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Anion-exchange Behavior of Nb, Ta, and Pa as Homologues of Db in HF/HNO$_3$ Solutions

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To find suitable conditions for the experimental study of anion-exchange behavior of element 105, dubnium (Db), we have investigated anion-exchange behavior of the group-5 elements Nb, Ta, and their pseudo homologue Pa in HF/HNO$_3$ media by a batch method using radiotracers of ^{95}Nb, ^{179}Ta, and ^{233}Pa. Clearly different adsorption behavior was observed among those homologues in the fluoride ion concentrations of 1×10^{-6} M < [F$^-$] < 2×10^{-2} M, suggesting that each element forms different anionic complexes. Based on the observed distribution coefficients of these elements, we propose appropriate experimental conditions to investigate fluoride complexation of Db.

1. Introduction

The transactinide element with atomic number $Z \geq 104$ is produced at accelerators using heavy ion-induced nuclear reactions as only one atom at a time because of the considerably low production rate and short half-life. Thus, the chemical properties of the transactinide element must be evaluated by single-atom base experiments and the chemical reaction system for such experiments should reach an equilibrium state fast enough within the lifetime of an objective transactinide nuclide. Partition methods as chromatographic systems with fast kinetics are applied to the chemical studies of the transactinide elements.[1,2]

Several studies on the solution chemistry of Db were conducted by applying rapid partition methods.[3–10] From the results of the experiments, it was found that the chemical behavior of Db is distinctively different from that of the closest homologue Ta and is similar to those of Nb and Pa.[4,5,7] As the fluoride anion is a very strong complexing agent for the group-5 elements, several chemical experiments of Db were conducted in HF solutions or in mixed solutions of HF with other strong mineral acids.[4,5,7–10] The results of the experiments showed that Db forms anionic fluoro complexes which are strongly retained on an anion-exchange resin.[10] The chemical properties of Db, however, have not yet been well clarified due to ambiguities of the data caused by insufficient statistics. In our previous works, distribution coefficients (K_d) of element 104 (Rf) were determined by anion-exchange experiments in HF and HF/HNO$_3$ solutions with AIDA (Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha-spectroscopy), and the fluoride complexation of Rf was studied in detail by comparing the results with those of its homologues.[11–13] We, in this work, have investigated anion-exchange behavior of Nb, Ta, and Pa in HF/HNO$_3$ media by a batch method to study the formation of their anionic fluoro complexes and to find suitable experimental conditions for the chemical study of Db.

2. Experimental

2.1. Preparation of radiotracers.

2.1.1. Preparation of mixed solution of ^{95}Nb and ^{179}Ta. Niobium-95 ($T_{1/2}$ = 34.97 d) and ^{179}Ta ($T_{1/2}$ = 665 d) were produced in proton bombardments on Zr and Hf metallic foil targets with natural isotopic abundance, respectively, using the RIKEN K70 AVF cyclotron. The incident energy of the proton beam was 14 MeV with the beam current of approximately 5 μA for the production of both ^{95}Nb and ^{179}Ta. Several hundreds to thousands kBq of the radiotracers were produced.

Purifications of Nb and Ta were individually carried out as follows. Each target foil was dissolved in 0.2 mL of concentrated HF solution in a polytetrafluoroethylene (PTFE) beaker. After evaporation to dryness, the residue was dissolved with 0.2 mL of 1 M HF and the solution was fed onto a chromatographic column (2.5 mm i.d. × 25 mm long for Nb, 2.5 mm i.d. × 10 mm long for Ta) filled with the anion-exchange resin (Dowex 1×8, 200–400 mesh, F$^-$ form). By washing the resin column with 1–2 mL of 1 M HF, most of by-products of the nuclear reaction such as lanthanide elements were eluted from the column, while the group 4 and 5 elements were retained on the resin. Three to five mL of the mixed solution of 9 M HCl/0.004 M HF was subsequently fed on the column to elute the target materials of Zr and Hf. Niobium was then eluted with 3 mL of 5 M HNO$_3$/0.2 M HF, while Ta was eluted with additional 30 mL of concentrated HF solution. The Nb and Ta effluents were separately collected in PTFE beakers and were evaporated to dryness. The above anion-exchange procedure was repeated until little residue remains in the beaker after the evaporation. Thereafter, Nb and Ta in the PTFE beakers were dissolved with a small amount of 1 M HF. After adding several drops of hydrogen peroxide (H$_2$O$_2$) into the solution, the mixture was heated to eliminate the decomposition products of the anion-exchange resin. The purified Nb and Ta radiotracers were dissolved with 1 M HF solution and mixed each other. The solution was stocked in a perfluoro alkoxy (PFA) vessel. X and γ rays of ^{179}Ta and ^{95}Nb were measured with a Ge semiconductor detector to ascertain the isolation of the elements.

2.1.2. Preparation of ^{233}Pa solutions. Protactinium-233 ($T_{1/2}$ = 27.0 d) was chemically separated from its α-decay parent ^{237}Np ($T_{1/2} = 2.144 \times 10^6$ y). Neptinium-237 with 69 kBq was dissolved with 0.2 mL of 9 M HCl, and then the solution was fed onto a column (2.5 mm i.d. × 25 mm long) filled with the anion-exchange resin (Dowex 1×8, 200–400 mesh, Cl$^-$ form). After washing the resin with 2 mL of 9 M HCl, Pa was eluted with 3 mL of 9 M HCl/0.025 M HF. The eluate was collected in a PTFE beaker. Remaining Np on the resin was eluted with distilled water and 0.2 M HNO$_3$. The effluent of the Pa fraction obtained was evaporated to dryness and underwent the same anion-exchange procedure to remove Np thoroughly.

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About 40 kBq of ^{233}Pa was obtained and stocked in 1 M HF solution in a PFA vessel.

2.2. Adsorption on PFA and PP surfaces. Adsorption of the group-5 elements Nb and Ta on glass, Pt, and even Teflon in concentrated HCl and HNO_3 was reported in Reference 3. As the adsorption interferes with precise batch-wise determination of distribution coefficients on the anion-exchange resin, we investigated the adsorption behavior of ^{95}Nb and ^{179}Ta on the surfaces of PFA and polypropylene (PP) test tubes used in this experiment. HF solutions of three different concentrations (10^{-4}, 10^{-2}, and 1 M) and mixed solutions of two different compositions (10^{-4} M HF/0.1 M HNO_3 and 10^{-2} M HF/0.1 M HNO_3) were used in the present adsorption experiment. After determination of the "initial reference radioactivity" of each solution, several mL of the radiotracer solutions were fed into the PFA and PP test tubes (12 mm i.d. × 140 mm long for PFA, 17 mm i.d. × 119 mm long for PP). Then, the solutions were well shaken and left. After some standing time, 30 μL of the solution was pipetted into a small PP container and was subjected to X- and γ-ray spectrometry. The ratio, R, of the radioactivity in each solution to the initial reference radioactivity of the solution was obtained as a function of the standing time to observe the time-dependent adsorption behavior of the radiotracers on the PFA and PP surfaces. The adsorption behavior of ^{233}Pa was also investigated in the same manner.

We confirmed that the adsorption of the radioisotopes on the pipettes made of PP is negligible. Only statistical errors were taken into account in the estimation of errors of the radioactivity ratios R. The concentrations of the HF and HNO_3 solutions were determined by titrations with standardized NaOH and $NaHCO_3$, respectively, before the experiments.

2.3. Ion-exchange kinetics. In order to determine the distribution coefficient in equilibrium, kinetics of the chemical reaction has to be examined. The distribution coefficient of an ion-exchange system is defined using a ratio of the radioactivity in the resin to that in the solution as

$$K_d = \frac{A_r V_s}{A_s W_r},$$

where A_r and A_s are the radioactivities (Bq) in the resin and the solution, respectively, V_s is the volume of the solution (mL), and W_r is the mass of the dry resin (g). By observing the time dependence of the K_d value, we examined the kinetics of the ion-exchange reaction which includes the coordination reaction of the metal element with the fluoride ions.

The resin used was the strongly basic anion exchanger MCI® GEL CA08Y supplied by Mitsubishi Chemical Corporation. The resin was washed with distilled water, and then stirred in 2 M HNO_3 and 2 M NaOH solutions alternately. After washing the resin with 2 M HNO_3 twice, the resin was washed with the distilled water several times and dried in a vacuum oven at 70 °C for 24 h.

Kinetics of the ion-exchange reaction was investigated for ^{95}Nb, ^{179}Ta, and ^{233}Pa in HF/0.1 M HNO_3 solutions with HF concentrations of 10^{-4}, 10^{-3}, 10^{-2}, 1, and 10 M. In a PP test tube, 8–200 mg of the dried resin and 3 mL of HF/HNO_3 solution containing 30–50 μL of the tracer solution were mixed. In each sample, 10^8–10^{12} atoms of the tracer nuclides were contained. Then, the tube was shaken for a certain time (shaking time). After centrifugation, 1 mL of the solution was pipetted in a small PP container and subjected to X- and γ-ray spectrometry with a Ge detector. The same treatment was conducted without the resin to determine the reference radioactivity of the solution. The radioactivity of each isotope on the resin was determined by subtracting the radioactivity in the supernatant solution from the reference radioactivity of the solution. We investigated a dependence of the K_d value on the shaking time that includes the time consumed for the centrifugation. Statistical errors were taken into account in the estimation of errors of the K_d values.

2.4. Determination of distribution coefficients. The K_d values of Nb, Ta, and Pa were determined in various concentrations of HF/HNO_3, where the concentration of HNO_3 was kept constant at 0.1 M. The experimental procedure was almost the same as that described in sec. 2.3. For the solutions with the HF concentration [HF] $\geq 10^{-2}$ M, the shaking time was 15 min, while the time was at least 5 h for the solutions with 10^{-3} M $\leq$ [HF] $< 10^{-2}$ M, and 1 day for those with [HF] $< 10^{-3}$ M. The shaking time was determined based on the results of the kinetic studies.

3. Results and Discussion

3.1. Adsorption on PFA and PP surfaces. Variations of the radioactivity ratios, R, which represent the adsorption of the radiotracers on the surfaces of the PFA and PP test tubes in HF and HF/HNO_3 solutions are shown as a function of elapsed time in Figure 1. It is found that the decrease of the ratio resulting from the adsorption on the surface of the tube is not observed for every element in the solutions with the fluoride ion concentration $[F^-] \geq 10^{-4}$ M. Here, the fluoride ion concentration was calculated using the dissociation constants of HF and HF_2^- reported in Reference 14. For the solutions with $[F^-] < 10^{-4}$ M, contrarily, the adsorption on the PFA and PP surfaces is observed for Ta after about 1 week. In such low F^- concentrations, hydrolytic species would be dominant for Ta;[15] various kinds of species including neutral complexes coexist in the solutions. To avoid the adsorption, we stocked the radiotracers in HF solutions with the concentrations of 10^{-2} M or higher and those mixed with 0.1 M HNO_3.

As a result, it is evident that influence of the adsorption of the group-5 elements on both the PP and PFA surfaces is negligible within 1 week for the determination of the K_d values in the solutions with $[F^-] > 10^{-6}$ M.

3.2. Ion-exchange kinetics. Variations of the K_d values of

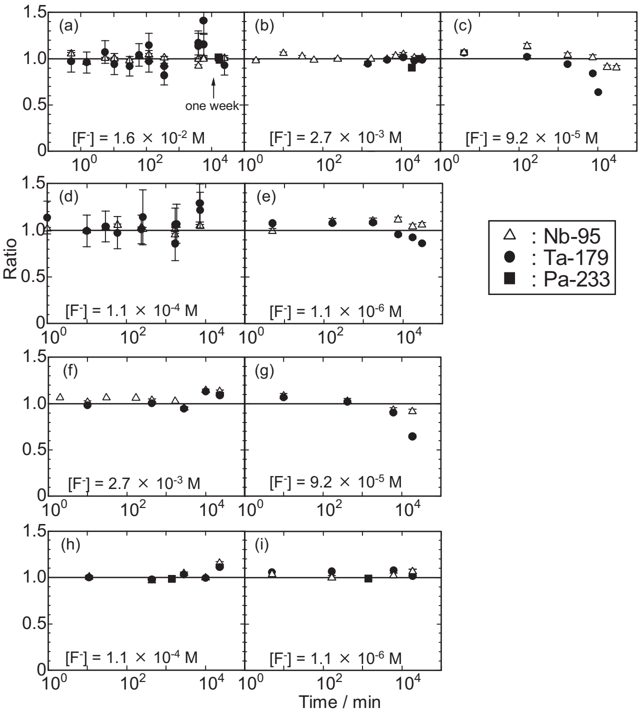

Figure 1. Adsorptions of Nb, Ta, and Pa on the surfaces of the (a)–(e) PFA and (f)–(i) PP test tubes as a function of elapsed time in (a) 1 M HF ($[F^-] = 1.6 \times 10^{-2}$ M), (b)(f) 10^{-2} M HF ($[F^-] = 2.7 \times 10^{-3}$ M), (c)(g) 10^{-4} M HF ($[F^-] = 9.2 \times 10^{-5}$ M), (d)(h) 10^{-2} M HF/0.1 M HNO_3 ($[F^-] = 1.1 \times 10^{-4}$ M), and (e)(i) 10^{-4} M HF/0.1 M HNO_3 ($[F^-] = 1.1 \times 10^{-6}$ M). The vertical axis denotes the radioactivity ratio, R, which is defined in the text. $R = 1$ (horizontal line) corresponds to no adsorption, while $R = 0$ means 100% adsorption.

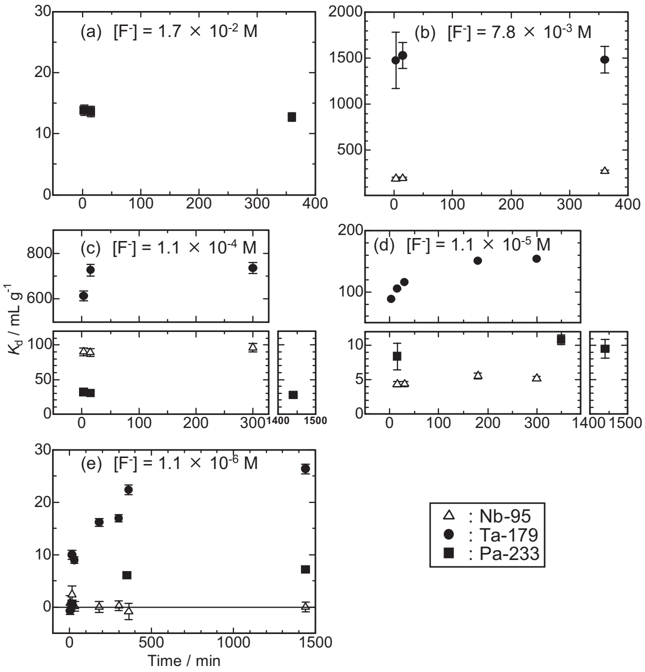

Figure 2. Variations of the distribution coefficients of Nb, Ta, and Pa on the anion-exchange resin as a function of the shaking time in the HF/HNO_3 solutions. The concentration of HNO_3 was constant (0.1 M). The concentrations of HF were (a) 10 M ($[F^-] = 1.7 \times 10^{-2}$ M), (b) 1 M HF ($[F^-] = 7.8 \times 10^{-3}$ M), (c) 10^{-2} M ($[F^-] = 1.1 \times 10^{-4}$ M), (d) 10^{-3} M ($[F^-] = 1.1 \times 10^{-5}$ M), and (e) 10^{-4} M ($[F^-] = 1.1 \times 10^{-6}$ M).

Nb, Ta, and Pa as a function of the shaking time are depicted in Figure 2. It is found that the ion-exchange kinetics depends on the fluoride ion concentration of the solution. The distribution coefficients do not change significantly over the shaking time ranging from 3 to 360 min, indicating that equilibrium kinetics is accomplished within 3 min in the solutions with $[F^-] \geq 7.8 \times 10^{-3}$ M. In the solutions with $[F^-] < 10^{-4}$ M, especially for Ta, it takes several hundreds min at most to achieve the ion-exchange equilibrium. This means that $[F^-]$ should be higher than 10^{-4} M in rapid ion-exchange experiments for short-lived isotopes of the group-5 elements to obtain chemical constants in equilibrium.

It is evident from the results of the kinetic studies that the K_d values in chemical equilibrium can be determined by the present batch experiments in the wide range of fluoride ion concentration, $[F^-] > 10^{-6}$ M, without the interference from the adsorption on the surfaces of the test tubes.

3.3. Distribution coefficients. Variations of the K_d values of Nb, Ta, and Pa as a function of $[F^-]$ are shown in Figure 3. The K_d values of the elements increase with increasing $[F^-]$, which reflects the successive formation of anionic fluoro complexes. The decreasing feature of the K_d values in the concentrated $[F^-]$ region would be due to the displacement of the anionic fluoro complexes of the group-5 elements on the resin through the HF_2^- anions.[16]

Clear differences in the adsorption behavior among the group-5 elements on the anion-exchange resin are observed. The large difference in the K_d values of the homologues Nb and Ta observed in the present study would arise from the fact that Ta forms fluoro complexes TaF_n^{5-n} while Nb is present as oxo-fluoro complexes $NbOF_n^{3-n}$ dominantly.[15–19] It is reported that Pa forms fluoro complexes PaF_n^{5-n} like Ta.[15–17] However, the observed K_d values of Pa are considerably smaller than those of Ta in the studied conditions. As an average charge of anionic complexes influences on the K_d value, the number of the fluoride anions bound with Pa possibly differs from that of Ta in the present conditions. The average charge of the metal complexes can be estimated from the relationship between the K_d values and the counter-anion (NO_3^-) concentration.[20,21] For more detailed discussion on the anionic fluoride complexation of the group-5 elements, therefore, further experiments to obtain K_d values as a function of the NO_3^- ion concentration are needed.

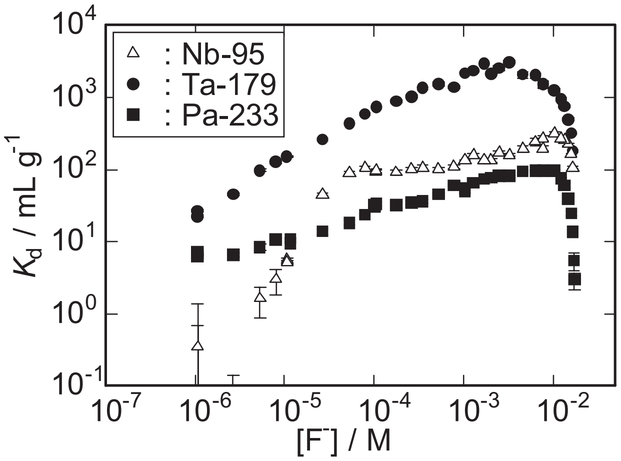

Figure 3. Distribution coefficients of Nb, Ta, and Pa in HF/HNO_3 solutions as a function of the fluoride ion concentration.

The differences in the anion-exchange behavior among the group-5 elements seem to originate from the differences in their chemical species. Fluoro complex formation of Db is expected to be discussed from experimental results on Db performed in the present chemical system. Taking into account the experimental restriction that chemical equilibrium should be achieved within the lifetime of ^{262}Db ($T_{1/2}$ = 34 s), the anion-exchange experiments must be carried out in the solutions with $[F^-] \geq 10^{-4}$ M. Furthermore, the distribution coefficient should be 10–500 mL/g to be determined using the microcolumn of AIDA.[11] From these standpoints, the experimental conditions at $[NO_3^-] = 0.1$ M would be appropriate for the anion-exchange experiments of Db on the assumption that Db behaves like Nb or Pa as reported in References 4, 5, and 7.

4. Conclusion

We found out the experimental conditions to obtain the distribution coefficients of the group-5 elements in anion-exchange chromatography with HF/HNO_3 solutions using the radiotracers of ^{95}Nb, ^{179}Ta, and ^{233}Pa. Anion-exchange behavior of Nb, Ta, and Pa was minutely examined in the wide range of the fluoride ion concentration. Clear differences in the behavior among Nb, Ta, and Pa were observed in the studied conditions, suggesting that each element forms different anionic fluoro complexes. The present result gives the reality to the rapid chemical experiment of Db in HF/HNO_3 media for the study of fluoride complexation.

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