On-line anion-exchange experiment of Nb and Ta in HF/HNO_3 mixture solution for Db chemistry

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Superheavy elements with atomic number $\geq$ 104 are placed at the 7th period of the periodic table. Owing to the influence of strong relativistic effects caused by their large positive nuclear charge, these elements are expected to have chemical properties different from those of lighter homologues. However, because these elements have very short half-lives and low production rates in nuclear reactions, it is difficult to determine their chemical properties.

Few studies on the aqueous chemistry of Db, a group-5 superheavy element, have been performed together with the lighter homologues Nb and Ta and the pseudo-homologue Pa. In the anion exchange in 13.9 M HF solution, the distribution coefficient (K_d) of Db was reported to be smaller than those of Nb and Ta but larger than that of Pa.[1] In 0.31 M HF/0.1 M HNO_3 solution, the adsorption of Db on the resin was showed to be clearly weaker than that of Ta and similar to those of Nb and Pa.[2] These studies suggest 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. Thus, the purpose of the present study is to investigate whether Db behaves like either Pa or Nb, particularly in high HF concentrations, which would enable us to deduce its chemical form: $[DbOF_4]^-$ or $[DbF_6]^-$. In this study, we performed on-line anion-exchange experiment of Nb and Ta in HF/HNO_3 mixture solution by using an automated rapid chemistry apparatus (ARCA) to determine the suitable experimental conditions for Db.

^{88g}Nb ($T_{1/2}$ = 14.5 min) and ^{170}Ta ($T_{1/2}$ = 6.7 min) were produced in the ^{nat}Ge(^{19}F, nx) and ^{nat}Gd(^{19}F, nx) reactions, respectively, using the RIKEN K70 AVF cyclotron. The reaction products transported by a He/KCl gas-jet system were deposited on a collection site of ARCA. Then, the products were dissolved in 0.1–14.5 M HF/1.0 M HNO_3 mixture solution. The solution was fed onto a small 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 fractions were collected in 7 polypropylene tubes. The products remaining in the column were stripped with 0.015 M HF/6.0 M HNO_3 mixed solution and were collected in another PP tube. These fractions assayed by γ-ray spectrometry with a Ge detector to obtain elution curves for Nb and Ta.

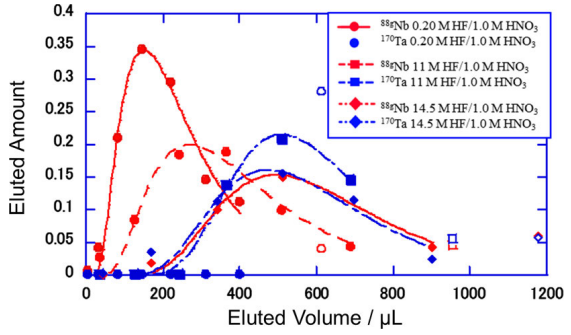

Fig. 1. Elution curves of ^{88g}Nb and ^{170}Ta in 0.20, 11, 14.5 M HF/1.0 M HNO_3 solutions.

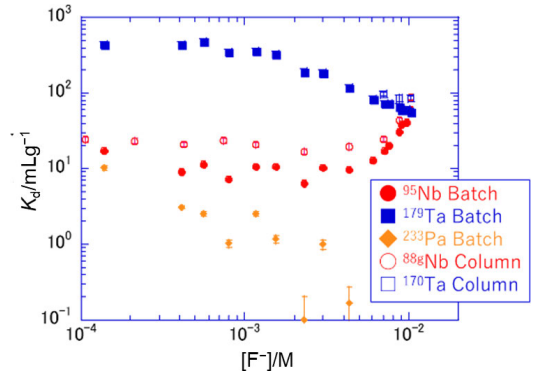

Fig. 2. Variation of the distribution coefficient, K_d, of Nb, Ta, and Pa as a function of [F^-].

Figure 1 shows, the elution curves of ^{88g}Nb and ^{170}Ta in 0.20, 11, and 14.5 M HF/1.0 M HNO_3 solutions. The eluted radioactivity $A(\nu)$ at effluent volume ν is expressed by the the following equation:

$$A(\nu) = A_{\max}\left\{-N(\nu_p - \nu)^2/(2\nu_p\nu))\right\} \quad (1)$$

where $A_{\max}$, N, and ν_p are maximum peak height, the number of theoretical plates, and the peak volume, respectively. The ν and ν_p values are corrected for the dead volume. The results of the fit are in good agreement with the experimental data. The K_d value based on the column chromatographic method is expressed as

$$K_d = \nu_p/m_r \quad (2)$$

where m_r is the mass of dry resin. The average m_r value was measured to be 5.7±0.6 mg. The K_d values obtained through the online column chromatography and a batch experiment conducted separately are plotted in Fig. 2.

The K_d values in the on-line experiment are larger than those in the batch experiment. However, the overall trend of K_d values, such as a sudden increase in the K_d value of Nb at around $[F^-]_{eq} = 5 \times 10^{-3}$ M, was reproduced. This suggests that the anion-exchange kinetics of Db may be fast in the present mixed solution, and the K_d values of Db may be obtained under the present conditions. In the near future, we will perform online experiments of Db to determine its K_d value.

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