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Adduct Formation of the Mixed Copper(II) 2-Thenoyltrifluoroacetonate-3-isopropyltropolonate Chelate with Tributyl Phosphate in Solvent-extraction Systems Containing These Ligands

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Synopsis. From the extraction data of copper(II) in a perchlorate solution into carbon tetrachloride containing 2-thenoyltrifluoroacetone (Htta), 3-isopropyltropolone (Hipt), and tributyl phosphate (tbp), the formation of an adduct mixed chelate, Cu(tta)(ipt)(tbp), together with the $Cu(tta)_2$, $Cu(tta)_2(tbp)$, Cu(tta)(ipt), and $Cu(ipt)_2$ species, was concluded, and the formation constant of this adduct mixed chelate was calculated.

Synergism in metal chelate-extraction systems by neutral ligands is, in most cases, attributed to the adduct formation of the extracted chelate with the ligand.[1,2] It is often that the formation constants of adduct chelates of a certain metal ion with a certain given neutral ligand are very different when the chelating extractant is different.[3]

In a previous paper, this difference in the stabilities of adduct metal chelates was demonstrated by the enhancement of copper(II) extraction with 2-thenoyltrifluoroacetone (TTA) and 3-isopropyltropolone (IPT) by adding tributyl phosphate (TBP);[4] the extraction with TTA was very much enhanced by TBP, but that with IPT was not. From these results, it was concluded that the $Cu(tta)_2$ chelate formed a stable adduct, $Cu(tta)_2(tbp)$, while the $Cu(ipt)_2$ chelate formed no TBP adduct. The formation constant of the TTA-TBP adduct chelate was calculated from the enhancement of the TTA extraction, determined as a function of the concentration of TBP.

In another previous paper, the extraction of copper(II) in solvent-extraction systems containing both TTA and IPT was studied, and from the data, the extraction of the mixed chelate, Cu(tta)(ipt), together with the $Cu(tta)_2$ and $Cu(ipt)_2$ chelates, was concluded. The extraction constant of the mixed chelate was calculated from the data obtained at various molar ratios of TTA and IPT.[5]

In the present study, we have measured the distribution ratio of copper(II) in solvent-extraction systems containing TTA, IPT, and TBP; we have concluded that the mixed chelate, Cu(tta)(ipt), formed an adduct with TBP, Cu(tta)(ipt)(tbp).

Experimental

Reagents. All of the reagents were of an analytical grade. The extractants were supplied by the Dojindo Co., Kumamoto (TTA), by the Takasago Perfumery Co., Kanagawa (IPT), and by the Kanto Kagaku Co., Tokyo (TBP).

All of the experiments were made in a manner similar to that previously reported[4,5] except that the amount of copper(II) in the present study was measured by an atomic-absorption method. The temperature was 25±0.3 °C. The hydrogen-ion concentration was in stoichiometric units, as in previous studies.

Statistical

In this paper all the species in the organic phase will be denoted by the subscript "org". As has been described above, no formation of $Cu(ipt)_2(tbp)$ species was found previously. Thus, if higher adducts containing more than one TBP are negligible, the distribution ratio of copper(II) in the presence of TTA, IPT, and TBP may be written as:

$$\begin{aligned} D &= ([\mathrm{Cu(tta)_2}]_{\mathrm{org}} + [\mathrm{Cu(tta)_2(tbp)}]_{\mathrm{org}} + [\mathrm{Cu(tta)(ipt)}]_{\mathrm{org}} \\ &\quad + [\mathrm{Cu(tta)(ipt)(tbp)}]_{\mathrm{org}} + [\mathrm{Cu(ipt)_2}]_{\mathrm{org}})[\mathrm{Cu^{2+}}]^{-1} \\ &= \{K\mathrm{ex}_{2,0}[\mathrm{Htta}]^2_{\mathrm{org}}(1+\beta^{\mathrm{tta}}_{1(\mathrm{org})}[\mathrm{tbp}]_{\mathrm{org}}) \\ &\quad + K\mathrm{ex}_{1,1}[\mathrm{Htta}]_{\mathrm{org}}[\mathrm{Hipt}]_{\mathrm{org}}(1+\beta^{\mathrm{mix}}_{1(\mathrm{org})}[\mathrm{tbp}]_{\mathrm{org}}) \\ &\quad + K\mathrm{ex}_{0,2}[\mathrm{Hipt}]^2_{\mathrm{org}}\}[\mathrm{H^+}]^{-2} \end{aligned} \tag{1}$$

where:

$$K\mathrm{ex}_{2,0} = [\mathrm{Cu(tta)_2}]_{\mathrm{org}}[\mathrm{H^+}]^2[\mathrm{Cu^{2+}}]^{-1}[\mathrm{Htta}]^{-2}_{\mathrm{org}} \tag{2}$$

$$K\mathrm{ex}_{1,1} = [\mathrm{Cu(tta)(ipt)}]_{\mathrm{org}}[\mathrm{H^+}]^2[\mathrm{Cu^{2+}}]^{-1}[\mathrm{Htta}]^{-1}_{\mathrm{org}}[\mathrm{Hipt}]^{-1}_{\mathrm{org}} \tag{3}$$

$$K\mathrm{ex}_{0,2} = [\mathrm{Cu(ipt)_2}]_{\mathrm{org}}[\mathrm{H^+}]^2[\mathrm{Cu^{2+}}]^{-1}[\mathrm{Hipt}]^{-2}_{\mathrm{org}} \tag{4}$$

$$\beta^{\mathrm{tta}}_{1(\mathrm{org})} = [\mathrm{Cu(tta)_2(tbp)}]_{\mathrm{org}}[\mathrm{Cu(tta)_2}]^{-1}_{\mathrm{org}}[\mathrm{tbp}]^{-1}_{\mathrm{org}} \tag{5}$$

$$\begin{aligned} \beta^{\mathrm{mix}}_{1(\mathrm{org})} &= [\mathrm{Cu(tta)(ipt)(tbp)}]_{\mathrm{org}}[\mathrm{Cu(tta)(ipt)}]^{-1}_{\mathrm{org}} \\ &\quad \times [\mathrm{tbp}]^{-1}_{\mathrm{org}} \end{aligned} \tag{6}$$

Results and Discussion

The organic solvent employed was carbon tetrachloride, and the aqueous phase contained 0.116 mol dm^{-3} of perchloric acid. The equilibrium constants defined by Eqs. 2 to 5 have already been reported in previous papers. They are given in Table 1, and they were employed for the analysis of the experimental data in the present study.

Several runs were made at various sets of concentrations of TTA, IPT, and TBP. It was found from the

TABLE 1. SUMMARY OF EQUILIBRIUM CONSTANTS[a)]
Aq. phase: 0.1 mol dm^{-3} perchlorate media.
Solvent: CCl_4.

Extraction constant		Ref.	Adduct-formation constant[b)]		Ref.
$\log K\mathrm{ex}_{2,0}$	−1.08	4	$\log \beta^{\mathrm{tta}}_{1(\mathrm{org})}$	2.27	4
$\log K\mathrm{ex}_{1,1}$	0.80	5	$\log \beta^{\mathrm{mix}}_{1(\mathrm{org})}$	1.63	present work
$\log K\mathrm{ex}_{0,2}$	0.95	4			

a) The definitions of the constants are given in Eqs. 2 to 6. b) $Cu(ipt)_2$ does not form any adduct with TBP.

TABLE 2. EXPERIMENTAL DATA

Aq. phase: 0.116 mol dm^{-3} $HClO_4$. Org. solvent: CCl_4.

	$[TBP]_{org}$	[Cu(II)]	$[Cu(II)]_{org}$	log D	log $\beta^{mix}_{1(org)}$
a)	0.02	9.40×10^{-5}	1.10×10^{-4}	0.07	1.56
	0.03	8.16×10^{-5}	1.22×10^{-4}	0.20	1.60
	0.05	6.82×10^{-5}	1.36×10^{-4}	0.30	1.54
	0.075	5.15×10^{-5}	1.52×10^{-4}	0.47	1.63
	0.1	4.21×10^{-5}	1.62×10^{-4}	0.58	1.65
b)	0.02	1.28×10^{-4}	7.60×10^{-5}	−0.23	1.67
	0.03	1.14×10^{-4}	9.05×10^{-5}	−0.10	1.75
	0.05	1.00×10^{-4}	1.04×10^{-4}	0.02	1.69
	0.075	8.90×10^{-5}	1.15×10^{-4}	0.11	1.64
	0.1	8.11×10^{-5}	1.23×10^{-4}	0.18	1.59
c)	0.02	1.56×10^{-4}	4.83×10^{-5}	−0.51	1.67
	0.03	1.47×10^{-4}	5.72×10^{-5}	−0.41	1.70
	0.05	1.39×10^{-4}	6.52×10^{-5}	−0.33	1.62
	0.075	1.29×10^{-4}	7.49×10^{-5}	−0.24	1.59
	0.1	1.16×10^{-4}	8.81×10^{-5}	−0.12	1.63
d)	0.02	1.74×10^{-4}	2.96×10^{-5}	−0.76	1.78
	0.03	1.76×10^{-4}	2.81×10^{-5}	−0.80	1.53
	0.05	1.71×10^{-4}	3.26×10^{-5}	−0.72	1.50
	0.075	1.58×10^{-4}	4.59×10^{-5}	−0.54	1.67
	0.1	1.59×10^{-4}	4.46×10^{-5}	−0.55	1.52

a) $[Htta]_{org}=0.1$ mol dm^{-3}, $[Hipt]_{org}=0.01$ mol dm^{-3}.
b) $[Htta]_{org}=0.05$ mol dm^{-3}, $[Hipt]_{org}=0.01$ mol dm^{-3}.
c) $[Htta]_{org}=0.025$ mol dm^{-3}, $[Hipt]_{org}=0.01$ mol dm^{-3}.
d) $[Htta]_{org}=0.01$ mol dm^{-3}, $[Hipt]_{org}=0.01$ mol dm^{-3}.

results that the distribution ratio could be well explained by assuming the formation of only one adduct mixed chelate other than the four species already found. The formation constant of the adduct mixed chelate was calculated by introducing the extraction data and the values of the four constants into Eq. 1. Table 2 shows the data and the values of $\beta^{mix}_{1(org)}$ thus obtained from each set of data. In this table, the only data employed were those obtained under conditions where more than 25% of the copper(II) species in the organic phase was in the form of the adduct mixed chelate. The average value was $\log\beta^{mix}_{1(org)}=1.63$, where the standard deviation was 0.08.

Figure 1 shows the percentage distribution of copper(II) species in the organic phase, as calculated by using the constants in Table 1. As may be seen from Fig. 1, the mixed species is always important in the high concentration range of TBP. For example, at $R=2$ and $[tbp]_{org}=0.1$ mol dm^{-3} more than 50% of the copper(II) in the organic phase is in the form of the adduct mixed chelate, Cu(tta)(ipt)(tbp).

The stability of adduct metal chelates in organic solvents is affected by several complicated factors, and no clear and systematic interpretation which allows a prediction of the stability of a certain given adduct metal chelate is available. Thus, we can not make any statistical estimation of the stability of the Cu(tta)(ipt)(tbp) adduct, even though we know the formation constants of the $Cu(tta)_2(tbp)$ and $Cu(ipt)_2(tbp)$ (the constant for the latter is zero). The present experimental results indicate that this adduct mixed chelate fairly stable, although it is less stable than the $Cu(tta)_2(tbp)$.

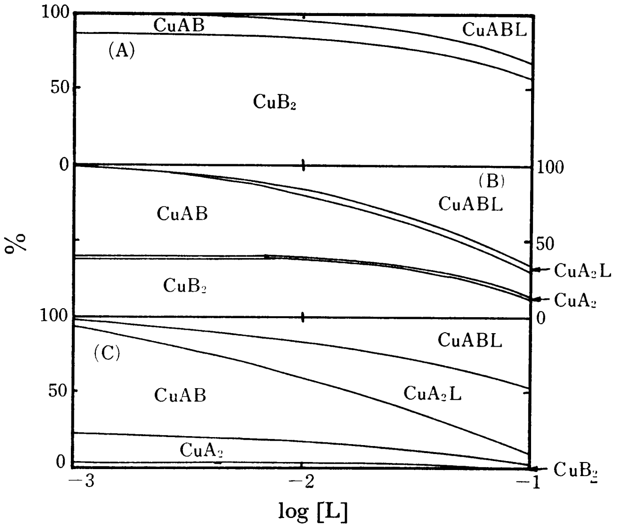

Fig. 1. The calculated percentage distribution of Cu(II) species in the organic phase as a function of the concentration ratio of the chelating extractants ($R=[HA]_{org}/[HB]_{org}$) and of L where HA is Htta, HB is Hipt, and L is tbp.
(A): $R=0.2$, (B): $R=2$, (C): $R=20$.

No quantitative study of such adduct mixed chelate seems ever to have been made in other solvent extraction systems, but we presume that similar species would be formed in several of them containing various different sets of a metal ion, a chelating ligand, and an adduct-forming ligand.

References

1) H. M. N. H., Irving, "Solvent Extraction Chemistry," North-Holland Publ. Co., Amsterdam (1967), p. 105.

2) T. V. Healy, "Solvent Extraction Chemistry Research," Wiley Interscience, New York (1969), p. 257.

3) T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry," Marcel Dekker, New York (1977).

4) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1727 (1964).

5) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 2013 (1964).