

Adsorption Behavior of ^{95}Nb and ^{179}Ta as Homologues of Element 105, Db, on Cation Exchanger in HF/HNO₃ Solution

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Adsorption behavior of the group-5 elements, ^{95}Nb and ^{179}Ta , on cation-exchange resin was studied in mixed solution of HF and HNO₃ (HF/HNO₃) as a model experiment of their heavier homologue, element 105 (dubnium, Db). Chemical reactions of these elements in the cation exchange rapidly reached the equilibrium. It was found that distribution coefficients of Nb and Ta decrease with increasing the fluoride ion concentration in the studied range of 10^{-7} – 10^{-5} M. Clear difference between Nb and Ta was observed in the variations of the distribution coefficients against the fluoride ion concentration. This would originate from their different chemical species of fluoride complexes. We propose the cation-exchange experiment of Db based on the present experimental results to understand its fluoride complex formation.

1. Introduction

Relativistic effects on orbital electrons become increasingly strong in transactinide elements with the atomic number $Z \geq 104$ because of high positive charges of nuclei of these heavy atoms. As a consequence of the mass increase of the inner shell electrons, these electrons are stabilized. In contrast, the outer shell electrons are destabilized due to enhanced shielding of the nuclear charge by the inner shell electrons. Thus, chemical properties of the transactinide elements cannot be deduced from those of lighter homologues.^{1,2} Chemical studies on these elements are very attractive for many chemists. Furthermore, studies of the transactinides produced in heavy-ion-induced nuclear reactions are fairly challenging. Because of low production rates and short half-lives of the transactinide nuclides, chemical experiments of these elements must be conducted on a single atom scale.³ Partition experiments such as column chromatography are required to be performed within the lifetime of an objective nuclide. In addition, chemical reactions should be fast to rapidly reach the equilibrium. These situations make it very difficult to study chemical properties of the transactinide elements. Prior to carrying out chemical experiments with the transactinide elements, therefore, we need to search for suitable chemical reaction systems and to determine appropriate conditions of the experiments for these elements. For these purposes, generally, chemical experiments using homologues of respective transactinide elements are performed. Through these experiments, we can also obtain comparative data to discuss the chemical properties of the transactinide elements.

So far, solution chemistry was conducted mainly for the lighter transactinide elements, rutherfordium, $_{104}\text{Rf}$, and dubnium, $_{105}\text{Db}$. For Db, only a few experiments to investigate its chemical behavior such as a distribution equilibrium in two-phase partition have been carried out^{4–6} after some primary chemical experiments such as a mutual separation.^{7–11} In our previous studies,^{12–15} anion- and cation-exchange behavior of Rf has been investigated in detail using the automated ion-

exchange separation apparatus coupled with the detection system for alpha spectroscopy (AIDA).¹⁶ Interesting results have been obtained especially in the fluoride complex formation; the properties of Rf are largely different from those of the homologues. Following these successful works, using the apparatus and method, adsorption behavior of Db on anion exchanger has been studied together with its homologues Nb and Ta and the pseudo-homologue Pa in HF⁶ and in the mixed solution of HF and HNO₃ (HF/HNO₃).⁴ In 13.9 M HF solution, the adsorption of Db on the resin is weaker than that of Nb and Ta, and is stronger than or equal to that of Pa within counting statistics.⁶ This provided the adsorption sequence of $\text{Ta} \approx \text{Nb} > \text{Db} \geq \text{Pa}$ which qualitatively follows inverse sequence of their ionic radii. In 0.31 M HF/0.1 M HNO₃, it was found that the adsorption behavior of Db is similar to that of Nb and Pa, while the adsorption of these elements is clearly weaker than that of Ta.⁴ The adsorption sequence of $\text{Ta} > \text{Nb} \geq \text{Db} \geq \text{Pa}$ is different from the order of the ionic radii, suggesting that chemical species in this solution should be different among these group-5 elements. In more dilute fluoride ion concentration, $[\text{F}^-]$, the behavior of the cationic fluoride complexes is expected to be investigated by cation-exchange method. The cation-exchange behavior of Db in addition to the anion-exchange one^{4,6} leads to further understanding of its fluoride complexation. The cation-exchange behavior of the cationic fluoride complexes of Nb and Ta is not well-known, although the cation-exchange technique has been applied to the chemical separations of these elements.^{17,18} It is difficult to investigate the behavior of these elements in aqueous solutions without ligand anions due to their instabilities and polymerizations in macro amounts.¹⁷

In this paper, we report adsorption behavior of Nb and Ta on cation-exchange resin in HF/HNO₃ solution using carrier-free radiotracers ^{95}Nb and ^{179}Ta to obtain fundamental information about cationic fluoride species of Nb and Ta and this is a model experiment of Db. After examining cation-exchange kinetics of ^{95}Nb and ^{179}Ta , distribution coefficients (K_d [mL g⁻¹]) in equilibrium are determined for these elements as a function of $[\text{F}^-]$. The fluoride complex formation of Nb and Ta are discussed based on the present results together with the results obtained in the anion-exchange experiment in the HF/HNO₃ solution.⁴

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2. Experimental

The nuclides ^{95}Nb ($T_{1/2} = 34.97$ d) and ^{179}Ta ($T_{1/2} = 665$ d) were produced in the proton bombardments of ^{nat}Zr and ^{nat}Hf metallic foil targets, respectively, at the RIKEN K70 AVF cyclotron. The incident energy of the proton beam was 14 MeV with the beam current of approximately 5 μA . The ^{95}Nb and ^{179}Ta radiotracer solutions were prepared by the same method as described in our previous paper¹⁹ and were stocked in 0.001 and 0.01 M HF solutions in perfluoro alkoxy (PFA) tubes.

The cation-exchange resin used was a strongly acidic cation exchanger MCI GEL CK08Y with a particle size of 25 μm supplied from Mitsubishi Chemical Corporation. The commercially available resin in the Na^+ form was washed with distilled water and then stirred in 2 M HNO_3 and 2 M NaOH solutions alternately three times. After stirred in 2 M HNO_3 , the resin was washed with distilled water until it is neutralized, and then dried in a vacuum oven at 70 $^\circ\text{C}$ for 24 h. After grinding the resin, it was kept in a desiccator.

Kinetics of the cation-exchange reaction for ^{95}Nb and ^{179}Ta was investigated in 10^{-5} , 10^{-4} , and 10^{-3} M HF/0.1 M HNO_3 solutions by measuring the time dependence of the K_d values in the cation exchange. The dried resin with a weight of 20–100 mg and 3 mL of HF/ HNO_3 solution containing the ^{95}Nb and ^{179}Ta radiotracer solution were mixed in a polypropylene (PP) tube. The mixture was shaken at 22 ± 1 $^\circ\text{C}$ and then separated by centrifugation. Mixing time which includes the time consumed for the shaking and centrifugation was varied between 10 and 2880 min. After centrifugation, 1 mL of the supernatant solution was precisely pipetted into a small polyethylene tube and it was subjected to γ -ray spectrometry using a Ge detector. A standard 1 mL solution of ^{95}Nb and ^{179}Ta was prepared in the same way without the resin and was subjected to γ -ray spectrometry. Non-adsorption of these radiotracers onto walls of PFA and PP tubes was also verified in 10^{-5} , 10^{-4} , and 10^{-3} M HF/0.1 M HNO_3 by the same method as that in Reference 19.

The distribution coefficient in an ion exchange is obtained from eq 1:

$$K_d = \frac{A_r V_s}{A_s m_r}, \quad (1)$$

where A_r and A_s are the radioactivities in the resin and solution, respectively, V_s is the volume of the solution (mL), and m_r is the mass of the dry resin (g). In the present experiment, the radioactivity in the resin, A_r , was evaluated by subtracting the radioactivity in the supernatant solution, A_s , from that in the standard solution.

According to the results of the above kinetics experiments, the K_d values of ^{95}Nb and ^{179}Ta in equilibrium were determined as a function of $[\text{F}^-]$ in 10^{-5} – 10^{-3} M HF/0.1 M HNO_3 with the mixing time of 1440 min.

3. Results and Discussion

In Figures 1 (a), 1(b), and 1(c), the K_d values of ^{95}Nb and ^{179}Ta in the cation exchange are shown as a function of the mixing time in 10^{-5} , 10^{-4} , and 10^{-3} M HF/0.1 M HNO_3 , respectively. The fluoride ion concentrations in these solutions were calculated to be 1.1×10^{-7} , 1.1×10^{-6} , and 1.1×10^{-5} M, respectively, using the dissociation constants of HF and HF_2^- .²⁰ As shown in Figures 1(a) to 1(c), the K_d values of Nb and Ta are almost constant in the studied time range of 10–2880 min, except for those of Ta at $[\text{F}^-] = 1.1 \times 10^{-7}$ M. This means that the cation-exchange and fluoride-complexation reactions reached the equilibrium states more rapidly than the studied time range. For Ta, in the lowest concentration solution at $[\text{F}^-] = 1.1 \times 10^{-7}$ M, these reactions might be relatively slow.

Figure 2 shows variations of the K_d values of ^{95}Nb and ^{179}Ta

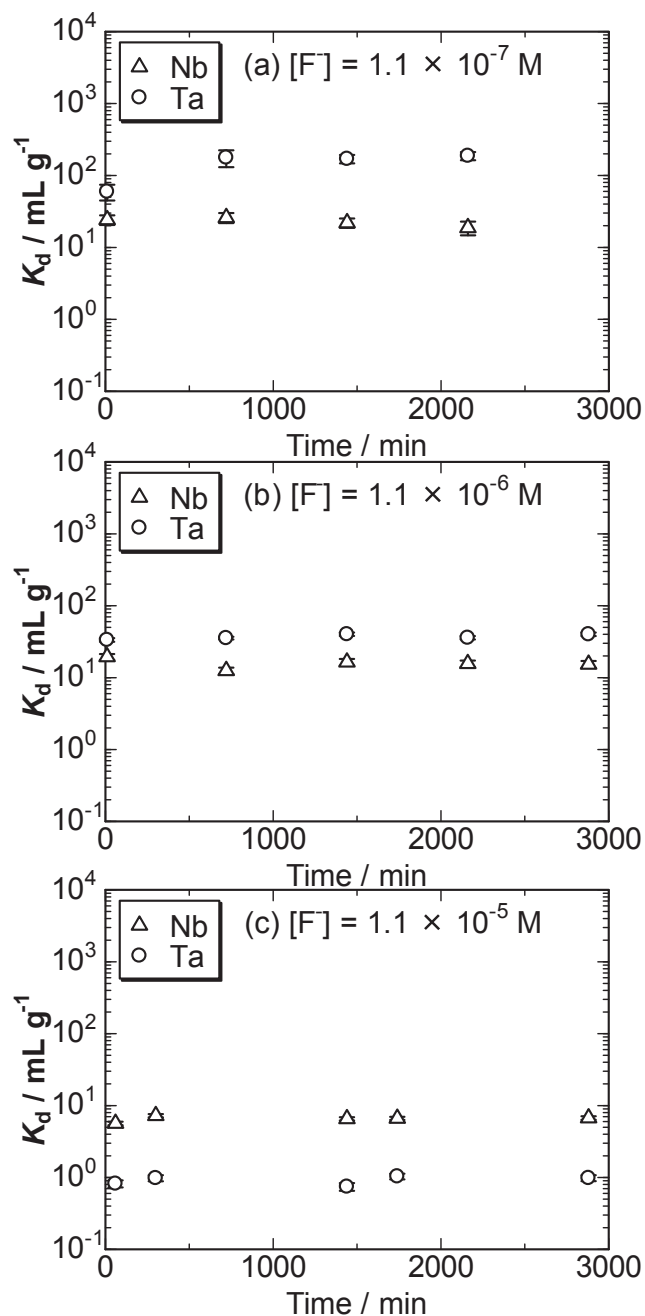


Figure 1. Distribution coefficients of ^{95}Nb and ^{179}Ta as a function of mixing time in (a) 10^{-5} , (b) 10^{-4} , and (c) 10^{-3} M HF/0.1 M HNO_3 solutions. The values of ^{95}Nb and ^{179}Ta are depicted by open triangles and open circles, respectively.

in the cation exchange as a function of $[\text{F}^-]$ in HF/0.1 M HNO_3 . For comparison, the K_d values of ^{95}Nb and ^{179}Ta in the anion exchange previously obtained in HF/0.1 M HNO_3 ⁴ are also plotted. As $[\text{F}^-]$ increases, the K_d values of Nb and Ta in the cation exchange decrease in the studied $[\text{F}^-]$ range between 10^{-7} and 10^{-5} M, representing that the abundance of the cationic complexes of Nb and Ta in the solution decreases with increasing $[\text{F}^-]$ owing to the consecutive formation of the neutral and anionic fluoride complexes. This result gives a consistent picture with their anion-exchange behavior that the K_d values increase with increasing $[\text{F}^-]$. The K_d values in both the cation and anion exchange are low around $[\text{F}^-]$ of 10^{-5} and 10^{-6} M for Nb and Ta, respectively, suggesting that the neutral complexes of these elements are dominant in each concentration range.

The stable oxidation states of Nb and Ta in aqueous solution are both +5 and their ionic radii in the same coordination

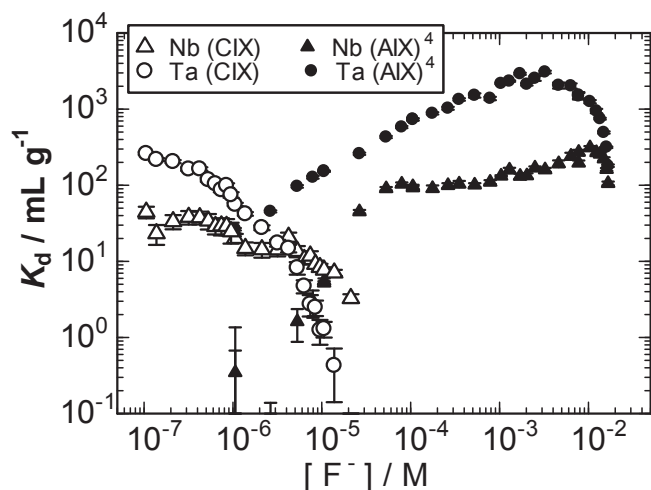


Figure 2. Distribution coefficients of ^{95}Nb and ^{179}Ta in the cation exchange (CIX) in $\text{HF}/0.1\text{ M HNO}_3$ solutions as a function of the fluoride ion concentration together with the data of ^{95}Nb and ^{179}Ta obtained in our previous anion-exchange (AIX) experiment⁴. The plots of ^{95}Nb and ^{179}Ta obtained in this work are depicted by open triangles and open circles, respectively, and those of ^{95}Nb and ^{179}Ta in the anion exchange are shown as closed triangles and closed circles, respectively.

number are almost the same. The charge densities of the complexes of Nb and Ta are, therefore, expected to be very close with each other if these metal ions form the complexes with the same configuration. Indeed, the group-4 elements Zr and Hf, having the +4 stable oxidation state and very close ionic radii, form the same complexes and represent similar adsorption behavior on resins.^{12–15} In contrast, the adsorption behavior on the cation- and also anion-exchange resin is clearly different between Nb and Ta as shown in Figure 2. In our previous report,⁴ different behavior between Nb and Ta in the anion-exchange distribution was attributed to the difference in their chemical species; Nb forms oxo-fluoro complexes and Ta forms fluoride complexes,^{21–24} which leads to higher K_d values of Ta than those of Nb. For the present results, therefore, it could be also suggested that Nb and Ta exist as different cationic species in the studied $[\text{F}^-]$ range between 10^{-7} and 10^{-5} M. Metal ions of Nb and Ta may form the complexes such as fluoride or oxo-fluoro species with different positive charges. Otherwise, Nb may form oxo-fluoro complexes having lower charge densities than those of the fluoride complexes the same as that in higher $[\text{F}^-]$ range,^{21–24} which leads to lower K_d values of Nb than Ta.

We are planning to perform the on-line cation-exchange experiment of Db as well as Nb and Ta under the present conditions. Formation of the cationic fluoride complexes of Db will be investigated by comparing the data for Db with the present ones for Nb and Ta. The comprehensive discussion with the results obtained in the anion- and cation-exchange experiments will further deepen understanding of the properties of the fluoride complexes of Db.

4. Conclusion

Cation-exchange behavior of ^{95}Nb and ^{179}Ta was studied in $\text{HF}/0.1\text{ M HNO}_3$ by batch method. It was found that reaction kinetics of both the elements in the cation exchange is fast under the present experimental conditions, whereas that of Ta in the solution with the lowest $[\text{F}^-]$ of 10^{-7} M may not be sufficiently fast. The K_d values of Nb and Ta decreased with increasing $[\text{F}^-]$, indicating that the neutral and anionic fluoride complexes are formed as $[\text{F}^-]$ increases. Adsorption behavior

on the cation-exchange resin was clearly different between Nb and Ta in the studied $[\text{F}^-]$ range of 10^{-7} – 10^{-5} M. This suggests that the chemical species of the fluoride complexes are different between these elements. The investigation on the cation-exchange behavior of Db under the present experimental conditions would lead to the further understanding of the fluoride complex formation of Db.

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