An XAS Study of the pH and Temperature Dependence of Uranium Speciation in Acetate and Citrate Solutions

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Introduction

Uranium forms strong, stable complexes with a wide variety of organic compounds, including biological materials, and is often found at high concentrations in organic rich-deposits (e.g. peat, coal). Its ability to form such complexes has been extensively utilized for cleaning up uranium contamination. The resultant uranyl-organic chelated species can be highly mobile within the environment and hence difficult to dispose of safely (see e.g. Choppin, 1992).

A variety of uranium organic species have been successfully studied using X-ray absorption spectroscopy. For example, in solid uranyl diacetate, Thompson et al., (1997) were able to demonstrate that XAS could resolve the six equatorial oxygen atoms into two shells with four of the oxygen atoms belonging to the bi-dentate acetate groups, the remaining two being part of water molecules. No study has previously investigated the structure of uranyl acetate complexes in aqueous solution. Allen et al., (1996) investigated the structures of uranyl tartrate, citrate and malate complexes in aqueous solution at 25°C. They concluded that the most likely structure for the complexes were dimers, $(UO_2)_2(L)_2$ with a U-U bond distance of ~3.93, the uranyl groups being bridged through the α -hydroxyl groups.

We have studied the speciation of uranium in the presence of the relatively simple and naturally abundant ligands citrate $[(HOOCCH_2)_2C(OH)COOH]$ and acetate $[CH_3COOH]$. Acetate and citrate molecules are stable to temperatures up to 200°C, and thus suitable for investigating speciation changes with increasing temperature. We have used the method of Mosselmans et al. (1996) to investigate speciation as a function of concentration, pH and temperature. Knowledge of the structure and stability of various uranyl-acetate and uranyl-citrate species will provide valuable information on the mode of uranium transport in nearsurface fluids in the presence of typical organic ligands.

Results

Solutions were prepared from solid uranyl acetate and uranyl nitrate and with the addition of citric and acetic acids. The pH was adjusted by adding small quantities of hydroxide. Samples were run sealed in silica tubes and heated using the cell of Seward et al., (1996). In all experiments the uranium was present as the linear, divalent uranyl ion, with a U-O distance of 1.78-1.79Å. There is no evidence of U-U interactions in any of the experiments within this study.

(i) Citrate Solutions.

At room temperature, there is a decrease in the equatorial U-O distances as the pH increases. At all temperatures up to 200°C the uranyl ion is co-ordinated equatorially to between 5 and 6 oxygen atoms at an average distance of 2.38Å. At low temperatures a second co-ordination sphere interaction with carbon is observed at a distance of approximately 2.9Å.

(ii) Acetate Solutions.

In solutions of 1.0 M acetate, pH 2.6, there is a decrease in the equatorial co-ordination number from 5.1 to 4.4 with a reduction in uranyl concentration from 0.1 M to 0.05 M at room temperature, a similar reduction was seen for solutions at lower pH.

There are no systematic variations of the equatorial U-O distances as a function of temperature and no other clear trends are observed with increasing temperature, although there are indications that speciation changes are occurring.

Conclusions

Increasing the pH of uranyl citrate solutions results in a contraction of the equatorial co-ordination shell. There are no observable speciation changes in these citrate solutions as a function of temperature.

Increasing pH in uranyl acetate solutions causes a reduction in the number of equatorially co-ordinated acetate ligands. A decrease in the equatorial co-ordination number is evident when the uranyl concentration is decreased from 0.1 M to 0.05 M possibly related to a replacement of water molecules by acetate ligands.

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