

EXAFS Studies of Uranium Ions in Calcium Chloride Hydrate Melts

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Introduction

Calcium chloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, has a melting point of 302 K. The molten $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is a concentrated electrolyte solution called "hydrate melt". Because of the limited amount of water, the chemical behavior of solute in it is different from that in usual aqueous solutions. In the present study, the coordination of UO_2^{2+} in CaCl_2 hydrate melts, $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$, was studied by U L_{III} edge extended X-ray absorption fine structure, EXAFS, spectroscopy.

Experimental*Sample preparation*

Calcium chloride hexahydrate (Fluka) was used as liquid after melting at 323 K. Uranyl dichloride hydrate, $\text{UO}_2\text{Cl}_2 \cdot n\text{H}_2\text{O}$, was prepared by drying up the aqueous solution containing UO_2Cl_2 with HCl. The UO_2^{2+} ion concentration used in the EXAFS measurements was 0.05 M (mol dm^{-3}).

EXAFS data acquisition and analysis

EXAFS measurements were carried out at BL27B beam-line of the Photon Factory in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. EXAFS measurements based on the U L_{III} -absorption edge ($E_0 = 17.180$ keV) were performed. All the solutions were measured in fluorescence mode using a Ge solid state detector. The EXAFS spectra were analyzed by using WinXAS ver. 3.1 code developed by Ressler [1].

Results

U L_{III} -edge k^3 -weighted EXAFS spectra and corresponding Fourier transforms, FT, are shown in Fig. 1. The FTs of the $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$ show axial oxygen atoms, O_{ax} , at 1.76 ± 0.02 Å, equatorial oxygen atoms, O_{eq} , at 2.41 ± 0.02 Å and an additional peak at the distance of 2.69 ± 0.02 Å indicative of Cl in the first coordination sphere. The intensity due to Cl increases with increasing chloride concentration (decreasing n). It should be noted that EXAFS analysis reflects only the average coordination and is not able to differentiate between coexisting species if the bond lengths are equal. Therefore, in the fit

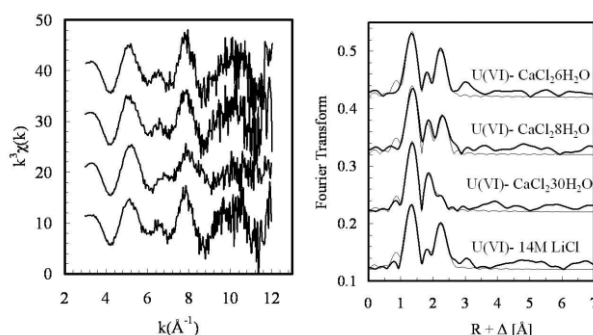


Fig. 1. U L_{III} -edge k^3 -weighted EXAFS data (left) and corresponding Fourier Transforms (right) taken over $k = 3 - 12$ Å⁻¹ for UO_2^{2+} as a function of hydration number, n in $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$: experimental data (bold line); theoretical curve fit (thin line).

procedure the bond lengths of possible solution species comprising $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{UO}_2(\text{H}_2\text{O})_{5-x}\text{Cl}_x^{2-x}$ are averaged to a common radial distribution. The Debye-Waller factors, σ^2 , were fixed for the EXAFS fit procedure to make the relation between O_{eq} and Cl comparable and avoid the correlation problems between coordination number, N , and σ^2 . The σ^2 for the U- O_{eq} and the U-Cl shell was fixed at 0.0075 and 0.0050 Å², respectively, as obtained from $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ in 0.1 M HClO_4 solution[2] and $\text{UO}_2\text{Cl}_4^{2-}$ [3]. With increasing the concentration of Cl⁻ (decreasing n), the coordination number N_{Cl} increased from 0.6 to 2.8 and the coordination number N_{Oeq} decrease from 3.5 to 1.5. These fit results indicate that even in a high concentration of Cl⁻ such as $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, a part of the equatorial shell consists of H_2O . The U-Cl distance remains nearly constant at 2.69 ± 0.02 Å for all samples. Coordination numbers N_{Cl} and N_{Oeq} in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ were similar to those in 14 M LiCl[3].

References

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