Solvent Extraction of Gold(I) from Alkaline Cyanide Solution with Synthesized Sulfoxide MSO under Assistance of TBP

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In this work the extraction performances of gold(I) from alkaline solution using a synthesized sulfoxide MSO with assistance of TBP and n-octanol were investigated in details. Several extraction parameters were studied. The results indicated that effective extraction of gold could be realized with increasing MSO concentration at a constant TBP concentration and a fixed phase ratio. TBP exhibited poor extraction for gold without MSO from alkaline cyanide solution, but it could facilitate MSO to transfer gold(I) even with a lower concentration of MSO. N-octanol had no extracting ability for gold(I), but effectively assisted MSO to extract gold(I). Using an organic phase containing 0.7 mol·L⁻¹ of MSO, 30% (v/v) TBP and 20% (v/v) n-octanol, the percentage extraction of gold reached 98.6%, and the fast extraction reaction equilibrium could be established within 2 min. The stripping behaviors of gold-laden organic phase were carried out using sodium thiosulfate (Na₂S₂O₃) solution. The percentage stripping of gold reached 92.6% when Na₂S₂O₃ concentration was 30 g·L⁻¹. Gold(I) could be extracted directly from alkaline cyanide solution efficiently using an organic phase composed of MSO, TBP and n-octanol, and efficiently stripped by Na₂S₂O₃ aqueous solution. Further study may fulfill its potential application in the extraction and separation of gold.

**Keywords:** solvent extraction, synthesized sulfoxide MSO; gold(I); TBP; n-octanol;

1. Introduction

The production of gold via hydrometallurgical processing combines a series of leaching, adsorption, precipitation, electro-winning or extraction operations. Usually, alkaline cyanide solution [1], thiosulfate solution [2], thiocyanate solution [3], and thiourea solution [4], are used to leach gold from its ores. Among
these methods, cyanidization still predominates for the obvious advantages, e.g. with a high leaching efficiency and mature technology. In the traditional production technology, the gold-laden organic phase is recovered mainly by activated charcoal adsorption, displacement/reduction with zinc dust or galvanic deposition. However, these methods have a few obvious drawbacks, such as losing partial gold product, rather long processes and higher content of impurities. Thus it is urgent to select efficient methods to substitute the traditional procedures so as to extract gold directly from alkaline cyanide solution. Solvent extraction has been proved to be a very efficient and practical approach for the recovery of precious metals even with low concentration [5]. During the past decades, there has been a renewed interest in solvent extraction of gold from alkaline solution, and some progress has been made not only in potential applications but also theoretical studies [6-10]. In summary, only a few applicable systems were suitable to extract gold directly from alkaline cyanide solutions, including amines, modified amines, guanidine, substituted guanidine, sulfoxide category materials as well as crown ethers [11-16].

In the present work, we have tried to extract gold directly from alkaline cyanide solution using a synthesized sulfoxide MSO as extractant with addition of tri-\textit{n}-butylphosphate (TBP) as a modifier and assistance of \textit{n}-octanol. The results indicated that almost all of the \text{Au(CN)}_2^- was extracted into the organic phase and most of the gold was transferred from the loaded organic phase into the aqueous phase during the stripping process. This method could provide a potential technology for gold recovery from alkaline cyanide solution in industry.

2. Experimental

2.1 Reagents

The synthesized sulfoxide MSO extractant (R\textsubscript{2}SO), which was mixture and the carbon number of R was C\textsubscript{5}-C\textsubscript{8} and percentage content of S was 10.40\%, was used as supplied by South China University of Technology, China. Its important parameters were presented as the following: $d = 0.899$ g·cm\textsuperscript{-3} (28°C), viscosity $\eta = 25$ mPa·S (25°C), boiling point ~ 300°C and characteristic absorption of IR of $\nu_{S=O} = 1025.34$ cm\textsuperscript{-1}. The IR spectrum of MSO is shown in Figure 1.

![Figure 1. IR spectrum of MSO](image)

Except K\text{Au(CN)}_2 ( purchased from Wenda Rare and Precious Reagents Factory in Tianjin, China), the other reagents were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). All reagents
were used directly as received without any purification in advance. The extractants of (MSO and TBP), three alcohols: \(n\)-pentanol, \(n\)-octanol and iso-octanol, stripping reagent of sodium thiosulfate (\(\text{Na}_2\text{S}_2\text{O}_3\)), all were analytical grade. Odourless kerosene (diluent) was chemical grade.

2.2 Feed solution and organic phase preparation

Feed solution of \(\text{KAu(CN)}_2\) (1.000 g \(\text{L}^{-1}\), \(\text{pH} = 10.0\)) was prepared by dissolving a calculated amount of \(\text{KAu(CN)}_2\) in deionized water. The \(\text{pH}\) of the aqueous solution was adjusted with 0.1 mol \(\text{L}^{-1}\) KOH solution. A series of \(\text{KAu(CN)}_2\) sub-solutions were obtained by diluting the mother solution. Organic phases were prepared by dissolving appropriate volume of MSO, TBP and alcohol reagents in odourless kerosene. In the preliminary experiments, chloroform (\(\text{CHCl}_3\)), \(n\)-hexane and cyclohexane were also selected to serve as diluents for MSO. The results suggested that if they were used as diluents, the disadvantages were clear, e.g. separation time of two phases prolonged (usually over 20 h) and muddy interface of aqueous and organic phases appeared. These did not favor the gold extraction from alkaline cyanide solution. However, the problems did not occur by using odourless kerosene as diluent.

2.3 Extraction Procedure and analytical method

All the experiments were carried out at room temperature. For determining the percentage extraction of gold(I), equal volumes (2.0 mL) of organic and aqueous phases were mixed in a 10 mL test tube, then the extraction system was shaken vigorously for a stipulated time, leading to attain extraction equilibrium in a preliminary experiment. After phase separation, the residual gold concentration of aqueous phase was determined using an atomic absorption spectrophotometer (WFX-110, from Ruili Analysis and Instrument Inc., Beijing, China). These results were further used to estimate the extraction efficiency of gold(I). The amount of extracted gold(I) was calculated from the differences in the metal concentrations in the aqueous phase between, before, and after the extraction.

3. Results and discussion

3.1 Effects of extractants and \(n\)-octanol concentration on gold extraction

In order to determine the effects of extractant concentration on gold extraction, experiments were performed as the following parameters were fixed: initial gold concentration of the aqueous phase, 100 mg \(\text{L}^{-1}\); organic/aqueous (O/A) phase ratio, 1.0; initial \(\text{pH}\) of aqueous solution, 10; and contact time of two phases, 10 min. The effect of MSO concentration on the percentage extraction of gold was investigated without addition of alcohol and with addition of 30\% (v/v) iso-octanol, \(n\)-pentanol or 30\% (v/v) \(n\)-octanol into the organic phase. The results are shown in Figure 2.

It was observed from Figure 2, by increasing MSO concentration in the range of 0 to 1.5 mol \(\text{L}^{-1}\), the percentage extraction of gold increased, but it was rather low and had only a slight enhancement when no alcohol, 30\% (v/v) 2-ethylhexanol or \(n\)-pentanol was added to the organic phase, and it only increased in the range from 0.5 to 17.8\% with no alcohol, from 0.6 to 25.4\% with 30\% (v/v) 2-ethylhexanol and from 0.8 to 40.8\% with 30\% (v/v) \(n\)-pentanol. However, with addition of 30\% (v/v) \(n\)-octanol into the organic
phase, the percentage extraction of gold had an enhanced value ranging from 54.5 to 89.6% under the same experimental conditions. The results indicated that alcohols with an alcohol with linear alkyl chain could promote the gold extraction better than those with branched alkyl chain hydroxyl group, the phenomena was similar with the previous work [18].

To further improve gold extraction using MSO as extractant, we tried to change the compositions of organic phase by adding TBP to the organic phase containing MSO. TBP (tributylphosphate) had been used to extract gold from alkaline cyanide solution [12]. In order to investigate the effect of TBP concentration on the extraction of gold without MSO in the organic phase, the experiments were performed with different TBP concentration when the other parameters were fixed: initial gold concentration, 100 mg·L⁻¹; organic/aqueous (O/A) phase ratio, 1.0; contact time of two phases, 30 min; pH of aqueous 10.0; n-octanol concentration, 30% (v/v). The results are shown as Figure 3.

As can be seen from Figure 3, although the percentage extraction of gold increased with increasing TBP concentration from 0 to 50% (v/v), TBP showed rather poor extraction performances for gold from alkaline cyanide solution, because the corresponding percentage extraction of gold had only a slight increase from 0.6 to 23.6%. The previous work shown than TBP could improve gold extraction from alkaline cyanide solution using other extractants, say CTAB (cetyltrimethylammonium bromide) [17]. Thus
we had projected a procedure in which a mixture composed of MSO and TBP was used to extract gold from alkaline cyanide solution. In these experiments the following parameters were fixed: initial gold concentration, 100 mg·L⁻¹; A/O, 1.0; contact time of two phases, 15 min; pH of aqueous phase, 10.0; n-octanol concentration of organic phase, 20%. The effect of compositions of mixture extractants composed of MSO and TBP on the percentage extraction of gold was investigated. The results are shown in Figure 4.

![Figure 4](image)

**Figure 4.** Effects of MSO and TBP concentrations on the gold extraction using an organic phase containing 20% n-octanol (v/v) but different TBP concentrations: ■, no TBP; ●, 10%(v/v) TBP; ▲, 20%(v/v) TBP; ▼, 30%(v/v) TBP

As can be seen from Figure 4, with a fixed TBP concentration, percentage extraction of gold increased by increasing MSO concentration in the range from 0.1 to 0.7 mol·L⁻¹; likewise with a fixed MSO concentration, percentage extraction of gold increased with increasing TBP concentration ranging from 10 to 30%. Thus gold could be extracted with a high percentage extraction even with a lower MSO concentration in organic phase in which appropriate amount of TBP was added to. For instance, the percentage extraction of gold reached 98.7% using an organic phase containing 0.7 mol·L⁻¹ MSO and 30% (v/v) TBP. In the contrast experiments performed as the above, the percentage extraction of gold was 89.6% even using a 1.3 mol·L⁻¹ MSO organic phase without addition of TBP.

3.2 Effect of n-octanol concentration on the extraction of gold

Based on the above results, n-octanol could promote gold extraction using MSO and TBP as extractants, but they did not eliminate the possibility if n-octanol itself could extract gold from alkaline cyanide solution. Thus the following experiments were carried out without addition of MSO and TBP but n-octanol in the organic phases. The results are shown in Table 1. From the Table 1, by increasing n-octanol concentration in the range of 0 to 40%(v/v), the residual gold concentrations of aqueous phase basically were equaled to the ones of the feed solutions. Namely, n-octanol showed no extraction for gold(I) from alkaline cyanide solution. However it could positively improve gold extraction with MSO and TBP. Similar results were obtained in previous study using DBC (dibutylcarbitol) and n-octanol to extract gold directly from alkaline cyanide solution [18] The improvement of gold extraction upon n-octanol addition possibly may be attributed to the solvation by n-octanol of the molecules composed of gold(I) and dibutyl sulfoxide and their subsequent transfer to the organic phase. A few reagents like phosphine oxides Cyanex 921 or Cyanex 923 also can directly extract gold from alkaline cyanide solution via the solvation effect [13].
Table 1. Effect of $n$-octanol concentration on gold extraction with organic phase without MSO and TBP

<table>
<thead>
<tr>
<th>$N$-octanol concentration % (v/v)</th>
<th>0</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual gold concentration (mg.L$^{-1}$)</td>
<td>100</td>
<td>99.9</td>
<td>99.8</td>
<td>99.9</td>
<td>99.8</td>
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3.3 Effect of contact time of phases on the extraction of gold

To investigate the contact time of two phases on the gold extraction, the feed solution in which gold concentration was 100 mg·L$^{-1}$ was extracted by the organic phase composed of 0.7 mol·L$^{-1}$ and 10, 30 or 50% (v/v) TBP, respectively, with a fixed O/A 1.0. The results are presented in Figure 5.

![Figure 5](#)

Figure 5. Effect of contact time of two phases on the gold extraction: ▲, (v/v) TBP; 10%; ▼, 30%(v/v) TBP; ♦, 50%(v/v) TBP

As can be detected from Figure 5, with a constant MSO concentration, by increasing TBP concentration of organic phase from 10 to 50%, the extraction reaction was fast under the experimental conditions, and the extraction equilibrium was established within 2 min because prolonging the contact time could not further increase the percentage extraction of gold. It also can be seen that more addition amount of TBP in organic phase could accelerate the extraction, for example, the equilibrium almost reached even for 1 min with addition of 30% (v/v) TBP while it was not established with addition of 10% (v/v).

3.4 Effect of organic/aqueous phase ratio on the extraction of gold

As a significant parameter plays a crucial role on metal extraction, organic/aqueous (O/A) phase ratio should be provided in the gold extraction. In these experiments, the following extraction parameters were fixed: initial gold concentration, 100 mg·L$^{-1}$; MSO concentration, 0.6 mol·L$^{-1}$; contact time of two phases, 5 min; pH of aqueous phase, 10.0; $n$-octanol concentration, 20% (v/v). Effect of O/A on the gold extraction was investigated using two organic phases containing 30% and 50% (v/v) TBP respectively. The results are shown in Figure 6.

As seen in Figure 6, by increasing O/A in the range from 0.1 to 1.0, percentage extraction of gold increased rapidly from 26.5 to 96.6 % (30% TBP) and 38.6 to 98.9% (50% TBP). Further increasing O/A from 1.0 to 1.5, the percentage extraction of gold increased slightly, from 96.6 to 98.1% (30% TBP) and
from 98.9 to 99.2% (50% TBP). In fact, between 0.6 and 1.0 of O/A, the increased extent of the percentage extraction of gold was not obvious, e.g. from 83.7 to 93.6 % (30% TBP) and 94.7 to 98.9 % (30% TBP) respectively, if gold extraction was performed using a O/A belonging to this range, gold could be transferred efficiently from aqueous phase to organic one. In addition, with higher TBP concentration in organic phase, gold could be extracted with high efficiency with a lower O/A, which further verified that TBP could favor improving gold extraction from alkaline cyanide solution with MSO. Based on the experiments, it is appropriate to control O/A between 0.6 and 1.0 for efficient extraction for gold.

3.5 Effect of pH of aqueous phase on the gold extraction

To examine the influence of pH of stock solution on the gold extraction, we had used two organic phases, in which MSO was each 0.6 mol·L\(^{-1}\) and \(n\)-octanol concentration each 20% (v/v), but TBP concentration was equal to 20% and 30% (v/v) respectively. Experiments were performed to investigate the effect of aqueous solution pH on gold extraction when initial gold concentration was controlled at 100 mg·L\(^{-1}\), O/A phase ratio 1.0 and contact time 5 min. The results of gold extraction percentage vs. pH are shown in Figure 7.

As shown in Figure 7, the percentage extraction of gold decreased from 94.6 to 12.3% (20% TBP) and
98.8 to 36.7% (30% TBP) respectively accompanying increase of pH from 8 to 13. However, it decreased slightly, e.g. from 94.6 to 91.4% (20% TBP) and 98.8 to 96.3% (30% TBP) correspondingly, as pH increased from 8 to 10. Further increasing pH of aqueous phase to 13, the percentage extraction of gold decreased tremendously, for example, from 91.4 to 12.3% (20% TBP) and 96.3 to 36.7% (30% TBP) respectively. Further experiments proved that when pH continued to increase until to 14 in the end, the percentage extraction of gold almost decreased to zero. For this reason, strong base solutions were used to strip gold loaded in organic phase. It can be observed from Figure 7, the organic phase with higher TBP concentration could increase the extraction pH of feed solution, i.e. higher TBP concentration of organic phase was favorable for gold extraction with MSO from alkaline cyanide solution with higher pH of aqueous phase. In fact, the pH values of the gold cyanide leaching solutions in industry are usually in the range of 8-10. Hence the initial pH of aqueous phase was fixed at 10.0 in this work.

3.6 Performances of stripping gold

To obtain high percentage stripping, Na$_2$S$_2$O$_3$ was used as stripping reagent. In these experiments, the following parameters were fixed: gold concentration in loaded organic phase 96.3 mg·L$^{-3}$ and mixing time 20 min. The effects of Na$_2$S$_2$O$_3$ concentration on gold striping are shown in Figure 8.

![Figure 8. Effect of Na$_2$S$_2$O$_3$ concentrations on gold stripping](image)

As seen in Figure, by increasing Na$_2$S$_2$O$_3$ concentration from 5 to 30 g·L$^{-1}$, the percentage stripping of gold increased. However, further increasing Na$_2$S$_2$O$_3$ concentration, gold stripping percentage decreased. Therefore the optimum stripping reagent concentration was 30 g·L$^{-1}$ or so. The percentage stripping of gold reached 92.6% using 30% g·L$^{-1}$ Na$_2$S$_2$O$_3$ solution after a single stripping operation for 20 min.

4. Conclusions

The behaviors of direct gold extraction from alkaline cyanide solution with a synthesized sulfoxide MSO with assistance of TBP and n-octanol were investigated. The percentage extraction of gold increased by increasing MSO, TBP and n-octanol concentration of organic phase, but decreased accompanying the accretion of pH of aqueous phase. Without MSO and TBP in the organic phase, n-octanol revealed no ability to extract gold from alkaline cyanide solution. The system composed of MSO, TBP and n-octanol could extract gold rapidly, with a fast equilibrium establishment within 2 min. The addition of TBP and
n-octanol could facilitate MSO even with a lower concentration to extract gold efficiently. The gold-loaded organic phase could be stripped by 30 g L\(^{-1}\) Na\(_2\)S\(_2\)O\(_3\) solution, and the percentage stripping of gold was 92.6%. In summary, the presented extraction system was favorable to directly extract gold(I) from alkaline cyanide solution, and the gold(I) extraction was more efficient than the previous report [13], and furthermore, separation time of two phases and equilibrium time were obvious shorter than other system [10,11].

References