A Study of Silver(I) Complexes with Some π-Donors and n-Donors in Chloroform by the Solvent Extraction Method

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The solvent extraction of silver(I) in a 0.1 M constant-ionic-strength solution into chloroform with 2-thenoyltrifluoroacetone(TTA) and with caproic acid was studied by means of radiometry. It was found that these extractions are enhanced by the addition of aliphatic and cyclic alkenes, of aromatic hydrocarbons, and of some n-donors. The enhancement of the extraction was explained in terms of the formation of molecular complexes of the silver(I)-TTA chelate or of silver(I) caproate in chloroform. By an analysis of the experimental data, the stability constant of the silver(I)-TTA chelate in the aqueous phase, and the stability constants of the molecular complexes in the chloroform phase with these donors, were determined. Some consideration was made of these results and of the possibility of the application of these extraction systems to analytical chemistry.

Many workers have reported the complex formation of silver(I) with various n-donor ligands, and the stability constants have been determined by various experimental techniques.[1] At the same time, some workers have also reported that silver(I) can form complexes with π-donor ligands, such as unsaturated aliphatic or aromatic hydrocarbons.[2,3]

The complex formation equilibria of silver(I) with n-donor ligands have been determined, in most cases, in aqueous solutions because the complexes with n-donors which are usually anionic have often been of interest to analytical and inorganic chemists from the standpoint of the chemical behavior of silver(I) in aqueous solutions. The π-donors are, on the other hand, usually uncharged, and they are often relatively insoluble in water. However, the complex formation of silver(I) with these ligands has also been determined in aqueous solutions or mixed solutions of water and polar organic solvents, because silver(I) salts with ordinary inorganic anions are insoluble in nonpolar organic solvents.

The formation of various other molecular complexes, however, has been studied very often in nonpolar organic solvents such as carbon tetrachloride,[2,3] in many cases, the formation constants of molecular complexes seem to be affected by the nature of the solvent—they are usually larger in organic solvents than in water.[2] This could be due to a great interaction of water molecules with various ionic or molecular substances; the comparison of the formation constants of a given complex in water and in other kinds of solvents should give some information about that complex.

The present study has been undertaken from this standpoint. The present authors have determined the complex formation of silver(I) extracted from aqueous solutions into chloroform as a chelate complex with thenoyltrifluoroacetone(TTA) or as a complex with caproic acid. Thenoyltrifluoroacetone and caproic acid were used in order to make silver(I) extractable into the organic solvent, and the complex formation was determined from the enhancement of the extraction due to the formation of molecular complexes in the organic phase. The stability constants thus obtained were compared with those determined in aqueous solutions, the results obtained in these different solvents were discussed. The effect of the formation of these molecular complexes on the solvent extraction of silver(I) with the chelating reagent or with the fatty acid was considered, and the possibility of the application of such extractions to analytical chemistry was discussed.

Experimental

Reagents. The silver-110 m tracer was obtained from the New England Nuclear Corp. U. S. A., as silver nitrate in a dilute nitric acid solution. It was diluted with 0.1 M nitric acid and used as the stock tracer solution. The quinoline and caproic acid were obtained from the Merck Co. Germany. The tributyl phosphate (TBP) and unsaturated hydrocarbons were obtained from Tokyo Kasei Co., and the TTA and trioctylphosphine oxide (TOPO), from Dojindo Co. All of the reagents were of a reagent-grade. TBP was washed with 0.1 M perchloric acid, water, and 0.1 M sodium hydroxide, and then several times with water. Chloroform was washed three times with water just before use. The other reagents were used without further purification. The concentration of the sodium hydroxide solution was determined by means of acid titration, and the concentrations of the other solutions were determined by means of gravimetry.

Procedures. All of the procedures were carried out in a thermostatted room at 25 °C. Stoppered glass tubes (volume, 20 ml) were used to equilibrate the two phases. For the experiments on the silver(I)-TTA chelate, sodium perchlorate solutions containing sodium hydroxide and a chloroform solution of TTA were placed in the tubes. After the two phases has been equilibrated by shaking them for one minute by hand, a certain amount of a silver(I) solution labelled by silver-110 m was added; the two phases were then again agitated by hand for three minutes and centrifuged. For the experiments on the silver(I) caproate complex, aqueous solutions containing sodium perchlorate and/or sodium caproate, and chloroform were placed in the tubes and the labelled silver(I) was added. The two phases were agitated for three minutes by hand and then centrifuged. The initial volumes of the two phases were always 5.0 ml, and

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[1] "The Stability Constants of Metal-Ion Complexes," ed. by L. G. Sillén and A. E. Martell, The Chemical Society Special Publication, No. 17 (1964).

[2] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day Inc., San Francisco (1964).

[3] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe", Springer, Berlin (1961).

the inoic strength of the aqueous phase was 0.1 M. The initial concentration of the silver(I) ion in the aqueous phase was 2×10^{-5} to 3×10^{-6} M. The concentration of TTA in the organic phase was 0.1 M. The concentration of caproate ions in the aqueous phase was 0.1 M unless otherwise stated. The pH of the aqueous phase at equilibrium was in a range from 7 to 8 in both cases.

A 2 ml portion was pipetted out from each equilibrated phase and transferred into a test tube. The γ-radioactivity was measured with a well-type(NaI) scintillation counter, and the distribution of silver(I) was calculated as follows;

$$D=\frac{[\mathrm{Ag(I)}]_{\mathrm{org,total}}}{[\mathrm{Ag(I)}]_{\mathrm{total}}}$$

$$=\frac{\gamma\text{-count-rate per ml of the organic phase}}{\gamma\text{-count-rate per ml of the aqueous phase}}$$

Statistical

The extraction of silver(I) in an aqueous solution with an organophilic and acidic extracting reagent, HA, can be written as follows:

$$\mathrm{Ag^+ + HA(org)} \rightleftarrows \mathrm{AgA(org) + H^+} \tag{1}$$

$$K_{\mathrm{ex}}=\frac{[\mathrm{AgA}]_{\mathrm{org}}[\mathrm{H^+}]}{[\mathrm{Ag^+}][\mathrm{HA}]_{\mathrm{org}}} \tag{2}$$

When the organic phase initially contains C_{HA}M of the extractant and when the volumes of the two phases are the same, the following equation can be used:

$$C_{\mathrm{HA}}=[\mathrm{HA}]_{\mathrm{org}}+[\mathrm{HA}]+[\mathrm{A^-}] \tag{3}$$

However, if the aqueous phase initially contains C_{OH}M of sodium hydroxide (which is smaller than C_{HA}M) and if the pH is not very high (that is, $[\mathrm{OH^-}]\ll 1$), the following equation can be used:

$$C_{\mathrm{OH}}\simeq[\mathrm{A^-}] \tag{4}$$

Thus, under such conditions, the concentration of the dissociated extractant anion, $[\mathrm{A^-}]$, in Eq. (4) can be calculated from the amount of sodium hydroxide added to the initial aqueous phase, regardless of the total concentration of the extractant in the system.

The distribution ratio of silver(I) into an inert solvent such as chloroform can be described as:

$$D=\frac{[\mathrm{Ag(I)}]_{\mathrm{org,total}}}{[\mathrm{Ag(I)}]_{\mathrm{total}}} \tag{5}$$

$$=\frac{[\mathrm{AgA}]_{\mathrm{org}}}{[\mathrm{Ag^+}]+[\mathrm{AgA}]+\cdots}=\frac{K_{\mathrm{dm}}\beta_1[\mathrm{A^-}]}{1+\beta_1[\mathrm{A^-}]+\cdots} \tag{6}$$

where β_1 is the stability constant of the silver(I) complex with the extractant in the aqueous phase and where K_{dm} is the distribution constant of the uncharged chelate between the two phases:

$$K_{\mathrm{dm}}=\frac{[\mathrm{AgA}]_{\mathrm{org}}}{[\mathrm{AgA}]} \tag{7}$$

From the acid dissociation constant and the distribution constant of HA, that is, $K_{\mathrm{a}}=[\mathrm{A^-}][\mathrm{H^+}]/[\mathrm{HA}]$ and $K_{\mathrm{d}}=[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}]$, we obtain:

$$[\mathrm{A^-}]=\frac{K_{\mathrm{a}}[\mathrm{HA}]_{\mathrm{org}}}{K_{\mathrm{d}}[\mathrm{H^+}]} \tag{8}$$

When no aqueous complex with $\mathrm{A^-}$ is formed, the following equation is obtained from Eqs. (6) and (8):

$$D=K_{\mathrm{dm}}\beta_1[\mathrm{A^-}]=K_{\mathrm{dm}}\beta_1K_{\mathrm{a}}K_{\mathrm{d}}^{-1}[\mathrm{HA}]_{\mathrm{org}}[\mathrm{H^+}]^{-1} \tag{9}$$

From Eqs. (2) and (9), we obtain:

$$K_{\mathrm{ex}}=K_{\mathrm{dm}}\beta_1K_{\mathrm{a}}K_{\mathrm{d}}^{-1} \tag{10}$$

When the metal complex forms molecular complexes with a neutral ligand, L, in the organic phase, the equilibrium can be written as:

$$\mathrm{AgA(org)}+n\mathrm{L(org)} \rightleftarrows \mathrm{AgAL}_n\mathrm{(org)} \tag{11}$$

$$\beta_n(\mathrm{org})=\frac{[\mathrm{AgAL}_n]_{\mathrm{org}}}{[\mathrm{AgA}]_{\mathrm{org}}[\mathrm{L}]_{\mathrm{org}}{}^n} \tag{12}$$

where $\beta_{n(\mathrm{org})}$ is the over-all stability constant of the "n-th" molecular complex in the organic phase.

The distribution ratio in such a system can be written as:

$$D=\frac{[\mathrm{AgA}]_{\mathrm{org}}+[\mathrm{AgAL}]_{\mathrm{org}}+[\mathrm{AgAL_2}]_{\mathrm{org}}+\cdots}{[\mathrm{Ag^+}]+[\mathrm{AgA}]+\cdots} \tag{13}$$

From Eqs. (6), (12), and (13), the following equation is obtained:

$$D=\frac{K_{\mathrm{dm}}\beta_1[\mathrm{A^-}]}{1+\beta_1[\mathrm{A^-}]+\cdots}\times(1+\beta_{1(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}+\beta_{2(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}{}^2+\cdots) \tag{14}$$

If the concentration, $[\mathrm{L}]_{\mathrm{org}}$, is kept at a constant value, $\mathrm{L_1}$, Eq. (14) can be written as:

$$D=C_{\mathrm{L}}\times\frac{K_{\mathrm{dm}}\beta_1[\mathrm{A^-}]}{1+\beta_1[\mathrm{A^-}]+\cdots} \tag{15}$$

where C_{L} is a constant which is equal to $(1+\beta_{1(\mathrm{org})}\mathrm{L_1}+\beta_{2(\mathrm{org})}\mathrm{L_1}^2+\cdots)$

If the concentration, $[\mathrm{A^-}]$, is kept at a constant value, $\mathrm{A_1}$, the following equation can be obtained from Eqs. (6) and (14):

$$D/D_{\mathrm{A}}=(1+\beta_{1(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}+\beta_{2(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}{}^2+\cdots) \tag{16}$$

where D_{A} is a constant which is equal to $K_{\mathrm{dm}}\beta_1\mathrm{A_1}(1+\beta_1\mathrm{A_1}+\cdots)^{-1}$ in such a case.

The stability constants, β_n and $\beta_{n(\mathrm{org})}$, and the distributation constant, K_{dm}, can be determined from the experimental results by a curve-fitting method.[4]

If only the first complex is formed in the aqueous phase, the log D *vs.* log $[\mathrm{A^-}]$ plot of the data represented by Eq. (15) can be fitted with the standard curve represented by Eq. (17), while if only the first complex is formed in the organic phase, the log D/D_{A} *vs.* log $[\mathrm{L}]_{\mathrm{org}}$ plot of the data represented by Eq. (16) can be fitted with the standard curve represented by Eq. (18):

$$Y=-\log(1+v^{-1});\ X=\log v \tag{17}$$

$$Y=\log(1+v);\ X=\log v \tag{18}$$

If both the first and second complexes are formed in the organic phase, the plot can be fitted with the following family of standard curves:

$$Y=\log(1+pv+v^2);\ X=\log v \tag{19}$$

The equilibrium constants can be obtained from the parameters of the fitted curve.

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[4] T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

Results

TTA Extraction. The extraction of silver(I) with TTA in chloroform is poor. The open circles in Fig. 1 gives the distribution ratio of silver(I) between chloroform and the aqueous phase as a function of the concentration of the TTA anion. The extraction is less than 10 percent even when the aqueous phase contains nearly 0.1 M TTA anions.

This extraction is enhanced very much if a molecular complex-forming ligand is added to the chloroform phase. Figure 1 also gives the extraction curves when the chloroform phase contains 5×10^{-1} M toluene, 1×10^{-2} M cyclohexene, or 1×10^{-3} M quinoline. It also gives the extraction curve of silver(I) with TTA in benzene. As may be seen from Fig. 1, each plot has two asymptotes, with slopes of +1 and 0. This fact indicates that the data can be represented by Eq. (15). The equilibrium constants obtained by the curve-fitting method are listed in Table 1.

Figures 2 to 6 show the enhancement of the extraction of the silver(I)-TTA chelate by an addition

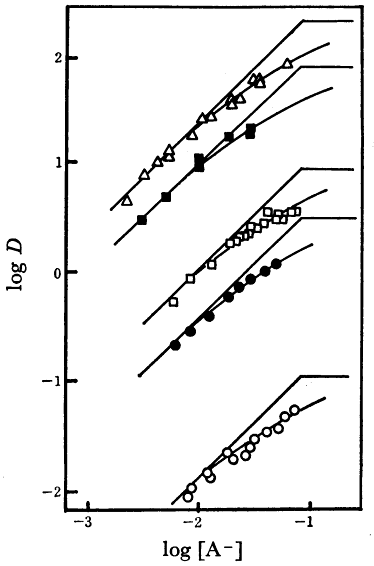

Fig. 1. Distribution ratio of Ag(I) as a function of the concentration of TTA anion. Org. phase: ○: $CHCl_3$, ●: $CHCl_3$ containing 5×10^{-1} M toluene, □: $CHCl_3$ containing 1×10^{-2} M cyclohexene, ■: benzene, △: $CHCl_3$ containing 1×10^{-3} M quinoline.

TABLE 1. EQUILIBRIUM CONSTANTS OBTAINED FROM Fig. 1

Organic solvent	$\log\beta_1$ a)	$\log K_{dm}'$ b)	$\log K_{ex}'$ c)
$CHCl_3$	1.10	−0.96	−7.94
$CHCl_3$ containing 5×10^{-1} M toluene	1.10	0.50	−6.48
$CHCl_3$ containing 1×10^{-2} M cyclohexene	1.10	0.94	−6.04
$CHCl_3$ containing 1×10^{-3} M quinoline	1.10	2.30	−4.68
C_6H_6	1.10	1.95	−4.78

a) $\beta_1=[AgA]/[Ag^+][A^-]$ in the aqueous phase where A^- is the dissociated TTA anion.
b) $K_{dm}'=K_{dm}C_L$ (K_{dm}, *cf.* Eq. (7) and C_L, *cf.* Eq. (15)).
c) $K_{ex}'=K_{ex}C_L$ (K_{ex}, *cf.* Eqs. (2) and (10) and C_L, *cf.* Eq. (15)).

These values are calculated from the values of K_{dm}' by using the following constants for TTA: $pK_a=6.23$, $\mu=0.1$[6] and $K_d=71$[5] ($CHCl_3$-0.1 M $NaClO_4$), $K_d=40$ (C_6H_6-0.1 M $NaClO_4$).[17]

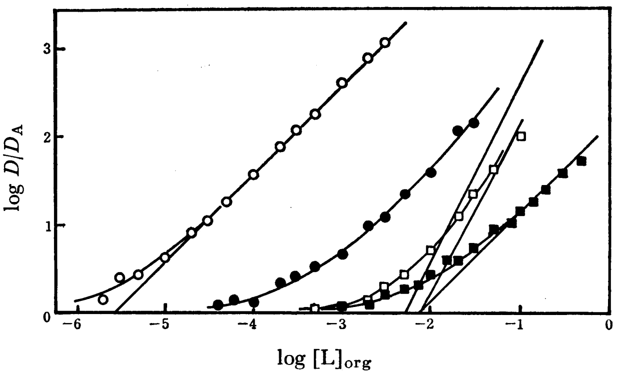

Fig. 2. Enhancement of Ag(I)-TTA extraction by an addition of one of the three ligands into $CHCl_3$. ○: quinoline, ●: TOPO, ■: TBP. Enhancement of Ag(I) caproate extraction by an addition of TOPO (□) into $CHCl_3$ is also shown.

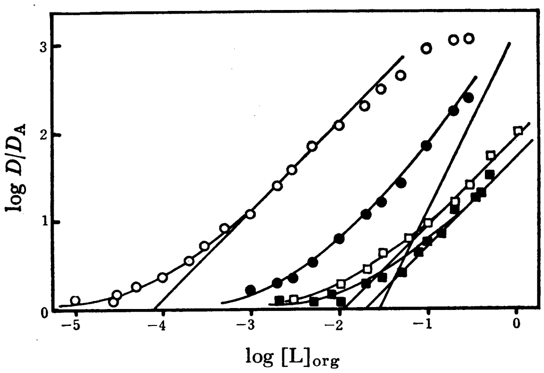

Fig. 3. Enhancement of Ag(I)-TTA extraction by an addition of one of the three ligands into $CHCl_3$. ○: 1-hexene, ●: mesitylene, ■: toluene. Enhancement of Ag(I) caproate extraction by an addition of 1-hexene (□) into $CHCl_3$ is also shown.

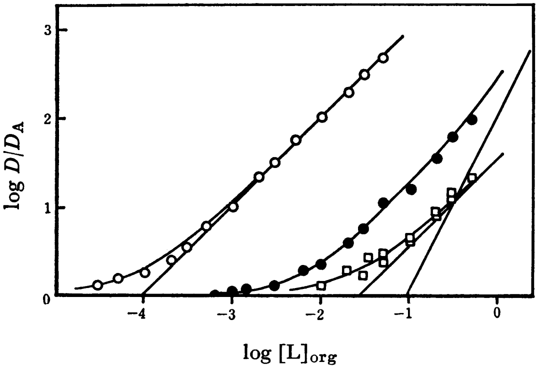

Fig. 4. Enhancement of Ag(I)-TTA extraction by an addition of one of the three ligands into $CHCl_3$. ○: cyclohexene, ●: *o*-xylene, □: benzene.

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[5] T. Sekine and Y. Hasegawa, "Solvent Extraction Research," ed. by A. S. Kertes and Y. Marcus, John Wiley & Sons (1969) p. 289.

[6] J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.* **72**, 2948 (1950).

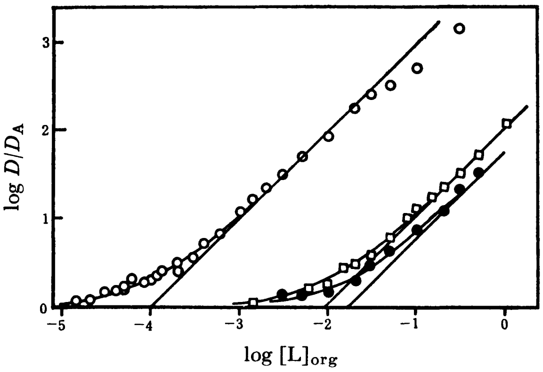

Fig. 5. Enhancement of Ag(I)-TTA extraction by an addition of one of the two ligands into $CHCl_3$. ○: 1-pentene, ●: *p*-xylene. Enhancement of Ag(I) caproate extraction by an addition of cyclohexene (□) into $CHCl_3$ is also shown.

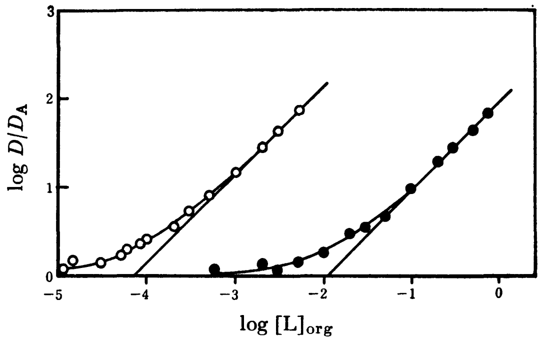

Fig. 6. Enhancement of Ag(I)-TTA extraction by an addition of one of the two ligands into $CHCl_3$. ○: 1-heptene, ●: *m*-xylene.

of the molecular complex-forming ligand to the chloroform phase. By the curve-fitting, it was concluded that both the first and second complexes are formed with *o*-xylene, mesitylene, and TOPO, while only the first complex is formed with the other ligands. The stability constants of these complexes were determined from the parameters of the fitted standard curve; they are given in Table 2. Table 2 also lists the literature stability constants of silver(I) complexes with these ligands in an aqueous solution.

Caproate Extraction. The extraction of silver(I) with the caproate ion into chloroform is also poor. The distribution ratio was found to be only $10^{-2.29}$ even when the concentration of the caproate ion is 0.1 M.[12] This extraction is also enhanced by the addition of 1-hexene, cyclohexene, or TOPO. Figures 2, 3, and 5 also show the enhancement of the silver(I) caproate extraction caused by these ligands. The data were analyzed by the curve-fitting method. The constants thus obtained are also listed in Table 2.

Discussion

The results in Fig. 1 and Table 1 show that the stability of the silver(I) complex with the TTA anion in the aqueous phase is rather small and that the distribution constant of the silver(I)-TTA chelate between chloroform and the aqueous phase is very small. It is known that β-diketones are not effective extractants for silver(I) (see, for example, Ref. 13). This seems

TABLE 2. STABILITY CONSTANTS FOR THE MOLECULAR COMPLEXES OF Ag(I)-TTA CHELATE AND Ag(I)-CAPROATE IN CHLOROFORM OR FOR SILVER COMPLEXES IN AQUEOUS 1 M (K, Ag)NO_3 SOLUTIONS WITH SOME π-DONORS AND *n*-DONORS AT 25°C

Donors	Present work (in chloroform)				From literature (in aqueous soln.)		
	AgTTA		AgCap.		Ag^+		Ref.
	log $\beta_{1(org)}$	log $\beta_{2(org)}$	log $\beta_{1(org)}$	log $\beta_{2(org)}$	log β_1	log β_2[a]	
Propene	—	—	—	—	1.94	—	7
1-Butene	—	—	—	—	2.08	—	8
1-Pentene	4.01	—	—	—	—	—	
1-Hexene	4.11	—	1.96	—	2.93	—	9
1-Heptene	4.12	—	—	—	—	—	
Cyclohexene	4.03	—	2.15	—	1.90	—	9
Benzene	1.55	—	—	—	0.38	−0.29	10
Toluene	1.70	—	—	—	0.47	−0.20	10
o-Xylene	2.17	2.12	—	—	0.46	−0.04	10
m-Xylene	1.94	—	—	—	0.48	−0.01	10
p-Xylene	1.78	—	—	—	0.42	−0.06	10
Mesitylene	2.56	3.08	—	—	0.26	—	11
TBP	2.15	—	—	—	—	—	
TOPO	3.58	4.20	2.73	4.26	—	—	
Quinoline	5.56	—	4.65[b]	—	—	—	

a) The stability constant is given as $\beta_2 = [Ag_2L^{2+}]/[Ag^+]^2[L]$. b) Taken from Ref. 12.

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7) C. K. N. Trueblood and H. J. Lucas, *J. Amer. Chem. Soc.*, **74**, 1338 (1952).

8) F. R. Hepner, K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1333 (1952).

9) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).

10) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

11) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950).

12) T. Sekine and D. Dyrssen, unpublished data.

13) J. Stary, "The Solvent Extraction of Metal Chelates," Pergamon Press, Oxford (1964).

to be because of this small distribution constants of of the silver(I) chelate. Since this distribution constant of the silver(I)-TTA chelate is much lower than that of the acid-form TTA (the distribution constant of TTA between chloroform and a 0.1 M sodium perchlorate solution has been reported to be 71[5])), it is assumed that the silver(I) ion in the TTA chelate interacts with water molecules in the aqueous phase rather strongly.

The results in Table 2 can be summarized as follows: (i) In all cases, the molecular complexes of silver(I) combined with the thenoyltrifluoroacetonate ion in chloroform are more stable than those with the caproate ion in chloroform and those of the silver(I) ion in aqueous solutions. (ii) The stabilities of the molecular complexes of the silver(I) TTA chelate with the three unsaturated aliphatic hydrocarbons and with cyclohexene are similar to one another. (iii) The stabilities of the molecular complexes with the aromatic hydrocarbons increase as the number of the methyl group increases. Among the three xylenes, the stability becomes larger in this order: ortho-, meta-, and para-xylene. On the other hand, the stability constants of the molecular complexes of Ag^+ in an aqueous solution with these ligands are not very different. (iv) The three n-donors also form stable molecular complexes. TOPO forms more stable complexes than does TBP, and quinoline forms the most stable first complex. (v) The stabilities of the molecular complexes of silver(I)-caproate with cyclohexene are similar to that of the silver(I) cyclohexene complex in an aqueous solution, but the molecular complex with 1-hexene in chloroform is somewhat less stable than the corresponding complex in the aqueous phase.

Although no information has been obtained about the structure of the complexes from only these distribution data, there is no doubt that TOPO, TBP, and quinoline form complexes through the lone-pair electrons on the oxygen or nitrogen atom, whereas the unsaturated hydrocarbons form complexes with the π-electrons.

It is remarkable that these donors form more stable complexes with the silver(I)-TTA chelate in chloroform than with the silver(I) ion in aqueous solutions. In the chloroform phase, the silver(I) in the TTA chelate is probably combined with the TTA anion through the lone-pair electrons on the two oxygens in the anion. At the same time, it is possible that both the complex and the ligand in the chloroform phase are combined with some molecules of water. In an aqueous solution, the silver(I) ion is probably hydrated with several water molecules; the ligands may also interact with some water molecules. The complex formation and the interaction of the silver atom and of the ligand with other molecules probably interfere with the formation of the molecular complexes to some extent. The stability constants are affected by many factors; thus, it seems to be very difficult to estimate the contributions of the interactions of TTA or of water molecules on the silver(I) or on the ligands. However, since the stability constants of the molecular complexes in the chloroform phase are much higher, even though the silver(I) is coordinated with TTA, the effect of the interactions with water molecules is probably very large.

In the present study, chloroform was employed as the organic solvent. However, as has been pointed out on the basis of various pieces of evidence, this solvent interacts with these molecular complex-forming ligands and probably also with the silver(I)-TTA chelate more strongly than do many other inert solvents, such as saturated hydrocarbons or carbon tetrachloride, and the stabilities of various molecular complexes in this solvent are usually lower than in the above other inert solvents. For example, in the adduct formation of various metal chelates with organophilic neutral ligands in solvent extraction systems, the stabilities of the molecular complexes are larger in carbon tetrachloride than in chloroform.[14]) Thus, the stabilities of the molecular complexes studied in the present paper may also be larger in other nonpolar solvents. It has also been reported that the stability of the molecular complexes of Ag^+ with alkenes is much lower in ethylene glycol than in water.[2]) This can not be compared with the present results, however, because this alcohol may also interact with the silver(I) and with the donors.

It may be reasonable to assume that the length of the hydrocarbon chain does not have any significant effect on the stabilities of the molecular complexes with the 1-alkenes, as can be seen in the cases of many ther chemical properties. At the same time, it may also be reasonable to assume that the stabilities of the molecular complexes increase in the order of the increase in the density of the π-electrons in the aromatic ring; a similar order of the stabilities was pointed out among the complexes between Ag^+ and substituted benzenes in an equivalent molar mixture of water and methyl alcohol.[15]) There seems to be no reasonable explanation of why this tendency of the stability of the molecular complexes does not appear in the complexes of Ag^+ with the same ligands in water (*cf.* Table 2).

The molecular complexes of various metal chelates, especially of TTA chelates, with these three n-donors have been determined from the enhancement of the metal-chelate extraction in solvent extraction systems, which is called "synergism".[14]) It is known that TOPO forms more stable adducts than does TBP. However, it was found that quinoline forms a less stable adduct with europium(III)-TTA chelates in chloroform than does TOPO or TBP;[16]) this seems to indicate that the stability order of adducts with ligands coordinating through an oxygen atom and through a nitrogen atom can be different when the central metal ion is different.

Carboxylic acids are said to form no chelate type complexes with various metal ions. Thus, the interaction

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14) T. V. Healy, "Solvent Extraction Research" ed. by A. S. Kertes and Y. Marcus, Wiley-Interscience, New York (1969) p. 257.

15) N. Ogimachi, L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **78**, 2210 (1956).

16) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **29**, 1475 (1967).

17) T. Sekine, Y. Hasegawa, and N. Ihara, *ibid.*, in press.

of silver(I) with the caproate anion should be weaker than in a complex with the TTA anion. This difference in the nature of the bond between silver(I) and the adjacent anion may cause a difference in the stability of the molecular complex of silver(I) with the donors studied in this work. However, since only the formation of molecular complexes with quinoline,[12)] and that of cyclohexene, 1-hexene, and TOPO complexes with silver(I) caproate, have been studied, no final conclusion can be drawn with regard to this interesting problem; further information is necessary in order to make a detailed discussion.

The synergism due to the molecular complex formation has been studied in many metal chelate extraction systems by using various n-donors. It is very remarkable that the silver(I)-TTA chelate shows a synergism with both n-donors and π-donors. Such molecular complexes of silver(I) with π-donors can be used for some analytical purpose. For example, although the extraction of silver(I) with β-diketones in an inert solvent is usually poor,[13)] the addition of 1×10^{-3} M quinoline makes the extraction quantitative, as may be seen from Fig. 1. When aromatic solvents such as benzene are used as the diluents of TTA, silver(I) can also be extracted nearly quantitatively (more than 90%).

The chelate extraction of silver(I) has often been carried out with dithizone or oxine. The dithizone extraction is excellent and is favorable for the colorimetry of silver, but it is interferred by many ions. The oxine extraction, on the other hand, is comparable with the present TTA extraction into, for example, benzene.[13)] However, the oxine extraction is not very specific. The metal extraction with TTA is also not very specific. However, since only a few metal ions form π-complexes with aromatic hydrocarbons, the synergism of TTA extraction with aromatic hydrocarbons may occur in only a few cases. Thus, when a sample solution containing various metal ions is pretreated by extraction with TTA in chloroform ($[A^-]<10^{-2}$ M), only silver(I) and a small number of metal ions may remain in the aqueous phase; thus, when the solution is shaken twice with benzene or toluene containing 0.1 M TTA (and $[A^-]\simeq10^{-2}$ M), only silver(I) will be extracted from the residue in the aqueous phase, while the other metal ions, such as alkaline earths, will remain in the aqueous phase. Such an extraction method seems to be quite favorable for the separation of silver(I) from among many other metal ions.