Solvent Extraction of Silver from Nitric Acid Solution with a Mixture of LIX84I and PC88A

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The solvent extraction of Ag(I) from nitrate solutions has been studied using a mixture of LIX84I and PC88A. The mixture showed significant synergism at a LIX84I/PC88A ratio of 0.8:0.2. In order to identify the extraction reaction, the effects of various parameters, such as the equilibrium pH value and extractant concentration, were studied based on the slope analysis method. From stripping studies, 3 mol/L of nitric acid was found to be the best stripping agent. This mixed extractant can be applied for the separation of Ag from a nitrate solution containing Ca, Si, Al, Re, and Ni.

1. Introduction

Silver is a precious metal that plays significant roles in many facets of human life [1]. It has been widely used in aesthetic, industrial, and technical fields due to its unique physical and chemical properties. Recently, its technical applications have been extended to producing brazing alloys, electrical and electronic products, photographic paper and film, and catalysts. In particular, Ag is the active species in Ag/ α -Al₂O₃, a series of catalysts used to manufacture acetaldehyde and formaldehyde from ethanol and methanol, respectively. The content of Ag in the catalyst can range from 10 – 40 wt% [2]. A large amount of spent catalysts are produced with the development of the petrochemical industry and considering the cost and potential toxicity of Ag, they will become an important alternative resource of Ag [3, 4]. Hydrometallurgical treatment is a popular technique to recover Ag from these resources, in which Ag and other minor elements are first leached using lixiviants such as nitric acid, hydrochloric acid, and cyanide solutions.

Solvent extraction is a selective method in the hydrometallurgical treatment of metals, ranging from laboratory- to industrial-scale operations. Extraction and separation of Ag from nitric acid, hydrochloric acid, and cyanide solutions have been investigated using individual extractants [5-14]. Synergistic extraction systems, which are different combinations of extractants, have also been studied for increasing the extraction efficiency or improving the selectivity for Ag. 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone in the presence of organophosphorus donors (TBP, TOP, TOPO) was used to extract silver from nitric acid solution at pH 3.0. Synergistic enhancement factors, *R*, ranged from 1.9 – 4.7 were obtained [15].

A literature survey suggests that few efforts have been made to extract Ag with LIX84I or its mixture with acidic extractants like PC88A. In our previous experiments (unpublished) of binary mixtures of the chelate extractant, LIX84I, and various acidic extractants (PC88A, Versatic 10, D2EHPA), we found that

adding PC88A to LIX84I could increase the efficiency of Ag extraction from nitric acid solutions. Therefore, some fundamental studies on the synergistic solvent extraction of Ag from nitric acid solutions were performed using a mixture of LIX84I and PC88A. In order to identify the extraction mechanism, the effects of some parameters, such as equilibrium pH and extractant concentration, were investigated. Finally, the feasibility of applying the mixture for the separation of Ag from nitrate solutions containing Ca, Si, Al, Re and Ni, is demonstrated.

2. Experimental

2.1 Reagents

2-hydroxy-5-nonyl acetophenone oxime (LIX84I, BASF, USA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A, 95%, Daihachi, Japan) were used as-received without further treatment. Kerosene (98 %, Daejung, Korea) was used as the diluent. The Ag solution was prepared by dissolving AgNO_3 (99.8 %, Daejung, Korea) in deionized water. HNO_3 (60 %, Daejung, Korea) was used to adjust the pH of the solution. All other reagents employed in this work were of analytical grade.

2.2 Solvent extraction procedure

Solvent extraction experiments were carried out by mixing equal volumes (20 mL) of aqueous and organic phases for 30 min using a shaker (VS-8480SF, Vision Scientific Co., LTD) at ambient temperature. Previous experiments showed 30 min was sufficient to reach equilibrium. After separation, the equilibrium pH value was measured with a pH meter (Thermo Orion Star A211). The concentration of metal ions in the aqueous phase was measured using an ICP emission spectrometer (ICPS-7500, Shimadzu). The concentration of metal ions in the organic phase was obtained by calculating the difference between the metal ion concentration in the aqueous phase before and after extraction. The distribution ratio, D , was calculated as the ratio of the concentration at equilibrium of the metal present in the organic phase to that in the aqueous phase.

3. Results and Discussion

3.1 Extraction of Ag with PC88A

Extraction of Ag from a nitric acid solution using PC88A as the extractant was investigated using the slope analysis method. The effect of the equilibrium pH on the extraction was investigated by varying the initial pH from 0 through 3, while the concentrations of PC88A and Ag were maintained at 0.5 and 0.001 mol/L, respectively. The results are presented as a plot

Figure 1. Extraction of Ag from nitric acid solution using PC88A as the extractant. (a) Plot of $\log D$ vs. equilibrium pH. (b) Plot of $\log D$ vs. $\log[\text{PC88A}]_2$.

of log D vs. equilibrium pH in Figure. 1 (a).

The extraction efficiency is found to increase with increasing equilibrium pH. The plot of log D vs. equilibrium pH is a straight line with a slope of 1.30 (~ 1), indicating the release of one mole of protons from the extractant during the extraction process. The effect of the concentration of PC88A on the extraction of Ag was investigated by varying the concentration of PC88A in the range 0.1–0.7 mol/L at a fixed initial pH of 3. The slope of the plot of log D vs. log PC88A (Figure. 1(b)) is 1.15 (~ 1), indicating that one mole of extractant was involved in the extraction. Since PC88A exists as a dimer [16], the extraction reaction can be represented as follows,

where $(\text{HA})_2$ denotes the dimer of PC88A.

The equilibrium constant, K , for eq(1) can be defined as,

$$K_{\text{ex}} = [\text{AgA}(\text{HA})][\text{H}^+] / \{[\text{Ag}^+][(\text{HA})_2]\} \quad (2)$$

$$K_{\text{ex}} = D[\text{H}^+] / [(\text{HA})_2] \quad (3)$$

Where

$$D = [\text{AgA}(\text{HA})][\text{H}^+] / [\text{Ag}^+] \quad (4)$$

Taking logarithm of Eq (4),

$$\log K = \log D - \text{pH} - \log [(\text{HA})_2] \quad (5)$$

The equilibrium concentration of the extractant was calculated by mass balance as follows,

$$[(\text{HA})_2] = [(\text{HA})_2]_{\text{initial}} - [\text{AgA}(\text{HA})] \quad (6)$$

The equilibrium constant was calculated by substituting the equilibrium concentration of the extractant, the value of the equilibrium pH and the distribution coefficients into eq.(5).

In the calculation of the equilibrium constant, the activity coefficients of the species were not considered, assuming they do not change significantly under the experimental conditions. The value of the equilibrium constant for Eq(1) was found to be 1.11×10^{-3} .

3.2 Extraction of Ag with LIX84I

Extraction of Ag from nitric acid solution using LIX84I as the extractant was

Figure 2. Extraction of Ag from nitric acid solution using LIX84I as the extractant. (a) Plot of logD vs. equilibrium pH. (b) Plot of logD vs. log[PC88A]₂.

investigated using the slope analysis method under conditions similar to that for PC88A. The concentration of Ag in the feed solution was fixed at 0.001 mol/L. Figure 2 (a) represents the effect of the equilibrium pH value on the extraction of Ag from the nitric acid solution with 0.5 mol/L of LIX84I. The extraction of Ag increases with increasing equilibrium pH. The plot of log D vs. the equilibrium pH is a straight line with a slope of 1.15 (~ 1), indicating the release of one mole of protons from the extractant during the extraction process. The effect of the concentration of LIX84I on the extraction of Ag was investigated by varying the concentration of LIX84I in the range 0.1– 0.7 mol/L at a fixed initial pH of 3. The slope of the plot of log D vs. log LIX84I (Figure 2 (b)) is 1.39 (~ 1), indicating that one mole of extractant is involved in the extraction. The extraction reaction can be represented as follows,

where HB denotes LIX84I.

The equilibrium constant of eq (7) was calculated using the same method as for Ag and PC88A. The value of the equilibrium constant for eq (7) was found to be 0.61×10^{-3} .

3.3 Extraction of Ag with a mixture of LIX84I and PC88A

Extraction of Ag from nitric acid solution using a mixture of LIX84I and PC88A as the extractant was investigated at an initial pH of 3.0. The total concentration of the binary mixture was maintained at 0.5 mol/L. The results are presented as a function of D to the mole fraction of LIX84I (X_{LIX84I}) in Figure 3. The distribution ratios of Ag using LIX84I and PC88A separately as extractants are also presented in Figure 3 for comparison. The individual extractant concentration is present at x-axis together with the same concentration of the extractant involved in the mixed extractant.

As shown in Figure 3, the extraction of Ag with PC88A or LIX84I alone increases with increasing extractant concentration. The maximum distribution ratios for Ag are 0.32 and 0.30 with 0.5 mol/L of LIX84I and 0.5 mol/L of PC88A, respectively. In the case of the mixed extractant, the distribution ratio of Ag increases from 0.30 to 4.55 (extraction percentage: 23% to 82%) with an increase in the mole fraction of LIX84I (X_{LIX84I}) from 0 to 0.8 and then decreases with a further increase in X_{LIX84I} . These results clearly indicate that there is synergism at $X_{\text{LIX84I}} = 0.8$. The magnitude of the synergism can be expressed by the synergistic enhancement factor, R, which is defined as,

$$R = D_{\text{mix}} / (D_{\text{LIX84I}} + D_{\text{PC88A}}) \quad (8)$$

where D_{mix} denotes the distribution ratio of the mixture of LIX84I and PC88A, while D_{LIX84I} and D_{PC88A} denote the distribution ratios of the individual LIX84I

Figure 3. Extraction of Ag from nitric acid solution using LIX84I, PC88A, and the mixture of LIX84I+PC88A. ([Ag] = 0.001 mol/L, initial pH = 3, [LIX84I+PC88A] = 0.5 mol/L.)

and PC88A solutions, respectively. For R, a value higher than 1 indicates synergistic extraction, whereas, a value lower than 1 suggests antagonism. The value of the synergistic enhancement factor obtained at a X_{LIX84I} of 0.8 is 7.34. The value of R for the synergistic extraction of Ag with 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone with TBP/ TOP/ TOPO, was 1.9 ~4.7. Thus, a significant synergism with the mixture of LIX84I and PC88A is demonstrated. The enhanced extraction efficiency may be related to an increase in the hydrophobic nature of the extracted complex, which occurs by the replacement of coordinated water molecules when PC88A is added to LIX84I.

3.4 Effect of the equilibrium pH value

In order to identify the extraction mechanism for Ag with a mixture of 0.4 mol/L of LIX84I and 0.1 mol/L of PC88A, the slope

analysis method was employed. The extraction experiments were carried out by varying the initial pH value of the feed solution in the range 1–3. The results are presented as a plot of log D vs. equilibrium pH in Figure 4. The distribution ratio of Ag increases with increasing equilibrium pH. The slope of the plot of log D vs. equilibrium pH is 1.01, suggesting that one mole of H^+ ions are liberated during the extraction process.

3.5 Effect of extractant concentration

The effect of the LIX84I concentration in the mixed extractant was investigated by varying the concentration of LIX84I in the mixture at fixed concentrations of PC88A (0.1 and 0.2 mol/L). The initial pH of the aqueous solution was 3.0. The results are shown in Figure 5 as a plot of log D vs. log [LIX84I]. The plots for both PC88A concentrations are linear and the slopes are approximately unity (1.46 and 1.35 at 0.1 and 0.2 mol/L PC88A, respectively). Similarly, the effects of varying the PC88A concentration at fixed concentrations of LIX84I are shown in Figure 6. The plots of log D vs. log [PC88A] are linear with slopes of approximately 0.3 (0.27 and 0.28 at 0.2 and 0.3 mol/L of LIX84I, respectively). The slope values in Figures 5 and 6 suggest that one mole of LIX84I and one mole of PC88A are involved in the extraction

Figure 4. Effect of equilibrium pH on the extraction of Ag from nitric acid solution using the mixture of 0.4 mol/L of LIX84I and 0.1 mol/L of PC88A. ($[\text{Ag}] = 0.001$ mol/L.)

Figure 5. Effect of LIX84I concentration on the extraction of Ag from nitric acid solution using the mixed extractants. ($[\text{Ag}] = 0.001$ mol/L, initial pH = 3.)

of Ag from the nitric acid solution. The deviation from the expected slope of unity when the PC88A concentration is varied can be explained by the amount of free LIX84I available. The increase in PC88A at a fixed concentration of LIX84I results in increasing molecular interaction between the two compounds, causing the concentration of free LIX84I in the solution to be reduced. Therefore, the slope of the plot is less than the expected value of unity. The same type of phenomenon was observed in the extraction of actinides by a mixture of thenoyltrifluoroacetone (HTTA) and tributyl phosphate (TBP), [17, 18] and the extraction of Pr by a mixture of Cyanex 301 and LIX63 [19].

Considering the effects of the equilibrium pH and the extractant concentration, the synergistic solvent extraction of Ag with a mixture of LIX84I and PC88A can be represented as follows.

where $(\text{HA})_2$ and HB denote the PC88A dimer and LIX84I, respectively.

The spectrophotometric data for the single LIX84 and PC88A extractants and that of their mixture are shown in Figure 7. Compared the spectrophotometric data for the mixture with that of the single extractants (PC88A/ LIX84), the decrease in intensity or disappearance of the peaks (3383cm^{-1} and 983cm^{-1} stand for N-H/O-H, P-OH, respectively) is probably due to the interaction between PC88A and LIX84I. A quantitative study will be carried out in future research.

3.6 Separation of Ag from associated metal ions by a mixture of LIX84I and PC88A

Silver is commonly associated with many metals, such as Ca, Si, Al, Re, and Ni, in spent Ag/ $\alpha\text{-Al}_2\text{O}_3$ catalysts and ores. In order to explore the

Figure 6. Effect of PC88A concentration on the extraction of Ag from nitric acid solution using the mixed extractants. ($[\text{Ag}] = 0.001 \text{ mol/L}$, initial pH = 3.)

Figure 7. The spectrophotometric data. a. 0.8 mol/L LIX84, b. 0.2 mol/L PC88A c. 0.8 mol/L LIX84+ 0.2 mol/L PC88A d. Loaded 0.8 mol/L LIX84+ 0.2 mol/L PC88A

possibility of separating Ag from these associated metals, extraction experiments were carried out using a mixture containing 0.4 mol/L of LIX84I and 0.1 mol/L of PC88A. The concentration of each element in the aqueous solution was maintained at 0.001 mol/L and the initial pH value of the aqueous solution was varied from 1 to 4. As shown in Figure 8, when the equilibrium pH value is higher than 1.83 (the corresponding initial pH value is 2), more than 80 % of the Ag can be extracted, while extraction of the other metals is negligible. This result indicates that the mixture of LIX84I and PC88A can selectively separate Ag from the associated metals, which is of industrial importance.

3.7 Stripping studies

In a commercial extraction process, stripping is imperative to recover metal from the loaded organic phase. Stripping of Ag from the loaded mixture of LIX84I and PC88A was investigated using various stripping reagents (see Table 1). The loaded organic phase was obtained by shaking an aqueous solution, which had an initial pH of 3.0, with a mixture of 0.4 mol/L of LIX84I and 0.1 mol/L of PC88A (as described in the experimental section). Stripping experiments were carried out by shaking equal volumes of the loaded organic phase and stripping agent. The results are presented in Table 1. Ag can be stripped quantitatively (> 80 %) from the loaded organic phase with HNO₃, a mixture of thiourea and HNO₃, and 1 mol/L of Na₂S₂O₃. In the case of stripping with HNO₃, the stripping percentage of Ag increases with an increase in the HNO₃ concentration and complete stripping is obtained when the concentration of HNO₃ is 3 mol/L or higher.

Figure 8. Effect of the equilibrium pH on the extraction of Ag from associated metal ions using the mixture of 0.4 mol/L of LIX84I and 0.2 mol/L of PC88A.

Table 1. Effect of different stripping reagents on the stripping (%) of Ag from the loaded mixed extractant.

Reagent	Stripping (%)
0.1 mol/L Thiourea	54.5
0.1 mol/L Thiourea + 0.1 mol/L HNO ₃	84.5
0.1 mol/L Thiourea + 0.5 mol/L HNO ₃	85.0
0.01 mol/L HNO ₃	46.6
0.05 mol/L HNO ₃	78.1
0.1 mol/L HNO ₃	80.3
0.5 mol/L HNO ₃	81.2
1 mol/L HNO ₃	82.9
3 mol/L HNO ₃	100
5 mol/L HNO ₃	100
1 mol/L Na ₂ S ₂ O ₃	85.3
25% NH ₃ ·H ₂ O	nil
1 mol/L NH ₄ Cl	8.9
1 mol/L (NH ₄) ₂ SO ₄	9.2

4. Conclusion

The extraction of Ag from nitrate solutions has been studied using LIX84I and PC88A, separately, as well as in a mixture. The mixture of LIX84I and PC88A was found to show a synergistic effect on the

extraction of Ag. The maximum value of the synergistic enhancement (7.34) was obtained at a LIX84I mole fraction of 0.8. Based on the slope analysis results, the synergistic extraction reaction was identified and the extracted complex was proposed as $\text{AgH}_2\text{A}_2\text{B}$. Complete stripping of Ag from the loaded mixture of LIX84I and PC88A was possible using a nitric acid solution. The mixed extractant system can be applied to separate Ag from nitrate solutions containing Ca, Si, Al, Re, and Ni, which is important in practical separations.

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