Recovery of Noble Metals by Hexadentate Ligand TPEN and Acidic Extractant D2EHPA

Kenji Takeshita1, Masaru Ishida1, Misako Kondo2, Yoshio Nakano2 and Yoshimi Seida3

1. Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503 Japan  E-mail: takeshit@res.titech.ac.jp
2. Department of Environmental Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502 Japan  E-mail: nakano@chemenv.titech.ac.jp
3. Department of Chemistry, Institute of Research and Innovation, 1201 Takada, Kashiwa 277-0861 Japan  E-mail:seida@iri.or.jp

ABSTRACT

A synergistic extraction system of trivalent gold ion (Au(III)) with an acidic extractant D2EHPA (di(2-ethylhexyl)phosphoric acid) and a hexadentate ligand TPEN (N,N,N',N'-tetrakis(2-pyridylmethyl)-1,2-ethylenediamine) was investigated and its applicability to the simultaneous recovery process of noble metals, Pd(II), Pt(II) and Au(III), from waste electric devices was discussed. Since Au(III) is present stably as an anionic complex, AuCl4^-, in aqueous chloride solution, Au(III) and noble metals cannot be recovered simultaneously by an acidic extractants such as D2EHPA. However, by the addition of TPEN in amounts equimolar with Au(III) in the aqueous phase, the extractability of Au(III) with D2EHPA was improved drastically. AuCl4^- is complexed strongly with TPEN in the aqueous phase and a cationic complex, Au(TPEN)3^+ is formed by the ligand exchange between chloride ion and nitrogen donor. The formation constant of Au(TPEN)3^+ was evaluated as about 10^{10} by the potentiometric titration technique. From these results, both the stoichiometry for the synergistic extraction of Au(III) with TPEN and D2EHPA (HR) and its extraction constant were determined as

\[ \text{AuCl}_4^- + \text{TPEN} + 3(\text{HR}) \rightarrow \text{Au}^{(\text{TPEN})R}3^+(\text{HR})_3 + 3\text{H}^+ + 4\text{Cl}^- \quad K_{ex}=10^{5.7} \]

TPEN acts as a powerful synergist for the extraction of Au(III) with D2EHPA. Thus, by introducing the proposed synergistic extraction system, Au(III) and other noble metals can be recovered simultaneously and effectively from aqueous chloride solution.

KEYWORDS

extraction, synergistic extraction, nitrogen-donor, TPEN, noble metal, gold, simultaneous recovery

INTRODUCTION

The recovery of noble metals, Au, Ag, Pd and Pt, from waste electric devices is very important from the viewpoint of resource protection. For example, about 0.01 g of gold is contained in a cellular phone.
This value corresponds to about 200 g of gold per 1 ton of waste phones. When considering that ore with the gold content of 10g/t is refined commercially, this fact indicates that waste electric devices are of great value as secondary resource (Shibata et al., 2002). So far many recovery processes of noble metals from scrap have been investigated. In these conventional processes, various extractants such as DBC(dibutylcarbitol), TBP(tributylphosphate) and D2EHPA (di(2-ethylhexyl)phosphoric acid) were used and the noble metals were recovered individually through several extraction processes (Zhao et al., 1998; Shijie et al., 1996). When the industrial-scale plant is operated, a large amount of secondary wastes are generated. If these noble metals are partitioned from base metals at the first stage of process, the generation of secondary wastes will be suppressed considerably. It is worthwhile to develop the simultaneous recovery process of noble metals.

The noble metals, Ag(I), Pd(II), Pt(II) and Au(III), are classified to soft metals by the Pearson’s HSAB (Hard and Soft Acids and Bases) theory. Therefore, the high selectivity of soft metals is required for the simultaneous recovery of noble metals. In the previous studies (Takeshita et al., 2003a; 2003b; 2004), a synergistic extraction system using an acidic extractant, D2EHPA, and a hexadentate ligand, TPEN, was proposed. TPEN has six nitrogen donors and is coordinated strongly with various metals, especially soft metals. The extraction separation of Cd(II) (soft metal) and Zn(II) was tested and it was found that the extractability of Cd(II) with D2EHPA was improved drastically by the addition of a slight amount of TPEN in the aqueous phase (Takeshita et al., 2003a). Next, a new extraction separation system of Cd(II) and Zn(II) with TPEN and Cyanex301 (di-(2,4,4,trimethy)dithiophosphonic acid) was investigated and the separation factor higher than 6500, which corresponds to about 300 times that without TPEN, was observed (Takeshita et al., 2003b; 2004).

In this study, the recovery of Au(III) by the synergistic extraction system with D2EHPA and TPEN and the extraction mechanism of Au(III) were investigated in details. Generally Au(III) is present as a stable chloraurate-complex ion, AuCl₄⁻, in aqueous chloride solution and cannot be extracted directly with an acidic extractant such as D2EHPA. However, the extractability of Au(III) with D2EHPA may be improved by the addition of TPEN in the similar manner as the previous study. Firstly, the complexation processes of TPEN and Au in the aqueous phase, namely the protonation of TPEN, the hydrolysis of Au(III) and the complexation of Au(III) and TPEN, were investigated by the potentiometric titration technique. Next, both the stoichiometry of extraction reaction and its equilibrium constant were evaluated quantitatively by the slope analysis technique. From these results, the applicability of this extraction process to the simultaneous recovery of Au(III) and other noble metals was discussed.

**EXPERIMENTAL**

**Synthesis of TPEN**

The synthesis procedure of TPEN was described in detail in the previous papers (Chang et al., 1990; Morss et al.,1997; Takeshita et al., 2003a). The summary of synthesis procedure was as follows. 2-(Chloromethyl)pyridine hydrochloride (60mmol, Wako Chemicals Co.LTD) in 5ml of water was
neutralized by adding 7.4 ml of 5.4 mol/L NaOH solution. Ethylenediamine (10mmol, Tokyo Kasei Co.LTD) was added dropwise in the solution. The pH value was kept in the range of 8.0 ± 0.1 by a pH-stat (AUT-501, DDK-TOA Co.) using 1mol/L NaOH solution. After stirred for 4 days, the white precipitate formed in the mixture was filtered off and washed several times with pure water. After drying, the precipitate was analyzed by elemental analysis, mass spectrometer, FT-IR and 1H-NMR. It was ascertained that the precipitate obtained was TPEN. The yield of TPEN was 30%

**Evaluation of complexation of TPEN and Au(III) in aqueous solution**

To clarify the extraction mechanism of Au(III) with TPEN and D2EHHPA, the protonation of TPEN, the hydrolysis of Au(III) and the complex formation of TPEN and Au(III) have to be investigated before the extraction tests. These complexation phenomena were analyzed by potentiometric titration technique. Three aqueous solutions dissolving TPEN (0.01M), HAuCl₄ (0.01M) and TPEN (0.01M) +HAuCl₄ (0.01M) mixture were prepared and titrated by an aqueous solution with NaOH (0.02M) and NaCl (0.09M). The potentiometric titrations were measured at 298K under N₂ atmosphere by an automatic titrator (AUT-501, DKK-TOA Co.). The titration curves were measured by adding dropwise the titrant in these aqueous solutions. From the features of curvature of these titration curves, the protonation constants of TPEN, the hydrolysis constants of Au(III) and the formation constant of Au-TPEN complex were determined by fitting the calculated titration curve to the experimental one. The calculation method of titration curve is described in details in the ‘Results and Discussion’.

The complex structure of Au and TPEN was studied by the UV absorption measurement. The content of TPEN in the aqueous solution was kept constant to 0.01M and that of Au was changed in the range of 0 to 0.023M. Seven aqueous solutions with different molar ratios of Au to TPEN were prepared. The ionic strength was adjusted to 0.1 by the addition of NaCl. The UV absorbance was measured in the range of 200 to 300 nm by a UV-VIS spectrometer (V-550, JASCO Co.).

**Extraction tests of Au(III) with D2EHHPA and TPEN**

Aqueous chloride solutions dissolving HAuCl₄ (2.54x10⁻⁴ mol/L), in which pH was adjusted in the range of 1 to 4, were prepared as aqueous phase. TPEN in amounts equimolar with Au(III) was added in the aqueous solutions. The ionic strength of these solutions was adjusted to 0.1 by addition of NaCl. 0.1, 0.25 and 0.5 mol/L D2EHHPA solutions diluted with toluene were prepared as organic phase. Equal volumes (10ml) of aqueous and organic solutions were placed in a vial, which was shaken vigorously at 25±0.1°C for 5min. After phase separation, the concentration of Au(III) in the aqueous phase was measured by an inductively coupled plasma spectrometer (ICPS-8100, Shimadzu Co.). The distribution ratio, D, defined as

\[ D = \frac{\text{concentration of Au(III) extracted in organic phase}}{\text{concentration of Au(III) remained in aqueous phase}} = \frac{C_{eq} - C_{aq}}{C_{aq}} \times \frac{V_{aq}}{V_{org}} \]  

(1)

was calculated from the concentration of Au(III) in the aqueous phase before and after the extraction.
operation, where \( C_0 \), \( C_{eq} \), \( V_{aq} \) and \( V_{org} \) denote the initial concentration of Au(III), the equilibrium concentration of Au(III), the volume of aqueous phase and that of organic phase, respectively. The changes in the distribution ratio with the initial concentration of D2EHPA and pH were measured.

RESULTS AND DISCUSSION

Protonation of TPEN in aqueous phase

The analysis of protonation of TPEN was studied in details in the previous paper (Takeshita et al., 2003a). By fitting the titration curve calculated from both the mass balance of TPEN and the charge balance to the experimental one, four dissociation constants of protonated TPEN molecules, defined as

\[
H(TPEN)^+ \rightarrow TPEN + H^+
\]

\[
K_1 = \frac{[TPEN][H^+]}{[H(TPEN)^+]} \tag{2}
\]

\[
H_2(TPEN)^{2+} \rightarrow H(TPEN)^+ + H^+
\]

\[
K_2 = \frac{[H(TPEN)^+][H^+]}{[H_2(TPEN)^{2+}]} \tag{3}
\]

\[
H_3(TPEN)^{3+} \rightarrow H_2(TPEN)^{2+} + H^+
\]

\[
K_3 = \frac{[H_2(TPEN)^{2+}][H^+]}{[H_3(TPEN)^{3+}]} \tag{4}
\]

\[
H_4(TPEN)^{4+} \rightarrow H_3(TPEN)^{3+} + H^+
\]

\[
K_4 = \frac{[H_3(TPEN)^{3+}][H^+]}{[H_4(TPEN)^{4+}]} \tag{5}
\]

were determined. The appropriate dissociation constants were given as \( K_1 = 10^{7.2} \), \( K_2 = 10^{4.8} \), \( K_3 = 10^{3.3} \) and \( K_4 = 10^{2.6} \), which were similar to those measured by Jensen et al. (Jensen et al., 2000).

**Figure 1** shows the pH dependence on the protonation of TPEN, which was calculated from the mass balance equation of TPEN substituting the appropriate \( K \) values. These results suggest that the protonation of TPEN has to be considered even in weakly acidic solution.

Complexation of Au(III) and TPEN in aqueous phase

In this section, both the hydrolysis of \( \text{AuCl}_4^- \) and the complex formation between Au(III) and TPEN are evaluated quantitatively. **Figure 2** shows the titration curve obtained from the aqueous solution dissolving 0.01M HAuCl₄, whose initial pH was adjusted to 2.0. For the hydrolysis of \( \text{AuCl}_4^- \), following reactions

\[
\text{AuCl}_4^- + H_2O \rightarrow \text{AuCl}_3(OH)^- + H^+ + \text{Cl}^- \quad \beta_1 = \frac{[\text{AuCl}_3(OH)^-][H^+][\text{Cl}^-]}{[\text{AuCl}_4^-]} \tag{6}
\]
\[
\begin{align*}
\text{AuCl}_3\text{(OH)}^- + H_2O &\rightarrow \text{AuCl}_2\text{(OH)}_2^- + H^+ + Cl^- & \beta_2 = \frac{[\text{AuCl}_2\text{(OH)}_2^-][H^+][Cl^-]}{[\text{AuCl}_3\text{(OH)}^-]} \\
\text{AuCl}_2\text{(OH)}_2^- + H_2O &\rightarrow \text{AuCl(OH)}_3^- + H^+ + Cl^- & \beta_3 = \frac{[\text{AuCl(OH)}_3^-][H^+][Cl^-]}{[\text{AuCl}_2\text{(OH)}_2^-]} \\
\text{AuCl(OH)}_3^- + H_2O &\rightarrow \text{Au(OH)}_4^- + H^+ + Cl^- & \beta_4 = \frac{[\text{Au(OH)}_4^-][H^+][Cl^-]}{[\text{AuCl(OH)}_3^-]}
\end{align*}
\]

should be considered. In the same manner as the analysis of protonation of TPEN (Takeshita et al., 2003a), the equilibrium constants, \( \beta_1 \) to \( \beta_4 \), can be determined by fitting the calculated titration curve to the experimental one. The titration curve can be calculated by solving simultaneously both the charge balance and the mass balance of Au(III). The charge balance is described as

\[
\left[\text{AuCl}_4^-\right]_0 + \frac{\beta_1}{[H^+][Cl^-]} + \frac{\beta_2}{[H^+][Cl^-]^2} + \frac{\beta_3}{[H^+]^2[Cl^-]} + \frac{\beta_4}{[H^+]^3[Cl^-]} + K_w + \frac{\text{v}_i}{v_i + \text{v}_\text{NaOH}} \cdot \frac{C_{\text{Na}^+}}{C_{\text{Na}^+}} = 0 
\]

where \( K_w, v_i, v_{\text{NaOH}}, C_{\text{Na}^+} \) and \( C_{\text{Na}^+} \) denote ionic product, initial volume of solution, volume of added titrant, initial concentration of Na\(^+\) and concentration of Na\(^+\) in titrant, respectively. Assuming that HAuCl\(_4\) is dissociated completely in the pH range above 2, the mass balance is described as

\[
v_i\left[\text{AuCl}_4^-\right]_0 - (v_i + v_{\text{NaOH}})\left[\text{AuCl}_4^-\right]_0 \left(1 + \frac{\beta_1}{[H^+][Cl^-]} + \frac{\beta_2}{[H^+][Cl^-]^2} + \frac{\beta_3}{[H^+]^2[Cl^-]} + \frac{\beta_4}{[H^+]^3[Cl^-]}\right) = 0
\]

The solid line in Fig.2 show a titration curve calculated from Eqs.(10) and (11). When the appropriate \( \beta \) values are selected, the calculated titration curve is in well agreement with the experimental data except the pH range above 8. In alkaline solution, the formation of Au(OH)\(_3\) participate has to be considered. The appropriate \( \beta \) values are determined as follows; \( \beta_1=10^{-5.7}, \beta_2=10^{-5.3}, \beta_3=10^{-5.3} \) and \( \beta_4=10^{-3.8} \).

Next, TPEN and HAuCl\(_4\) were added in the aqueous phase and the formation of Au-TPEN complex was observed by the UV-VIS spectrometer. The content of TPEN was adjusted in the range of 0.1 to 2.3 times the concentration of Au(III). Figure 3a shows the UV spectra in the wavelength range of 200 to 300 nm. The peaks at 235 and 260 nm are assigned as the absorption of Au-TPEN complex and free TPEN, respectively. Figure 3b shows the changes in these peak heights with the molar ratio of Au to TPEN. The peak height of TPEN decreases with increasing the molar ratio of Au to TPEN. This is because of the decrease in the concentration of free TPEN by the formation of Au-TPEN complex. For the change in the peak height of Au-TPEN complex (235 nm), the maximal absorption was observed at the Au-TPEN ratio of 1:1. This means that the ratio of Au to TPEN in the Au-TPEN complex is given as 1:1. Thus, the formation of Au-TPEN complex can be described as

\[
\begin{align*}
\text{AuCl}_3\text{(OH)}^- + 2\text{TPEN} &\rightarrow \text{Au-TPEN}_2^- + 2\text{H}^+ + 3\text{Cl}^- & \text{Max. Abs. at 235 nm, } \text{Au:TPEN = 1:1} \\
\text{AuCl}_2\text{(OH)}_2^- + \text{TPEN} &\rightarrow \text{Au-TPEN}_3^- + \text{H}^+ + 3\text{Cl}^- & \text{Max. Abs. at 260 nm, } \text{Au:TPEN = 1:2} \\
\text{AuCl(OH)}_3^- + \text{TPEN} &\rightarrow \text{Au-TPEN}_4^- + \text{H}^+ + 4\text{Cl}^- & \text{Max. Abs. at 300 nm, } \text{Au:TPEN = 1:3}
\end{align*}
\]
The equilibrium constant for the formation of Au-TPEN complex, $K_{TPEN}$, was determined by the potentiometric titration method. An aqueous solution with TPEN (0.02M), HAuCl$_4$ (0.02M) and HCl (0.09M) was prepared and titrated by an aqueous solution with NaOH (0.02M) and NaCl (0.09M) at 298K in N$_2$ atmosphere. Figure 4 shows the measured titration curve. The titration curve is quite different from that without TPEN (Fig.2). The titration curve was increased rapidly after 75ml of titrant was added. Such feature of titration curve indicates that the formation constant of Au-TPEN complex is very large. Both the mass balance of Au and the charge balance considering the formation of Au-TPEN complex were derived and the titration curve was calculated. Solid line in this figure represents the titration curves calculated under the condition that $K_{TPEN}$=10$^{10}$. This large value indicates that more than 99% of Au is complexed with TPEN in the pH range above 2 by the addition of TPEN in amounts equimolar with AuCl$_4^-$.

**Extraction of Au(III) with D2EHPA and TPEN**

In this section, the synergistic extraction of Au(III) with D2EHPA and TPEN is evaluated quantitatively. Figure 5 shows the effect of the addition of TPEN on the extraction of Au(III) with D2EHPA. In the case without TPEN (Fig.5(a)), no extraction of Au was observed in the wide range of pH and D2EHPA, however, by the addition of TPEN in amounts equimolar with Au(III) (Fig.5(b)), the
extraction behavior was improved drastically. The extraction percent increased with increasing the concentrations of D2EHPA and pH. These results suggest that the cationic Au-TPEN complex, \( \text{Am(TPEN)}^{3+} \), is extracted to the organic phase by the cation exchange with D2EHPA. Since D2EHPA is present as a dimmer in toluene, the cation exchange between \( \text{Am(TPEN)}^{3+} \) and D2EHPA dimmer, \( (HR)_2 \), can be represented as

\[
\text{Au(TPEN)}^{3+} + n(\text{HR})_2 \rightarrow \text{Au(TPEN)R}_n(\text{HR})_{2n-3} + 3\text{H}^+ \quad K_{\text{ex}}
\]

where \( K_{\text{ex}} \) and \( n \) denote the extraction constant and the number of D2EHPA dimmer coordinated with Au, respectively. As stated in the former section, most of Au(III) is coordinated with TPEN in the pH range above 2, when TPEN in amounts equimolar with Au(III) is added. Therefore, the presence of free Au(III) is not considered for the analysis of extraction mechanism.

The \( n \)-value of Eq.(13) can be determined by the slope analysis technique. The extraction constant \( (K_{\text{ex}}) \) is given as

\[
K_{\text{ex}} = \frac{[\text{Au(TPEN)R}_n(\text{HR})_{2n-3}][\text{H}^+]}{[\text{Au(TPEN)}^{3+}][\text{(HR)}_2]^n} = D \frac{[\text{H}^+]}{[\text{(HR)}_2]^n}
\]

where \( D \) denotes the distribution ratio defined as Eq.(1). Therefore, the logarithm of Eq.(14) is given as

\[
\log D + 3\log[\text{H}^+] = \log K_{\text{ex}} + n \log[(\text{HR})_2]
\]

Then, the concentration of free dimmer, \( [(\text{HR})_2] \), is given approximately as \( [(\text{HR})_2] \approx [(\text{HR})_2]_0 \) from the relation of \( [(\text{HR})_2]_0 \gg [\text{Au}]_0 \). Figure 6 shows the relation of \( (\log D+3\log[\text{H}^+]) \) vs. \( \log[(\text{HR})_2] \). The slope is given as about 3 and the extraction constant, \( K_{\text{ex}} \), is evaluated as \( 10^{-4.3\pm0.3} \) from the intercept value. Thus, the overall extraction reaction and its extraction constants \( (K_{\text{ex}}) \)
[mol³/L³]) are given as

\[
\text{AuCl}_4^- + 3(\text{TPEN})_2 \rightleftharpoons \text{Au}(\text{TPEN})_3(\text{HR})_3 + 3\text{H}^+ + 4\text{Cl}^- \quad K_{\text{ex}} = K_{\text{ex}} \cdot K_{\text{TPEN}} = 10^{5.7} (16)
\]

These results suggest that the synergistic extraction system with TPEN and D2EHPA is very powerful for the recovery of Au(III). Figure 7 shows the pH dependence on the complex formation in aqueous and organic phases. Au(III) forms Au(TPEN)³⁺ in the pH range above 1.5 and Au(TPEN)³⁺ is extracted to the organic phase as Au(TPEN)R₃(HR)₃ in the pH range above 2. Then, the formation of minor complexes such as the protonated TPEN and the hydrolyzed Au is suppressed completely, because the formation constant of Au(TPEN)R₃(HR)₃ is very large.

As stated in the ‘Introduction’ in this paper, Au(III), which is present as anion complex in aqueous chloride phase, cannot be extracted with an acidic extractant. However, by the addition of a slight amount of TPEN, Au(III) is extracted to the organic phase by the cation-exchange reaction between Au(TPEN)³⁺ and D2EHPA. These results indicate that Au(III) can be recovered effectively from the weakly acidic solution together with noble metal ions such as Pd(II) and Pt(II) by introducing this synergistic extraction system. In Fig.8, the results of extraction tests of Au(III) and Pd(II) in aqueous chloride solution were compared. The extraction of Pd(II) as well as Au(III) was improved drastically by the addition of TPEN. These results suggest that the synergistic extraction system with TPEN and D2EHPA is applicable to the simultaneous recovery process of noble metals.

CONCLUSIONS

(1) AuCl₄⁻ is complexed strongly with TPEN in the aqueous phase and converted to a cationic complex, Au(TPEN)³⁺ by the addition of TPEN in amounts equimolar with Au(III). The formation constant of
Au(TPEN)$^{3+}$ is evaluated as about $10^{10}$. Under these conditions, more than 99% of Au is complexed with TPEN in the pH range above 2 and then the formation of minor complexes, such as protonated TPEN and hydrolyzed Au, was suppressed completely.

(2) Au(III) is extracted to the organic phase by the cation-exchange reaction between Au(TPEN)$^{3+}$ and D2EHPA. Both the stoichiometry of extraction reaction and its extraction constant are given as

$$
\text{AuCl}_4^- + \text{TPEN} + 3(\text{HR})_2 \rightarrow \text{Au}^{3+}(\text{TPEN})\text{R}_3(\text{HR})_2 + 3\text{H}^+ + 4\text{Cl}^- \quad K_{\text{ex}}=10^{5.7}
$$

TPEN acts as a powerful synergist for the extraction of Au(III) with D2EHPA. By introducing the proposed synergistic extraction system, Au(III) and other noble metals can be recovered simultaneously and effectively from aqueous chloride solution.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. Kenneth L. Nash, Washington State University, U.S.A., for valuable discussions on the synthesis and complexation of TPEN.

REFERENCES


Takeshita, K., K.Watanabe, Y.Nakano and M.Watanabe, Solvent extraction separation of Cd(II) and Zn(II) with the organophosphorus extractant D2EHPA and the aqueous nitrogen-donor ligand TPEN, Hydrometallurgy, 70 , 63-71 (2003a)

