

Structural study of zirconium in aqueous solution for transactinide element research

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Introduction

According to the actinide concept, the 5f electron series ends with element 103, lawrencium (Lr), and a new 6d transition metal, transactinide, series is predicted to begin with element 104, rutherfordium (Rf). So far, we have studied an anion-exchange behavior of Rf homologues together with the lighter Zr and Hf in HCl. The results have clearly shown that the behavior of Rf is quite similar to that of Zr and Hf, indicating Rf is the member of the group 4 elements [1]. To discuss the anion structure of Rf, Zr and Hf in HCl, we study structure of Zr in various concentration of HCl with the EXAFS method.

Experimental

ZrCl₄ were dissolved with 1 M to 11.5 M HCl. The concentration of Zr was adjusted to 0.01 M for each sample solution. Each sample was sealed in a polyethylene bag and set to the beam line of BL27B. The Zr-K edge EXAFS spectra were measured with the fluorescence mode using a 7-element pure-Ge solid state detector.

Results and Discussion

The Fourier transformed EXAFS spectra of the Zr-K edge are shown in Fig. 1, in which the phase shifts were not corrected. In the range of 1 to 10 M HCl, the most intense peak is observed at 1.77 Å that corresponds to the distance of the Zr-O bond. At > 9 M HCl, this peak broadens with the concentration of HCl due to the increase of the condition from the Zr-Cl bond at 2.0 Å. In 1 M to 5 M solution, the peak observed at 1.25 Å is originated from Z=O and its intensity decreases with the concentration of HCl. While in 1 and 3 M solution, an extremely characteristic peak derived from Zr-Zr is observed at 3.3 Å. This suggests that Zr forms a binuclear complex in these low concentrations. Thinking about the decrease of the intensity of the Zr=O peak and the growing up of the Zr-Cl peak with the HCl concentration, it is suggested that a Zr anion, such as [ZrCl₆]²⁻, is produced in the higher concentration of HCl solution by the substitution of the Zr=O to the Zr-Cl in terms of the insertion of Cl⁻ ions to the coordination positions. These dramatic changes of the ligands in the Zr anion provide the good account for the result of the adsorption behavior of Zr on the anion exchange resin [1]. In the next

experiments, we will try to reveal the structure of Hf in HCl solution.

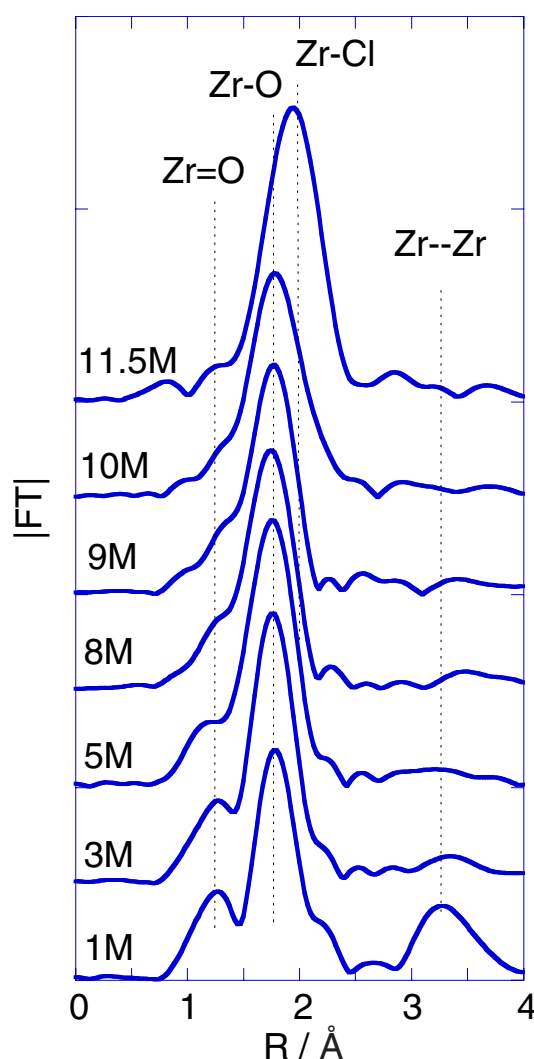


Figure 1. Fourier transformed EXAFS spectra of Zr-K edge:

Reference

[1] H. Haba et al., J. Nucl. Radiochem. Sci. **3**, 143 (2002).

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