



## Study of Extraction of Silver(I) in Nitric Acid Media by 2-Ethylhexyl Octyl Sulfide

JINFEI LI, YAN LIU and ZHANGJIE HUANG\*

Department of Chemistry, Yunnan University, Kunming 650091, P.R. China

\*Corresponding author: Fax: +86 871 65032180; Tel: +86 871 6688875; E-mail: zhjhuang@ynu.edu.cn

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Extraction performance of Ag(I) was studied using 2-ethylhexyl octyl sulfide as extractant from nitric acid media. Ag(I) transferring was depended on the 2-ethylhexyl octyl sulfide and nitric acid concentration, phase ratio (O/A), contact time and Ag(I) concentration in stock solution. By controlling 2-ethylhexyl octyl sulfide and nitric acid concentration, Ag(I) could be separated effectively from mixing solution containing Pt(IV), Rh(III), Fe(III), Cu(II), Co(II), Zn(II) and Ni(II) impurities when 2-ethylhexyl octyl sulfide and nitrate acid concentration were fixed at 6 % (v/v) and 4 M, respectively. Silver(I) loaded in organic phase was stripped effectively with thiourea solution.

**Keywords:** Silver, Solvent extraction, 2-Ethylhexyl octylsulfide.

### INTRODUCTION

Silver is one of the most useful noble metals, due to its excellent physico-chemical properties. It is widely used in various industries, *e.g.*, jewelry, photography, batteries, electroplating, catalyst, anticorrosive alloys and antimicrobial materials, *etc.*<sup>1-3</sup>. It is estimated that about 12 % of the world's silver resources are used in the production of light-sensitive devices. In the refining of precious metals, silver is either left in the leach residue, or recovered as a precipitate of silver chloride in the initial stage of refining in the majority of current process flowsheets. However, small or even considerable amounts of silver are not completely separated as precipitates from other precious metals which remain dissolved in aqueous solutions. Further treatment is required for the separation and recovery of silver. Various hydrometallurgical processes such as adsorption<sup>4-10</sup>, supported liquid membrane<sup>11-13</sup>, ion exchange<sup>14</sup> and solvent extraction<sup>15,16</sup> are used for the recovery of silver. Solvent extraction has been considered as a most efficient technique for the recovery and separation of silver from aqueous solutions. Various extractants, such as calixarene derivatives<sup>17-21</sup>, open-chain ether and thioether derivatives<sup>22</sup>, crown ether derivatives<sup>23,24</sup>, phosphorus derivatives<sup>25</sup>, pyridine derivatives<sup>26,27</sup>, sulfur-containing extractants<sup>28</sup>, *etc.*, have been suggested to be suitable for silver(I) solvent extraction. However, these methods are not so reliable for routine application because these methods suffer the drawbacks such as low selectivity, high costs, lack of chemical stability, *etc.*<sup>29-31</sup>. Therefore, high selectivity, low costs and more chemically stable extractants are desired from the practical point of view.

In the present work, the solvent extraction of silver(I) from nitric acid media by 2-ethylhexyl octyl sulfide (EHOS) has been investigated. Various parameters affecting the percentage extraction of silver(I), such as the diluting agents, the concentrations of 2-ethylhexyl octyl sulfide, contact time, phase ratio (O/A), initial silver(I) concentration and nitric acid concentration in aqueous phase, were investigated. Thiourea was selected to strip silver(I) from the loaded organic phase. The results showed that almost all of silver (I) (> 99 %) was extracted into the organic phase during extraction and that most of silver(I) (> 98 %) was transferred from the loaded organic phase into the aqueous phase during the stripping process. The proposed method possesses higher selectivity than the reported methods.

### EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan) was used to measure the concentration of Ag(I). The operating conditions were carried out according to the recommendations of manufacturer. The wavelength selected for Ag is 328.1 nm.

**Silver(I) stock solution (10 g L<sup>-1</sup>):** A weighed amount of silver nitrate was dissolved in nitric acid solution (4 mol L<sup>-1</sup>). The solution was transferred into a 250 mL of volumetric flask.

2-Ethylhexyl octyl sulfide (EHOS) was synthesized in our laboratory as literature<sup>32</sup>. The organic phase was prepared by dissolving a weighed amount of 2-ethylhexyl octyl sulfide in kerosene.

**General extraction procedure:** Equal volumes (30 mL) of both phases were mixed and vigorously shaken for 3 min, which was sufficient enough to attain equilibrium in a preliminary experiment. After phase separation, the concentration of Ag(I) in aqueous solution was determined by an atomic absorption photometer. These results were further used to estimate the extraction efficiency of metal. The amount of extracted metal ion was calculated according to the differences in the metal concentrations of the aqueous phase before and after the extraction.

**Influences of the diluents:** In order to choose an appropriate diluting agents for the Ag(I) extraction system, various diluting agents were studied, such as kerosene, methyl benzene, dimethyl benzene, chloroform and benzene. Their experiments were performed as the following parameters were fixed: Initial Ag(I) concentration in the aqueous phase  $500 \text{ mg L}^{-1}$ , organic/aqueous (O/A) phase ratio 1, nitric acid concentration in aqueous solution  $4 \text{ mol L}^{-1}$ , concentration of 2-ethylhexyl octyl sulfide 6 % (v/v) and mixing time 3 min. The results are shown that the solubility for Ag(I)-EHOS adduct decreased in the following order: kerosene > benzene > dimethyl benzene > methyl benzene. Finally, kerosene was selected as the appropriate diluting agents.

## RESULTS AND DISCUSSION

**Influences of the concentration of extractant:** To investigate the effect of 2-ethylhexyl octyl sulfide (EHOS) concentration on the extraction performances of Ag(I), the experiments were performed at the fixed conditions. The results are shown in Fig. 1. As can be seen from Fig. 1, 2-ethylhexyl octyl sulfide dissolved in kerosene with the extractant concentration varying from 2 to 10 % (v/v). The percentage extraction of Ag(I) increased in the range from 43.1 to 99.2 % by increasing 2-ethylhexyl octyl sulfide concentration from 2 to 6 % (v/v). Further increasing 2-ethylhexyl octyl sulfide concentration from 6 to 10 % (v/v), the percentage extraction of Ag(I) only had a slight increase (from 99.2 to 99.4 %). 6 % (v/v) 2-ethylhexyl octyl sulfide was needed for quantitative extraction of Ag(I) from a nitric acid solution containing  $500 \text{ mg L}^{-1}$  silver.

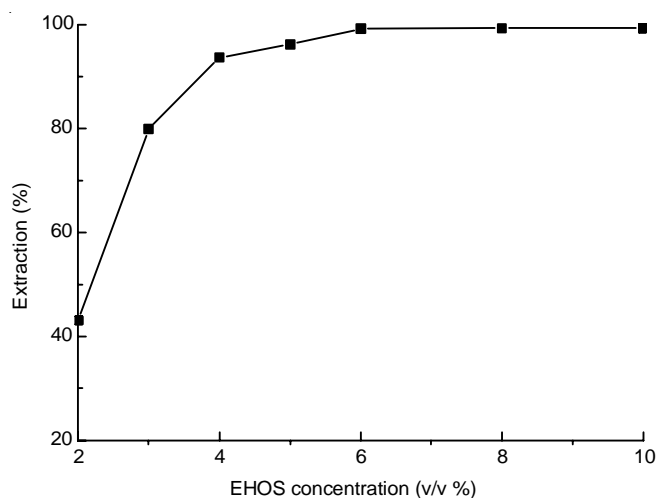


Fig. 1. Effect of extractant concentration on the extraction of Ag(I);  $C_{\text{Ag(I)}}$ :  $500 \text{ mg L}^{-1}$ ,  $C_{\text{HNO}_3}$ :  $4 \text{ mol L}^{-1}$ , O/A: 1.0, contact time: 3 min

**Influences of silver concentration:** The influence of the variation of the initial Ag(I) concentration in the aqueous phase on the extraction has been studied. These tests were carried out with nitric acid concentration in aqueous solution,  $4 \text{ mol L}^{-1}$ ; 2-ethylhexyl octyl sulfide concentration in the organic phase, 6 % (v/v); and mixing time, 3 min. The results are presented in Fig. 2. As can be seen in Fig. 2, with increasing initial Ag(I) concentration from 100 to  $500 \text{ mg L}^{-1}$ , the percentage extraction of Ag(I) merely has a slight decrease (from 99.6 to 99.2 %). Further increasing initial Ag(I) concentration from 500 to  $800 \text{ mg L}^{-1}$ , the percentage extraction of Ag(I) decreases rapidly (from 99.2 to 73.4 %).

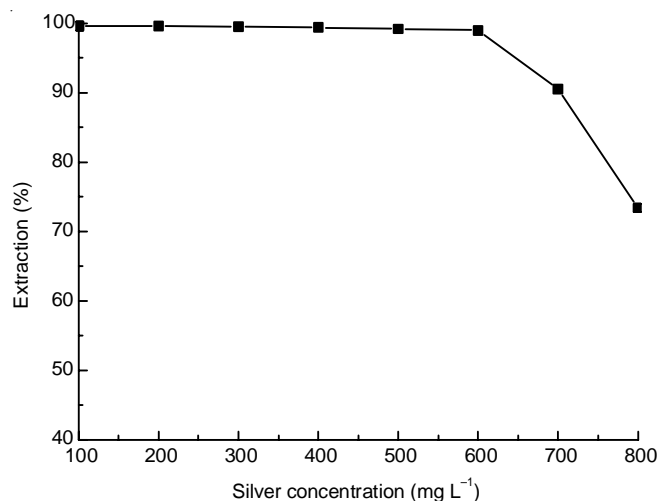


Fig. 2. Effect of silver concentration on the extraction of Ag(I);  $C_{\text{EHOS}}$ : 6 % (v/v), O/A: 1.0, contact time: 3 min,  $C_{\text{HNO}_3}$ :  $4 \text{ mol L}^{-1}$

**Influences of nitric acid concentration:** The effect of nitric acid concentration on the extraction of Ag(I) is shown in Fig. 3. Fig. 3 indicated that the concentration of nitric acid in aqueous phases strongly affects the extraction ability of 2-ethylhexyl octyl sulfide. With increasing concentration of nitric acid in aqueous phases from 0.1 to  $4.0 \text{ mol L}^{-1}$ , the percentage extraction of Ag(I) increased from 24.1 to 99.2 %. By further increasing concentration of nitric acid from 4 to 6, the percentage extraction of Ag(I) kept constant. Therefore,  $4 \text{ mol L}^{-1}$   $\text{HNO}_3$  was adopted in all subsequent experiments.

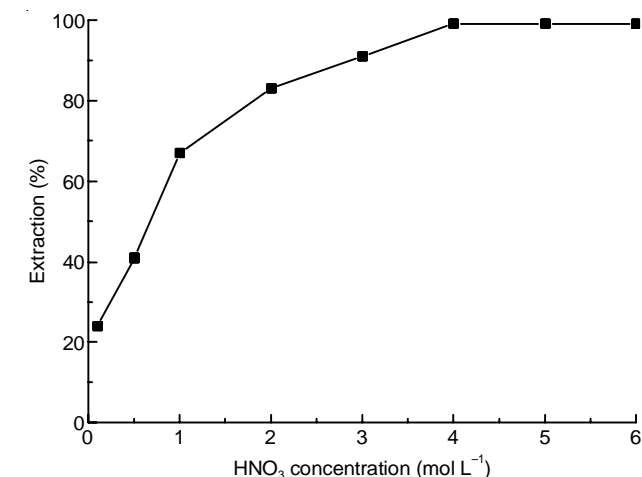


Fig. 3. Effect of  $\text{HNO}_3$  concentration on the extraction of Ag(I);  $C_{\text{Ag(I)}}$ :  $500 \text{ mg L}^{-1}$ ,  $C_{\text{EHOS}}$ : 6 % (v/v), O/A: 1 contact time: 3 min

**Influences of contact time:** To extract Ag(I) efficiently by controlling an optimal contact time of aqueous and organic phases, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 4. Contact time was determined by measuring the metal content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 1 to 5 min. The percentage extraction of Ag(I) increased in the range from 72.5 to 99.2 % by in increased of contact time from 1 to 3 min. Further increasing contact time from 3 to 5 min, the percentage extraction of Ag(I) kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of silver was found to be about 3 min.

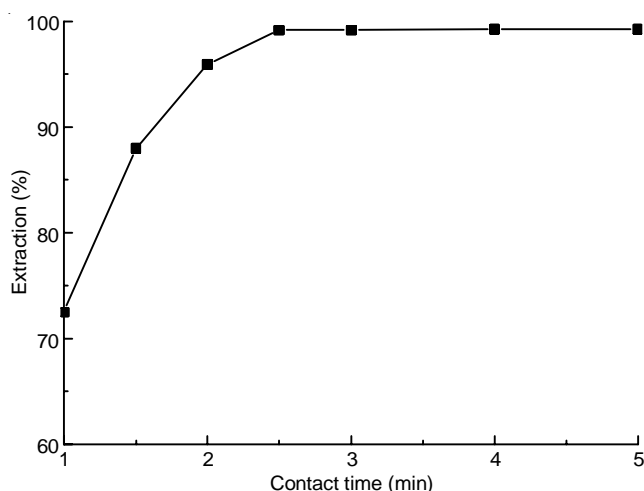


Fig. 4. Effect of contact time on the extraction of Ag(I);  $C_{Ag(I)}$ : 500 mg L<sup>-1</sup>,  $C_{EHOS}$ : 6 % (v/v), O/A: 1,  $C_{HNO_3}$ : 4 mol L<sup>-1</sup>

**Influences of organic/aqueous (O/A) phase ratio:** To obtain optimal O/A for extraction of Ag(I), the following experiments were performed at other fixed extraction parameters. The results are shown in Fig. 5. As can be seen from Fig. 5, by increasing O/A from 0.2 to 1.0, the percentage extraction of Ag(I) increased from 28.5 to 99.2 %. By further increasing O/A from 1.0 to 3, the percentage extraction of

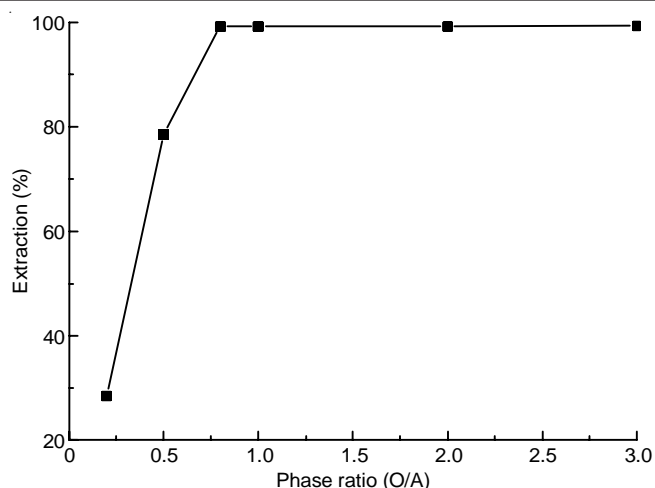


Fig. 5. Effect of phase ratio (O/A) on the extraction of Ag(I);  $C_{Ag(I)}$ : 500 mg L<sup>-1</sup>,  $C_{EHOS}$ : 6 % (v/v), contact time: 3 min,  $C_{HNO_3}$ : 4 mol L<sup>-1</sup>

Ag(I) kept constant. Therefore, Ag(I) can be extracted efficiently by controlling organic/aqueous (O/A) phase ratio, 1.0.

#### Verification of separating Ag(I) from mixed solution:

A synthetic mixing stock solution containing Ag(I), Pt(IV), Rh(III), Fe(III), Cu(II), Co(II), Zn(II) and Ni(II) impurities, was prepared by concocting their solutes in 4 M HNO<sub>3</sub>. The mixed aqueous solution was extracted with 6 % (v/v) 2-ethylhexyl octyl sulfide when the O/A and contact time was controlled as 1 and 3 min, respectively. The experiments showed that the percentage extraction of Ag(I) was more than 99 %, indicating Ag(I) was extracted completely, while Pt(IV), Rh(III), Fe(III), Cu(II), Co(II), Zn(II) and Ni(II) was not extracted basically. In present experimental range, extraction percentages of impurities were lower than 1 %. Based on this process, Ag(I) can be separated efficiently from a mixing solution containing Pt(IV), Rh(III), Fe(III), Cu(II), Co(II), Zn(II) and Ni(II) impurities. The composition of the solution and percentage extractions of metal ions are shown in Table-1.

Table-2 compares the characteristic data of the proposed method with other solvent extraction of silver methods reported in literatures. As can be seen, the proposed method possesses high selectivity than the reported methods.

TABLE-1  
COMPOSITION OF THE MIXED SOLUTION AND PERCENTAGE EXTRACTIONS OF METAL IONS

Metal ion	Ag(I)	Pt(IV)	Rh(III)	Fe(III)	Cu(II)	Zn(II)	Ni(II)	Co(II)
Concentration (mg L <sup>-1</sup> )	500	600	200	450	650	350	250	300
Extraction (%)	99.1	0.8	0.3	0.8	0.6	0.3	0.2	0.7

TABLE-2  
COMPARISON OF THE REPORTED EXTRACTANTS FOR SILVER WITH 2-ETHYLHEXYL OCTYL SULFIDE

Extractants	Media	Selectivity	Ref.
Calix[4]arenethiotetramide	Nitric acid	Heavy metals were co-extracted	17
Homocalixpyridine	Nitric acid	Cu(II) was co-extracted	32
Acyclic tetrathioethers	Picrate	Zn(II), Co(II) Ni(II), Cu(II) were co-extracted	22
Diaza-18-crown-6	Picrate	Zn(II), Co(II) Ni(II), Cu(II) were co-extracted	23
Thiacrown ethers	Picrate	Cu(II) was co-extracted	24
Triphenylphosphine oxide	Nitric acid	Fe(III), Cu(II), Zn(II) were co-extracted	25
1,2-bis(Diphenylphosphinyl)ethane	Nitric acid	Fe(III), Cu(II), Zn(II) were co-extracted	25
Tridentate pyridine	Perchlorate	Zn(II), Co(II) Ni(II), Cu(II) were co-extracted	26
Dithiocarbonate derivatives	Perchlorate	Pt(IV) caused precipitation	28
2-Ethylhexyl octyl sulfide	Nitric acid	Pt(IV), Rh(III), Fe(III), Cu(II), Co(II), Zn(II) and Ni(II) were not co-extracted	This work

**Stripping properties of silver:** In the present work, thiourea solution was employed as the stripping reagent of silver loaded organic phase. The stock silver-loaded organic phase was prepared by the same extraction procedure as described above. In the following experiments, the organic phase loaded with  $500 \text{ mg L}^{-1}$  Ag(I) was used. The experiments were carried out at the following fixed parameters: contact time of the two phases, 6 min; aqueous/organic (A/O) phase ratio, 1.0. As can be seen from Fig. 6, by increasing thiourea concentration from 0.1 to 0.5 (wt %), the percentage stripping of Ag(I) increased from 64.1 to 98.8 %. By further increasing concentration of thiourea from 0.5 to 1.0 (wt %) the percentage stripping of Ag(I) kept constant. The stripping was quantitative when 0.5 (wt %) thiourea solution was used.

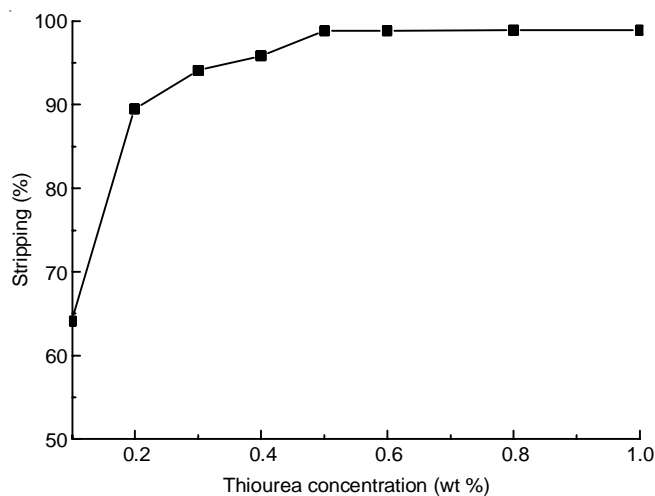


Fig. 6. Effect of stripping reagent concentration on the stripping of Ag(I); A/O: 1.0, contact time: 6 min

## Conclusion

2-Ethylhexyl octyl sulfide (EHOS) diluted in kerosene was effective to extract Ag(I) from nitrate acid media using a suitable extraction parameters:  $C_{\text{Ag(I)}} = 500 \text{ mg L}^{-1}$ , 2-ethyl-hexyl octyl sulfide concentration: 6 % (v/v),  $\text{HNO}_3$  concentration: 4.0 M, phase ratio O/A = 1.0, contact time  $t = 3$  min. The above parameters were also workable and practical for separation of Ag(I) from mixing stock solution containing impurities such as Pt(IV), Rh(III), Fe(III), Cu(II), Co(II), Zn(II) and Ni(II). Under the controlled conditions, Ag(I) could be separated efficiently. The proposed method possesses high selectivity than the reported methods. The present technology is full of potential application on the extraction and separation of Ag(I) in nitric acid media.

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