Solvent Extraction of Precious Metals with o-(2-Ethylhexylthio)aniline and N-Phenyl-N’-[o-(2-ethylhexylthio)phenyl]thiourea

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Abstract
o-(2-Ethylhexylthio)aniline (ETA) and N-phenyl-N’-[o-(2-ethylhexylthio)phenyl]thiourea (PEPT) were newly synthesized in order to develop selective extractants for precious metals. These extractants were designed to form coordination bonds among metal ion, nitrogen and sulfur atoms and they were effective in the solvent extraction of precious metals. ETA was found to be highly selective palladium(II) and gold(III) over platinum(IV) and base metals. PEPT has selectively extracted palladium(II), gold(III) and platinum(IV) over base metals such as copper(II), nickel(II) and cobalt(II). The extraction equilibrium of gold(III) with ETA was reported from hydrochloric acid solution.

1 Introduction
The precious metals such as silver, gold, palladium and platinum are important metals in industries such as catalyst, battery and electronics. The high prices of these metals have stimulated the investigation of their separation, concentration and purification by solvent extraction techniques. The extraction technique of metal ions with chelating reagents has been used for hydrometallurgy and the treatment of wastewater. With the depletion of many high-grade ores, methods for effecting ore concentration have become increasingly important, and there is increased demand to process low-grade materials. [1] In recent years, the development of solvent extraction systems as an alternative for precious metals removal have been reconsidered. [2] Since separation and purification of these metals are the difficult process because of their chemical behavior in chloride media, it is essential to develop a more efficient recovery process for the extraction and separation. [3,4]

In this paper, the newly solvent extraction reagents, o-(2-ethylhexylthio)aniline (ETA) and N-phenyl-N’-[o-(2-ethylhexylthio)phenyl]thiourea (PEPT), which can expect the specific extraction behavior for precious metals, have been synthesized to examine the selectivity and extraction equilibrium for metal ion. The characteristics that ETA and PEPT can coordinate with both ‘hard’ nitrogen atom and ‘soft’ sulfur atom, leads to the complex formation with precious metals that is extractable into organic solvents.
2 Experimental

2.1 Reagent

ETA was synthesized from aminothiophenol and 2-ethylhexylbromide in DMF at 273 K by a conventional method. Water and chloroform were added to the reaction mixture and then the two phases were separated. Chloroform phase was washed by 1.0 M (M = mol dm$^{-3}$) hydrochloric acid, followed by 1.0 M sodium hydroxide. The product was purified by distillation under vacuum. The final product was brown liquid.

PEPT was synthesized from ETA and phenyl isothiocyanate in ethanol at 333 K. The residue was washed by methanol-water mixture. The product was recrystallized from hexane and ethyl acetate. The final product was white powder. The identification of these products was carried out using FT-IR, $^1$H-NMR and $^{13}$C-NMR spectra. The purity was verified to be about 97 and 96 % (ETA and PEPT), respectively.

2.2 Extraction experiments

Organic phase was prepared by diluting extractants with chloroform on a gravimetric basis. Aqueous solutions of metals were prepared by dissolving the metal chloride in hydrochloric acid. The initial concentration of each metal was about 1 x 10$^{-3}$ M. The measurement of extraction equilibria was carried out by a batchwise method. Equal volumes of aqueous and organic phases were shaken in the flask immersed in the thermostated water bath maintained at 30 °C to attain equilibrium. Equilibrium was reached within 24 h in the extraction of metals from the hydrochloric acid. The initial and equilibrium concentrations of metal in the aqueous phase were determined by using Hitachi model Z-8000 atomic absorption spectrophotometer.

3 Results and Discussion

3.1 Selectivity of ETA and PEPT for various metals from hydrochloric acid

Figure 1 shows the effect of hydrochloric acid concentration on the extraction of various metals with ETA. As seen from this figure, ETA can extract only palladium(II) and gold(III) over platinum(IV) and base metals such as copper(II), nickel(II) and cobalt(II). In addition, only palladium(II) among all the metals was almost completely extracted over the whole concentration region of hydrochloric acid. In particular, palladium(II) and gold(III) were extracted over platinum(IV). Figure 2 shows the effect of hydrochloric acid concentration on the extraction of various metals with PEPT. PEPT can almost completely extract mercury(II), palladium(II) and gold(II) over the whole concentration region of hydrochloric acid. Platinum(IV) was extracted only in the low concentration region of hydrochloric acid. PEPT can extract palladium(II) and gold(III) over base metals such as copper(II), nickel(II) and cobalt(II). Thus separation of precious metals from base metals was achieved.

The differences between ETA and PEPT were that platinum(IV) was extracted by PEPT in the low concentration region of hydrochloric acid and mercury(II) was completely extracted by PEPT over the whole concentration region of hydrochloric acid. Thus ETA has high selectivity for particular metals. ETA and PEPT have high affinity to precious metals because these two extractants have sulfur atom.
3.2 Extraction equilibrium of gold(III) with ETA.

ETA is an effective extractant for the separation of palladium(II) and gold(III) from base metals. A quantitative investigation was conducted on the extraction equilibrium of gold(III) from hydrochloric acid by examining the effect of the concentrations of reactant species on the distribution ratio to specify the extraction reaction and evaluate the equilibrium constants.

Figure 3 shows the effect of the hydrochloric acid concentration on the distribution ratio. The distribution ratio decreases with the increase in hydrochloric acid concentration.

Figure 4 shows the effect of the hydrogen ion concentration on the distribution ratio at a fixed concentration of the chloride ion ([Cl\(^-\)] = 2.0 M). The distribution ratio slightly decreases with the increase in the hydrogen ion concentration in the low hydrogen ion concentration region. In the high hydrogen ion concentration
region of the hydrogen ion, the distribution ratio abruptly decreases with the increase in the hydrogen ion concentration. In addition, Fig. 4 shows the effect of the chloride ion concentration on the distribution ratio at the fixed concentration of the hydrogen ion ([H+] = 0.1 M). The distribution ratio decreases with the increase in the chloride ion concentration.

Figure 5 shows the effect of the extractant concentration on the distribution ratio of gold(III). The distribution ratio increases with the increase in the extractant concentration. The plotted points appear to lie on straight lines with the slope of 1. From the results mentioned above, it can be concluded that gold(III) is extracted according to the following extraction reactions.

\[
\begin{align*}
RNS + H^+ + Cl^- & \rightarrow RNSHCl : K_{ex1} \\
RNS + AuCl_3 & \rightarrow RNSAuCl_3 : K_{ex2}
\end{align*}
\]

where the mass balance is expressed by following equation.

\[ [RNS]_0 \approx [RNS] + [RNSHCl] \]  

The distribution ratio is expressed from Eqs.(1) - (3) by follows,

\[ D = K_{ex2} [RNS]_0 \alpha_3 / (1 + K_{ex1} [H^+] [Cl^-]) \]

where \[ \alpha_3 = \beta_3[Cl^-]^3/(1 + \Sigma \beta_i[Cl^-]^i) \]
\[ \beta_1 = 3.2 \times 10^8 [M^{-1}], \beta_2 = 4.7 \times 10^{16} [M^{-2}], \beta_3 = 3.7 \times 10^{23} [M^{-3}], \beta_4 = 4.4 \times 10^{29} [M^{-4}] \] \[\text{[6]}\]

The extraction equilibrium constants were determined to be \( K_{ex1} = 4.9 [M^{-2}] \) and \( K_{ex2} = 8.5 \times 10^9 [-] \), respectively. The solid lines in Figs. 4 and 5 are the theoretical ones based on Eq.(4). The theoretical lines are in good agreement with the experimental results.

**References**