



	Experiment title: EXAFS study on the complexation of Am(III) with lactate as a function of the pH-value	Experiment number: 20-01-747
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Names and affiliations of applicants (* indicates experimentalists): Daniel R. FRÖHLICH*¹, Andrej SKERENCAK-FRECH*², Ugras KAPLAN*², Carsten KOKE*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 lactate has been investigated as a function of the pH at room temperature under ambient air conditions. Six samples have been prepared. The concentrations of Am(III) and lactate ranged between 0.1–0.3 mmol/L and between 4.0–9.0 mmol/L, respectively, whereas the pH was varied between 1 and 7 by addition of HClO₄ 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 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 [YbL¹Lactate](CF₃SO₃)₂ (L¹ is a heptadentate ligand) [3] in which lactate is bound “side-on” to Yb (Yb replaced by Am). The theoretical model was fit to the raw k³-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 neighbours are located in the first coordination sphere at a distance of 2.47 Å. Whereas no carbon is found in the coordination sphere of Am(III) at pH ≤ 2, the coordination number with respect to carbon increases from 1.0 at pH 3.0 to 2.2 at pH 5.3. At higher pH N(C) decreases due to beginning formation of Am(III) hydroxy species. The coordinating carbon atoms are located at 3.41–3.43 Å, the distal C/O atoms of lactate are located at 4.32–4.36 Å. 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 lactate in the coordination sphere of Am(III).

The carbon distance of 3.42 ± 0.01 Å clearly points out that lactate coordinates in a “side-on” mode to Am(III). In the case of an “end-on” coordination through the carboxylic function only, a much shorter distance < 3 Å would be expected as it has been observed for Am(III) acetate complexes [4].

The experimentally determined coordination numbers have been compared to the values expected from thermodynamic calculations using the stability constants for the formation of [AmLac_n]³⁻ⁿ (n = 1–3) given in the NIST database 46.8 (log β₁⁰ = 3.04, log β₂⁰ = 5.22, log β₃⁰ = 7.32). For all samples, the expected and obtained result are in very good agreement.

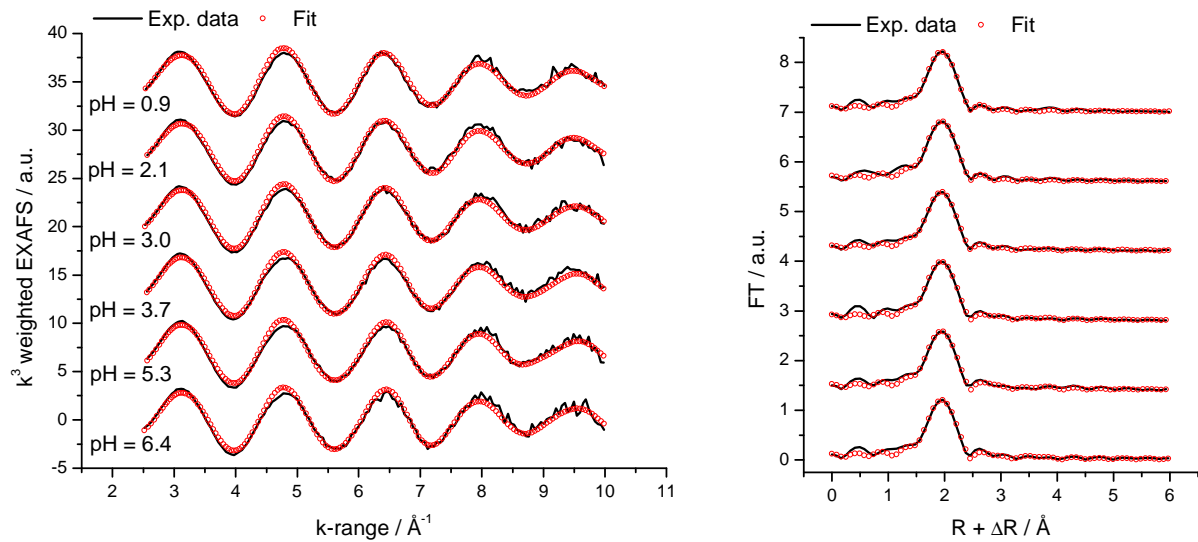


Figure 1: Left: Raw k^3 -weighted Am L_{III} -edge EXAFS spectra (black dots) of Am(III) in the presence of lactate as a function of the pH together with the best fit from EXAFSPAK (red lines). Right: Corresponding Fourier Transforms.

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		0.9	2.1	3.0	3.7	5.3	6.4
O	N	10.9 (3)	10.4 (3)	10.6 (3)	10.4 (4)	10.2 (3)	10.0 (4)
	R / Å	2.47 (1)	2.47 (1)	2.47 (1)	2.47 (1)	2.47 (1)	2.47 (1)
	σ^2 / Å ²	0.0104 (4)	0.0099 (4)	0.0103 (4)	0.0103 (4)	0.0100 (5)	0.0094 (5)
C_{coord}^*	N	-	-	1.0 (4)	1.6 (4)	2.2 (4)	1.7 (5)
	R / Å	-	-	3.43 (4)	3.43 (3)	3.41 (2)	3.42 (2)
C/O_{dist}^{**}	R / Å	-	-	4.34 (5)	4.36 (4)	4.36 (3)	4.32 (4)
ΔE_0 / eV		-1.7 (3)	-1.5 (3)	-1.4 (2)	-1.4 (3)	-1.4 (3)	-1.3 (3)
Reduced error without C shells		0.1357	0.1460	0.1282	0.1678	0.1671	0.1978
Reduced error with C shells		-	-	0.1266	0.1578	0.1430	0.1843
k-range / Å ⁻¹		2.54-9.99	2.56-9.98	2.53-9.99	2.56-9.98	2.56-9.98	2.52-9.99

* σ^2 held constant at 0.005 Å², ** N coupled to C shell and σ^2 held constant at 0.005 Å²

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