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Solvent Extraction of Several Divalent Metal Ions with 4-Isopropyltropolone into Chloroform in the Absence and Presence of Trioctylphosphine Oxide

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The solvent extraction of divalent metal ions, manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) in aqueous 0.1 mol dm^{-3} sodium nitrate solutions with 2-hydroxy-4-(1-methylethyl)-2, 4, 6-cycloheptatrien-1-one (4-isopropyltropolone; Hipt) into chloroform was studied in the absence and presence of trioctylphosphine oxide (TOPO). When the concentration of metal ions (M^{2+}) was 1×10^{-5} to 1×10^{-4} mol dm^{-3} in the initial aqueous solutions, the extracted species of the metal ions in the absence of TOPO were only the mononuclear complex, $M(ipt)_2$, with copper(II); these species were both the mononuclear complex, $M(ipt)_2$, and the mononuclear self-adduct complex, $M(ipt)_2\cdot Hipt$, with zinc(II); they were both the mononuclear complex, $M(ipt)_2$, and the dinuclear complex, $M_2(ipt)_4$, with cobalt(II) and cadmium(II); and they were predominantly the dinuclear complex, $M_2(ipt)_4$, with nickel(II) and manganese(II). It was also found that the extraction of manganese(II), cobalt(II), nickel(II), zinc(II), and cadmiun(II) was enhanced when TOPO was added into the organic phase. This was explained in terms of the formation of mononuclear adduct complex, $M(ipt)_2TOPO$, from $M(ipt)_2$, $M(ipt)_2\cdot Hipt$, and/or $M_2(ipt)_4$. The extraction constants for those species were determined. The extractability and the tendency to form dinuclear complexes are discussed.

2-Hydroxy-4-(1-methylethyl)-2,4,6-cycloheptatrien-1-one(4-isopropyltropolone, Hinokitiol; Hipt) is an effective chelating extractant for several metal ions, as was demonstrated by Dyrssen with twenty four metal ions already in 1962.[1] The extraction of metal ions from weakly acid aqueous solutions into chloroform with this reagent is approximately quantitative with most of these metal ions under suitable conditions. The extracted species with this extractant was described to be in the "self-adduct" chelate complex form with many metal ions: When a metal ion, M^{m+}, was extracted with Hipt, the extracted species was often in the $M(ipt)_m\cdot Hipt$ form. Thus, the extraction was m+1 order dependent on the concentration of the reagent in the acid form when the hydrogen-ion concentration was kept constant. However, it was found recently that when cobalt(II) was extracted with 4-isopropyltropolone in toluene, the distribution ratio was dependent not only on the concentration of extractant but also on the initial concentration of cobalt(II) in the aqueous phase: It was higher when the metal concentration was higher but under otherwise identical conditions.[2] This was estimated to be due to extraction of polynuclear chelate complexes. On the other hand, it was reported in other papers[3,4] that the distribution ratio of thallium(I) and silver(I) with 4-isopropyltropolone into chloroform was not dependent on the metal concentration. Thus extraction of polynuclear species of these two metal ions did not occur.

The present work was undertaken in order to determine the extraction behavior of metal ions with this reagent; furthermore, especially we want to investigate the extraction of polynuclear chelate complexes and also adduct chelate complexes with a solvating type ligand (synergism). The metal ions studied were manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmiun(II) and the solvating type ligand was trioctylphosphine oxide (TOPO). The initial metal concentration in the aqueous phase was 1×10^{-5} to 1×10^{-4} mol dm^{-3}. This concentration range is much higher than the tracer levels in the previous study;[1] consequently, there was much more possibility to find extractions of polynuclear complexes.

Experimental

All of the reagents were of reagent grade. The 4-isopropyltropolone was obtained from Takasago Koryo Co. Trioctylphosphine oxide (TOPO) was obtained from Dojindo Laboratories. These reagents were purified by recrystallization from cyclohexane. The chloroform was washed several times with water and was used within a week after the purification. Aqueous solutions of the metal ions were supplied by Wako Pure Chemical Industries, Ltd. and they were used as the stock solution. The solvent-extraction experiments were carried out in a thermostated room at 298 K.

The two-phase distribution of 4-isopropyltropolone in the absence and presence of TOPO was determined as follows. A 10 cm^3 portion of chloroform solution containing 1×10^{-3} to 0.1 mol dm^{-3} of 4-isopropyltropolone and none or 1×10^{-3} to 0.2 mol dm^{-3} of TOPO and the same volume of an aqueous solution containing 0.010 mol dm^{-3} nitric acid and 0.090 mol dm^{-3} sodium nitrate were placed in a stoppered glass tube (capacity 50 cm^3). The two phases were agitated for one hour and then centrifuged off. Then the aqueous phase was transferred into another tube and agitated with a portion of chloroform. The amount of 4-isopropyltropolone extracted into this chloroform was determined from the optical absorption at 320 nm.

The extraction of metal ions was studied as follows. A portion of 0.1 mol dm^{-3} sodium nitrate solution containing a certain amount of acetate buffer (the total acetate concentration was 1×10^{-3} to 0.01 mol dm^{-3}) or nitric acid was placed in the stoppered glass tube; then a 10 cm^3 portion of chloroform containing 2×10^{-3} to 0.1 mol dm^{-3} of 4-isopropyltropolone and none or 1×10^{-3} to 0.2 mol dm^{-3} of TOPO was added. The two phases were agitated vigorously in order to equilibrate the reagents in the two-phase system and then an aqueous solution containing 1×10^{-5} to 1×10^{-4} mol dm^{-3} of one of the metal ions was added. Then the two phases were vigorously agitated for one hour and then centrifuged off, except when manganese(II) was extracted. When the metal ion was manganese(II), the two phases were agitated for 10 to 30s in order to prevent the oxidation which occurred during a prolonged two-phase agitation. The metal ions in the equilibrated organic phase were stripped by 0.1 to 4 mol dm^{-3} nitric acid. The metal content in this stripped solution and that in the equilibrated aqueous phase were determined by atomic absorption spectrometry. The hydrogen-ion concentration in the equilibrated aqueous phase was measured by potentiometry.

Statistical

In the present paper, any chemical species in the organic phase is denoted by the subscript "org", and one in the aqueous phase is given without any subscript. The volume of the two liquid phases is assumed to be the same. The metal ion is represented by M^{2+} and the 4-isopropyltropolone is denoted by HA. The two-phase distribution and acid dissociation equilibrium of HA can be written as:

$$\mathrm{HA} \rightleftarrows \mathrm{HA}_{\mathrm{(org)}}; \qquad K_{\mathrm{d}} = [\mathrm{HA}]_{\mathrm{org}}[\mathrm{HA}]^{-1}. \tag{1}$$

$$\mathrm{HA} \rightleftarrows \mathrm{H}^{+} + \mathrm{A}^{-}; \qquad K_{\mathrm{a}} = [\mathrm{H}^{+}][\mathrm{A}^{-}][\mathrm{HA}]^{-1}. \tag{2}$$

From these equations, the concentration of extractant anion, A^-, can be calculated by the following equation:

$$[\mathrm{A}^{-}] = [\mathrm{HA}]_{\mathrm{initial}}/(1+(K_{\mathrm{d}}+1)[\mathrm{H}^{+}]K_{\mathrm{a}}^{-1}). \tag{3}$$

When polynuclear metal species are extracted, the distribution ratio of metal ions, $[\mathrm{M(II)}]_{\mathrm{org,total}}/[\mathrm{M(II)}]_{\mathrm{aq,total}}$, can be written as:

$$\begin{aligned} D &= \Sigma\Sigma j[\mathrm{M}_j\mathrm{A}_{2j}\cdot a\mathrm{HA}]_{\mathrm{org}}/\Sigma[\mathrm{MA}_p{}^{2-p}] \\ &= \Sigma\Sigma jK_{\mathrm{ex}ja}[\mathrm{M}^{2+}]^{(j-1)}[\mathrm{A}^{-}]^{2j}[\mathrm{HA}]_{\mathrm{org}}{}^{a}/\Sigma\beta_p[\mathrm{A}^{-}]^{p} \end{aligned} \tag{4}$$

where

$$K_{\mathrm{ex}ja} = [\mathrm{M}_j\mathrm{A}_{2j}\cdot a\mathrm{HA}]_{\mathrm{org}}/[\mathrm{M}^{2+}]^{j}[\mathrm{A}^{-}]^{2j}[\mathrm{HA}]_{\mathrm{org}}{}^{a} \tag{5}$$

$$\beta_p = [\mathrm{MA}_p{}^{2-p}]/[\mathrm{M}^{2+}][\mathrm{A}^{-}]^{p}. \tag{6}$$

In the presence of TOPO, the distribution ratio of the divalent metal ions can be written as:

$$\begin{aligned} D &= (\Sigma\Sigma j[\mathrm{M}_j\mathrm{A}_{2j}\cdot a\mathrm{HA}]_{\mathrm{org}} \\ &\quad +\Sigma\Sigma\Sigma j[\mathrm{M}_j\mathrm{A}_{2j}(\mathrm{TOPO})_b\cdot a\mathrm{HA}]_{\mathrm{org}})/\Sigma[\mathrm{MA}_p{}^{2-p}] \\ &= (\Sigma\Sigma K_{\mathrm{ex}ja}j[\mathrm{M}^{2+}]^{(j-1)}[\mathrm{A}^{-}]^{2j}[\mathrm{HA}]_{\mathrm{org}}{}^{a} \\ &\quad +\Sigma\Sigma\Sigma K_{\mathrm{ex}jab}[\mathrm{M}^{2+}]^{(j-1)}[\mathrm{A}^{-}]^{2j}[\mathrm{HA}]_{\mathrm{org}}{}^{a}[\mathrm{TOPO}]_{\mathrm{org}}{}^{b} \\ &\quad /\Sigma\beta_p[\mathrm{A}^{-}]^{p}, \end{aligned} \tag{7}$$

where

$$\begin{aligned} K_{\mathrm{ex}jab} &= [\mathrm{M}_j\mathrm{A}_{2j}(\mathrm{TOPO})_b\cdot a\mathrm{HA}]_{\mathrm{org}} \\ &\quad /[\mathrm{M}^{2+}]^{j}[\mathrm{A}^{-}]^{2j}[\mathrm{HA}]_{\mathrm{org}}{}^{a}[\mathrm{TOPO}]_{\mathrm{org}}{}^{b}. \end{aligned} \tag{8}$$

The data can be calculated on the basis of a certain equation by using a least squares computer program.

Results

Two-Phase Distribution Equilibrium of 4-Isopropyltropolone in the Absence and Presence of Trioctylphosphine Oxide. It was found that the distribution ratio of 4-isopropyltropolone was not dependent on the initial concentration of this reagent in the range of 1×10^{-3} to 0.2 mol dm^{-3}. This suggests that the dimerization of Hipt in chloroform should be negligible. The two phase distribution of 4-isopropyltropolone was also measured when the organic phase contained 1×10^{-3} to 0.2 mol dm^{-3} TOPO. It was found that the distribution ratio of this reagent was not dependent on the concentration of TOPO. Thus the association of Hipt with TOPO in the organic phase in this concentration range was negligible. The value of two-phase distribution constant of 4-isopropyltropolone, K_{d} in Eq. 1, was determined to be $10^{3.37}$. The value of acid dissociation constant, K_{a} in Eq. 2, when the aqueous phase contained 0.1 mol dm^{-3} sodium salt was taken from Ref. 1 to be $10^{-7.04}$.

Extraction of Metal Ions with 4-Isopropyltropolone in the Absence of Trioctylphosphine Oxide. Figure 1 gives the extraction curves of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) as a function of the concentration of 4-isopropyltropolonate anion in the aqueous phase in the absence and presence of 0.1 mol dm^{-3} of TOPO when the initial concentration of metal ion in the aqueous phase is 1×10^{-4} mol dm^{-3}. The details of the statistical treatments of these data are further described later, with the extraction data of cobalt(II) and zinc(II) as the example.

Figure 2 gives the extraction curves of cobalt(II) as a function of the concentration of 4-isopropyltropolonate anion in the aqueous phase when the initial concentration of metal ion is 1×10^{-5} (closed symbols) and 1×10^{-4} (open symbols) mol dm^{-3}. As can be seen from Fig. 2, the distribution ratio of cobalt(II) is higher when the metal concentration in the initial aqueous phase is higher but the other conditions are identical. This can be explained on the assumption that the extracted metal species are not only mononuclear but also polynuclear. Moreover, even when the concentration of 4-isopropyltropolone in the organic phase is different, the data fall on the same curve. As can be seen from Eq. 4, this indicates that the metal ion in the extracted species does not combine with Hipt molecules, that is, self-adduct species are not extracted.

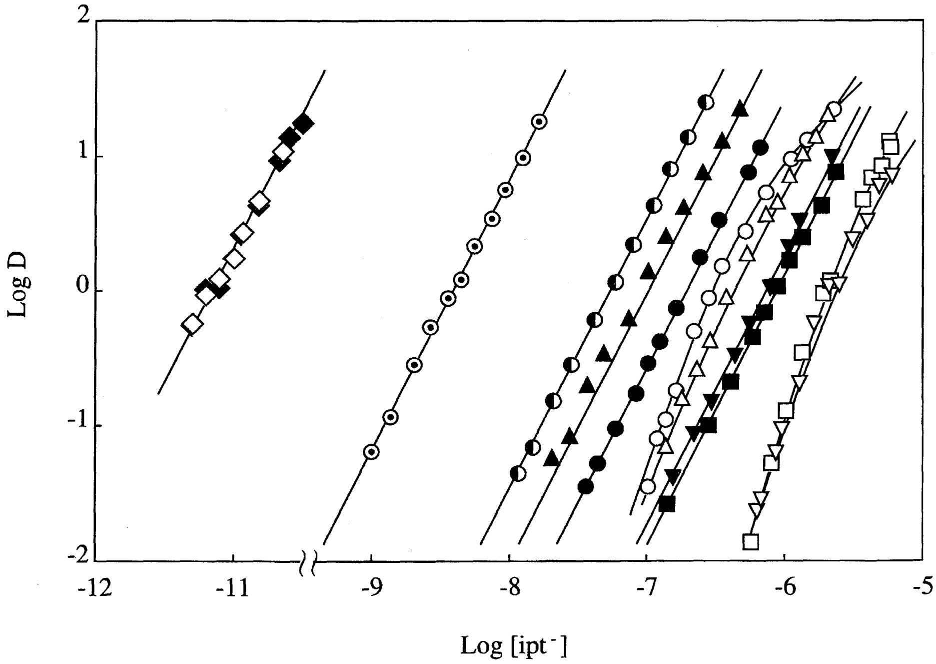

Fig. 1. Distribution ratio of manganese(II) (□,■), cobalt(II) (△,▲), nickel(II) (○,●), copper(II) (◇,◆), zinc(II) (◑,◉), and cadmium(II) (▽,▼) as a function of the concentration of 4-isopropyltropolonate anion in the absence and presence of TOPO, respectively. The initial concentration of metal ions is 1×10^{-4} mol dm^{-3} and that of 4-isopropyltropolone is 0.01 mol dm^{-3} for copper(II) and 0.1 mol dm^{-3} for other five metal ions. The solid lines were calculated on the basis of Eqs. 4 and 7 by using the values of constants in Table 1.

In order to determine the extent of extraction of polynuclear species, the following statistical treatments were carried out. The total metal concentration in the aqueous phase is written as:

$$[\mathrm{M(II)}]_{\mathrm{aq,total}} = [\mathrm{M}^{2+}] + [\mathrm{M(ipt)}^{+}] + \cdots = [\mathrm{M}^{2+}](1 + \beta_1[\mathrm{ipt}^-] + \cdots). \quad (9)$$

Thus the concentration of metal ions in the aqueous phase at equilibrium can be written as:

$$[\mathrm{M}^{2+}] = [\mathrm{M(II)}]_{\mathrm{aq,total}}/(1+\beta_1[\mathrm{ipt}^-] + \cdots). \quad (10)$$

The total metal concentration in the organic phase can be written as follows, when the formation of self-adduct, $\mathrm{M(ipt)_2}\cdot\mathrm{Hipt}$, is negligible:

$$\begin{aligned}[\mathrm{M(II)}]_{\mathrm{org,total}} &= [\mathrm{M(ipt)_2}]_{\mathrm{org}} + 2[\mathrm{M_2(ipt)_4}]_{\mathrm{org}} + \cdots \\ &= K_{\mathrm{ex10}}[\mathrm{M}^{2+}][\mathrm{ipt}^-]^2 + 2K_{\mathrm{ex20}}[\mathrm{M}^{2+}]^2[\mathrm{ipt}^-]^4 + \cdots. \quad (11)\end{aligned}$$

By introducing Eq. 10 into Eq. 11, the following equation is obtained:

$$\begin{aligned}[\mathrm{M(II)}]_{\mathrm{org,total}} = \; & K_{\mathrm{ex10}}[\mathrm{M}^{2+}]_{\mathrm{aq,total}}[\mathrm{ipt}^-]^2/(1 + \beta_1[\mathrm{ipt}^-] + \cdots) \\ & + 2K_{\mathrm{ex20}}[\mathrm{M}^{2+}]^2[\mathrm{ipt}^-]^4/(1+\beta_1[\mathrm{ipt}^-] + \cdots)^2 + \cdots. \quad (12)\end{aligned}$$

On the basis of Eq. 12, the extraction of polynuclear species may be known from the slope of the $\log[\mathrm{M(II)}]_{\mathrm{org,total}}$ vs. $\log[\mathrm{M}^{2+}]_{\mathrm{aq,total}}[\mathrm{ipt}^-]^2/(1+\beta_1[\mathrm{ipt}^-]+\cdots)$ plot, as was described in previous papers.[5—10)] The data were calculated by a successive approximation method using a least squares computer program. After trials, the best-fit was obtained by assuming the extraction of $\mathrm{Co(ipt)_2}$ and $\mathrm{Co_2(ipt)_4}$, and formation of the first complex $\mathrm{Co(ipt)^+}$ in the aqueous phase. The values of K_{ex10}, K_{ex20}, and β_1 which gave the best-fit are listed in Table 1. Figure 3 gives the $\log[\mathrm{Co(II)}]_{\mathrm{org,total}}$ vs. $\log[\mathrm{Co}^{2+}]_{\mathrm{aq,total}}[\mathrm{ipt}^-]^2/(1+\beta_1[\mathrm{ipt}^-])$ plot when β_1 is the best-fit value, $10^{5.7}$. The solid lines in Fig. 2 in the absence of TOPO and in Fig. 3 were calculated on the basis of Eqs. 4 and 12 by using the values of constants in Table 1. The dotted lines in Fig. 3 are the calculated plots when the complex in the aqueous phase is assumed to be negligible. The data of the other metal ions in Fig. 1 except zinc(II) were also analyzed in the same manner. The extracted species was only the mononuclear complex, $\mathrm{M(ipt)_2}$, with copper(II); these species were both the mononuclear complex, $\mathrm{M(ipt)_2}$, and dinuclear complex, $\mathrm{M_2(ipt)_4}$, with cobalt(II) and cadmium(II); and they were predominantly the dinuclear complex, $\mathrm{M_2(ipt)_4}$, with nickel(II) and manganese(II) under these experimental conditions. The extraction constants of these metal ions and the formation constants of aqueous complexes which were obtained from the experimental data by the successive approximation method are listed in Table 1.

The extraction data of zinc(II) could not be explained by Eq. 12. Figure 4 gives the extraction curves of zinc(II) as a function of the concentration of 4-isopropyltropolonate anion in the aqueous phase, when the initial concentration of metal ion is 1×10^{-5} (closed symbols) and 1×10^{-4} (open symbols) mol dm^{-3}. As can be seen from Fig. 4, the distribution ratio of zinc(II) is not dependent on the metal con-

Table 1. Summary of the Equilibrium Constants for Solvent Extraction of Divalent Metal Ions with 4-Isopropyltropolone in the Absence and Presence of Trioctylphosphine Oxide

	Log K_{ex10}[a)]	Log K_{ex11}[b)]	Log K_{ex20}[c)]	Log β_1	Log β_2	Log K_{dimer}	Log $\beta_{\mathrm{(org)self1}}$	Log K_{ex101}[d)]
Manganese(II)	—	—	26.8	—	—	—	—	13.1
Cobalt(II)	12.5	—	29.5	5.7	—	4.5	—	15.1
Nickel(II)	—	—	30.4	6.1	11.4	—	—	14.4
Copper(II)	22.3	—	—	—	—	—	—	—
Zinc(II)	13.9	15.4	—	—	—	—	1.5	17.8
Cadmium(II)	10.3	—	26.7	4.9	—	6.1	—	13.2

The chemical form of extracted species is as follows (cf. Eqs. 5 and 8). a) $M(ipt)_2$. b) $M(ipt)_2Hipt$. c) $M_2(ipt)_4$. d) MA_2TOPO.

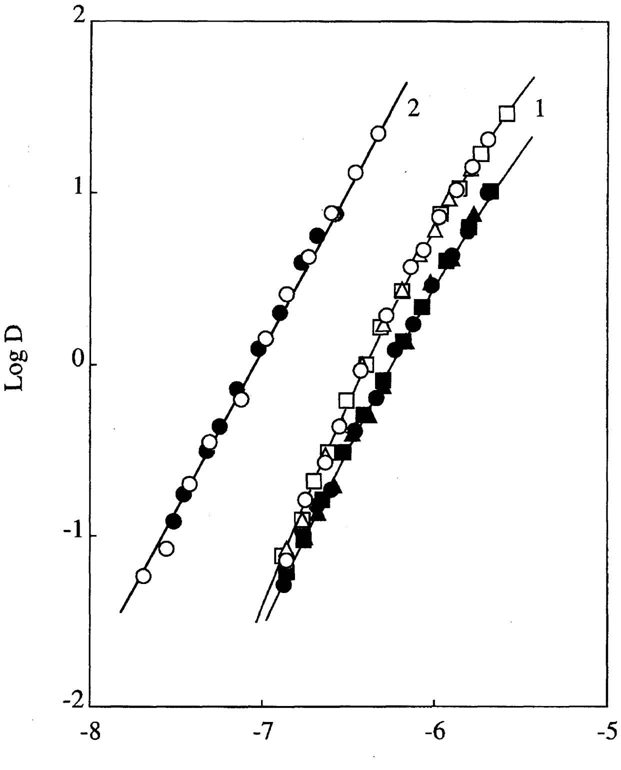

Fig. 2. Distribution ratio of 1×10^{-4} (open symbols) and 1×10^{-5} mol dm^{-3} (closed symbols) cobalt(II) as a function of the concentration of 4-isopropyltropolonate anion in the absence (No.1) and presence of TOPO (No.2). The initial concentration of 4-isopropyltropolone is 0.1 mol dm^{-3} (○,●), 0.05 mol dm^{-3} (△,▲) 0.02 mol dm^{-3} (□,■). The solid lines were calculated on the basis of Eqs. 4 and 7 by using the values of constants in Table 1.

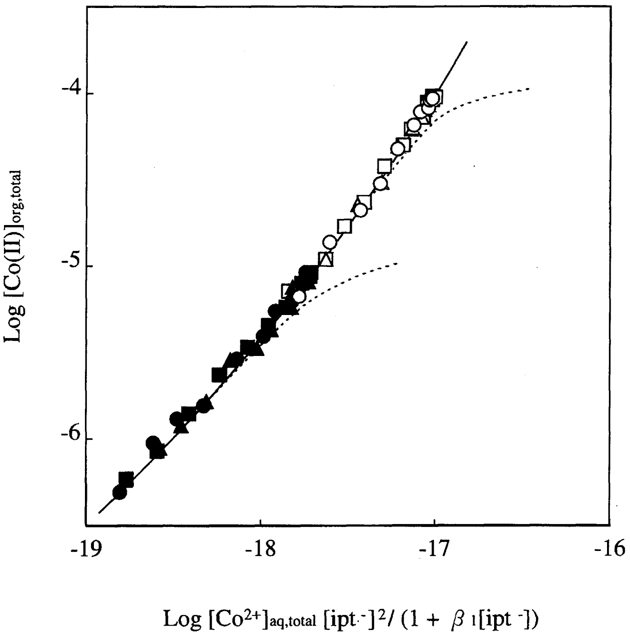

Fig. 3. The log $[\mathrm{Co(II)}]_{\mathrm{org,total}}$ vs. log $[\mathrm{Co}^{2+}]_{\mathrm{aq,total}}\,[\mathrm{ipt}^-]^2/(1+\beta_1[\mathrm{ipt}^-])$ plot in the absence of TOPO when β_1 is $10^{5.7}$. The symbols are the same as in Fig. 2. The solid line is calculated on the basis of Eq. 12 by using the values of constants in Table 1. The dotted lines are the calculated plots when the complexes in the aqueous phase are neglected.

centration when the concentration of 4-isopropyltropolonate anion in the aqueous phase, $[A^-]$, is identical. However, the extraction of zinc(II) is different when the concentration of 4-isopropyltropolone in the organic phase, $[HA]_{\mathrm{org}}$, is different. This can be explained in terms of the extraction of a mononuclear species, $Zn(ipt)_2$, and a self-adduct species, $Zn(ipt)_2\cdot a Hipt$. Furthermore, the plots of extraction data of zinc(II) in Fig. 4 are straight lines with a slope of +2 and, consequently, the complexes in the aqueous phase should be negligible under these conditions. The data were analyzed on the basis of the following equation which was introduced from Eq. 4:

$$\begin{aligned} D &= ([\mathrm{Zn(ipt)_2}]_{\mathrm{org}} + [\mathrm{Zn(ipt)_2\cdot Hipt}]_{\mathrm{org}} \\ &\quad + [\mathrm{Zn(ipt)_2\cdot 2Hipt}]_{\mathrm{org}} + \cdots)/[\mathrm{Zn}^{2+}] \\ &= K_{\mathrm{ex10}}[\mathrm{ipt}^-]^2 + K_{\mathrm{ex11}}[\mathrm{ipt}^-]^2[\mathrm{Hipt}]_{\mathrm{org}} \\ &\quad + K_{\mathrm{ex12}}[\mathrm{ipt}^-]^2[\mathrm{Hipt}]_{\mathrm{org}}^2 + \cdots \end{aligned} \tag{13}$$

$$\begin{aligned} &= K_{\mathrm{ex10}}[\mathrm{ipt}^-]^2(1 + \beta_{\mathrm{(org)self1}}[\mathrm{Hipt}]_{\mathrm{org}} + \\ &\quad \beta_{\mathrm{(org)self2}}[\mathrm{Hipt}]_{\mathrm{org}}^2 + \cdots), \end{aligned} \tag{14}$$

where

$$\beta_{\mathrm{(org)self}a} = [\mathrm{Zn(ipt)_2\cdot}a\mathrm{Hipt}]_{\mathrm{org}}/[\mathrm{Zn(ipt)_2}]_{\mathrm{org}}[\mathrm{Hipt}]_{\mathrm{org}}^{a}. \tag{15}$$

The following equation can be introduced from Eqs. 13 and 14:

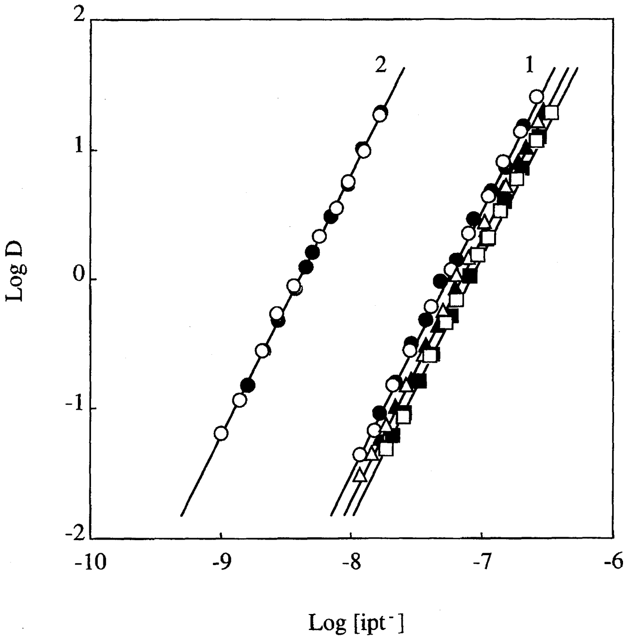

Fig. 4. Distribution ratio of 1×10^{-4} (open symbols) and 1×10^{-5} mol dm^{-3} (closed symbols) zinc(II) as a function of the concentration of 4-isopropyltropolonate anion in the absence (No. 1) and presence of TOPO (No. 2). The symbols are the same in Fig. 2. The solid lines were calculated on the basis of Eqs. 4 and 7 by using the values of constants in Table 1.

$$D[\mathrm{ipt}^-]^{-2} = K_{\mathrm{ex10}} + K_{\mathrm{ex11}}[\mathrm{Hipt}]_{\mathrm{org}} + K_{\mathrm{ex12}}[\mathrm{Hipt}]_{\mathrm{org}}^{\ 2} + \cdots \tag{16}$$

$$= K_{\mathrm{ex10}}(1 + \beta_{(\mathrm{org})\mathrm{self1}}[\mathrm{Hipt}]_{\mathrm{org}}$$

$$= +\beta_{(\mathrm{org})\mathrm{self2}}[\mathrm{Hipt}]_{\mathrm{org}}^{\ 2} + \cdots). \tag{17}$$

The open circles in Fig. 5 gives the $\log D[\mathrm{ipt}^-]^{-2}$ vs. $\log\,[\mathrm{Hipt}]_{\mathrm{org}}$ plot of zinc(II) on the basis of Eqs. 16 and 17 when $[\mathrm{ipt}^-]$ is $10^{-7.7}$ mol dm^{-3}. As is seen from Fig. 5, the slope of the plot changes from 0 to +1 and this also indicates the extraction of both $\mathrm{Zn(ipt)_2}$ and $\mathrm{Zn(ipt)_2{\cdot}Hipt}$. The extraction constant of zinc(II) and the formation constant of the self-adduct thus obtained are listed in Table 1. The solid lines in Figs. 4 and 5 were calculated on the bases of Eqs. 4 and 17 by using the values of constants in Table 1.

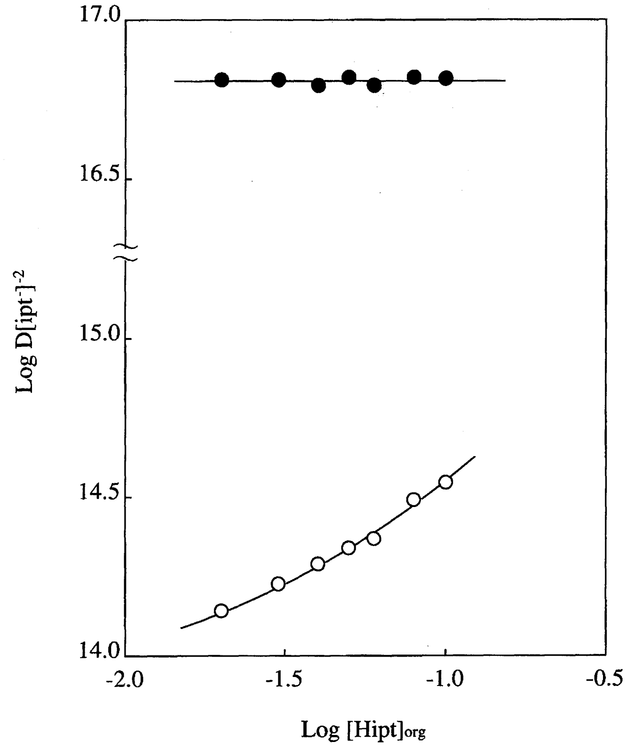

Fig. 5. The $\log D[\mathrm{ipt}^-]^{-2}$ vs. $\log\,[\mathrm{Hipt}]_{\mathrm{org}}$ plot of zinc(II) in the absence (open symbols) and presence (closed symbols) of TOPO. The initial concentration of zinc(II) is 1×10^{-4} mol dm^{-3} and the concentration of 4-isopropyltropolonate anion is $10^{-7.7}$ mol dm^{-3}. The solid lines were calculated on the basis of Eq. 16 by using the values of constants in Table 1.

Synergistic Effect of 4-Isopropyltropolone and Trioctylphosphine Oxide on the Extraction of Metal Ions. As can be seen from Fig. 1, the extraction of these metal ions is enhanced by the addition of TOPO except copper(II). Figures 2 and 4 also give the extraction curves of cobalt(II) and zinc(II) as a function of the concentration of 4-isopropyltropolonate anion in the aqueous phase in the presence of 0.1 mol dm^{-3} TOPO . As can be seen from Fig. 2, the extraction curve of cobalt(II) in the presence of 0.1 mol dm^{-3} TOPO is not dependent on the initial concentration of metal ions in the aqueous phase. The results of manganese(II), nickel(II), and cadmium(II) also indicate that the extraction curves were not dependent on the initial concentration of metal ions. This shows that only mononuclear TOPO adduct complexes are extracted with all of these four metal ions. The closed symbols in Fig. 5 give the $\log D[\mathrm{ipt}^-]^{-2}$ vs. $\log\,[\mathrm{Hipt}]_{\mathrm{org}}$ plot of zinc(II) when $[\mathrm{ipt}^-]$ is $10^{-8.5}$ mol dm^{-3} in the presence of 0.1 mol dm^{-3} TOPO. As can be seen from Fig. 5, the distribution ratio of zinc(II) in the presence of 0.1 mol dm^{-3} TOPO is not dependent on the concentration of 4-isopropyltropolone in the organic phase, $[\mathrm{HA}]_{\mathrm{org}}$, as long as the concentration of 4-isopropyltropolonate anion in the aqueous phase, $[\mathrm{A}^-]$, is identical. Thus no adduct of $\mathrm{Zn(ipt)_2}$ which combines both TOPO and 4-isopropyltropolone molecules in the organic phase, should be formed. It can be concluded that the addition of TOPO forms only a mononuclear TOPO adduct even when the extracted species is a dinuclear species or when it is a self-adduct species in the absence of TOPO. In other words, the formation of TOPO adduct dissociates the dinuclear species or the self-adduct species.

Figure 6 gives the dependence of extraction of the six metal ions as a function of the concentration of TOPO in the organic phase when the concentration of 4-isopropyltropolonate anion in the aqueous phase is kept constant. As can be seen from Fig. 6, each plot has asymptotes with slopes 0 and +1 except copper(II). Thus it can be concluded that the TOPO adduct should always be in the chemical form of $\mathrm{M(ipt)_2TOPO}$ under these conditions.

The data are analyzed on the basis of Eq. 7 by the least squares computer program and the values of constants, K_{ex101}

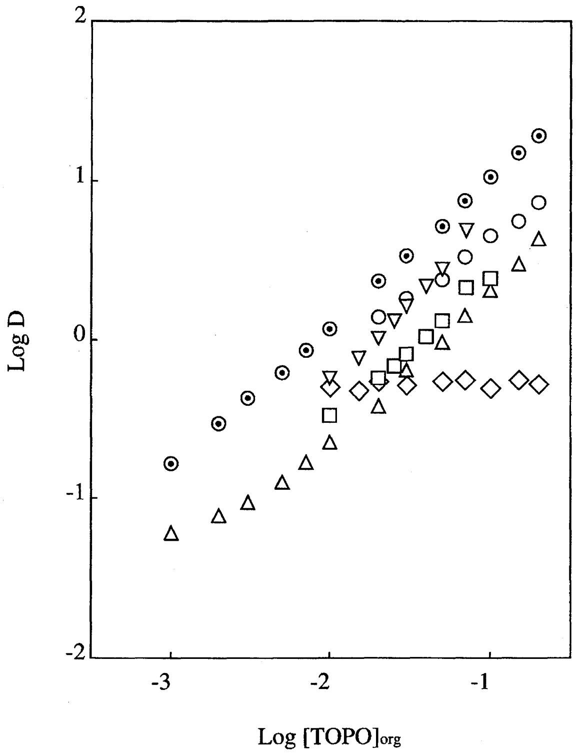

Fig. 6. Distribution ratio by the addition of TOPO as a function of the quantity $[\mathrm{TOPO}]_{\mathrm{org}}$. Initial concentration of metal ions is 1×10^{-5} mol dm^{-3}. (□): manganese(II) when [ipt$^-$] is $10^{-5.9}$ mol dm^{-3}, (△): cobalt(II) when [ipt$^-$] is $10^{-6.9}$ mol dm^{-3}, (○): nickel(II) when [ipt$^-$] is $10^{-6.3}$ mol dm^{-3}, (◇): copper(II) when [ipt$^-$] is $10^{-11.3}$ mol dm^{-3}, (○): zinc(II) when [ipt$^-$] is $10^{-7.9}$ mol dm^{-3}, and (▽): cadmium(II) when [ipt$^-$] is $10^{-5.7}$ mol dm^{-3}.

in Eq. 8, obtained are given in Table 1. The solid lines in Figs. 2 and 4 are ones calculated on the basis of Eq. 7 into which is introduced the values of constants in Table 1. Furthermore, the following adduct formation constant in the organic phase could be calculated by using the values of K_{ex101} and K_{ex10}, and K_{ex101} and K_{ex20} in Table 1.

$$\mathrm{M(ipt)_{2(org)}} + \mathrm{TOPO_{(org)}} \rightleftarrows \mathrm{M(ipt)_2TOPO_{(org)}};$$

$$\beta_{\mathrm{(org)mono}} = [\mathrm{M(ipt)_2TOPO}]_{\mathrm{org}} / [\mathrm{M(ipt)_2}]_{\mathrm{org}}[\mathrm{TOPO}]_{\mathrm{org}} \tag{18}$$

$$= K_{\mathrm{ex101}} / K_{\mathrm{ex10}}. \tag{19}$$

$$\mathrm{M_2(ipt)_{4(org)}} + 2\mathrm{TOPO_{(org)}} \rightleftarrows 2\mathrm{M(ipt)_2TOPO_{(org)}};$$

$$\beta_{\mathrm{(org)di}} = [\mathrm{M(ipt)_2TOPO}]_{\mathrm{org}}^2 / [\mathrm{M_2(ipt)_4}]_{\mathrm{org}}[\mathrm{TOPO}]_{\mathrm{org}}^2 \tag{20}$$

$$= K_{\mathrm{ex101}}^2 / K_{\mathrm{ex20}}. \tag{21}$$

The values of $\beta_{\mathrm{(org)mono}}$ and $\beta_{\mathrm{(org)di}}$ are given in Table 2.

Discussion

The results that only the $\mathrm{M(ipt)_2}$ species is extracted with copper(II) and both the $\mathrm{M(ipt)_2}$ and $\mathrm{M(ipt)_2{\cdot}Hipt}$ species are extracted with zinc(II) agree with the results in the previous work.[1] Thus, we concluded that the tendency to form dinuclear species of the copper(II) and zinc(II) is very small. It is known that copper(II) and zinc(II) usually form more stable complexes than the other four metal ions of the present study. However, these results do not seem to explain the reason why the copper(II) and zinc(II) complexes do not form polynuclear species in the organic phase. Furthermore, with the zinc(II) complexes, no clear evidence for the extraction of any dinuclear species even when the concentration of 4-isopropyltropolone in the organic phase, $[\mathrm{HA}]_{\mathrm{org}}$, is low and the molar ratio of $\mathrm{Zn(ipt)_2{\cdot}Hipt}$ to $\mathrm{Zn(ipt)_2}$ is not high. Thus the absence of formation of dinuclear species of zinc(II) complex should not be due to the fact that two self-adduct molecules can not associate with each other to form dinuclear species.

Table 2. Summary of the Formation Constants of 4-Isopropyltropolonate Complexes with TOPO

	Log $\beta_{\mathrm{(org),mono}}$	Log $\beta_{\mathrm{(org),di}}$
Manganese(II)	—	−0.6
Cobalt(II)	2.6	0.7
Nickel(II)	—	−1.6
Copper(II)	—	—
Zinc(II)	3.9	—
Cadmium(II)	2.9	−0.3

The extraction of only dinuclear species with nickel(II) and manganese(II) and that of both mononuclear and dinuclear species with cobalt(II) and cadmium(II) was not described in the previous work.[1] This was because the experiments were carried out by using radioactive tracers and thus the metal concentration was much lower than that in the present work. The conclusion is that the extracted species should essentially be in the dinuclear form with nickel(II) and manganese(II) even when $\log D$ is -1, that is, even when the concentration of the metal ion in the complex in the organic phase is 1×10^{-6} mol dm^{-3}. Thus it is assumed that the following dimerization constant should be very high:

$$2\mathrm{M(ipt)_{2(org)}} \rightleftarrows \mathrm{M_4(ipt)_{4(org)}}. \tag{22}$$

$$K_{\mathrm{dimer}} = [\mathrm{M_2(ipt)_4}]_{\mathrm{org}} / [\mathrm{M(ipt)_2}]_{\mathrm{org}}^2 = K_{\mathrm{ex20}} / K_{\mathrm{ex10}}^2. \tag{23}$$

On the other hand, the constant, K_{dimer}, of cobalt(II) and cadmium(II) can be calculated by using the values of the extraction constants, K_{ex10} and K_{ex20} on the basis of Eq. 23. The value of K_{dimer} of cobalt(II) and cadmium(II) are given in Table 1. As can be seen from Table 1, if more than 90% of the manganese(II) and the nickel(II) complex would be in the dimer form, the value of K_{dimer} of these metal complexes should be equal to or even higher than $10^{8.7}$ and the value will be much greater than that for the cobalt(II) and cadmium(II) complex in the same solvent.

It is often found that the solvent extraction of nickel(II) is much inferior to that of cobalt(II) under identical conditions.[11,12] However, as can be seen from Fig. 1, the extractions of cobalt(II) and nickel(II) with 4-isopropyltropolone are rather similar to each other. The poorer extraction of nickel(II) than cobalt(II) under identical conditions with a certain extractant is often explained in terms of stronger hydration of the nickel(II) complexes than the cobalt(II) complexes. Although the stability of a certain nickel(II) complex in an aqueous solution is rather similar or even a little higher than that of the cobalt(II) complex with the same ligand, this stronger hydration of the complex should interfere more with the extraction of the nickel(II) than cobalt(II). For these reasons, the extraction from the aqueous phase is more difficult with the nickel(II) complex than with the cobalt(II) complex. The similar extraction of cobalt(II) and nickel(II) with 4-isopropyltropolone in the present study should be because the extractability of the dinuclear species are rather similar.

The enhancement of solvent extraction of these metal ions except copper(II) by the addition of TOPO should be due to the adduct formation of the extracted metal chelate: the synergistic effect. It is important that all of the metal adduct chelates of the five metal ions are mononuclear species. This indicates that the formation of the dinuclear species in the organic phase is very much interfered with by the addition of TOPO. No assumption can be made for the structure of dinuclear complexes and for the chemical species which connects the two chelate complex molecules or two metal ions in the dinuclear complexes, only from the extraction data. However, we conclude that the TOPO combines with the central metal ion in the chelate and this addition of TOPO lowers the ability of the material to bridge the two mononuclear species or two metal ions. Thus although the adduct formation with TOPO enhances the extraction, the TOPO also impairs the extraction of the dinuclear species of manganese(II), cobalt(II), nickel(II), and cadmium(II) as is found with the solvent extraction of some metal ions with a carboxylic acid into chloroform in the presence of TOPO.[9,10] The extracted species of zinc(II) are both $Zn(ipt)_2$ and $Zn(ipt)_2 \cdot Hipt$ in the absence of TOPO, while $Zn(ipt)_2TOPO$ is also formed in the presence of TOPO. Although the ratio $[Zn(ipt)_2 \cdot Hipt]_{org}/[Zn(ipt)_2]_{org}$ should be constant even when TOPO is added, as long as $[Hipt]_{org}$ is kept constant, as is seen from Eq. 13 to Eq. 17, the ratio $[Zn(ipt)_2TOPO]_{org}/[Zn(ipt)_2 \cdot Hipt]_{org}$ is higher when $[TOPO]_{org}$ is higher. Thus the TOPO adduct, $Zn(ipt)_2TOPO$. should be dominant in the organic phase when TOPO concentration is high.

The smaller enhancement of extraction as the 4-isopropyltropolonate complex of nickel(II) and manganese(II) than that of cobalt(II) and cadmium(II) by an addition of TOPO can be explained in terms of the dissociation of the dinuclear species when the TOPO adduct is formed. As can be seen from Table 2, the adduct formation constant of mononuclear species is related with the dimerization constant, K_{dimer}, of the mononuclear species for cobalt(II) and cadmium(II) in Table 1. The adduct formation constants from mononuclear species, $\beta_{\text{(org)mono}}$, of cobalt(II) and cadmium(II) are rather similar, but the formation constant of the TOPO adduct from the dinuclear species, $\beta_{\text{(org)di}}$, of cobalt(II) is higher than cadmium(II), as can be seen from Table 2. For this reason, the enhancement of extraction by an addition of TOPO is much higher with cobalt(II) than that with cadmium(II) when the metal concentration is high and thus the dinuclear species is predominant under the conditions of the present study. This should be due to the fact that the dimerization constant of cadmium(II) is two orders higher than cobalt(II) complex and since the adduct with TOPO is, in both cases, mononuclear, $M(ipt)_2TOPO$. Both of them are formed by the dissociation of dinuclear species and this should be much easier with the cobalt(II) complex than with the cadmium(II) complex. The smaller enhancement of the extraction by an addition of TOPO with nickel(II) and manganese(II) than cobalt(II) and cadmium(II) should be due to the same reason: The dissociation of the dinuclear species of these two metal ions should be much more difficult than cobalt(II) and cadmium(II). The largest enhancement of extraction by an addition of TOPO with zinc(II) should be due to no formation of dinuclear complex of zinc(II).

It is well known that the extracted metal species with several carboxylic acids are often polynuclear complexes containing different numbers of undissociated acid molecules. This is often related with the tendency that the reagent itself is present in the organic phase as species dimerized by hydrogen bonding. However, not very much is known about the extraction of polynuclear metal species when the extractant is a chelating type. One of such examples is the solvent extraction of several divalent metal ions with 8-quinolinol and 2-methyl-8-quinolinol.[13—15] Furthermore, as was written, 4-isopropyltropolone is present as a mononuclear form in the organic phase which should indicate that 4-isopropyltropolone has a much smaller tendency of hydrogen bonding in the organic phase than carboxylic acids. However, copper(II), which is extracted only as the mononuclear species with 4-isopropyltropolone, is extracted with several carboxylic acids as polynuclear species in several solvent extraction systems.[5—8] These indicate that further studies are necessary in order to understand the difference of the formation of polynuclear complexes in the organic solvents when the ligand is different.

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