EXAFS Investigation of Th(IV)–N,N-Di-alkylamides Complexes

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Introduction
In our previous research work, the obtained bond distance between uranium(VI) and oxygen of N,N-dialkylamides are 2.40 Å for N,N-diocyt.butanamide (DOBA) and 2.31 Å for N,N-di(2-ethyl)hexyl(2,2-dimethyl)propanamide (D2EHDMPA) [1]. The bond distance of U(VI)-O=C(amide) depended on amides structure, especially carbonyl alkyl branching on α-position. In this study, we investigated Th(IV) complexes with these N,N-dialkylamides in the organic solution by extended X-ray absorption fine structure(EXAFS).

Experimental
N,N-dialkylamides: DOBA and D2EHDMPA were synthesized in our laboratory (Fig.1). The thorium samples were made as following procedures. 1) 1.0 ml of 1 M DOBA-n-dodecane as an organic solvent was shaken with the same volume of 5.0 M nitric acids containing 40 mM of Th4+. Equal volumes (0.5 mL) of aqueous and pre-equilibrated organic phases containing Th(IV) were shaken for 10 minutes in a thermostatic atmosphere at 298 K within ±0.1 K. After the equilibration, the system was centrifuged at 5000 rpm for 5 minutes. After centrifugation, 0.45 mL organic solution was separated and used as sample. 2) 0.5 mL of ethanol as an organic solvent containing 0.8 M DEH2DMPA was added to the same volume of ethanol solution containing 40 mM of Th4+. After mixture these solution, 0.45 mL ethanol solution was used as samples.

The EXAFS measurement was carried out at beam line BL27B station using the fluorescence and the transition methods. The measurement was carried out Th-LIII (16.30 keV) absorption edge. The extraction data of EXAFS oscillation from absorption spectra were carried out by WinXAS Ver. 3.1[2]. The theoretical parameters for curve fittings of the EXAFS spectra were calculated using FEFF 8.20 [3].

Results and Discussion

Figure 1a shows the raw k³-weighted Th LIII-edge EXAFS spectra and the corresponding fourier transforms (FT) of Th(IV)-DOBA complex in n-dodecane prepared by the solvent extraction methods. The first peak of the RSF is based on two oxygen atoms of DOBA and 4 oxygen atoms of the nitrate ions which coordinated to Th by bidentate fashion and 2 nitrogen atoms of nitrate ions. The obtained bond distance between Th(IV) and carbonyl oxygen of DOBA is 2.32 Å which is shorter than that of U(VI)-DOBA complex (2.40 Å ; which showed at introduction). This result shows that DOBA coordinates to Th(IV) more strongly than U(VI).

Figure 1b shows the raw k³-weighted Th LIII-edge EXAFS spectra and the corresponding fourier transforms (FT) of Th(IV)-D2EHDMPA complex in ethanol (Th : amide = 1 : 20). The first peak of the RSF is based on two oxygen atoms of water molecules and 4 oxygen atoms of the nitrate ions which coordinated to Th by bidentate fashion and 2 nitrogen atoms of nitrate ions. The obtained bond distance between thorium(IV) and oxygen of water molecule is 2.35 Å. This result means that Th(IV) does not combine with D2EHDMPA in ethanol solution, even if D2EHDMPA exists superfluously because the steric hindrance around carbonyl oxygen of D2EHDMPA increased with introducing tert-butyl group to carbonyl carbon atom.

References

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