Study of anion exchange equilibrium of Zr and Hf in H_2SO_4 for Rf experiment

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Clarifying the chemical properties of superheavy elements with atomic number $Z \geq 104$ is an intriguing and important subject. These elements are produced by accelerators using heavy-ion-induced nuclear reactions. The production rates of these elements are low, and their half-lives are short ($T_{1/2} \leq 1$ min). Therefore, chemical studies on these elements are conducted on a single-atom basis.[1]

The chemical properties of superheavy elements have been discussed by comparing their chemical behavior with that of lighter homologous elements. The solution chemistry of superheavy elements has been studied mainly for element 104, Rf. In these studies, experiments on Rf and homologous elements was carried out under the same conditions, but even for homologous elements, equilibrated data were obtained only under a few conditions. In particular, it was reported that the chemical reaction kinetics between Zr and Hf are different in H_2SO_4.[2] Equilibrated data are necessary to discuss chemical properties such as complex formation. Therefore, the observation of equilibration and the equilibrated distribution data are very important to characterize the sulfate complex formation of Rf. In our previous study, we performed anion-exchange experiment with ^{88}Zr, ^{175}Hf, and ^{234}Th and determined the suitable experimental condition for Rf.[3] In this work, we performed online anion-exchange experiments with Zr and Hf by using AMBER[4] as the model experiment of Rf.

^{85}Zr and ^{169}Hf were produced in the ^{nat}Ge(^{18}O, xn)^{85}Zr and ^{nat}Gd(^{18}O, xn)^{169}Hf reactions, respectively, using the K70 AVF cyclotron at RIKEN. The nuclear reaction products were transported using a gas-jet system to the chemistry laboratory and deposited on the collection site of AMBER for 60 s. Then, the deposited sample was dissolved in 0.21–0.27 mL of 0.16–0.72 M H_2SO_4. The solution sample entered the chemical reaction container containing the anion-exchange resin (MCI GEL CA08Y). After shaking the container with a vortex mixer for 10–600 s, only the solution phase was pushed out of the container by using compressed air, and was assayed by γ-ray spectroscopy. The residual Zr and Hf species adsorbed on the resin were stripped by washing the resin five times with 0.25 mL of 1 M H_2SO_4. Subsequently, the resin was conditioned with H_2SO_4 for the next anion exchange. A control experiment was also performed without the resin to determine the radioactivity of the control solution. The Q_d values were determined from the following equation:

$$Q_d = A_r V_s / A_s w_r = (A_c - A_s) V_s / A_s w_r \qquad (1)$$

where A_r, A_s, and A_c are radioactivities of the resin, the solution, and the control solution, respectively; V_s is the volume (mL) of the solution; and wr is the mass of the dry resin (g).
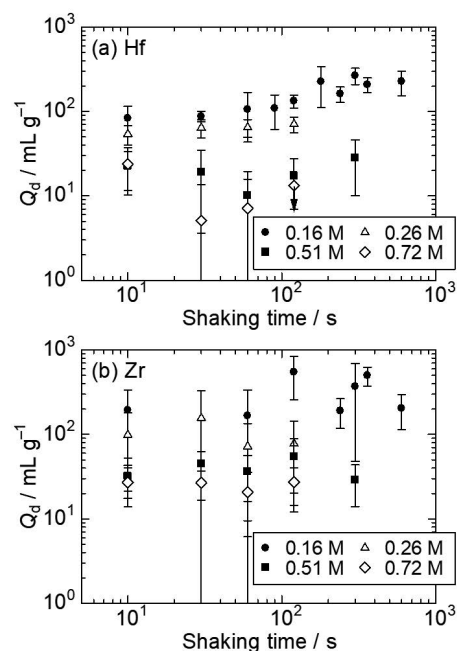
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Fig. 1. The Q_d values of (a) Hf and (b) Zr in anion exchange as a function of shaking time.

The activity of ^{85}Zr was very low, and the Q_d values of Zr had large errors. Figures 1(a) and 1(b) show the time dependence of the Q_d values of Hf and Zr, respectively. The Q_d values of Hf are constant within the errors in the entire time range studied in 0.26–0.72 M H_2SO_4. In 0.16 M H_2SO_4, the Q_d values of Hf become constant within the errors after 180 s. From the time when the Q_d values became constant within error, the anion-exchange reaction reaches equilibrium within 180 and 10 s in 0.16 and ≥ 0.26 M H_2SO_4, respectively. From these results, it is seen that the anion-exchange reaction kinetics is slow in low concentration of H_2SO_4. It is suggested that the anion-exchange kinetics of Rf may be slow in low concentration of H_2SO_4. In the case of Zr, the Q_d values are constant within the error in the entire time range studied in 0.16–0.72 M H_2SO_4. However, from this result, the discussion of anion-exchange reaction equilibrium for Zr is difficult, because the obtained Q_d values have large error.

In any case, we need to perform experiments with Zr again using enough activity of Zr isotopes. To obtain the small variations' Q_d values of small variations, we need to suitably adjust the ratio of W_r and V_s, when we perform the control experiment. For Hf, the Q_d values in 0.51 and 0.72 M H_2SO_4 have large errors; therefore, we plan to perform experiments under this condition again using increased resin weight.

References
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