

# Structure of $\text{Yb}^{3+}$ Aquo Ion and Chloro Complexes in Aqueous Solutions up to 500°C and 270 MPa

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## Introduction

X-ray absorption fine structure (XAFS) has proven to be a very useful tool for the study of the local structure of ions in aqueous solutions. However, progress in x-ray absorption spectroscopy of aqueous solutions at hydrothermal conditions has been limited by corrosivity and signal efficiency of high P-T cells. In the study of the lanthanide ions in hydrothermal fluids, signal efficiency owing to the thickness and type of window material of the cell has been a particularly important barrier to overcome. We have successfully solved the problem of signal efficiency through recent improvements of the hydrothermal diamond anvil cell by laser drilling grooves in the diamond windows [1]. We report here on XAFS measurements used to determine the structure of the  $\text{Yb}^{3+}$  ion in aqueous solutions over a range of temperatures from 25° to 500°C and pressures up to 270 MPa. These data are part of a larger study on the behavior of lanthanides in aqueous solutions at high temperatures and pressures.

## Methods and Materials

Fluorescence Yb  $L_3$ -edge spectra were collected separately from nitrate (0.006*m* Yb/0.16*m*  $\text{HNO}_3$ ) and chloride (0.006*m*  $\text{YbCl}_3$ /0.017*m*  $\text{HCl}$ ) aqueous solutions within a hydrothermal diamond anvil cell from 25° to 500°C and up to 270 MPa. The hydrothermal diamond anvil cell has been described in detail elsewhere [2]. XAFS spectra were collected at the Yb  $L_3$ -edge (8944 eV) on the undulator PNC-CAT ID-20 beamline of APS at Argonne National Laboratory. A 13-element Ge detector was used to collect the x-ray fluorescence from the sample, as a means of XAFS data acquisition. The detector was placed in the standard horizontal 90° orientation to the incident x-ray beam. The Si(111) crystals of the monochromator were detuned by 30-40% as a means of harmonic reduction in the incident x-ray beam. Each spectrum was measured for approximately 20 min. The slits before the monochromator were positioned at 2.4 mm (width)  $\times$  1.2 mm (height), while the ones after the monochromator were adjusted to 0.96 mm

(width)  $\times$  0.875 mm (height). Kirkpatrick-Baez mirrors were used to focus the beam, giving roughly a 25- $\mu\text{m}$  circular spot with a flux of  $5 \times 10^{11}$  photons/s at the x-ray energy of 8900 eV. The incident and transmitted x-ray beams were detected by using gas ionization chambers (10.2-cm and 30.5-cm lengths, respectively) filled with dry nitrogen gas. Up to six scans were collected at each P-T point. Small Bragg diffraction peaks in the spectra were observed occasionally. In this case, Bragg peaks were removed by rotating the cell by up to  $\pm 4^\circ$  relative to the incident beam direction, in the plane of the synchrotron radiation.

The data analysis was made by using the FEFFIT2.54 software program [3, 4]. This program employs a nonlinear, least square fit to the theoretical standards calculated by using FEFF8 theoretical code [5]. Fitting was made simultaneously in *r*-space (the Fourier transformed space) and filtered *k*-space (inverse Fourier transformed space). Fitting parameters included the coordination number ( $N_i$ ), radial distance ( $R_i$ ), XAFS Debye-Waller factor ( $\sigma_i^2$ ) and  $\Delta E_0$ , which compensates for the mismatch between  $E_0$  and its theoretical estimate.

## Results

The structure results for nitrate-bearing and chloride-bearing solutions are in Tables 1 and 2, respectively. The  $\text{Yb}^{3+}$  is found to persist as an aquo ion in the nitrate solution throughout the P-T range of the study. The Yb-O distance of the  $\text{Yb}^{3+}$  aquo ion in the nitrate solution exhibits a uniform reduction at a rate of 0.02 Å/100°C, while the number of oxygens decreases from  $8.3 \pm 0.6$  to  $4.8 \pm 0.7$  while going from 25° to 500°C. No evidence for nitrate complexes was found from measurements made on this solution. The  $\text{Yb}^{3+}$  is found to persist as an aquo ion up to 150°C in the chloride aqueous solution. In the 300° to 500°C range, chloro complexes occur in the solution, most likely of the type  $\text{Yb}(\text{H}_2\text{O})_{\delta-n}\text{Cl}_n^{+3-n}$  ( $\delta \approx 7$ ). The Yb-Cl distance of the chloro ytterbium(III) complexes decreases uniformly at a rate of about 0.02 Å/100°C, while the number of chlorines increases from  $0.5 \pm 0.3$  to  $1.8 \pm 0.2$  in the 300° to 500°C temperature range.

Table 1. Structure results from fitting of XAFS spectra measured from a 0.006m Yb/0.16m HNO<sub>3</sub> aqueous solution.

Temp	$\Delta E_{0(\text{Yb-O})}$	$N_{\text{O}}$	$R_{\text{Yb-O}}$	$\sigma^2_{\text{Yb-O}}$	$\mathfrak{R}$ -Factor
25°C	12.5 ± 0.5	8.3 ± 0.6	2.33 ± 0.01	0.007 ± 0.001	0.006
150°C	10.8 ± 0.9	7.8 ± 0.8	2.29 ± 0.01	0.013 ± 0.003	0.016
300°C	11.3 ± 1.0	6.2 ± 0.7	2.28 ± 0.01	0.016 ± 0.003	0.006
400°C	10.4 ± 1.1	4.8 ± 0.6	2.26 ± 0.01	0.017 ± 0.003	0.008
500°C	10.9 ± 1.1	4.8 ± 0.7	2.24 ± 0.02	0.017 ± 0.004	0.011

Table 2. Structure results from fitting of XAFS spectra measured from a 0.006m YbCl<sub>3</sub>/0.017m HCl aqueous solution.

Temp	$\Delta E_{0(\text{Yb-O})}$	$\Delta E_{0(\text{Yb-Cl})}$	$N_{\text{O}}$	$N_{\text{Cl}}$	$R_{\text{Yb-O}}$	$R_{\text{Yb-Cl}}$	$\sigma^2_{\text{Yb-O}}$	$\sigma^2_{\text{Yb-Cl}}$	$\mathfrak{R}$ -Factor
25°C	7.2 ± 0.5	—	8.3 ± 0.5	—	2.328 ± 0.007	—	0.007 ± 0.001	—	0.003
150°C	4.7 ± 0.4	—	8.5 ± 0.4	—	2.316 ± 0.006	—	0.012 ± 0.001	—	0.002
300°C	4.0	6.5	6.5 ± 0.5	0.5 ± 0.3	2.306 ± 0.007	2.60 ± 0.04	0.012	0.006	0.009
400°C	4.0	6.5	5.1 ± 0.6	1.6 ± 0.3	2.29 ± 0.01	2.57 ± 0.01	0.016	0.007	0.014
500°C	4.0	6.5	5.1 ± 0.3	1.8 ± 0.2	2.294 ± 0.008	2.566 ± 0.009	0.019	0.009	0.004

Conversely, the Yb-O distance undergoes a lower uniform reduction at a rate of 0.007 Å/100°C, while the number of oxygens reduces from 8.3 ± 0.5 to 5.1 ± 0.3 when going from 25° to 500°C in the same solution.

## Discussion

Our room temperature results shown in Table 1 are in excellent agreement with the structure results for hydrated Yb<sup>3+</sup> obtained from previous studies. While our measurements are insensitive to the precise geometry of the inner hydration shell, the number of oxygen ligands (8.3) is consistent with the square antiprismatic structure of the Yb<sup>3+</sup> aquo ion determined from molecular dynamics simulations made by Kowall et al. [6].

Our results from analysis of spectra measured from the chloride solution sample (in Table 2) at room temperature indicate that the Yb<sup>3+</sup> ion is hydrated with approximately eight equidistantly positioned water molecules in the inner hydration sphere. We do not find evidence for chloro complex formation in this solution at room temperature. These results are in excellent agreement with those obtained by Cossy et al. [7], Yaita et al. [8], and Allen et al. [9]. In addition, these results are consistent with our structure data for the hydrated Yb<sup>3+</sup> ion in our nitrate solution measured at room temperature. Our results for chloro speciation of Yb<sup>3+</sup> in the chloride solution under elevated P-T conditions qualitatively agree well with thermodynamic calculations made by Haas et al. [10] and are in agreement with results from solubility measurements made by Gammons et al. [11].

The relaxation in the structure of the Yb<sup>3+</sup> aquo ion and of the chloro ytterbium(III) complexes is attributed to

hydrogen bond breaking occurring in the outer hydration shell, resulting in the unbalanced Yb-ligand interaction forces contracting the ligands inward toward the cation at elevated temperatures.

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