

## Extraction and Electrochemical Behaviors of Au(III) using Phosphonium-Based Ionic Liquids

**Authors :** Kyohei Yoshino, Masahiko Matsumiya, Yuji Sasaki

**Abstract :** Recently, studies have been conducted on Au(III) extraction using ionic liquids (ILs) as extractants or diluents. ILs such as piperidinium, pyrrolidinium, and pyridinium have been studied as extractants for noble metal extractions. Furthermore, the polarity, hydrophobicity, and solvent miscibility of these ILs can be adjusted depending on their intended use. Therefore, the unique properties of ILs make them functional extraction media. The extraction mechanism of Au(III) using phosphonium-based ILs and relevant thermodynamic studies are yet to be reported. In the present work, we focused on the mechanism of Au(III) extraction and related thermodynamic analyses using phosphonium-based ILs. Triethyl-n-pentyl, triethyl-n-octyl, and triethyl-n-dodecyl phosphonium bis(trifluoromethyl-sulfonyl)amide,  $[P_{222x}][NTf_2]$ , ( $X = 5, 8, \text{ and } 12$ ) were investigated for Au(III) extraction. The IL-Au complex was identified as  $[P_{2225}][AuCl_4]$  using UV-Vis-NIR and Raman spectroscopic analyses. The extraction behavior of Au(III) was investigated with a change in the  $[P_{222x}][NTf_2]$ IL concentration from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-1}$  mol  $dm^{-3}$ . The results indicate that Au(III) can be easily extracted by the anion-exchange reaction in the  $[P_{222x}][NTf_2]$ IL. The slope range 0.96-1.01 on the plot of  $\log D$  vs  $\log[P_{222x}][NTf_2]$ IL indicates the association of one mole of IL with one mole of  $[AuCl_4^-]$  during extraction. Consequently,  $[P_{222x}][NTf_2]$  is an anion-exchange extractant for the extraction of Au(III) in the form of anions from chloride media. Thus, this type of phosphonium-based IL proceeds via an anion exchange reaction with Au(III). In order to evaluate the thermodynamic parameters on the Au(III) extraction, the equilibrium constant ( $\log K_{ex}'$ ) was determined from the temperature dependence. The plot of the natural logarithm of  $K_{ex}'$  vs the inverse of the absolute temperature ( $T^{-1}$ ) yields a slope proportional to the enthalpy ( $\Delta H$ ). By plotting  $T^{-1}$  vs  $\ln K_{ex}'$ , a line with a slope range 1.129-1.421 was obtained. Thus, the result indicated that the extraction reaction of Au(III) using the  $[P_{222x}][NTf_2]$ IL ( $X=5, 8, \text{ and } 12$ ) was exothermic ( $\Delta H=-9.39$ - $11.81$  kJ mol $^{-1}$ ). The negative value of  $T\Delta S$  ( $-4.20$ - $5.27$  kJ mol $^{-1}$ ) indicates that microscopic randomness is preferred in the  $[P_{222x}][NTf_2]$ IL extraction system over  $[P_{22212}][NTf_2]$ IL. The total negative alternation in Gibbs energy ( $-5.19$ - $6.55$  kJ mol $^{-1}$ ) for the extraction reaction would thus be relatively influenced by the  $T\Delta S$  value on the number of carbon atoms in the alkyl side length, even if the efficiency of  $\Delta H$  is significantly influenced by the total negative alternations in Gibbs energy. Electrochemical analysis revealed that extracted Au(III) can be reduced in two steps: (i) Au(III)/Au(I) and (ii) Au(I)/Au(0). The diffusion coefficients of the extracted Au(III) species in  $[P_{222x}][NTf_2]$  ( $X = 5, 8, \text{ and } 12$ ) were evaluated from 323 to 373 K using semi-integral and semi-differential analyses. Because of the viscosity of the IL medium, the diffusion coefficient of the extracted Au(III) increases with increasing alkyl chain length. The  $4f7/2$  spectrum based on X-ray photoelectron spectroscopy revealed that the Au electrodeposits obtained after 10 cycles of continuous extraction and electrodeposition were in the metallic state.

**Keywords :** au(III), electrodeposition, phosphonium-based ionic liquids, solvent extraction

**Conference Title :** ICIL 2023 : International Conference on Ionic Liquids

**Conference Location :** Tokyo, Japan

**Conference Dates :** December 04-05, 2023