



# Comparative solvent extraction study of silver(I) by MEHPA and Cyanex 302 as acidic extractants in a new industrial diluent (MIPS)



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## ABSTRACT

The experimental results for the solvent extraction of silver ions from acidic aqueous media with bis(2,4,4-trimethylpentyl) monothiophosphonic acid (Cyanex 302) and a mixture of mono and di(2-ethylhexyl) phosphoric acid and di(2-ethylhexyl)phosphoric acid (MEHPA) as the ligand, diluted with an industrial paraffinic solvent are presented. The effects of the influential parameters such as pH, contact time, extractant type, extractant concentration and temperature were investigated. The results of the solvent extraction of silver ions from the solutions showed that extraction of the silver ions increased with increasing pH, extractant concentration and temperature. The stoichiometry of the extracted metal species by Cyanex 302 and MEHPA with silver ions was 1.0:1.5 and 1.0:4.0, respectively. The results of solvent extraction showed that a quantitative extraction of silver ions was feasible in a single stage within 3 min only at the condition of  $O/A = 1$ , silver ions concentration of  $0.035 \text{ mol L}^{-1}$ ,  $\text{pH}_{\text{eq}} = 7.0$  for  $[\text{MEHPA}] = 0.4 \text{ M}$  and  $\text{pH}_{\text{eq}} = 6.5$  for  $[\text{Cyanex 302}] = 0.05 \text{ M}$ , respectively. The stripping of silver from the loaded organic carried out with nitric acid showed quantitative stripping for MEHPA (97.2%).

The composition of the extracted species in the organic phase was proposed to be  $\text{AgL}(\text{HL})_{(4x-1)(\text{org})}$  and  $\text{AgL}(\text{HL})_{(1.5x-1)(\text{org})}$ , for MEHPA and Cyanex 302, respectively. The thermodynamic analysis of the temperature effects showed that the extraction processes were endothermic and standard enthalpy change for both extractants were positive.

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## 1. Introduction

Silver is a relatively rare precious metal, with broad applications and growing demand as the natural sources of silver are decreasing. There is a great deal of interests in silver recovery for both environmental and economic reasons (Park and Fray, 2009). Nowadays, most of the silver globally is recovered from scraps such as photographic and X-ray films, jewelry and catalysts (Ajiwe and Anyadiegwu, 2000). During the past three decades, electrolysis (Pillai and Chung, 2008), precipitation (Rivera et al., 2007), flotation (Zouboulis, 1995), ion-exchange (Matulionyte et al., 2007), adsorption (Kononova et al., 2007), solid phase extraction (Hu et al., 2003), electro coagulation (Mohan and Pittman, 2006), cementation (Miller et al., 1990), bio-sorption (Fujiwara et al., 2007), liquid membranes (Othman et al., 2006; Laki et al., 2015), reverse osmosis (Koseoglu and Kitis, 2009) and solvent extraction (Stankovic et al., 2008) have been used for silver recovery.

Each method has its own benefits and shortcomings. In cementation method, the recycled solution becomes contaminated by metal ions derived from the reducing agent (Dimeska et al., 2006). Electrochemical

deposition and chemical precipitation, from dilute liquors are not economical or cost effective in terms of energy or chemicals (Devi et al., 2000).

Contrary to all of the above methods, solvent extraction using low-cost extractants is recognized as an emerging technique and a large variety of the extractants have been developed and tested for extraction of different metal ions (El-Shahawi et al., 2007; Matulionyte et al., 2007). Some important advantages of this method such as simplicity, flexibility, economic benefits, rapidity, higher enrichment factors, lower costs and being environmentally friendly etc. predominate over other techniques (Sole and Hiskey, 1995). The solvent extraction process has been reported as a potential technique for recovering metal ions from solutions.

Since the salts of metal ions of interest are insoluble in organic solvents, the extraction process requires the introduction of an extractant that will combine with the metal ions to form an organic soluble species (Alam et al., 1997; Hubicki and Hubicka, 1995; Sevdic et al., 1990). One of the most important factors that influence the selectivity of a solvent extraction system is the choice of a suitable extractant. Dicarboxylic acids, aliphatic amines, aromatic amines, amino acids, and hydroxyl acids are usually used as extractants for metal ion (Kimura and Shono, 1987). In this regard, the use of organic phosphorus extractants has

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increased steadily because of their excellent selective nature in forming complexes under specific conditions (Brian, 1993; Darvishi et al., 2005; Reddy et al., 2004a, 2004b).

The most frequently reported organic phosphorus extractants for the metal ions are bis(2-ethylhexyl) phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl) phosphonic acid (Cyanex 272) and 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC 88A). Sulfur substituted phosphinic acids like Cyanex 302, Cyanex 301 and Cyanex 923 are known to be employed as extractants for the transition metal ions (Devi and Mishra, 2010; Devi et al., 2000; Kumar Singh et al., 2009; Paiva, 1993; Sarkar and Dhadke, 2000; Sole and Hiskey, 1995). Several organophosphorous compounds such as Cyanex 272, D2EHPA, Cyanex 301, and Cyanex 302 have also been employed for the extraction of silver and other transition metal ions (Amamrani et al., 1999; Arroyoa et al., 2008; Baba et al., 1986; Ennassef et al., 1995; Lee et al., 2005; Nathsarma and Devi, 2006; Otu and Westland, 1990; Sarangi et al., 1999; Sole et al., 1994).

Previous studies have been carried out on solvent extraction of silver ions from nitrate, sulfate or even chloride media using sulfur-containing (Alam et al., 1997) and other extractants such as tri-isobutyl phosphine sulfide (Baba et al., 1986), thiocrown ethers (Dietze et al., 1989), thio-urea based reagents (Zuo and Muhammed, 1990), o-dibutylphenyl amino phenyl methanethio phosphonate (Sevdić et al., 1990), and calix[4]arene (Ohto et al., 1997).

It is well known that diluents play an important role in the solvent extraction of metal ions. In the field of solvent extraction technology, the diluent constitutes a rather important part in the economy of the process. The diluent has to be inexpensive, less toxic, should have almost negligible loss and give good solubility to the extractant and its various compounds. Hence, several properties need to be considered in selecting the suitable diluents (Sanjay and Mansing, 2002).

In this study, two organic phosphorus extractants (MEHPA and Cyanex 302) were applied to study silver ion recovery from nitrate solutions. To the authors' knowledge, application of commercial MEHPA mixed esters for solvent extraction of silver ions from aqueous solutions is completely new. The influence of the concentrations of extractants and silver ions, temperature, contact time and pH of aqueous phase on separation efficiency was investigated. Important parameters in the design of solvent extraction process such as stoichiometry, distribution coefficient, extraction rate were compared for both extractants.

## 2. Experimental

### 2.1. Materials

Silver nitrate, nitric acid (69.1% purity) and sodium hydroxide (99.0% purity) were of analytical reagent grade from Merck, Germany. A mixture of mono and di(2-ethylhexyl) phosphoric acid and di(2-ethylhexyl)phosphoric acid – MEHPA – (a mixture of 55% monoester and 45% diester) was bought from Merck and bis(2,4,4-trimethylpentyl) mono thiophosphonic acid (Cyanex 302) was supplied from Sigma-Aldrich and were used without further purification. A new industrial solvent, which mainly consists of paraffinic and naphthenic hydrocarbons in the range of C<sub>10</sub>–C<sub>14</sub> (Table 1), was used as an inert diluent for the extractants and supplied from Marun Petrochemical Company, Iran (MIPS: Marun Industrial Petrochemical Solvent). Demineralized water (<0.5 µS/cm) was used for preparation of the desired solutions.

### 2.2. Methods

The aqueous feed solutions were prepared by dissolving an appropriate amount of AgNO<sub>3</sub> in demineralized water. The pH of each solution was adjusted by dilute solutions of nitric acid or sodium hydroxide. The organic solutions were prepared by dissolving the

**Table 1**  
The specifications of the industrial paraffinic solvent.

| Parameter   | Value        | Unit               |
|---|--------------|--------------------|
| <n-C <sub>10</sub>                                  | Max 0.5%     | Mole %             |
| n-C <sub>10</sub> <sup>+</sup> to n-C <sub>11</sub> | Min 40%      | Mole %             |
| n-C <sub>12</sub> <sup>+</sup> to n-C <sub>13</sub> | Max 50%      | Mole %             |
|   | Min 43%      |                    |
| >n-C <sub>13</sub>                                  | Max 56%      | Mole %             |
|   | Max 1.5%     |                    |
| Aromatic and water                                  | Max 100      | mg/kg              |
| Total sulfur content                                | Max 1        | mg/kg              |
| Kinematic viscosity                                 | 1.96 @ 20 °C | cSt                |
| Density   | 0.85         | g mL <sup>-1</sup> |

extractant (MEHPA or Cyanex 302) in MIPS in which the extractants dissolved quickly. Equal aliquots of the feed solution containing precise concentration of silver ions and an equal volume of the organic solution (O: A = 1:1) containing Cyanex 302 or MEHPA in MIPS were mixed in the thermostatic bath at the desired temperature until the equilibrium was established. The extraction experiments were carried out in a thermostated bath (with accuracy of ±0.1 °C) equipped with a shaking basket (Julabo, SW-20C). The primary experiments indicated that 3 min of contact time was adequate to establish the extraction equilibrium, however, the mixing/contact time was adjusted at 10 min in all experimental conditions to ensure that the equilibrium was reached. Then, the mixture was carefully transferred into a separatory funnel and the aqueous phase was carefully separated and centrifuged for 10 min and next its equilibrium pH was measured. The pH values of the initial and equilibrated aqueous solutions were determined by a digital pH meter (Metrohm model 700) and the viscosity of the organic phases were measured by a Stabinger viscometer (Anton Paar, SVM 3000) equipped with a precise thermostatic water bath (with accuracy of ±0.1 °C). Density (ρ) measurements of MEHPA and Cyanex 302 in industrial solvent at different temperatures were carried out using hydrometer (Anton Paar, DMA 4500 ME) based on the proven oscillating U-tube principle ensuring highly accurate density values.

### 2.3. Analysis

After the phase separation (around 20 s), an aqueous phase was carefully separated from the organic phase. The concentration of silver ions in the aqueous phase was analyzed by the Atomic Absorption Spectrophotometer (AAS) Model, PerkinElmer AA 700 after suitable dilutions with 0.05 M HNO<sub>3</sub>. In most cases, for silver analysis, the samples were diluted to the concentration of 5–10 mg/L in order to bring it within the linear working range of the equipment sensitivity. The concentration of silver ions in the organic phase was calculated from the difference between the aqueous phase concentrations before and after extraction. The distribution coefficient was calculated from the ratio of metal ion concentrations in organic/aqueous phases. The extraction efficiency (%) was calculated using Eq. (1).

$$E = \left[ \frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

where, C<sub>0</sub> is the initial concentration of metal ions in the feed solution and C<sub>t</sub> is the metal ion concentration in the feed solution after time interval, t.

## 3. Results and discussion

### 3.1. Determination of equilibrium contact time

The extraction of silver ions was studied by equilibrating solution containing 0.035 M of silver, 0.4 M MEHPA and 0.05 M Cyanex 302 at

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