Chemistry

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Structure of Zirconium Complex in HCl Solution for Chemical Characterization of Transactinide Element Rf

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Introduction

According to the actinide concept, the 5f electron series ends with element 103, lawrencium (Lr), and a 6d transition metal, transactinide, series is predicted to begin with element 104, rutherfordium (Rf). So far, we have studied anion-exchange behavior of Rf together with the lighter homologues Zr and Hf in HCl [1]. The results have clearly shown that the behavior of Rf is quite similar to that of Zr and Hf, indicating that Rf is the member of the group-4 elements. To discuss the anion complex structure of Rf in HCl, the structural information of Zr and Hf is indispensable. In this paper, we report the structure of the Zr complex in 1 M to 11.5 M HCl determined by the EXAFS method.

Experimental

Commercially available $ZrCl_4$ powder was dissolved with 1 to 11.5 M HCl. The concentration of Zr was adjusted to 0.01 M. The sample was sealed in a polyethylene bag and set to the BL27B beam line. The Zr-K edge EXAFS spectra were measured with the fluorescence mode using a 7-element Ge solid-state detector array.

Results and Discussion

The adsorption behavior of Zr on the anion-exchange resin indicated that Zr cation and/or neutral complexes are dominant in HCl solutions up to 7 M. Beyond 7 M, the adsorption rate increases with the HCl concentration and becomes almost 100% at 10 M. In the observed Fourier transformed EXAFS spectra for 1-10 M HCl, the most intense peak appears at the distance corresponding to the Zr-O bond. At > 9 M HCl, this peak broadens with an increase of the HCl concentration due to an increase of the contribution from the Zr-Cl bond. A peak originating from Z=O is observed in 1-5 M, while in 1 and 3 M, an extremely characteristic peak derived from Zr-Zr is observed [2]. Spectral simulations were performed with the FEFF8, and the obtained parameters, the number of neighboring atoms N, the distance to the neighboring atom R (Å) are listed in table 1. The R values for the Zr-O shell are 2.20 – 2.23 Å, and the N are 6 – 7 up to 9 M. Above 10 M, Cl^- are substituted for H_2O and /or OH^- with an increase of the concentration of HCl, and the Zr-Cl shell with 2.43 Å appears. This structural change is consistent with the tendency of the distribution coefficient (K_d) of Zr on anion-exchange resins.

References

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Table 1. Simulated structural parameters by FEFF8. N and R (Å) are indicating the number of neighboring atoms and the distance to the neighboring atom, respectively.

[HCl]	Zr-O		Zr-Cl		Zr=O		Zr---Zr		Zr---O	
(M)	N	R	N	R	N	R	N	R	N	R
1.0	6	2.21			1	1.63	1	3.58	4	4.95
3.0	6	2.20			0.5	1.63	0.5	3.58		
5.0	6	2.21			0.8	1.63				
8.0	6	2.22								
9.0	7	2.23								
10.0	4	2.21	3	2.43						
11.5			6	2.43						