

## EXTRACTION BEHAVIOR OF SILVER( I ) WITH THENOYLTRIFLUOROACETONE AND A THIA-CROWNETHER

Susumu OGAWA<sup>\*1</sup>, Naoki HIRAYAMA<sup>†</sup>, Takaharu HONJO<sup>\*1</sup>, and Kenji CHAYAMA<sup>‡2</sup>

<sup>\*1</sup>Graduate School of Natural Science & Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

<sup>‡2</sup>Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada-ku, Kobe 658-8501, Japan

The extractability of Ag(I) with TTA in benzene was enhanced in the presence of HTCO. The extraction equilibrium was reached within 5 min. It was found that Ag(I) is extracted as the ion-pair complex, Ag(I) (HTCO) TTA. From the slope analysis, it was estimated that the Ag(I) species was oxidized to Ag(II) as an ion-pair complex, Ag(II) (HTCO) (TTA)<sub>2</sub>. The presence of  $\pi$  electrons or chlorine atoms in diluent molecules such as benzene, toluene, monochlorobenzene, and chloroform, may affect the oxidation of Ag(I) during the extraction.

### 1. Introduction

A thiacrownether, 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO), having sulfur atoms in place of all the oxygen atoms of a crown ether, 18-crown-6 (18C6), may be used in the ion-pair extraction of heavy metal ions of soft bases such as Cu(I), Pd(II), Ag(I), Cd(II), and Pt(II) [1, 2]. Traces of Ag(I) can be separated by using dicyclohexano-18-crown-6 (DC18C6) based on the formation of an extractable ion-pair product in hydrochloric acid media containing potassium thiocyanate [3].

In the present work, some factors affecting the chelate extraction behavior of Ag(I) using thenoyltrifluoroacetone (TTA), TTA-18C6, and TTA-HTCO systems have been investigated.

## 2. Experimental

### 2.1 Apparatus

A Hitachi model Z-6100 polarized Zeeman atomic absorption spectrophotometer was used for the determination of Ag(I). The phases were mixed by shaking using a Taiyo model SR-II reciprocating shaker. A Tomy Seiko model CD-50R swing type centrifuge was used for the phase separation. The pH measurements were performed with a Hitachi-Horiba model F-12 pH meter.

### 2.2 Materials

A standard stock solution (1000 ppm) of Ag(I) was purchased from Kanto Chemical Co. Ltd.. Deionized distilled water (DDW) was prepared with a Barnstead Nano-pure apparatus, and was used in all experiments. Buffer solutions were prepared by dissolving a weighed quantity of lithium acetate ( $\text{CH}_3\text{COOLi}$ , Katayama Chemical Co. Ltd.), 2-morpholinoethanesulfonic acid (MES, Dojindo Co. Ltd.), 3-morpholinopropanesulfonic acid (MOPS, Dojindo Co. Ltd.) in DDW, and by dilution to an appropriate volume. The ionic strength reagent used was mainly lithium nitrate ( $\text{LiNO}_3$ , Katayama Chemical Co. Ltd.), although nitrates of other alkali metals were also used.

Nitric acid (Kanto Chemical Co. Ltd.) and/or a solution of lithium hydroxide ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ) were used for pH adjustment. 1,4,7,10,13,16-Hexathia-cyclooctadecane (HTCO), synthesized according to the method by Black and McLean[4], was used. 18-crown-6 (18C6) was purchased from Merck Co. Ltd.. Thenoyltrifluoroacetone (TTA) was purchased from Dojindo Co. Ltd.. All chemicals and solvents were of analytical or guaranteed reagent grade, and were used without further purification.

### 2.3 Procedures

An aqueous solution (10 ml) containing  $10^{-5}$  M Ag(I) and 0.01M  $\text{CH}_3\text{COOLi}$ , MES and MOPS, as buffer solutions, was placed in a centrifuge tube (50 ml) having a ground-glass stopper. The ionic strength was adjusted to 0.1 with alkali metal nitrates ( $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$ ). The aqueous solution was shaken mechanically with the same volume (10 ml) of an organic solvent containing  $10^{-1}$  M TTA,  $10^{-1}$  M TTA- $5 \times 10^{-4}$  M 18C6, and  $10^{-1}$  M TTA- $5 \times 10^{-4}$  M HTCO in benzene for 20 min at room temperature ( $25 \pm 2$  °C), respectively. Both phases were separated by centrifugation at 2,000 rpm for 5 min. The pH of the aqueous phase was measured again by means of a pH meter, and the obtained values were used as the pH at

extraction equilibrium. Then 7 ml of the organic phase after extraction was shaken with 7 ml of 0.1 M nitric acid for 10 min, and then centrifuged. The concentrations of Ag(I) in the aqueous phase after extraction and back extraction were measured by flame atomic absorption spectrometry at 338.3 nm .

### 3. Results and Discussion

#### 3.1 Effect of Shaking time

In order to ascertain the shaking time required to reach equilibrium in the extraction of Ag(I), the extractability of Ag(I) with TTA and/or TTA-HTCO in benzene was determined for various shaking times (15 s ~ 30 min) at fixed pH conditions (at pH 5.5 and 6.5 for the Ag-TTA systems, 5.5 and 5.9 for the Ag-TTA-HTCO systems). It was found that extraction equilibrium for Ag(I) was reached within 5 min.

#### 3.2 Influence of buffer reagents

Buffer solutions such as  $\text{CH}_3\text{COOLi}$ , MES, and MOPS did not affect the extraction of Ag(I). By contrast, TAPS,  $\text{Na}_2\text{B}_4\text{O}_7$ , and EPPS interfered with the extraction of Ag(I) at  $\text{pH} > 7$ . Therefore, the study was carried out at  $\text{pH} < 7$ .

#### 3.3 Effect of ionic strength reagents

The effect of ionic strength reagents such as  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$  on the extraction of Ag(I) in the TTA-HTCO-benzene system was investigated. The results of  $\log D$  vs,  $\Delta \text{pH}$  ( $\text{pH}$  shift) plots are shown in Fig 1.

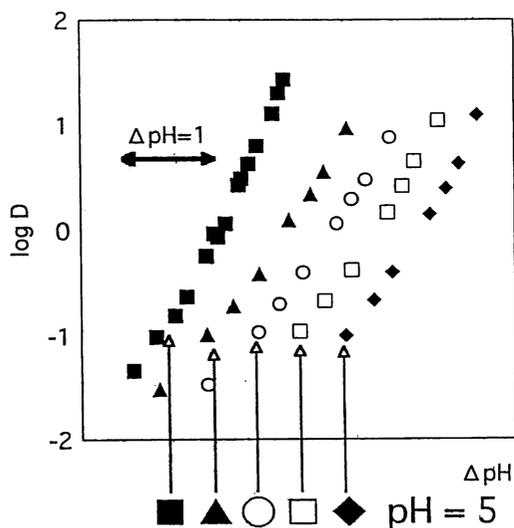


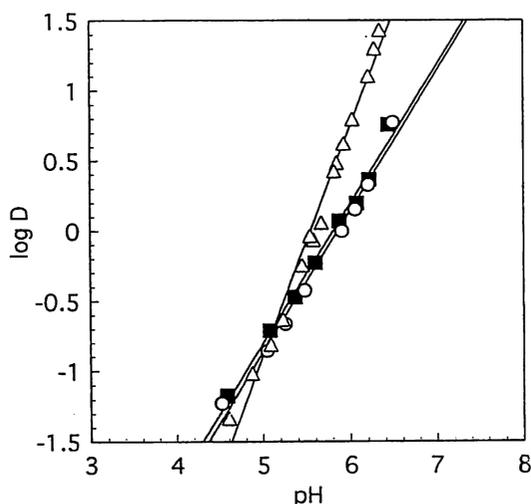
Fig. 1 Effect of ionic strength reagent in the Ag-TTA-HTCO-benzene system

■ :  $\text{LiNO}_3$ , ▲ :  $\text{NaNO}_3$ , ○ :  $\text{KNO}_3$ , □ :  $\text{RbNO}_3$ , ◆ :  $\text{CsNO}_3$

It was found that all nitrates except for  $\text{LiNO}_3$  lowered the extractability of  $\text{Ag(I)}$ . This result shows that the host-guest interaction between HTCO and an alkali metal ion influences the extraction of  $\text{Ag(I)}$ . Judging from the cavity radius of HTCO (0.16 nm) [5], and the ionic radii of alkali metals [6], such as Li (0.076 nm), Na (0.102 nm), K (0.138 nm), Rb (0.152 nm), and Cs (0.167 nm), Li is too small to interact moderately with HTCO. However, the other alkali metal ions fit and interact with HTCO. Therefore,  $\text{LiNO}_3$  was used as the ionic strength reagent in subsequent extraction tests.

#### 4.4 Extraction behavior of the $\text{Ag-TTA}$ complex with or without crown ethers

Extraction studies for  $\text{Ag(I)}$  with the TTA, TTA-18C6, and TTA-HTCO-benzene systems were carried out. The plots of  $\log D$  vs. pH are shown in Fig 2.



**Fig. 2** Plots of  $\log D$  vs. pH for the  $\text{Ag(I)-TTA}$ , TTA-18C6, and TTA-HTCO-benzene systems

■: TTA, ○: TTA-18C6, △: TTA-HTCO

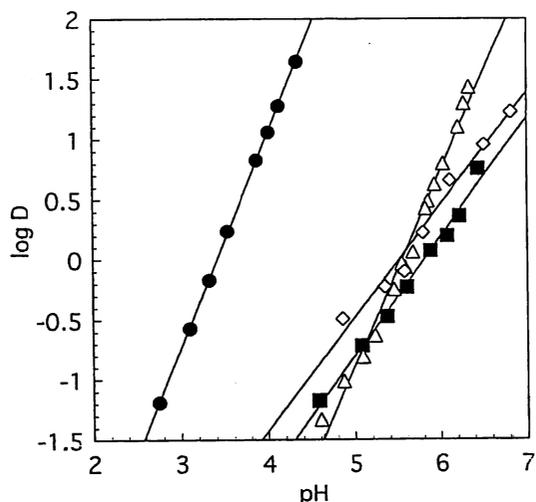
The extraction behavior of  $\text{Ag(I)}$  in the TTA-18C6-benzene system was almost the same as that for the TTA system alone. In other words, 18C6 does not form an adduct with the  $\text{Ag(TTA)}$  complex. Furthermore, the complex formation constant of  $\text{Ag(I)}$  with 18C6 in water is  $10^{1.50}$  [7]. Therefore, it is obvious that 18C6 does not form a host-guest complex with  $\text{Ag(I)}$  in the aqueous phase. On the contrary, the complex formation constant of  $\text{Ag(I)}$  with HTCO in water was reported previously as

more than  $10^8$  [8]. Therefore, Ag(I) in the aqueous phase is completely changed to the Ag-HTCO host-guest complex, and it was considered that Ag(I) is extracted into the organic phase as the ion-pair complex, Ag(I) (HTCO) TTA. The slopes of log D vs. pH plots of the Ag(I) in Fig. 2 were 0.99 and 1.00 for TTA and TTA-18C6, respectively. It was found that one proton is released during the extraction of Ag(I) in the TTA and the TTA-18C6-benzene systems. On the contrary, the slope of the log D vs. pH plot for Ag(I) in the TTA-HTCO-benzene system was 1.63, and it was assumed that more than one proton is released. This result is abnormal, because the release of only one proton is needed for the formation of an uncharged species between Ag(I) and TTA.

### 3.5 Some aspects of the composition of the Ag(I) extracted species

Extraction behavior in the Ag-TTA, the Ag-TTA-HTCO, the Cu(I)-TTA-HTCO-benzene, and the Cu(II)-TTA-HTCO-benzene systems was compared. The plots of log D vs. pH are shown in Fig. 3. From these results, the plots in the Ag-TTA and the Ag-TTA-HTCO-benzene systems were almost parallel to those in Cu(I)-TTA-HTCO-benzene, and Cu(II)-TTA-HTCO-benzene systems, respectively.

Therefore, it was considered that, with HTCO, Ag(I) was extracted with the release of two protons. The slope of the plots of log D vs. log [TTA]<sub>o</sub> for Ag(I) with the TTA and the TTA-HTCO-benzene systems was unity and two, respectively.



**Fig. 3** Comparison of the Ag(I)-TTA and the Ag(I)-TTA-HTCO, the Cu(I)-TTA-HTCO, and the Cu(II)-TTA-HTCO extraction systems

■: Ag-TTA, △: Ag-TTA-HTCO, ◇: Cu(I)-TTA-HTCO, ●: Cu(II)-TTA-HTCO

It was assumed that two TTA molecules react with Ag(I) in the

TTA-HTCO-benzene system. From these results, the extracted Ag(I) species in the TTA-HTCO-benzene system is concluded to be either the ion-pair complex,  $M\text{Ag(I)}(\text{HTCO})(\text{TTA})_2$  or  $\text{Ag(II)}(\text{HTCO})(\text{TTA})_2$ , where M is a monovalent cation. In the former case, the extractability of the species must depend on the strength of hydration of M(I). However, the highest extractability of the species was observed for  $M(\text{I}) = \text{Li}$ , which has a relatively high hydration number. Therefore, the former conclusion seems to be untenable. As mentioned above, complex formation between Ag(I) and HTCO is strong. Furthermore, it has been reported previously that Ag(I) (HTCO) is often oxidized to Ag(II) (HTCO) under certain oxidative conditions[9, 10]. From these facts, it was concluded that formation of the complex,  $\text{Ag(II)}(\text{HTCO})(\text{TTA})_2$  occurred in the extraction of Ag(I) in the presence of HTCO. The extraction and back extraction of Ag in the Ag-TTA-HTCO-benzene system were also ascertained to be reversible

### 3.6 Effect of the organic diluents

To evaluate the effect of the organic diluent on the extraction of Ag(I), the extraction behavior of Ag(I) into several types of diluents such as benzene, 4-methyl-2-pentanone (MIBK), toluene, 1-octanol, monochlorobenzene, and chloroform, was studied. The plots of log D vs. pH for these extraction systems are shown in Fig. 4.

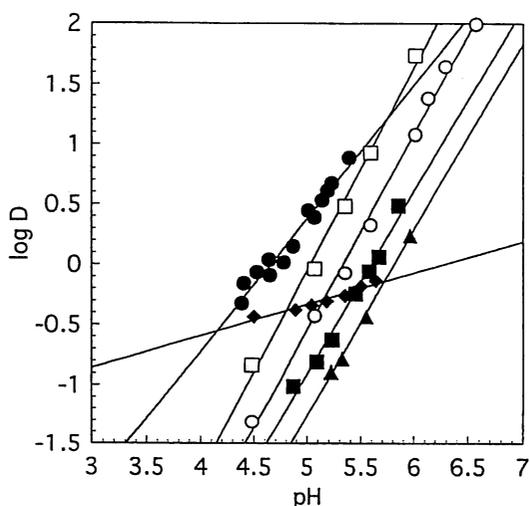


Fig. 4. Effect of the organic diluent in the Ag(I)-TTA-HTCO system

■: benzene, ●: MIBK, ▲: toluene, ◆: 1-octanol,  
□: monochlorobenzene, ○: chloroform

The extraction behavior of Ag(I) into toluene, monochlorobenzene, and chloroform was similar to that for benzene. In other words, the use of these diluents also may cause the abnormal Ag(I) extraction behavior. On the contrary, the slope in MIBK was nearly unity. This result shows that Ag(I) is extracted into MIBK as Ag(I) (HTCO) (TTA) without oxidation. In addition, the slope in 1-octanol was far less than unity. However, the reason of this phenomenon is unknown at present. From these results, it was estimated that the presence of  $\pi$ -electrons and chloride atoms in the diluent molecules may affect the oxidation of Ag(I) in the TTA-HTCO extraction system.

#### 4. Conclusion

When Ag(I) was extracted with TTA in the presence of HTCO in benzene, the buffer solutions ( $\text{CH}_3\text{COOLi}$ , MES, MOPS, TAPS,  $\text{Na}_2\text{B}_4\text{O}_7$ , and EPPS) at  $\text{pH} < 7$ , and the ionic strength reagent ( $\text{LiNO}_3$ ) did not affect the extraction of Ag(I). It was found that Ag(I) is extracted as the ion-pair complex, Ag(I) (HTCO) TTA within 5 min. It was shown that Ag(I) is oxidized to Ag(II) as an ion-pair complex, Ag(II) (HTCO) (TTA)<sub>2</sub> in diluents having  $\pi$ -electrons or chlorine atoms in the diluent molecules during extraction.

#### References

- 1) K. Chayama, M. Fujimoto and E. Sekido, *Mem. Konan. Univ. Sci. Ser.*, **1994**, 25.
- 2) T. Honjo, *Bunseki, "Solvent Extraction: Crown Ether"*, **1997**, 127.
- 3) C.T. Camagong and T. Honjo, *Anal. Bioanal. Chem.*, **373**, 856 (2002).
- 4) D. St. C. Black and I. A. McLean, *Tetrahedron Lett.*, **1969**, 3961.
- 5) T. Igarashi and M. Suzuki, *Kanagawa Daigaku Kenkyu Hokoku*, **21**, 30 (1983).
- 6) T. Inui, A. Nakahara, O. Yamauchi and Y. Yoshikawa, *Kaitei Kagaku*, **1981**, 178.
- 7) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7620 (1976).
- 8) K. B. Yatsimirskii, A. Yu. Nazarenko, V. V. Pavllshchuk and P. E. Strizhak, *Dokl. Akad. Nauk. Ukr. SSR. Ser. B.*, **1988**, 60.
- 9) A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, G. Reid, A. Taylor and M. Schroder, *Polyhedron*, **8**, 513 (1989).
- 10) A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, G. Reid, A. Taylor and M. Schroder, in A. J. L. Pombeiro and J. A. McCleverty, *"Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds"*, Klumer, Amsterdam, **1993**, 121.