

Solution coordination chemistry of uranium in the binary UO_2^{2+} - SO_4^{2-} and the ternary UO_2^{2+} - SO_4^{2-} - OH^- system, a combined EXAFS and ^{17}O NMR study.

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Introduction

UO_2^{2+} forms binary complexes $\text{UO}_2(\text{SO}_4)_n^{2-2n}$, $n = 1 - 3$ in slightly acid solution. The complexes are moderately strong, $\beta_1 \approx 50$, and different experimental techniques (potentiometry, spectrophotometric measurements, and TRLFS) have been used to determine the composition and stability of these species [1-3]. The occurrence of uranium (10^{-5} M) and sulfate (3×10^{-2} M) in some ground and surface waters indicates that uranyl sulfate species may be important for the understanding of the mobility of uranium in nature. At higher pH a number of different ternary complexes containing both hydroxide/oxide and sulfate are formed. This was first shown by Peterson [4] who determined the conditional hydrolysis constants of U(VI) in 1.5 M Na_2SO_4 , and showed that both the stoichiometry and the equilibrium constants were different from those previously found in perchlorate media. This can only be explained by the formation of ternary complexes containing coordinated sulfate. An attempt to determine the stoichiometry with respect to sulfate was first made by Grenthe and Lagerman, who studied the system at different total concentrations of sulfate and from these data proposed the stoichiometry and stability of the major ternary complexes: $(\text{UO}_2)_2(\text{OH})_2(\text{SO}_4)_2^{2-}$, $(\text{UO}_2)_3(\text{OH})_4(\text{SO}_4)_4^{4-}$, and $(\text{UO}_2)_5(\text{OH})_8(\text{SO}_4)_6^{10-}$ [5]. Equilibrium analysis used in [1-3] gives only the analytical composition and the amounts of species present in solution, these are in general in rapid equilibrium. Information about chemical structure and dynamics of the systems must be obtained using other experimental methods. The structure and dynamics of aqueous uranyl sulfato species are poorly understood. Infrared (IR) and Raman measurements gave no clear answer regarding the mode of co-ordination of sulfate, unidentate, bridging or chelating, to UO_2^{2+} [6, 7], however the authors assume that a bridging bidentate behaviour is more likely at $\text{SO}_4:\text{U}$ ratios, > 5 . In this study we have determined the structure and dynamics in the systems outlined above. Two sets of experiments have been made: determination of the mode of coordination of sulfate using U L_{III} -edge EXAFS spectroscopy; ^{17}O -NMR spectroscopy to determine the reaction dynamics in the binary and ternary system.

Experimental

EXAFS measurements. Samples were prepared by taking aliquots of the acidic $\text{UO}_2(\text{ClO}_4)_2$ stock solution to get a final uranyl concentration of 0.05 M. The sulfate concentration in the acidic test solutions (samples A - C) was adjusted using H_2SO_4 or Na_2SO_4 . The pH of sample D was adjusted with NaOH. Speciation calculations were made using known equilibrium constants and the program SOLGASWATER [8]. Solid $\text{UO}_2\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$, was synthesised as described in [9] and was mixed with polyethylene and then pressing to give pellets with a diameter of 13 mm. EXAFS data were recorded at the Rossendorf Beamline (ROBL) at the ESRF in Grenoble. The transmission spectra were measured at room temperature using a cooled Si(111) double crystal monochromator of fixed-exit type ($E = 5\text{-}35$ keV). The higher harmonics were rejected by two Si and Pt coated mirrors. For energy calibration of the sample spectra, the spectrum from a Zr foil was recorded simultaneously.

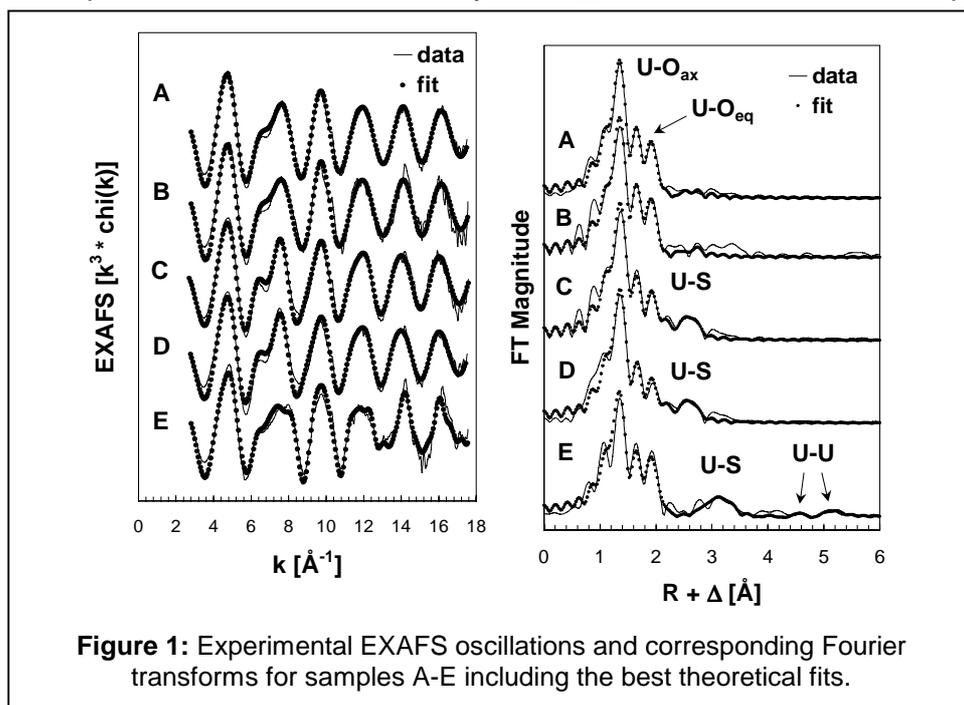
The ionisation energy of the U L_{III} electron, E_0 , was arbitrarily defined as 17 185 eV. The data were treated using the WinXAS software [10]. Theoretical backscattering phase and amplitude functions, $\delta(k)$ and $F(k)$, used in data analysis were calculated for the test compound, $\text{UO}_2\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$ [11], using the FEFF7 [12] program.

NMR measurements. The ^{17}O NMR spectra were measured using 10 mm sample tubes, on a Bruker AM400 spectrometer at -5°C , unless otherwise mentioned. 5% D_2O in the test solutions were used to obtain locked mode. The probe temperature was adjusted using a Bruker Eurotherm variable temperature control unit and was measured by a calibrated Pt-100 resistance thermometer. The chemical shifts are given in ppm, using external water as a reference. The ^{17}O -NMR measurements were made using an acidic ^{17}O -enriched uranyl stock solution prepared as described previously using H_2^{17}O (29% ^{17}O Campro Science) [13]. The line widths were determined by fitting a Lorentzian curve function to the measured signal using the WIN-NMR program [14].

Results and discussion

EXAFS in the $\text{UO}_2^{2+}\text{-SO}_4^{2-}$ System. The isolated EXAFS oscillations and corresponding Fourier transforms for samples A to C and E are shown in Fig. 1. The obtained structural parameters are given in Tab. 1.

In all samples uranium is surrounded by two O_{ax} atoms at $1.77 \pm 0.01 \text{ \AA}$. Approximately five



O_{eq} atoms are coordinated to the linear uranyl group at 2.39-2.43 \AA in the equatorial plane. In sample C, where $\text{UO}_2(\text{SO}_4)_2^{2-}$ is the dominant species, approximately two sulfur atoms were located at 3.11 \AA from uranium. This is in agreement with the value 3.07 \AA , reported by Blatov *et al.* in the solid $\text{UO}_2\text{SO}_4 \cdot 2\text{CH}_3\text{CON}(\text{CH}_3)_2$, where SO_4^{2-} is bidentate coordinated to UO_2^{2+} [15]. The U-S distance is longer, 3.63 \AA , if sulfate is monodentate and bridging, like in $\text{UO}_2\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$. There was also evidence for U-U interactions. The U-U distance at 5.40 \AA can be clearly identified (8.2 % of the total EXAFS oscillation). The U-U distance at 4.80 \AA was included according to the crystal structure (3.8 % of the total EXAFS oscillation). In samples A and B it is difficult to localise the S backscatterer. In sample B one could

Table 1: Fit parameters to U L_{III} edge EXAFS data in the binary uranyl sulfate system (Samples A-C, and E) and the ternary uranyl hydroxide sulfate system (Sample D); ΔE_0 set at -7.0 eV. XRD values from reference [11] are in parenthesis.

Sample	Scattering Path	N	σ^2 (Å ²)	R (Å)	Residuals
A 82% UO ₂ SO ₄ (aq) 12% UO ₂ ²⁺	U-O _{ax}	1.9 ± 0.2	0.0013	1.77 ₃	11.5
	U-O _{eq}	5.0 ± 0.4	0.0084	2.41 ₂	
	U-S	1f	0.0105	3.11f	
B 50% UO ₂ SO ₄ (aq) 50% UO ₂ (SO ₄) ₂ ²⁻	U-O _{ax}	1.9 ± 0.2	0.0013	1.77 ₂	18.7
	U-O _{eq}	5.0 ± 0.4	0.0082	2.40 ₄	
	U-S	1f	0.0086	3.14 ₀	
C 12% UO ₂ SO ₄ (aq) 88% UO ₂ (SO ₄) ₂ ²⁻	U-O _{ax}	2.0 ± 0.2	0.0013	1.78 ₁	13.4
	U-O _{eq}	5.0 ± 0.4	0.0107	2.43 ₇	
	U-S	2.2 ± 0.5	0.0075	3.11 ₃	
D 10% UO ₂ (SO ₄) ₂ ²⁻ 50% (UO ₂) ₅ (OH) ₈ (SO ₄) ₆ ¹⁰⁻ 20% (UO ₂) ₃ (OH) ₄ (SO ₄) ₃ ⁴⁻ 20% (UO ₂) ₂ (OH) ₂ (SO ₄) ₂ ²⁻	U-O _{ax}	2.0 ± 0.2	0.0017	1.78 ₂	14.4
	U-O _{eq}	5.0 ± 0.4	0.0119	2.43 ₄	
	U-S	2.1 ± 0.5	0.0072	3.10 ₅	
E UO ₂ SO ₄ ·2.5H ₂ O	U-O _{ax}	1.7 ± 0.2 (2)	0.0011	1.77 ₀ (1.76 ₀)	17.5
	U-O _{eq}	4.9 ± 0.4 (5)	0.0066	2.39 ₃ (2.40 ₉)	
	U-S	1.1 ± 0.3 (1)	0.0020	3.62 ₅ (3.58 ₃)	
	U-U	0.8 ± 0.2 (1)	0.0075	4.87 ₀ (4.81 ₀)	
	U-U	0.9 ± 0.2 (1)	0.0045	5.40 (5.44 ₄)	

f: held constant during the fit.

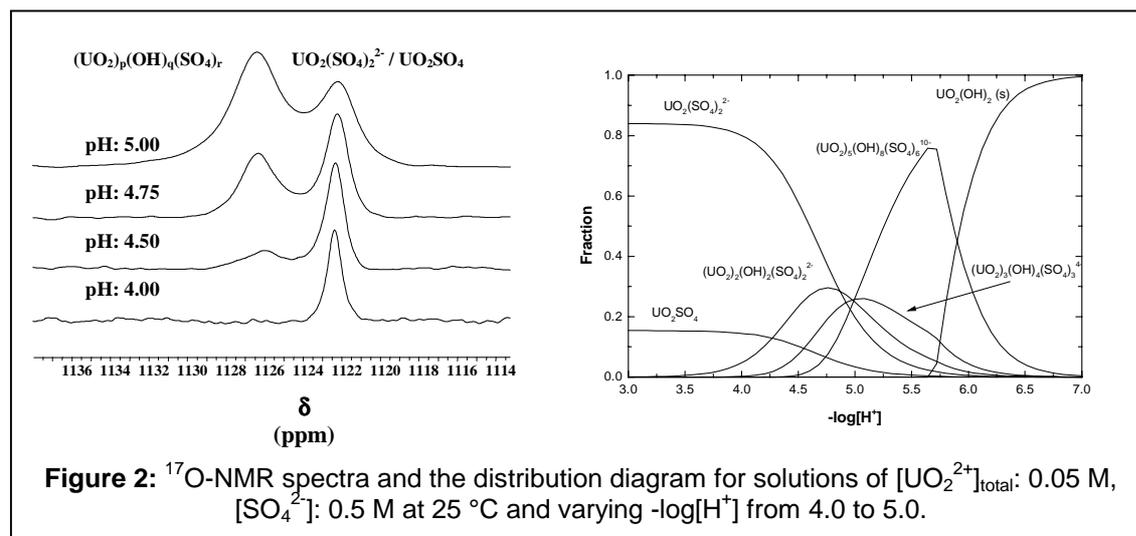
assume both a shorter U-S distance at 3.11 Å and a longer U-S distance at about 3.60 Å. We found it unlikely, considering the results from sample C, that samples A and B contained a monodentate bonded sulfate and therefore included a U-S distance fixed at 3.11 Å in the model. The short U-S distance in samples A and B are supported by the presence of a residual oscillation after subtraction the model EXAFS oscillation obtained without including the U-S shell. This remaining oscillation showed in all solutions the same pattern at a k range of 2.8 to 9.2 Å⁻¹. The resulting peak was FT filtered and the oscillation could be described using a U-S distance of 3.16 Å. However, from the results of the samples A and B alone one cannot conclude the presence of a bidentate sulfate. But by considering all information the EXAFS data indicate clearly that SO₄²⁻ is bonded in a bidentate fashion to the uranyl unit in solution.

¹⁷O-NMR studies of the UO₂²⁺-SO₄²⁻ System (for detailed information see [16]). The line width and the chemical shift increase with the sulfate concentration is a result of the formation of uranyl sulfate complexes. The only observed peak in the binary system indicates a fast exchange between the complexes on the ¹⁷O-NMR time-scale. The measured line shape can then give information about the dynamics of the system, using the matrix formalism introduced by Reeves and Shaw [17]. The chemical environment of the uranyl ion is changing by sulfate exchange which takes place via two pathways, and the pseudo first order rate constants describing the exchange between UO₂²⁺ and UO₂SO₄, $k_{1(obs)}$, and between UO₂SO₄ and UO₂(SO₄)₂²⁻, $k_{2(obs)}$, can be determined from the line width using the formalism described above. The following reactions can contribute to the pseudo first order rate constants: a) UO₂²⁺ + SO₄²⁻ ⇌ UO₂SO₄ [$k_1=(3.4±0.5) × 10^3 M^{-1}s^{-1}$], b) UO₂²⁺ + UO₂(SO₄)₂²⁻ ⇌ 2UO₂SO₄ [$k_2=(2.1±0.3) × 10^5 M^{-1}s^{-1}$], c) UO₂SO₄ + SO₄²⁻ ⇌ UO₂(SO₄)₂²⁻ [$k_3=(1.4±0.2) × 10^3 M^{-1}s^{-1}$], and d) U*O₂²⁺ + UO₂SO₄ ⇌ U*O₂SO₄ + UO₂²⁺ [$k_4=(9.3±0.8) × 10^4 M^{-1}s^{-1}$]. Similar type of reactions were observed in the case of the binary uranyl-fluoride system [18]. The mechanism consists of two steps, a faster bonding of a chelating sulfate, $k_1 = 3.4 × 10^3 M^{-1}s^{-1}$, to form the neutral complex UO₂SO₄, which is followed by the coordination

of a second sulfate with $k_3 = 1.4 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$. These rate constants are similar to those measured for the binary uranyl-fluoride system [18]. Szabó *et al.* found a rate constant of $k_{m,n} \sim 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the fluoride exchange reactions and suggested an intimate mechanism of the Eigen-Wilkins type. The experimental findings, $k_x \sim 7 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, indicate that the rate of complex formation is not strongly dependent on the entering ligand, F^- ($k_{m,n} \sim 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in [18]) or SO_4^{2-} , supporting an Eigen-Wilkins mechanism.

EXAFS in the UO_2^{2+} - SO_4^{2-} -OH System. Figure 1 depicts a typical example for the EXAFS data measured in the ternary system. The results (Table 1, sample D) showed no significant differences from the binary uranyl sulfate system. Approximately two sulfur atoms were measured at 3.10 Å indicating that SO_4^{2-} is bonded as a chelate in the uranyl hydroxo species. We can exclude single bonded bridging, but not chelating bridging co-ordination, *c. f.* the structure proposals in Grenthe and Lagerman. Sulfate may like chromate [19] act as a bidentate bridging ligand to stabilize the polynuclear hydroxo complexes. According to the structural model of Grenthe and Lagerman and the coordination geometry of uranyl in polynuclear hydroxo complexes, it is not possible to coordinate more than 1.5 sulfates per uranyl unit. The theoretical coordination number of sulfur in sample D is between 1.2 and 1.5. The error in the coordination number using EXAFS is large, but the second number is not inconsistent with the theoretical value. Calculations using a fixed coordination number of 1.5 showed no significant changes in the results. A residual value of 14.8 was obtained compared to 14.4 when the coordination number was not fixed. No peaks corresponding to a U-U interaction between 4 and 6 Å were observed. Nevertheless, this is not an indication that the ternary species are not formed, the potentiometric measurements (see [16]) and the ^{17}O -NMR investigations clearly show the presence of polynuclear species. The measured EXAFS oscillations represents the sum of all absorber-backscatterer shell contributions. Such contributions which are out of phase, may result in the disappearance of a U-U peak. CaCO_3 is one example for such "out-of-phase" effects [20]. Thompson *et al.* found that distant contributions from U (4.9 to 5.2 Å) are weak and therefore might be difficult to detect in samples of unknown composition (see structural parameters of $\text{UO}_2\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$ in Tab. 1) [21]. An other example might be the weak U-U interaction at 4.92 Å in $[(\text{UO}_2)_3(\text{CO}_3)_6]^{6-}$ [22].

^{17}O -NMR in the UO_2^{2+} - SO_4^{2-} -OH System. ^{17}O -NMR was applied for the first time to obtain structural and dynamic information about this complicated system. ^{17}O -NMR spectra



measured at $0.05 \text{ M } \text{U}^*\text{O}_2^{2+}$ in $2 \text{ M } \text{NaClO}_4 + 0.5 \text{ M } \text{Na}_2\text{SO}_4$ and 25°C are summarized in Fig. 2.

The appearance of a second peak in addition to the peak of the binary species, which then dominates the spectra at increasing $-\log[\text{H}^+]$ is a clear indication for the formation of ternary uranyl sulfate hydroxide species, as expected from the speciation calculations. The integrals

of the two peaks give information on the amount of uranium present as mononuclear and polynuclear complexes. This quantity was compared with that calculated from the equilibrium constants. The agreement between the two values was within 15%, which is within the accuracy of the two measurements. The only broad peak at 1126.2 ppm shows that it is not possible to identify the different polynuclear complexes, very likely because of the small chemical shift difference and the fast exchange between them. From the experiments we have made it is not possible to get more concrete information about the dynamics of the ternary systems. Co-ordination of sulfate to the polynuclear hydroxide complexes results in a fairly large change in the chemical shift of the "yl"-oxygens, from 1120 ppm in $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and 1124.7 ppm in $(\text{UO}_2)_3(\text{OH})_5^+$ measured by Jung et al. [23], to 1126.2 ppm in the ternary system.

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