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Solvent extraction of gold(I) from alkaline cyanide solutions by the cetylpyridinium bromide/tributylphosphate system

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ABSTRACT

This paper explores the solvent extraction of $KAu(CN)_2$ from alkaline cyanide solutions using quaternary ammonium cetylpyridinium bromide (CPB) as an extractant with the addition of tributylphosphate (TBP) as a modifier. It also investigates the influence of several variables on gold extraction, including the molar ratio (β) of CPB to Au(I), the volume percentage of TBP (φ_{TBP}), NaCl concentration, phase ratio (AQ/ORG), and gold concentration in the aqueous phase. The results indicate that nearly all of the Au(I) (>98%) was transferred from the aqueous phase into the organic phase when $\beta = 1$ and $\varphi_{TBP} = 30$ vol%. We also carried out experiments for treating 20 L synthetic aurocyanide solution containing 10 mg/L Au(I) with column-shaped extraction equipment. The results demonstrated the recovery of more than 94.5% of Au(I) after two successive stages of extraction, and the Au(I) concentration in the raffinate was less than 0.5 mg/L. KSCN solution was used to strip the gold-loaded organic phase, and about 90% of Au(I) could be reverse extracted into the aqueous phase when the KSCN concentration reached 3.0 mol/L. The results obtained in this paper establish that the CPB/TBP extraction system has potential for practical application in the extraction and separation of gold from alkaline aurocyanide solutions.

1. Introduction

Gold is normally leached using an aqueous alkaline cyanide solution. Subsequently, the pregnant leachate solution undergoes zinc powder cementation or activated carbon adsorption for enrichment. During the past decades, studies on direct solvent extraction of Au(I) from alkaline cyanide leaching solution have received much attention since Mooiman and Miller (1983, 1986) published their well-known work. Their results indicated that the addition of organic phosphorus oxide compounds to simple amine extraction systems could significantly increase the basicity of simple amines, which meant the recovery of gold in alkaline cyanide solutions by simple amines might be possible. Thereafter, various extractants and modifiers (Alguacil et al., 1994; Alguacil, 1998, 1999; Adams, 2003; Sastre et al., 1999; Aguayo et al., 2007; Jiang et al., 2005; Zhang et al., 2001a,b; Pan, 2008) were selected to optimize the extraction system to increase loading capacity, improve selectivity, and reduce emulsification, as well as other practical considerations. Quaternary ammonium salts (Alguacil, 1990) have also been used to extract $Au(CN)_2^-$ due to their high gold-loading capacity over a broad range of pH. We introduced a new quaternary ammonium salt extraction system (Zhang et al., 2001b; Chen et al., 2005; Yang et al., 2008) using cetyltrimethylammonium bromide (CTAB) to extract Au(I) from an aurocyanide leaching solution. We first added CTAB to the aurous cyanide aqueous solution at a molar ratio of CTAB to $Au(CN)_2^- = 1:1$; we then used tributylphosphate (TBP) as the organic phase, and extracted nearly all the gold (>98% extraction) in the aqueous phase. However, it was difficult to strip gold from such a loaded organic phase. In addition, previous studies have emphasized the extraction reaction mechanism, and the results obtained were all from g/L-level experiments, whereas gold concentration in industrial heap leaching solutions was very low—only about 1 mg/L to 20 mg/L—and far from practical industrial application levels.

To obtain further information and better knowledge of the chemistry of gold extraction by the new quaternary ammonium salt extraction system, in this work we attempted to study another typical cationic surfactant, cetylpyridinium bromide (CPB, structure in Fig. 1) in the extraction of low concentration of Au(I) ($[Au]_{aq} = 10$ mg/L) from alkaline cyanide solutions, using tributylphosphate (TBP) as a modifier. Different from CTAB, CPB is a pyridine derivatives cationic surfactant with a longer carbon–hydrogen chain. In the organic phase, the affinity between CPB^+ and $Au(CN)_2^-$ must be weaker than that of $CTAB^+$ due to the conjugation effects of the pyridine ring, which may lead to easier stripping. KSCN was selected to strip gold(I) from the loaded organic phase. The results showed that all of the $Au(CN)_2^-$ could be extracted into the organic

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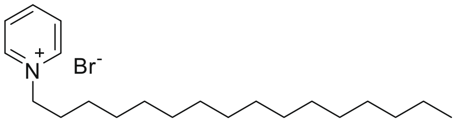

Fig. 1. Structure of cetylpyridinium bromide (CPB).

phase during extraction process, and that most of the gold (90%) could be reverse extracted into the aqueous phase during the stripping process.

2. Experiment

2.1. Reagents

Analytical Reagent (A.R.) grade cetylpyridinium bromide, potassium thiocyanate (KSCN), tributylphosphate (TBP) and *n*-dodecane were supplied by Beijing Chemical Reagent Co. and $KAu(CN)_2$ (99%) was prepared according to the literature (Cao, 1988). Other chemicals used were all commercially available reagents of analytical grade. Distilled water was used in all studies.

The organic phase was prepared by dissolving TBP (typically 30 vol%) in *n*-dodecane. A synthetic solution of Au(I) ($[Au]_{aq}$ = 10 mg/L, typically) was prepared from analytical grade $KAu(CN)_2$ dissolved in NaCl solution (pH 10.5, $[NaCl]_{aq}$ = 0.2 mol/L, typically). CPB was added to the aurous cyanide solution, with the equal molar ratio (1/1) of CPB versus Au(I) in advance.

2.2. Extraction and stripping of $KAu(CN)_2$

In the extraction experiments, 10.0 mL organic phase, previously balanced with deionized water (pH 10.5), was equilibrated with 10.0 mL aqueous phase in the 60-mL separating funnel by shaking for 10 min at 25 ± 1 °C on an automatic shaker. Preliminary kinetic tests indicated that equilibrium was attained within 5 min. After 10 min of contact, the mixture was centrifuged for clear phase separation. The gold concentration in the aqueous phase was determined by atomic absorption spectrometry using a Hitachi Z2000 spectrophotometer. Gold in the organic phase was estimated by mass balance. In the stripping experiments, the gold-loaded organic phase ($[Au]_{org}$ = 1.98 g/L) was prepared using the same extraction procedure as described above. Au(I) stripping experiments were carried out by mechanically shaking the organic phase and KSCN aqueous solution in a separating funnel at room temperature for 20 min.

Pilot extraction experiments were run in column-shaped extraction equipment as shown in Fig. 2. The diameter of each column was 8×10^{-2} m by 1.0 m. The top one-third of the column functioned as a mixing chamber, and the remainder of the column served as a settling chamber. A mechanical stirrer was assembled in each mixing chamber. Before performing the Au(I) extraction experiment, 2 L NaCl solution with concentrations of 0.2 mol/L and 200 mL 30 vol% TBP were added to the first and second extraction columns. During the extraction process, the candidate Au(I) solution—molar ratio of CPB to $KAu(CN)_2$ of 1—was pumped into the mixing chamber at a flow rate of 4 L/h. In the extraction columns, the phases are contacted by drops of the heavy phase (aurocyanide solutions) falling through the continuous light phase (30 vol% TBP). The extraction raffinate flowed from the bottom of the column and into the next extraction column. After two successive stages of extraction, 10 mL per 2 L raffinate was removed from the outflow solution for analysis. To decrease the loss of TBP carried from the out-flow aqueous phase in the extraction process, we used another accessional extraction column with 100 mL *n*-dodecane after two successive extraction stages to arrest the dissolved TBP in the aqueous phase.

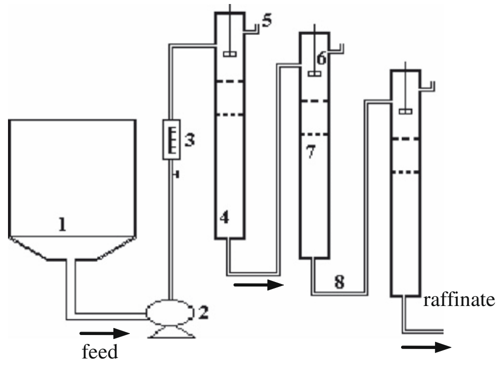

Fig. 2. Schematic diagram of gold(I) extraction from alkaline cyanide solution. (1) Feed tank; (2) Water pump; (3) Float-type flow meter; (4) Extraction column; (5) Entrance of organic phase; (6) Stirrer; (7) Baffle; (8) Conduit.

3. Results and discussion

3.1. Effects of the molar ratio of CPB to Au(I) in the aqueous phase on the extraction of gold

To determine the influence of CPB on the extraction of Au(I), we investigated the effect of the molar ratio of CPB to Au(I) in the aqueous phase. Fig. 3 shows the results. Initially, the extraction percentage linearly increases with an increase of CPB until the molar ratio of CPB to aurocyanide, β reaches 1, and then it levels off with a further increase of β. When β reaches 1, 99% efficiency is achieved. This indicates that the molar ratio of CPB to $Au(CN)_2^-$ in the extracted complex is l. Compared to Br^-, the $Au(CN)_2^-$ anion is comparatively bulky and less hydrated. When CPB is added in the aqueous phase, $Au(CN)_2^-$ will replace Br^- to form ion-pairs with CPB^+. The ion-pair $[CPB^+][Au(CN)_2^-]$ will be more easily solvated by the TBP than the $[CPB^+][Br^-]$ ion-pair, resulting in a greater extraction percentage of gold.

3.2. Effects of the volume percentage of TBP on extraction of gold

The effect of concentration of the modifier TBP on the extraction of Au(I) has been studied by varying the volume percentage of TBP (φ_{TBP}) from 0 vol% to 60 vol% using *n*-dodecane as diluents.

Fig. 4 shows the extraction percentage of gold as a function of the TBP content (in volume percentage). The modifier TBP played an important role during the extraction. Without the TBP, almost

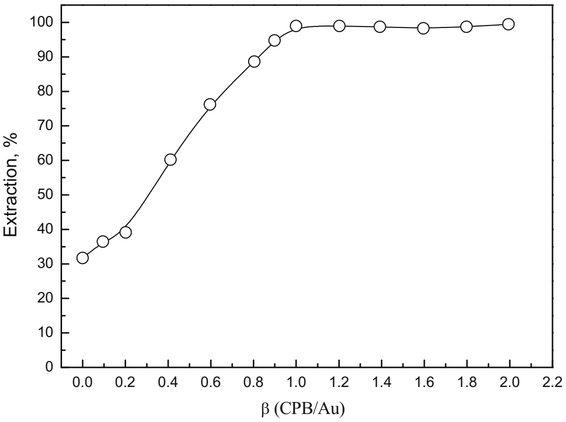

Fig. 3. Effect of the molar ratio (β) of CPB to Au(I) on the extraction of gold ($[Au]_{aq}$ = 10 mg/L, $[NaCl]_{aq}$ = 0.2 mol/L, φ_{TBP} = 30 vol%).