Anion and cation exchange of Pa in HF/HCl mixture solution for Db chemistry

T. Yokokita*[1] and H. Haba*[1]

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)]

F^- ion is a very strong complexing agent for the group-5 elements (Nb and Ta). The fluoride complex species of the heaviest group-5 element, dubnium (Db), is very interesting (Db forms $[DbOF_x]^{n-}$ or $[DbF_x]^{n-}$) 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 anion- and cation-exchange experiments of Pa (pseudo homologue of Db) in HF/HCl mixture solution to determine the suitable experimental condition of Db and obtain comparable data for Db.

^{233}Pa was obtained as an α-decay daughter of ^{237}Np in the following procedure. First, ^{237}Np in 9 M HCl containing ^{233}Pa was fed onto the TK400 resin's (TRISKEM) column. ^{237}Np was then eluted with 9 M HCl and ^{233}Pa was adsorbed on the resin. The adsorbed ^{233}Pa species was eluted with 1 M HCl. The eluent containing the Pa tracers was evaporated and dissolved in 9 M HCl. Then, Pa nuclide was purified by anion-exchange column chromatography using a procedure found in Ref. 3).

In the anion-exchange experiments, the anion-exchange resin (MCI GEL CA08Y) was added in 0.25 mL of HF/HCl mixture solution containing ^{233}Pa 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 standardized NaOH solution before the experiments. In all anion-exchange experiments, control experiments without the resin were performed. We also performed cation-exchange experiments of Pa using a cation-exchange resin (MCI GEL CK08Y). The experimental procedures were the same as the anion-exchange experiments. The K_d values were determined from the following equation:

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

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 w_r is the mass (g) of the dry resin. A_c denotes the radioactivity of the control solution.

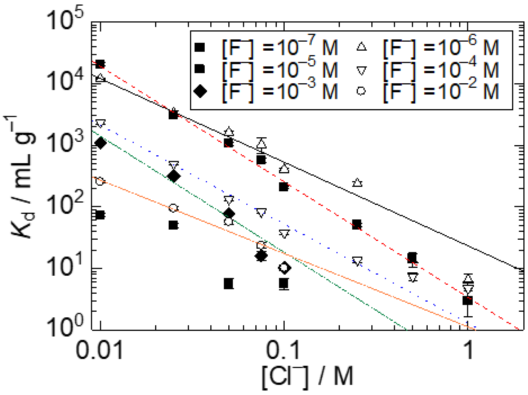

Fig. 1. K_d values of Pa in anion exchange as a function of Cl^- concentration.

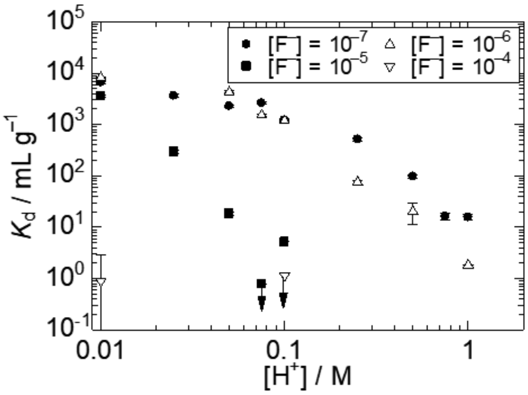

Fig. 2. K_d values of Pa in cation exchange as a function of H^+ concentration.

The K_d values of Pa as a function of Cl^- concentration in the anion-exchange experiment are shown in Fig. 1. In anion exchange, the K_d values of Pa linearly decrease with increasing concentration of Cl^- in $[F^-] = 10^{-6} - 10^{-2}$ M. These results indicate that Pa forms anionic complexes in the studied conditions. The slope values between log K_d and log$[Cl^-]$ are −1.4, −1.9, −1.6, −1.9, and −1.2 in $[F^-] = 10^{-6}$, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} M, respectively. These results indicated that the net charge of the adsorbed Pa species are −2 and −1.

The K_d values of Pa as a function of H^+ concentration in the cation-exchange experiment are shown in Fig. 2. The K_d values of Pa were $> 10^3$ mL g^{-1} and Pa was adsorbed on the resin in $[F^-] = 10^-7 - 10^-5$ M and $[H^+] = 0.01$ M. These results indicate that Pa forms cationic species in these F^- concentrations. The linear relation between log K_d and log $[H^+]$ is not obtained. It is suggested that some cationic Pa species coexist and/or Pa forms chloride complexes.

Recently, we produced ^{95}Nb and ^{179}Ta (homologues of Db) in the ^{nat}Zr(d, xn)^{95}Nb and ^{nat}Hf(d, xn)^{179}Ta reactions, respectively. We plan to study anion- and cation-exchange behavior of Nb and Ta in HF/HCl using these tracers for Db chemistry.

References

1) A. Türler, V. Pershina, Chem. Rev. **113**, 1273 (2013).
2) Y. Kasamatsu *et al.*, J. Radioanal. Nucl. Chem. **279**, 371 (2009).
3) Y. Kasamatsu *et al.*, J. Nucl. Radiochem. Sci. **8**, 69 (2007).

*1 RIKEN Nishina Center