XAFS Study of Actinide Coordination Structure in Np(IV)-fulvates

M. A. Denecke,[1] C. M. Marquardt,[1] J. Rothe,[1] K. Dardenne,[1] M. P. Jensen[2]

[1]Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, Karlsruhe, Germany
[2]Chemistry Division, Argonne National Laboratory (ANL), Argonne, IL, U.S.A.

Introduction

Humic substances (HSs), which include humin, humic acid (HA), and fulvic acid (FA), are structurally complex macromolecules, ubiquitous in soils and natural waters as a consequence of the degradation of plant and animal residues [1]. HA and FA show a high affinity for complexing metal cations. For this reason, HSs have been studied extensively for their environmental and biochemical importance (e.g., Reference 2).

Investigations of the actinide-binding properties of HA and FA implicate carboxylate groups (-COO⁻) as the primary functional groups complexing metal ions [3]. According to the charge neutralization model [4], the number of binding sites for complexing each metal cation is the number required to compensate for the cation valence charge. In this model, the loading capacity (LC) is introduced as the maximum amount of metal cation that a HS can complex under a given set of conditions, normalized to the total molar HS concentration. In general, the LC of HS for actinide cations increases as a function of pH. The LC increase is greater the larger the effective charge on the actinide is [4]. For example, the slope of LC vs. pH follows the order $Np^{4+} >> Am^{3+} > UO_2^{2+} > NpO_2^+$ [5]. The LC of FA for Np(IV) exhibits a remarkably large increase, going from pH_c 1.0 to 1.5 [6]. The aim of this study is to ascertain if this anomalous LC increase is associated with a change in the metal-ligand interaction.

To this end, the coordination of tetravalent neptunium complexed with FA at pH_c 1.0 to 1.5 is determined by using extended x-ray absorption spectroscopy. From analysis of the Np L3-edge EXAFS (extended x-ray absorption fine structure), structural metric parameters are obtained: coordination number (N), bond distance (R), EXAFS Debye-Waller factor (σ^2), and relative shift in L3 ionization potential (ΔE_0) [7]. For comparison, the hydration number and bond distances of the Np(IV) aquo ion are also determined.

Methods and Materials

Two different FAs are used. Both are isolated from geological formations associated with proposed nuclear waste disposal sites: Boom clay interstitial water in Belgium and Gorleben groundwater in Germany. Sample preparation is described in Reference 8. The Np(IV)-fulvates are measured as wet pastes in 0.5 mm Ø polyethylene vials. The acidic Np(IV) solution (1 M $HClO_4$) is measured in a polyacrylic cuvette with a 10-mm path length. The Np L3-edge EXAFS are recorded in fluorescence mode by using a nine-element Ge detector and Si(111) monochromator crystals at the APS Basic Energy Sciences Synchrotron Radiation Center (BESSRC) 12-BM experimental station. The photon energy is calibrated relative to the point of inflection in an x-ray absorption near-edge structure (XANES) spectrum of a Zr foil, defined as 17,998 eV.

Treatment of data and analysis of EXAFS spectra are done by using the WinXAS program [9]. E_0 is defined as the energy of the white line in the sample XANES. Single scattering theoretical backscattering amplitude and phase shift functions calculated by using FEFF7 [10] are used in modeling the data.

Results

The k^3-weighted EXAFS spectra and their corresponding Fourier transforms (FTs) are shown in Fig. 1. The EXAFS pattern of both the Np(IV):Gorleben-FA and the Np(IV):Boom clay-FA are similar. There is a change in the oscillation fingerprint near k = 8-9 Å⁻¹ and a slight amplitude reduction between spectra of the samples prepared at pH_c 1.5 and those prepared at pH_c 1.0. A distinct shoulder on the high R side of the first FT peak is present in the FTs of all samples. This indicates that two distances may be present.

The Fourier filtered oscillation of this FT peak for all samples (not shown) shows a beat node interference pattern near k ~ 9 Å⁻¹, evidence for the presence of two nearest neighbor oxygen distances. From the beat node k value (k_{bn}), the bond distance difference between the two interfering coordination shells estimated from $\Delta R = n*\pi/2k_{bn}$ [11] is 0.17 Å for these samples.

Fits of the EXAFS equation to Fourier filtered data are initially performed by using a model with two oxygen coordination shells. The metric parameters obtained from these fits are then used as starting parameters for fits to the raw EXAFS data. Metric parameters obtained from these fits are listed in Table 1. The values obtained for the Np(IV) aquo ion are comparable to those previously reported [12]. This confirms that the amplitude and phase functions used in the analysis are correct.

The Np(IV)-fulvate complexes have two distinct nearest neighbor oxygen distances. The first distance is
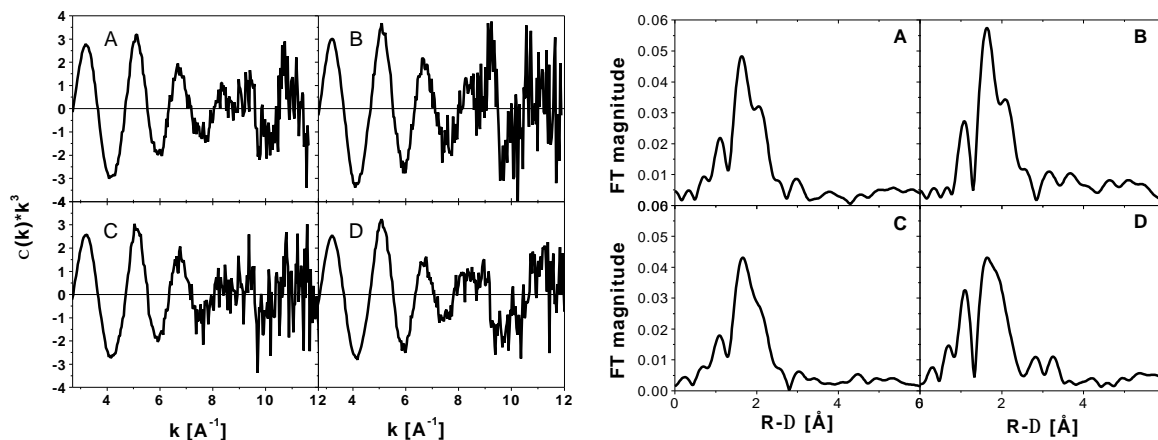
FIG. 1. k^3-weighted EXAFS (left) and their corresponding FT (right) of the Np(IV)-fulvates studied.
A = Np(IV):Gorleben-FA, $-log[H^+] = 1.5$.   B = Np(IV):Gorleben-FA, $-log[H^+] = 1.0$.
C = Np(IV):Boom clay-FA, $-log[H^+] = 1.5$.   D = Np(IV):Boom clay-FA, $-log[H^+] = 1.0$.

short, in a range of 2.24 to 2.27 Å. Fit results for the second, longer distance yield five to seven oxygen atoms at 2.41 to 2.44 Å. The ΔR for these two distances is comparable to the value for ΔR estimated from k_{bn}. The N value for the first distance obtained in the fits varies considerably, from a range of 2 to 4 for fits to raw data to a range of 3 to 6 for fits to filtered data (not shown).

There is evidence for a chlorine atom that is more distant than the two oxygen shells in three of the samples. The fit residual or difference between the experimental and theoretical EXAFS of the two oxygen shells is not merely noise but displays oscillations. The FT of the residual exhibits a peak at a distance uncorrected for phase shift at 2.7 Å. This peak can be modeled very well with a Cl atom at an interatomic distance of 3.03-3.10 Å (see Fig. 2). A Np-Cl shell with a comparable distance has been observed in /a Np(IV)-humate studied by another group [13].

No Np-Np scattering peak is observed in the EXAFS spectra. None of the EXAFS or difference spectra [14]

have a signature of a heavy backscatterer. There is also no large variation in the measured white line intensities of all the sample XANES, including the Np(IV) aquo ion. In contrast, the XANES white line intensity decreases markedly as it goes from the Th(IV) aquo ion to a colloidal suspension to a $Th(OH)_4(am)$ precipitate [15]. If polynuclear species and/or eigencolloids form in the Np(IV)-fulvates, then we would expect a similar white line intensity decrease in the Np L3-edge XANES.

Discussion

Unlike the EXAFS results reported for metal cation coordination in Hf(IV):HA and Th(IV):HA [16] and for the equatorial bond lengths in Np(V):HA [14] and U(VI):HA [3], the first coordination sphere in both Np(IV):FA's studied has two oxygen distances. There is

Table 1. Results of fits to the EXAFS data described in text.

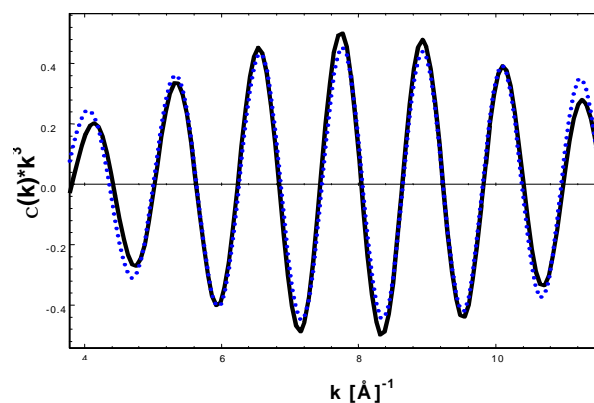| Sample	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Np(IV):Gorleben-FA,	3.4	2.25	0.001	
pH$_c$ 1.5 (A)	5.8	2.43	0.003	-2.6
Np(IV):Gorleben-FA,	3.7	2.26	0.001	
pH$_c$ 1.0 (B)	7.1	2.43	0.005	-2.5
Np(IV):Boom clay-FA,	4.2	2.27	0.005	
pH$_c$ 1.5 (C)	5.0	2.44	0.005	-2.5
Np(IV):Boom clay-FA,	2.3	2.24	0.001	
- pH$_c$ 1.0 (D)	6.6	2.41	0.006	-2.5
Np(IV) aquo ion (E)	10.5	2.39	0.005	-1.5

FIG. 2. k^3-weighted Fourier filtered EXAFS (line) and corresponding theoretical fit (dots) for a Cl atom (N = 0.8, R = 3.10 Å) isolated from the Np(IV): Gorleben-FA, $-log[H^+] = 1.0$ spectrum in Fig. 1B.

also evidence for a single chlorine atom at 3.03-3.10 Å in three samples. From comparison to other known tetravalent actinide complexes [8], the shorter distance (~2.25 Å) is interpreted as belonging to a strong Lewis base; in this case, a hydroxyl ligand. We attribute the longer distance to an average Np-O distance for coordinating fulvate carboxylate groups and oxygen atoms of other coordinating ligands (e.g., water molecules). No evidence for the formation of polynuclear species or eigencolloids is observed.

The Cl atom found at 3-3.1 Å from Np(IV) is at a distance that is more than 0.2 Å longer than the distance observed for the chloride ion directly bound to Np(IV) [17]. The distance observed here is closer to what one would expect for a perchlorate ion coordinated to the Np(IV). A direct coordinating ClO_4^- appears unusual. However, another research group independently found a comparable Np-Cl distance in Np(IV):HA [13], which supports this result. Study of the potential of HSs to affect novel complexation behavior is certainly required.

The observed LC "anomaly" for tetravalent neptunium lies in the presence of mixed Np-fulvate complexes, $Np(OH)_xFA(IV-x)$. The LC is calculated by assuming a charge neutralization of the Np^{4+} cation through formation of a Np-FA(IV) complex, where the FA(IV) denotes four functional groups from fulvate neutralizing the Np^{4+} cation charge [4]. For each coordinating hydroxyl group, one less functional group from the fulvate is needed to neutralize the $Np(OH)_x^{(4-x)+}$ cation charge. The presence of $Np(OH)_2FA(II)$, for example, would reduce the calculated LC by half of that predicted by assuming a charge neutralization with a Np-FA(IV) complex. Because of the difficulty in determining the exact number of hydroxyl ligands bound to Np^{4+}, however, we cannot define x in $Np(OH)_xFA(IV-x)$ from the EXAFS analysis. The presence of ligating ClO_4^- complicates the situation. It does not change the interpretation, however, that the LC anomaly is due to a reduction of actual charge, through mixed complex formation, assumed to be neutralized by the fulvate.

References
[1] M. N. Jones and N. D. Bryan, Adv. Colloid Interface Sci. **78**, 1-48 (1998).
[2] G. Davies et al., J. Chem. Soc., Dalton Trans., 4047-4060 (1997).
[3] M. A. Denecke, T. Reich, S. Pompe, M. Bubner, K.-H. Heise, H. Nitsche, P. G. Allen, J. J. Bucher, N. M. Edelstein, D. K. Shuh, and K. R. Czerwinski, Radiochim. Acta **82**, 103 (1998).
[4] J. I. Kim and K. R. Czerwinski, Radiochim. Acta **73**, 5 (1996).
[5] European Commission, report EUR-19610-EN, edited by G. Buckau (Directorate-General for Research, Brussels, Belgium, 2000), p. 23.
[6] C. M. Marquardt, V. Pirlet, and J. I. Kim, Wissenschaftliche Berichte Forschungszentrum Karlsruhe **6524**, 45 (2000).
[7] D. C. Koningsberger and R. Prins, *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (John Wiley & Sons, New York, NY, 1988).
[8] M. A. Denecke, C. M. Marquardt, J. Rothe, K. Dardenne, and M. P. Jensen, J. Nucl. Sci. Technol. (accepted).
[9] T. Ressler, J. Physique IV **7**, C2-269 (1997).
[10] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. Eller, Phys. Rev. B **52**, 2995 (1995).
[11] G. Martens, P. Rabe, N. Schwentner, and A. Werner, Phys. Rev. Lett. **39**(22), 1411 (1977).
[12] P. G. Allen, J. J. Bucher, D. K. Shuh, N. M. Edelstein, and T. Reich, Inorg. Chem. **36**, 4676 (1997).
[13] T. Reiche et al. (private communication.
[14] M. A. Denecke, K. Dardenne, C. M. Marquardt, J. Rothe, and M. P. Jensen, *Proceedings of the Second OECD-NEA Workshop on Speciation, Techniques and Facilities for Radioactive Materials at Synchrotron Light Source* (Grenoble, France, 10-12 September 2000).
[15] J. Rothe, M. A. Denecke, V. Neck, R. Müller, and J. I. Kim, Inorg. Chem. **41**, 249-258 (2002).
[16] M. A. Denecke, D. Bublitz, J. I. Kim, H. Moll, and I. Farkes, J. Synchrotron Rad. **6**, 394 (1999).
[17] P. G. Allen, J. J. Bucher, D. K. Shuh, N. M. Edelstein, and I. Craig, Inorg. Chem. **39**, 595 (2000).