Anion and cation exchange of Pa 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 \((T_{1/2} \leq 1 \text{ min})\). Thus, chemical studies on these elements are conducted on a single-atom basis.\(^{1}\)

\( \text{F}^- \) 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 \([\text{DbOF}_x]^n-\) or \([\text{DbF}_x]^n-\)) because Nb and Ta form different fluoride complexes (Nb: \([\text{NbOF}_3]^2-\); Ta: \([\text{TaF}_3]^2-\)) in 0.1–10 M HF \(([\text{F}^-] = 8.9 \times 10^{-3} - 1.9 \times 10^{-2} \text{ M})\).\(^{2}\) 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.

\(^{233}\text{Pa}\) was obtained as an \( \alpha \)-decay daughter of \(^{237}\text{Np}\) in the following procedure. First, \(^{237}\text{Np}\) in 9 M HCl containing \(^{233}\text{Pa}\) was fed onto the TK400 resin’s (TRISKEM) column. \(^{237}\text{Np}\) was then eluted with 9 M HCl and \(^{233}\text{Pa}\) was adsorbed on the resin. The adsorbed \(^{233}\text{Pa}\) species were 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 \(^{233}\text{Pa}\) 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 \( \gamma \)-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:

\[
K_d = A_r V_r/A_s w_t = (A_c - A_r) V_s/A_s w_t
\]

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

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 \([\text{F}^-] = 10^{-6} - 10^{-2} \text{ M}\). 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 \([\text{F}^-] = 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, \) and \(10^{-2} \text{ M}\), 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 \( > 10^3 \text{ mL g}^{-1}\) and Pa was adsorbed on the resin in \([\text{F}^-] = 10^{-7} - 10^{-5} \text{ M}\) and \([\text{H}^+] = 0.01 \text{ M}\). These results indicate that Pa forms cationic species in these \( \text{F}^-\) concentrations. The linear relation between log \( K_d \) and log[\( \text{H}^+\)] is not obtained. It is suggested that some cationic Pa species coexist and/or Pa forms chloride complexes.

Recently, we produced \(^{95}\text{Nb}\) and \(^{179}\text{Ta}\) (homologues of Db) in the \( ^{\text{nat}}\text{Zr}(d, xn)^{95}\text{Nb} \) and \( ^{\text{nat}}\text{He}(d, xn)^{179}\text{Ta} \) 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