

Evidence of Dimer Formation for the Uranium (VI) -Diglycolamide (DGA) Complexes in Solution

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Introduction

A number of studies concerning carboxylate compounds of uranyl in the solid state have been published^{1,2}. Furthermore, the crystal structures of the polyfunctional ligand iminodiacetate (IDA) and oxydiacetate (ODA) uranium complexes recently have been reported³. Elucidation of coordination structures of oxygen donor ligand to actinyl ion is significant on the standpoint of molecular design for separation agent for actinide. In this study, the uranyl (VI) complexes with the diglycolamide (DGA) derivative, *N,N'*-dimethyl-*N,N'*-diphenyl-diglycolamide (DMDPhDGA), one of the promising ligands for the separation of actinides from the high level radioactive waste, were determined in solution by EXAFS methods.

Experimental

Sample Preparation

All the chemicals were reagent grade (the purities were more than 99%). The sample solutions were prepared by the extraction of uranium (VI) with the DMDPhDGA in CHCl₃ from 3M HNO₃ solution. On the basis of the stoichiometry from the dependencies of the distribution ratio on metal concentration, two uranium are included in an extracted complex. The uranium concentrations were estimated to be 1mM from the distribution ratio.

EXAFS Measurement and Analysis

The U L_{III}-EXAFS spectra were measured in the fluorescence mode using 7 elements semi-conductive detector at the BL27B, PF of KEK. The data extraction and reduction of EXAFS oscillation from absorption spectra were carried out by WinXAS V.2.3⁴. The theoretical parameters for curve fittings of the EXAFS spectra were calculated using FEFF8⁵.

Results and Discussion

The radial structural function of U(VI)-DMDPhDGA complexes in solution is shown in Fig.1. The selected structural parameters were listed in Table 1. The interaction with uranium are mainly 5, U=O_{ax}, U-O_{eq1}, and 2 U-C, and U-U. Especially, the U-U interaction is a significant evidence for the formation of dimer like the model structure in Fig.1. The bond distance of U-U is about 4.0 Å, and agrees with the previous uranium study³ within fitting error. The small peak at 3Å is attributed to

the multiple scattering from the O=U=O. The DMDPhDGA usually behaves as a tridentate ligand. The bond distance between uranium and ether oxygen (U-O_{eq2}), however, is slightly large from the distance with oxygen of carbonyl (U-O_{eq1}), suggesting that DMDPhDGA coordinates with semi-tridentate fashion.

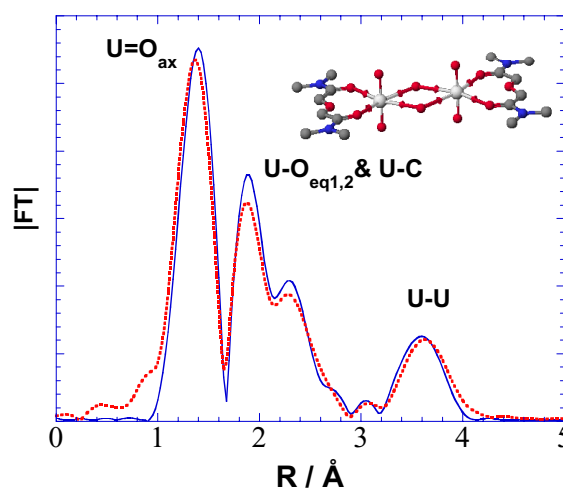


Figure1. The radial structural function of U(VI)-DMDPhDGA complexes in solution. Solid line: Raw data; Dotted line: fitting data

Table 1: Structural Parameters of U(VI)-DMDPhDGA complex

Interaction	N	R/Å	σ^2
U=O _{ax}	2	1.80	0.001
U-O _{eq1}	4	2.40	0.003
U-O _{eq2}	2	3.03	0.003
U-U	1	4.00	0.004

*N: coordination number; R: bond distance; σ^2 : Debye waller factor.

References

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