EXTRACTION EQUILIBRIUM OF SILVER(I) WITH TRIISOBUTYLPHOSPHINE SULFIDE FROM NITRATE MEDIA

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Measurement of the extraction equilibrium of silver(I) from nitric acid and aqueous ammonium nitrate solutions with triisobutylphosphine sulfide (TBPS) in toluene was carried out at 303 K to examine the effects of the concentrations of nitrate and hydrogen ions and silver in the aqueous phase as well as that of the extractant. It was found that the extraction equilibrium is explained in terms of the solvation of silver(I) by TBPS with simultaneous transfer of a nitrate ion into the organic phase to form an ion-pair and that the extracted species in the organic phase is the sliver : TBPS 1 : 2 complex.

Introduction

Organophosphorus compounds containing the phosphoryl group ($\geqslant P=O$), such as tributylphosphate (TBP) and trioctylphosphine oxide (TOPO) have been extensively used as extractants for various metals and acids on both analytical and commercial scale. However, the sulfur analogues of these compounds have received only a little attention;[1-3,5,7,9] it has not been well examined what changes are brought about in the extraction properties of organophosphorus compounds by the replacement of phosphoryl group with thiophosphoryl group as the donating group.

Recently, American Cyanamid Co. developed a new commercial extractant, CYANEX 471, the active species of which is triisobutylphosphine sulfide,[6] as a selective extractant for silver(I) and palladium(II).[10]

In the present study, the authors investigated the extraction equilibrium of silver(I) with triisobutylphosphine sulfide (TBPS), from nitric acid and aqueous ammonium nitrate solutions as a part of a series of investigations of the solvent extraction of noble metals with sulfur-containing extractants.

1. Experimental

1.1 Reagents

CYANEX 471 extractant as delivered from American Cyanamid Co. is a white crystalline solid with molecular weight 234. TBPS was purified from CYANEX 471 by recrystallization from water–ethanol. The purified reagent was confirmed by element analysis as follows.

	C	H
Found (%)	61.34	11.48
Calculated (%)	61.49	11.61

Organic phase was prepared by diluting TBPS with toluene on a gravimetric basis. The aqueous silver(I) solution was prepared by dissolving silver nitrate into nitric acid or aqueous ammonium nitrate solutions. In experiments to examine the effect of the nitrate ion concentration, pH of the aqueous ammonium nitrate solution was kept constant at pH = 5 by addition of a small amount of aqueous sodium hydroxide solution. In addition, the initial silver concentration was kept constant at 1×10^{-3} mol/dm^3 in all experiments except in that to examine the effect of silver concentration. All chemicals used were of analytical reagent grade.

1.2 Extraction and analytical procedures

Equal volumes (1.5×10^{-2} dm^3) of the organic and aqueous phases were shaken for 30 minutes in a 0.1-dm^3 stoppered glass flask in a thermostat-bath maintained at 303 K. It was confirmed that equilibrium was attained within 30 minutes in the preliminary experiments.

After equilibration, the two phases were separated and the silver content in the aqueous phase was determined by atomic absorption spectrochemical analysis using a Nippon Jarrell-Ash model AA-782 spectrophotometer. That in the organic phase was calculated from the difference between the initial and equilibrium concentrations of silver in the aqueous phase.

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2. Results and Discussion

Stoichiometric relation of the extraction of monovalent metals such as Ag(I) from nitrate media by a neutral coordinating ligand such as TBPS ($=\bar{S}$) is described as follows.

$$Ag^+ + NO_3^- + n\bar{S} \rightleftharpoons \overline{AgS_nNO_3} \quad K_e \qquad (1)$$

where the silver ion is coordinately solvated by TBPS through a sulfur atom, the donating atom, and is paired with a nitrate ion in the organic phase as in the cases of extraction with oxygen-containing neutral solvating extractants such as TBP and TOPO. The equilibrium constant of the above extraction reaction, K_e, is written as follows.

$$K_e = \frac{[\overline{AgS_nNO_3}]}{[Ag^+][NO_3^-][\bar{S}]^n} \qquad (2)$$

In the regions of low concentration of nitrate ion and low pH, the concentration of free silver ion ($[Ag^+]$) in Eq. (2) can be approximated by the total concentration of silver in the aqueous phase (C_{Agw}), because the formation of an ion-pair $Ag^+NO_3^-$ and ammine complexes, $Ag(NH_3)_i^+$, can be ignored and, in addition, the concentration of the unreacted extractant, $[\bar{S}]$, is approximated to its initial concentration (C_{B0}). From Eq. (2), the logarithm of the distribution ratio, D, is expressed by Eq. (3) in this region.

$$\log D = \log[NO_3^-] + n \log C_{B0} + \log K_e$$
$$= \log[NO_3^-] + a \qquad (3)$$

where

$$a = n \log C_{B0} + \log K_e \qquad (4)$$

Figure 1 shows the plots of the experimental results based on Eq. (3). Straight lines of slope 1 were obtained for both media in the low concentration range of nitrate ion. The values of a defined by Eq. (4) were evaluated from the intercepts of these straight lines with the ordinate for each value of C_{B0} and were plotted against $\log C_{B0}$ as shown in **Fig. 2**. Obviously, the plotted points lie on a straight line of slope 2, which suggests that $n=2$ in Eq. (4). Therefore, the stoichiometric relation of this extraction reaction is expressed as follows.

$$Ag^+ + NO_3^- + 2\bar{S} \rightleftharpoons \overline{AgS_2NO_3} \quad K_e \qquad (5)$$

The extraction equilibrium constant, K_e, was evaluated from the value of the intercept of the straight line with the ordinate as $K_e = 7.08 \times 10^6$ $(dm^3/mol)^3$ for both media.

However, in the higher-concentration region of nitrate ion, the distribution ratios for both media deviate downward from the straight lines with increasing concentration of nitrate ion. Furthermore,

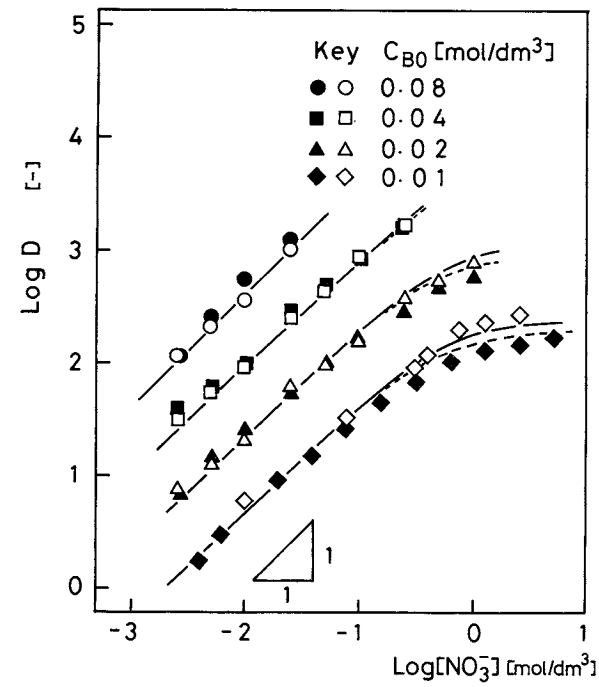

Fig. 1. Equilibrium distribution of silver(I) from nitrate media with TBPS in toluene.
Keys: open, nitric acid; filled, ammonium nitrate.

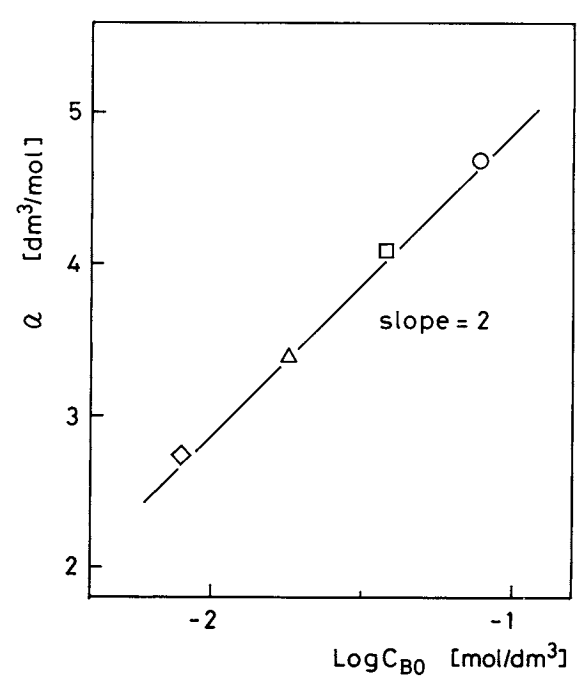

Fig. 2. Relation between a and $\log C_{B0}$.

those from aqueous ammonium nitrate solution are slightly lower than those from nitric acid solution. This is considered to be due to the formations of an ion-pair, $Ag^+NO_3^-$, and silver–ammine complexes, $Ag(NH_3)_i^+$, in the aqueous phase, which are unlikely to be extracted by TBPS, and also to the decrease in concentration of the free extractant.

In the case of extraction from nitric acid, the ion-pair formation of silver cation with nitrate ion is

described as follows.

$$Ag^+ + NO_3^- \rightleftharpoons Ag^+NO_3^- \quad K_1 \tag{6}$$

where $K_1 = 1.82\,dm^3/mol$.[8)]
Therefore, the concentration of free silver ion ($[Ag^+]$) is expressed as follows.

$$[Ag^+] = \frac{C_{Agw}}{1 + K_1[NO_3^-]} = \alpha_1 C_{Agw} \tag{7}$$

where

$$\alpha_1 = 1/(1 + K_1[NO_3^-]) \tag{8}$$

Further, the total concentration of the extractant in the organic phase (C_{B0}) and the initial concentration of silver in the aqueous phase (C_{Ag0}) are expressed as follows, respectively.

$$C_{B0} = [\bar{S}] + 2[\overline{AgS_2NO_3}] \tag{9}$$

$$C_{Ag0} = C_{Agw} + [\overline{AgS_2NO_3}] \tag{10}$$

Combination of Eqs. (2), (7) and (10) gives

$$C_{Agw} = C_{Ag0}/(1 + \gamma[\bar{S}]^2) \tag{11}$$

where

$$\gamma = K_e \alpha_1 [NO_3^-] \tag{12}$$

The mass balance equation of the extractant in the organic phase expressed by Eq. (9) is reduced to a cubic equation with respect to the concentration of unreacted extractant ($[\bar{S}]$), as is expressed by Eq. (13) using Eqs. (11) and (12).

$$\gamma[\bar{S}]^3 + (2\gamma C_{Ag0} - \gamma C_{B0})[\bar{S}]^2 + [\bar{S}] - C_{B0} = 0 \tag{13}$$

The distribution ratio is given by

$$D = \frac{[\overline{AgS_2NO_3}]}{C_{Agw}} = \frac{C_{Ag0}}{C_{Agw}} - 1 = \gamma[\bar{S}]^2 \tag{14}$$

The solid line in Fig. 1 is the calculated result from Eqs. (13) and (14) for the extraction from nitric acid.

Figure 3 shows the effect of silver concentration in the aqueous phase for the various concentrations of TBPS on its distribution ratio in the extraction from nitric acid. The solid lines in Fig. 3 represent the calculated curves obtained from Eqs. (13) and (14). The calculated curves are in good agreement with the experimental results. Since the plotted points in Fig. 3 cover the region where the ratio, $C_{B0}/[\overline{Ag}]$, ranges from 80 ($C_{B0} = 0.08$ mol/dm^3) up to 2.2 ($C_{B0} = 0.01$ mol/dm^3), the equilibrium relation between the two phases can be satisfactorily interpreted by the extraction reaction expressed by Eq. (5) in this region.

On the other hand, in the case of extraction from aqueous ammonium nitrate media, it is further necessary to take account of the formation of silver–ammine complexes, described as follows.

$$Ag^+ + iNH_3 \qquad Ag(NH_3)_i^+ \quad \beta_i \ (i = 1\text{–}2) \tag{15}$$

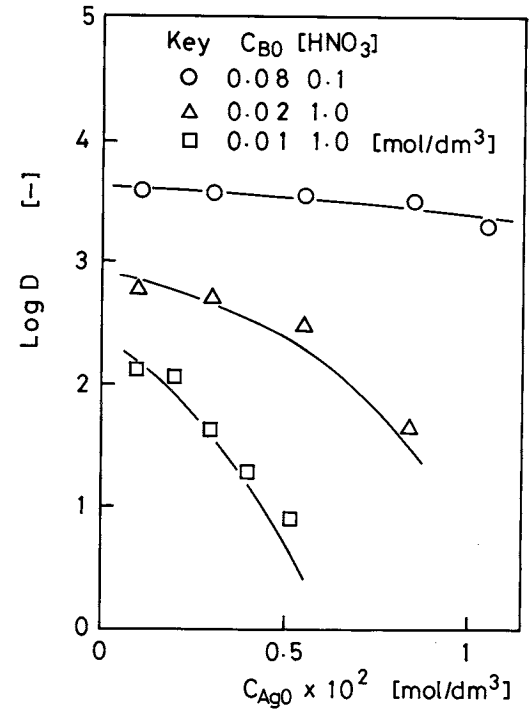

Fig. 3. Effect of initial concentration of silver(I) in aqueous phase on distribution ratio of silver(I).

where β_i denotes the stability constant of the ammine complexes; these values are $\beta_1 = 2.51 \times 10^3$ dm^3/mol and $\beta_2 = 2.51 \times 10^7$ (dm^3/mol)^2.[8)] Taking account of Eqs. (6) and (15), the concentration of free silver cation can be expressed as follows.

$$[Ag^+] = \frac{C_{Agw}}{1 + \sum_{i=1}^{2} \beta_i [NH_3]^i + K_1[NO_3^-]} \tag{16}$$

In addition, the concentration of free ammonia is related to that of ammonium ion through the equilibrium relation described as follows.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad K_A \tag{17}$$

where $K_A = 5.5 \times 10^{-10}$ mol/dm^3.[4)] The concentration of ammonium ion under the present experimental conditions, where the concentration of silver is much less than that of ammonium ion, can be approximated as

$$[NH_4^+] \simeq [NO_3^-] \tag{18}$$

Consequently, Eq. (16) is reduced to Eq. (19), taking account of Eqs. (17) and (18).

$$[Ag^+] = \frac{C_{Agw}}{1 + \sum_{i=1}^{2} \beta'_i/[H^+]^i + K_1[NO_3^-]} = \alpha_2 C_{Agw} \tag{19}$$

where

$$\beta'_i = \beta_i (K_A[NO_3^-])^i \tag{20}$$

$$\alpha_2 = 1 \Big/ \left(1 + \sum_{i=1}^{2} \beta_i'/[H^+]^i + K_1[NO_3^-]\right) \quad (21)$$

The broken line in Fig. 1 is the result for the extraction from ammonium nitrate media calculated in a manner similar to that from nitric acid media using Eq. (19) instead of using Eq. (7).

Further, **Fig. 4** shows the dependency of pH on the distribution ratio. It is evident that the distribution ratio is independent of pH in the region pH < 5, while it decreases with increasing pH in the high pH region, which can be attributed to the formation of silver-ammine complexes. The solid line in Fig. 4 represents the calculated result in the same manner mentioned above. The calculated curve is in good agreement with the experimental results.

Conclusion

The extraction equilibrium of silver(I) from nitric acid and aqueous ammonium nitrate solutions with TBPS in toluene was studied at 303 K. It is concluded that silver(I) is extracted according to the following extraction reaction.

$$Ag^+ + NO_3^- + 2\bar{S} \rightleftharpoons \overline{AgS_2NO_3} \quad K_e$$

This equation can satisfactorily interpret the experimental results over the range where the ratio, $C_{B0}/[\overline{Ag}]$, ranges from 80 up to 2.2. The extraction equilibrium constant, K_e, was evaluated as $K_e = 7.08 \times 10^6$ $(dm^3/mol)^3$.

Acknowledgment

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Nomenclature

C_{Ag0}	= initial concentration of silver in aqueous phase	[mol/dm^3]
C_{Agw}	= total concentration of silver in aqueous phase	[mol/dm^3]
C_{B0}	= initial concentration of triisobutylphosphine sulfide	[mol/dm^3]
D	= ratio of equilibrium concentration of silver in organic phase to that in aqueous phase	[—]
K_A	= dissociation constant of ammonium ion	[mol/dm^3]
K_e	= equilibrium constant for extraction reaction of silver by triisobutylphosphine sulfide	[(dm^3/mol)^3]

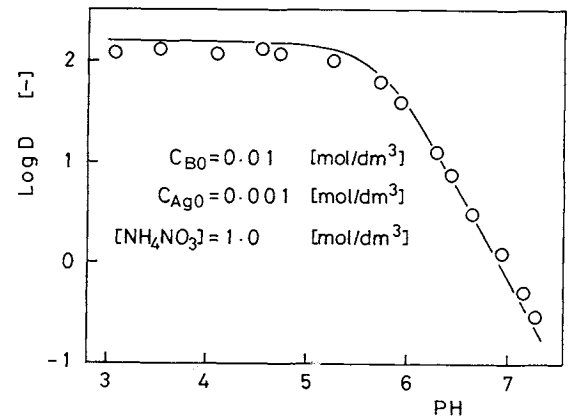

Fig. 4. Effect of hydrogen ion concentration on distribution ratio of silver(I).

K_1	= formation constant of ion-pair defined by Eq. (6)	[dm^3/mol]
n	= number of triisobutylphosphine sulfide molecules solvated to silver cation in organic phase	[—]
S	= species of triisobutylphosphine sulfide	
β_i	= stability constant of i-th ammine complex of silver cation	[(dm^3/mol)^i]
β_i'	= i-th constant defined by Eq. (20)	[(mol/dm^3)^i]
[ ]	= concentration	[mol/dm^3]

⟨Subscript⟩

0	= initial	

⟨Superscript⟩

—	= organic phase	

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