27B/2003G068

Structure of Zirconium TBP Complex in HCl Solution

Kazuhiko AKIYAMA [*1], Hiromitsu HABA [2], Kazuaki TSUKADA [1], Masato ASAI[1], Tsuyoshi YAITA[1], Atsushi TOYOSHIMA[1, 3], Yuichiro NAGAME[1]
[1]Japan Atomic Energy Research Institute, Ibaraki 319-1195, Japan
[2]The Institute of Physical and Chemical Research (RIKEN), Saitama 351-0198, Japan
[3]Osaka University, Osaka 560-0043, Japan

Introduction

The extraction behavior of Rf using tributyl phosphate (TBP) from HCl solution was reported by research groups of LBNL [1] and GSI [2], individually. However, their results were inconsistent with each other for the experimental difficulties. Recently, we have successfully studied the anion exchange behavior of Rf by use of the automatic rapid chromatographic apparatus "AIDA" [3]. To clarify the TBP extraction behavior of Rf, we prepared the reversed-phase chromatographic resin modified with TBP for the loading material of the micro column of AIDA. The purpose of this work is to determine the structure of Zr complexes adsorbed on the resin.

Experimental

MCI GEL CHP20Y (Mitsubishi Chemical, Styrene-DivinylBenzene) as a base material was stirred in the high purity methanol. TBP was added dropwisely to the mixture and stirred overnight. After that, TBP/methanol mixture was dried at the ambient temperature for the evaporation of methanol and at 110 °C for removing the residual water. Commercially available $ZrCl_4$ powder was dissolved in 7 M, 8 M and 11.9 M HCl. The concentration of Zr was adjusted to 0.02 M. These solutions were mixed with the TBP resin and filtered by the suction filtration. The resin on the filter paper 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 detector array.

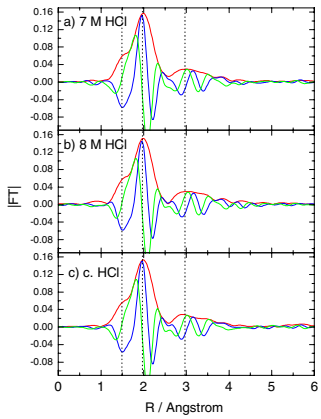

Figure 1. Fourier transformed EXAFS spectra of Zr complexes in the TBP resin at a) 7 M, b) 8 M, and c) 11.9 M HCl.

Results and Discussion

Figure 1 shows Fourier transformed EXAFS spectra of Zr complexes adsorbed on the TBP resin in 7 M, 8 M and conc. HCl solutions. These three spectra are the same with each other and exhibit three dominant peaks at approximately 1.5, 2.0, and 3.0 Å (without the phase-shift correction). This indicates that the structure of the Zr complex adsorbed on the TBP resin is same in the studied HCl concentrations 7 M to 11.9 M. We modeled the Zr TBP complex as $ZrCl_4(TBP)_2$ besed on the reported uranyl TBP complex and the Zr monobutylphosphate (MBP) and dibutylphosphate (DBP) complexes [4,5]. The spectral simulation using this model structure was performed with the FEFF7 code. The simulated radial distribution function (RDF) reproduces the experimental Fourier transformed EXAFS spectra as shown in figure 2 (only single scattering paths are displayed). From this simulation and the fact that TBP extracts the neutral complexes, it is reasonable that Zr is adsorbs to the TBP resin as the $ZrCl_4(TBP)_2$ form.

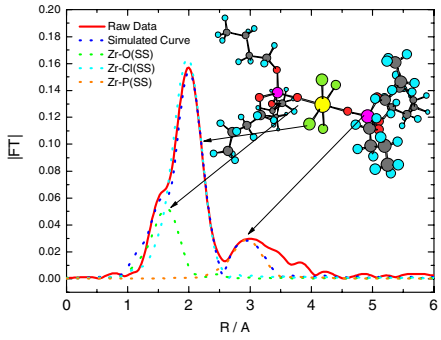

Figure 2. Simulated RDF and experimental Fourier transformed EXAFS spectra of the Zr TBP complex. Simulated R, N, and σ^2 values are 2.1, 2, and 0.005 for the Zr-O phase, 2.45, 4, and 0.005 for the Zr-Cl phase, and 3.43, 2, and 0.005 for the Zr-P phase, respectively.

References

[1] C. D. Kacher et al., Radiochim. Acta 75, 127 (1996).
[2] R. Günther et al., Radiochim. Acta 80, 121 (1998).
[3] H. Haba et al., J. Am. Chem. Soc. 126, 5219 (2004).
[4] C. Miyake et al., J. Nucl. Sci. Technol. 27, 256 (1990).
[5] J. H. Burns, Inorg. Chem. 20, 3868 (1981).

* kakiyama@popx.tokai.jaeri.go.jp