Solvent Extraction of Copper(I) and (II) as Thiocyanate Complexes with Tetrabutylammonium Ions into Chloroform and with Trioctylphosphine Oxide into Hexane

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The solvent extraction of copper(II) in 1 mol dm^{-3} Na(SCN, NO$_3$), in which the thiocyanate concentration was 0.01 to 1 mol dm^{-3}, with tetrabutylammonium ions (tba$^+$) into chloroform and with trioctylphosphine oxide (TOPO) into hexane was studied. Also, the solvent extraction of copper(I), which was formed by reducing copper(II) by ascorbic acid in these aqueous solutions, was studied. By a statistical analysis of the extraction data, it was concluded that copper(I) was extracted as tba$^+$Cu^I(SCN)$_2^-$ and Cu^{I}SCN(TOPO)$_3$, and copper(II) was extracted as (tba$^+$)$_2$Cu^{II}(SCN)$_4^{2-}$ and Cu^{II}(SCN)$_2$(TOPO)$_3$. Although copper(I) was extracted with both extractants better than copper(II) in the lower thiocyanate concentration range, copper(II) was extracted better in the higher thiocyanate concentration range. This was concluded to be due to better extraction of the extractable species of copper(I) than those of copper(II); however, copper(I) formed unextractable complexes much more than did copper(II) in the higher thiocyanate concentration range in the aqueous phase.

Keywords   Solvent extraction, copper(I), copper(II), thiocyanate complex, tetrabutylammonium ion, trioctylphosphine oxide

In a previous paper[1], it was reported that the extraction of a small amount, 1×10^{-5} mol dm^{-3}, of copper(II) in aqueous 0.1 mol dm^{-3} sodium nitrate solutions containing less than 1×10^{-3} mol dm^{-3} thiocyanate ions into 4-methyl-2-pentanone (MIBK) was negligible. The extraction of copper(II) was also negligible from these aqueous solutions into chloroform with bulky cations, tetrabutylammonium ions (tba$^+$). These were concluded to be due to the negligible complex formation of copper(II) in such a low thiocyanate concentration range. On the other hand, it was also found that copper(II) in these solvent extraction systems could be extracted when an effective reductant, ascorbic acid, was added to the aqueous phase. The extracted species were found to be Cu^{I}SCN and Na$^+$Cu^I(SCN)$_2^-$ into MIBK in the absence of tba$^+$ and tba$^+$Cu^I(SCN)$_2^-$ into chloroform in the presence of tba$^+$. Thus, when ascorbic acid was present, copper(II) in the aqueous phase was extracted as copper(I) thiocyanate complexes, though it was assumed that only copper(II) was present in the aqueous phase. However, it was also found that copper(II) in sodium thiocyanate solutions was extracted into MIBK when the thiocyanate concentration was higher than 0.1 mol dm^{-3}, though the extraction was not quantitative.[2] In the present study, copper initially in the form of Cu^{2+} was added into aqueous 1 mol dm^{-3} Na(SCN, NO$_3$) solutions where the thiocyanate concentration was 0.01 to 1 mol dm^{-3} and containing none or an amount of ascorbic acid. The copper was then extracted with

TOPO into hexane and also with tba$^+$ into chloroform. Under such conditions, it was concluded that copper(I) was extracted in the presence of ascorbic acid and copper(II) was extracted in the absence of this reducing reagent.
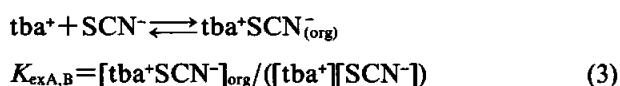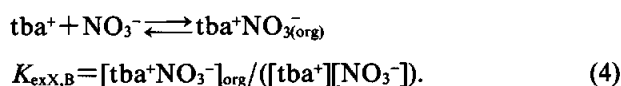
Statistical

In the present paper, any chemical species in the organic phase is denoted by the subscript "org" while that in the aqueous phase is denoted by the lack of any subscript. The initial concentration is denoted by the subscript "init". The volume of the two liquid phases is assumed to be the same. The distribution ratio of copper(I) and (II) in a liquid–liquid system can be defined as:

$$D_I = [\text{Cu(I)}]_{\text{org,total}} / [\text{Cu(I)}]_{\text{total}} \tag{1}$$

$$D_{II} = [\text{Cu(II)}]_{\text{org,total}} / [\text{Cu(II)}]_{\text{total}}. \tag{2}$$

The extraction equilibrium of tba$^+$ as an ion-pair with thiocyanate ions and with nitrate ions can be written as follows:

$$\text{tba}^+ + \text{SCN}^- \rightleftharpoons \text{tba}^+\text{SCN}^-_{(\text{org})}$$

$$K_{\text{exA,B}} = [\text{tba}^+\text{SCN}^-]_{\text{org}} / ([\text{tba}^+][\text{SCN}^-]) \tag{3}$$

$$tba^+ + NO_3^- \rightleftharpoons tba^+NO_{3(org)}^-$$

$$K_{exX,B} = [tba^+NO_3^-]_{org}/([tba^+][NO_3^-]). \tag{4}$$

When no formation of ion-pairs in the aqueous phase is assumed, the concentration of tba^+ at the initial stage can be written as:

$$[tba^+]_{init} = [tba^+] + [tba^+SCN^-]_{org} + [tba^+NO_3^-]_{org}$$

$$+ \Sigma a[(tba^+)_a Cu^{II}(SCN)_b^{2+a-b}]_{org}$$

$$+ \Sigma c[(tba^+)_c Cu^I(SCN)_d^{1+c-d}]_{org}. \tag{5}$$

However, since the initial tba^+ concentration is always much higher than the total concentration of copper complex species in the organic phase, the terms of the extracted copper(I) and (II) complexes in Eq. (5) should be negligible, and can then be rewritten as:

$$[tba^+]_{init} = [tba^+] + [tba^+SCN^-]_{org} + [tba^+NO_3^-]_{org}$$

$$[tba^+] = [tba^+]_{init}/(1 + K_{exA,B}[SCN^-] + K_{exX,B}[NO_3^-]). \tag{6}$$

In such systems, the extraction of these ion-pairs also decreases the concentration of thiocyanate and nitrate ions in the aqueous phase, and the following equations can be written as:

$$[SCN^-]_{init} = [SCN^-] + [tba^+SCN^-]_{org}$$

$$[NO_3^-]_{init} = [NO_3^-] + [tba^+NO_3^-]_{org}$$

$$[SCN^-] = [SCN^-]_{init}/(1 + K_{exA,B}[tba^+]) \tag{7}$$

$$[NO_3^-] = [NO_3^-]_{init}/(1 + K_{exX,B}[tba^+]). \tag{8}$$

By using Eqs. (6), (7) and (8), the free tba^+ concentration in the aqueous phase, which is available for the extraction of copper complexes, and the concentration of thiocyanate and nitrate ions in the aqueous phase at equilibrium can be calculated.

When TOPO is used as the extractant, it can be assumed that the amount of TOPO in the aqueous phase should be much smaller than that in the organic phase, and that the following equation can be written by neglecting the TOPO in the aqueous phase as:

$$[TOPO]_{org,init} = [TOPO]_{org} + [HNO_3 \cdot TOPO]_{org}$$

$$+ [HSCN \cdot TOPO]_{org}$$

$$+ \Sigma e[Cu^{II}(SCN)_2(TOPO)_e]_{org}$$

$$+ \Sigma f[Cu^ISCN(TOPO)_f]_{org}. \tag{9}$$

Here, the TOPO concentration in hexane is always assumed to be much higher than the total concentration of extracted copper complexes, and that the extraction of sodium thiocyanate and sodium nitrate with TOPO is assumed to be negligible under the conditions of the present study. In previous papers[3,4], the extraction equilibrium of nitric and thiocyanic acid with TOPO was written as:

$$H^+ + NO_3^- + TOPO_{(org)} \rightleftharpoons HNO_3 \cdot TOPO_{(org)}$$

$$K_{exHNO3} = [HNO_3 \cdot TOPO]_{org}/([H^+][NO_3^-][TOPO]_{org})$$

$$\tag{10}$$

$$H^+ + SCN^- + TOPO_{(org)} \rightleftharpoons HSCN \cdot TOPO_{(org)}$$

$$K_{exHSCN} = [HSCN \cdot TOPO]_{org}/([H^+][SCN^-][TOPO]_{org}).$$

$$\tag{11}$$
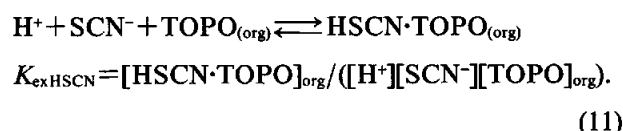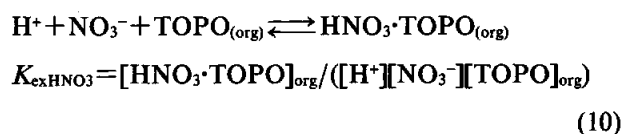
By introducing Eqs. (10) and (11), Eq. (9) can be rewritten as:

$$[TOPO]_{org} = [TOPO]_{org,init}/(1 + K_{exHNO3}[H^+][NO_3^-]$$

$$+ K_{exHSCN}[H^+][SCN^-]). \tag{12}$$

In such systems, the extraction of these acids with TOPO decreases the concentration of the thiocyanate and nitrate ions in the aqueous phase and the following equations can be written:

$$[SCN^-]_{init} = [SCN^-] + [HSCN \cdot TOPO]_{org}$$

$$[NO_3^-]_{init} = [NO_3^-] + [HNO_3 \cdot TOPO]_{org}$$

$$[SCN^-] = [SCN^-]_{init}/(1 + K_{exHSCN}[H^+][TOPO]_{org}) \tag{13}$$

$$[NO_3^-] = [NO_3^-]_{init}/(1 + K_{exHNO3}[H^+][TOPO]_{org}). \tag{14}$$

By using Eqs. (12), (13) and (14), the free TOPO concentration in hexane, which is available for the extraction of copper complexes, and the concentration of thiocyanate and nitrate ions in the aqueous phase at equilibrium can be calculated.
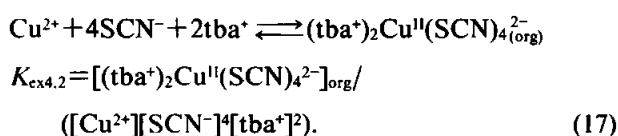
Extraction of copper(II)

Since it was assumed from the experiments in the present study that the extracted species of copper(II) with tba^+ should be in the form of $(tba^+)_2Cu^{II}(SCN)_4^{2-}$, the following equation can be written:

$$D = [(tba^+)_2Cu^{II}(SCN)_4^{2-}]_{org}/(\Sigma[Cu^{II}(SCN)_n^{2-n}]), \tag{15}$$

where $n \geq 0$. The stability constants for the copper(II) thiocyanate complexes in the aqueous phase can be written as:

$$\beta_n = [Cu^{II}(SCN)_n^{2-n}]/([Cu^{2+}][SCN^-]^n). \tag{16}$$

The extraction of the copper(II) thiocyanate complex with tba^+ can be written as:

$$Cu^{2+}+4SCN^-+2tba^+ \rightleftharpoons (tba^+)_2Cu^{II}(SCN)_{4(org)}^{2-}$$

$$K_{ex4,2}=[(tba^+)_2Cu^{II}(SCN)_4^{2-}]_{org}/$$

$$([Cu^{2+}][SCN^-]^4[tba^+]^2). \qquad (17)$$

By introducing Eqs. (16) and (17), Eq. (15) can be rewritten as:

$$D=K_{ex4,2}[SCN^-]^4[tba^+]^2/(1+\Sigma\beta_{n+1}[SCN^-]^{n+1}) \qquad (18)$$

$$D/[tba^+]^2=K_{ex4,2}[SCN^-]^4/(1+\Sigma\beta_{n+1}[SCN^-]^{n+1}). \qquad (18')$$

Since it was assumed from the experiments in the present study that the extracted species of copper(II) with TOPO should be in the form of $Cu^{II}(SCN)_2(TOPO)_3$, the following equation can be written:

$$D=[Cu^{II}(SCN)_2(TOPO)_3]_{org}/(\Sigma[Cu^{II}(SCN)_2^{2-n}]), \qquad (19)$$

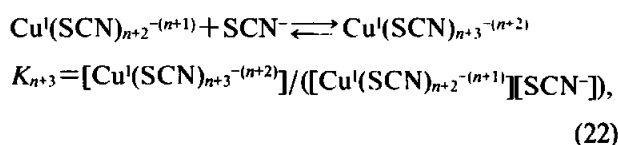where $n\geqq0$. The extraction of the copper(II) thiocyanate complex with TOPO can be written as:

$$Cu^{2+}+2SCN^-+3(TOPO)_{(org)}\rightleftharpoons$$

$$Cu^{II}(SCN)_2(TOPO)_{3(org)}$$

$$K_{ex2,3(TOPO)}=[Cu^{II}(SCN)_2(TOPO)_3]_{org}/$$

$$([Cu^{2+}][SCN^-]^2[TOPO]_{org}^3). \qquad (20)$$
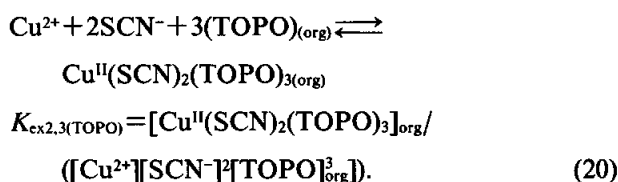
By introducing Eqs. (16) and (20), Eq. (19) can be rewritten as:

$$D=K_{ex2,3(TOPO)}[SCN^-]^2[TOPO]_{org}^3/$$

$$(1+\Sigma\beta_{n+1}[SCN^-]^{n+1}) \qquad (21)$$

$$D/[TOPO]_{org}^3=K_{ex2,3(TOPO)}[SCN^-]^2/$$

$$(1+\Sigma\beta_{n+1}[SCN^-]^{n+1}). \qquad (21')$$

Extraction of copper(I)

Under the conditions of the copper(I) extraction experiments in the present study, all of the copper species can be assumed to be in the monovalent state. Since the Cu^+ and Cu^ISCN in the aqueous phase was assumed to be negligible, the stability constants of the copper(I) thiocyanate complexes in the aqueous phase can only be written in the following way:

$$Cu^I(SCN)_{n+2}^{-(n+1)}+SCN^-\rightleftharpoons Cu^I(SCN)_{n+3}^{-(n+2)}$$

$$K_{n+3}=[Cu^I(SCN)_{n+3}^{-(n+2)}]/([Cu^I(SCN)_{n+2}^{-(n+1)}][SCN^-]), \qquad (22)$$

where $n\geqq0$.

Since it was assumed from the experiments in the present study that the extracted species of copper(I) with tba$^+$ should be in the form of $tba^+Cu^I(SCN)_2^-$, the following equation can be written:

$$D=[tba^+Cu^I(SCN)_2^-]_{org}/\Sigma[Cu^I(SCN)_{n+2}^{-(n+1)}], \qquad (23)$$

where $n\geqq0$. The extraction constant with tba$^+$ can be written as:

$$Cu(SCN)_2^-+tba^+\rightleftharpoons tba^+Cu^I(SCN)_{2(org)}^-$$

$$K_{ex2,1}=[tba^+Cu^I(SCN)_2^-]_{org}/([Cu(SCN)_2^-][tba^+]). \qquad (24)$$
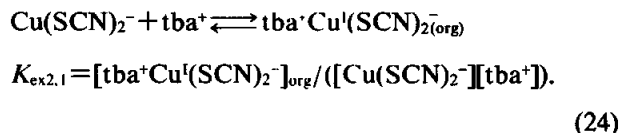
Thus, Eq. (23) can be rewritten as:

$$D=K_{ex2,1}[tba^+]/(1+K_3[SCN^-]+K_3K_4[SCN^-]^2+\cdots) \qquad (25)$$

$$D/[tba^+]=K_{ex2,1}/(1+K_3[SCN^-]+K_3K_4[SCN^-]^2+\cdots). \qquad (25')$$

Since it was assumed from the experiments in the present study that the extracted species of copper(I) with TOPO should be in the form of $Cu^ISCN(TOPO)_3$, the following equation can be written:

$$D=[Cu^ISCN(TOPO)_3]_{org}/\Sigma[Cu(SCN)_{n+2}^{-(n+1)}], \qquad (26)$$

where $n\geqq0$. The extraction constant with TOPO under the conditions of the present study should be written as:

$$Cu^I(SCN)_2^-+3(TOPO)_{(org)}\rightleftharpoons$$

$$Cu^ISCN(TOPO)_{3(org)}+SCN^-$$

$$K_{ex1,3(TOPO)}=[Cu^ISCN(TOPO)_3]_{org}[SCN^-]/$$

$$([Cu^I(SCN)_2^-][TOPO]_{org}^3). \qquad (27)$$
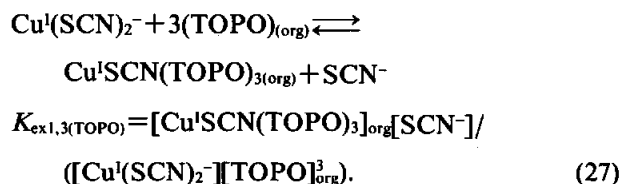
Equation (26) can be rewritten as:

$$D=K_{ex1,3(TOPO)}[TOPO]_{org}^3/([SCN^-](1+K_3[SCN^-]$$

$$+K_3K_4[SCN^-]^2+\cdots)) \qquad (28)$$

$$D/[TOPO]_{org}^3=K_{ex1,3(TOPO)}/([SCN^-](1+K_3[SCN^-]$$

$$+K_3K_4[SCN^-]^2+\cdots)). \qquad (28')$$

Experimental

All of the reagents were of analytical grade. Sodium nitrate and sodium thiocyanate were recrystallized three times from water. Chloroform was washed several times with water before use. Trioctylphosphine oxide was recrystallized from cyclohexane.

All of the solvent extraction procedures were carried out in a thermostated room at 298 K. A stock sodium thiocyanate solution was prepared by dissolving sodium thiocyanate crystals in water; the concentration was determined by titration with a standard silver(I) nitrate solution. Copper(II) nitrate was dissolved in nitric acid,

and the copper concentration in the solution was determined by EDTA titration.   Stoppered glass tubes (capacity 20 cm³) were used for the solvent extraction experiments.   The vessels were covered by aluminum foil in order to avoid any effect of light.   The aqueous solution was prepared by mixing 1 mol dm⁻³ sodium thiocyanate and 1 mol dm⁻³ sodium nitrate.   Then, a small amount of nitric acid was added in order to adjust the initial hydrogen-ion concentration, 1.00×10^{-2} mol dm⁻³, and a solution containing tba⁺NO₃⁻ was added. Then, a solution of ascorbic acid was added to the aqueous solution just before starting the experiment in order to reduce copper(II) to copper(I).   The aqueous solution was placed in a tube, and a portion of chloroform was added.   After the two phases had been agitated for about 5 min, and an amount of copper(II) nitrate solution was added.   The initial copper concentration in the aqueous phase was 2×10^{-5} mol dm⁻³.   The volume of the two phases was both 6 cm³.   The two phases were agitated for a certain given time and centrifuged.   The copper extracted into the organic phase was stripped by 1 mol dm⁻³ nitric acid.   The copper content in this aqueous solution and that in the equilibrated aqueous phase were determined by atomic absorption spectrometry.   The hydrogen-ion concentration was determined by potentiometry using a solution containing 1.00×10^{-2} mol dm⁻³ nitric acid and 0.99 mol dm⁻³ sodium nitrate as the standard of $-\log[H^+]$ is 2.00.

For the solvent extraction of copper(I) with TOPO, an aqueous solution containing no tba⁺NO₃, but otherwise identical to that mentioned above, was prepared.   The aqueous solution was placed in a tube and hexane containing TOPO was added.   The procedures thereafter were the same as those for extraction with tba⁺.

The solvent extraction of copper(II) was carried out in a similar manner to that of copper(I), except that ascorbic acid was not added.

A determination of the stability constants of copper(II) thiocyanate complexes in the aqueous phase was carried out by a chelate-extraction method in a similar manner as that described previously.[2]

Results

Copper(I) and (II) in the thiocyanate solutions were extracted as anionic thiocyanate complexes with tetra-butylammonium ions (tba⁺) and as non-charged thiocyanate complexes with trioctylphosphine oxide (TOPO). When copper(II) was extracted, the equilibrium was found to be established by two-phase agitation for 30 s; the distribution ratio did not change when the two phases were further agitated for at least 60 s.   Thus it was concluded that the extraction of copper(II) with either tba⁺ or TOPO should reach equilibrium by two-phase agitation for 30 s.   In the present study, the two phases were always agitated for 30 s for the extraction of copper(II).   However, the distribution ratio of copper(II) increased due to two-phase agitation for a
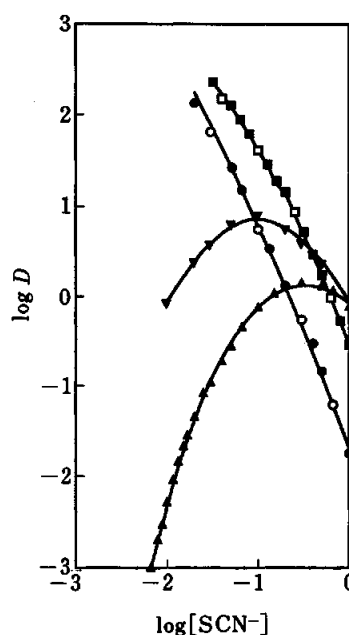

Fig. 1   Solvent extraction of copper(I) and (II) in 1 mol dm⁻³ Na(SCN,NO₃) into chloroform with 1×10^{-3} mol dm⁻³ tba⁺ (initial value in the aqueous phase) and that into hexane with 0.01 mol dm⁻³ TOPO (initial value in the organic phase). For the copper(I) extraction, 0.01 mol dm⁻³ ascorbic acid is added into the aqueous phase.   Copper(I) extraction with tba⁺ (■: forward extraction and □: backward extraction) and with TOPO (●: forward extraction and ○: backward extraction).   Copper(II) extraction with tba⁺ (▲) and TOPO (▼).

longer time, for example for 1 h.   This should have been due to a partial reduction of the extracted copper(II) thiocyanate complex to a copper(I) thiocyanate complex, as was found previously concerning the extraction of a copper(II) thiocyanate complex into MIBK.[5]   For the experiments with copper(I), ascorbic acid was always added to an aqueous solution containing Cu²⁺ at the initial stage.   The initial concentration of ascorbic acid in the aqueous phase was 0.01 mol dm⁻³.   Since the distribution ratio of copper was not affected, even when the ascorbic acid concentration was twice or half of this concentration, it was concluded that the complex formation of copper(I) with ascorbic acid in the aqueous phase was negligible, and that 0.01 mol dm⁻³ ascorbic acid was sufficient to reduce copper(II) to copper(I). The aqueous solution was then agitated with an organic solvent for 30 min.   Since no change in the distribution ratio of copper was found when the two phases were further agitated in the presence of ascorbic acid, two-phase agitation for 30 min was sufficient to reach the extraction equilibrium of copper(I).

Figure 1 gives the solvent extraction curves of copper(I) and (II) from 1 mol dm⁻³ Na(SCN,NO₃) initially containing 0.01 mol dm⁻³ hydrogen ions with TOPO into hexane and with tba⁺ into chloroform. These data were analyzed on the basis of Eqs. (18), (21),

(25) and (28) in which the concentration of TOPO and tba⁺ at equilibrium was calculated by Eqs. (6) and (12), as it will be further described. The calculation was performed using a least-squares computer program. From these, the extracted species was concluded to be in the form of (tba⁺)₂Cuᴵᴵ(SCN)₄⁻ and tba⁺Cuᴵ(SCN)₂⁻ for extraction with tba⁺, and Cuᴵᴵ(SCN)₂(TOPO)₃ and CuᴵSCN(TOPO)₃ for extraction with TOPO. The best-fit values of the constants for the data in Fig. 1, obtained by a statistical analysis, are listed in Table 1. The solid lines for the extraction data in Fig. 1 were calculated on the basis of Eqs. (18), (21), (25) and (28) and the constants given in Table 1. As can be seen from Fig. 1, the calculated values fit well with the experimental data, which should indicate that the statistical analysis for these data was made reasonably.

Back-extraction experiments of copper(I) were made as follows. An organic solution initially containing essentially only copper(I) in the form of a thiocyanate complex with tba⁺, tba⁺Cuᴵ(SCN)₂⁻, or with TOPO, CuᴵSCN(TOPO)₃, was prepared by the solvent extraction method. Each organic solution containing one of these thus-prepared complexes was agitated with an aqueous thiocyanate solution containing no ascorbic acid for 30 s. The copper in the two phases was then determined. Examples of the distribution data obtained by back-extraction experiments are also given in Fig. 1 by open symbols. As can be seen from Fig. 1, the distribution data of copper obtained by the back-extraction procedure agree well with those obtained by forward-extraction experiments, but otherwise identical conditions. It was found that the distribution ratio of copper did not change even in the absence of ascorbic acid, at least during two-phase agitation for 3 min in the thiocyanate concentration range. Thus, the copper(I) in the aqueous phase was not readily oxidized, at least within such a short time under the conditions.

The dependence of the distribution ratio of copper on the concentration of the extractant was further examined. Both thiocyanate and nitrate ions were extracted with tba⁺. These extractions lowered the tba⁺ concentration as well as the thiocyanate and nitrate concentrations in the aqueous phase. Thus, corrections for both tba⁺ and thiocyanate concentrations were necessary in order to determine the dependence of extraction of copper on the tba⁺ concentration, even when the initial thiocyanate and nitrate concentrations were kept constant. Figures 2(a) and 2(b) give the corrected distribution ratio of copper(II) and (I) as a function of the tba⁺ concentration at equilibrium, which was calculated based on Eq. (6). The slope of the plot of copper(II) in Fig. 2(a) is +2, while that of the plot of copper(I) in Fig. 2(b) is unity. These results indicate that the number of tba⁺ in the extracted species is two for the copper(II) complex and one for the copper(I) complex. These also indicate that the statistical analysis of the extraction data with tba⁺ in Fig. 1, which was made in the same manner as given here, should be reasonable. Figures 3(a) and 3(b) give the corrected
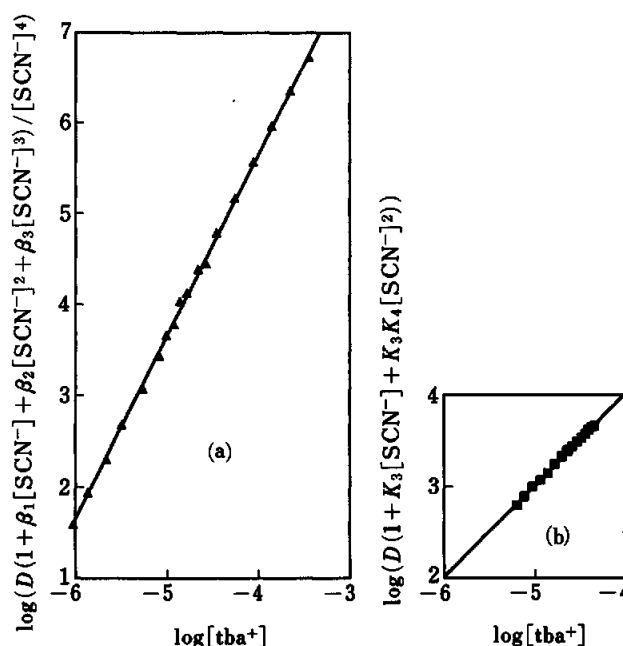

Fig. 2 Dependence of copper extraction on the calculated tba⁺ concentration at equilibrium in the aqueous phase. (a) Extraction of copper(II): aq. phase, 1 mol dm⁻³ Na(SCN, NO₃) containing 0.066 mol dm⁻³ SCN⁻ at initial and no ascorbic acid; org. phase, chloroform. (b) Extraction of copper(I): aq. phase, 1 mol dm⁻³ Na(SCN, NO₃) containing 0.1 mol dm⁻³ SCN⁻ and 0.01 mol dm⁻³ ascorbic acid at initial; org. phase, chloroform.
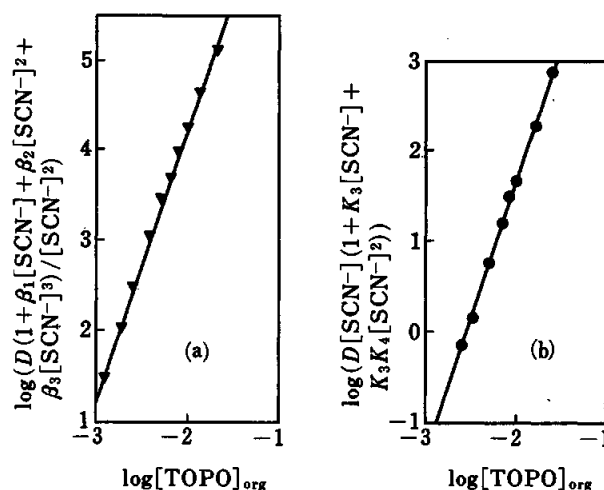

Fig. 3 Dependence of the copper extraction on the calculated TOPO concentration at equilibrium in the organic phase. (a) Extraction of copper(II): aq. phase, 1 mol dm⁻³ Na(SCN, NO₃) containing 0.1 mol dm⁻³ SCN⁻ at initial and no ascorbic acid; org. phase, hexane containing TOPO. (b) Extraction of copper(I): aq. phase, 1 mol dm⁻³ Na(SCN, NO₃) containing 0.2 mol dm⁻³ SCN⁻ and 0.01 mol dm⁻³ ascorbic acid at initial; org. phase, hexane containing TOPO.

distribution ratio of copper(II) and (I) as a function of the free TOPO concentration in the organic phase. The concentration of TOPO given in these figures was

Table 1 Extraction and stability constants for copper thiocyanate complexes

(a) Copper(I)

log $K_{ex1,3(TOPO)}$	log $K_{ex2,1}$	log K_3	log K_4
7.65	8.01	2.75	0.46

(b) Copper(II)

log $K_{ex2,3(TOPO)}$	log $K_{ex4,2}$	log β_1	log β_2	log β_3
10.2	13.7	1.52	2.75	2.95

Table 2 Extraction constants used for the calculation of the concentration of tba$^+$ and TOPO at equilibrium

(a) TOPO

log K_{exHSCN}	log K_{exHNO3}	log $K_{exNaSCN}$	log $K_{exNaNO3}$
2.5[a]	0.85[b]	0.38[c]	nil

(b) tba$^+$

log $K_{exA,B}$	log $K_{exX,B}$
2.2[d]	1.08[d]

a. Ref. 4.   b. Ref. 3.   c. Ref. 6.   d. Ref. 7.

corrected on the basis of Eq. (12) for the decrease in the concentration due to the extraction of HSCN·TOPO and HNO$_3$·TOPO in a similar manner as has been reported.[3,4] The slopes of the plots in Figs. 3(a) and 3(b) are both +3. This indicates that the number of TOPO molecules in the extracted species in hexane should be three. From this, it was also assumed that the data given in Fig. 1 were analyzed reasonably. The values of the constants obtained from the experimental data are given in Table 1.

When the concentration of tba$^+$ or TOPO was higher than that in the experiments shown in Fig. 1, a better extraction was obtained, as can be seen from Figs. 2(a) and 2(b) as well as Figs. 3(a) and 3(b), which can also be calculated by using the constants given in Table 1 on the basis of Eqs. (18), (21), (25) and (28). When the initial TOPO concentration was 0.1 mol dm^{-3}, the extractions of both copper(I) and (II) were quantitative (log $D > 2$) in the thiocyanate concentration range from 0.01 to 0.1 mol dm^{-3}. When the initial tba$^+$ concentration was 0.01 mol dm^{-3}, the extraction of copper(I) was quantitative in the thiocyanate concentration range from 0.01 to 0.1 mol dm^{-3} and that of copper(II) was nearly quantitative when the thiocyanate concentration was above 0.1 mol dm^{-3}.

In the present study, the extraction of copper(I) as thiocyanate complexes was carried out when the thiocyanate concentration was higher than 0.02 mol dm^{-3}. This was because the recovery of copper(I) from both phases was not quantitative when the thiocyanate concentration was in the range from 1×10^{-3} to 0.02 mol dm^{-3}. In a previous paper[1], it was described that the solvent extraction of copper(I) as thiocyanate complexes was reproducible, and that the recovery of the initially added copper from both phases was quantitative when the thiocyanate concentration was lower than 1×10^{-3} mol dm^{-3}; the aqueous phase was 0.1 mol dm^{-3}

Na(SCN, NO$_3$) in this previous study. On the other hand, solvent extraction experiments of copper(I) as thiocyanate complexes were not successful in the thiocyanate concentration range from 1×10^{-3} to 0.02 mol dm^{-3} because the recovery of copper from both phases was not quantitative and not reproducible. This may have been because the Cu^{I}SCN complex is not stable in the aqueous phase; it may precipitate or be adsorbed on the vessel wall or on the liquid-liquid interface.

Discussion

Both copper(I) and copper(II) in the aqueous thiocyanate solutions are extractable into the organic phase as non-charged complexes with TOPO and as anionic complexes with tba$^+$. As can be seen from Fig. 1, each set of experimental data are well fitted with the calculated extraction curve. This suggests that the assumption for the chemical form of the extracted species should be reasonable, and that the equilibrium constants for the chemical species in these systems should also be reasonable. The experimental data given in Fig. 1 were obtained when the initial concentration of the extractant, TOPO or tba$^+$, was identical for each series of experiments. However as has already been pointed out in previous papers[3,4], TOPO extracts not only the metal complex but also the thiocyanate and nitrate ions. The extractable species with TOPO should have been sodium nitrate, sodium thiocyanate, thiocyanic acid and nitric acid in the present study. From the literature[6], it can be assumed that the extraction of sodium nitrate should be negligible. The amount of sodium thiocyanate extracted with TOPO can be calculated using the extraction constant in this previous study to be 2.4×10^{-6} mol dm^{-3} when the aqueous thiocyanate concentration is the highest, 1 mol dm^{-3}; thus, only 7.2×10^{-6} mol dm^{-3} of TOPO should combine with sodium thiocyanate as [Na(TOPO)$_3$]$^+$SCN$^-$; this amount is less than 0.1% of the initial TOPO concentration. However, the extraction of both nitric and thiocyanic acids with TOPO into hexane should be taken into account. The extraction of HSCN·TOPO was better than that of HNO$_3$·TOPO. Thus, when the thiocyanate concentration is higher, the free TOPO concentration which is available for the extraction of complex should be lower than when the thiocyanate concentration is lower. When the initial concentration of nitric acid in the aqueous phase was 0.01 mol dm^{-3} and that of TOPO in the hexane phase was 0.01 mol dm^{-3}, the hydrogen-ion concentration in the aqueous phase at equilibrium was experimentally found to be 8.5×10^{-3}, 7.2×10^{-3} and 4.0×10^{-3} mol dm^{-3} if the initial thiocyanate concentration in the aqueous phase was 0.01, 0.1 and 1 mol dm^{-3}, respectively. This caused a great change in the free TOPO concentration. When the initial thiocyanate concentration in the aqueous phase was 0.01, 0.1 and 1 mol dm^{-3}, the free TOPO concentration in the organic phase should become 9.2×10^{-3}, 7.9×10^{-3} and 4.4×10^{-3} mol dm^{-3}, respectively.

Thus, the TOPO concentration at equilibrium, which should be introduced for calculating the extraction constants on the basis of Eqs. (21) and (28), is nearly 92.0%, 79.4% and 44.3% of the initial concentration when the thiocyanate concentration is 0.01, 0.1 and 1 mol dm^{-3}, respectively. Thus, the distribution ratio of copper(I) and (II) should be lower than the calculated value obtained by assuming the initial TOPO concentration, that is, 0.01 mol dm^{-3}. Furthermore, this extraction of thiocyanic acid with TOPO should make the free thiocyanate concentration lower than the initial value. However, by a calculation based on Eq. (13), the change in the free thiocyanate concentration was only slight over the entire thiocyanate concentration range of the present study. The calculated curves for the TOPO extraction in Fig. 1 were obtained after a correction for the decrease in the free TOPO concentration was made. The effect of a change in the free TOPO concentration on the extraction can be corrected by dividing the distribution ratio by the cubic of the calculated TOPO concentration at equilibrium. Figure 4 gives data concerning the distribution ratio given in Fig. 1 thus normalized with respect to the TOPO concentration. As can be seen from Figs. 1 and 4, the distribution ratio of copper(II) by TOPO extraction decreases after a maximum due to a further increase in the thiocyanate concentration. However, this decrease in the distribution ratio appears to be greater using the experimental data given in Fig. 1 than with the normalized data given in Fig. 4. This is because a decrease in the distribution ratio in Fig. 1 is caused by both the formation of an unextractable anionic complex, and by a decrease in the free TOPO concentration; however, the decrease in the distribution ratio due to the change in the free TOPO concentration is corrected in Fig. 4. The smaller decrease in the distribution ratio of the TOPO extraction of copper(I) due to an increase in the thiocyanate concentration in Fig. 4 than in Fig. 1 is also due to the same reason.

A correction for the thiocyanate and nitrate concentrations in the aqueous phase should also be made in the tba$^+$ extraction systems. The extraction of thiocyanate ions with tba$^+$ is better than that of nitrate ions. Thus, when the thiocyanate concentration is higher, the tba$^+$ concentration which is available for the extraction of the complex should be lower than when the thiocyanate concentration is lower. When the thiocyanate concentration in the aqueous phase was 0.01, 0.1 and 1 mol dm^{-3} and when the initial tba$^+$ concentration was 1×10^{-3} mol dm^{-3}, the free tba$^+$ concentration in the aqueous phase at equilibrium was calculated to be 6.9×10^{-5}, 3.6×10^{-5} and 6.3×10^{-6} mol dm^{-3}, respectively. Thus, in order to calculate the degree of extraction as an anionic thiocyanate complex of copper(I) and (II) on the basis of Eqs. (18) and (25), a correction for the decrease in the free tba$^+$ concentration in the aqueous phase is indispensable. The tba$^+$ concentration is markedly affected by the thiocyanate and nitrate concentration. The curves for extraction with tba$^+$ in Fig. 1 were obtained with both copper(I) and (II) when the initial tba$^+$ concentration was
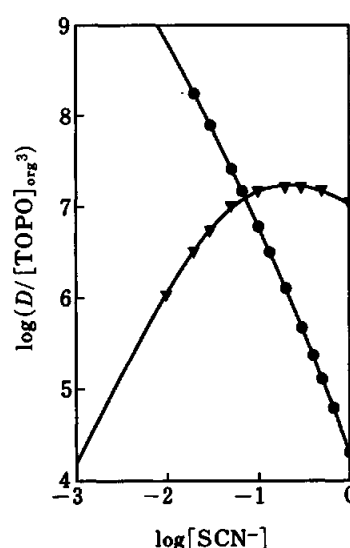

Fig. 4 Dependence of the copper(I) and (II) extraction on the SCN$^-$ concentration in the aqueous phase normalized with the TOPO concentration at equilibrium. Aq. phase, 1 mol dm^{-3} Na(SCN,NO$_3$) containing no ascorbic acid (▼) for copper(II) and 0.01 mol dm^{-3} ascorbic acid (●) for copper(I); org. phase, hexane initially containing 0.01 mol dm^{-3} TOPO.

always 1×10^{-3} mol dm^{-3}. The distribution ratio of copper(I) should be divided by the first order of the free tba$^+$ concentration in the aqueous phase, while the distribution ratio for copper(II) should be divided by the square of the free tba$^+$ concentration in order to correct for any change in the free tba$^+$ concentration. These corrected values are given in Figs. 5(a) and (b). As can be seen from Fig. 5(a), the corrected extraction curve of copper(II) with tba$^+$ is steeper than the curve for the experimental data in Fig. 1. However, the corrected extraction curve of copper(I) as a function of the free tba$^+$ concentration in Fig. 5(b) is less steep than the curve for the experimental data in Fig. 1. The slope of the log D vs. log[SCN$^-$] plot of copper(II) in Fig. 1 decreases after a maximum at about 0.1 mol dm^{-3} thiocyanate. The plot log(D/[tba$^+$]^2) vs. log[SCN$^-$] in Fig. 5(a) has no maximum, and the slope of the curve gradually decreases. There is no maximum for copper(I) extraction in both the plot for the corrected extraction data in Fig. 5(b) and that for experimental data in Fig. 1. These show that a correction for the concentration of the extractant is very important in order to understand the equilibrium.

Copper(I) forms much more stable thiocyanate complexes than does copper(II), which should cause a great difference in the extraction of copper(I) and (II). From the formation constants of copper(I) and (II) in the aqueous phase, the molar ratio of the complex species in the aqueous phase was calculated, as given in Fig. 6. It was not possible to determine the stability constants of the lower thiocyanate complexes of copper(I) in the present study. Such a difficulty was also encountered
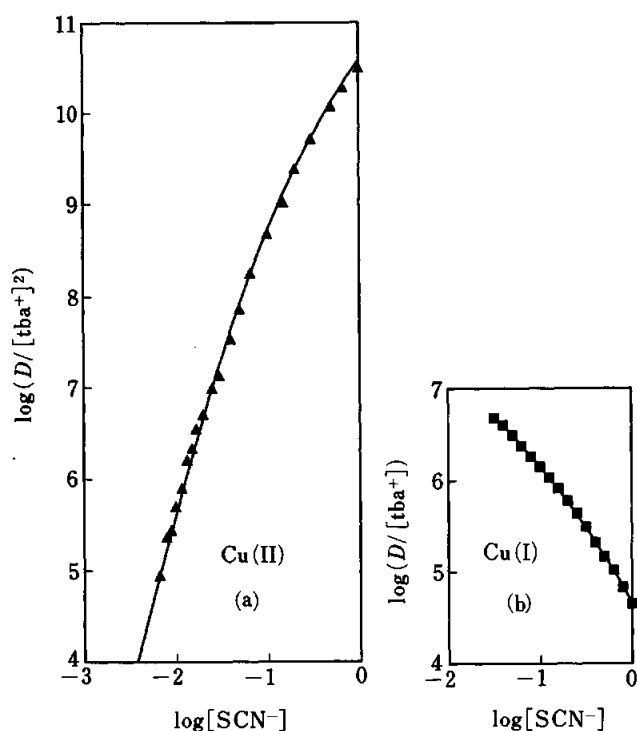
Fig. 5 Dependence of the copper(I) and (II) extraction on the SCN⁻ concentration in the aqueous phase normalized with the tba⁺ concentration at equilibrium. Aq. phase, 1 mol dm⁻³ Na(SCN,NO₃) containing 1×10⁻³ mol dm⁻³ tba⁺ at initial and no ascorbic acid (▲) for copper(II) and 0.01 mol dm⁻³ ascorbic acid (■) for copper(I); org. phase, chloroform.
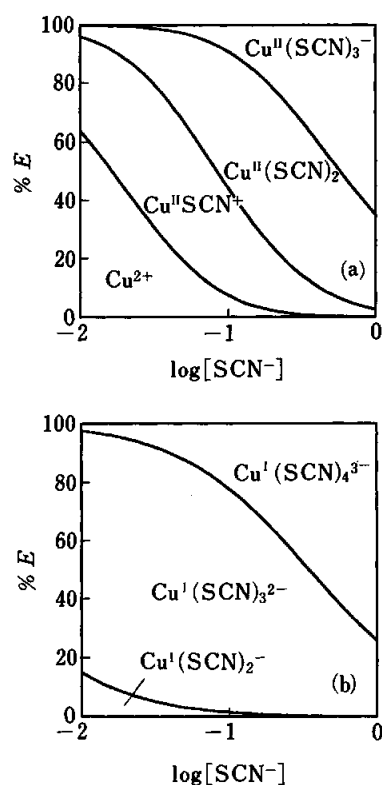

Fig. 6 The molar ratio of copper(I) and (II) species in the aqueous phase as a function of the thiocyanate concentration calculated using the stability constants of the complexes given in Table 1.

when silver(I) was extracted from thiocyanate solutions with tba⁺ into chloroform in a previous study.[7] The extraction of silver(I) could be studied when the aqueous phase contained only anionic complexes. It is mentioned that the extraction constant of tba⁺[M(SCN)₂⁻]org in Eq. (24) is much higher for copper(I) ($K_{ex2,1}$=10⁸·⁰¹) than for silver(I)[7] ($K_{ex2,1}$=10⁵·³⁸). Since the molar volume of the anionic copper(I) complex should not be very different from that of the anionic silver(I) complex, the much higher extraction constant of the copper(I) complex can be explained in terms of a more hydrophilic nature of the silver(I) complex.

The extracted species of copper(II) as the anionic thiocyanate complex with tba⁺ is not tba⁺Cu^{II}(SCN)₃⁻, but (tba⁺)₂Cu^{II}(SCN)₄²⁻. In the present study, the copper(II) thiocyanate complexes in the aqueous phase was also determined by a chelate extraction method in a similar manner as described previously.[2] The obtained values agree well with those obtained by an analysis of the extraction data with TOPO and with tba⁺ in Fig. 1, which are listed in Table 1. The extractable anionic complex Cu^{II}(SCN)₄²⁻ was negligible in the aqueous phase based on calculation, even at the highest thiocyanate concentration. A similar situation of negligible species in the aqueous phase was also found when copper(I) was extracted with TOPO. Although the Cu^{I}SCN(TOPO)₃

species was extracted into hexane, this complex in the aqueous phase was calculated from the experiments data in Fig. 1 to be negligible within the experimental accuracy.

Few reports have been published on solvent extraction studies of copper(I) thiocyanate complexes. On the other hand, there have been many reports on the solvent extraction of copper(II) thiocyanate complexes. Although the extraction of copper(II) anionic thiocyanate complex with bulky cations was also reported[8-10], the equilibrium involved in the solvent extraction systems was not statistically analyzed in these previous papers. The extracted species of copper(II) thiocyanate complexes with tributylphosphate were suggested to be ion-pairs with a hydrogen ion or a potassium ion in a previous paper.[11]

As can be seen from the results of the present study, copper(I) could be present in aqueous solutions as stable anionic thiocyanate complexes under the conditions studied. On the other hand, when the thiocyanate concentration was lower than 1×10⁻³ mol dm⁻³, it was concluded that although only the copper(I) thiocyanate complex was extracted into the organic phase of the solvent extraction system, the copper in the aqueous phase was assumed to be essentially in the divalent state even when the reducing agent, ascorbic acid, was

present.[1] Even under such conditions, the distribution ratio was constant when the two-phase agitation was further continued for a certain time. This indicated that the amount of extraction of copper from the aqueous to the organic phase should be the same as the amount of back-extraction of copper from the organic to the aqueous phase under such conditions. Thus, a circulation of copper should occur between the aqueous phase, where the copper is mainly in the divalent state, and the organic phase, where the copper is mainly in the monovalent state. This indicates that the copper(I) which was back-extracted from the organic to the aqueous phase should have been oxidized to copper(II) most probably by the dissolved atmospheric oxygen in the aqueous phase, even in the presence of ascorbic acid, if the thiocyanate concentration was lower than $1 \times 10^{-3} mol dm^{-3}$. However, such oxidations should be negligible when the thiocyanate concentration is higher than $0.01 mol dm^{-3}$. It was reported in a previous paper[5] and also found in the present study that the extracted copper(II) thiocyanate complex was partially reduced in the organic phase, and that the distribution ratio gradually changed when two-phase agitation was continued for a longer time. From this point of view, even when the distribution ratio of copper reached a certain value and did not change due to further two-phase agitation for a certain time period, as given in the copper in the two oxidation states in these two-liquid systems should still be regarded as being in a transient equilibrium.

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