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-thienyltrifluoracetone (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 were reported in the analysis and discussion of our results.

Radiotracers of 88Zr (T1/2 = 83.4 d) and 175Hf (T1/2 = 70 d) were produced in the 89Y(d, 3n) and 248Cm(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:

$$D = \frac{A_o V_o}{A_a V_a},$$  \hspace{1cm} (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 (MIV) with HDEHP, the extraction reaction would be described by the following equation:

$$M^{IV} + 4(HDEHP)_{2o} \rightleftharpoons M(HDEHP \cdot DEHP)_{4o} + 4H^+.$$  \hspace{1cm} (2)

From eq. (2), the log D vs. log ([(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 Zr(HDEHP·DEHP)4 and Hf(HDEHP·DEHP)4, respectively, in 3 M HClO4. In 1 M HClO4, the slope value of the log D vs. log ([(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 ZrOH3+ and HfOH3+ 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