Anion exchange of element 104, Rf, at 0.11 M H_2SO_4 by using batch-type solid-liquid extraction apparatus, AMBER

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The relativistic effect of 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 deviate from the periodicity of their lighter homologues in the periodic table. Thus, it is important and interesting to investigate the chemical properties of these elements. Thus 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 for Rf at equilibrium, a 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 with Rf and its homologous elements. By using AMBER, we have already performed online anion-exchange experiments with Zr and Hf in H_2SO_4 as the model experiments for Rf and determined the anion-exchange experimental condition of Rf as 0.1–0.7 M H_2SO_4.[4] In this work, we performed online anion-exchange experiments with Rf and Hf at 0.11 M H_2SO_4 by using AMBER to examine the equilibrium time for the distribution of the elements and determine their K_d values.

In the online anion exchange of Rf and Hf, we simultaneously produced ^{261}Rf and ^{169}Hf ($T_{1/2} = 3.24$ min) by the bombardment of a mixture of ^{248}Cm and ^{nat}Gd mixture with ^{18}O beams delivered by 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 were dissolved with 0.24 mL of 0.11 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, after being passed 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 α/SF detection system[5] and evaporated quickly to dryness using hot He gas and a halogen heat lamp. Subsequently, using the detection system's robot arm, the Ta disk was subjected to rapid γ-ray measurement 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 radioactivities in the resin and solution phases, the volume of the solution phase, and the mass of the dry resin.

We conducted 327 anion-exchange and 135 control cycles, and observed a total of 96 α events from the decay of ^{261}Rf and its daughter nuclide ^{257}No ($T_{1/2} = 24.5$ s), including 14 time-correlated α-α correlations. The event ratios of ^{261}Rf between the resin and solution phases were estimated from the α events. The K_d values of Hf were constant in all the time ranges studied (10–90 s), 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 10 mL g^{-1}. This indicates that Rf is not adsorbed on the resin. In turn, this is considered to suggest that Rf does not form an anionic sulfate complex at 0.11 M H_2SO_4, though there is a possibility that counter ions of HSO_4^- and SO_4^{2-} are preferentially adsorbed on the resin. It should be noted that that we cannot exclude the possibility that the kinetics of Rf is significantly slower than that of Zr and Hf. The K_d values at 0.1 M H_2SO_4 follow the order of Zr > Hf $\gg$ Rf, and this sequence is consistent with the trend predicted by theoretical calculation.[6] Furthermore, in a cation-exchange study in H_2SO_4/HNO_3, the sequence of the K_d values was reported to be Rf > Hf $\geq$ Zr.[7] These results indicate that the sulfate complexation of Rf is weaker than those of lighter homologues.

From the present work, we found that Rf is not adsorbed on the anion-exchange resin at 0.11 M H_2SO_4 within 10–90 s. However, it is not clear whether Rf avoids forming the anionic sulfate complex in this studied condition. We need additional anion-exchange experiments of Rf at a lower counter-ion concentration.

References
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