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XAFS study of Au complexes in the solvent extraction system

Hirokazu NARITA*[1], Mikiya TANAKA[1], Tsuyoshi YAITA[2], Yoshihiro OKAMOTO[2]
[1]Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
[2]Quantum Beam Science Directorate, Japan Atomic Energy Agency, Koto 1-1-1, Sayo, Hyogo 679-5148, Japan

Introduction

Solvent extraction techniques have been widely employed for the recovery of precious metals from chloride solutions [1]. We have studied O-donor and/or S-donor compounds as the gold extractants from HCl solution [2, 3]; however, the structure of the Au extracted complexes has not been clarified yet. Therefore, this work investigated the local structures of Au in the extracted complexes with *N,N*-di-*n*-octyl-hexanamide, DOHA ($(C_8H_{17})_2NC(O)\textit{n}\text{-}C_5H_{11}$), *N,N'*-dimethyl-*N,N'*-di-*n*-octyl-thiodiglycolamide, TDGA ($\{CH_3(\textit{n}\text{-}C_8H_{17})NC(O)CH_2\}_2S$) and di-*n*-hexyl sulfide, DHS ($(\textit{n}\text{-}C_6H_{13})_2S$).

Experimental

The extracted complexes were prepared by solvent extraction (org. phase: 0.5 M extractant in 2-ethylhexanol — aq. phase: 0.1 M Au in 1.0 M HCl) and then allowing to stand for 1d at room temperature. They were sealed in a polyethylene bag with a Teflon spacer. All of XAFS spectra were measured in transmission mode at the BL-9C station in the KEK-PF. The experimental data were analyzed by WinXAS Ver. 2.3 [4] and fit using theoretical phase and amplitudes calculated from the program FEFF 8 [5].

Results and Discussion

Figure 1 shows the XANES spectra of the solid state $HAuCl_4 \cdot 2H_2O$ (Ausol), Au in 1.0 M HCl solution (Auaq), the DOHA, DHS and TDGA extracted complexes. The XANES spectra are divided into two types: (1) Ausol, Auaq and DOHA; (2) DHS and TDGA. The Au in the solid and aqueous solution samples is trivalent and the shape of their XANES displays a typical trivalent one [6]; therefore, Au(III) is dominant in the DOHA extracted complex. Structural parameters of Auaq and the DOHA complex are determined from curve fitting. The obtained result indicates that the inner coordination sphere of Au(III) in the extracted complex is almost the same as that in the HCl solution (DOHA: 4.3 Cl atoms at 2.28 Å, Auaq: 4 Cl atoms at 2.28 Å); that is, $AuCl_4^-$ is dominant. This is consistent with the slope analysis result in the Au(III) extraction study with DOHA, which shows that an ion-pair reaction between $AuCl_4^-$ and the protonated DOHA likely occurs [3].

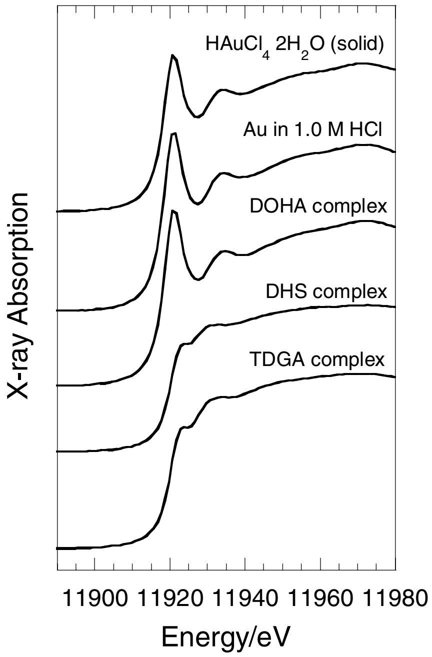

Fig.1 Au L_{III}-edge XANES spectra of the solid and solution states Au(III) samples and the extracted complexes.

For the DHS and TDGA extracted complexes, the XANES spectra show that the Au is probably monovalent [6]. This means that the extracted Au(III) was reduced to Au(I). Yuan et al. suggested that the reduction of Au(III) to Au(I) results in oxidation of the dialkyl sulfides [7]. To fully understand the mechanism of Au(III) binding and reduction by sulfur-containing extractants, more study is required.

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* hirokazu-narita@aist.go.jp