

EXAFS Studies of Thorium(IV) Ion in Concentrated Chloride Hydrate Melts

Akihiro UEHARA^{1,*}, Toshiyuki FUJII¹, Haruaki MATSUURA²,
Hajimu YAMANA¹ and Yoshihiro OKAMOTO³

¹Division of Nuclear Engineering Science, Research Reactor Institute, Kyoto University,
2-1010, Asashiro Nishi, Kumatori, Sennan, Osaka, 590-0494, Japan

²Research Laboratory for Nuclear Reactor, Tokyo Institute of Technology,
2-12-1, Ookayama, Meguro, Tokyo, 152-8550, Japan

³Quantum Beam Science Directorate, Japan Atomic Energy Agency,
2-4, Shirakatashirane, Tokai, Ibaraki 319-1195, Japan

Introduction

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 behaviour to solutes. Dependence of the activity coefficient of ions on the water content shows a different trend compared to that in the water-abundant solutions [1]. In order to clarify the characteristic variation of the activity coefficient of ions of *f*-elements in hydrate melts, some spectroscopic analyses have been performed. These are: electronic absorption spectrometry; fluorescence spectrometry; emission lifetime analysis; and extended X-ray absorption fine structure, better known as EXAFS analysis [2-4]. In the present study, we studied the coordination spheres of the Th⁴⁺ ion in CaCl₂·6H₂O melt and concentrated CaCl₂ solution by EXAFS measurement.

Experimental

Sample preparation

Calcium chloride hexahydrate (Fluka) was used as liquid after melting at 323 K. Thorium chloride, ThCl₄, hydrate was prepared from thorium nitrate hydrate with hydrochloric acid at 623 K. The thorium 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 Th L_{III}-absorption edge ($E_0 = 16.27$ 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 [5].

Results

Figure 1 shows the k^3 -weighted EXAFS spectra for Th⁴⁺ 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 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. The curve fit results for the spectrum (1.5 M HClO₄) shows that Th⁴⁺ is surrounded by 9.6 water molecules at 2.41 Å. This hydration number

was less than that estimated by Moll et al. [6] for the same medium.

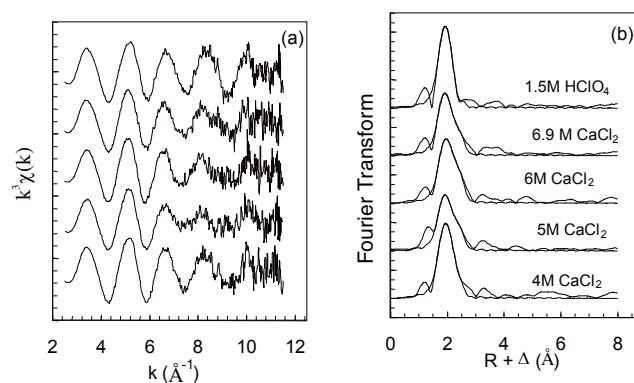


Fig. 1. Th L_{III}-edge k^3 -weighted EXAFS data (a) and corresponding Fourier transforms (b) taken over $k = 2.5 - 11.5$ Å⁻¹ for Th⁴⁺. Debye-Waller factor σ^2 value of the Th–O shell was fixed in the fit to 0.007 Å² as obtained for the Th⁴⁺ perchlorate solution, and that of the Th–Cl shell was fixed to 0.005 Å² as the same value for U(IV) [7].

In the series of CaCl₂ systems, EXAFS oscillation patterns gradually changed with the Cl⁻ concentration. The largest peak at $R + \Delta = 1.92$ Å was independent of the Cl⁻ concentration. With the increase of water content from 6.9 to 4 M CaCl₂, coordination number of chloride ion N_{Cl} in the Th⁴⁺ coordination sphere decreased from 1.9 to 1.5, while coordination number of water molecule N_O in it increased from 7.6 to 8.8. The combined coordination number $N_O + N_{Cl}$ in CaCl₂ solutions was the same with that in 1.5 M HClO₄ within the analytical uncertainty.

References

- [1] Y. Marcus, Ion Solvation Wiley, New York (1985).
- [2] P.G. Allen, et al., Inorg. Chem., 36 (1997) 4676.
- [3] C. Hennig, et al., Inorg. Chem., 44 (2005) 6655.
- [4] A. Uehara, et al., OECD-NEA, 15 (2009) 197.
- [5] T. Ressler, J. Synchrotron Radiat., 5 (1998) 118.
- [6] H. Moll, et al., Inorg. Chem., 38 (1999) 1975.
- [7] A. Uehara, et al., submitted.

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