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Solvent Extraction of Copper(I) and Copper(II) from Aqueous Halide Solutions with Tetrabutylammonium Ions into Chloroform

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The solvent extraction of copper(I) and copper(II) from 1 mol dm^{-3} Na(X, NO$_3$), where X$^-$ is Cl$^-$, Br$^-$, or I$^-$, as ion-pairs of anionic halide complexes with tetrabutylammonium ions (tba$^+$) into chloroform was studied in the absence and presence of a reducing agent, ascorbic acid. The extraction of copper(II) with 2-thenoyltrifluoroacetone (Htta) in chloroform from these aqueous solutions was also studied. In the absence of ascorbic acid, the extraction of copper which was added as Cu^{2+} with tba$^+$ was negligible from chloride and bromide solutions but tba$^+$Cu$^{\mathrm{II}}$I$_3{}^-$ and (tba$^+$)$_2$Cu$^{\mathrm{II}}$I$_4{}^{2-}$ were extracted from iodide solutions. In the presence of ascorbic acid, the extraction of tba$^+$Cu$^{\mathrm{I}}$X$_2{}^-$ was found from all of these halide solutions. Only copper(II) was extracted with Htta from these solutions. The distribution ratio was lower when the halide concentration was higher due to formation of copper(II) complexes in the absence of ascorbic acid and it was much lower in the presence of this reducing agent due to formation of copper(I) complexes, which were stabler than the copper(II) complexes. From the extraction data with tba$^+$ and with Htta, the formation constants of copper(I) and copper(II) halide complexes from Cu^{2+} in the aqueous phase as well as the extraction constants of certain complexes into the organic phase were determined. It was concluded that the dominant metal species in the aqueous phase was Cu^{2+} when the halide concentration was low even in the presence of the reducing agent and thus copper(I) anionic complexes were extracted into the organic phase and the molar ratio of copper(I) complex species to Cu^{2+} in the aqueous phase was higher at higher halide concentrations.

Copper(I) and copper(II) are extractable as halide complexes from aqueous chloride, bromide, and iodide solutions with various extractants.[1,2] Among these, bulky cations such as quaternary ammonium ions, diantipyrylmethane, and cationic dyes were used for the extraction of anionic copper(I) and copper(II) halide complexes.[3—11] However, not much is known about the equilibrium among the chemical species of copper in these liquid–liquid systems.

In this paper, the solvent extraction of copper, which was initially added in the form of Cu^{2+} from chloride, bromide, and iodide solutions with tetrabutylammonium ions, into chloroform was studied in the absence and presence of a reducing agent, ascorbic acid. It was found that copper(II) anionic complexes were extracted only from iodide solutions but copper(I) anionic complexes were extracted from all of these halide solutions when the reducing agent was present. Furthermore, it was also found that even when a copper(I) anionic complex was extracted in the presence of the reducing agent, the copper in the aqueous phase were not always in the monovalent state. From the extraction data with tba$^+$, the formation constants of copper(I) and copper(II) halide complexes and the extraction constants of certain complexes were determined. Copper(II) is known to be extracted well with several chelating extractants and its extraction with a certain chelating extractant should be different from that of copper(I). The effect of the reducing agent on the extraction of copper(II) with Htta (1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione(thenoyltrifluoroacetone)) was examined in the absence and presence of halide ions to discover how the oxidation states of copper in the aqueous phase were affected by the reducing agent. The complex formation of copper(I) and copper(II) was also examined by this Htta extraction in the absence and presence of ascorbic acid and the formation constants of the complexes were obtained from the change in the distribution ratio of the metal chelate extraction.

Experimental

All the reagents were of analytical grade. Chloroform was purified by agitating it several times with water before use. The chelating extractant, thenoyltrifluoroacetone (Htta), which was obtained from Dojindo Laboratories, was purified by recrystallization from cyclohexane. Sodium nitrate was recrystallized three times from water. Tetrabutylammonium nitrate obtained from Kanto Chemical Co., Inc. was dried and used without further purification.

All the solvent extraction experiments were done in a thermostatted room at 298 K. Stock solutions of sodium chloride, bromide, and iodide were prepared by dissolving crystals of the salt in water and the halide concentration was measured by titration with a standard silver nitrate solution. Sodium nitrate solutions were prepared by dissolving a weighed amount of sodium nitrate crystals in water. Standard copper(II) nitrate solutions were prepared by dissolving copper(II) nitrate crystals in an aqueous sodium nitrate solution. A standard copper(II) nitrate solution was obtained from Kanto Chemical Co., Inc. and stock copper(II) solutions were prepared by dilution of it with a sodium nitrate solution. The copper concentration in these solutions were measured by an EDTA titration method. Stoppered glass tubes (capacity 20 cm^3) were used for the solvent extraction experiments. The vessels were covered by aluminum foil to avoid effects of light. An amount of 1 $\text{mol}\,\text{dm}^{-3}$ $Na(X, NO_3)$ solutions where X^- was Cl^-, Br^- or I^- was placed in a tube and a portion of aqueous tetrabutylammonium nitrate ($tba^+NO_3^-$) solution was added. The hydrogen-ion concentration was adjusted to 1.00×10^{-2} $\text{mol}\,\text{dm}^{-3}$ by addition of nitric acid. In certain experiments, some ascorbic acid solution was added as the reducing agent just before the experiments. The initial ascorbic acid concentration was 0.01 $\text{mol}\,\text{dm}^{-3}$. Then a portion of chloroform was placed in the tube and the two phases were agitated for about 5 min and some copper(II) nitrate solution was added. The initial copper concentration in the aqueous phase was 2×10^{-5} $\text{mol}\,\text{dm}^{-3}$. The volume of the two phases was 6 cm^3. The two phases were vigorously agitated usually for 30 min and they were centrifuged off. The copper in the chloroform phase was stripped by agitation with 1 $\text{mol}\,\text{dm}^{-3}$ nitric acid. The copper in this nitric acid solution and that in the equilibrated aqueous phase was measured by atomic absorption spectrometry. The hydrogen-ion concentration was measured by potentiometry using a solution containing 1.00×10^{-2} $\text{mol}\,\text{dm}^{-3}$ nitric acid and 0.99 $\text{mol}\,\text{dm}^{-3}$ sodium nitrate as the standard of $-\log\,[H^+]$ 2.00.

Solvent extraction experiments of copper(II) in these aqueous solutions were also done in the absence of ascorbic acid but otherwise under identical conditions as above and the two phases were agitated for 30 s.

A series of chelate extraction experiments was made when the aqueous phase was 1 $\text{mol}\,\text{dm}^{-3}$ $Na(X, NO_3)$ containing 2×10^{-5} $\text{mol}\,\text{dm}^{-3}$ of copper(II) and none or 0.01 $\text{mol}\,\text{dm}^{-3}$ ascorbic acid. The aqueous phase was agitated with chloroform containing Htta for 30 s or for 30 min.

The extraction of ion-pairs of the reagents, tba^+X^-, into chloroform was measured as follows. A portion of 1 $\text{mol}\,\text{dm}^{-3}$ NaX solution containing an amount of tba^+ nitrate was placed in a tube and the same volume of chloroform was added. The two phases were agitated for 5 min and then centrifuged off. The aqueous phase was transferred into another tube and an excess of sodium picrate, 2×10^{-3} $\text{mol}\,\text{dm}^{-3}$, was added. This aqueous solution was agitated with the same volume of chloroform and the tba^+ in the aqueous solution was extracted as ion-pairs with picrate ions, tba^+pic^-. It was confirmed that the extraction of tba^+ under these conditions was quantitative. The ion-pairs (tba^+pic^-) thus extracted were measured from the optical absorption of the picrate ions at 370 nm.

Results

In this paper, any chemical species in the organic phase is denoted by a subscript "org" while that in the aqueous phase is denoted by lack of any subscript. The subscript "init" denotes the concentration at the beginning. The aqueous phase always contained 0.01 $\text{mol}\,\text{dm}^{-3}$ hydrogen ions at the beginning. The volume of the two liquid phases was always the same. It was found that the change in the hydrogen-ion concentration was negligible before and after the two-phase agitation in all the experiments. For the statistical analysis of the data, it was assumed that when copper(I) and copper(II) are extracted with tba^+ from an aqueous solution into an organic solvent, the distribution ratio can be written as:

$$D = ([\mathrm{Cu(I)}]_{\mathrm{org,total}} + [\mathrm{Cu(II)}]_{\mathrm{org,total}})/([\mathrm{Cu(I)}]_{\mathrm{total}} + [\mathrm{Cu(II)}]_{\mathrm{total}}). \quad (1)$$

When anionic halide complexes are extracted with the bulky cations, tba^+, a general equation for each term in Eq. 1 can be written as:

$$[\mathrm{Cu(I)}]_{\mathrm{org,total}} = [\mathrm{Cu^IX}]_{\mathrm{org}} + \sum[(\mathrm{tba}^+)_a\mathrm{Cu^IX}_{a+1}{}^{-a}]_{\mathrm{org}} \quad (2)$$

$$[\mathrm{Cu(II)}]_{\mathrm{org,total}} = [\mathrm{Cu^{II}X_2}]_{\mathrm{org}} + \sum[(\mathrm{tba}^+)_b\mathrm{Cu^{II}X}_{b+2}{}^{-b}]_{\mathrm{org}} \quad (3)$$

$$[\mathrm{Cu(I)}]_{\mathrm{total}} = [\mathrm{Cu}^+] + \sum[\mathrm{Cu^IX}_c{}^{1-c}] \quad (4)$$

$$[\mathrm{Cu(II)}]_{\mathrm{total}} = [\mathrm{Cu}^{2+}] + \sum[\mathrm{Cu^{II}X}_d{}^{2-d}]. \quad (5)$$

1. Extraction of Halide and Nitrate Ions with tba^+. When an aqueous 1 $\text{mol}\,\text{dm}^{-3}$ $Na(X, NO_3)$ solution containing tba^+ was agitated with chloroform, both tba^+X^- and $tba^+NO_3^-$ were extracted. The extraction equilibrium of tba^+ as ion-pairs with halide ions and with nitrate ions can be written by assuming no formation of ion-pairs in the aqueous phase and no dissociation of the extracted ion-pairs in chloroform as:

$$\mathrm{tba}^+ + \mathrm{X}^- \rightleftharpoons \mathrm{tba}^+\mathrm{X}^-{}_{\mathrm{(org)}}$$
$$Kex_{\mathrm{A.B}} = [\mathrm{tba}^+\mathrm{X}^-]_{\mathrm{org}}/([\mathrm{tba}^+][\mathrm{X}^-]) \quad (6)$$

$$\mathrm{tba}^+ + \mathrm{NO_3}^- \rightleftharpoons \mathrm{tba}^+\mathrm{NO_3}^-{}_{\mathrm{(org)}}$$
$$Kex_{\mathrm{NO3.B}} = [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}}/([\mathrm{tba}^+][\mathrm{NO_3}^-]). \quad (7)$$

The concentration of tba^+ at the beginning can be written as:

$$[\mathrm{tba}^+]_{\mathrm{init}} = [\mathrm{tba}^+] + [\mathrm{tba}^+\mathrm{X}^-]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}} + \sum a[(\mathrm{tba}^+)_a\mathrm{Cu^IX}_{a+1}{}^{-a}]_{\mathrm{org}} + \sum b[(\mathrm{tba}^+)_b\mathrm{Cu^{II}X}_{b+2}{}^{-b}]_{\mathrm{org}}. \quad (8)$$

However, since $[tba^+]_{init}$ is always much higher than the total concentration of copper species, the terms of extracted copper complexes in Eq. 8 can be neglected and it can be rewritten as:

$$[\mathrm{tba}^+]_{\mathrm{init}} = [\mathrm{tba}^+] + [\mathrm{tba}^+\mathrm{X}^-]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}}. \quad (9)$$

By introducing Eqs. 6 and 7 into Eq. 9, the following equation is obtained:

$$[\mathrm{tba}^+] = [\mathrm{tba}^+]_{\mathrm{init}}/(1 + Kex_{\mathrm{A,B}}[\mathrm{X}^-] + Kex_{\mathrm{NO3,B}}[\mathrm{NO_3}^-]). \quad (10)$$

The extraction of tba^+X^- was measured when the aqueous phase contained no nitrate and thus it was 1 $\text{mol}\,\text{dm}^{-3}$ NaX. The results are given in Table 1. The extraction of these ion-pairs should decrease the concentration of X^- and NO_3^- in the aqueous phase and the following equations can be written.

$$[\mathrm{X}^-]_{\mathrm{init}} = [\mathrm{X}^-] + [\mathrm{tba}^+\mathrm{X}^-]_{\mathrm{org}}$$
$$[\mathrm{NO_3}^-]_{\mathrm{init}} = [\mathrm{NO_3}^-] + [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}}$$
$$[\mathrm{X}^-] = [\mathrm{X}^-]_{\mathrm{init}}/(1 + Kex_{\mathrm{A,B}}[\mathrm{tba}^+]) \quad (11)$$

$$[\mathrm{NO_3}^-] = [\mathrm{NO_3}^-]_{\mathrm{init}}/(1 + Kex_{\mathrm{NO3,B}}[\mathrm{tba}^+]) \quad (12)$$

On the basis of Eqs. 10, 11, and 12, the concentration of tba^+, halide ions, and nitrate ions in the aqueous phase at equilibrium can be calculated. The extraction constant of nitrate ions used for the data analysis was taken from a previous

Table 1. Distribution Ratio of tba^+, $[tba^+X^-]_{org}[tba^+]^{-1}$, at Various tba^+ Concentrations Where X^- is Cl^-, Br^- or I^-

$[tba^+]_{init}$	$\log D_{tba^+}$		
	Cl^-	Br^-	I^-
1.995E-4	−0.082	1.101	
2.512E-4	−0.076	1.102	
3.162E-4	−0.095	1.117	
5.012E-4	−0.089	1.113	
6.310E-4	−0.097	1.115	
7.943E-4	−0.093	1.113	
1.000E-3	−0.089	1.116	
2.000E-3			2.835
4.000E-3			2.810
5.000E-3			2.832
6.000E-3			2.810
7.000E-3			2.821
8.000E-3			2.825
1.000E-2			2.826
Calculated constants of $\log Kex_{A,B}$			
	Cl^-	Br^-	I^-
	−0.09 (±0.02)	1.11 (±0.02)	2.82 (±0.03)

Aq phase: 1 $mol\,dm^{-3}$ NaX. Org. phase: Chloroform.
$Kex_{A,B} = [tba^+X^-]_{org}[tba^+]^{-1}[X^-]^{-1}$ (cf. Eq. 6).
The constant $Kex_{NO3,B} = 10^{1.08}$ (cf. Eq. 7) employed for the calculation was taken from Ref. 12.

paper.[12] The extraction of halide ions and nitrate ions with tba^+ was very marked and thus the concentration of tba^+ in the aqueous phase was changed very much by the extraction of tba^+X^- and $tba^+NO_3^-$. For this reason, correction of the tba^+ concentration for the statistical analysis of the metal extraction data on the basis of Eq. 10 should be made. These extractions also lowered the concentration of halide and nitrate ions. The change was especially large with iodide ions. Thus, when it was necessary, corrections were also made for the concentration of halide ions in the aqueous phase on the basis of Eq. 11.

2. Extraction of Copper with tba^+ in the Absence of Ascorbic Acid. When the aqueous phase, 1 $mol\,dm^{-3}$ $Na(X, NO_3)$, contained no ascorbic acid, the extraction of copper from chloride and bromide solutions after the two-phase agitation for 10 s, for 30 s and for 30 min was negligible ($\log D < -2$) throughout the ligand concentration range from 0.01 to 1 $mol\,dm^{-3}$ when the initial tba^+ concentration in the aqueous phase was 1×10^{-3} $mol\,dm^{-3}$. On the other hand, copper which was initially added in the form of Cu^{2+} was found to be extracted from iodide solutions even in the absence of ascorbic acid. No difference in the distribution ratio of copper was found when the two phases were agitated for 10 s and for 30 s. This indicates that the extraction of copper from the iodide solutions reached a transient equilibrium within a short time and that the reduction of Cu^{2+} with the iodide ions is negligible during these extractions. However, when the two phases were agitated for more than 1 min, an increase in the distribution ratio occurred and it continued furthermore when the two phases were agitated for a longer time. This should be due to the copper in the two phases being copper(II) when the two-phase agitation was done for a short time such as 30 s, but the copper(II) was gradually reduced to copper(I) in the presence of the iodide ions if the two-phase agitation was further continued. No change in the color of the aqueous and organic phase was found during the two-phase agitation. Thus, oxidation of the iodide ions by the dissolved atmospheric oxygen or nitric acid which should give the color of I_2 and/or $tba^+I_3^-$ in the both phases should be negligible. Figure 1 gives the distribution ratio of copper(II) as a function of the iodide concentration when the initial tba^+concentration is 1×10^{-3} $mol\,dm^{-3}$. Figure 2 gives the dependence of the distribution ratio of copper(II) on the tba^+ concentration in the aqueous phase, which initially contained 0.1 $mol\,dm^{-3}$ iodide ions. The data in Figs. 1 and 2 were obtained after the two-phase agitation for 30 s. The tba^+ and iodide concentration in these figures were calculated on the basis of Eqs. 10 and 11. Since the dependence of the distribution of copper(II) on the tba^+ concentration in Fig. 2 was first to second order and thus the extraction of anionic copper(II) iodide complexes with one and two tba^+ ions as ion-pairs was assumed. The data in Figs. 1 and 2 were analyzed on the basis of the following equation which was introduced from Eqs. 1, 3, 5, and 9.

$$\begin{aligned} D &= ([tba^+Cu^{II}I_3^-]_{org}+[(tba^+)_2Cu^{II}I_4^{2-}]_{org}) \\ &\qquad /([Cu^{2+}]+\sum[Cu^{II}I_d^{2-d}]) \\ &= ((Kex_{3,1}[tba^+][I^-]^3+Kex_{4,2}[tba^+]^2[I^-]^4)/(1+\sum\beta^{II}{}_d[I^-]^d) \end{aligned} \tag{13}$$

where, $Kex_{3,1} = [tba^+Cu^{II}I_3^-]_{org}[tba^+]^{-1}[Cu^{2+}]^{-1}[I^-]^{-3}$ and

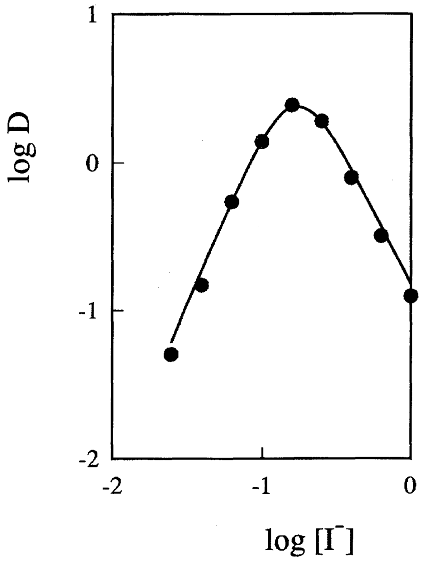

Fig. 1. Extraction of copper(II) in 1 $mol\,dm^{-3}$ $Na(I, NO_3)$ into chloroform with tba^+. The two phases were agitated for 30 s. Aq phase: 1 $mol\,dm^{-3}$ $Na(I, NO_3)$ containing 1×10^{-3} $mol\,dm^{-3}$ tba^+ at initial and 0.01 $mol\,dm^{-3}$ hydrogen ions. Org. phase: Chloroform. The solid line was calculated on the basis of Eq. 13 and the constants in Table 2 by assuming no copper(I) species.

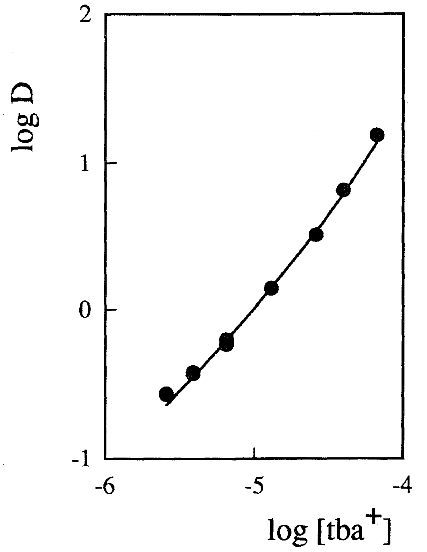

Fig. 2. Dependence of the copper(II) extraction on the tba$^+$ concentration in the aqueous phase. The two phases were agitated for 30 s. Aq phase: 1 mol dm^{-3} Na(I, NO$_3$) containing 0.1 mol dm^{-3} I$^-$ at initial and 0.01 mol dm^{-3} hydrogen ions. Org. phase: Chloroform. The solid line was calculated on the basis of Eq. 13 and the constants in Table 2 by assuming no copper(I) species.

$Kex_{4,2}=[(\text{tba}^+)_2\text{Cu}^{\text{II}}\text{I}_4^{2-}]_{\text{org}}[\text{tba}^+]^{-2}[\text{Cu}^{2+}]^{-1}[\text{I}^-]^{-4}$.

The values of extraction constant, $Kex_{3,1}$ and $Kex_{4,2}$, and the value of formation constant of copper(II) iodide complex in the aqueous phase were calculated by using a least squares computer program. No reasonable values of β^{II}_1, β^{II}_2, and β^{II}_3 were obtained by this calculation and the formation of Cu$^{\text{II}}$I$^+$, Cu$^{\text{II}}$I$_2$, and Cu$^{\text{II}}$I$_3{}^-$ were not concluded. Thus, only the Cu^{2+} and Cu$^{\text{II}}$I$_4{}^{2-}$ species were assumed in the aqueous phase. The value of the constant, β^{II}_4, is listed in Table 2. The calculated concentration of tba$^+$ in the aqueous phase at equilibrium was different from the initial value. For example, when the initial iodide concentration was 0.1 mol dm^{-3} and 1 mol dm^{-3}, the tba$^+$ concentration in the aqueous phase at equilibrium was found to be only 1.3 and 0.20% of the initial concentration when it was 1×10^{-3} mol dm^{-3}. Furthermore, the calculated concentration of iodide ions at equilibrium was also somewhat lower than the initial value. For example, when the initial tba$^+$ concentration was 1×10^{-3} mol dm^{-3} and 1×10^{-2} mol dm^{-3} and the initial iodide concentration was 0.1 mol dm^{-3}, the iodide concentration at equilibrium was 99.1 and 91.6% of the initial concentration. The calculated curve given in Figs. 1 and 2 was obtained by introducing the concentrations of tba$^+$ and iodide ions at equilibrium and the value of constants ($Kex_{3,1}$, $Kex_{4,2}$, and β^{II}_4 in Table 2) into Eq. 13.

Table 2. Formation and Extraction Constants of Copper(II) Complexes in Aqueous 1 mol dm^{-3} Na(X, NO$_3$)

X$^-$	logβ^{II}_1	logβ^{II}_2	logβ^{II}_3	logβ^{II}_4
Cl$^-$	−0.4	—	—	—
Br$^-$	−0.1	—	—	—
I$^-$	—	—	—	3.1

X$^-$	log$Kex_{3.1}$	log$Kex_{4.2}$
I$^-$	8.0	13.3
SCN$^-$	—	13.7[a)]

a) Ref. 13.

3. Extraction of Copper with tba$^+$ in the Presence of Ascorbic Acid. When the aqueous phase, 1 mol dm^{-3} Na(X, NO$_3$), contained ascorbic acid, the copper that was initially added as Cu^{2+} was extracted into chloroform with tba$^+$ from all the halide solutions. The distribution ratio of copper became a certain value after the two-phase agitation for a few minutes and it did not change after further agitation, at least for 30 min. Thus, the two-phase agitation was continued for 30 min in all the experiments in the presence of ascorbic acid. Figure 3 gives the extraction curve of copper from the aqueous halide solutions containing 0.01 mol dm^{-3} ascorbic acid and 1×10^{-3} mol dm^{-3} tba$^+$ at initial as a function of the calculated halide concentration at equilibrium. As is seen from Fig. 3, the extraction curve in all the systems is nearly a straight line with a slope of +2 in the lowest halide concentration range. It is also seen that the slope of the plot decreases gradually upon an increase in the halide concentration and the distribution ratio of copper

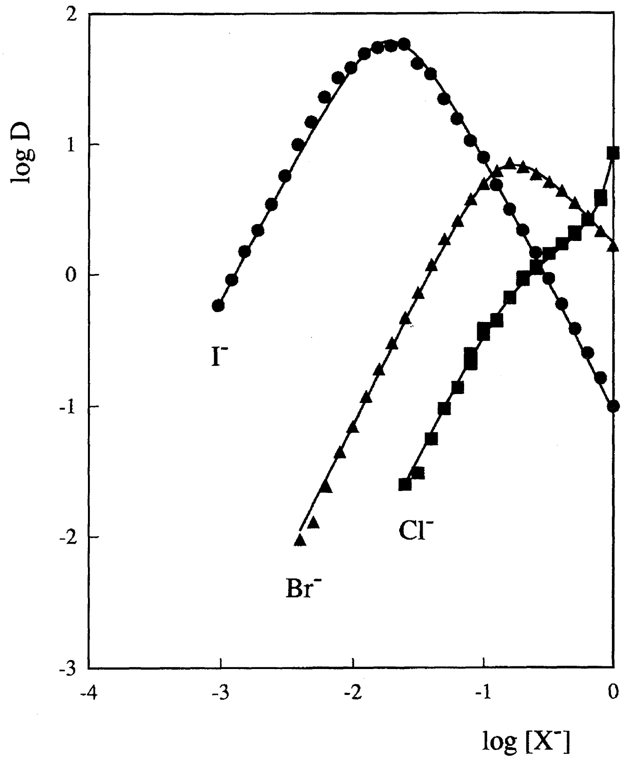

Fig. 3. Extraction of copper(I) in 1 mol dm^{-3} Na(X, NO$_3$) into chloroform with tba$^+$. The two phases were agitated for 30 min. Aq phase: 1 mol dm^{-3} Na(X, NO$_3$) containing 1×10^{-3} mol dm^{-3} tba$^+$ and 0.01 mol dm^{-3} ascorbic acid at initial and 0.01 mol dm^{-3} hydrogen ions. Org. phase: Chloroform. The solid line was calculated on the basis of Eq. 20 and the constants in Tables 2 and 3.

decreases after a maximum in the bromide and iodide systems. This is due to the formation of unextractable higher anionic complexes at higher halide concentrations in the both systems, and also to the decrease in the tba$^+$ concentration caused by the extraction of tba$^+$I$^-$ in the iodide system. No decrease in the distribution ratio of copper is found upon an increase in the chloride concentration and the slope of the plot in Fig. 3 increases even in the highest chloride concentration range. This is due to the increase in the free tba$^+$ concentration in the aqueous phase by an increase in the chloride concentration, which decreases the nitrate concentration. This occurs because the extraction of tba$^+$NO$_3{}^-$ is better than that of tba$^+$Cl$^-$. This effect is especially marked in the highest chloride concentration range as is seen from Fig. 3. The dependence of the distribution ratio of copper on the tba$^+$ concentration was further examined. Figure 4 gives the data when the initial chloride and bromide concentration was 0.1 mol dm^{-3} and 0.05 mol dm^{-3}, respectively, and when the initial iodide concentration was 1×10^{-3} mol dm^{-3} and 1×10^{-2} mol dm^{-3}. The decrease in the chloride and bromide concentration in the aqueous phase at equilibrium from the initial concentration due to the extraction of tba$^+$Cl$^-$ and tba$^+$Br$^-$ was calculated to be negligible in all the concentration ranges. (the decrease was less than 1% from the initial concentration). On the other hand, the decrease in the iodide concentration upon the extraction of tba$^+$I$^-$ was not negligible, as was described (the largest decrease was about 8% with the data in Figs. 3 and 4). The value of vertical axis in Fig. 4 gives the calculated value, $D/[\mathrm{X}^-]^2$: this should normalize the change in the halide concentration in the aqueous phase. The decrease in the tba$^+$ concentration at equilibrium from the initial value was calculated on the basis of Eq. 10 and the value of the horizontal axis gives the corrected one. As is seen from Fig. 4, the distribution ratio of copper is first order dependent on the tba$^+$ concentration in the aqueous phase. Since the distribution ratio of copper in the presence of ascorbic acid was higher than that obtained in the absence, except in the highest iodide concentration range, it can be assumed that the extracted species was copper(I) anionic complexes in the chloride and bromide systems and that was also mainly copper(I) anionic complex in the iodide system. Thus the extracted species was assumed to be in the form of tba$^+$Cu$^{\mathrm{I}}$X$_2{}^-$ from the dependence of the distribution ratio on the tba$^+$ concentration in Fig. 4. From these assumptions, the data given in Figs. 3 and 4 were treated on the basis of the following equation which is introduced from Eq. 1 to Eq. 5.

$$\begin{aligned} D &= [\mathrm{tba^+Cu^IX_2{}^-}]_{\mathrm{org}}/([\mathrm{Cu(I)}]_{\mathrm{total}}+[\mathrm{Cu(II)}]_{\mathrm{total}}) \\ &= Kex_{2,1}[\mathrm{tba^+}][\mathrm{X^-}]^2[\mathrm{e^-}]/(C[\mathrm{e^-}](1+\textstyle\sum\beta^{\mathrm{I}}{}_c[\mathrm{X^-}]^c) \\ &\quad +(1+\textstyle\sum\beta^{\mathrm{II}}{}_d[\mathrm{X^-}]^d)) \end{aligned} \tag{14}$$

The formation constants in Eq. 14 are defined as:

$$\mathrm{Cu^+} + c\mathrm{X^-} \rightleftharpoons \mathrm{Cu^IX}_c^{1-c}$$
$$\beta^{\mathrm{I}}{}_c = [\mathrm{Cu^IX}_c^{1-c}][\mathrm{Cu^+}]^{-1}[\mathrm{X^-}]^{-c} \tag{15}$$

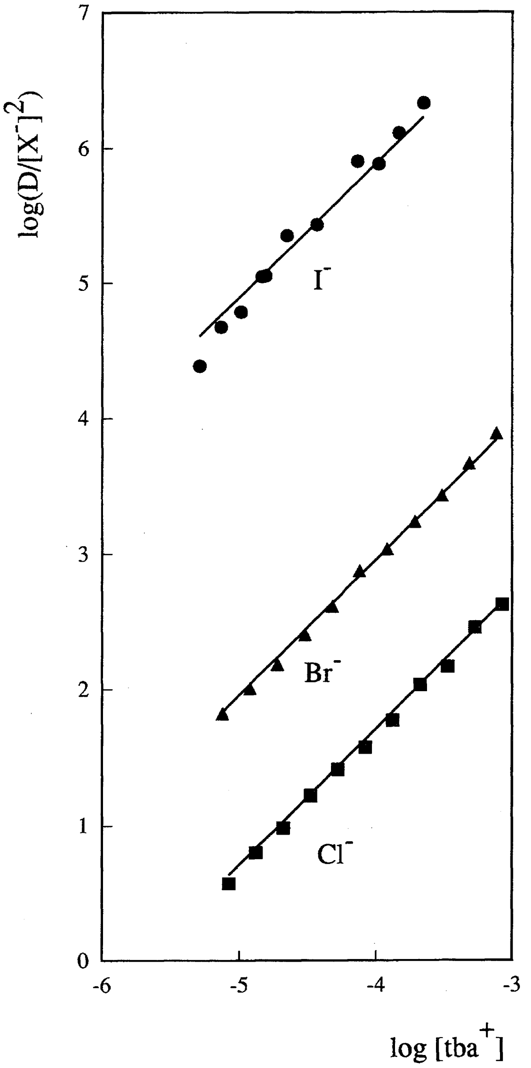

Fig. 4. Dependence of copper(I) extraction on the tba$^+$ concentration in the aqueous phase. The two phases were agitated for 30 min. The distribution ratio is normalized to the change in the halide concentration. Aq phase: 1 mol dm^{-3} Na(X, NO$_3$) containing 0.01 mol dm^{-3} ascorbic acid at initial and 0.01 mol dm^{-3} hydrogen ions. Org. phase: Chloroform. The solid line was calculated on the basis of Eq. 20 and the constants in Tables 2 and 3.

$$\mathrm{Cu^{2+}} + d\mathrm{X^-} \rightleftharpoons \mathrm{Cu^{II}X}_d^{2-d}$$
$$\beta^{\mathrm{II}}{}_d = [\mathrm{Cu^{II}X}_d^{2-d}][\mathrm{Cu^{2+}}]^{-1}[\mathrm{X^-}]^{-d}. \tag{16}$$

The extraction constant, $Kex_{2,1}$, and the constant C are defined as:

$$\mathrm{Cu^{2+}} + \mathrm{e^-} + 2\mathrm{X^-} + \mathrm{tba^+} \rightleftharpoons \mathrm{tba^+Cu^IX_2^-}{}_{(\mathrm{org})}$$
$$Kex_{2,1} = [\mathrm{tba^+Cu^IX_2{}^-}]_{\mathrm{org}}[\mathrm{Cu^{2+}}]^{-1}[\mathrm{X^-}]^{-2}[\mathrm{tba^+}]^{-1}[\mathrm{e^-}]^{-1} \tag{17}$$

$$\mathrm{Cu^{2+}} + \mathrm{e^-} \rightleftharpoons \mathrm{Cu^+}$$
$$C = [\mathrm{Cu^+}][\mathrm{Cu^{2+}}]^{-1}[\mathrm{e^-}]^{-1}. \tag{18}$$

Since the concentration of reducing agent was constant and it was in large excess to the total copper and since the hydrogen-ion concentration was also constant in this study, the term $[e^-]$ can be regarded as a certain constant value. Thus, the following conditional constant, $Kex^*_{2,1}$ and C^*, can be defined:

$$Kex^*_{2,1} = Kex_{2,1}[e^-]$$
$$C^* = [Cu^+][Cu^{2+}]^{-1} = C[e^-] \qquad (19)$$

and by using these constants, Eq. 14 can be rewritten as:

$$D = Kex^*_{2,1}[tba^+][X^-]^2/(C^*(1+\sum\beta^{I}_c[X^-]^c)+(1+\sum\beta^{II}_d[X^-]^d)). \qquad (20)$$

By statistical analysis of the data on the basis of Eq. 20, the values of $Kex^*_{2,1}$, $C^*\beta^{I}_c$, and β^{II}_d were measured. The value of C^* could not be obtained from the results of experiments in this study and only the value of K^*_n which is defined by the following equation could be obtained:

$$Cu^{2+} + e^- + cX^- \rightleftarrows Cu^{I}X_c{}^{1-c}$$
$$K^*_n = C^*\beta^{I}_c. \qquad (21)$$

The values obtained are listed in Table 3. The solid curves in Fig. 3 and the straight lines in Fig. 4 are calculated on the basis of Eq. 20 which was introduced the values of constants in Table 3 and the values of the tba^+ and X^- concentration in the aqueous phase at equilibrium.

4. Extraction with Htta. The solvent extraction of copper(II) from 1 mol dm^{-3} $NaNO_3$ solutions with 0.1 mol dm^{-3} Htta into chloroform was measured as a function of the hydrogen-ion concentration. The extraction constant and the distribution ratio may be written as:

$$Cu^{2+} + 2Htta_{(org)} \rightleftarrows Cu^{II}(tta)_{2(org)} + 2H^+$$
$$Kex_{(Htta)} = [Cu^{II}(tta)_2]_{org}[H^+]^2[Cu^{2+}]^{-1}[Htta]_{org}{}^{-2} \qquad (22)$$

$$D_0 = [Cu^{II}(tta)_2]_{org}[Cu^{2+}]^{-1} = Kex_{(Htta)}[Htta]_{org}{}^2[H^+]^{-2}. \qquad (23)$$

Since the extraction of $Cu^{I}tta$ was assumed to be negligible, this term is not given in the equations. When halide complexes of copper(I) and copper(II) are formed in the aqueous phase of such a chelate extraction system and when they are not extractable into chloroform, the distribution ratio of copper can be written as:

$$D = [Cu^{II}(tta)_2]_{org}/([Cu^+] + \sum[Cu^{I}X_c{}^{1-c}] + [Cu^{2+}] + \sum[Cu^{II}X_d{}^{2-d}]). \qquad (24)$$

On the basis of Eqs. 15, 16, 22, and 23, Eq. 24 can be rewritten as:

$$D = Kex_{(Htta)}[Htta]_{org}{}^2[H^+]^{-2}/([Cu^+][Cu^{2+}]^{-1}(1+\sum\beta^{I}_c[X^-]^c) + (1+\sum\beta^{II}_d[X^-]^d)) \qquad (25)$$

$$D/D_0 = 1/([Cu^+][Cu^{2+}]^{-1}(1+\sum\beta^{I}_c[X^-]^c)+(1+\sum\beta^{II}_d[X^-]^d)). \qquad (26)$$

Thus, when the value D/D_0 is measured as a function of the halide concentration, the data can be analyzed on the basis of Eq. 26. As it will be considered, the value, $[Cu^+][Cu^{2+}]^{-1}$, should always be constant when the concentration of the reducing agent and that of hydrogen ions in the aqueous phase is constant. It was found that the $\log D$ vs. $-\log[H^+]$ plot was a straight line of a slope +2. This indicates that the extraction of copper with Htta is well explained on the basis of Eqs. 22 and 23.

The extraction equilibrium of copper from 1 mol dm^{-3} Na(X, NO_3) with 0.1 mol dm^{-3} Htta into chloroform was established by the two-phase agitation for 30 s in the absence of ascorbic acid and for 3 min in its presence. Since no change in the distribution ratio of copper was found when the two phases were further agitated in the presence of ascorbic acid, the data obtained after the two-phase agitation for 30 min was used for the data analysis. In the iodide system, the extraction with Htta in the absence of ascorbic acid after the two-phase agitation for 30 s was similar to that obtained after the two-phase agitation for 10 s and thus the data after the two-phase agitation for 30 s were used for the statistical analysis. It was found that a further two-phase agitation in the iodide system caused a gradual decrease in the distribution ratio of copper which was assumed to be due to the reduction of copper(II) to copper(I) by the iodide ions. The data of Htta extraction are given in Figs. 5(a), 5(b), and 5(c). As is seen from these figures, the distribution ratio of copper decreases upon an increase in the halide concentration in the absence of ascorbic acid and it decreases very much in the presence of this reducing agent. The following equation can be introduced for the data in the absence of ascorbic acid on the basis of Eq. 25 by assuming that copper(I) species are negligible.

$$D = Kex_{(Htta)}[Htta]_{org}{}^2[H^+]^{-2}/(1+\sum\beta^{II}_d[X^-]^d) \qquad (27)$$

The formation constants of copper(II) halide complexes are listed in Table 2. In the presence of ascorbic acid, the data were analyzed by assuming that copper(I) and copper(II) halide complexes should be formed in the aqueous phase and the extraction of the $Cu^{I}(tta)$ species into chloroform should be negligible. The larger decrease in the distribution ratio in the presence of ascorbic acid should be due to that the

Table 3. Formation and Extraction Constants of Copper(I) Complexes in Aqueous 1 mol dm^{-3} Na(X, NO_3)

X^-	tba^+ extraction	Htta extraction	tba^+ extraction	Htta extraction
	$\log K^*_2$	$\log K^*_2$	$\log K^*_3$	$\log K^*_3$
Cl^-	1.5	1.6	—	—
Br^-	—	—	2.6	2.8
I^-	—	—	5.2	5.7

X^-	$\log Kex^*_{2,1}$
Cl^-	5.7
Br^-	7.0
I^-	9.9

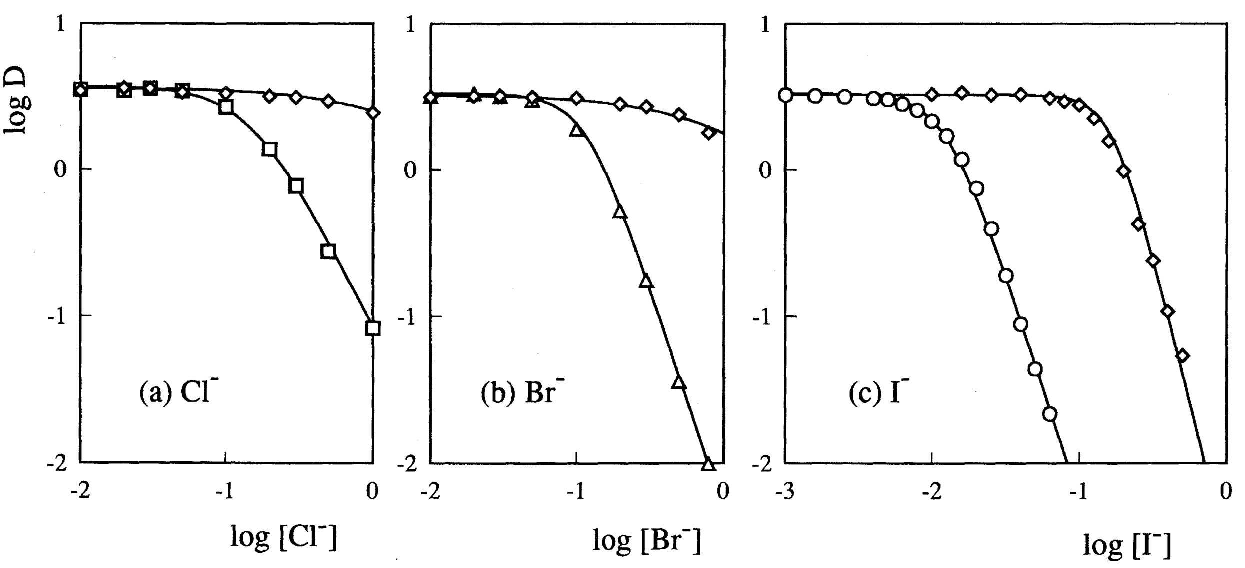

Fig. 5. Extraction of copper(II) with Htta as a function of halide concentration in the absence and presence of reducing agent. The two phases were agitated for 30 s (◇) and 30 min (□△○). Aq phase: 1 mol dm^{-3} Na(X, NO$_3$) containing 0.01 mol dm^{-3} hydrogen ions and no ascorbic acid (◇) or 0.01 mol dm^{-3} ascorbic acid (□△○). Org. phase: Chloroform containing 0.1 mol dm^{-3} Htta. The solid line was calculated on the basis of Eq. 28 and the constants in Tables 2 and 3.

copper(I) halide complexes are more stable than the copper(II) halide complexes. Thus the following equation in the presence of ascorbic acid can be introduced on the basis of Eqs. 19 and 25.

$$D = Kex_{(\mathrm{Htta})}[\mathrm{Htta}]_{\mathrm{org}}{}^{2}[\mathrm{H}^{+}]^{-2} \Big/ (C^{*}(1+\textstyle\sum\beta^{\mathrm{I}}{}_{c}[\mathrm{X}^{-}]^{c})+(1+\textstyle\sum\beta^{\mathrm{II}}{}_{d}[\mathrm{X}^{-}]^{d})) \quad (28)$$

The data were analyzed by using the least square computer program on the basis of Eq. 28. As was described, the value C^* which gives the value of $[\mathrm{Cu}^+][\mathrm{Cu}^{2+}]^{-1}$ could not be determined and thus only the conditional constant, K_n^*, $C^*\beta_c^{\mathrm{I}}$, could be determined also by the Htta extraction method.

Discussion

The statistical analysis of the extraction data with tba$^+$ in Figs. 1 and 2 and Figs. 3 and 4 was made on the basis of Eq. 13 and Eq. 20, respectively. Since the distribution ratio of copper in Figs. 1 and 2 was not affected by the change in the agitation time from 10 to 30 s, the extraction equilibrium should be reached and the reduction of copper(II) should be negligible under these conditions. The value of formation constant of the copper(II) iodide complex, $\beta^{\mathrm{II}}{}_4$, obtained by the two extraction methods agrees to each other and thus the assumption on the basis of the tba$^+$ extraction data that the formation of $\mathrm{Cu^{II}I^+}$, $\mathrm{Cu^{II}I_2}$, and $\mathrm{Cu^{II}I_3}^-$ complexes is negligible are also supported by the results of Htta extraction in Fig. 5(c). As was reported previously,[13] copper(II) in thiocyanate solutions was extracted with tba$^+$ into chloroform as $(\mathrm{tba^+})_2\mathrm{Cu^{II}(SCN)_4}^{2-}$. The constant, $Kex_{4,2}=10^{13.7}$, for the extraction of this thiocyanate complex is nearly similar to that of $(\mathrm{tba^+})_2\mathrm{Cu^{II}I_4}^{2-}$ in this study, $Kex_{4,2}=10^{13.3}$. The molar ratio of copper(I) and copper(II) species in the aqueous phase can be calculated on the basis of Eqs. 4, 5, 15, and 16 and the constants in Tables 2 and 3 as shown in Fig. 6(a) to

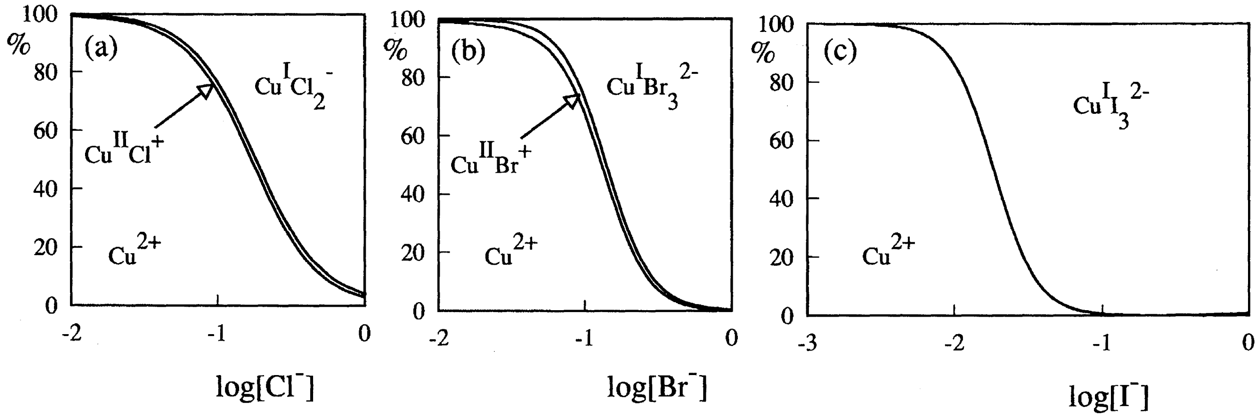

Fig. 6. The calculated molar ratio of copper species in the aqueous phase as a function of the halide concentration using the formation constants of the complexes given in Tables 2 and 3. The molar ratio of $\mathrm{Cu^{II}I_4}^{2-}$ is less than 1% in all the concentration range and can not be indicated clearly in Fig. 6(c).

Fig. 6(c).

The formation constant of the copper(I) species in the aqueous phase given in Table 3 are conditional formation constants of the chemical species but these values are valid only under the conditions where the concentration of the reducing agent and the hydrogen ions are certain given values, that is, both are 0.01 mol dm^{-3} in this study. Under such conditions, the value C^* which gives $[\mathrm{Cu}^+][\mathrm{Cu}^{2+}]^{-1}$ should be constant even when the halide ions are present or absent, the halide ions are chloride, bromide, or iodide and the concentration of the halide ions is different. Although the value of C^* cannot be determined by the experimental method used in this study, it should be assumed that $[\mathrm{Cu}^+]$ is much smaller than $[\mathrm{Cu}^{2+}]$ and thus C^* is much smaller than 1. This is seen from the Htta extraction data in Fig. 5(a) to Fig. 5(c): The copper extraction with Htta was not affected by addition of the ascorbic acid when the halide concentration was low. If a large amount of Cu^+ would be formed in the aqueous phase under such conditions, the Htta extraction should be lowered because the extraction of Cu^+ with Htta should be negligible as it could be assumed from the extraction data of silver(I) with Htta in chloroform which was found only at high pH such as 7 to 8.[14] From these, it is clear that the copper species is mainly Cu^{2+} in the lower halide concentration range even in the presence of ascorbic acid. The extracted species in the chloride and bromide systems were mainly $\mathrm{tba}^+\mathrm{Cu}^{\mathrm{I}}\mathrm{X}_2{}^-$. In the iodide extraction systems, although the copper(II) anionic iodide complexes are effectively extracted together with tba^+ in the absence of ascorbic acid, still the extracted species in the presence of ascorbic acid is calculated to be nearly only the $\mathrm{tba}^+\mathrm{Cu}^{\mathrm{I}}\mathrm{I}_2{}^-$ species. The formation constants for $\mathrm{Cu}^{\mathrm{I}}\mathrm{Cl}_2{}^-$ and $\mathrm{Cu}^{\mathrm{I}}\mathrm{Br}_3{}^{2-}$ obtained by the two experimental methods agree with each other but that for $\mathrm{Cu}^{\mathrm{I}}\mathrm{I}_3{}^{2-}$ obtained by the Htta extraction method is a little higher than that obtained by the tba^+ extraction method as is seen from Table 3. Up to now, this cannot be well explained.

Under the conditions of this study, both copper(I) and copper(II) were present in the system when the reducing agent was present. The complex formation and the solvent extraction equilibria of copper(II) in the systems can be obtained by the experiments in the absence of the reducing agent. No separation of copper(I) and copper(II) could be made experimentally in this study and thus only the total amount of copper in the two phases was measured by the atomic absorption method. For this reason, the chemical behavior of the copper(I) species was estimated from the difference of the distribution ratio of total copper in the absence and presence of the reducing agent but under otherwise identical conditions. Thus from the analysis of the solvent extraction data, not only the formation of the metal complexes in the different oxidation states but also their redox reactions can be learned reasonably.

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