Chloride Complexation of Zr and Hf in HCl Investigated by Extended X-ray Absorption Fine Structure Spectroscopy: Toward Characterization of Chloride Complexation of Element 104, Rutherfordium (Rf)

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Chloride complexation of the group-4 elements Zr and Hf in 8.0–11.9 M HCl is investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy to characterize chloro complexes of the transactinide element, rutherfordium (Rf). The complexes of Zr and Hf successively vary with the concentration of HCl from a hydrated complex $[M(H_2O)_8]^{4+}$ at 8.0 M to a hexachloro complex $[MCl_6]^{2-}$ at 11.9 M (M = Zr and Hf). The present structural changes of the Zr and Hf complexes well reflect the previously studied anion-exchange behavior of Zr and Hf in HCl. From both the EXAFS and anion-exchange results, we suggest that Rf forms the same complexes as those of Zr and Hf in HCl, and that the complexation strength of the hexachloro complexes of the group-4 elements, $[MCl_6]^{2-}$ (M = Zr, Hf, and Rf), is in the sequence of Rf > Zr > Hf.

Chemical characterization of the transactinide elements with atomic numbers $Z \geq 104$ is an extremely interesting and challenging subject in modern nuclear and radiochemistry.[1–5] A most important and interesting question is to clarify chemical properties of these newly-synthesized heavy elements and to elucidate the influence of relativistic effects on chemical properties of these heaviest elements.[1,5–7] The transactinide elements (nuclides) are produced in accelerators in heavy-ion-induced nuclear reactions. Because of the short half-lives and extremely low production rates of these nuclides, chemical experiments with transactinides must be done on an atom-at-a-time scale; spectroscopic studies to characterize chemical species of these elements are not applicable. Experiments with the transactinide elements are usually conducted together with expected lighter homologs in the periodic table using partition methods.[1–5] Observed chemical behavior of the transactinide elements is compared to that of the homologs, and then their properties are discussed based on comparative studies with the homologs.

Pioneering anion-exchange studies of the first transactinide element, rutherfordium (Rf, $Z = 104$), in HCl were performed by Hulet et al.[8] and then Czerwinski et al.[9] The results demonstrated that the chloride complexation of Rf is stronger than that of the trivalent actinide elements and is similar to that of the expected lighter homologs Zr and Hf. In a previous report from our group,[10] the adsorption behavior of Rf together with Zr and Hf on an anion-exchange resin in 4.0–11.5 M HCl was systematically studied using an automated rapid ion-exchange separation apparatus. It was found that the adsorption behavior of Rf is very similar to those of Zr and Hf, suggesting that Rf is a typical member of the group-4 elements. The adsorption strength in the order of Rf > Zr > Hf was also clarified. To deepen our understanding of the anion-exchange behavior and to characterize chemical complexes of Rf, structural data of Zr and Hf complexes in HCl are essentially required. Further, structural information of Rf inferred from comparative studies with Zr and Hf is also available to perform theoretical molecular orbital calculations and to discuss the electronic structure of Rf.

The extended X-ray absorption fine structure (EXAFS) measurements can provide information on the local environment around the central atom such as the atomic number (Z), the number of neighboring atoms (N), and their distance from the central atom (R). In the present work, we have measured the EXAFS spectra of Zr and Hf complexes in 8.0–11.9 M HCl and those of Zr complexes on an anion-exchange resin equilibrated with 9.0–11.9 M HCl. The structural changes of these complexes with the HCl concentration are discussed by referring to our anion-exchange results for Zr and Hf.[10] Based on both the EXAFS and anion-exchange results for the chloride complexation of Zr and Hf, we discuss the formation of chloro complexes of Rf in HCl.

Experimental

Commercially available $ZrCl_4$ and $HfCl_4$ powders were dissolved with 8.0, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, and 11.9 M HCl to obtain 0.01 M concentration of Zr and Hf. The concentrations of the HCl solutions were determined by titration with a standardized

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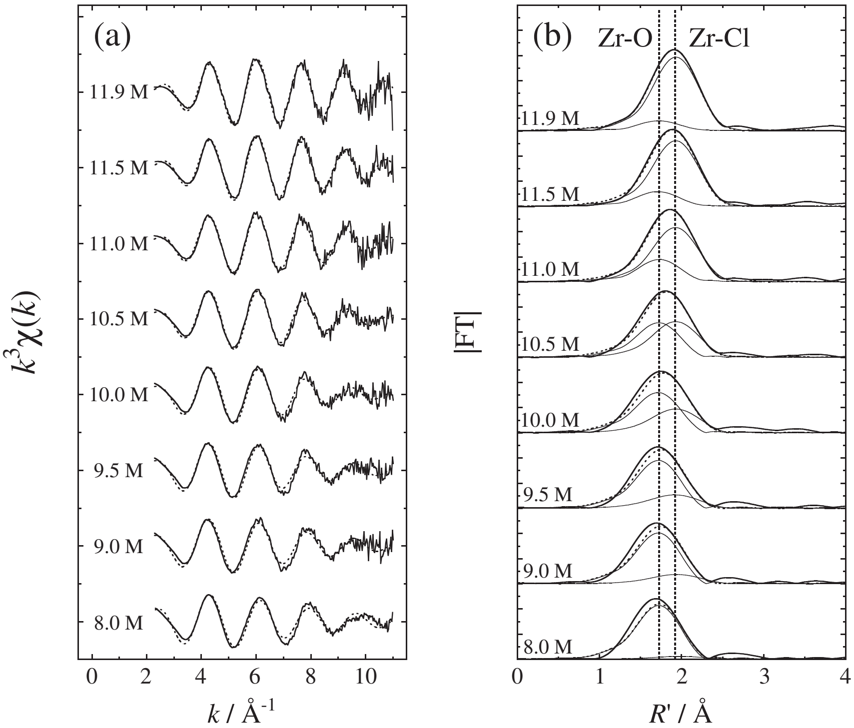

Figure 1. (a) The k^3-weighted raw EXAFS spectra of the Zr complexes in 8.0, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, and 11.9 M HCl (thick solid curves) and (b) the corresponding radial structural functions (thick solid curves). The theoretical fits by FEFF 7 (Ref. 12) are shown by dotted curves. The radial structural functions are decomposed into two components for the shells M–O and M–Cl (thin solid curves). The peak positions for the Zr–O and Zr–Cl shells are indicated by vertical dashed lines.

NaOH solution. Five hundred μL of each sample solution was pipetted and sealed in a polyethylene bag. For the resin samples, the anion-exchange resin used was MCI GEL CA08Y, supplied by Mitsubishi Chemical Corporation in a chloride form, a strongly basic quaternary-amine polymer with a particle size of 22 ± 2 μm. 100 mg of CA08Y and 5 mL of the 0.002 M Zr solutions in 9.0, 10.0, and 11.9 M HCl were added into a polypropylene tube and were equilibrated for 30 min. The mixture was sealed in the polyethylene bag. It is noted that the distribution coefficient (K_d) of Zr on CA08Y is more than 140 mL g^{-1} at $\geq$9.0 M where most of Zr–chloro complexes are adsorbed on the resin.[10]

EXAFS spectra were collected at BL27B of the High Energy Accelerator Research Organization Photon Factory (KEK-PF) using a Si(111) monochromator. Measurements were performed in the fluorescence mode at the Zr K edge and the Hf L_{III} edge with a 7-element Ge detector. Twenty-five to 40 scans were collected for each sample to obtain statistically significant data.

The EXAFS spectra were analyzed according to standard procedures using the WinXAS 3.1 code.[11] The radial structural functions were obtained by Fourier transformation of the EXAFS oscillations in the k space in the range of 2.3–11.0 Å^{-1} for Zr and 1.5–11.0 Å^{-1} for Hf. Fitting analyses were conducted using the backscattering amplitude and phase shift parameters calculated by the ab initio curved-wave multiple-scattering program FEFF 7.[12] Free parameters were the Debye–Waller factor (σ^2), the distance to the neighboring atom (R), the number of neighboring atoms (N), and the relative energy threshold (ΔE_0). The fixed reduction factor ($S_0{}^2$) was included in the present analysis to make it possible to systematically compare the complex structures of Zr and Hf as a function of the HCl concentration. The reduction factor of $S_0{}^2 = 1.10$ was determined by assuming the octahedral hexachloro complex of Zr, $[ZrCl_6]^{2-}$, in 11.9 M HCl as suggested by Raman spectroscopic studies;[13,14] N was fixed to 6, and $S_0{}^2$, σ^2, R, and ΔE_0 were free. Errors estimated from the fits to well-characterized model compounds are ±20% for N and ±0.02 Å for R.

Results and Discussion

The k^3-weighted raw EXAFS spectra of the Zr complexes in 8.0, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, and 11.9 M HCl are shown in Figure 1a together with the theoretical fits by FEFF 7 indicated by dotted curves. The corresponding radial structural functions are depicted in Figure 1b. Note that the R' shown in Figure 1b is not corrected for the EXAFS phase shifts. The analytical results for Hf are given in Figure 2. The fitting parameters, N, R, σ^2, and ΔE_0 for Zr and Hf complexes are summarized in Tables 1 and 2, respectively.

The structural changes of the Zr and Hf complexes are very similar to each other in the HCl concentration range studied. In Figures 1b and 2b, the radial structural functions (thick solid curves) are successfully decomposed into two components corresponding to the shells of M–O and M–Cl (M = Zr and Hf) as shown by thin solid curves. The peak positions for these shells are indicated by vertical dashed lines. At 8.0 M, the M–O peak from the M–OH_2 and/or M–OH bonds is dominant for both Zr and Hf. The R values were determined to be 2.23 and 2.20 Å for the Zr–O and Hf–O shells, respectively, and the N values are 7.4 and 8.0. It is known that the M–OH_2 and M–OH distances in the various oxygen-containing compounds in eight-coordination are in the ranges 2.20–2.29 and 2.10–2.14 Å, respectively.[15] Thus, the water-containing complex structure of

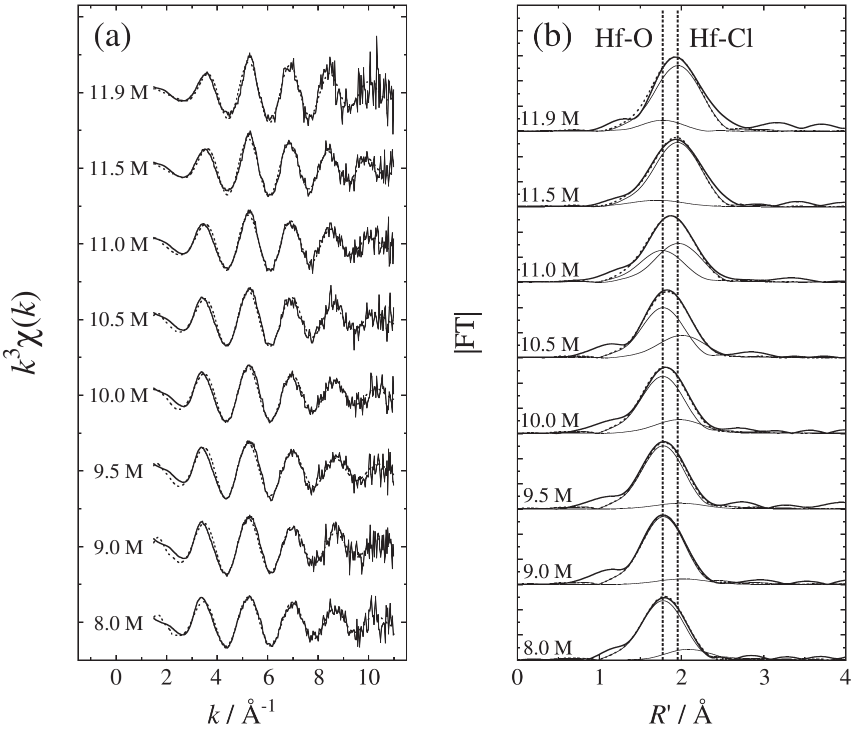

Figure 2. (a) The k^3-weighted raw EXAFS spectra of the Hf complexes in 8.0, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, and 11.9 M HCl and (b) the corresponding radial structural functions. See the caption of Figure 1 for other details.

Table 1. EXAFS Structural Parameters of the Zr Complexes in 8.0–11.9 M HCl

[HCl] /M	Zr–O				Zr–Cl			
	N	R /Å	σ^2	ΔE_0 /eV	N	R /Å	σ^2	ΔE_0 /eV
8.0	7.4	2.23	0.0082	2.90	0.7	2.56	0.0209	9.80
9.0	7.5	2.23	0.0088	0.61	1.4	2.48	0.0161	4.51
9.5	6.7	2.23	0.0083	0.37	2.3	2.48	0.0165	2.51
10.0	6.1	2.24	0.0088	−0.20	3.0	2.47	0.0126	1.92
10.5	4.2	2.23	0.0065	−0.30	3.7	2.46	0.0098	0.46
11.0	2.0	2.23	0.0030	−1.36	5.0	2.46	0.0084	−1.01
11.5	1.3	2.22	0.0032	−5.22	6.1	2.46	0.0086	−0.54
11.9	0.6	2.21	0.0008	−5.15	6.3	2.46	0.0075	−0.81

Table 2. EXAFS Structural Parameters of the Hf Complexes in 8.0–11.9 M HCl

[HCl] /M	Hf–O				Hf–Cl			
	N	R /Å	σ^2	ΔE_0 /eV	N	R /Å	σ^2	ΔE_0 /eV
8.0	8.0	2.20	0.0090	5.21	0.7	2.43	0.0063	17.81
9.0	8.6	2.20	0.0083	5.65	0.8	2.40	0.0163	14.77
9.5	8.2	2.20	0.0085	5.17	0.9	2.41	0.0165	9.99
10.0	7.7	2.20	0.0089	4.75	1.7	2.40	0.0132	8.42
10.5	6.1	2.20	0.0075	4.73	2.5	2.42	0.0118	5.91
11.0	4.9	2.20	0.0106	4.43	3.7	2.41	0.0092	3.71
11.5	2.5	2.19	0.0256	3.40	6.8	2.41	0.0103	2.33
11.9	1.0	2.19	0.0038	3.59	6.6	2.41	0.0098	2.97

$[M(H_2O)_8]^{4+}$ is deduced at 8.0 M. Recently, Hagfeldt et al.[16] investigated the complex structures of the hydrated Zr^{4+} and Hf^{4+} ions in concentrated $HClO_4$ by means of EXAFS. Although the Zr–O and Hf–O distances were determined to be 2.187 ± 0.003 and 2.160 ± 0.012 Å, respectively, as in the eight-coordination, these distances are somewhat smaller than the present ones; Hagfeldt et al.[16] pointed out that their experiment cannot rule out the possibility of a seven-coordinated complex with smaller bond distances ($\approx$2.14 Å for Zr–O and $\approx$2.13 Å for Hf–O). As shown in Figures 1b and 2b, the peak intensity for the M–O shell decreases with an increase of the HCl concentration, while the peaks corresponding to the shell of M–Cl with $R = 2.46$ and 2.41 Å for Zr and Hf, respectively, appear. The N values for M–Cl at 11.9 M are 6.3 and 6.6 for Zr and Hf, respectively, and those for M–O are negligible. The present result confirms the octahedral complex structure of $[MCl_6]^{2-}$ suggested by the Raman spectroscopic studies.[13,14] The present Zr–Cl bond distance agrees well with the literature data of 2.461 ± 0.020 Å averaged for the 24 solid crystals containing $[ZrCl_6]^{2-}$,[17–37] while that for Hf is also consistent with 2.447 ± 0.019 Å for the 14 solid crystals[21,23,27,29,32–35,38–40] within the error limit of the present EXAFS method (±0.02 Å).

In Figure 3, the k^3-weighted raw EXAFS spectra of the Zr complexes adsorbed on the anion-exchange resin CA08Y at 9.0, 10.0, and 11.9 M HCl are shown together with the corresponding radial structural functions. As shown in Figure 3b, only the Zr–Cl peak is observed for the resin samples. The parameters, N, R, σ^2, and ΔE_0, are summarized in Table 3. The average values of $R = 2.48$ Å and $N = 5.9$ agree well with those of the Zr complexes in 11.9 M HCl (see Table 1). The complex structure of Zr and presumably of Hf on the binding site of the anion-exchange resin was found to be $[MCl_6]^{2-}$.

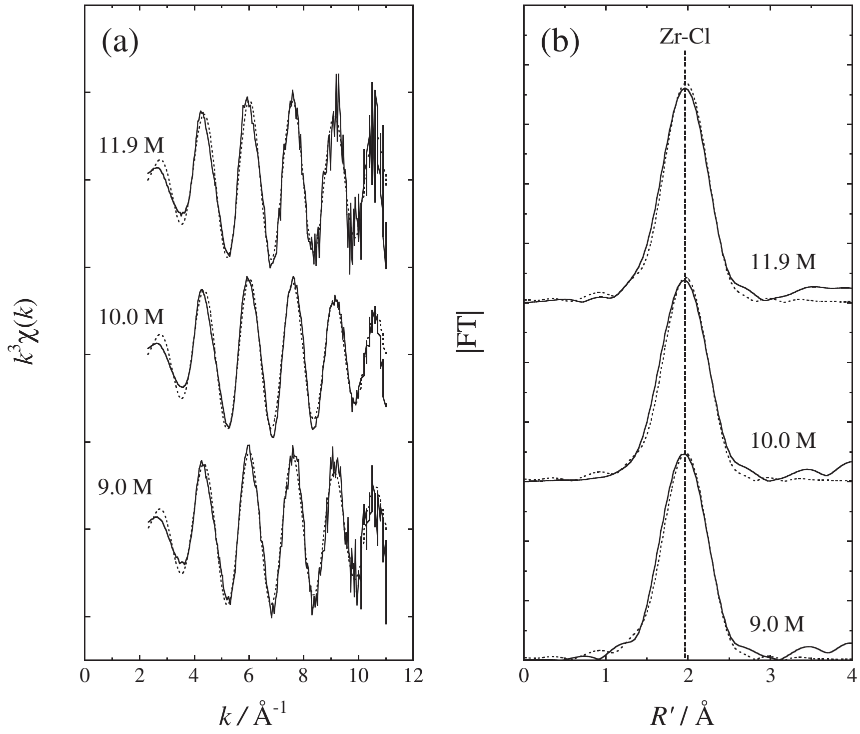

Figure 3. (a) The k^3-weighted raw EXAFS spectra of the Zr complexes adsorbed on the anion-exchange resin CA08Y in 9.0, 10.0, and 11.9 M HCl (solid curves) and (b) the corresponding radial structural functions (solid curves). The theoretical fits by FEFF 7 (Ref. 12) are shown by dotted curves. The peak position for the Zr–Cl shell is indicated by a vertical dashed line.

Table 3. EXAFS Structural Parameters of the Zr Complexes Adsorbed on the Anion-Exchange Resin at 9.0, 10.0, and 11.9 M HCl

[HCl]/M	Zr–Cl			
	N	R/Å	σ^2	ΔE_0/eV
9.0	6.0	2.48	0.0058	0.78
10.0	5.9	2.48	0.0058	0.94
11.9	5.8	2.48	0.0049	1.01

The ratios ρ of the N value for M–Cl ($=N_{\rm Cl}$) to the sum of N for M–Cl and M–O ($=N_{\rm Cl}+N_{\rm O}$) are shown in Figure 4 as a function of the HCl concentration. The data for Zr and Hf are depicted by closed squares connected with a solid curve and by closed circles with a dotted curve, respectively. The ρ values increase smoothly with an increase of the HCl concentration, reflecting that the chlorinating reaction $[\rm M(H_2O)_8]^{4+} \rightarrow [\rm MCl_6]^{2-}$ successively proceeds. It is noted that the onset HCl concentration, at which the ρ value starts to increase, for Zr is apparently lower than that for Hf. This indicates that the affinity of the $\rm Cl^-$ ion for Zr is stronger than that for Hf.

Previously, we measured the distribution coefficients ($K_{\rm d}$) of Zr and Hf on the anion-exchange resin CA08Y in 1.0–11.5 M HCl by a batch method using the radiotracers ^{88}Zr and ^{175}Hf.[10] The $K_{\rm d}$ values of Zr and Hf are shown in Figure 5a. In the HCl concentration range of <7 M, the $K_{\rm d}$ values of Zr and Hf are almost constant, <10 mL g^{-1}, while at the higher HCl concentration, the $K_{\rm d}$ values steeply increase to 1.5×10^4 mL g^{-1} for Zr and 4.5×10^3 mL g^{-1} for Hf at 11.5 M. This increase of the $K_{\rm d}$ value indicates that the component of the hexachloro complex of $[\rm MCl_6]^{2-}$ adsorbed on the CA08Y resin increases with an increase of the HCl concentration. The separation factors $K_{\rm d}$(Zr)/$K_{\rm d}$(Hf) are also plotted in Figure 5b by open diamonds. The $K_{\rm d}$(Zr)/$K_{\rm d}$(Hf) values are 2–3 at <7 M, increase with the HCl concentration up to about 10, and again decrease to 3 at 11.5 M. The ratios of the ρ value of Zr to that of Hf, ρ(Zr)/ρ(Hf), are compared in Figure 5b by closed diamonds. The ρ(Zr)/ρ(Hf) value also shows a peak at around 9.5 M that comes from the difference in the onset HCl concentration for

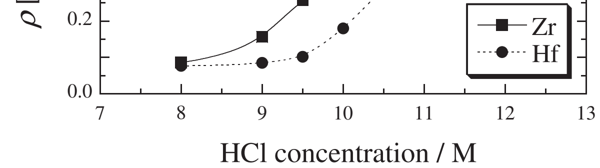

Figure 4. Variations of the ratio ρ of the N value for M–Cl ($=N_{\rm Cl}$) to the sum of N for M–Cl and M–O ($=N_{\rm Cl}+N_{\rm O}$) as a function of the HCl concentration. The data for Zr and Hf are depicted by closed squares connected with a solid curve and closed circles with a dotted curve, respectively.

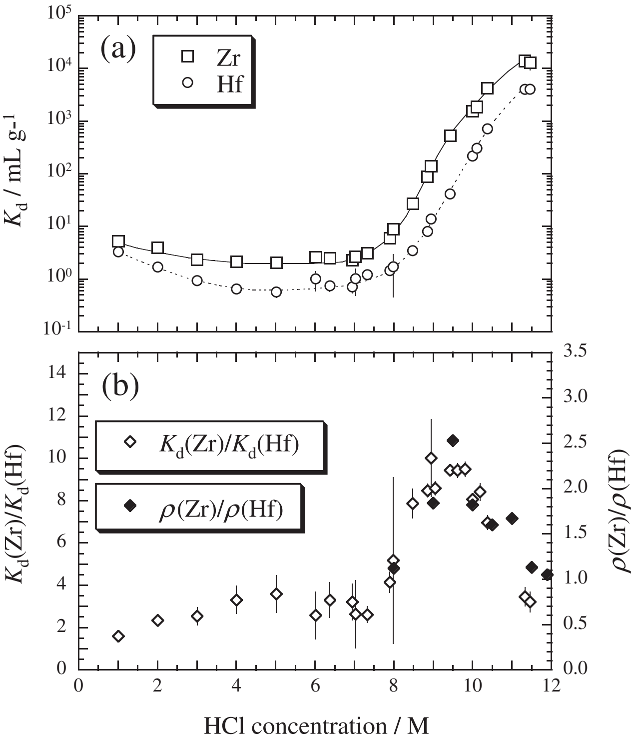

Figure 5. (a) Variations of the distribution coefficients (K_d) for Zr (open squares) and Hf (open circles) on the anion-exchange resin CA08Y as a function of the HCl concentration (Data from Ref. 10). (b) Variations of the separation factor K_d(Zr)/K_d(Hf) (open diamonds) and the ρ(Zr)/ρ(Hf) ratios (closed diamonds) as a function of the HCl concentration.

the chloride complexation of Zr and Hf (see Figure 4). It is found that the variation of the K_d values of Zr and Hf reasonably reflect the structural changes of the complexes deduced from the present EXAFS measurements.

In a previous report,[10] the adsorption probabilities (%ads) of Rf on CA08Y, which were the measure of the K_d value, were determined from 1893 cycles of anion-exchange experiments in 4.0–11.5 M HCl. The variations of the %ads values of ^{85}Zr, ^{169}Hf, and ^{261}Rf are shown as a function of the HCl concentration in Figure 6. The %ads values of Rf increase with an increase of the HCl concentration from $4.5_{-3.2}^{+6.3}$% at 4.0 M to 97_{-6}^{+3}% at 11.5 M. This adsorption behavior of Rf is quite similar to that of Zr and Hf, and is typical of the group-4 elements. It should be also noted here that the onset HCl concentration for Rf is clearly lower than that for Zr. The anion-exchange results together with those of the EXAFS studies clearly suggest that Rf forms the same complexes as those of Zr and Hf in HCl: $[Rf(H_2O)_8]^{4+} \rightarrow [RfCl_6]^{2-}$, and that the chloride complexation of Rf is stronger than that of the homologs Zr and Hf.

Conclusion

The structural changes of Zr and Hf complexes, $[M(H_2O)_8]^{4+} \rightarrow [MCl_6]^{2-}$, were determined by EXAFS as a function of HCl concentration at 8.0–11.9 M. The onset HCl concentration for the chloride complexation of Zr is lower than that of Hf, indicating that the affinity of the Cl$^-$ ion for Zr is stronger than that for Hf. Taking into account the anion-exchange results, it was suggested that Rf also forms the same complexes as those of Zr and Hf, $[Rf(H_2O)_8]^{4+} \rightarrow [RfCl_6]^{2-}$, and that the affinity of Cl$^-$ for these metal ions is in the following sequence Rf > Zr > Hf.

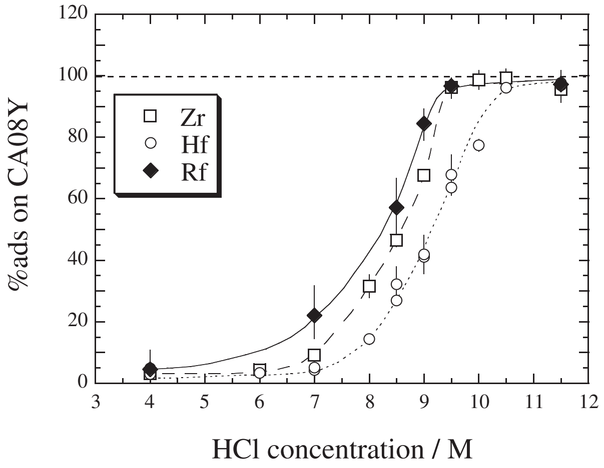

Figure 6. Variations of the adsorption probabilities (%ads) for Zr (open squares), Hf (open circles), and Rf (closed diamonds) on the anion-exchange resin CA08Y as a function of the HCl concentration (Data from Ref. 10).

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