Study on Solvent Extraction Behavior of Zirconium and Hafnium as Homologs of Rutherfordium (Element 104) with Chelate Extractant

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VI. 1. Study on Solvent Extraction Behavior of Zirconium and Hafnium as Homologs of Rutherfordium (Element 104) with Chelate Extractant

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Introduction

The elements with atomic numbers \( Z \geq 104 \) are called superheavy elements (SHEs). The SHEs can be produced only in the heavy-ion induced nuclear reactions. Because of short half-lives and low production rates of SHEs, chemical investigation of SHEs must be performed on atom-at-a-time scale. For these experimental restrictions, the chemical properties of SHEs are poorly known. In the region of SHEs, it is predicted that relativistic effects on orbital electrons may induce deviations from the periodicity of the chemical properties based on extrapolations from lighter homologs in the Periodic Table\(^{1,2}\). Therefore, the chemical studies of SHEs are extremely fascinating and challenging subjects.

We are planning to investigate the aqueous chemical behavior of element 104, rutherfordium (Rf). So far, aqueous chemical studies on Rf have been carried out mainly with inorganic ligands such as halide ions\(^{3,4}\). However, little has been reported on chemical experiments of Rf with organic ligands. In this study, as model experiments of Rf, we carried out the solvent extraction of zirconium (Zr) and hafnium (Hf), which are lighter homologs of Rf, using 2-thenoyltrifluoroacetone (TTA) as a chelate extractant.

Experimental

Radiotracers

Radiotracers of \(^{88}\text{Zr} (T_{1/2} = 83.4 \text{ d})\) and \(^{175}\text{Hf} (T_{1/2} = 70 \text{ d})\) were separately produced in the \(^{89}\text{Y} (p, 2n)\) and \(^{175}\text{Lu} (p, n)\) reactions, respectively, using the AVF cyclotron at Tohoku University. A pellet of \(\text{Y}_2\text{O}_3\) (190 mg/cm\(^2\)) and a Lu metal foil (125 \(\mu\)m thickness) were used as targets. The incident energy of the proton beam was 16 MeV. The produced
Radiotracers were chemically separated from the target materials through anion exchange separations and were stored in 1 M HNO₃ solution.

**Solvent extraction procedure**

Aqueous solution of 1 M HNO₃ (600 μL) containing ⁸⁸Zr and ¹⁷⁵Hf tracers was mixed with an equal volume of TTA in toluene solution in a polypropylene tube, and the mixture was mechanically shaken at 25 °C. After equilibration, the mixture was centrifuged for 30 seconds, and 420 μL aliquots of each phase were transferred to separate polypropylene tubes. The radioactivity of each phase was measured by a Ge detector, and the distribution ratio \(D\) was calculated as the ratio of radioactivity of organic phase to that of aqueous phase.

**Results and Discussion**

Figure 1 shows the dependences of \(D\) values of ⁸⁸Zr and ¹⁷⁵Hf in 1 M HNO₃ solution as a function of shaking time with TTA in toluene solution (0.01 M TTA for Zr and 0.025 M TTA for Hf). It seems that the \(D\) values of ⁸⁸Zr and ¹⁷⁵Hf become constant in shaking time of 5 hours. Therefore, we selected shaking time of 5 hours in the following experiments.

Figure 2 shows the log \(D\) vs. log [TTA] plot in 1 M HNO₃-TTA in toluene system. It is well-known that the chemical behavior of Zr is remarkably similar to that of Hf. However, the results showed that the \(D\) value of ⁸⁸Zr was approximately 10 times greater than that of ¹⁷⁵Hf. Therefore, it is very interesting to compare extraction behavior of Rf in this extraction system with that for Zr and Hf. A weighted least-squares fit to the data showed straight line with slopes of 3.3 for both Zr and Hf. The slope of this plot indicates the number of TTA molecules involved in the extraction reaction. Therefore, this result suggests that the main extracted TTA complexes of Zr and Hf possibly contains three TTA molecules and one OH⁻ or NO₃⁻ ion as ligand in this experimental condition. This would be confirmed through extraction experiments in 1 M HClO₄ solution because the formation of perchlorate complexes of metal ions may be neglected.

For solvent extraction experiments of Rf, rapid chemical operations are required because of its short half-life of around 1 min. For this purpose, we are developing rapid solvent extraction apparatus using flow injection analysis (FIA) technique⁵. In the near future, extraction experiments of Zr and Hf with the FIA system will be performed for Rf experiment.

**Acknowledgments**
We would like to thank the operating staff of AVF cyclotron at Tohoku University for providing the stable proton beam.

References


Figure 1. The dependence of distribution ratios of $^{88}$Zr and $^{175}$Hf as a function of shaking time. Aqueous phase is 1 M HNO$_3$ solution, and organic phase is TTA in toluene solution (0.01 M TTA for Zr and 0.025 M TTA for Hf).

Figure 2. The log D vs. log [TTA] plot in 1 M HNO$_3$-TTA in toluene system.