© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 70, 1867—1873 (1997)

Solvent Extraction of Anionic Silver(I) Thiocyanate Complex as Ion-Pairs with Tetrabutylammonium Ions into Chloroform and 4-Methyl-2-pentanone

Yasunobu Ohmiya, Nguyen Thi Kim Dung, and Tatsuya Sekine*

Department of Chemistry, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162

(Received February 21, 1997)

Solvent extraction of silver(I) from aqueous 1 mol dm^{-3} Na(SCN, NO$_3$) solutions, where the thiocyanate ion concentration was higher than 1×10^{-3} mol dm^{-3} and pH was 3, into chloroform and into 4-methyl-2-pentanone (MIBK) was studied in the presence of tetrabutylammonium ions (tba$^+$) at 298 K. The extraction equilibria of the ion-pairs, tba$^+$SCN$^-$ and tba$^+$NO$_3{}^-$ into these solvents were also determined. The experimental data were well explained by extraction of tba$^+$Ag(SCN)$_2{}^-$ into chloroform and both tba$^+$Ag(SCN)$_2{}^-$ and Na$^+$Ag(SCN)$_2{}^-$ into MIBK and by formation of Ag(SCN)$_n{}^{1-n}$, where n was 2 to 4 in the aqueous phase. More than half of the initial amount of tba$^+$ in the aqueous phase was extracted as tba$^+$SCN$^-$ and tba$^+$NO$_3{}^-$. The analysis of the extraction data of silver(I) should be made by taking the decrease in the tba$^+$ concentration due to these extractions into account. No dissociation of the ion-pairs was found in chloroform but the extracted ion-pairs were partially dissociated in MIBK. In the presence of 1×10^{-3} mol dm^{-3} tba$^+$ in the initial aqueous phase, the extraction of silver(I) was much better into MIBK than into chloroform under otherwise identical conditions. The extraction and dissociation constants of the above species and the stability constants of the anionic thiocyanate complexes of silver(I) in the aqueous phase were calculated.

Several metal ions can be extracted as thiocyanate complexes into polar organic solvents such as 4-methyl-2-pentanone (MIBK),[1] but the extraction is usually poor into nonpolar organic solvents such as chloroform. In the course of a further study in our laboratory, it was found that the extraction of metal thiocyanate complexes was much better in the presence of bulky cations. The extraction was possible even into chloroform as ion-pairs of anionic thiocyanate complexes with tetrabutylammonium ions (tba$^+$). At the same time, the thiocyanate ions and the nitrate ions in the aqueous phase were also extracted as ion-pairs with tba$^+$ into chloroform and MIBK. Thus, the extraction equilibrium should be understood by considering the extraction of not only the anionic thiocyanate complexes but also that of these anions in the aqueous phase. Furthermore, the extracted ion-pairs partially dissociate in the organic phase when the solvent is MIBK. The statistical analysis of the equilibrium in the system should be made by taking the dissociation of ion-pairs in the organic phase into account.

In the present paper, the solvent extraction of silver(I) in aqueous 1 mol dm^{-3} Na(SCN, NO$_3$) solutions into chloroform and into MIBK is described. The thiocyanate concentration is higher than 1×10^{-3} mol dm^{-3} even though the solubility of silver(I) thiocyanate is low in aqueous solutions and thus precipitation of silver(I) thiocyanate is negligible. Still silver(I) is present as anionic complexes when the thiocyanate concentration is not low. Both chloroform and MIBK are chosen as the solvent in order to discover the effect of dissociation of ion-pairs which could occur in MIBK but not in chloroform. The results are statistically analyzed on the basis of the complex formation in the aqueous phase, the extraction of anionic complexes as ion-pairs with tba$^+$, by assuming the dissociation of the ion-pairs in MIBK. The extraction of tba$^+$ with thiocyanate and nitrate ions is also measured because it causes a decrease in the concentration of both tba$^+$ and thiocyanate ions in the aqueous phase. It is found that the solvent extraction of anionic silver(I) thiocyanate complexes into these solvents is quite different, but still the equilibrium can be well explained by analyzing the data on the basis of formation and extraction of the thiocyanate anionic complexes by similar statistical treatments of the experimental data. It is also found that the decrease in the tba$^+$ concentration by the extraction of anions and the dissociation of ion-pairs in the organic phase is very important in order to understand the extraction equilibria of silver(I).

Experimental

All the solvent extraction experiments were carried out in a thermostated room at 298 K. All the reagents employed were of reagent grade. Stoppered glass tubes (capacity 20 cm^3) were used for the agitation of the two liquid phases. The MIBK was washed with dilute perchloric acid, a dilute aqueous sodium hydroxide solution, and then several times with water. The chloroform was washed several times with water before use. The concentration of sodium thiocyanate in the stock solution was determined by titration with a standard silver nitrate solution. The initial aqueous phase was 1 mol dm^{-3} Na(SCN,NO$_3$) containing 5×10^{-6} mol dm^{-3} silver(I) and none or a certain amount of tba$^+$. The pH of this solution was adjusted at about 3 with a small amount of nitric acid. The volume of the two phases was always 5 cm^3. The vessels were covered by an aluminum foil in order to keep the samples in the dark and to minimize the effect of light. The two phases were agitated by a mechanical shaker for 30 min and centrifuged off. The extracted silver(I) in the organic phase was stripped by 1 $\mathrm{mol\,dm^{-3}}$ sodium thiocyanate solution, which was found to be sufficient in order to recover the extracted silver(I) into the aqueous phase as anionic thiocyanate complexes.[2] The silver(I) content in the aqueous solutions was determined by an atomic absorption method.

The extraction of either SCN^- or $\mathrm{NO_3}^-$ as ion-pairs with tba^+ was measured in a similar manner to that explained in previous papers.[3,4] The extracted tba^+ with SCN^- or $\mathrm{NO_3}^-$ was stripped by repeating agitations with water and then extracted as ion-pairs with picrate ions into chloroform. The amount of tba^+ was determined by spectrophotometry of the extracted picrate ions.

Statistical

All the chemical species in the organic phase are denoted by the subscript "org" and those in the aqueous phase are shown without any subscript. The volumes of the two liquid phases are assumed to be the same.

The formation of anionic silver(I) complexes with thiocyanate ions in the aqueous phase can be written by step-wise formation equilibrium as:

$$\begin{gathered}\mathrm{Ag(SCN)}_{n-1}{}^{2-n} + \mathrm{SCN}^- \rightleftharpoons \mathrm{Ag(SCN)}_n{}^{1-n}\\ K_n = [\mathrm{Ag(SCN)}_n{}^{1-n}]/([\mathrm{Ag(SCN)}_{n-1}{}^{2-n}][\mathrm{SCN}^-]).\end{gathered}\tag{1}$$

When the uninegative complex, $\mathrm{Ag(SCN)_2}^-$, is extracted as ion-pairs with tba^+, the equilibrium can be written as:

$$\begin{gathered}\mathrm{Ag(SCN)_2}^- + \mathrm{tba}^+ \rightleftharpoons \mathrm{tba^+Ag(SCN)_2}^-{}_{\mathrm{(org)}}\\ K_{\mathrm{extba}} = [\mathrm{tba^+Ag(SCN)_2}^-]_{\mathrm{org}}/([\mathrm{tba}^+][\mathrm{Ag(SCN)_2}^-]).\end{gathered}\tag{2}$$

When this ion-pair undergoes dissociation in the organic phase, the equilibrium can be written as:

$$\begin{gathered}\mathrm{tba^+Ag(SCN)_2}^-{}_{\mathrm{(org)}} \rightleftharpoons \mathrm{tba}^+{}_{\mathrm{(org)}} + \mathrm{Ag(SCN)_2}^-{}_{\mathrm{(org)}}\\ K_{\mathrm{diss}} = [\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{Ag(SCN)_2}^-]_{\mathrm{org}}/[\mathrm{tba^+Ag(SCN)_2}^-]_{\mathrm{org}}.\end{gathered}\tag{3}$$

When the anionic complex is extracted as ion-pairs with Na^+ in the aqueous phase, the equilibrium can be written as:

$$\begin{gathered}\mathrm{Ag(SCN)_2}^- + \mathrm{Na}^+ \rightleftharpoons \mathrm{Na^+Ag(SCN)_2}^-{}_{\mathrm{(org)}}\\ K_{\mathrm{exNa}} = [\mathrm{Na^+Ag(SCN)_2}^-]_{\mathrm{org}}/([\mathrm{Na}^+][\mathrm{Ag(SCN)_2}^-]).\end{gathered}\tag{4}$$

When the extraction of non-charged complex, AgSCN, is negligible and this complex is also negligible in the aqueous phase, the distribution ratio in the solvent extraction system can be written as:

$$\begin{aligned}D = {}&([\mathrm{Na^+Ag(SCN)_2}^-]_{\mathrm{org}} + [\mathrm{tba^+Ag(SCN)_2}^-]_{\mathrm{org}} + [\mathrm{Ag(SCN)_2}^-]_{\mathrm{org}})\\ &/([\mathrm{Ag(SCN)_2}^-] + [\mathrm{Ag(SCN)_3}^{2-}] + [\mathrm{Ag(SCN)_4}^{3-}]).\end{aligned}\tag{5}$$

When the solvent is chloroform, the extraction of the ion-pair, $\mathrm{Na^+Ag(SCN)_2}^-$, is assumed to be negligible. Furthermore, the dissociation of the extracted species with tba^+, $\mathrm{tba^+Ag(SCN)_2}^-$, should also be negligible in this solvent; then the distribution ratio of silver(I) can simply be written as:

$$\begin{aligned}D = {}&[\mathrm{tba^+Ag(SCN)_2}^-]_{\mathrm{org}}/([\mathrm{Ag(SCN)_2}^-]\\ &+[\mathrm{Ag(SCN)_3}^{2-}] + [\mathrm{Ag(SCN)_4}^{3-}]).\end{aligned}\tag{6}$$

By introducing Eqs. 1 and 2, Eq. 6 can be rewritten as:

$$D = K_{\mathrm{extba}}[\mathrm{tba}^+]/(1 + K_3[\mathrm{SCN}^-] + K_3K_4[\mathrm{SCN}^-]^2).\tag{7}$$

By introducing Eqs. 1, 2, and 3, Eq. 5 can be rewritten as:

$$\begin{aligned}D = {}&(K_{\mathrm{exNa}}[\mathrm{Na}^+] + K_{\mathrm{extba}}[\mathrm{tba}^+] + K_{\mathrm{extba}}K_{\mathrm{diss}}[\mathrm{tba}^+][\mathrm{tba}^+]_{\mathrm{org}}{}^{-1})\\ &/(1 + K_3[\mathrm{SCN}^-] + K_3K_4[\mathrm{SCN}^-]^2).\end{aligned}\tag{8}$$

The solvent extraction of thiocyanate ions in the aqueous phase may be written as:

$$\begin{gathered}\mathrm{tba}^+ + \mathrm{SCN}^- \rightleftharpoons \mathrm{tba^+SCN}^-{}_{\mathrm{(org)}}\\ K_{\mathrm{exAB}} = [\mathrm{tba^+SCN}^-]_{\mathrm{org}}/([\mathrm{tba}^+][\mathrm{SCN}^-]).\end{gathered}\tag{9}$$

The dissociation equilibrium of the extracted $\mathrm{tba^+SCN^-}$ in the organic phase can be written as:

$$\begin{gathered}\mathrm{tba^+SCN}^-{}_{\mathrm{(org)}} \rightleftharpoons \mathrm{tba}^+{}_{\mathrm{(org)}} + \mathrm{SCN}^-{}_{\mathrm{(org)}}\\ K_{\mathrm{dissAB}} = [\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{SCN}^-]_{\mathrm{org}}/[\mathrm{tba^+SCN}^-]_{\mathrm{org}}.\end{gathered}\tag{10}$$

The solvent extraction of nitrate ions in the aqueous phase with tba^+ and the dissociation of the extracted $\mathrm{tba^+NO_3}^-$ species can be written as:

$$\begin{gathered}\mathrm{tba}^+ + \mathrm{NO_3}^- \rightleftharpoons \mathrm{tba^+NO_3}^-{}_{\mathrm{(org)}}\\ K_{\mathrm{exXB}} = [\mathrm{tba^+NO_3}^-]_{\mathrm{org}}/([\mathrm{tba}^+][\mathrm{NO_3}^-])\end{gathered}\tag{11}$$

$$\begin{gathered}\mathrm{tba^+NO_3}^-{}_{\mathrm{(org)}} \rightleftharpoons \mathrm{tba}^+{}_{\mathrm{(org)}} + \mathrm{NO_3}^-{}_{\mathrm{(org)}}\\ K_{\mathrm{dissXB}} = [\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{NO_3}^-]_{\mathrm{org}}/[\mathrm{tba^+NO_3}^-]_{\mathrm{org}}.\end{gathered}\tag{12}$$

From the mass and charge balance, the following equations can be written:

$$\begin{aligned}[\mathrm{tba}^+]_{\mathrm{init}} = {}&[\mathrm{tba}^+] + [\mathrm{tba}^+]_{\mathrm{org}} + [\mathrm{tba^+SCN}^-]_{\mathrm{org}} + [\mathrm{tba^+NO_3}^-]_{\mathrm{org}}\\ &+[\mathrm{tba^+Ag(SCN)_2}^-]_{\mathrm{org}}\end{aligned}\tag{13}$$

$$[\mathrm{tba}^+]_{\mathrm{org}} = [\mathrm{SCN}^-]_{\mathrm{org}} + [\mathrm{NO_3}^-]_{\mathrm{org}} + [\mathrm{Ag(SCN)_2}^-]_{\mathrm{org}}.\tag{14}$$

By the extraction of thiocyanate ions as ion-pairs with tba^+ and as $\mathrm{Ag(SCN)}_n{}^{1-n}$ complexes, the thiocyanate concentration in the aqueous phase at equilibrium should be lower than the initial one. In order to calculate the thiocyanate concentration at equilibrium, the following equation may be used:

$$\begin{aligned}[\mathrm{SCN}^-]_{\mathrm{init.}} = {}&[\mathrm{SCN}^-] + 2[\mathrm{Ag(SCN)_2}^-] + 3[\mathrm{Ag(SCN)_3}^{2-}]\\ &+ 4[\mathrm{Ag(SCN)_4}^{3-}] + [\mathrm{tba^+SCN}^-]_{\mathrm{org}} + [\mathrm{SCN}^-]_{\mathrm{org}}\\ &+ 2[\mathrm{tba^+Ag(SCN)_2}^-]_{\mathrm{org}} + 2[\mathrm{tba^+Ag(SCN)_2}^-]_{\mathrm{org}}.\end{aligned}\tag{15}$$

Results

1. Extraction of SCN^- and $\mathrm{NO_3}^-$ with tba^+ and Dissociation of Ion-Pairs. The solvent extraction of SCN^- and $\mathrm{NO_3}^-$ with tba^+ was examined in the absence of silver(I). Figure 1 gives the distribution ratio of tba^+ between MIBK or chloroform and 1 $\mathrm{mol\,dm^{-3}}$ NaSCN and also between

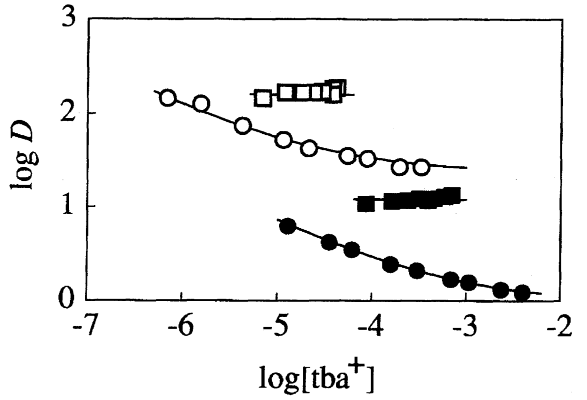

Fig. 1. Extraction curves of tba^+SCN^- (open symbols) or $tba^+NO_3^-$ (closed symbols) as a function of aqueous tba^+ concentration into chloroform (squares) or MIBK (circles). The curves are calculated on the basis of Eqs. 18 and 19.

these solvents and 1 mol dm^{-3} $NaNO_3$ as a function of the concentration of tba^+ at equilibrium, which was obtained experimentally. The data were analyzed on the basis of the following equations:

$$D_{\mathrm{tbaA}} = ([\mathrm{tba}^+]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{SCN}^-]_{\mathrm{org}})/[\mathrm{tba}^+] \tag{16}$$

$$D_{\mathrm{tbaX}} = ([\mathrm{tba}^+]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}})/[\mathrm{tba}^+]. \tag{17}$$

By introducing Eqs. 9, 10, 11, and 12, Eqs. 16 and 17 can be rewritten when the anions are only thiocyanate or only nitrate as in theses experiments:

$$D_{\mathrm{tbaA}} = K_{\mathrm{exAB}} + K_{\mathrm{exAB}}{}^{1/2}K_{\mathrm{dissAB}}{}^{1/2}[\mathrm{tba}^+]^{-1/2} \tag{18}$$

$$D_{\mathrm{tbaX}} = K_{\mathrm{exXB}} + K_{\mathrm{exXB}}{}^{1/2}K_{\mathrm{dissXB}}{}^{1/2}[\mathrm{tba}^+]^{-1/2}. \tag{19}$$

The data in Fig. 1 were analyzed on the basis of Eqs. 18 and 19 by using a least-squares computer program. The constants obtained are listed in Table 1. The curves in Fig. 1 were calculated on the basis of Eqs. 18 and 19 by introducing the values of constants in Table 1.

The extraction of NaSCN and $NaNO_3$ into chloroform and into MIBK was found to be slight and thus the extraction of these species will not be considered in the statistical analysis of data in the present study.

2. Solvent Extraction of Silver(I) into Chloroform. In the absence of tba^+, the solvent extraction of silver(I) into chloroform was negligible within the limit of experimental accuracy. Thus, the extraction of either AgSCN or $Na^+Ag(SCN)_2^-$ should be negligible and, when no dissociation of the extracted ion-pairs is assumed, Eq. 7 can be employed for the data analysis. Figure 2 gives the extraction data of silver(I) in the presence of tba^+ into chloroform by the squares. The data were analyzed on the basis of Eq. 7. For this analysis, the concentrations of tba^+ and SCN^- in the aqueous phase at equilibrium were calculated on the basis of Eqs. 13 and 15. The analysis of extraction data of silver(I) was made by using these values of tba^+ and SCN^- concentrations. The values of constants obtained are listed in Table 1. The curve was drawn on the basis of Eq. 7, into which were introduced the values of the constants in Table 1.

Since the calculated curve fits well with the experimental data, the following assumptions should be reasonable: (i)

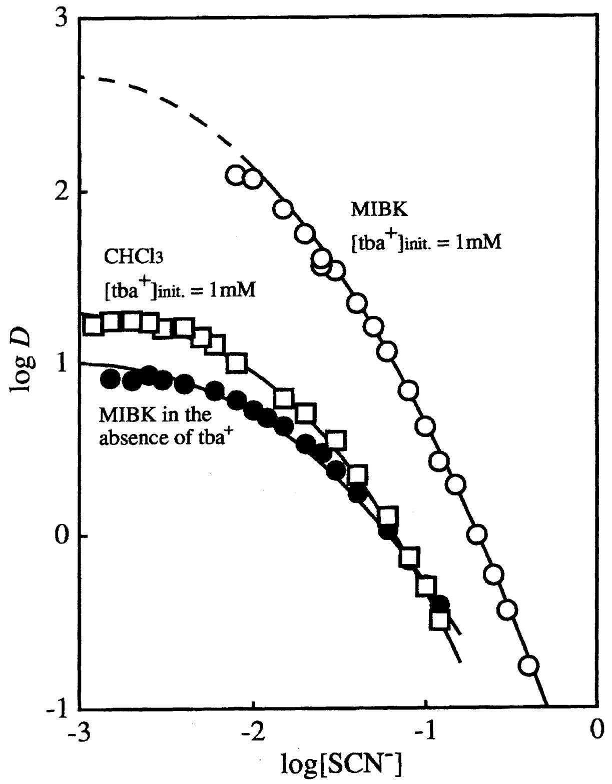

Fig. 2. Extraction curves of silver(I) as a function of thiocyanate concentration into chloroform (open squares) or MIBK in the absence (closed circles) and presence (open circles) of tba^+. The curves are calculated on the basis of Eq. 7 (chloroform) or Eq. 8 (MIBK). Since no accurate experimental data are obtained in the lower thiocyanate concentration range than 0.01 mol dm^{-3} with the open circles, the calculate extraction curves cannot be compared with experimental data, thus the calculated curve in this region is drawn by broken line.

Table 1. Summary of Equilibrium Constants

Solvent	$\log K_{\mathrm{exNa}}$	$\log K_{\mathrm{extba}}$	$\log K_{\mathrm{diss}}$	$\log K_{\mathrm{exAB}}$	$\log K_{\mathrm{exXB}}$	$\log K_{\mathrm{dissAB}}$	$\log K_{\mathrm{dissXB}}$	$\log K_3$	$\log K_4$
MIBK	0.98	5.72	−3.30	1.3	−0.02	−3.31	−3.38	1.83	1.22
$CHCl_3$	Nil	5.38	Nil	2.2	1.08	Nil	Nil	1.83	1.22

Org. phase: MIBK or $CHCl_3$.

Aq phase: 1 mol dm^{-3} $NaNO_3$ solution containing a certain amount of NaSCN and none or a certain amount of tba^+ and the pH of aqueous phase is kept at 3±0.2.

The values of constants obtained in Ref. 2 under similar experimental conditions were: $\log K_{\mathrm{exNa}}=1.02$, $\log K_3=1.81$, and $\log K_4=1.27$.

only the $\text{tba}^+\text{Ag(SCN)}_2{}^-$ species was extracted from the aqueous phase in which the anionic silver(I) thiocyanate complexes were formed, (ii) the dissociation of the extracted ion-pairs is negligible, and (iii) the extraction of AgSCN and $\text{Na}^+\text{Ag(SCN)}_2{}^-$ species was negligible.

The assumptions that the extracted silver(I) species was only in the $\text{tba}^+\text{Ag(SCN)}_2{}^-$ form and the dissociation of the ion-pairs was negligible were further examined by measuring the extraction of silver(I) from aqueous 1 mol dm^{-3} NaNO_3 solution initially containing 0.01 mol dm^{-3} NaSCN as a function of the initial tba^+ concentration in the aqueous phase. Figure 3 gives the results by the squares. The extraction curve was also calculated on the basis of Eq. 7 into which the values of constants in Table 1 were introduced. As is seen from Fig. 3, the calculated extraction curve fits well with the experimental data. Thus, it can also be concluded that the assumptions mentioned above are reasonable.

3. Solvent Extraction of Silver(I) into MIBK. The extraction data of silver(I) into MIBK in the absence of tba^+ were given in Fig. 2 by closed circles. These data were analyzed by the following equation, derived from Eq. 5 by assuming that Ag^+ and AgSCN in the aqueous phase were negligible and the dissociation of the extracted $\text{Na}^+\text{Ag(SCN)}_2{}^-$ was negligible:

$$D = K_{\text{exNa}}[\text{Na}^+]/(1 + K_3[\text{SCN}^-] + K_3K_4[\text{SCN}^-]^2) \tag{20}$$

where $[\text{Na}^+]$ was unity.

The equilibrium constants obtained by the statistical analysis of data on the basis of Eq. 20 were listed in Table 1. The values also agree with those already reported from our laboratory which were obtained when the pH of the aqueous phase was 5.5. The extraction was enhanced very much by an addition of tba^+ into the aqueous phase. The open circles in Fig. 2 give the results. It was also assumed that, even in the presence of tba^+, the extraction of ion-pairs, $\text{Na}^+\text{Ag(SCN)}_2{}^-$, which is the dominant extracted species into this solvent in the absence of tba^+ should occur. Calculations were made by assuming the dissociation of the extracted ion-pairs, $\text{tba}^+\text{Ag(SCN)}_2{}^-$, but no dissociation of $\text{Na}^+\text{Ag(SCN)}_2{}^-$ and also negligible extraction of other species such as AgSCN and $(\text{tba}^+)_2\text{Ag(SCN)}_3{}^{2-}$. The dissociation constants of the extracted silver(I) species finally obtained are listed in Table 1.

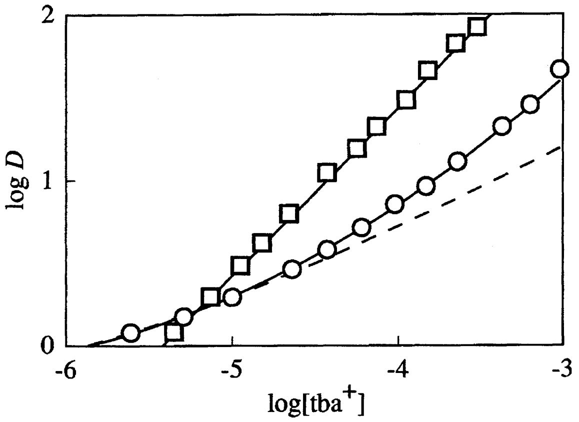

Fig. 3. Extraction curves of silver(I) as a function of aqueous tba^+ concentration into chloroform (squares: $[\text{SCN}^-]_{\text{initial}} = 0.01$ mol dm^{-3}) or MIBK (circles: $[\text{SCN}^-]_{\text{initial}} = 0.1$ mol dm^{-3}). The solid lines are calculated on the basis of Eq. 7 (chloroform) or Eq. 8 (MIBK), and the broken line is calculated when the extracted species, $\text{tba}^+\text{Ag(SCN)}_2{}^-$, is completely dissociated in MIBK on the basis of Eq. 27. The curve is tentatively drawn to fit the data at tba^+ concentration 2×10^{-6} mol dm^{-3}.

The dependence of the extraction into MIBK on the initial tba^+ concentration when the thiocyanate concentration is 0.1 mol dm^{-3} is given in Fig. 3 by circles. In order to calculate the values of K_{extba} in Eq. 2 and the dissociation constant in Eq. 4, the following equation is introduced from Eqs. 8, 13, and 14:

$$Y = K_{\text{extba}}(1 + K_{\text{diss}}[\text{tba}^+]_{\text{org}}{}^{-1}) \tag{21}$$

where $Y = D(1 + K_3[\text{SCN}^-] + K_3K_4[\text{SCN}^-]^2) - K_{\text{exNa}}[\text{tba}^+]^-$.

The $\log Y$ vs. $\log\,[\text{tba}^+]_{\text{org}}$ plot was made from the data given in Fig. 3. It has two asymptotes which can be written as:

$$\lim\,([\text{tba}^+]_{\text{org}} \to \infty) \qquad \log Y = \log K_{\text{extba}}$$
$$\lim\,([\text{tba}^+]_{\text{org}} \to 0) \qquad \log Y = \log K_{\text{extba}} + \log\,(K_{\text{diss}}[\text{tba}^+]_{\text{org}}{}^{-1})$$

From the parameters of each asymptote, the values of $\log K_{\text{extba}}$ and $\log K_{\text{diss}}$ were determined, as given in Table 1.

The solid curve for the open circles in Fig. 2 and that for the circles in Fig. 3 were calculated by introducing these values into Eq. 8 and into Eqs. 2, 3, and 8.

Discussion

As is seen from Fig. 1 and also from the results of the extraction of silver(I) into chloroform in Fig. 2, the curve calculated by assuming no dissociation of ion-pairs in the organic phase fits well with the experimental data. Thus it should be reasonable to assume no dissociation of all the ion-pairs, $\text{tba}^+\text{NO}_3{}^-$, tba^+SCN^-, and $\text{tba}^+\text{Ag(SCN)}_2{}^-$ in chloroform. These results are reasonable, because the solvation of chloroform on these species should be slight and the dielectric constant is low (ε=4.9 at 20 °C).[5] On the other hand, the partial dissociation of ion-pairs with tba^+ in MIBK should be taken into account, though it was negligible with $\text{Na}^+\text{Ag(SCN)}_2{}^-$, as was pointed out in the previous paper[2] and as was found in the present study. From the equilibrium and dissociation constants in Table 1, it was calculated that, when 1×10^{-4} to 1×10^{-2} mol dm^{-3} tba^+ was initially present in 1 mol dm^{-3} NaSCN, 99 to 93% of the tba^+ is extracted into MIBK and about 87 to 29% of the extracted tba^+SCN^- dissociated in the MIBK phase, respectively. When the aqueous phase is 1 mol dm^{-3} NaNO_3, it is also calculated that, when 1×10^{-4} to 1×10^{-2} mol dm^{-3} tba^+ was initially present, 87 to 60% of the tba^+ is extracted together with $\text{NO}_3{}^-$, and 82 to 21% of the extracted ion-pairs dissociate in the organic phase, respectively. As can be seen from Fig. 1, the extraction of these ion-pairs is better into chloroform that into MIBK, except in the lower concentration range where more dissociation occurs, as is seen from Eqs. 18 and 19.

In Fig. 2, each line was calculated on the basis of Eq. 7 or Eq. 8 into each of which were introduced the values of constants in Table 1. The lines fit well with the experimental data. Although the composition of the silver(I) thiocyanate complexes in the aqueous phase at a certain thiocyanate concentration is the same for all the extraction data of the three extraction systems, the shapes of the three extraction curves are quite different. The extraction into MIBK in the absence of tba^+ was reported in the previous paper.[2] The experimental data and equilibrium constants obtained in the absence of tba^+ in the present paper, which are listed in Table 1, agree well with those obtained in the previous paper under similar conditions, which are given in the footnote of Table 1. No dissociation of the ion-pairs is assumed in the statistical analysis of the extraction data into MIBK in the absence of tba^+ where only $Na^+Ag(SCN)_2{}^-$ is extracted, and into chloroform with tba^+ where only $tba^+Ag(SCN)_2{}^-$ is extracted. However, the shapes of these extraction curves are different. This is because, when silver(I) is extracted into MIBK, the concentration of the counter ion, Na^+, is always 1 $mol\,dm^{-3}$ but with the extraction into chloroform, the concentration of the counter ion, tba^+, is not constant because of its extraction with $NO_3{}^-$ and also the extraction with SCN^- is different even when the initial concentration of tba^+ in the aqueous phase is constant, 1×10^{-3} $mol\,dm^{-3}$. Since no dissociation of ion-pairs was concluded from the extraction data into chloroform, the $[tba^+]_{org}$ term in Eq. 13 can be neglected. Moreover, since the concentration of silver(I) was much lower than the total concentration of tba^+, the $[tba^+Ag(SCN)_2{}^-]_{org}$ term in Eq. 13 could also be neglected. Thus the following equation can be introduced:

$$[tba^+] = [tba^+]_{init.}(1+K_{exAB}[SCN^-]+K_{exXB}[NO_3{}^-])$$
$$= [tba^+]_{init.}/\{1+K_{exAB}[SCN^-]+K_{exXB}(1-[SCN^-])\}. \quad (22)$$

The slope of the plot in the presence of tba^+ in Fig. 2 is steeper with the extraction into MIBK than into chloroform. Since the extracted species is, in all the cases, only $Ag(SCN)_2{}^-$, the decrease in the molar ratio of this species to the total silver(I) in the aqueous phase should decrease the extraction. Figure 4 gives the calculated molar ratio of the silver species in the aqueous phase as a function of the thiocyanate concentration by using the stability constants in Table 1. As is seen from Fig. 4, the extractable species is more than 90% when $[SCN^-]$ is 1×10^{-3} $mol\,dm^{-3}$, but it is about 5 and 0.5% when it is 0.1 and 0.3 $mol\,dm^{-3}$, respectively. Thus the formation of higher anionic complexes, $Ag(SCN)_3{}^{2-}$ and $Ag(SCN)_4{}^{3-}$, lowers the extraction of silver(I) in these systems. Furthermore, since one anionic complex is extracted with one tba^+, the decrease of the tba^+ concentration also decreases the extraction of the silver(I) complex. When the extraction into MIBK in the absence of tba^+ is examined, the counter ion is Na^+ and its concentration is essentially constant, 1.0 $mol\,dm^{-3}$. When the counter ion is tba^+, a decrease in the tba^+ concentration in the aqueous phase is caused by an increase in the thiocyanate concentration and, consequently, the extraction of silver(I) is decreased, as can be seen from Eqs. 7, 13, and 14. This decrease in the tba^+ concentration is due to the facts that the extraction of tba^+ together with thiocyanate ion is better than that of nitrate ion as is seen from the values of K_{exAB} and K_{exXB} in Table 1. Figure 5 gives the calculated value of the tba^+ concentration in the aqueous phase as a function of the thiocyanate concentration when the initial tba^+ concentration is 1×10^{-3} $mol\,dm^{-3}$. The tba^+ concentrations in the aqueous phase at equilibrium, which were necessary for the calculation of the curves in the MIBK system, were experimentally obtained; the values in the chloroform system were calculated on the basis of Eqs. 9, 11, and 13 and the values K_{exAB} and K_{exXB} in Table 1. As is seen from Fig. 5, a 92.5% portion of tba^+ is already extracted into chloroform when the thiocya-

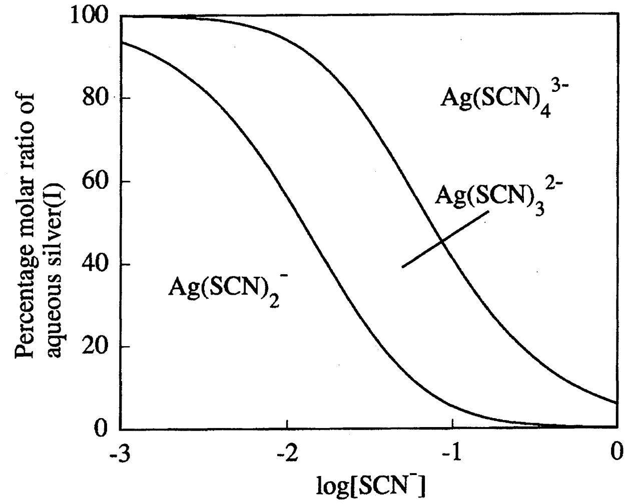

Fig. 4. Calculated molar ratio of aqueous Ag(I) species at equilibrium as a function of thiocyanate concentration by using equation $A/(1+10^{1.83}[SCN^-]+10^{3.05}[SCN^-]^2)$ where A is 1, $10^{1.83}[SCN^-]$, and $10^{3.05}[SCN^-]^2$ respectively for $Ag(SCN)_2{}^-$, $Ag(SCN)_3{}^{2-}$, and $Ag(SCN)_4{}^{3-}$.

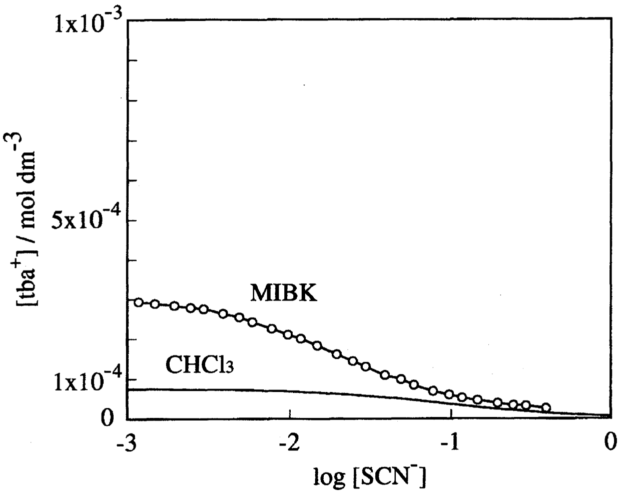

Fig. 5. The change in the tba^+ concentration in the aqueous phase which is 1 $mol\,dm^{-3}$ $Na(SCN, NO_3)$ by the extraction as $tba^+NO_3{}^-$ and tba^+SCN^- when the initial tba^+ concentration is 1×10^{-3} $mol\,dm^{-3}$.

nate concentration is 1×10^{-3} mol dm^{-3} and a portion more than 96% is extracted when the thiocyanate concentration is 0.1 mol dm^{-3}. On the other hand, about a 70% portion is extracted into MIBK from the aqueous phase when the thiocyanate concentration is 1×10^{-3} mol dm^{-3} and a portion more than 94% is extracted when the thiocyanate concentration is 0.1 mol dm^{-3}. The amount of tba$^+$ extracted into the organic phase increases by an increase in the thiocyanate concentration in both the systems but since the difference in the extractability of tba$^+$NO$_3{}^-$ and tba$^+$SCN$^-$ is larger into MIBK than into chloroform, an increase in the thiocyanate concentration causes a greater decrease of the tba$^+$ concentration in the MIBK system, as is seen from Fig. 5. This causes a steeper decrease of the distribution ratio of silver(I) thiocyanate by an increase in the thiocyanate concentration in the extraction into MIBK than that into chloroform.

From the statistical analysis, it is assumed that the Ag$^+$ and AgSCN species is negligible under the conditions of the present study. Since the solubility of AgSCN is very low in the aqueous phase,[6)] precipitates should be formed when the Ag$^+$ species is present in the aqueous phase containing SCN$^-$. On the other hand, when silver(I) forms anionic complexes in the aqueous phase, the precipitation of AgSCN should be negligible as long as no formation of precipitates of the anionic complexes with the bulky cations occurs.

It is seen from Fig. 2 that tba$^+$ is much more effective than Na$^+$ as the counter ion of Ag(SCN)$_2{}^-$. This is because tba$^+$ is much bulkier than Na$^+$. As is seen from Table 1, the extraction constants of Ag(SCN)$_2{}^-$ as ion-pairs with tba$^+$ (K_{extba}) is about five orders greater than with Na$^+$ (K_{exNa}). It can be calculated that the distribution ratio with the extraction with tba$^+$ into MIBK is $10^{2.7}$ when the initial thiocyanate concentration is 1×10^{-3} mol dm^{-3}. This can not be obtained experimentally because it is too high to be determined accurately. On the other hand, that for the extraction as ion-pairs with Na$^+$ is 1.0, as is seen from Fig. 2. This very large difference between the K_{exNa} and K_{extba} due to the difference in the size of the counter cations also causes the difference in the dissociation of the extracted species. The dissociation of Na$^+$Ag(SCN)$_2{}^-$ in MIBK is negligible while that of tba$^+$Ag(SCN)$_2{}^-$ is not negligible. If the concentration of dissociated tba$^+$ in the organic phase is changed, it will affect the dissociation of the ion-pairs of the anionic silver(I) complex with tba$^+$. Therefore, it should also affect the dependence of the extraction of silver(I) on the thiocyanate concentration. As is seen from Fig. 3, the plot of extraction into chloroform as a function of the aqueous tba$^+$ concentration is a straight line of +1. This can be well explained by Eq. 7; the dissociation of the extracted species is negligible in chloroform. On the other hand, the slope of the plot for the extraction into MIBK also in the presence of tba$^+$ is smaller. When silver(I) thiocyanate complex would be extracted only with tba$^+$ and the extracted ion-pairs would dissociate completely, the extraction equilibrium may be given as:

$$\mathrm{tba}^+ + \mathrm{Ag(SCN)_2}^- \rightleftarrows \mathrm{tba}^+_{\mathrm{(org)}} + \mathrm{Ag(SCN)_2}^-{}_{\mathrm{(org)}}$$

$$K_{\mathrm{exdiss}} = [\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{Ag(SCN)_2}^-]_{\mathrm{org}}/([\mathrm{tba}^+][\mathrm{Ag(SCN)_2}^-]). \quad (23)$$

Then the distribution ratio should be given by the following equation instead of Eq. 6:

$$D = [\mathrm{Ag(SCN)_2}^-]_{\mathrm{org}}/([\mathrm{Ag(SCN)_2}^-] + [\mathrm{Ag(SCN)_3}^{2-}] + [\mathrm{Ag(SCN)_4}^{3-}]) \quad (24)$$

$$= K_{\mathrm{exdiss}}[\mathrm{tba}^+][\mathrm{tba}^+]_{\mathrm{org}}{}^{-1}/(1 + K_3[\mathrm{SCN}^-] + K_3K_4[\mathrm{SCN}^-]^2). \quad (25)$$

By assuming that $[\mathrm{Ag(SCN)_2}^-]_{\mathrm{org}}$ would be much lower than $[\mathrm{SCN}^-]_{\mathrm{org}}$ and $[\mathrm{NO_3}^-]_{\mathrm{org}}$ in Eq. 4, the following equation can be written:

$$[\mathrm{tba}^+]_{\mathrm{org}} = [\mathrm{tba}^+]^{1/2}(K_{\mathrm{exAB}}K_{\mathrm{dissAB}}[\mathrm{SCN}^-] + K_{\mathrm{exXB}}K_{\mathrm{dissXB}}[\mathrm{NO_3}^-])^{1/2}. \quad (26)$$

From Eqs. 25 and 26, the following equation can be written:

$$D = K_{\mathrm{exdiss}}[\mathrm{tba}^+]^{1/2}(K_{\mathrm{exAB}}K_{\mathrm{dissAB}}[\mathrm{SCN}^-] + K_{\mathrm{exXB}}K_{\mathrm{dissXB}}[\mathrm{NO_3}^-])^{-1/2}/(1 + K_3[\mathrm{SCN}^-] + K_3K_4[\mathrm{SCN}^-]^2). \quad (27)$$

Thus the slope of log D as a function of [tba$^+$] when [SCN$^-$] is constant should be +1/2, as was also pointed out.[4)] In Fig. 3, an example of the calculated plot (broken line) when complete dissociation is assumed. The calculation of the broken line was made by introducing the values of K_{exAB}, K_{dissAB}, K_{exXB}, K_{dissXB}, K_3, and K_4 in Table 1 into Eq. 27 and by assuming the value K_{exdiss} as $10^{2.7}$. the value of K_{exdiss} is tentatively calculated to fit the line with the data in the lowest tba$^+$ concentration. As is seen from Fig. 3, the slope of the plot of the experimental data of the extraction with MIBK is between +1/2 and +1 and this also indicates partial dissociation of the extracted tba$^+$Ag(SCN)$_2{}^-$ species in the organic phase.

In the present study, the extracted silver(I) species is the "ternary complex", Na$^+$Ag(SCN)$_2{}^-$ or tba$^+$Ag(SCN)$_2{}^-$. When the change in the concentration of the cation and the dissociation of the ion-pairs in the organic phase is negligible, as in the extraction into MIBK in the absence of tba$^+$, the data analysis is rather simple. However, in the presence of tba$^+$, the extraction data obtained in the form of log D as a function of log [SCN$^-$] should be analyzed by considering the extraction of the third component, tba$^+$. Furthermore, the partial dissociation of the extracted ion-pairs, tba$^+$Ag(SCN)$_2{}^-$, tba$^+$SCN$^-$, and tba$^+$NO$_3{}^-$ makes the equilibrium complicated. This partial dissociation of the extracted species seems to have not been considered previously.

The chemical behavior of silver(I) in aqueous thiocyanate solutions has been studied very much. The number of reported values of stability constants of silver(I) thiocyanate complexes is very many.[6—10)] Since the solubility of the silver(I) thiocyanate is low, most of such studies were made at rather high thiocyanate concentrations, as in the present study. This is due to the fact that the precipitation can be avoided by anionic complex formation. This indicates that the solvent extraction of the uncharged complex, AgSCN, should be difficult: Under the conditions where this complex is extractable, precipitation in the aqueous phase should make the experiments very difficult. Thus not many have been studied with the solvent extraction of silver(I) thiocyanate.[11—15] However, the solvent extraction of silver(I) in thiocyanate solutions seems to be favorable as anionic complexes by using bulky cations.

It was found in the present study that the recovery of silver(I) from the both phases became poorer when the thiocyanate concentration was lower than 1×10^{-3} mol dm^{-3}. This should be due to precipitation of AgSCN on the vessel wall and/or on the interface.

The assumption that the extracted species into MIBK in the absence of tba$^+$ is $Na^+Ag(SCN)_2{}^-$ indicates this difficulty of extraction of AgSCN. The extraction in the absence of tba$^+$ into MIBK is not very effective, but that in the presence of tba$^+$ is effective, especially when the thiocyanate concentration is low, as is seen from Fig. 2.

The results in the present study show that the solvent extraction of anionic metal complexes with bulky cations is much more effective than the extraction of the metal ion as neutral complex. This was also observed when the metal ion was copper(I) in the thiocyanate complexes.[4] However, the chemical equilibria involved in the solvent extraction systems are much more complicated, especially when partial dissociation of the extracted ion-pairs occurs in the organic phase. Thus a careful consideration is necessary for the statistical analysis of the extraction of anionic metal complexes, especially when the organic solvent is polar.

References

1) T. Morimoto, S. Ochiai, and T. Sekine, *Anal. Sci.*, **4**, 255 (1988).

2) T. Sekine, M. Kashima, J. Tsuda, and Y. Ohmiya, *Solvent Extr. R. & D., Jpn.*, **2**, 112 (1995).

3) J. Noro and T. Sekine, *Bull. Chem. Soc. Jpn.*, **65**, 1910 (1992).

4) A. Nasu, A. Yoshikawa, J. Noro, and T. Sekine, *Anal. Sci.*, **12**, 411 (1996).

5) T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry," Marcel Dekker, New York (1977), pp. 48—50.

6) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, Spec. Pub. No. 17 (1964) and Spec. Pub. No. 25 (1971).

7) D. D. Marco, A. Bellomo, F. Licastro, and A. Casale, *Ann. Chim.*, **74**, 617 (1984).

8) D. D. Marco, *Zetz. Nauk.-Politech. Lodz., Technol. Chem. Spozyw*, **621**, 71 (1994).

9) A. Survila, G. Cesiulis, and T. Jankauskas, *Liet. TSR Mokslu Akad. Darb., Ser. B*, **4**, 11 (1985).

10) K. I. Tudoryanu, P. K. Migal, and L. F. Konishesku, *Zh. Neorg. Khim.*, **35**, 129 (1990).

11) M. Ziegler, *Angew. Chem.*, **70**, 745 (1958).

12) M. Ziegler, H. Sbrzesny, and O. Glemser, *Z. Anal. Chem.*, **171**, 250 (1959).

13) A. S. Reddy and M. L. Reddy, *Radiochem. Radioanal. Lett.*, **59**, 133 (1983).

14) S. Armed, A. Rusheed, and M. S. Bhatti, *J. Radioanal. Nucl. Chem.*, **122**, 75 (1988).

15) V. O. Kodyukevich, V. L. Giruts, and V. I. Kuznetsov, *Zh. Neorg. Khim.*, **37**, 954 (1992).