EXAFS analysis of uranium(IV) and thorium(IV) complexes in concentrated CaCl_2 solutions

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Summary. The coordination of U^{4+} and Th^{4+} in concentrated CaCl_2 solutions is studied by U and Th L_{III} edge extended X-ray absorption fine structure (EXAFS) spectroscopy. With the decrease of concentration of CaCl_2 from 6.9 to 4 M, the Cl^- ion coordination number N_{Cl} in the U^{4+} coordination sphere decreases from 3.4 to 1.3, while the hydration number N_{O} increases from 4.5 to 6.7. The combined coordination number $N_{\text{O}} + N_{\text{Cl}}$ of U^{4+} in concentrated Cl^- solution (8.0), is lower than that in 1.5 M perchloric acid aqueous solution (9.0). For Th^{4+} , the decrease of concentration from 6.9 to 4 M CaCl_2 , the coordination number N_{Cl} in the Th^{4+} coordination sphere decreased slightly from 1.9 to 1.5, while coordination number N_{O} increased from 7.6 to 8.8. The $N_{\text{O}} + N_{\text{Cl}}$ of Th^{4+} in concentrated Cl^- solution (9.0), is similar to that in 1.5 M perchloric acid. The bond distance of U–Cl (2.67 Å), is shorter than that of Th–Cl (2.76 Å), because of low coordination number N_{O} to U^{4+} . By adding HCl into the system, the U^{4+} and Th^{4+} coordination sphere is unchanged. The coordination structures of U^{4+} and Th^{4+} in concentrated LiCl is also discussed.

1. Introduction

Highly concentrated aqueous solutions of inorganic electrolytes give a characteristic chemical behavior when compared to their behavior in the water abundant solutions [1]. This is related to the limited amount of water. In order to understand the speciation of *f*-elements in highly concentrated electrolytes, various spectroscopic analyses have been performed [2–11]. They included: electronic absorption spectrometry [2, 3]; fluorescence spectrometry [4]; emission lifetime analysis [5, 6]; and extended X-ray absorption fine structure, better known as EXAFS analysis [7–11]. According to our EXAFS measurements for UO_2^{2+} in concentrated calcium chloride (CaCl_2) solution, the coordination number of Cl^- in the coordination sphere of UO_2^{2+} decreased

from 2.2 to 1.8 with the increase of water content from 6.9 to 4.7 M CaCl_2 , while the coordination number of H_2O increased from 1.4 to 2.1 [3]. The bond distance between uranium and oxygen of the water molecule, $\text{U}-\text{O}_{\text{eq}}$, as determined for 14 M LiCl was found to be shorter than the value reported for 14 M LiCl + 0.01 M HCl [7]. This is because the interaction between H^+ ions and hydrate water molecule depresses the hydration of UO_2^{2+} , and this results in the longer bond distance of $\text{U}-\text{O}_{\text{eq}}$. On the other hand, enough data of U^{4+} in high concentrated chloride solutions has not been obtained because of the oxidation of U^{4+} in this environment. Hennig *et al.* [9] developed an electrochemical cell for *in-situ* EXAFS measurement to prepare U^{4+} from UO_2^{2+} by the controlled potential electrolysis in concentrated LiCl solutions. They found that the combined coordination number of Cl^- and H_2O of the U^{4+} species was 9 at low concentration of Cl^- and a smaller coordination number of 8 for 9 M LiCl.

In connection with tetravalent uranium, the coordination sphere of tetravalent thorium also has been studied and compared with that of U(IV) [12, 13]. Moll *et al.* [13] determined that the coordination number of H_2O for both ions is 10.8 ± 0.5 in 1.5 M perchloric acid. The distances in the U^{4+} and Th^{4+} coordination sphere are 2.42 ± 0.01 and 2.45 ± 0.01 Å, respectively. However, there are few reports which measured or reported the coordination sphere of Th^{4+} in high concentrated chloride solutions.

In the present study, we studied the coordination spheres of the U^{4+} and Th^{4+} in concentrated CaCl_2 and LiCl solution by EXAFS measurement. From the results obtained and the reported data [3, 4], we discuss the difference in the coordination environment of U(IV) and Th(IV) complexes for these concentrated media. EXAFS spectra in concentrated chloride ion with and without H^+ were measured.

2. Experimental

2.1 Sample preparation

Anhydrous uranium tetrachloride was prepared by the chlorination of U_3O_8 with CCl_4 at 723 K [14]. The product was identified by X-ray diffraction spectrometry (XRD) as well

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as by thermal gravimetric and differential thermal analyses (TG-DTA) to be the anhydrous UCl_4 . Thorium tetrachloride hydrate was prepared by adding hydrochloric acid to thorium nitrate pentahydrate and drying up the solution. This procedure was repeated for three times to completely exchange the nitrate ion of the salt for chloride ion. When pH was measured after dissolving the product in distilled water, the ratio of mol concentration of H^+ to that of the product dissolved was negligible. 6.9 M CaCl_2 ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) was melted at 323 K, and then the solution was used in the supercooled state at room temperature. The concentration of calcium chloride was adjusted by adding deionized water to 6.9 M CaCl_2 . Concentrated LiCl solutions (14 M) were prepared from anhydrous LiCl . The synthesized uranium tetrachloride was dissolved in the concentrated electrolyte solutions. Concentrations of U(IV) and Th(IV) in EXAFS samples were 0.04 M and 0.05 M, respectively. As references for EXAFS, two solutions were prepared: (1) a 0.04 M U^{4+} solution in 1.5 M HClO_4 and (2) a 0.05 M Th^{4+} solution in 1.5 M HClO_4 . All the chemical reagents were of reagent grade. Two cm^3 of each sample were sealed in a thin polyethylene bag which was fabricated for the X-ray measurement. A 5 mm thick Teflon plate, which has a hole of 8 mm diameter, was set inside the bag in order to keep the light path to be 5 mm. The sample preparations were carried out in the glove box in an argon atmosphere to avoid the oxidation of the metal ions. When the absorption spectra of these samples were measured after EXAFS experiments, the UV-Vis absorption peak corresponding to U(VI) was not observed. It was confirmed that U(IV) was not oxidized to form U(VI) since samples were prepared in an argon atmosphere and U(IV) was highly coordinated by Cl^- in concentrated Cl^- solutions.

2.2 EXAFS data acquisition and analysis

XAFS measurements were carried out in the BL27B beamline [15] of the Photon Factory at the High Energy Accelerator Research Organization (KEK), Japan. Hard X-ray ranging from 5 to 20 keV are available in this beamline with a Si(111) double-crystal monochromator. Monochromatic X-ray energy was calibrated by using copper and zirconium metal foil. XAFS measurements were performed based on the U L_{III} -absorption edge ($E_0 = 17.15$ keV) and Th L_{III} -absorption edge ($E_0 = 16.27$ keV). All solutions were measured in fluorescence mode using a Ge solid state detector at room temperature. The XAFS spectra were analyzed by using WinXAS ver. 3.1 code developed by Ressler [16]. Multiple XAFS scans were collected from each sample at ambient temperature (298 K), and the results were averaged. The EXAFS data were curve fit using theoretical phase and amplitudes calculated from the program FEFF 8 Rehr *et al.* [17]. The structures of UCl_4 [18] and $\text{U(H}_2\text{O)}_4(\text{SO}_4)_2$ [19] for U(IV) and $\text{Ba}_2\text{U(C}_2\text{O}_4)_4 \cdot 8\text{H}_2\text{O}$ for Th(IV) were used. Due to increasing noise levels at higher k -range, data analysis was restricted to the k -range 2.5–11.5 $\text{\AA}^{-1}$ for U^{4+} and Th^{4+} . The amplitude reduction factor, S_0^2 , was defined as 0.9 in the FEFF calculation and fixed to that value in the data fits. The fitted energy shift parameter, ΔE_0 , was linked for all shells. Bessel function was used as a window function for the Fourier transforms.

3. Results

3.1 U^{4+} complexes

Fig. 1a shows the k^3 -weighted EXAFS spectra for U^{4+} chloride solutions. Fig. 1b shows their corresponding Fourier transforms (FTs), along with those for U^{4+} in 1.5 M HClO_4 as a reference, *i.e.*, 0 M Cl^- . The perchlorate ion is known to be a noncomplexing ligand for actinide ions because of its weak coordination ability, especially in aqueous solution [20]. Therefore, actinide species in an aqueous perchlorate medium are considered to be pure hydrate complexes. The EXAFS spectrum of U^{4+} in 1.5 M HClO_4 consists of a single oscillation pattern, producing only one FT peak at $R + \Delta = 1.92$ $\text{\AA}$, which corresponds to the oxygen atoms of water molecules in the primary coordination sphere of the spherically coordinating U^{4+} . Structural results of the standard EXAFS shell fitting including phase correction are summarized in Table 1. The curve fit results for the spectrum shows that U^{4+} is surrounded by 9 water molecules at 2.40 $\text{\AA}$. Recently, the coordination number of water molecules N_0 in perchlorate medium is reported to be 9 and 10 as determined by EXAFS [9, 10, 13]. This is larger than the coordination number N_0 of 8 as determined by large-angle X-ray scattering [12]. According to the relativistic density functional theory, the coordination number N_0 of 9 was predicted [21].

EXAFS oscillation patterns gradually changed with decreasing Cl^- concentration from 6.9 to 4 M CaCl_2 (sample U-C, U-D, U-E and U-F in Table 1), especially in the k range over 9 $\text{\AA}^{-1}$. Their FTs display a systematic change with decreasing Cl^- concentration. The largest peak at $R + \Delta$

Fig. 1. U L_{III} -edge k^3 -weighted EXAFS data (a) and corresponding Fourier transforms (b) taken over $k = 2.5\text{--}11.5$ $\text{\AA}^{-1}$ for U^{4+} as a function of Cl^- concentration.

Table 1. EXAFS structural parameters for U⁴⁺ chloride solutions.

		[Cl ⁻] mol kg ⁻¹	U–O		U–Cl		N _O + N _{Cl}	ΔE ₀ (eV)
			N _O	R (Å)	N _{Cl}	R (Å)		
U–A	1.5 M HClO ₄	0	9.0 ± 1.4	2.40	–	–	9.0 ± 1.4	7.0
U–B	14 M LiCl	20.2	4.2 ± 0.6	2.42	3.7 ± 0.6	2.68	7.9 ± 0.8	7.4
U–C	6.9 M CaCl ₂	18.5	4.5 ± 0.7	2.40	3.4 ± 0.5	2.67	7.9 ± 0.8	5.9
U–D	6 M CaCl ₂	15.1	4.9 ± 0.7	2.39	3.1 ± 0.5	2.66	8.0 ± 0.9	5.2
U–E	5 M CaCl ₂	12.0	6.3 ± 0.9	2.42	1.8 ± 0.3	2.69	8.1 ± 1.0	6.7
U–F	4 M CaCl ₂	9.24	6.7 ± 1.0	2.43	1.3 ± 0.2	2.66	8.0 ± 1.0	6.1
U–G	6 M CaCl ₂ + 0.001 M HCl	15.1	5.5 ± 0.8	2.41	2.5 ± 0.4	2.68	8.0 ± 0.9	6.5
U–H	6 M CaCl ₂ + 0.1 M HCl	15.3	4.9 ± 0.7	2.41	3.2 ± 0.5	2.66	8.1 ± 0.9	6.2

Errors in distances R are ± 0.02 Å, errors in coordination numbers N are $\pm 15\%$. The Debye–Waller factor σ^2 was held constant for the shells U–O, $\sigma^2 = 0.009$ Å² and U–Cl, $\sigma^2 = 0.005$ Å², respectively. A k range of 2.5–11.5 Å⁻¹ was used.

$\Delta = 2.15$ Å in 6.9 M CaCl₂ shifts to a lower R range, while the largest peak is observed at $R + \Delta = 2.00$ Å in 4 M CaCl₂. As expected from the FTs in Fig. 1b, systematic changes are found for coordination numbers N_O and N_{Cl} as a function of Cl⁻ concentration as shown in Table 1. Here, a Debye–Waller factor σ^2 value of the U–O shell was fixed in the fit to be 0.009 Å² as obtained for the U⁴⁺ perchlorate solution, and that of the U–Cl shell was fixed to be 0.005 Å² assuming the same value as obtained for U(VI) [11]. The coordination number N_O increases gradually, while the coordination number N_{Cl} decreased with decreasing Cl⁻ concentration as shown in Table 1. This indicates that water molecules are replaced by Cl⁻ ion in high Cl⁻ concentration solutions. These results imply that UV-VIS-NIR absorption spectra change with Cl⁻ concentration as previously reported [3]. It is noted that the combined coordination number $N_O + N_{Cl}$ in concentrated Cl⁻ solutions (samples U–B to U–H) was 8, which is lower than that in 1.5 M HClO₄ aqueous solution. Decreasing of $N_O + N_{Cl}$ in 9 M LiCl was reported by Hennig *et al.* [9]. This is because the coordination sphere of U(IV) was occupied by Cl ion with a larger ionic size. However, the U–O and U–Cl bond distances are not significantly changing with the Cl⁻ concentration.

When 14 M LiCl (sample U–B) was used instead of CaCl₂ to compare the effect of cation size on the U⁴⁺ coordination, the coordination number N_O decreased and N_{Cl} increased compared with those in 6.9 M CaCl₂ (sample U–C). This suggested that coordination numbers are dependent upon the water activity of 14 M LiCl (0.11) and 6.9 M CaCl₂

(0.19) [22], *i.e.*, coordination number N_O is lower at the solution with lower water activity.

We have reported that the coordination structure of UO₂²⁺ was affected by addition of H⁺, *i.e.*, the U–O bond distance at high Cl⁻ concentration is shortened when H⁺ ions are added because of interactions between the H⁺ ion and the water molecules of UO₂²⁺ [11]. The effect of H⁺ ion on the coordination of U⁴⁺ in high concentration of Cl⁻ was investigated using 6 M CaCl₂ with 0.001 M HCl (sample U–G) or 0.1 M HCl (sample U–H). However, clear differences between sample U–D, U–G and U–H were not observed for the coordination numbers and bond distances.

3.2 Th⁴⁺ complexes

Fig. 2 shows the k^3 -weighted EXAFS spectra for Th⁴⁺ in chloride solutions (a) and their corresponding FTs (b), along with those for Th⁴⁺ in 1.5 M HClO₄ as a reference. The EXAFS spectrum of Th⁴⁺ in 1.5 M HClO₄ (sample Th–A) consists of a single oscillation pattern, producing only one FT peak at $R + \Delta = 1.92$ Å corresponding to the oxygen atoms of water molecules. Structural results of the standard EXAFS shell fitting including phase correction are summarized in Table 2. The curve fit results for the spectrum show that Th⁴⁺ is surrounded by 9.6 water molecules at 2.41 Å. Our results are less than that estimated by Moll *et al.* [13] in the same media.

EXAFS oscillation patterns gradually changed with decreasing Cl⁻ concentration from 6.9 to 4 M CaCl₂ (samples Th–C, Th–D and Th–E in Table 2). The peak position at $R +$

Table 2. EXAFS structural parameters for Th⁴⁺ chloride solutions.

		[Cl ⁻] mol kg ⁻¹	Th–O		Th–Cl		N _O + N _{Cl}	ΔE ₀ (eV)
			N _O	R (Å)	N _{Cl}	R (Å)		
Th–A	1.5 M HClO ₄	0	9.6 ± 1.4	2.41	–	–	9.6 ± 1.4	5.9
Th–B	14 M LiCl	20.2	4.7 ± 0.7	2.42	2.7 ± 0.4	2.76	7.4 ± 0.8	7.4
Th–C	6.9 M CaCl ₂	18.5	7.6 ± 1.1	2.41	1.9 ± 0.3	2.75	9.5 ± 1.2	9.0
Th–D	6 M CaCl ₂	15.1	7.7 ± 1.2	2.43	2.2 ± 0.3	2.76	9.9 ± 1.2	8.6
Th–E	4 M CaCl ₂	9.24	8.8 ± 1.3	2.42	1.5 ± 0.2	2.73	10.3 ± 1.3	7.6
Th–F	6 M CaCl ₂ + 0.001 M HCl	15.1	7.5 ± 1.1	2.44	1.9 ± 0.3	2.75	9.4 ± 1.2	9.0
Th–G	6 M CaCl ₂ + 0.1 M HCl	15.3	7.8 ± 1.2	2.44	2.0 ± 0.3	2.75	9.8 ± 1.2	8.9

Errors in distances R are ± 0.02 Å, errors in coordination numbers N are $\pm 15\%$. The Debye–Waller factor σ^2 was held constant for the shells Th–O, $\sigma^2 = 0.009$ Å² and Th–Cl, $\sigma^2 = 0.005$ Å², respectively. A k range of 2.5–11.5 Å⁻¹ was used.

Fig. 2. Th L_{III} -edge k^3 -weighted EXAFS data (a) and corresponding Fourier transforms (b) taken over $k = 2.5$ – $11.5 \text{\AA}^{-1}$ for Th^{4+} as a function of Cl^- concentration.

$\Delta = 1.92 \text{\AA}$ is almost independent of Cl^- concentration. With the increase of water content from 6.9 to 4 M CaCl_2 , coordination number N_{Cl} in the Th^{4+} coordination sphere slightly decreased from 1.9 to 1.5, while coordination number N_{O} increased from 7.6 to 8.8 as shown in Table 2 though 15% error for each plot was taken into account. Here, a Debye–Waller factor σ^2 value of the Th–O shell was fixed in the fit to $0.007 \text{\AA}^2$ as obtained for the Th^{4+} perchlorate solution, and that of the Th–Cl shell was fixed to $0.005 \text{\AA}^2$ assuming the same value for U(IV). It was also found that the combined coordination number $N_{\text{O}} + N_{\text{Cl}}$ in concentrated Cl^- solution was similar to that in 1.5 M HClO_4 aqueous solution.

The FT of 14 M LiCl (sample Th–B) was significantly changed compared with 6.9 M CaCl_2 (sample Th–C), a splitting of the FT peak was observed corresponding to well resolved Th–O and Th–Cl backscattering. The coordination number N_{O} in sample Th–B was lower and the coordination number N_{Cl} was higher than that in sample Th–C. It was noted that the combined coordination number $N_{\text{O}} + N_{\text{Cl}}$ in 14 M LiCl solution was about 8 which is lower than that of CaCl_2 series.

The effect of H^+ ion on the coordination of Th^{4+} in high concentration of Cl^- was investigated using 6 M CaCl_2 with 0.001 M HCl (sample Th–F) or 0.1 M HCl (sample Th–G). However, clear differences were not observed for the coordination numbers and bond distances.

4. Discussion

In perchloric acid solution (samples U–A and Th–A), the coordination number N_{O} of U^{4+} is 9.0, which is smaller than

that of Th^{4+} 9.6. According to the bond valence sum calculation [10], coordination number $N_{\text{O}} < 10$ of U^{4+} is smaller than that of Th^{4+} , 10. Results of the calculation agree with the result obtained in this experiment. On the other hand, coordination number N_{O} of both U^{4+} and Th^{4+} , 10.8 ± 0.5 , in similar condition reported by Moll *et al.* [13] was larger than those obtained in this study. The U–O bond distance, $2.40 \text{\AA}$, is similar to the Th–O bond distance, $2.41 \text{\AA}$. However, the U–O bond distance is about $0.03 \text{\AA}$ shorter than Th–O bond distance reported by Moll *et al.* [13].

In concentrated calcium chloride solutions (samples U–C to U–F and Th–C to Th–E), it is noted that the U–Cl bond distance, $2.67 \text{\AA}$, is significantly shorter than Th–Cl bond distance, $2.75 \pm 0.02 \text{\AA}$, while the U–O bond distance, $2.41 \pm 0.02 \text{\AA}$, is similar to the Th–O bond distance, $2.42 \pm 0.02 \text{\AA}$. Fig. 3 shows dependence of coordination numbers N_{O} and N_{Cl} for U^{4+} and Th^{4+} on the water activity in concentrated CaCl_2 and LiCl. The coordination sphere of U^{4+} is well affected by water activity, *i.e.*, the coordination number N_{Cl} to U^{4+} decrease and coordination number N_{O} increase with increase of water activity. This result indicates that ligands coordinated to U^{4+} are exchanged from Cl^- to H_2O with increase of water activity. On the other hand, coordination number N_{Cl} in the Th^{4+} coordination sphere slightly decreased from 1.9 to 1.5 and coordination number N_{O} slightly increased from 7.6 to 8.8 with increase of water activity.

These results indicate that the hydration of Th(IV) is stronger than that of U(IV) even in highly concentrated chloride solutions. The combined coordination number $N_{\text{O}} + N_{\text{Cl}}$ of U^{4+} was determined to be 8 which is obviously lower than those of Th^{4+} 9.5 because of low coordination number

Fig. 3. Dependence of coordination numbers N_{O} and N_{Cl} on the water activity $a_{\text{H}_2\text{O}}$ in concentrated CaCl_2 and LiCl. ●: N_{O} and ■: N_{Cl} in CaCl_2 , ○: N_{O} and □: N_{Cl} in LiCl. (a) is for U(IV), (b) is for Th(IV). Plot of $a_{\text{H}_2\text{O}} = 1$ shows sample A (1.5 M HClO_4).

N_O of U^{4+} . Since the stability constant of $U^{4+}-Cl$ ($\log \beta_1 = 2.6$) [23] is larger than that of $Th^{4+}-Cl$ ($\log \beta_1 = 2.0$) [24], the coordination number of Cl to U^{4+} should be larger than that to Th^{4+} in the same concentration of Cl. This trend was observed consistently and with those expected.

It is of interest that coordination number N_O of Th^{4+} in LiCl is quite smaller than that estimated from results of $CaCl_2$ systems (Fig. 3b). Hydration of Th^{4+} might be sensitive to the co-existed cations with strong polarizing power.

The effect of small amount of H^+ ion on the coordination of U^{4+} and Th^{4+} in high Cl^- concentration was investigated (samples U-D, U-G, U-H, Th-D, Th-F and Th-G), however, significant dependences of bond distances and coordination numbers were not observed. This suggests that the $U^{4+}-OH_2$ and $Th^{4+}-OH_2$ bond distances were not affected by adding of H^+ .

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