

## Observation of the chemical reaction equilibria of element 104, rutherfordium: Solid-liquid extraction of Rf, Zr, Hf and Th with Aliquat 336 resin from HCl†

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It is important to investigate the chemical properties of superheavy elements (SHEs) with an atomic number ( $Z$ )  $\geq 104$ . Especially, in solution chemistry, we can study various non-volatile complexes. Thus far, two-phase partition methods, such as ion exchange and extraction, have been usually applied to SHEs. In these experiments, a rapid chemical separation is repeated many times by online chemical experiments using automated chemistry apparatus. The distribution coefficient ( $K_d$ ) in a solid-liquid extraction or the distribution ratio ( $D$ ) in a liquid-liquid extraction is often used in solution chemistry investigations for SHEs. These values are defined as the ratio of the elemental (radioactivity) concentrations of the two phases at equilibrium. However, there have been no previous experimental observations of equilibrium states for SHEs, although the experimental conditions in many previous studies were carefully adjusted based on the behaviours of homologues. To obtain the equilibrium  $K_d$  values for SHEs, we previously developed a new automated solid-liquid extraction apparatus for online use (AMBER).<sup>1)</sup> Herein, we applied the AMBER-based method to element 104, Rf.

In the online solid-liquid extraction of Rf and Hf, we simultaneously produced  $^{261}\text{Rf}$  ( $t_{1/2} = 68$  s) and  $^{169}\text{Hf}$  ( $t_{1/2} = 3.24$  min) by the bombardment of a  $^{248}\text{Cm}$  and  $^{152}\text{Gd}$  mixture with  $^{18}\text{O}$  beams delivered by the K 70 AVF cyclotron at RIKEN. The products were transported to a chemistry room by a He/KCl gas-jet system. The transported products were deposited on the collection site of AMBER's dissolution equipment for  $\sim 2$  min, and were dissolved in HCl. The solution sample was injected into a chemical reaction container containing 28 wt% Aliquat 336 resin (anion exchanger). After shaking the container with a shaker for 10, 30 and 60 s, only the solution phase was discharged from the container, passing through a PTFE filter, by compressed air for 10 s. The discharged solution was collected in a Ta disk on the round table of an automated rapid  $\alpha$ /SF detection system, and evaporated quickly to dryness using hot He gas and the halogen heat lamp. Subsequently, using the detection system's robot arm, the Ta disk was rapidly transferred into an  $\alpha$ -particle detection chamber for  $\alpha$ -particle measurements for  $\sim 800$  s. After that, the sample was assayed by  $\gamma$ -ray measurement with a Ge detector for the monitor of  $^{169}\text{Hf}$ . We also performed control experiments without the resin to determine the standard radioactivity of the solution sample.

Control experiments were carried out in 7.9 M HCl with 10-s shaking and in 9.0 M HCl with 10-s and 30-s shaking. Solid-liquid extraction experiments were carried out in 7.9 M HCl with 10-, 30- and 60-s shaking and in 9.0 M HCl with 10-s shaking. The ratios of the element concentrations between the resin and solution phases ( $Q_d$ ) in  $\text{mL g}^{-1}$  were determined from the radioactivities in the resin and the solution phases, the volume of the solution phase, and the mass of the dry resin.

The solid-liquid extraction of  $^{89\text{g.m}}\text{Zr}$  and  $^{173}\text{Hf}$  in the online experiment was performed at the Research Center for Nuclear Physics (RCNP), Osaka University in a similar way to the extraction of  $^{261}\text{Rf}$ . The solid-liquid extraction of  $^{88}\text{Zr}$ ,  $^{175}\text{Hf}$  and  $^{234}\text{Th}$  in the offline experiments (usual batch method) was also performed.

In the Rf experiment, we conducted a total of 379 extraction procedure cycles, and registered 132  $\alpha$  events from the decay of  $^{261}\text{Rf}$  and its daughter nuclide  $^{257}\text{No}$  ( $t_{1/2} = 24.5$  s), including 23 time-correlated  $\alpha$ - $\alpha$  correlation. The event ratios of  $^{261}\text{Rf}$  between the resin and solution phases were estimated from these  $\alpha$  events.

The  $Q_d$  values of Rf, Zr and Hf were constant in all the time ranges studied, indicating that equilibrium in the extraction of Rf (7.9 M HCl), as well as Zr and Hf, was accomplished within 10 s. This finding represents the first observation of the equilibrium state of the extraction reactions for SHEs on a one-atom-at-a-time basis, and the  $K_d$  value of Rf at equilibrium was obtained. Based on these results, we performed extraction experiment of Rf in 9.0 M HCl with shaking for 10 s, and obtained a lower limit for the  $K_d$  value  $> 1.4 \times 10^3 \text{ mL g}^{-1}$  (95% confidence).

For the dependence of the  $K_d$  values of Rf, Zr, Hf and Th on the HCl concentration, the  $K_d$  values of Zr and Hf in the online experiment were in good agreement with those in the offline experiment. The  $K_d$  value of Rf in 9.0 M HCl was higher than that in 7.9 M HCl, which indicates that the abundance of anionic chloride complexes of Rf increases with increasing the HCl concentration. The  $K_d$  value of Rf was close to that of Zr in 7.9 M HCl, while the value of Rf in 9.0 M HCl was clearly higher than the values of Zr and Hf by one and two orders, respectively. The significant difference in the  $K_d$  values among Rf, Zr and Hf in the HCl system was shown for the first time in this study by determining the  $K_d$  values of Rf. This result might suggest the possibility that Rf forms chloride complexes with a different configuration to its lighter homologues.

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### Reference

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