

XAFS analysis of $\text{UO}_2(\text{NO}_3)_x(\text{TcO}_4)_{2-x}(\text{TBP})_2$

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Introduction

In the nuclear fuel re-processing, technetium exists as per-technetate ion. The per-technetate ion is comparatively large tetrahedral structure which consists of four oxygen, while the effective charge is comparatively smaller than other anion. Therefore, it is extracted in ion pair as a pertechnetic acid by tri-butyl phosphate(TBP) easily. Furthermore, the per-technetate ion is co-extracted with counters ions such as UO_2^{2+} , Pu^{4+} and Zr^{4+} with TBP. However, there is few reported about structural analysis of these co-extracted complexes until now. In this study, the structural analysis of the co-extracted complexes were performed about Tc-complexes $\text{UO}_2(\text{NO}_3)_x(\text{TcO}_4)_{2-x}(\text{TBP})_2$ [1].

Experimental

The technetium samples were made as following procedure. 1 ml of n-dodecane as an organic solvent containing 30 % tri-butyl phosphate was shaken with the same volume of the various nitric acid containing 40 mM of UO_2^{2+} with about 0.7 M of TcO_4^- . After centrifugation, 0.45 ml of the organic solution was separated to use as a sample. 0.45 ml of Tc-U-TBP complex solution was enclosed in polyethylene tube. The XAFS measurement carried out at beam line BL27B. The absorption edges were 17.16 keV for U(L_{III}), and 21.05 keV for Tc(K).

Results and Discussion

The radial structural functions of Tc-K XAFS for Tc-U-TBP complex in dodecane prepared by the solvent extraction method is shown in Fig.1. The first peak in the sample is attributed to the four oxygen atoms of TcO_4^- ion. The bond distance of Tc-O, i.e. about 1.74 Å, agrees well with the previous data [2]. Generally, technetium is further extracted in the presence of U(VI) ion in the solvent extraction with TBP. Therefore, technetium is regarded to behave as a counter ion in the extraction of uranium. Accordingly, the peaks around 3.2 Å (in RSF) can be attributed to the Tc-U interaction. The curve fitting for the $\text{UO}_2\text{-TcO}_4\text{-NO}_3\text{-TBP}$ complexes of Tc-K XAFS is also shown in Fig.1. The bond distance of Tc-O and Tc-U are about 1.74 Å and 3.59 Å, respectively. These structural analysis data suggest that TcO_4^- ion coordinates to uranium with bidentate fashion instead of a nitrate ion in the Tc co-extraction system. The comparison of radial structural functions of U-L_{III} XAFS for $\text{UO}_2(\text{TcO}_4)(\text{NO}_3)(\text{TBP})_2$, $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ and $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ are shown in Fig.2. The U-O(O-Tc) and U-Tc of $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)(\text{TBP})_2$ are also confirmed, and a significant evidence of TcO_4^- for direct coordination to UO_2^{2+} . The distance of U-Tc is 3.60 Å, which well agrees with the Tc-K XAFS result. The interaction of uranium are mainly 5, U=O_{axial}, U-O_{eq1} (O=P), U-O_{eq2}

(O2-NO), U-O_{eq3} (O-Tc), and U-Tc. The bond distance of the U-O_{eq3} (O-Tc): 2.97 Å is longer than the U-O_{eq2} (O2-NO): 2.51 Å and U-O_{eq1} (O=P): 2.31 Å. Therefore, TcO_4^- would be weaker interaction than the other oxygen.

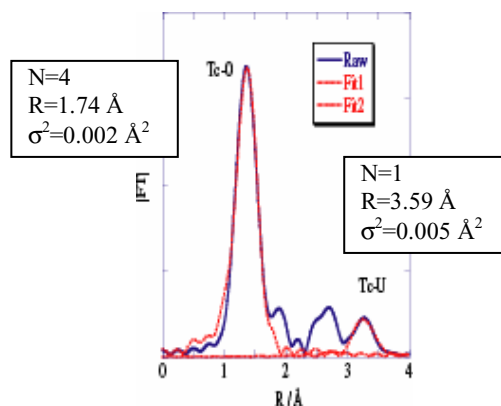


Fig.1. The radial structural functions and the curve fitting of Tc K-EXAFS spectra on the basis of $\text{UO}_2\text{-TcO}_4\text{-NO}_3\text{-TBP}$ model.

* The N, R, σ^2 present the coordination number, bond distance, and debye-waller factor, respectively.

**The phase shifts were not corrected.

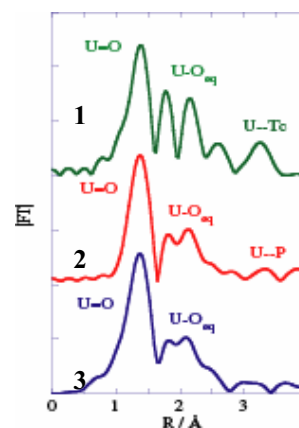


Fig.2. The comparison of radial structural functions of Tc-ligand complexes.

1 : $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)(\text{TBP})_2$, 2 : $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$, 3 : $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$

*The phase shifts were not corrected.

References

- [1] S.Suzuki et al., Physica Scripta, T115, 306(2005).
[2] P.G.Allen et al., Radiochimica. Acta, 76,77(1997)

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