Anion exchange of Nb and Ta in HF/HCl mixture solution for Db chemistry

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Clarifying the chemical properties of superheavy elements with atomic number (Z) $\geq$ 104 is an intriguing and important subject. These elements are produced at accelerators using heavy-ion-induced nuclear reactions. The production rates of these elements are low, and their half-lives are short ($T_{1/2} \leq 1$ min). Thus, chemical studies on these elements are conducted on a single-atom basis.[1)]

The fluoride ion is a very strong complexing agent for group-5 elements (Nb and Ta). The fluoride complex species of the heaviest group-5 element, dubnium (Db), is very interesting (Db forms oxyfluoride or fluoride complexes) because Nb and Ta form different fluoride complexes (Nb: $[NbOF_5]^{2-}$; Ta: $[TaF_7]^{2-}$) in 0.1–10 M HF ($[F^-] = 8.9 \times 10^{-3} - 1.9 \times 10^{-2}$ M).[2)] To determine the fluoride complex species of Db, we plan to perform an ion-exchange study of Db. In this study, we performed an anion-exchange experiment on Nb and Ta in HF/HCl mixture solutions to determine the suitable experimental conditions and obtain comparable data for Db.

We produced ^{95}Nb and ^{179}Ta in the ^{nat}Zr(d, xn) and ^{nat}Hf$(d, xn)^{179}$Ta reactions (nat = natural isotopic abundance), respectively, by using the RIKEN AVF cyclotron. These radiotracers were purified by the anion-exchange method using the procedure reported in Ref. 3).

In the anion-exchange experiments, the anion-exchange resin (MCI GEL CA08Y) was added to 0.25 mL of an HF/HCl mixture solution containing both ^{95}Nb and ^{179}Ta in a PP tube, and the mixture was shaken using a mixer. Next, the resin was removed by centrifugation. Subsequently, the filtrate was pipetted into another tube, weighed, and subjected to γ-ray spectrometry using a Ge detector. The concentration of HF and HCl was determined by titration with a standardized NaOH solution before the experiments. In all anion-exchange experiments, control experiments without the resin were performed. The K_d values were determined from the following equation:

$$K_d = A_r V_s / A_s w_r = (A_c - A_s) V_s / A_s w_r, \qquad (1)$$

where A_r and A_s are the radioactivities on the resin and in the solution, respectively; V_s is the volume (mL) of the solution; and wr is the mass (g) of the dry resin. A_c denotes the radioactivity of the control solution.

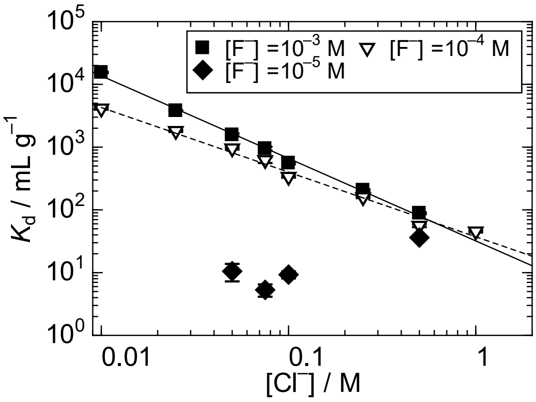

Fig. 1. K_d values of Nb in anion exchange as a function of Cl^- concentration.

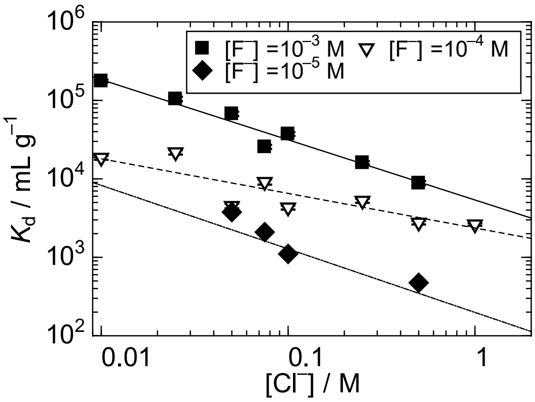

Fig. 2. K_d values of Ta in anion exchange as a function of Cl^- concentration.

The K_d values of Nb and Ta as a function of Cl^- concentration in the anion-exchange experiment are shown in Figs. 1 and 2, respectively. The values of Nb and Ta linearly decrease with increasing Cl^- concentration, except for Nb in $[F^-] = 10^{-5}$ M. These results suggest that Nb and Ta form anionic complexes in $[F^-] \geq 10^{-4}$ and $\geq 10^{-5}$ M, respectively. The slope values between $\log K_d$ and $\log [Cl^-]$ of Nb are -1.1 ± 0.1 and -1.3 ± 0.1 in $[F^-] = 10^{-4}$ and 10^{-3} M, respectively. These results indicate that the net charge of the adsorbed Nb species is -1. For Ta, the slope values between $\log K_d$ and $\log [Cl^-]$ are -0.8 ± 0.1, -0.4 ± 0.1, and -0.8 ± 0.4 in $[F^-] = 10^{-5}$, 10^{-4}, and 10^{-3} M, respectively. These results indicate that the net charge of the adsorbed Ta species is -1 at $[F^-] = 10^{-5}$ and 10^{-3} M. However, at $[F^-] = 10^{-4}$ M, the net charge of the adsorbed Ta species cannot be determined.

We also obtained the K_d values of Nb and Ta as a function of F^- concentration in [HCl] = 0.1 M. We also obtained those of Pa in our previous study.[4)] The sequence of the K_d values is Ta > Nb > Pa, and it is consistent with that in the HF/HNO_3 mixture system.[2,3)] This point suggests that the effect of the chloride ion is small for the complexation agent. On the other hand, another study is needed to check the effect of chloride ion.

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References

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