant ionic media is here different from the data of analytical experiments. For example, the extraction curve of indium(III) from 4M Na(SCN, ClO_4) into hexol or TBP-hexane has a peak where the ligand concentration is about 2×10^{-1}M; on the other hand, the extraction curves from thiocyanate solutions decrease with the decrease in the anion concentration, and also, according to the extraction of ion-pairs with perchlorate ions, the curves are very different from each other in the lower ligand-concentration region. The analysis of the equilibrium in such systems, in which the ionic concentrations are not kept constant, is very difficult.

The extraction of a charged indium(III) species which was negligible in quantity into hexane containing a small amount of TBP is very remarkable in these polar solvents. For the extraction of charged species as ion pairs, both solvation on the central metal ion and a polar nature (or a high dielectric constant) of the organic solvent are important. The solvation should be largest in MIBK, and this is probably the reason why MIBK shows the best extraction in most cases. The tendency for the large extraction of anionic complexes into nitrobenzene, which does not have a large ability for the solvation, may be due to the very high dielectric constant of this solvent. These properties in hexol are between those of these two organic solvents, and the intermolecular hydrogen bonds in this solvent must play an important role, although further information on the distribution equilibria of various species will be necessary before a detailed discussion of the extraction behavior will become possible.

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