Anion exchange of Rf in H_2SO_4 using the batch-type solid-liquid extraction apparatus AMBER

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The relativistic effect on orbital electrons is relatively more pronounced for heavy elements. In particular, the chemical properties of superheavy elements (SHEs) with atomic number $Z \geq 104$ are expected to deviate from the periodicity of their lighter homologues in the periodic table. Thus, it is important and interesting to investigate the chemical properties of SHEs. So far, ion-exchange experiments on SHEs have been conducted to determine the distribution coefficients (K_d), which are defined as the ratio of the elemental concentrations of the two phases.[1] However, those values at equilibrium have not been obtained in most studies. To obtain the K_d values at equilibrium, the batch-type solid-liquid extraction apparatus called AMBER was developed,[2] and the equilibrium K_d values on the chloride complexation of Rf were successfully obtained in an Aliquat 336/HCl system.[3]

To study the sulfate complexation of Rf, we plan to perform anion-exchange experiments of Rf and its homologous elements. In our previous study, by using AMBER, we obtained the K_d value of Rf in 0.11 M H_2SO_4.[4] The obtained K_d value of Rf is ~10 mL g^{-1}, probably indicating that Rf does not form anionic species or that counter ions of HSO_4^- and SO_4^{2-} inhibit the adsorption of Rf on the anion-exchange resin. In this study, to reduce the effect of counter ions, we performed an anion-exchange experiment of Rf in 0.060 M H_2SO_4, which is lower than 0.11 M.

In the anion exchange of Rf and Hf, we simultaneously produced ^{261}Rf ($T_{1/2}$ = 68 s) and ^{169}Hf ($T_{1/2}$ = 3.24 min) by the bombardment of a mixture of ^{248}Cm and natGd with an ^{18}O beam delivered from the K70 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 3 min and dissolved with 0.24 mL of 0.060, 0.30, and 0.46 M H_2SO_4. The solution sample was injected into a chemical reaction container containing the anion-exchange resin (MCI GEL CA08Y). After shaking the container with a shaker for 10, 30, and 90 s, only the solution phase was discharged from the container through a PTFE filter with compressed air. The discharged solution was collected in a Ta disk on the round table of an automated rapid α/SF detection system[5] and evaporated quickly to dryness using hot He gas and a halogen heat lamp. Subsequently, the Ta disk was transferred to the position under a Si PIN photodiode detector, and α-particle measurement was performed. After the α-particle measurement, the γ-ray was measured with a Ge detector to monitor ^{169}Hf. We also performed control experiments with 10-s shaking without the resin to determine the standard radioactivity of the solution sample. The K_d values were determined from the radioactivity in the resin and solution phases, the volume of the solution phase, and the mass of the dry resin.

We conducted 390 anion-exchange and 92 control cycles, and observed a total of 73 α events from the decay of ^{261}Rf and its daughter nuclide ^{257}No ($T_{1/2}$ = 24.5 s), including 10 time-correlated α–α correlations. The radioactivity ratios of ^{261}Rf between the resin and solution phases were estimated from the α events. In 0.060 M H_2SO_4, the K_d values of Hf were constant in all the studied time ranges, indicating that equilibrium in the anion exchange of Hf was accomplished within 10 s. Those of Rf were also constant in all the time ranges studied, yielding values of approximately 20 mL g^{-1}. This indicates that Rf is not adsorbed on the resin.

We also obtained the K_d values of Rf, Zr, Hf, and Th in 0.060–0.46 M H_2SO_4. The obtained K_d values of Rf are low ($\leq$25 mL g^{-1}) in the entire studied H_2SO_4 concentration range. In contrast, the K_d values of Zr, Hf, and Th are $\geq$70 mL g^{-1} at 0.060 M H_2SO_4. These results suggest that Rf does not form anionic species and that Zr, Hf, and Th form anionic species in this studied condition. The K_d values at 0.060 M H_2SO_4 follow the order of Zr > Hf $\gg$ Th > Rf, and this sequence is consistent with the trend predicted by theoretical calculation.[6] On the other hand, the sequence of K_d values is Th > Rf > Hf $\geq$ Zr in the cation exchange in the H_2SO_4/HNO_3 system.[7] In the future, we plan to discuss the chemical species of Rf in this studied condition from the obtained anion-exchange behavior of Rf, Zr, Hf, and Th and chemical species of Zr, Hf, and Th.

References
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