



## Extraction of Gold(III) in Hydrochloric Acid Media by 2-Ethyl Hexyl Cyclohexyl Sulfide

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A new extractant of 2-ethyl hexyl cyclohexyl sulfide was synthesized and used as an extractant for Au(III) from hydrochloric acid solution. Gold(III) was extracted quantitatively with 2-ethyl hexyl cyclohexyl sulfide in kerosene. Sodium sulfite solution could be used as stripping agent. Extraction parameters of Au(III), including 2-ethyl hexyl cyclohexyl sulfide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio, sodium sulfite concentration and hydrochloric acid concentration of aqueous phase, were studied. Almost all of the Au(III) (> 99 %) was transferred from the aqueous phase into the organic phase. Most of the Au(III) (> 98 %) in the organic phase can be stripped with sodium sulfite aqueous solutions. The proposed method possesses wider range of acidity than the reported methods.

**Keywords:** Gold, Solvent extraction, 2-Ethyl hexyl cyclohexyl sulfide.

### INTRODUCTION

Gold is a metal which is widely used in various industries, e.g., electrical systems, fuel cells, catalysts, biomedical area, etc.<sup>1-3</sup>. Various hydrometallurgical processes such as ion exchange<sup>4-5</sup>, adsorption and solvent extraction are used for the recovery of gold.<sup>6-9</sup> Solvent extraction has been considered as a most efficient technique for the recovery and separation of gold from hydrochloric acid media. Many extractants for gold have been reported, such as dibutylcarbitol, methyl isobutyl ketone, ammonium extractants and phosphorus extractants<sup>10-12</sup>. However, the methods reported are not so reliable for routine application because these methods suffer due to the drawbacks such as selectivity of Au(III), operating condition, nature of diluents, critical pH range etc.<sup>13,14</sup>. Sulfur containing ligands are highly selective for the extraction of Au(III) and have been widely used in the extraction of this species<sup>15,16</sup>.

In the present work, a new extractant 2-ethylhexyl cyclohexyl sulfide (EHCHS) was synthesized and its extraction behaviour towards Au(III) from hydrochloric acid solution was also studied, by controlling important parameters like extractant concentration, acidity, contact time, phase ratio and concentration of stripping agent. The proposed method possesses wider range of acidity than the reported methods<sup>17-23</sup>.

### EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan)

was used to measure the concentration of Au(III). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Au 242.8 nm. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

**Au(III) stock solution (10 g L<sup>-1</sup>):** A weighed portion of gold metal was dissolved in aqua regia (120 mL). When the metal was completely dissolved, the solution was evaporated to nearly dryness. Residual HNO<sub>3</sub> was removed by adding 30 mL of 6 mol L<sup>-1</sup> HCl and evaporated to nearly dryness again and this was repeated 3 times. The solution was transferred into a 250 mL of volumetric flask. The organic phases with desired extractant concentration were obtained by dissolving a definite volume of 2-ethyl hexyl cyclohexyl sulfide (EHCHS) in kerosene.

**Synthesis of 2-ethyl hexyl cyclohexyl sulfide (EHCHS):** EHCHS was synthesized according to the following procedure: cyclohexyl mercaptan (11.6 g), ethanol (70 mL) and sodium hydroxide (5 g) were put in a round-bottom fitted with a mechanical stirrer and condenser and the mixture was heated for about 0.5 h. 2-ethylhexyl bromide (24.8 g) was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 2 h. The residual solid was filtered after cooling down and the ethanol was removed and EHCHS was obtained. Its structure (Fig. 1) was verified by <sup>1</sup>H NMR and <sup>13</sup>C NMR. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.57-2.52 (m, 1H), 2.50-2.49 (m, 2H), 1.97-1.96 (m, 2H), 1.76-1.75 (m,

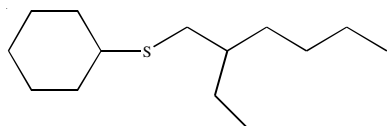


Fig. 1. Structure of 2-ethyl hexyl cyclohexyl sulfide (EHCHS)

2H), 1.62-1.60 (m, 1H), 1.47-1.26 (m, 14H), 0.91-0.86 (m, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 44.45, 40.02, 34.88, 34.21, 32.90, 29.30, 26.55, 26.32, 26.02, 23.37, 14.45, 11.18 ppm

**General extraction procedure:** Equal volumes (10 mL) of both phases were mixed and vigorously shaken for 4 min, which was sufficient enough to attain equilibrium in a preliminary experiment. After phase separation, the concentration of Au(III) 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 between, before and after the extraction.

## RESULTS AND DISCUSSION

**Influences of the extractant concentration:** To investigate the effect of 2-ethyl hexyl cyclohexyl sulfide (EHCHS) concentration on the extraction performances of Au(III), the experiments were performed at the fixed conditions. The results are shown in Fig. 2. As can be seen from Fig. 2, EHCHS dissolved in kerosene with the extractant concentration varying from 2 to 15 % (v/v). The percentage extraction of Au(III) increased in the range from 17.8 to 99.1 % by increasing

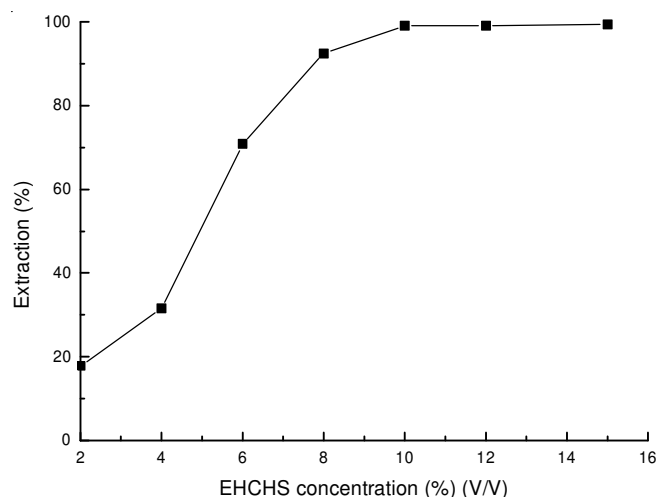


Fig. 2. Effect of extractant concentration on the extraction of Au(III).  $C_{\text{Au(III)}}$ : 0.1 g  $\text{L}^{-1}$ ,  $C_{\text{HCl}}$ : 0.1 to 4 mol  $\text{L}^{-1}$ , O/A: 1, contact time: 4 min

EHCHS concentration from 2 to 10 % (v/v). Further increasing concentration of EHCHS from 10 to 15 % (v/v), the percentage extraction of Au(III) only had a slight increase (from 99.1 to 99.5 %). 10 % (v/v) EHCHS was needed for quantitative extraction of Au(III) from a hydrochloric acid solution containing 0.1 g  $\text{L}^{-1}$  gold.

**Influences of hydrochloric acid concentration:** The effect of hydrochloric acid concentration on the extraction of Au(III) is studied. The extraction curve indicated the percentage of extraction of Au(III) kept constant with the increase of HCl concentration, from 0.1 mol  $\text{L}^{-1}$  to 4.0 mol  $\text{L}^{-1}$ . No effect of acidity on the quantitative extraction of gold. Therefore, 0.1 mol  $\text{L}^{-1}$  to 4 mol  $\text{L}^{-1}$  HCl was adopted in all subsequent experiments.

Table-1 compares the characteristic data of EHCHS with other extractants for gold reported in literatures. As can be seen, the proposed method possesses wider range of acidity than the reported methods.

**Influences of contact time:** To extract Au(III) 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. 3. 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 6 min. The percentage extraction of Au(III) increased in the range from 52.5 to 99.1 % by increasing of contact time from 1 to 4 min. Further increasing contact time from 4 to 6 min, the

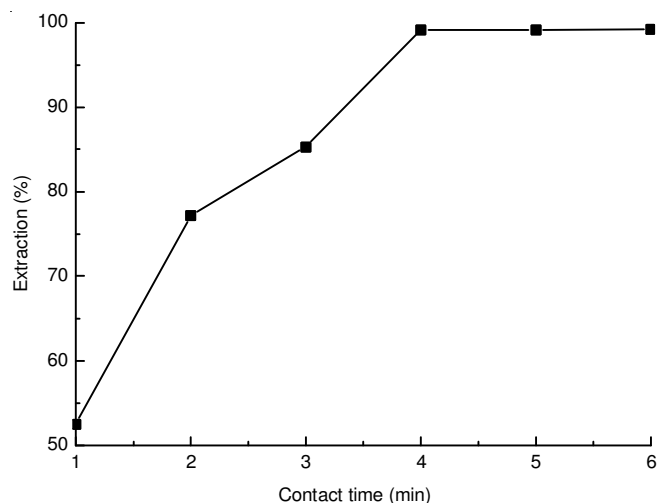


Fig. 3. Effect of contact time on the extraction of Au(III).  $C_{\text{Au(III)}}$ : 0.1 g  $\text{L}^{-1}$ ,  $C_{\text{EHCHS}}$ : 10 % (v/v), O/A: 1,  $C_{\text{HCl}}$ : 0.1 to 4 mol  $\text{L}^{-1}$

TABLE-1  
COMPARISON OF THE PUBLISHED EXTRACTANTS FOR GOLD WITH EHCHS

Extractants	Range of acidity	Stripped	Reference
DibutylCarbitol	1 M HCl media	1 Moxalic acid	17
N-n-octylaniline	0.1 M HCl media	7 M ammonia	18
Cyanex 925	6 M HCl media	water	19
Cyanex 471X	1 M HCl media	Sodium thiosulphate	20
ODMBAC	1 M HCl media		21
Benzoylthioureas	0.01 M HCl media		22
Pyrazolone	1 M HCl media		23
EHCHS	0.1-4 M HCl media		This work

percentage extraction of Au(III) kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of gold was found to be about 4 min.

**Influences of organic/aqueous (O/A) phase ratio:** To obtain optimal O/A for extraction of Au(III), the following experiments were performed at other fixed extraction parameters. The results are shown in Fig. 4. As can be seen from Fig. 4, by increasing O/A from 0.5 to 1.0, the percentage extraction of Au(III) increased from 48 to 99.1 %. By further increasing O/A from 1 to 3, the percentage extraction of Au(III) kept constant. Therefore, Au(III) can be extracted efficiently by controlling organic/aqueous (O/A) phase ratio, 1.

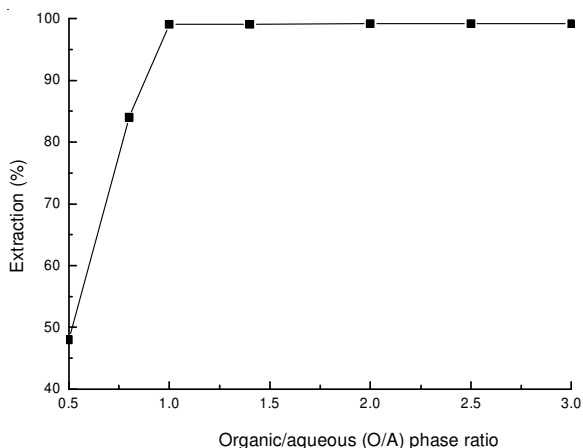


Fig. 4. Effect of O/A on the extraction of Au(III).  $C_{Au(III)}$ :  $0.1 \text{ g L}^{-1}$ ,  $C_{EHCHS}$ : 10 % (v/v), contact time: 4 min,  $C_{HCl}$ : 0.1 to  $4.0 \text{ mol L}^{-1}$

**Stripping properties of gold:** Gold loaded in the organic phase was stripped with various stripping agents, such as sodium sulfite, ammonia and thiourea as stripping agents. In the following experiments, the organic phase loaded with  $0.1 \text{ g L}^{-1}$  Au(III) was used. The experiments were carried out at the following fixed parameters: contact time of the two phases, 5 min; aqueous/organic (A/O) phase ratio, 1. The results show that gold can not be stripped from organic phase with thiourea and ammonia solution. Sodium sulfite solution can be used as the effective stripping agent. As can be seen from Fig. 5, by increasing sodium sulfite concentration from 0.5 to 1.5 (wt. %), the percentage stripping of Au(III) increased from 54.5 to 98.5 %. By further increasing concentration of sodium sulfite from 1.5 to 3.5 (wt. %) the percentage stripping of Au(III) kept constant. The stripping was quantitative when 1.5 (wt. %) sodium sulfite solution was used.

## Conclusion

The solvent extraction of Au(III) from hydrochloric acid solutions were investigated using 2-ethylhexylcyclohexyl sulfide diluted in kerosene. Extraction parameters of Au(III) were obtained and summarized as the following: 2-ethylhexylcyclohexyl sulfide (EHCHS) concentration, 10 % (v/v); organic/aqueous (O/A) phase ratio, 1; hydrochloric acid concentration of aqueous solution,  $0.1 \text{ mol L}^{-1}$  to  $4 \text{ mol L}^{-1}$ ; contact time of two phases 4 min. Au(III) loaded in organic phase could be stripped efficiently using an aqueous solution containing sodium sulfite. The proposed method possesses wider range of acidity than the reported methods.

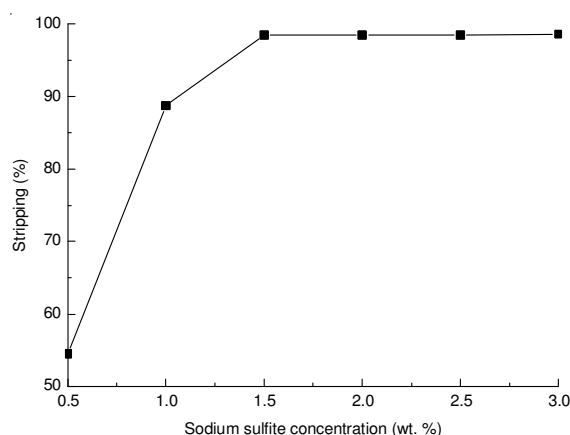


Fig. 5. Effect of stripping reagent concentration on the stripping of Au(III). O/A: 1, contact time: 5 min

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