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EXAFS Studies of Uranium(IV) Ion in Calcium Chloride Hydrate Melts

Akihiro UEHARA[1,*], Toshiyuki FUJII[1], Haruaki MATSUURA[2], Nobuaki SATO[3],
Hajimu YAMANA[1] and Yoshihiro OKAMOTO[4]
[1]Division of Nuclear Engineering Science, Research Reactor Institute, Kyoto University,
2-1010, Asashironishi, Kumatori, Osaka, 590-0494, Japan
[2]Research Laboratory for Nuclear Reactor, Tokyo Institute of Technology,
2-12-1, Ookayama, Meguro, Tokyo, 152-8550, Japan
[3]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1, Katahira, Aoba, Sendai 980-8577, Japan
[4]Quantum Beam Science Directorate, Japan Atomic Energy Agency,
2-4, Shirakatashirane, Tokai, Ibaraki 319-1195, Japan

Introduction

The molten hydrated salt, which is generally called hydrate melt, is a very highly concentrated electrolyte. Because of the limited amount of water, the hydrate melt gives a characteristic chemical behavior to solutes within it. Allen et al. [1] and Hennig et al. [2] have recently investigated the structure of UO_2^{2+} and U^{4+} complexes in concentrated LiCl solutions by EXAFS spectrometry. In the present study, we studied the coordination spheres of the U^{4+} in $CaCl_2{\cdot}nH_2O$ and concentrated LiCl solution by EXAFS measurement.

Experimental

Sample preparation

Calcium chloride hexahydrate (Fluka) was used as liquid after melting at 323 K. Uranium tetrachloride hydrate, UCl_4, was synthesized from Uranyl nitrate hydrate with hydrogen chloride at 623 K. The U^{4+} ion concentration used in the EXAFS measurements was 0.02 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 [3].

Results

U L_{III}-edge k^3-weighted EXAFS spectra and corresponding Fourier transforms, FT, are shown in Fig. 1. The three peaks were observed at $\Delta + R$ = 1.3, 1.9, and 2.2 Å in FT. The second and third far peaks were assigned to be the coordinations of U–O and U–Cl. Since no acid exists in our U^{4+} systems, if U^{4+} is partly oxidized to be UO_2^{2+}, the XAFS spectrum should possesses a peak at a shorter distance corresponding to axial oxygen atoms, $U–O_{ax}$, of UO_2^{2+} (1.76 Å). To verify this, the UV-VIS absorption spectra of all samples were checked. It was found that, in the absence of HCl, the U^{4+} was not oxidized to form UO_2^{2+}. The similar peak has been observed in the EXAFS spectrum for 9 M LiCl + 0.1M HCl [2], in which its origin was not clarified. According to a structural study by the density functional theory [4], the U–O distance of a hydrolysis species $U(OH)_2^{2+}$ was calculated to be 1.92 to 2.14 Å. This is shorter than the U–O distance corresponding to the hydration (2.45 Å). The first peak possibly originates from the hydrolysis. The most possible second and third far peaks were tentatively analyzed under the assumption that the first peak can be excluded. The Debye-Waller factor, σ^2, value of the U–O shell was fixed in the fit to 0.0070 $Å^2$, as obtained for the U^{4+} aquo ion, and that of the U–Cl shell was fixed to 0.0050 $Å^2$ assuming the same value as obtained for UO_2^{2+}. The coordination numbers N_O and N_{Cl} in $CaCl_2{\cdot}6H_2O$ were close to those in 14 M LiCl even in similar concentration of Cl^-. The coordination circumstance of U^{4+} would not be affected by the kinds of the cations in the concentrated solution.

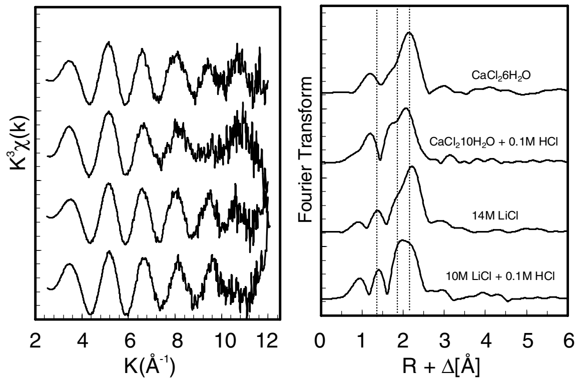

Fig. 1. U L_{III}-edge k^3-weighted EXAFS data (left) and corresponding Fourier transforms (right) taken over k = 2.6 – 12 $Å^{-1}$ for U^{4+}.

References

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*auehara@rri.kyoto-u.ac.jp