Anion-exchange behavior of Db in HF/HNO_3 solution

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The superheavy elements with atomic number ≥104 are located in the 7th period of the periodic table. Because of the relativistic effects caused by the large positive charge of their atomic nuclei, they are expected to have different chemical properties from those of lighter homologues. However, since these elements have very short half-lives and low production rates, it is difficult to reveal their chemical properties.

The aqueous chemistry of Db was studied in comparison with its lighter homologues Nb and Ta and the pseudohomologue Pa. Previous studies on the aqueous chemistry of the fluoride complex of Db suggested that Db would form $[DbOF_4]^-$ like Nb or $[PaOF_5]^{2-}$ and/or $[PaF_7]^{2-}$ like Pa, but not $[DbF_6]^-$ like Ta.[1,2] However, there was no significant difference in the K_d values between Nb and Pa in the solutions in which Db anion-exchange experiments were performed. Therefore, it was not possible to determine whether Db was similar to Nb or Pa, and it is also difficult to determine the chemical species of the fluoride complex of Db.

In our previous work, we revealed that there is a large difference in the K_d values between Nb and Pa in the mixture solution of HF and 1.0 M HNO_3.[3] The different K_d values for Nb and Pa imply that they have different chemical species. Thus, it is considered that the chemical species of Db can be determined by obtaining the K_d value of Db in this mixed solution and comparing it with those of Nb and Pa. In this study, we performed online anion-exchange experiments of Db in HF/1.0 M HNO_3 mixture solution using automated rapid chemistry apparatus (ARCA) to identify the chemical species of the fluoride complex of Db.

The online anion-exchange chromatography of ^{262}Db, ^{88g}Nb, and ^{170}Ta was performed. The nuclides were produced in the ^{248}Cm(^{19}F, xn), ^{nat}Ge(^{19}F, nx), and ^{nat}Gd(^{19}F, nx) reactions, respectively, at the RIKEN K70 AVF cyclotron. In the ^{262}Db and ^{170}Ta experiments, the products were transported by the He/KCl gas-jet system and were deposited on the collection site of ARCA for 120 s. Subsequently, the products were dissolved in a solution of 14.5 M HF/1.0 M HNO_3. The solution was fed onto the micro chromatographic column (1.6 mm *i.d.* × 7 mm) filled with anion-exchange resin (MCI GEL CA08Y) at a flow rate of 1.0 mL/min. The effluent was collected on two Ta disks as fractions 1 and 2. The remaining products in the column were stripped with a solution of 0.015 M HF/6.0 M HNO_3 and collected on another two Ta disks as fractions 3 and 4.

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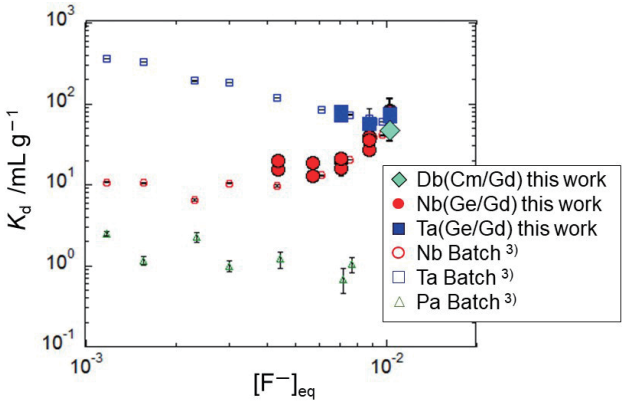

Fig. 1. Distribution coefficients, K_d, of Nb, Ta, Pa, and Db.

These disks were rapidly evaporated to dryness and subjected to α-particle measurements with an automated rapid α/SF detection system.[4] After the measurement, γ-rays of ^{170}Ta were monitored with Ge detectors.

In the ^{88g}Nb and ^{170}Ta experiments, the transported reaction products were deposited on the collection site of ARCA and were dissolved in a solution of 4.4–14.5 M HF/1.0 M HNO_3. Subsequently, the solution was fed onto the microcolumn under the same experimental conditions as those for Db. The effluent fractions were collected in 7 polypropylene(PP) tubes, and the remaining products were collected in another PP tube. These fractions were assayed by γ-ray spectrometry with a Ge detector.

We conducted 350 anion-exchange experiments and observed 5α events from ^{262}Db. Its adsorption probability on the resin was determined by the α counts found in fractions 1–4. The K_d value of Db was determined using the relation between K_d and the adsorption probability (%ads) of Nb and Ta studied in our previous work.[3] Figure 1 shows the K_d values of Nb, Ta, Pa, and Db. The K_d value of Db is close to that of Nb, while it is significantly larger than that of Pa. In our previous study, we found a large difference in the K_d value trends between Nb and Pa. The increase in the K_d value of Nb indicates a change in the chemical species from $[NbOF_4^-]$ to $[NbF_6^-]$. In contrast, the K_d value of Pa decreased monotonically, implying that the Pa species retains its form in this $[F^-]$ region. The present result suggests that Db is similar to the behavior of Nb, and the chemical species of Db chage from fluoro-oxo complex to fluoride like Nb.

In the near future, we will perform further anion-exchange experiments to observe the variation in K_d values of Db and identify the fluoride complex of Db.

References

1) K. Tsukada *et al.*, Radiochim. Acta, **97**, 83 (2009).
2) Y. Kasamatsu *et al.*, Chem Letts, **38**, 1084 (2009).
3) S. Adachi *et al.*, RIKEN Accel. Prog. Rep. **53**, 162 (2020).
4) H. Haba *et al.*, RIKEN Accel. Prog. Rep. **45**, 204 (2012).