ESRF	Experiment title: Coordination sphere of the uranyl ion in solutions of perchloric and triflic acid	Experiment number: CH–618
Beamline :	Date of experiment:	Date of report :
	Tom. April 10, 1999 to. June 12, 1999	August 20, 1999
Shifts:	Local contact(s):	Received at ESRF:
21	Dr. Tobias Reich, ROBL CRG	
Names and affiliations of applicants (* indicates experimentalists): Rémi Barillon, Isabelle Billard*, Jean-Marc Jung, Klaus Lützenkirchen*, Isabelle Rossini*, Laurent Sémon*		
Institut de Recherches Subatomiques Chimie Nucléaire F–67037 STRASBOURG Cedex 2		

Report (preliminary):

Highly acidic uranium(VI) solutions play an important role in the spent nuclear fuel cycle. In this context, the interaction of uranyl ions (UO_2^{2+}) with perchloric (HClO₄) and triflic acid (CF₃SO₃H) have previously been studied [1] with laser fluorescence spectroscopy. The fluorescence life times of uranium were found to generally increase with acidity. The effect is related to the number of H₃O⁺ ions, but it remains largely unexplained on a molecular level. The aim of the present investigations is to determine the coordination sphere of uranyl ions in solutions of up to 12 M perchloric and 10 M triflic acid by extended X–ray absorption fine structure spectroscopy (EXAFS).

Uranium L_{III} -edge EXAFS spectra were measured in transmission mode at the Rossendorf beam line (ROBL) of the ESRF using a Si(111) double–crystal monochromator. The EXAFS spectra were analyzed according to standard procedures using the program EXAFSPAK and theoretical scattering phases and amplitudes calculated with the scattering code FEFF [2].

For the perchlorate solutions, uranium is found to be coordinated with two axial oxygen atoms (O_{ax} , at a distance R=1.76 Å) and a single shell of 4.8±0.3 equatorial oxygen atoms (O_{eq} , at R=2.41 Å). No chlorine scattering contribution is observed at room temperature EXAFS

measurements. We conclude that $UO_2^{2^+}$ is coordinated with five water molecules and that the electrostatic interaction with the CIO_4^- ions takes place over longer distances. This is consistent with an EXAFS measurement of solid $UO_2(CIO_4)_2$, where chlorine scattering could neither be observed. Crystal structure data of this compound [3] show that the perchlorate tetrahedra are separated from uranium at U–Cl distances of 5.40 - 6.17 Å.

In the case of triflic acid uranium is again found to be coordinated with two O_{ax} and five O_{eq} atoms (four O_{eq} atoms for a concentration of 10 M). In addition, a contribution by sulphur atoms to the EXAFS signal was observed for acid concentrations larger than 6 M (Fig. 1). The U–S distance was determined as 3.59 Å. The measured distances indicate that the triflate group is coordinated with uranium via one of its oxygen atoms in a monodentate fashion. The number of coordinated sulphur atoms could not yet be determined to better than 2 ± 1. Additional information will be obtained from an X-ray diffraction measurement of solid UO₂(CF₃SO₃)₂.

At the highest acid concentration (10 M) uranium is coordinated with only four O_{eq} . One possible explanation is the formation of a $UO_2^{2^+}$ complex with four triflate ions and no water molecule for steric reasons. Again, more precise information on the number of coordinated sulphur atoms will help to elucidate this question. The coordination change at 10 M concentration is paralleled by a sharp increase of the uranium fluorescence life time from 5 μ s (8 M) to 30 μ s (10 M) [1]. Hence, the drastic life time variation would be related to a change in the coordination sphere of uranium.

- [1] M. Bouby, I. Billard, A. Bonnenfant, G. Klein, Chem. Phys. 240 (1999) 353.
- [2] S.I. Zabinsky et al, Phys. Rev. B 52 (1995) 2995.
- [3] N.W. Alcock, F.F.S. Esperas, J. Chem. Soc. Dalton Trans. (1977) 893.



Fig. 1: k^3 -weighted uranium L_{III}edge EXAFS spectrum (left) and its Fourier transform (right) of a 10^{-2} M U(VI) solution in 10 M triflic acid.