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Uranyl-citrate speciation in acidic aqueous solutions—an XAS study between 25 and 200 °C

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Abstract

Speciation of uranium(VI) in citrate (2-hydroxypropane-1,2,3-tricarboxylic acid) solutions between 25 and 200 °C, at pH values between 0.8 and 3.7 and at citrate/U ratios between 0.5 and 50 has been investigated using U L_{III}-edge X-ray absorption spectroscopy (XAS). At 25 °C and Cit/U>2, we observed a decrease in U–O_{eq} bond distance as pH was increased, accompanied by an increase in the number of coordinating O atoms around the uranyl ion. This indicates a speciation change due to polymerisation of the monomer $[UO_2(cit)]^-$, present around pH 1, to form the dimer $[(UO_2)_2(cit)_2]^{2-}$ at pH 1.8 and above. The dimer $[(UO_2)_2(cit)_2]^{2-}$ is bridged via the alcohol groups of the citrate ligand. At Cit/U≤2, hydrolysis species appear to dominate at room temperature. Upon heating, no speciation changes were observed, however evidence from U–O_{eq} bond distances and coordination numbers strongly suggests that uranyl-citrate species are present in solution up to 200 °C. Above 200 °C, decomposition of the citrate ligand was observed. The existence of the uranyl-citrate species in the temperature range 25–200 °C demonstrates the importance of including citrate and other organic ligands in models of uranium transport.

Keywords: Uranium; Citrate; Structure; Stability; High temperature; XAS

1. Introduction

Carboxylic acids are ubiquitous in a wide range of geologic environments including surface waters and sedimentary basin fluids where concentrations may be of the order of μg/L and mg/L, respectively (Thurman, 1985). The extent to which metals are transported as metal-organic complexes in aqueous fluids has been widely discussed and investigated in recent years (for

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example, Giordano, 1994; Shock and Koretsky, 1993, 1995 and references therein). The solubilities of many minerals have been observed to increase as a result of the presence of organic acids at low temperatures (see, for example, Bevan and Savage, 1989; Wieland and Stumm, 1992; Wogelius and Walther, 1991). The potential for organic complexation to enhance metal mobility in fluids at elevated temperatures for example basinal brines, hydrothermal fluids and discharges associated with proposed radioactive waste repositories, is considerable (see for example Benezeth and Palmer, 2000; Hennet et al., 1988; Ragnarsdottir et al., 2001).

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 for example peat and coal (Choppin, 1992). Interaction with humic and fulvic acids may be important in controlling uranium migration in soils and natural waters where significant levels of these compounds and other organic acids (for example oxalic and citric acids) are observed. Complexation with organic carboxyl groups also appears to be an important process in formation of some uranium ore deposits (Landais, 1996; Read et al., 1998; Sicree and Barnes, 1996; Spiriakis, 1996; Wood, 1996). The ability of uranium to form complexes with organic compounds has been extensively utilised for cleaning up uranium contamination in soils and in the nuclear industry where chelating agents are common constituents of fluids used to clean reactors (Sellers, 1983). The resultant uranyl-organic chelated species can be highly mobile and potentially highly bioavailable within the environment and hence difficult to dispose of safely (Brooks et al., 1998; Robinson et al., 1998).

Citric acid is a common constituent of domestic and industrial wastes including low-level radioactive wastes, and also occurs naturally in surface environments. Citrate forms strong water soluble complexes with both U(VI) and U(IV) over a wide range of pH. Uranyl-citrate complexes have been utilised in both in-situ and ex-situ methods to mobilise uranium in contaminated soils (Francis et al., 1999; Huang et al., 1998a,), including its addition as an amendment to enhance phytoextraction (Huang et al., 1998b). Additions of, for example, 10 mmol citric acid (pH 2) to uranium contaminated soils (750 mg kg^{-1}) have been shown to increase uranium concentrations in the shoots of *Brassica juncae* to levels in excess of 3500 mg kg^{-1} within 1 week. One advantage of using citrate rather than other organic ligands is that these complexes are reported to readily biodegrade under alkaline conditions or to photodegrade, and hence subsequent uranium mobility can be controlled (Huang et al., 1998a; Dodge and Francis, 1994, 1997). Other investigations have however shown that the uranyl-citrate complexes can be resistant to biodegradation at neutral-acidic conditions (Francis et al., 1992), with the structure of the complex being the dominant factor. Where the hydroxyl groups of the citrate are all involved in bonding to U biodegradation does not occur.

To predict the mobility of uranium in the environment in the presence of chelating agents, it is therefore important to understand the speciation and structure of the complexes formed over a range of pH conditions and their thermal stability. X-ray absorption spectroscopy (XAS) is a useful tool that can provide direct information on the local structural environment of metals in aqueous solutions containing chelating agents (for example Deneke et al., 1997a; Mosselmans et al., 2001; Bailey et al., 2004). Our aim in this study was to investigate the speciation and structure of uranyl-citrate complexes formed in aqueous solution using XAS over a wide range of citrate to uranium ratios (0.5–50) and temperatures (25–200 °C) and in a pH range where hydrolysis of the uranyl ion is minimal pH (0.8–3.7).

2. Previous work

Speciation in the uranium–citric acid system has been extensively studied at room temperature using potentiometric and spectrophotometric methods (Table 1). Above pH~3, hydrolysis of the uranyl ion can become increasingly important. The majority of investigations of the uranyl-citrate system have concentrated on establishing complexes formed under acidic conditions (pH<4) where hydrolysis is minimal due to the strength of the complexes formed. Early studies reached conflicting conclusions as to the species formed. Heitner and Bobtelsky (1954) reported the monomer $[UO_2cit]^-$ in the pH range 4–7