Online anion-exchange experiment of ^{89m}Zr in the Adogen 464/HNO_3 system for the chemical research of Rf

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Chemical elements with $Z \geq 104$ are called superheavy elements (SHEs) and synthesized by heavy-ion-induced nuclear reactions using accelerators. The chemical properties of SHEs are almost entirely unknown because of the very low cross sections of their nuclides and short half-lives ($T_{1/2} \leq 1$ min). Some chemical experiments on $_{104}$Rf in an aqueous solution were reported; however, its chemical properties are not sufficiently understood owing to limited experimental methods. We previously developed an automated batch-type solid-liquid extraction apparatus (AMBER) and investigated the anion-exchange behavior of Rf in HCl and H_2SO_4 to obtain the distribution coefficients (K_d) of Rf under chemical equilibrium conditions.[1,2)]

In this study, we focus on the formation of the Rf nitrate complexes. The clear difference between the complexation of Th (pseudo homologue of Rf) and those of Zr and Hf (homologues) in HNO_3 is known; Th forms an anionic complex with large coordination numbers of 10 and/or 12, while Zr and Hf do not. We found in a previous study that anion-exchange reactions using the Adogen 464 resin in HNO_3 reach chemical equilibrium in 60 s. This suggests that this resin is suitable for ^{261}Rf ($T_{1/2} = 68$ s) experiments. We also optimized the experimental condition for ^{261}Rf with long-lived radiotracers, ^{88}Zr, ^{175}Hf, and ^{234}Th.[3)] To check the stability of AMBER in the accelerator-online situation, we performed the online anion-exchange experiments of ^{89m}Zr in the Adogen 464/HNO_3 system as a model experiment of ^{261}Rf.

^{89m}Zr ($T_{1/2} = 4.16$ min) was produced in the ^{89}Y$(d, 2n)^{89m}$Zr reaction. A d beam with 24-MeV energy was extracted from the K70 AVF cyclotron at RIKEN. The nuclear-reaction products were transported to the chemistry laboratory by using a He/KCl gas-jet system and deposited on AMBER for 60 s. Then, ^{89m}Zr was dissolved in 270 μL of 8.1 M HNO_3. The solution was loaded into a chemical reaction container containing 32 mg of the Adogen 464 resin. After shaking the container with a vortex mixer for 30–120 s, only the liquid phase was pushed out of the container by compressed air. Then, the solution samples were collected in a 0.5 mL PP tube, and the 587.8-keV γ rays of ^{89m}Zr were counted with a Ge detector. The residual ^{89m}Zr adsorbed on the resin was stripped by washing the resin four times with about 150 μL of 0.1 M HCl. Subsequently, the resin was conditioned with 8.1 M HNO_3 twice. This procedures was repeated 30 times. The distribution coefficient (K_d) was determined by the equation

$$K_d = (A_{STD} - \alpha A_s)V/\alpha A_s w,$$

where A_s and A_{STD} are the radioactivities of ^{89m}Zr in the resin and the control solution, respectively; V is the volume of the aqueous phase (mL); and w is the mass of the dry resin (g). Note that α is a correction factor that accounts for the adsorption of some ^{89m}Zr in the reaction container.

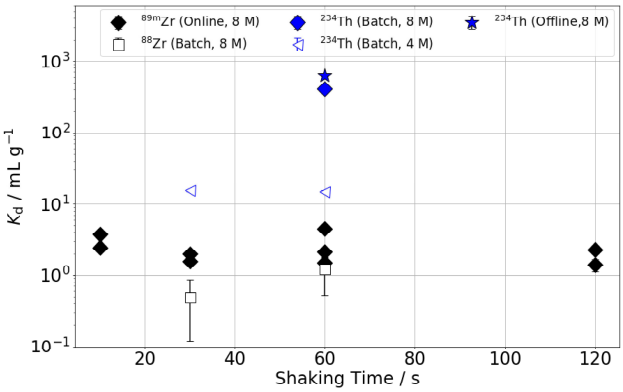

Fig. 1. K_d values of Zr and Th in the Adogen 464/HNO_3 system.

Figure 1 shows the K_d values of ^{89m}Zr using accelerator-online AMBER ("Online" in the figure) as a function of shaking time, along with those of ^{88}Zr and ^{234}Th previously obtained by AMBER in the offline condition and PP tube ("Offline" and "Batch" in the figure, respectively). The K_d of ^{89m}Zr for all shaking times are consistent with the values obtained under equilibrium conditions (60 s) in the batch experiments. This result indicates that the distribution coefficient can be obtained under the conditions of online experiments for the short-lived ^{261}Rf.

In 30 consecutive anion-exchange experiments, the K_d values of ^{89m}Zr are obtained reproducibly. We have previously confirmed good reproducibility for the K_d values of ^{234}Th by AMBER under the offline condition.[3)] Therefore, a wide range of K_d values of anion exchange in HNO_3 can be obtained in consecutive experiments by AMBER. Irrespective of the behavior of Rf in the system, we should be able to obtain reliable K_d values for Rf.

In this study, the applicability of the anion-exchange experiment to Rf in the Adogen 464/HNO_3 system us-

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ing AMBER was demonstrated by the success of the model experiment with the short-lived nuclei ^{89m}Zr. In addition to the ^{261}Rf experiment, we plan to conduct theoretical studies on Rf nitrate complexes using DFT calculations.

References

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