Solvent extraction of Zr and Hf using soft ligands toward chemical study of Rf

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Superheavy elements $(Z \ge 104)$ are only synthesized using heavy-ion-induced nuclear reactions. These heavy nuclides generally have short half-lives and low production rates. This makes it difficult to investigate their chemical properties. Element 104, rutherfordium (Rf), is the lightest element in transactinide elements. Previous studies on the solution chemistry of Rf have reported that Rf exhibits similar chemical behavior to those of group 4 elements (Zr and Hf), and also that the interactions of Rf with hard bases, such as OH^- and F^- are weaker than those of group 4 elements.¹⁻³ We aim to explore the solution chemistry of Rf by solvent extraction experiments using hard and soft donor ligands. For this purpose, we focused on dialkyl phosphates and dialkyl dithiophosphates, and selected commercially available dibutyl phosphate (HDBP, (CH₃(CH₂)₃O)₂POOH) and diethyl dithiophosphate (HDEDTP, (CH₃CH₂O)₂PSSH) as extractants. It is known that HDBP can extract Zr from aqueous solution.⁴⁾ In this study, we performed solvent extraction of Zr and Hf tracers with the above reagents to investigate the applicability to 261 Rf ($T_{1/2} = 68$ s) experiments. We show the results of the time required to reach the solvent extraction equilibria of Zr and Hf.

We produced the ⁸⁸Zr and ¹⁷⁵Hf isotopes in the ⁸⁹Y(d, 3n) and ^{nat}Lu(d, xn) reactions, respectively, by using the RIKEN AVF cyclotron. In extraction, 1 M HNO₃ was used for aqueous phases, and 0.1 M HDBP or HDEDTP in CCl₄ was used for organic phases. The aliquot aqueous phase and organic phase were mixed and shaken for at least 1 hour to be equilibrated preliminarily. After centrifugation, both solutions were separated. Then, 10 μ L of 1 M HNO₃ containing ⁸⁸Zr or ¹⁷⁵Hf, 490 μ L of aqueous phase, and 500 μ L of organic phase were mixed and shaken for a certain time. After centrifugation, the solutions were separated into an organic and an aqueous phase. Distribution ratio D was determined from Eq. (1).

$$D = [\mathbf{M}]_{\mathbf{o}} / [\mathbf{M}]_{\mathbf{w}} = A_{\mathbf{o}} m_{\mathbf{w}} d_{\mathbf{o}} / A_{\mathbf{w}} m_{\mathbf{o}} d_{\mathbf{w}}$$
(1)

where [M] is the concentration of metal ions in each phase, A is the radioactivity of each phase, m is the mass of each phase, d is the density of each phase. Subscripts "o" and "w" indicate the value of the organic and aqueous phases, respectively. Solvent extraction experiments were performed at 20°C.

Figure 1 shows the dependence of the distribution ratio of Hf in the 1 M HNO_3/CCl_4 system. It was found that reactions in this system reached equilibrium

1000 ▲ HDBP 100 ▲ HDEDTP 10 Ω 1 0.1 * ^ 0.01 0 10 20 30 40 50 60 Shaking time / min

Fig. 1. Dependence of the distribution ratio of Hf in the 1 M $\rm HNO_3/\rm CCl_4$ system on shaking time.

in less than 1 min when either HDBP or HDEDTP was used. The results suggest that these reaction systems are suitable for ²⁶¹Rf experiments. Figure 2 shows the dependence of the distribution ratio of Zr in the 1 M HNO₃/CCl₄ system on the shaking time. Although the data having large errors are included, it is suggested that chemical reactions of Zr also reach to equilibrium state rapidly. In addition, the distribution ratios of Zr are found to be smaller than those of Hf. The distribution ratio using HDEDTP has not yet been obtained. We plan to obtain distribution ratios of Zr in extraction by HDBP and HDEDTP from 1 M HNO₃/CCl₄ with smaller errors to compare the extraction behavior of Zr and Hf and to investigate their chemical species extracted in this system.



Fig. 2. Dependence of the distribution ratio of Zr in the $1 \text{ M HNO}_3/\text{CCl}_4$ system on shaking time.

References

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