

## Fluoride Complexation of Element 104, Rutherfordium

Hiromitsu Haba,<sup>\*,†,‡</sup> Kazuaki Tsukada,<sup>†</sup> Masato Asai,<sup>†</sup> Atsushi Toyoshima,<sup>†,§</sup>  
 Kazuhiko Akiyama,<sup>†</sup> Ichiro Nishinaka,<sup>†</sup> Masaru Hirata,<sup>†</sup> Tsuyoshi Yaita,<sup>†</sup>  
 Shin-ichi Ichikawa,<sup>†</sup> Yuichiro Nagame,<sup>†</sup> Ken-ichiro Yasuda,<sup>†</sup> Yutaka Miyamoto,<sup>†</sup>  
 Tetsuya Kaneko,<sup>†</sup> Shin-ichi Goto,<sup>||</sup> Sawako Ono,<sup>||</sup> Toshiyuki Hirai,<sup>||</sup> Hisaaki Kudo,<sup>||</sup>  
 Mitsuru Shigekawa,<sup>§</sup> Atsushi Shinohara,<sup>§</sup> Yasuji Oura,<sup>⊥</sup> Hiromichi Nakahara,<sup>⊥</sup>  
 Keisuke Sueki,<sup>⊗</sup> Hidetoshi Kikunaga,<sup>○</sup> Norikazu Kinoshita,<sup>○</sup> Naoya Tsuruga,<sup>○</sup>  
 Akihiko Yokoyama,<sup>○</sup> Minoru Sakama,<sup>#</sup> Shuich Enomoto,<sup>‡</sup> Matthias Schädel,<sup>▽</sup>  
 Willy Brüchele,<sup>▽</sup> and Jens V. Kratz<sup>◆</sup>

*Contribution from the Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan, Cyclotron Center, RIKEN, Wako, Saitama 351-0198, Japan, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, Faculty of Science, Niigata University, Niigata, Niigata 950-2181, Japan, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan, Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan, Faculty of Science, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan, School of Health Sciences, University of Tokushima, Tokushima, Tokushima 770-8509, Japan, Gesellschaft für Schwerionenforschung, D-64291 Darmstadt, Germany, and Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany*

Received December 19, 2003; E-mail: haba@riken.jp

**Abstract:** Fluoride complexation of element 104, rutherfordium (Rf), produced in the  $^{248}\text{Cm}(^{18}\text{O},5n)^{261}\text{Rf}$  reaction has been studied by anion-exchange chromatography on an atom-at-a-time scale. The anion-exchange chromatographic behavior of Rf was investigated in 1.9–13.9 M hydrofluoric acid together with those of the group-4 elements Zr and Hf produced in the  $^{18}\text{O}$ -induced reactions on Ge and Gd targets, respectively. It was found that the adsorption behavior of Rf on anion-exchange resin is quite different from those of Zr and Hf, suggesting the influence of relativistic effects on the fluoride complexation of Rf.

## 1. Introduction

Increasingly strong relativistic effects on the valence electrons of transactinide elements can induce deviations in chemical properties from the periodicity based on lighter homologues in the periodic table.<sup>1</sup> The first transactinide element, rutherfordium (Rf), is expected to be a group-4 member with a ground-state electronic configuration of  $[\text{Rn}]5f^{14}6d^27s^2$ , though relativistic calculations have predicted configurations such as  $6d^27s^2$ ,  $7s^27p^2$ , and  $6d7s^27p$ .<sup>1</sup> Extremely low production yields and short half-lives of transactinide nuclei force us to perform rapid, efficient, and repetitive experiments with single atoms. For single-atom chemistry, the classical law of mass action is no longer valid, because the atom cannot exist in the different

chemical forms taking part in the chemical equilibrium at the same time. The chemical study needs to be carried out on the phenomena that give the same results for only a few atoms and for macro amounts. Such requirements limit the chemical study to only the phenomena of fast kinetics by techniques such as ion-exchange chromatography, gas chromatography, solvent extraction, and other procedures with rapid attainment of a chemical equilibrium. Guillaumont et al.<sup>2</sup> defined an equilibrium constant for reactions with very small numbers of atoms in terms of the probabilities of finding the atom in one phase or the other and concluded that it is valid to combine the results of many separate single-atom experiments to get statistically significant results. Although several attempts have been made to study chemical properties of Rf by solvent extraction and ion-exchange methods in aqueous solutions, some of these experiments show conflicting results and some others are criticized due to unsatisfactory experimental conditions.<sup>1</sup> Furthermore, few quantitative data such as equilibrium constants and/or distribution coefficients, which are essential for the discussion of the influence of relativistic effects, are available at present.

<sup>†</sup> Japan Atomic Energy Research Institute.

<sup>‡</sup> RIKEN.

<sup>§</sup> Osaka University.

<sup>||</sup> Niigata University.

<sup>⊥</sup> Tokyo Metropolitan University.

<sup>⊗</sup> University of Tsukuba.

<sup>○</sup> Kanazawa University.

<sup>#</sup> University of Tokushima.

<sup>▽</sup> Gesellschaft für Schwerionenforschung.

<sup>◆</sup> Universität Mainz.

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A monofunctional anion-exchange resin with a strongly basic group provides an extremely simple and rapid technique for the determination of the complexing strength, ionic radius, and ionic charge of an anion in aqueous solution. Thus, we have studied the anion-exchange behavior of Rf together with those of lighter homologues of group-4 elements Zr and Hf in 4.0–11.5 M HCl and 8.0 M HNO<sub>3</sub>.<sup>3</sup> It has been found that the adsorption trends of Rf in HCl and HNO<sub>3</sub> are very similar to those of Zr and Hf, clearly indicating that Rf is a typical group-4 member.

Reported in this paper is our recent result of the anion-exchange study of Rf in hydrofluoric acid. HF is one of the best media on anion-exchange resin, because hydrolysis needs not be taken into consideration due to the high complexing strength of the fluoride ion. Previous studies<sup>4,5</sup> of the fluoride complexation of Rf have shown that Rf forms anionic fluoride complexes like its lighter homologue Hf in 0.2 M HF and in the mixed acid solution of 0.27 M HF/0.1 and 0.2 M HNO<sub>3</sub>. Recently, a different adsorption behavior between Rf and its homologues Zr and Hf was observed in anion- and cation-exchange studies in 0.0001–0.1 M HF/0.1 M HNO<sub>3</sub>.<sup>6</sup> A slight correction<sup>1,7</sup> of the original distribution coefficients ( $K_d$ ) did not modify the conclusions.<sup>6</sup> Also cited is an extraction study of fluoride complexes of Ti, Zr, Hf, and Rf into triisooctylamine (TiOA) from 0.5 to 4 M HF,<sup>8</sup> which shows some evidence for extraction of Rf into TiOA from 0.5 M HF.

In the present study, we first measured  $K_d$  values of Zr and Hf on the anion-exchange resin in 0.97–26.4 M HF under static conditions, i.e., in batch experiments, using the long-lived radiotracers <sup>89</sup>Zr and <sup>175</sup>Hf. In the experiments with the short-lived <sup>261</sup>Rf, the anion-exchange behavior of <sup>261</sup>Rf, <sup>85</sup>Zr, and <sup>169</sup>Hf was investigated under dynamic conditions, i.e., in chromatographic experiments, using the automated ion-exchange separation apparatus coupled with the detection system for alpha ( $\alpha$ ) spectroscopy, AIDA.<sup>3,9</sup> The  $K_d$  values of Rf on the anion-exchange resin were successfully determined with AIDA by running cycles of the anion-exchange experiments 4226 times within the concentration range of HF from 1.9 to 13.9 M. The complexing strength of the Rf fluoride is discussed by comparing with those of Zr and Hf and also with the theoretical prediction by the relativistic molecular density-functional calculations.<sup>10,11</sup>

## 2. Experimental Section

**2.1. Batch Experiments.** The radiotracers <sup>89</sup>Zr (half-life  $T_{1/2} = 78.41$  h) and <sup>175</sup>Hf ( $T_{1/2} = 70$  days) were produced in the <sup>89</sup>Y( $p,n$ ) and <sup>175</sup>Lu( $p,n$ ) reactions, respectively, using the JAERI tandem accelerator and the RIKEN K70 AVF cyclotron. These tracers were chemically separated from the target materials and stored in polypropylene vessels in 0.1 M HF solutions. The chemical separation procedures were almost the same as those described in ref 12.

The anion-exchange resin used was MCI GEL CA08Y, supplied by Mitsubishi Chemical Corporation, a strongly basic quaternary-amine polymer with a particle size of  $22 \pm 2 \mu\text{m}$ . The commercially available CA08Y in the chloride form was converted to the fluoride form by washing in the column with 26 M HF. Then, the resin was washed thoroughly by the batch method with H<sub>2</sub>O and dried to a constant weight at 80 °C in a vacuum oven. A 10–200 mg portion of CA08Y and 3 mL of the 0.97–26.4 M HF solution containing 50  $\mu\text{L}$  of the tracer solution were placed in a polypropylene tube and shaken for 100 min at 20 °C. After centrifugation, 1 mL of the aqueous phase was precisely pipetted into a polyethylene tube and subjected to  $\gamma$ -ray spectrometry using a Ge detector. As a standard sample, 50  $\mu\text{L}$  of the tracer solution was diluted to 1 mL with 0.1 M HF in another polyethylene tube. Control experiments without the CA08Y resin were also performed for exclusion of sorption on the inner wall of the polypropylene tube. The numbers of <sup>89</sup>Zr and <sup>175</sup>Hf atoms used for each batch experiment were  $10^{10}$  and  $10^{11}$ , respectively. The concentration of the HF solution was determined by titration with a standardized NaOH solution.

**2.2. On-Line Chromatographic Experiments. 2.2.1. Production of <sup>261</sup>Rf, <sup>85</sup>Zr, and <sup>169</sup>Hf.** The isotope <sup>261</sup>Rf ( $T_{1/2} = 78$  s) was produced in the <sup>248</sup>Cm(<sup>18</sup>O, $5n$ ) reaction with a 94-MeV <sup>18</sup>O beam. The <sup>248</sup>Cm target of 610  $\mu\text{g cm}^{-2}$  thickness and 5 mm diameter was prepared by electrodeposition of Cm(NO<sub>3</sub>)<sub>3</sub> in 2-propanol onto a 2.4 mg cm<sup>-2</sup> beryllium backing foil. The beam intensity was approximately 300 particle nA. It is important to perform Rf experiments together with Zr and Hf under identical conditions to find different chemical behavior among the homologues. Therefore, Gd (39.3%-enriched <sup>152</sup>Gd of 36  $\mu\text{g cm}^{-2}$  thickness) was admixed in the <sup>248</sup>Cm target to simultaneously produce Hf isotopes. The 108.5-MeV <sup>18</sup>O beam, delivered from the JAERI tandem accelerator, passed through a HAVAR vacuum window (2.0 mg cm<sup>-2</sup>), the helium cooling gas (0.09 mg cm<sup>-2</sup>), and the beryllium target backing, and it finally entered the target material at the energy of 94 MeV. At this incident energy, the excitation function for the <sup>248</sup>Cm(<sup>18</sup>O, $5n$ )<sup>261</sup>Rf reaction exhibits the maximum cross section of  $13 \pm 3$  nb.<sup>13</sup> This results in an expected production rate of about 2 atoms min<sup>-1</sup> under the present experimental condition.

To investigate the behavior of Zr and Hf, <sup>85</sup>Zr ( $T_{1/2} = 7.86$  min) and <sup>169</sup>Hf ( $T_{1/2} = 3.24$  min) were simultaneously produced in the <sup>nat</sup>Ge(<sup>18</sup>O, $xn$ ) and <sup>nat</sup>Gd(<sup>18</sup>O, $xn$ ) reactions, respectively (nat = natural isotopic abundance). The <sup>nat</sup>Gd target of 370  $\mu\text{g cm}^{-2}$  thickness and 5 mm diameter was electrodeposited on a 2.7 mg cm<sup>-2</sup> beryllium backing, and then on the resulting <sup>nat</sup>Gd target, the <sup>nat</sup>Ge target of 660  $\mu\text{g cm}^{-2}$  thickness was deposited by vacuum evaporation.

Reaction products recoiling out of the target were stopped in helium gas (~1 bar), attached to KCl aerosols generated by sublimation of the KCl powder at 640 °C, and continuously transported through a Teflon capillary (2.0 mm i.d., 20 m long) to the chemistry laboratory. The transport efficiency of <sup>261</sup>Rf was estimated to be 35%.<sup>13</sup>

**2.2.2. Anion-Exchange Chromatography.** The on-line anion-exchange chromatography was performed using AIDA.<sup>3,9</sup> This apparatus

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consists of a modified automated rapid chemistry apparatus (ARCA)<sup>14</sup> which is a miniaturized computer-controlled liquid chromatography system and a newly developed automated on-line  $\alpha$ -particle detection system. Two different microcolumns, 1.6 mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm, were used for the measurements of a wide range of  $K_d$  values.

The nuclear reaction products transported by the He/KCl gas-jet system were deposited on the collection site of AIDA. After deposition for 125 s, <sup>261</sup>Rf and <sup>169</sup>Hf were dissolved in a 240 (260)<sup>15</sup>  $\mu$ L HF solution of various concentrations of 13.9, 11.6, 7.7, 5.8, 4.8, and 3.9 (3.0, 2.4, and 1.9) M and were fed onto the column at a flow rate of 740 (1000)  $\mu$ L min<sup>-1</sup>, which corresponds to 0.88 (6.1) column volumes s<sup>-1</sup>. The effluent was collected on a tantalum disk as fraction 1 and evaporated to dryness using hot helium gas and a halogen heat lamp. The remaining Rf and Hf in the column were eluted with 210 (200)  $\mu$ L of 4.0 M HCl at a flow rate of 1000  $\mu$ L min<sup>-1</sup>. In the previous experiments,<sup>3</sup> we found that 200  $\mu$ L of 4.0 M HCl was enough to strip Rf as well as Zr and Hf from the anion-exchange column. The 4.0 M HCl effluent was collected on another tantalum disk and was evaporated to dryness as fraction 2. The pair of tantalum disks, fractions 1 and 2, was automatically transferred to an  $\alpha$ -spectrometry station equipped with eight 600 mm<sup>2</sup> passivated ion-implanted planar silicon (PIPS) detectors. Counting efficiencies of each detector ranged from 30% to 40% depending on geometrical differences of the dried sources, and its  $\alpha$ -particle energy resolution was 110–200 keV fwhm. All events were registered event by event. After the  $\alpha$ -particle measurement, the 493 keV  $\gamma$ -ray of <sup>169</sup>Hf was monitored with Ge detectors for every third or fourth pair of the Rf samples to determine the distribution of Hf and its chemical yield. The chemical yield of Hf including deposition and dissolution efficiencies of the aerosols was approximately 60%.

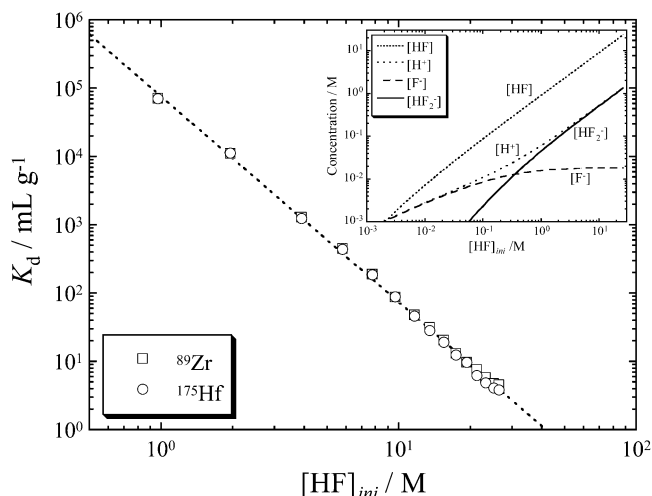
In the experiments with <sup>85</sup>Zr and <sup>169</sup>Hf, the reaction products deposited on the collection site of AIDA were dissolved in 3.9–17.4 M HF and fed onto the microcolumn under the same experimental condition as those with <sup>261</sup>Rf. The number of <sup>85</sup>Zr and <sup>169</sup>Hf atoms present in each anion-exchange experiment was about 10<sup>6</sup>. The effluent fractions were collected in 7 polyethylene tubes and were assayed by  $\gamma$ -ray spectrometry with Ge detectors to evaluate the sorption of Zr and Hf on the resin and to obtain their elution curves.

### 3. Results and Discussion

**3.1. Batch Experiments.** The distribution constant  $K$  in unit of mL g<sup>-1</sup> of the atoms in question between the resin and the solution was obtained using the following equation:

$$K = \frac{A_r V_s}{A_s W_r}, \quad (1)$$

where  $A_r$  and  $A_s$  are the radioactivities in the resin and the solution, respectively,  $V_s$  is the volume of the acid solution (mL), and  $W_r$  is the mass of the dry resin (g). If the radioactivity ratio of  $A_r A_s^{-1}$  represents the distribution of a single chemical species containing the atom in question between the resin and the solution,  $K$  is identical with the distribution coefficient  $K_d$ . The following discussion is carried on with the assumption that the radioactive atoms are mostly bound to a single chemical species. In Figure 1, the variation of the  $K_d$  values of <sup>89</sup>Zr and <sup>175</sup>Hf on CA08Y is shown by open squares ( $\square$ ) and open circles ( $\circ$ ), respectively, as a function of the initial HF concentration,  $[\text{HF}]_{\text{ini}}$ .



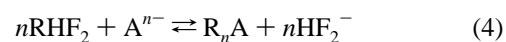
**Figure 1.** Variation of the distribution coefficient,  $K_d$ , of <sup>89</sup>Zr and <sup>175</sup>Hf on the anion-exchange resin CA08Y as a function of the initial HF concentration,  $[\text{HF}]_{\text{ini}}$ . The data for Zr and Hf are shown by open squares ( $\square$ ) and open circles ( $\circ$ ), respectively. The linear relationship with slope  $-3.0 \pm 0.1$  in the  $\log K_d$ – $\log[\text{HF}]_{\text{ini}}$  plot is indicated by a dotted line. The inset shows the variation of  $[\text{HF}]$ ,  $[\text{H}^+]$ ,  $[\text{F}^-]$ , and  $[\text{HF}_2^-]$  as a function of  $[\text{HF}]_{\text{ini}}$ .

As shown in Figure 1, the  $K_d$  values of Zr and Hf are identical with each other, and both decrease with an increase of  $[\text{HF}]_{\text{ini}}$ . A linear relationship with a slope of  $-3.0 \pm 0.1$  was found in the  $\log K_d$ – $\log[\text{HF}]_{\text{ini}}$  plot as indicated by a dotted line, although the slope and the observed linear relationship cannot be straightforwardly understood in terms of the anionic state of the fluoride complex without knowing the activity coefficients of the chemical species involved (the mean stoichiometric activity coefficients of hydrofluoric acid in aqueous solutions are available up to 4 M HF<sup>16</sup>).

As HF is a weak acid, equilibrations among HF,  $\text{H}^+$ ,  $\text{F}^-$ , and  $\text{HF}_2^-$  in the solution are established in the following two chemical relations.<sup>17</sup>

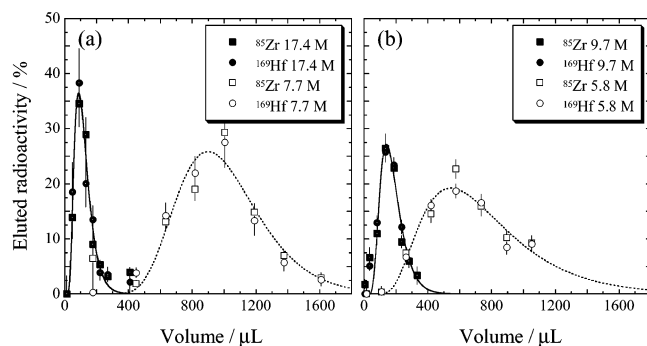


The concentrations of HF,  $\text{H}^+$ ,  $\text{F}^-$ , and  $\text{HF}_2^-$  in the solution can be calculated on the basis of the law of mass action using the dissociation constants  $K_1 = 935 \text{ M}^{-1}$  and  $K_2 = 3.12 \text{ M}^{-1}$  for the first (eq 2) and second (eq 3) equilibria, respectively.<sup>17</sup> The inset of Figure 1 shows the variation of  $[\text{HF}]$ ,  $[\text{H}^+]$ ,  $[\text{F}^-]$ , and  $[\text{HF}_2^-]$  as a function of  $[\text{HF}]_{\text{ini}}$ . Above 1 M HF, the concentration of the anionic  $\text{HF}_2^-$  species is more than 1 order of magnitude higher than that of  $\text{F}^-$ , and  $[\text{HF}_2^-]$  increases linearly with an increase of  $[\text{HF}]_{\text{ini}}$ :  $\log[\text{HF}_2^-] \approx \log[\text{HF}]_{\text{ini}} - 1.3$ . Thus, the decrease of the  $K_d$  values of Zr and Hf with  $[\text{HF}]_{\text{ini}}$  shown in Figure 1 is explained as the displacement of the metal complex from the binding sites of the resin with  $\text{HF}_2^-$  as the main anionic species in the solution, although any quantitative discussion requires the knowledge of the activities of the chemical species involved. Assuming that the adsorption equilibrium of an anion  $\text{A}^{n-}$  with the charge state  $n-$  can be represented by the equation



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(15) The values given in parentheses refer to the condition when the 1.0 mm i.d.  $\times$  3.5 mm column was used.



**Figure 2.** Elutions of  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  from (a) the 1.6 mm i.d.  $\times$  7.0 mm column in 17.4 and 7.7 M HF at a flow rate of  $740 \mu\text{L min}^{-1}$  and from (b) the 1.0 mm i.d.  $\times$  3.5 mm column in 9.7 and 5.8 M HF at a flow rate of  $1000 \mu\text{L min}^{-1}$ . The eluted radioactivities of  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  are depicted by squares ( $\blacksquare$ ,  $\square$ ) and circles ( $\bullet$ ,  $\circ$ ), respectively. The solid (—) and dotted (⋯) curves indicate the results of the theoretical fits by the Glueckauf equation.<sup>18</sup> The numbers of theoretical plates  $N$  were fitted to  $4.8 \pm 0.5$  and  $4.6 \pm 0.5$  for the 1.6 mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm columns, respectively. The peak volumes  $\bar{v}$  for the 1.6 mm i.d.  $\times$  7.0 mm column are  $88 \pm 3$  and  $900 \pm 30 \mu\text{L}$  at 17.4 and 7.7 M HF, respectively, while those for the 1.0 mm i.d.  $\times$  3.5 mm one are  $140 \pm 10$  and  $550 \pm 20 \mu\text{L}$  at 9.7 and 5.8 M, respectively.

where R represents the resin, the equilibrium constant can be expressed in terms of the law of mass action as

$$K_{A^{n-}} = \frac{[\text{R}_n\text{A}][\text{HF}_2^-]^n}{[\text{RHF}_2][\text{A}^{n-}]} \quad (5)$$

**3.2. On-Line Chromatographic Experiments.** In Figure 2, typical elution curves for  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  simultaneously produced from the Ge/Gd target are shown for the experiments with (a) the 1.6 mm i.d.  $\times$  7.0 mm column in the 17.4 and 7.7 M HF solution at a flow rate of  $740 \mu\text{L min}^{-1}$  and with (b) the 1.0 mm i.d.  $\times$  3.5 mm one in the 9.7 and 5.8 M HF at a flow rate of  $1000 \mu\text{L min}^{-1}$ . The percentages of the eluted radioactivities of  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  are depicted by squares and circles, respectively, and they are nearly the same as expected from the same  $K_d$  values in the batch experiment (see Figure 1). According to the Glueckauf equation of chromatography,<sup>18</sup> the eluted radioactivity  $A(v)$  with the effluent volume  $v$  is represented by the following equation:

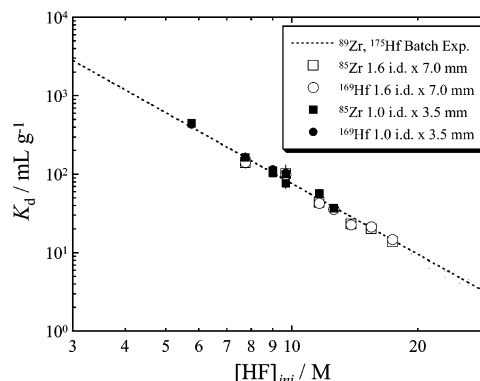
$$A(v) = A_{\text{max}} \exp\left\{-\frac{N(\bar{v} - v)^2}{2\bar{v}v}\right\} \quad (6)$$

where parameters  $A_{\text{max}}$ ,  $N$ , and  $\bar{v}$  are the maximum peak height, the number of theoretical plates, and the peak volume, respectively. It is noted here that the  $v$  and  $\bar{v}$  values are corrected for the dead volume of the columns, which are 40 and  $25 \mu\text{L}$  for the experiments with the 1.6 mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm columns, respectively. The results of the theoretical fit by eq 6 are shown by the solid (—) and dotted (⋯) curves in Figure 2, showing good agreements between the experiments and the Glueckauf equation.<sup>18</sup>

In the dynamic chromatographic system, the  $K_d$  value is described as

$$K_d = \bar{v}/m_r \quad (7)$$

where  $m_r$  is the mass of the dry resin.<sup>18</sup> The average  $m_r$  values were measured to be  $6.6 \pm 0.3$  and  $1.3 \pm 0.1 \text{ mg}$  for the 1.6



**Figure 3.** Variation of the distribution coefficient,  $K_d$ , of  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  on the anion-exchange resin CA08Y obtained from the chromatographic experiments as a function of the initial HF concentration,  $[\text{HF}]_{\text{ini}}$ . The data from the 1.6 mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm columns are depicted by open ( $\square$ ,  $\circ$ ) and closed ( $\blacksquare$ ,  $\bullet$ ) symbols, respectively. The dotted line indicates the  $K_d$  values of  $^{89}\text{Zr}$  and  $^{175}\text{Hf}$  from the batch experiment.

mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm columns, respectively. In Figure 3, the  $K_d$  values of Zr and Hf calculated by eq 7 are shown by open and closed symbols for the experiments with the columns of 1.6 mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm, respectively. The  $K_d$  values from the different columns are consistent with each other. The dotted line indicates the  $K_d$  values of  $^{89}\text{Zr}$  and  $^{175}\text{Hf}$  obtained from the batch experiment mentioned in section 3.1. The  $K_d$  values deduced from the dynamic column method agree well with those from the static batch one. This indicates that the  $K$  value in eq 1 is equal to the  $K_d$  value defined in eq 7 for a single chemical species, and also that the ion-exchange processes taking place in the present column experiment such as the one shown in eq 4 reach an equilibrium state fast enough.

The results of the  $^{261}\text{Rf}$  experiments are summarized in Table 1, where the initial HF concentration  $[\text{HF}]_{\text{ini}}$ , the total  $^{18}\text{O}$  beam dose, the number of cycles of the experiment, the chemical yield determined by  $^{169}\text{Hf}$  radioactivity measurements, the number of observed  $\alpha$  particles of  $^{261}\text{Rf}$  and of its daughter  $^{257}\text{No}$  ( $\alpha$ ) and correlated  $\alpha$  particle pairs of  $^{261}\text{Rf}$  and  $^{257}\text{No}$  ( $\alpha$ - $\alpha$ ) in fractions 1 and 2, and the percent adsorptions (%ads) of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  are listed. From the 4226 cycles of the ion-exchange experiments, a total of 266  $\alpha$  events from 78-s  $^{261}\text{Rf}$  (8.28 MeV)<sup>19</sup> and its daughter 25-s  $^{257}\text{No}$  (8.22, 8.27, 8.32 MeV)<sup>19</sup> were registered in the energy range 8.00–8.36 MeV, including 25 time-correlated  $\alpha$  pairs of  $^{261}\text{Rf}$  and its daughter  $^{257}\text{No}$ . The event ratio between  $\alpha$  singles and  $\alpha$ - $\alpha$  correlations was estimated to be 11:1 taking the counting efficiency of the detector ( $\sim 35\%$ ), the recoil effect of  $^{257}\text{No}$ , and the decay of  $^{261}\text{Rf}$  and  $^{257}\text{No}$  into consideration. The observed event ratio of 266:25 is reasonably consistent with the estimated event ratio within the counting statistics.

From the radioactivities  $A_1$  and  $A_2$  observed in fractions 1 and 2, respectively, the %ads values on CA08Y were evaluated using the equation

$$\% \text{ads} = \frac{100A_2}{A_1 + A_2} \quad (8)$$

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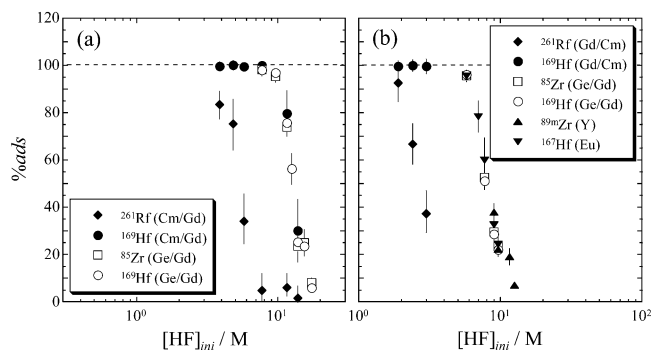
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**Table 1.** Summary of the Anion-Exchange Experiments of  $^{261}\text{Rf}$  in HF Solutions

[HF] <sub>ini</sub> (M)	total beam dose ( $\times 10^{17}$ )	no. cycles of the experiment	chemical yield (%)	$\alpha$ -count in fraction 1		$\alpha$ -count in fraction 2		%ads of $^{261}\text{Rf}$ (%)	%ads of $^{169}\text{Hf}$ (%)
				$\alpha$	$\alpha$ - $\alpha$	$\alpha$	$\alpha$ - $\alpha$		
13.9	1.75	849	51 $\pm$ 13	43	5	1	0	1.5 <sup>+5.2</sup> <sub>-1.5</sub>	30 $\pm$ 14
11.6	1.64	631	66 $\pm$ 19	35	2	2	0	6.0 <sup>+6.0</sup> <sub>-3.7</sub>	80 $\pm$ 10
7.7	0.775	322	66 $\pm$ 20	23	1	1	0	4.8 <sup>+7.2</sup> <sub>-4.8</sub>	99.8 $\pm$ 1.6
5.8	0.653	271	72 $\pm$ 17	16	1	6	0	34.0 <sup>+11.7</sup> <sub>-9.5</sub>	99.6 $\pm$ 1.9
4.8	0.326	179	84 $\pm$ 16	5	0	10	2	75.2 <sup>+10.4</sup> <sub>-11.0</sub>	100.1 $\pm$ 1.2
3.9	1.06	532	65 $\pm$ 16	10	0	31	4	83.4 <sup>+3.6</sup> <sub>-6.1</sub>	99.4 $\pm$ 1.7
3.0	1.02	465	57 $\pm$ 17	24	2	10	2	37.3 <sup>+9.6</sup> <sub>-8.2</sub>	99.5 $\pm$ 3.1
2.4	1.28	501	54 $\pm$ 19	13	1	17	3	66.6 <sup>+8.8</sup> <sub>-8.5</sub>	99.8 $\pm$ 2.5
1.9	1.36	476	47 $\pm$ 16	3	0	16	2	92.5 <sup>+5.9</sup> <sub>-7.9</sub>	99.5 $\pm$ 2.4

The corrections for the radioactive decay, and the background from cosmic rays and electronic noise, etc., were considered for  $A_1$  and  $A_2$ . The average background count rate was determined in a long counting interval after the Rf experiment as  $3.2 \times 10^{-6}$  counts  $\text{s}^{-1}$  for each detector in the  $\alpha$  energy range of interest. According to the procedure described in ref 20, the contribution of  $^{257}\text{No}$  formed from  $^{261}\text{Rf}$  during the collection time before the chemical separation was taken into account on the basis of the standard equations of growth and decay and the %ads values of No determined in the separate experiments using  $^{255}\text{No}$  produced in the  $^{248}\text{Cm}(^{12}\text{C},5n)$  reaction. It was found that the %ads values of No are independent of  $[\text{HF}]_{\text{ini}}$  and the average values are 4.8% and 3.4% for the 1.6 mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm columns, respectively. The  $A_1 + A_2$  values of Rf divided by the total beam doses and the chemical yields for each  $[\text{HF}]_{\text{ini}}$  run are equal to each other within the errors, suggesting a good reproducibility of the present experiments. The asymmetric error limits of the %ads values of  $^{261}\text{Rf}$  were evaluated from the counting statistics of the observed  $\alpha$  events based on the 68% confidence intervals for Poisson distributed variables.<sup>21</sup> On the other hand, the errors associated with the chemical yields and the %ads of  $^{169}\text{Hf}$  represent the standard deviation in the  $\gamma$ -ray measurements of every third or fourth pair of the Rf samples in each  $[\text{HF}]_{\text{ini}}$ .

The %ads values of Rf, Zr, and Hf are shown in Figure 4 as a function of  $[\text{HF}]_{\text{ini}}$  for the experiments with (a) the 1.6 mm i.d.  $\times$  7.0 mm column and with (b) the 1.0 mm i.d.  $\times$  3.5 mm one. The data observed for  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  that are simultaneously produced from the Cm/Gd target are shown by closed diamonds ( $\blacklozenge$ ) and closed circles ( $\bullet$ ), respectively, while those for  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  from the Ge/Gd target observed in a separate run are shown by open squares ( $\square$ ) and open circles ( $\circ$ ), respectively. The %ads values of Zr and Hf were also measured for the 1.0 mm i.d.  $\times$  3.5 mm column in separate experiments using  $^{89\text{m}}\text{Zr}$  and  $^{167}\text{Hf}$  produced in the  $^{89}\text{Y}(p,n)$  and  $^{167}\text{Eu}(^{19}\text{F},xn)$  reactions, respectively. They are included in Figure 4b by closed triangles ( $\blacktriangle$ ) for  $^{89\text{m}}\text{Zr}$  and by closed inverse triangles ( $\blacktriangledown$ ) for  $^{167}\text{Hf}$ . As shown in Figure 4a,b, the %ads values of Zr and Hf obtained by the on-line experiments in different experiments using different targets agree well, and they decrease steeply with an increase of  $[\text{HF}]_{\text{ini}}$  above  $\sim 8$  M for the 1.6 mm i.d.  $\times$  7.0



**Figure 4.** Variation of the percent adsorption, %ads, of Rf, Hf, and Zr on the anion-exchange resin CA08Y, obtained with (a) the 1.6 mm i.d.  $\times$  7.0 mm column and with (b) the 1.0 mm i.d.  $\times$  3.5 mm one, as a function of the initial HF concentration,  $[\text{HF}]_{\text{ini}}$ . The data for  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  obtained from the Cm/Gd target are shown by closed diamonds ( $\blacklozenge$ ) and closed circles ( $\bullet$ ), respectively, while those for  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  from the Ge/Gd target are by open squares ( $\square$ ) and open circles ( $\circ$ ), respectively. In part b, the %ads values of  $^{89\text{m}}\text{Zr}$  and  $^{167}\text{Hf}$  produced from the  $^{89}\text{Y}$  and  $^{167}\text{Eu}$  targets, respectively, are also included.

mm column and above  $\sim 5$  M for the 1.0 mm i.d.  $\times$  3.5 mm one, while the %ads of Rf decreases at much smaller  $[\text{HF}]_{\text{ini}}$ .

It is important to evaluate the  $K_d$  values of Rf to establish variations of chemical properties, to compare with theoretical predictions, and to determine thermodynamic constants. Because of the short half-life and low production yield of  $^{261}\text{Rf}$ , however, it is unrealistic to directly determine the  $K_d$  values of Rf from the elution curves based on eqs 6 and 7. Therefore, we deduced the  $K_d$  values of Rf in the following way, assuming that the kinetics in the complexation and ion-exchange processes of Rf are as fast as those for Zr and Hf and that a single complex anionic species of Rf is involved in the ion-exchange process between the solid and liquid phases.

In Figure 5a,b, the correlations between the %ads shown in Figure 4 and the  $K_d$  values of Zr and Hf shown in Figure 1 are plotted by the same symbols as used in Figure 4 for the two kinds of columns. The %ads of Zr and Hf are found to be smoothly correlated with  $K_d$ , and they can be fitted by the following relationship with the free parameters  $a$ ,  $b$ , and  $c$  as shown by solid curves ( $-$ ) in Figure 5a,b.

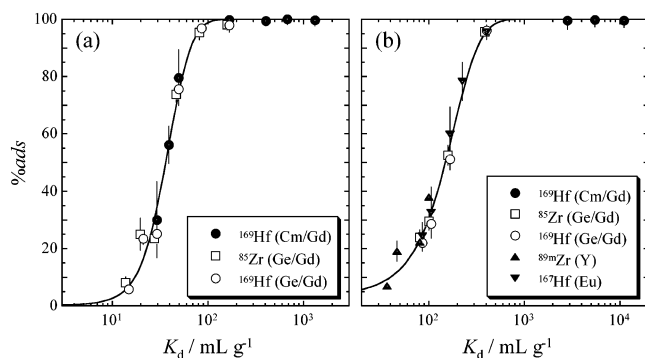
$$\% \text{ads} = 100 \exp[-a \exp\{-b(K_d - c)\}] \quad (9)$$

Then, the %ads of Rf from the dynamic column method with a fixed volume of the effluent as described above can be transformed into the  $K_d$  values using eq 9. The results are shown by diamonds in Figure 6 together with those of Zr and Hf by

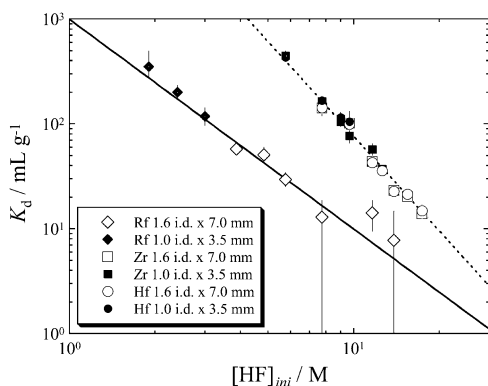
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**Figure 5.** Variation of the percent adsorption, %ads, of Zr and Hf on the anion-exchange resin CA08Y, obtained with (a) the 1.6 mm i.d.  $\times$  7.0 mm column and with (b) the 1.0 mm i.d.  $\times$  3.5 mm one, as a function of the distribution coefficient,  $K_d$ . The data for  $^{169}\text{Hf}$  obtained from the Cm/Gd target are shown by closed circles ( $\bullet$ ), while those for  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  from the Ge/Gd target are by open squares ( $\square$ ) and open circles ( $\circ$ ), respectively. In part b, the %ads values of  $^{89\text{m}}\text{Zr}$  and  $^{167}\text{Hf}$  produced from the  $^{89}\text{Y}$  and  $^{167}\text{Eu}$  targets, respectively, are also included.



**Figure 6.** Variation of the distribution coefficient,  $K_d$ , of Rf, Zr, and Hf on the anion-exchange resin CA08Y as a function of the initial HF concentration,  $[\text{HF}]_{\text{ini}}$ . The  $K_d$  values of Rf, Zr, and Hf are shown by diamonds, squares, and circles, respectively. The data from the 1.6 mm i.d.  $\times$  7.0 mm and 1.0 mm i.d.  $\times$  3.5 mm columns are depicted by open ( $\circ$ ,  $\square$ ,  $\diamond$ ) and closed ( $\bullet$ ,  $\blacksquare$ ,  $\blacklozenge$ ) symbols, respectively. Linear relationships with slopes  $-2.0 \pm 0.3$  for Rf and  $-3.0 \pm 0.1$  for Zr and Hf in the  $\log K_d$ – $\log[\text{HF}]_{\text{ini}}$  plot are indicated by the solid (—) and dotted (---) lines, respectively.

the same symbols as used in Figure 3. The errors associated with the  $^{261}\text{Rf}$  data were propagated from the error limits of the %ads values in Table 1. As shown by a solid line, the  $K_d$  values of Rf decrease linearly with an increase of  $[\text{HF}]_{\text{ini}}$ , and they are smaller than those of Zr and Hf for the same  $[\text{HF}]_{\text{ini}}$  as expected from the smaller %ads in Figure 4. The slope of  $-2.0 \pm 0.3$  of  $\log K_d$  against  $\log[\text{HF}]_{\text{ini}}$  for Rf differs from the slope of  $-3.0 \pm 0.1$  for Zr and Hf, indicating that different anionic fluoride complexes are formed. The errors are evaluated from the least-

squares fitting in Figure 6. The slope analysis based on the law of mass action of eqs 4 and 5 indicates that Rf is present as the hexafluoride complex  $\text{RfF}_6^{2-}$  similar to the well-known  $\text{ZrF}_6^{2-}$  and  $\text{HfF}_6^{2-}$  at the lower  $[\text{HF}]_{\text{ini}}$ <sup>22,23</sup> whereas Zr and Hf are present in the forms of  $\text{ZrF}_7^{3-}$  and  $\text{HfF}_7^{3-}$  at the higher  $[\text{HF}]_{\text{ini}}$  as suggested in refs 22 and 23. The lower coordination number as well as the lower adsorbability of Rf suggests that expected relativistic effects would influence the fluoride complexation of Rf.

Recently, relativistic molecular density-functional calculations of the electronic structure of hexafluoride complexes  $\text{MF}_6^{2-}$  ( $\text{M} = \text{Zr}, \text{Hf}, \text{and Rf}$ ) were performed, and the free energy change  $\Delta E_c$  for various fluorination reactions of Rf was compared with those of Zr and Hf.<sup>10</sup> It is reported that the complex formation of Rf in HF solutions is weaker than those of Zr and Hf when the fluorination starts from non-hydrolyzed cations, though the above formation shows the inverse trend as the fluorination process starts from hydrolyzed species or fluoro complexes. On the other hand, we have carried out the relativistic density functional calculations on the stability of hexafluoride ( $\text{MF}_6^{2-}$ ) and heptafluoride complexes ( $\text{MF}_7^{3-}$ ), assuming the octahedral and pentagonal bipyramidal structures, respectively.<sup>11</sup> The trend in the orbital overlap population between the valence d orbitals of  $\text{M}^{4+}$  and the valence orbitals of  $\text{F}^-$  was found to be  $\text{Zr} \approx \text{Hf} > \text{Rf}$ , suggesting that the Rf complex is less stable than those of Zr and Hf for both the  $\text{MF}_6^{2-}$  and  $\text{MF}_7^{3-}$  complex structures.

#### 4. Conclusions

The distribution coefficients of Rf together with the lighter homologues of the group-4 elements Zr and Hf were first measured by anion-exchange chromatography in the concentration range 1.9–13.9 M HF on an atom-at-a-time scale. It was clearly shown that the adsorption of Rf on the anion-exchange resin is smaller than those of Zr and Hf. The observed large different adsorption behavior between Rf and its homologues Zr and Hf suggests that the relativistic effect strongly influences the fluoride complexation of Rf.

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