

## Solvent extraction of Rf in the Aliquat 336/HCl system using flow-type extraction apparatus

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Superheavy elements (SHEs) with  $Z \geq 104$  are synthesized by heavy-ion-induced nuclear reactions. It is very difficult to investigate the chemical properties of SHEs because of the low production rates and short half-lives of these nuclides.<sup>1)</sup> In the solution chemistry of SHEs, ion-exchange and extraction experiments were so far performed for mainly element 104, Rf and 105, Db. Especially for fluoride complexation, various interesting data were obtained.<sup>1)</sup> To deepen the understanding of the halide complexation of Rf, we aim at investigating the chloride complexation of Rf. In our previous studies, we investigated the solid-liquid extraction behavior of Rf using Aliquat 336 as an extractant by confirming the extraction reaction equilibrium for the first time.<sup>2,3)</sup> The distribution coefficient ( $K_d$ ) of Rf was acquired. In the results, the variation of the  $K_d$  value of Rf with HCl concentration showed a slightly different tendency from those of Zr and Hf, and the sequence of the  $K_d$  values was different from that for fluoride complexation. In this study, we developed an online solvent extraction apparatus and performed solvent extraction experiments of Zr, Hf, and Rf in the Aliquat 336/HCl system for further investigation of the chloride complexation of Rf.

We first investigated the dependence of the distribution ratios ( $D$ ) of Zr and Hf on Aliquat 336 concentration ([Aliquat 336]) by a batch method to determine the net charge of the extracted anionic chloride complexes. We used 7.8–11.2 M HCl as the aqueous phase and  $\text{CHCl}_3$  or  $\text{CCl}_4$  as the organic phase, and we used carrier-free radiotracers of  $^{88}\text{Zr}$  ( $T_{1/2} = 83.4$  d) and  $^{175}\text{Hf}$  ( $T_{1/2} = 70$  d).

Consequently, the slopes in the  $\log D$  versus  $\log$  [Aliquat 336] plots of Zr and Hf were both 1.9 in  $\text{CHCl}_3$  as shown in Fig. 1, suggesting that the bivalent chloride complex is extracted. On the other hand, the slopes in  $\text{CCl}_4$  were 1.2 for both Zr and Hf, which suggests that the monovalent chloride complex is dominantly extracted. These results imply that different chloride complexes (net charge) would be extracted for different organic solvents:  $\text{CHCl}_3$  and  $\text{CCl}_4$ .

A flow-type solvent extraction apparatus called the flow Injection Solvent Extraction apparatus (ISE), which is suitable for online extraction experiments with short-lived isotopes of SHEs, was developed and its performance was checked by solvent extraction with Zr and Hf. Subsequently, as a model experiment of Rf, the online liquid-liquid extraction using ISE was performed with the AVF cyclotron in the Research Center for Nu-

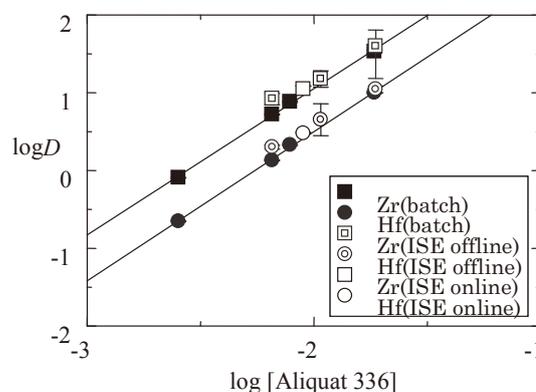


Fig. 1. Dependence of the  $D$  values of Zr and Hf on Aliquat 336 concentration in  $\text{CHCl}_3$  at 11.2 M HCl.

clear Physics, Osaka University (RCNP) by using  $^{89\text{m}}\text{Zr}$  ( $T_{1/2} = 4.18$  min) and  $^{173}\text{Hf}$  ( $T_{1/2} = 23.4$  h) produced in the  $^{\text{nat}}\text{Sr}(\alpha, xn)$  and  $^{\text{nat}}\text{Yb}(\alpha, xn)$  reactions, respectively. The  $D$  values acquired with ISE in 9.3–11.2 M HCl were in good agreement with those acquired by the batch method as shown in Fig. 1, suggesting applicability of the present method to the Rf experiment.

Recently, we produced  $^{261}\text{Rf}$  ( $T_{1/2} = 68$  s) and  $^{169}\text{Hf}$  ( $T_{1/2} = 3.24$  min) in the  $^{248}\text{Cm}(^{18}\text{O}, 5n)^{261}\text{Rf}$  and  $^{\text{nat}}\text{Gd}(^{18}\text{O}, xn)^{169}\text{Hf}$  reactions, respectively, by using the RIKEN AVF cyclotron, and carried out the solvent extraction of Rf in the Aliquat 336/HCl system (the organic solvent is  $\text{CHCl}_3$  or  $\text{CCl}_4$ ). The reaction products were transported by a He/KCl gas-jet system to the chemistry room and dissolved in 9.3 M HCl with a dissolution apparatus.<sup>3)</sup> The solution was injected to ISE. After phase separation by ISE, we collected the two phases on different Ta plates and the samples were assayed by alpha-particle measurement by the automated rapid  $\alpha$ /SF detection system. After alpha particle measurement, we measured  $\gamma$ -ray activities of  $^{169}\text{Hf}$  in the samples with Ge detectors.

We carried out 667 extraction cycles. We observed good reproducibility for the  $D$  values of Hf and the average  $D$  values of Hf are equivalent to the values obtained in the batch experiment. The chemical yield including dissolution efficiency was approximately 40%. In the alpha-particle measurement, we detected 118 counts of  $^{261}\text{Rf}$  and  $^{257}\text{No}$ , and the  $D$  values of Rf are now under analysis.

### References

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