ESRF	**Experiment title:** EXAFS study of the pH dependence of Am(III) complexation with acetate	**Experiment number**: EV-37
Beamline: BM 20	**Date of experiment**: from: 25.01.2014 to: 28.01.2014	**Date of report**:
Shifts: 9	**Local contact(s)**: André ROSSBERG	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Daniel R. FRÖHLICH*,[1], Andrej SKERENCAK-FRECH*,[2], Nicole BAUER*,[1,2], Petra J. PANAK[1,2]

[1] Physikalisch-Chemisches Institut, Ruprecht Karls Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany
[2] Insitut für Nukleare Entsorgung (INE), Karlsruhe Institut für Technologie (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany

Report:

The complexation of Am(III) with acetate has been investigated as a function of the pH at ambient air conditions. Six samples have been prepared. The concentrations of Am(III) and acetate were held constant at 1 mM and 0.2 M, respectively, whereas the pH was varied between 1 and 6 by addition of $HClO_4$ or NaOH solution (exact pH values are given in Table 1). 200 µL of each sample solution were encapsulated in an Eppendorf vial sealed in PE foil and measured by EXAFS spectroscopy. EXAFS spectra were recorded at the Am L_{III}-edge (18515 eV) in fluorescence mode at room temperature using the 13-element Ge detector positioned at an angle of 90 °C to the incoming beam. Analysis of the spectra was performed with the software packages EXAFSPAK [1] and FEFF8.40 [2]. The scattering phases and amplitudes were calculated using the crystal structure of $Eu(CH_3COO)_2 \times 0.5\ H_2O$ [3] (Eu replaced by Am). The theoretical modal was fit to the raw k^3-weighted Am L_{III}-edge EXAFS spectra.

The experimental EXAFS spectra and related Fourier Transforms are shown in Figure 1, the fit parameters are summarized in Table 1. In all cases, about 10 oxygen neighbors at a distance of 2.47-2.49 Å are found in the first coordination sphere which is in good agreement with oxygen distances reported in the literature for Am(III) and other trivalent actinides in aqueous solution [4]. At pH 1-2 no carbon shells could be fit to the spectra, at higher pH the coordination number with respect to carbon increases continuously with increasing pH from 0.4 to 2.0. The carboxylic and distal carbon atoms of acetate are located at 2.78-2.84 and 4.39-4.41 Å, respectively. These values are in the same range as An-C distances obtained for acetate complexes with U(VI) ($C_{carboxyl}$; 2.87-2.91 Å [5-7] C_{distal}: 4.36), Np(V) ($C_{carboxyl}$: 2.91-2.93 Å [8]) and Np(VI) ($C_{carboxyl}$: 2.87 Å, C_{dist}: 4.38 Å [8]).

The significance of the carbon contribution to the EXAFS fit is checked by comparing the reduced errors of the fits with and without carbon shell. As can be taken from Table 1, the reduced error for sample 3-6 is lower with the carbon shells which confirms the presence of acetate in the coordination sphere of Am(III).

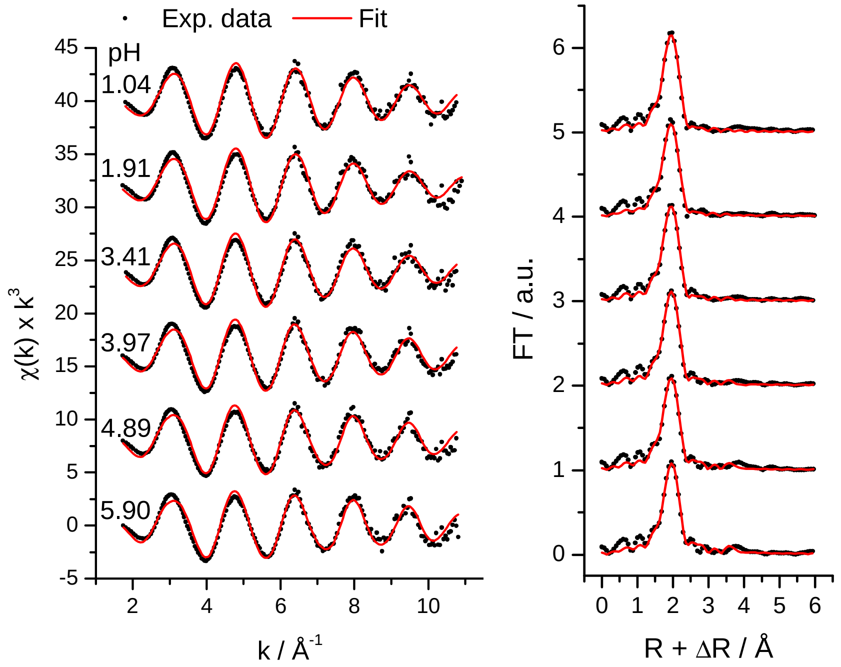

Figure 1: Left: Raw k^3-weighted Am L_{III}-edge EXAFS spectra (black dots) of 1 mM Am(III) in 0.2 M NaAc solution as a function of the pH together with the best fit from EXAFSPAK (red lines). Right: Corresponding Fourier Transforms.

Table 1: Fit parameters for the raw k^3-weighted Am L_{III}-edge EXAFS spectra shown in Figure 1.

Sample		1	2	3	4	5	6
pH		1.04	1.91	3.41	3.97	4.89	5.90
O	N	10.1 (3)	10.1 (4)	10.4 (5)	10.2 (4)	10.7 (5)	10.4 (5)
	R / Å	2.47 (1)	2.47 (1)	2.48 (1)	2.49 (1)	2.49 (1)	2.49 (1)
	σ^2 / Å²	0.009 (1)	0.009 (1)	0.009 (1)	0.009 (1)	0.010 (1)	0.009 (1)
$C_{carboxyl}$*	N	-	-	0.4 (4)	1.0 (3)	1.6 (0.4)	2.0 (4)
	R / Å	-	-	2.78 (7)	2.81 (3)	2.83 (2)	2.84 (1)
C_{dist}**	R / Å	-	-	4.39 (9)	4.41 (4)	4.41 (3)	4.41 (2)
ΔE_0 / eV		-2.0 (3)	-2.1 (3)	-1.6 (4)	-1.0 (3)	-1.0 (4)	-0.3 (4)
Reduced error without C shells		0.192	0.217	0.185	0.177	0.219	0.234
Reduced error with C shells		-	-	0.183	0.174	0.213	0.214
k-range / Å^{-1}		1.8-10.8	1.8-10.8	1.8-10.8	1.7-10.8	1.7-10.8	1.8-10.8

* σ^2 held constant at 0.003 Å², ** N of C_{dist} linked to N of the $C_{carboxyl}$, σ^2 held constant at 0.003 Å², S_0^2 set to 0.9 in all cases, uncertainties obtained from the EXAFSPAK fit are given in parantheses.

Acknowledgement

This work was supported by the German Federal Ministry of Economics and Technology (BMWi, Project 02E11031). We acknowledge the ESRF for provision of synchrotron beam time and thank A. Roßberg, C. Henning and A.C. Scheinost for the experimental support during the EXAFS measurements at ROBL.

References

[1] G.N. George et al., SSRL (2000). [2] A.L. Ankudinov et al., *Phys. Rev. B* **65** (2002) 104107. [3] P. Starynowicz, *J. Alloys. Compd.*, **268** (1998) 47. [4] P.G. Allen et al., *Inorg. Chem.* **39** (2000) 595. [5] C. Lucks et al., *Inorg. Chem.* **51** (2012) 12288. [6] J. Jiang et al., *Dalton Tran.* **51** (2002) 12288. [7] E.H. Bailey et al., *Geochim. Cosmochim. Acta* **68** (2004) 1711. [8] K. Takao et al., *Inorg. Chem.* **48** (2009) 8803.