

Solvent extraction behavior of Zr and Hf with di(2-ethylhexyl)phosphoric acid for aqueous chemistry of Rf

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Studies on the complex formation of element 104, rutherfordium (Rf), in aqueous solutions have been mainly performed using inorganic ligands such as halide ions.^{1, 2)} Few experiments with organic ligands have been reported and little is known about the complex formation between Rf and organic ligands. In a previous study,³⁾ we reported the solvent extraction behavior of zirconium (Zr) and hafnium (Hf), which are lighter homologs of Rf, with a chelating agent, 2-thenoyltrifluoroacetone (TTA), to find suitable experimental conditions for complexation studies of Rf. As another candidate for the chelate extraction of Rf, di(2-ethylhexyl)phosphoric acid (HDEHP) was used in this study; HDEHP is widely used in analytical chemistry in addition to TTA, and many experimental data with HDEHP was reported in the analysis and discussion of our results.

Radiotracers of ⁸⁸Zr ($T_{1/2} = 83.4$ d) and ¹⁷⁵Hf ($T_{1/2} = 70$ d) were produced in the ⁸⁹Y($d, 3n$) and ^{nat}Lu(d, xn) reactions, respectively, using the RIKEN K70 AVF cyclotron. Metal foils of Y and Lu (of 100 and 125 μm thickness, respectively) were used as targets. The incident energy of the deuteron beam was 24 MeV. The produced radiotracers were chemically separated from the target materials through an anion exchange and a solvent extraction method. A perchloric acid solution of 600 μL containing ⁸⁸Zr and ¹⁷⁵Hf radiotracers was mixed with an equal volume of HDEHP in toluene in a perfluoroalkoxy (PFA) sample tube. The mixture was shaken for 2 hours at 25 °C. After centrifugation for 1 min, a 420 μL aliquot from each phase was separately pipetted into a polypropylene tube. The radioactivity of each phase was measured with a Ge detector, and the distribution ratio (D) was evaluated using the following equation:

$$D = (A_o/V_o)/(A_a/V_a), \quad (1)$$

where A denotes the radioactivity of either ⁸⁸Zr or ¹⁷⁵Hf, V is the volume of the aqueous or organic phase, and the subscripts a and o refer to the aqueous and organic phases, respectively.

The D values of ⁸⁸Zr and ¹⁷⁵Hf in 3 M HClO₄ are shown in Fig. 1 as a function of the HDEHP concentration in toluene. In the previous TTA extraction experiment,³⁾ the D values of Zr was 10 times that of Hf, while the order of the D values was reversed in the extraction with HDEHP as shown in Fig. 1. The reason for this difference between TTA and HDEHP extraction is a very interesting topic for the chemical studies of Rf as well as Zr and Hf chemistry.

However, at present, we need further investigation for the interpretation of this result. HDEHP is known to form a dimer species,⁴⁾ and the dimer of HDEHP coordinates to metal ions as chelating agent. Therefore, in the extraction of tetravalent metal ions (M^{4+}) with HDEHP, the extraction reaction would be described by the following equation:



From eq. (2), the $\log D$ vs. $\log [(\text{HDEHP})_2]$ plot is expected to show a linear relation with a slope of 4. This slope value indicates the number of HDEHP dimer molecules involved in the extraction reaction, and the extraction mechanism can be deduced from a slope analysis of the plot. A least-squares fit to the data in Fig. 1 showed a good linear relation with a slope of 3.9 ± 0.1 for both of ⁸⁸Zr and ¹⁷⁵Hf. Therefore, this result suggests that the main extracted species of Zr and Hf would be $\text{Zr}(\text{HDEHP} \cdot \text{DEHP})_4$ and $\text{Hf}(\text{HDEHP} \cdot \text{DEHP})_4$, respectively, in 3 M HClO₄. In 1 M HClO₄, the slope value of the $\log D$ vs. $\log [(\text{HDEHP})_2]$ plot was 3.0 ± 0.1 for both Zr and Hf. Because these two elements have a great tendency to hydrolyze, the formation of hydrolyzed species such as ZrOH^{3+} and HfOH^{3+} might affect the extraction process. This change of extraction mechanism with acid concentration was also observed in the previous results with TTA.

For the Rf experiment, a rapid solvent extraction experiment of Zr and Hf using the flow injection analysis (FIA) technique will be performed with the HDEHP and TTA extraction system.

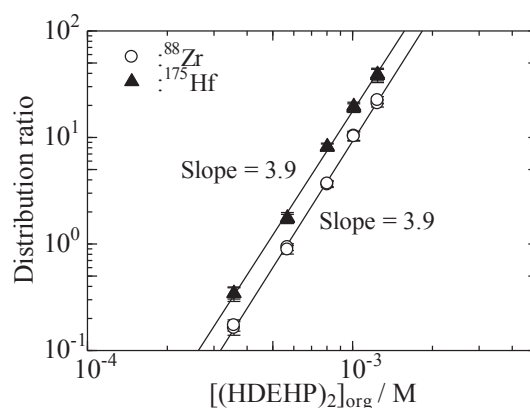


Fig. 1. Dependences of the distribution ratios of ⁸⁸Zr and ¹⁷⁵Hf in 3 M HClO₄ against the dimeric HDEHP concentration in toluene.

References

- 1) H. Haba et al., *J. Nucl. Radiochem. Sci.* **3**, 143 (2002).
- 2) H. Haba et al., *J. Am. Chem. Soc.* **126**, 5219 (2004).
- 3) A. Tanaka et al., *RIKEN Accel. Prog. Rep.* **48**, 288 (2015).
- 4) N. Miralles et al., *Anal. Sci.* **8**, 773 (1992).

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