chemistry

A study of uranium speciation in acetate solutions at temperatures from 25 to 250°C

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We report U L3-edge XAS analysis results from a study of the speciation of U(VI) in acetate solutions between 25 and 250 ºC, at pH's between 1.82 and 2.57 and [acetate]:[U] ratios of 0.5 to 50. At 25 ºC in excess acetate there are at least two acetate ligands in the equatorial plane with a U-O bond distance of 2.44 Å. At elevated temperatures with excess acetate, acetate is still coordinated but the speciation mixture appears more complicated. Less evidence exists for acetate coordination when [acetate]:[U] ratio is unity or below. pH within this limited range appears to have little effect on the uranyl speciation.

Keywords: Uranium, EXAFS, high-temperature solutions

1. Introduction

Knowledge of uranyl solution speciation enables an understanding of the mode of U transport in near surface fluids. Many recent studies have examined U solubility, mobility and precipitation response, e.g. Duff *et al.* (1997); Valsami-Jones & Ragnarsdottir, (1997). Normally U mobility in near-surface environments is redox-controlled, with U(VI) species being highly soluble and mobile while U(IV) tends to form insoluble phases. U forms strong stable soluble complexes with a wide-variety of organic compounds, including biological materials. Such complexation has been used for cleaning up U-contaminated soil by the nuclear industry (Francis *et al.*, 1999).

Raman studies of uranyl in acetate-containing solutions at room temperature have been published recently by Nguyen-Trung *et al.* (1992) and Quilès & Burnea (1998). The former looked at solutions with [acetate]:[U] ratios of between 1 and 100, and reported no acetate coordination below a pH of 3.. Above that value they saw bidentately coordinating acetate in inner sphere complexes of the form $UO_2(OAc)_n$: n =1,2 or 3 depending on the pH and [acetate:U] ratio. At pH >2.5 Quilès & Burnea report similar complexes 1n solutions with [acetate]:[U] ratios of between 1 and 3; but they interpret one of the acetate ligands in $UO_2(OAc)_n$ (n =1 and 2) as bonding in a pseudo-bridging mode, where only one of the acetate oxygens binds to the uranium, while the other one hydrogen bonds to a hydrogen atom on a ligated water molecule. Comparison with pseudo bridged calcium acetate complexes suggests that the U-OAc distance in a pseudo-bridging complex is likely to be in the range 2.35- 2.40 Å.

Allen *et al.* (1996) has investigated U speciation with tartrate, citrate and malate solutions using U L3-edge EXAFS at room temperature, while we have previously successfully studied U complexation in nitrate, chloride and carbonate solutions at elevated temperature (Schofield *et al.*, 1999; Bailey *et al.*, 2000). Here, we present results from a U L3-edge EXAFS study of uranyl(VI) in acetate-containing solutions at temperatures up to 250 ºC.

2. Experimental

The solutions were made up in deionised water with uranyl acetate and acetic acid except when the [U]:[acetate] ratio was less than 1:2 when uranyl nitrate was used. The pH was adjusted by adding nitric acid or sodium hydroxide, and measured using a calomel reference electrode before the solutions were sealed in silica tubes. Data has been recorded on 7 solutions, whose compositions are shown in Table 1, at temperatures between 25 and 250 ºC; here, we report a selection of the results on solutions a to d, which also illustrate the trends seen in the results of the other three solutions.

Table 1. The composition of each solution

Solution Label	a	b	c	d	e	f	g
[U] M	0.1	0.1	0.05	0.05	0.05	0.05	0.05
[Acetate] M	5.0	1.0	0.05	0.025	5.0	1.0	0.1
pH	1.8	2.6	2.1	2.1	1.8	2.6	3.8

X-ray absorption spectra were collected at Station 9.2 of the S.R.S., Daresbury Laboratory in transmission mode using a Si(220) double crystal monochromator detuned to 50% to remove higher harmonics. The X-ray intensity was measured with noble gas-filled ion chambers. The tubes were heated in an aluminium oven (Seward *et al.*, 1997). Data was recorded to 15 k ($Å^{-1}$) during three different visits to the Synchrotron. In the first, data was collected in step-scanning mode with 3 scans being collected on each sample at each temperature. In the last two visits data was recorded in QuEXAFS mode (Murphy *et al.*, 1995) with 6 ten-minutes scans being recorded on each sample. The first and last dataset were compared to check no sample transformation had occurred during the data collection process.

The data was reduced using the SRS programs EXCALIB and EXBROOK, then simulation was done of k^3-weighted data using the program EXCURV98 (Binsted, 1998) (Figure 1). Phase shifts were *calculated ab initio* using Von Barth ground state and Hedin-Lundquist exchange potentials. Studies have shown using such phase shifts, an amplitude reduction factor of 1 is appropriate (Roy & Gurman, 1999). The data was modelled initially using single scattering only with two shells of oxygen atoms of which the number in the second (equatorial) shell was refined; the number in the first (axial) shell was fixed at 2. Attempts to split the second set of oxygen atoms into two shells at different distances were unsuccessful. Two fit indices are quoted in Table 2, R and reduced χ^2 (Berry *et al.* 2000). As it is assumed that the uncertainty is the same at each datum and the uncertainty in the theory is difficult to quantify, the values of reduced χ^2 quoted have been used for comparative purposes only.

After setting the number of second shell atoms at the nearest integral value a full multiple scattering refinement was performed using the Rehr-Albers approximation (Rehr and Albers, 1990). Then the difference in experimental and theoretical spectra was plotted. In many cases this showed a peak at 2.8-3.0 Å, which has a small amplitude compared to the two oxygen shells (Figure 1).

This peak was only judged significant if its height was greater than 4 units in the Fourier transform, where the height of O_{ax} and O_{eq} peaks are typically 25 and 12, respectively. Adding carbon atoms to the model produced no improvement in the reduced χ^2, as the number of variables used in the model increases from 6 to 8. Hence no values for the U-C distance are given in this paper.
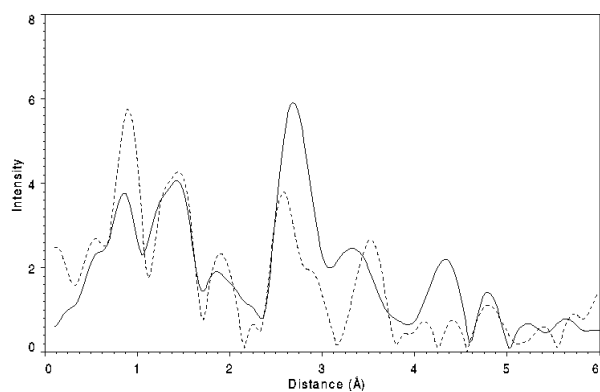
Figure 1. Phase-shifted Fourier transform difference plots for solutions a (———) and d (- - -) at 25ºC showing the carbon peak present in solution a.

3. Results and Discussion

A representative selection of the parameters obtained from the EXAFS simulation is shown in Table 2. An example of the fits achieved is shown in Figure 2. Contour maps of the fit index with the variation of two parameters while the rest were held constant were produced to estimate the error in the shell radius values at 1%, and in the number of atoms in the second oxygen shell at 15%.
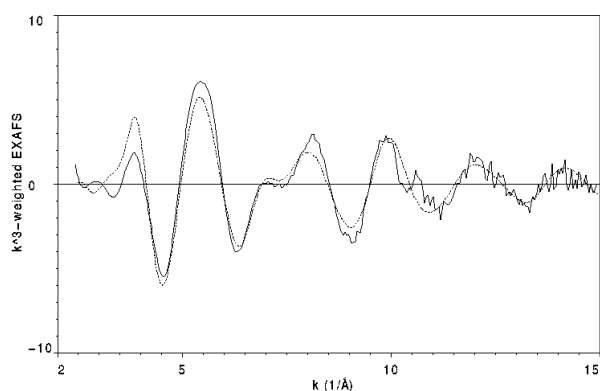

Figure 2 k^3-weighted U L3-edge EXAFS for solution a at 25 ºC. (——— experimental, - - - simulation)

For the 10-50 fold excess acetate solutions, at room temperature there is a slightly increased U-O distance in the equatorial shell compared to that of the solvated uranyl ion, $UO_2(OH_2)_5$, in solutions of uranyl nitrate. There we found *ca*. 5 O atoms at *ca*. 2.41 Å in the equatorial plane at temperatures between 25 and 150 ºC, with U-O$_{ax}$ = 1.77 Å. Above 180 ºC the average equatorial coordination number decreased to *ca*. 3.6 by 250 ºC with a small decrease (0.05 Å) in the U-O$_{eq}$. bond length (Schofield *et al.*, 1999). The longer U-O distance found here, the Fourier transform evidence, and that in the solid state acetate coordinates bidentately to $(UO_2)^{2+}$ (U-OAc = 2.46-2.47 Å) strongly suggest that the mean equatorial coordination includes two bidentate acetate ligands. This result contrasts with the Raman

study of Nguyen-Trung *et al.* (1992), who saw no uranyl-acetate complexes in solution below pH 3. We see evidence of either water coordinating in the equatorial plane or further acetate coordination. At higher temperatures the picture is less clear, since XAFS gives a mean picture and the system leads to a complicated equilibrium. However, in solution d the U-O$_{eq}$. bond length is longer than we found at similar temperatures for solvated Uranyl. Thus we believe acetate is still coordinating, though there may be less acetate coordination and a lower total coordination number. There is no predominant species present, thus the carbon shell is less distinct. In all cases the inclusion of multiple scattering modelled the peak in the Fourier transform at 3.6 Å, thus we saw no evidence for dimers. There are no clear trends with increasing pH though the speciation changes in the 2.6 pH solution are more pronounced.

Table 2 Best-fit parameters from EXAFS simulations

Solution / Temperature (ºC)	Number of O atoms in shell	Shell Radius (Å)	Debye-Waller factor $2\sigma^2 (Å^2)$	R factor Reduced χ^2	F.T. Evidence of shell at 2.8-3.0 Å
a	2.0	1.79	0.007	40.1	Yes
25	4.8	2.44	0.017	3.1	
a	2.0	1.79	0.007	38.2	No
125	4.2	2.43	0.017	3.5	
a	2.0	1.79	0.005	47.3	Yes
240	4.7	2.41	0.027	4.2	
b	2.0	1.78	0.007	48.5	Yes
25	5.1	2.43	0.018	6.7	
b	2.0	1.78	0.006	42.9	Yes
125	4.5	2.42	0.018	5.3	
b	2.0	1.79	0.005	42.2	No
250	3.9	2.41	0.021	4.5	
c	2.0	1.77	0.004	38.3	Yes
25	5.0	2.41	0.016	3.1	
c	2.0	1.78	0.005	46.1	Yes
250	5.0	2.40	0.025	5.6	
d	2.0	1.78	0.005	34.7	No
25	4.9	2.41	0.015	2.5	
d	2.0	1.76	0.003	47.0	Yes
250	5.2	2.36	0.029	4.9	

When the [acetate]:[U] ratio is smaller at 1:2 - 1:1 there is less evidence of acetate coordination at room temperature. Each uranyl cannot be coordinated to two acetate groups and thus the EXAFS evidence for coordination relies more on the U-O bond length and the second shell number. Our best-fit parameters are very similar to those obtained for nitrate solutions at similar [U], temperatures and pH's (Schofield *et al.*, 1999), where the uranyl ion is coordinated by 5 water molecules in the equatorial plane at room temperature. In those solutions we observed no nitrate coordination except at high temperature. The U-ONO$_2$ distance in $UO_2(NO_3)_2.6H_2O$ solid is 2.49 Å, while the bidentately-coordinated U-OAc distance in sodium triacetato- dioxouranium(VI) is 2.47 Å. Thus the U-Oeq distance will provide little evidence for which ligand, if any, is bidentately coordinated. But the evidence from our nitrate work indicates that no nitrate coordination occurs in these solutions at this temperature. At 250 ºC the picture is less clear, the mean U-O$_{eq}$ distances are shorter than at lower temperature, but the Fourier transform difference spectra suggest acetate may coordinate at this temperature. This perhaps suggests at these low [acetate]:[U] ratios the acetate does not coordinate bidentately to the uranyl ion except

at high temperature, whether it coordinates in a pseudo-bridging mode is cannot be determined from the data; vibrational (Raman) studies would assist in confirming this.

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