



Short communication

A new approach for monitoring and controlling the extraction of gold by tri-butyl phosphate from chloride media



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ARTICLE INFO

Article history:

Received 20 May 2015

Revised 5 October 2015

Accepted 7 October 2015

Available online 27 October 2015

Keywords:

Solvent extraction

Gold

Oxidation-Reduction Potential (ORP)

Tri-butyl phosphate (TBP)

ABSTRACT

The objective of this work was to control and monitor the solvent extraction process of gold chloride by tri-butyl phosphate (TBP) through measuring Oxidation Reduction Potential (ORP). The results effectively indicate the application of ORP measurement approach in on-line monitoring/controlling the process of gold chloride solvent extraction. This approach showed that any decrease in gold extraction leads to an increase in ORP value. Based on this finding and by applying the slope analysis method, it was proved that Au tetrachloride is the predominant anion in aqueous phase and each mole of Au is absorbed by three moles of TBP. Considering the fact that a variety of ions are extracted from aqueous media in solvent extraction process a new equilibrium would be created. On the basis of Nernst equation, the electrochemical potential of system is changed. This research aims at anticipating the kind and concentration of ionic species based on the potential value of solution.

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1. Introduction

Solvent extraction is known to be an efficient technique for the separation and recovery of metal ions, which has received a lot of attention due to its advantages, such as ease of application, low cost, and recoverability of components (Alamdari et al., 2012; Xing et al., 2012). Studying, working on and experiencing solvent extraction for many years, the authors believe that this technique is still on up and coming, especially on an industrial scale.

This is especially true when the solvent extraction process involves different species. An example of such a solvent extraction process is the extraction of Au from chloride media. Due to the electrochemical nature of different Au chloride complexes, it will be useful to base the analysis of such systems on electrochemical criteria. As an example, measuring the electro-conductivity of the extractant and the $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solutions in dry di-butyl carbitol (DBC), Mironov (2013) showed that the contribution of the ionic subsystem (H^+ , HAuCl_4 , $(\text{HAuCl}_4)_2$, $\text{H}(\text{AuCl}_4)_2^-$, and $\text{H}_2(\text{AuCl}_4)^+$) increases when Au concentration in the organic phase is raised. Other common characteristics that can be used for ionic species identification are through ORP. ORP can be considered as the

tendency of a system to accept or donate electrons when a change occurs in ionic species.

TBP is a reasonably priced reagent with low solubility in water and good extraction performance. It has been commonly used as an organic extractant in the metal extraction species from acidic solutions. Tocher et al. (1964) and Yadav and Khopkar (1970) successfully separated Au from chloride media Using TBP as an extractant.

In the present work, TBP was chosen as an extractant for tetrachloroauric ion extraction and the effects of parameters such as hydrochloric acid, Au and TBP concentration on solvent extraction processes were identified and analyzed. The slope analysis method is also used to identify the extraction reaction of Au by TBP from a chloride solution. Furthermore, in order to monitor the changes in the concentration of Au species in the aqueous phase during Au extraction by the organic phase, the ORP was employed and the corresponding data was electrochemically justified.

2. Materials and methods

Stock gold chloride solution was prepared by dissolving analytical grade Hydrogen gold tetrachloride ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, MERK Chemical Co., Germany) in double distilled water. Analytical grade TBP (FLUKA, Switzerland) and commercial grade kerosene (Isfahan Refinery Co.) were used as the extractant and the diluent respectively for preparing the stock organic solutions.

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Batch experiments were conducted in a flask containing equal volumes (20 mL) of aqueous and organic phases with different initial concentrations of Au (68–500 mg/L) and hydrochloric acid (0.25–10 mol/L). The time required to reach equilibrium, based on our preliminary studies, was set to 30 min. The metal content of the aqueous phase was determined by atomic absorption spectroscopy (Varian, A240) and that of the organic phase was estimated by mass balance calculations. The ORP was measured by *Pt standard electrode in KCl* and then converted to SHE standard (Hach Company, 2012).

3. Results and discussion

3.1. Effect of HCl concentration on Au extraction

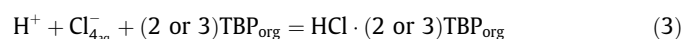
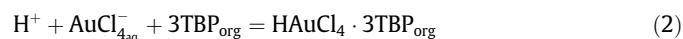
The effect of hydrochloric acid concentration on the extraction of gold at different concentration of TBP is shown in Fig. 1a. %E is defined in the form of Eq. (1):

$$\%E = \frac{[Au]_{org}}{[Au]_{aqueous} + [Au]_{org}} \quad (1)$$

As it can be seen, Au extraction percentage increases intrinsically with an increase in the concentration of hydrochloric acid concentration. At low TBP concentration, from 0.025 to 0.1 M, the increasing concentration of HCl causes a sharp increase in the percentage of extracted gold. However, the concentration of hydrochloric acid concentration on Au extraction in higher concentrations of TBP, over 0.25 M, has no significant effect. Under this condition, more than 90% of gold is extracted. Alamdari et al. (2012) reported that the protonated TBP molecules were able to extract anionic species such as ReO_4^- and MoO_4^- ; this mechanism, i.e. ion association reaction, is also acceptable for $AuCl_4^-$ extraction by TBP. Thus, higher HCl concentrations lead to a greater number of protonated TBP molecules that, in turn, result in an increase $AuCl_4^-$ in extraction percentage.

3.2. Effect of Au initial concentration

Fig. 1b illustrates the effect of HCl concentration on Au extraction percentage for different initial Au concentrations. Two distinct trends are observed in the Au extraction curves: (1) descending trends (for 65 and 130 mg/L Au concentrations), and (2) ascending trends (300 and 600 mg/L Au concentrations). When Au initial concentration is high (>300 mg/L), increasing HCl concentration has a significant effect on Au extraction; while at low Au concentrations (<130 mg/L), the extraction percentage decreases at higher HCl concentrations. In order to shed more light on the $AuCl_4^-$ extraction by TBP, it is beneficial to consider the major reactions occurring in this system. The solvent extraction and acid adsorption reaction are expressed, respectively, as follows:



Based on Eq. (2), Au extraction generally increases by increasing H^+ concentration for high initial concentrations of Au (300 and 500 mg/L). However, despite the fact that metal is preferred to acid extraction, according to Eq. (3), at low initial concentrations of Au (65 and 130 mg/L), an increase in HCl concentration results in a reduction in the concentration of free TBP molecules and causes a decrease in the affinity of TBP for Au extraction.

3.3. Effect of electrochemical potential in solvent extraction process

Gold metal, under standard conditions and in the presence of chloride ions is oxidized to Au^{3+} and Au^+ , which subsequently produces anions, respectively (Eqs. (4) and (5)).



The Nernst equation calculates the equilibrium potential for ionic species based on any change on the valence and concentration of that ion at ambient temperature. Equilibrium potential (E) and pH is changed in respect to any variation at chlorine and gold ions in this system (Finkelstein and Hancock, 1974). Here, calculated potentials of different ionic species of gold using the Nernst equation are reported in Table 1. These results are also in compatibility with Pourbaix diagram drawn by FACTSAGE software.

As it can be seen in Table 1, Au, $AuCl_4^-$ and $AuCl_2^-$ are in equilibrium with each other. Clearly, an increase in Cl^- or decrease in Au concentration leads to a decrease in the potential value so the equilibrium potential for these species changes from 0.88 to 0.97 V.

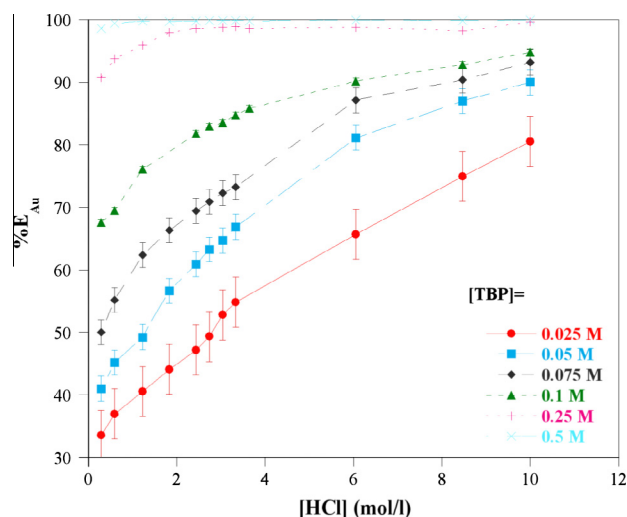


Fig. 1a. Gold extraction percent against of HCl concentration on for different TBP concentration for an initial aqueous Au concentration of 500 mg/L.

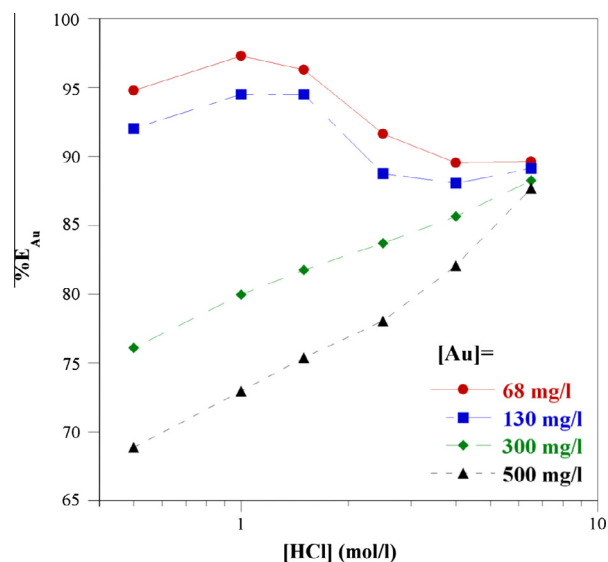


Fig. 1b. Au extraction percent against HCl concentration for different initial gold concentration, at ambient temperature and 0.1 M TBP.

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