

## Fluoro complex formation of Rf and Db

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*Abstract* – We present a study of fluoro complex formation of the transactinide elements, rutherfordium (Rf) and dubnium (Db), at JAEA (Japan Atomic Energy Agency). The transactinide nuclides <sup>261</sup>Rf and <sup>262</sup>Db were produced in the reactions <sup>248</sup>Cm(<sup>18</sup>O,5n) and <sup>248</sup>Cm(<sup>19</sup>F,5n), respectively, at the JAEA tandem accelerator. Ion-exchange behavior of Rf and Db together with their lighter homologues in HF/HNO<sub>3</sub> mixed solutions has been investigated with a rapid ion-exchange separation apparatus AIDA. It has been found that fluoro complexation of Rf is significantly different from that of the homologues. A large difference in the adsorption behavior of Db and the homologue Ta on the anion-exchange resin has been also observed.

*Keywords* – Rutherfordium, Dubnium, Fluoro complexation, Ion-exchange chromatography, Atom-at-a-time chemistry

Fluoro complexation of Rf and Db was investigated through ion-exchange chromatography based on an atom-at-a-time scale together with their lighter homologues in hydrofluoric and nitric acid (HF/HNO<sub>3</sub>) mixed solutions.

The isotopes of 78-s <sup>261</sup>Rf and 32-s <sup>262</sup>Db were produced via the <sup>248</sup>Cm(<sup>18</sup>O,5n) and <sup>248</sup>Cm(<sup>19</sup>F,5n) reactions, respectively, at the JAEA tandem accelerator. Ion-exchange chromatographic behavior of Rf and Db, and their homologues was investigated with the apparatus AIDA [1].

In the anion-exchange experiments, distribution coefficients ( $K_d$ ) of Rf and the homologues were measured as a function of the nitrate ion concentration [NO<sub>3</sub><sup>-</sup>] at the constant fluoride ion concentration [F<sup>-</sup>] = 3 × 10<sup>-3</sup> M. From the log  $K_d$  vs. log [NO<sub>3</sub><sup>-</sup>] plot, we unequivocally determined the species of Rf on the binding sites of the resin as the hexafluoro complex [RfF<sub>6</sub>]<sup>2-</sup>. The homologues are also to be present as [MF<sub>6</sub>]<sup>2-</sup> (M = Zr, Hf), while the absolute  $K_d$  values of Rf are about two-orders of magnitude smaller than those of the homologues. In the log  $K_d$  against log [F<sup>-</sup>] relation, the result indicated that at [NO<sub>3</sub><sup>-</sup>] = 0.01 M, the formation of [MF<sub>6</sub>]<sup>2-</sup> for Zr and Hf occurs at [F<sup>-</sup>] ~ 10<sup>-5</sup> M, while that of [RfF<sub>6</sub>]<sup>2-</sup> starts at around 10<sup>-3</sup> M. There was about two-orders of magnitude difference in the fluoride ion concentration between Rf and the homologues for the formation of the hexafluoro complexes. This clearly demonstrates that the formation of the fluoro complexes of Rf is much weaker than those of the homologues Zr and Hf [2].

Cation-exchange behavior of Rf and the homologues in HF/0.1 M HNO<sub>3</sub> was also studied with the same manner as those in the anion-exchange experiments. The  $K_d$  values of Rf on the resin decreased with increasing [F<sup>-</sup>] in the range of 5 × 10<sup>-5</sup> - 3 × 10<sup>-4</sup> M due to the consecutive formation of fluoride complexes, while for the homologues the decreasing features of  $K_d$  were observed at about one-order of magnitude lower [F<sup>-</sup>] [3]. These results indicate that the transition from cationic to neutral and then anionic fluoro complexes of the group-4 elements requires higher [F<sup>-</sup>] for Rf than for the homologues.

The present result establishes the following sequence of the strength of fluoro complex formation, Zr ~ Hf > Rf that is the definite confirmation of the previously obtained results in HF solution [1].

The anion-exchange experiment of Db has been conducted in HF/HNO<sub>3</sub> solution with AIDA based on the model experiments with the homologues Nb, Ta and Pa [4]. The preliminary result indicates that the adsorption of Db on the anion-exchange resin is quite different from that of the homologue Ta, while that is close to the adsorption of Nb and the pseudo-homologue Pa. To obtain more accurate data of Db with high statistics, an improved AIDA system, AIDA-II [5], based on continuous sample collection and evaporation of effluents, and successive  $\alpha$ -particle measurement, has been developed. The status of the apparatus will be briefly introduced.

The present study at JAEA has been carried out in collaboration with RIKEN, Niigata University, Osaka University, Tokyo Metropolitan University, Kanazawa University, University of Tsukuba, Gesellschaft für Schwerionenforschung (GSI), and Mainz University.

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