

Structure of the UO_2^{2+} – SO_4^{2-} Ion Pair in Aqueous Solution

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The structure of the ion pairs formed in aqueous uranyl sulfate solutions has been investigated with high-energy X-ray scattering. Sulfate binds to the uranyl as a monodentate ligand in equimolar solutions. The geometry of the ion pair is very similar to configurations found in crystalline structures; in particular, the U–O–S angle is bent in solution as well as in the solid state. It can therefore be concluded that an U–O–S angle of 143° is an intrinsic property of the uranyl sulfate bond and not due to packing effects or interaction with the water in the primary solvation shell.

Introduction

The doubly charged uranyl UO_2^{2+} and sulfate SO_4^{2-} ions are known to form uncharged ion pairs in solution. Evidence for their formation was inferred from extended X-ray absorption fine structure (EXAFS) measurements,¹ infrared and Raman spectroscopic measurements,^{2,3} measurements of partial molar volumes and heat capacities,⁴ an anomalously decreasing compressibility with increasing salt concentration,⁵ and the low ionic conductivity of UO_2SO_4 solutions, together with the small mean activity coefficient.⁶ A review of published formation constants is given in ref 7. Despite these numerous studies little is known about the ion-pair structure in aqueous solution. The only direct structural evidence of the uranyl coordination in solution comes from the position of the sulfur backscatter peak in the EXAFS data, which is difficult to extract, so that a definitive determination of the sulfate coordination, as mono- or bidentate, has not been possible. Recent theoretical work on UO_2^{2+} and PuO_2^{2+} sulfates⁸ assumes bidentate coordination

for SO_4^{2-} about the actinyl. We report results from high-energy X-ray scattering experiments designed to determine the structure of the uranyl sulfate ion pair.

Uranyl and sulfate ions exhibit a rich solid-state chemistry. The literature⁹ reveals 24 structures containing both the uranyl and the sulfate ions. The published structures that also contain the hydroxide ion are significantly different from those remaining structures that do not, the latter of which are more relevant to our experimental conditions, namely acidic solutions. Both monodentate and bidentate coordination are realized in the remaining structures. Bidentate coordination is the less common, occurs never as the only coordination mode, and occurs only in structures that have a sulfate/uranyl ratio larger than one.

Ion pairing is thought to become increasingly more important at higher temperatures. The rationale for this assumption is that the dielectric constant of the solvent water decreases with increasing temperature and therefore the ion–ion interactions become stronger. Conductivity data from salt solutions such as sodium chloride can be interpreted as indicating the formation of large ion clusters at high temperature.¹⁰ It is interesting to note that UO_2SO_4 solutions separate into two liquid phases at high temperatures,^{11,12} a heavier solution concentrated in uranyl and sulfate and a lighter solution dilute in these ions. Although a temperature-dependent study of the ion pairs in UO_2SO_4 was not the intention in this work, one may expect that extended ion

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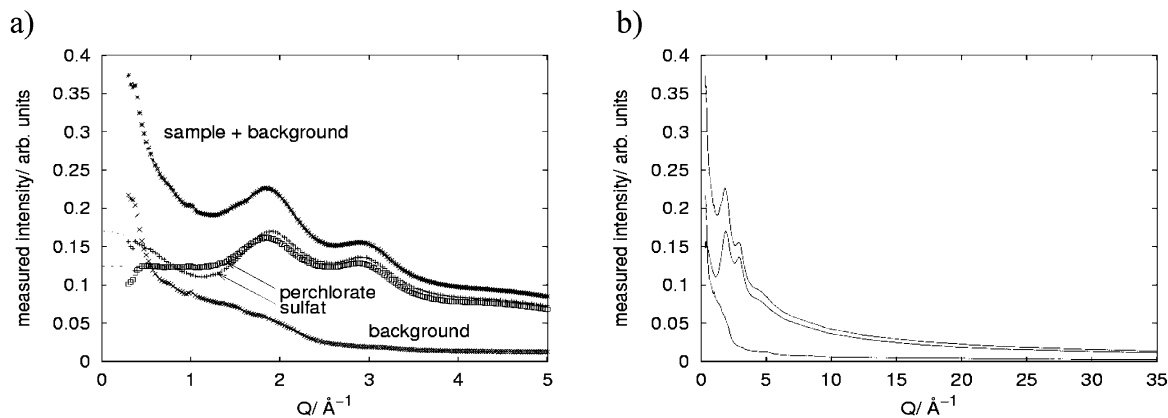


Figure 1. (a) Comparison of the scattering intensities from UO_2SO_4 and $\text{UO}_2(\text{ClO}_4)_2$ solutions and the instrumental background intensity at $Q < 5 \text{ \AA}^{-1}$. (b) Scattering intensity over the entire momentum-transfer range covered. From top to bottom: sample (UO_2SO_4 solution) + background and sample and background separately.

clustering at high temperature could be responsible for this unusual behavior.

Experimental Section

Materials and Sample Preparation. A solution of a molality of 0.5 mol kg^{-1} UO_2SO_4 was prepared by dissolution of 150 mg (0.5 mmol) of $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ in a mixture of 50 mg (0.5 mmol) of concentrated sulfuric acid (Aldrich) and 983 mg of deionized water. Solutions of $\text{UO}_2(\text{ClO}_4)_2$ were prepared in an analogous manner by dissolving $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ in perchloric acid (Aldrich). UO_2SO_4 solutions prepared in this way have a pH of 2.0 (interpolated from the values given in ref 13), a pH high enough that sulfate is predominantly present as SO_4^{2-} and not HSO_4^- . To confirm the water content of the uranium trioxide the concentration of UO_2^{2+} of a solution of the $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ in diluted sulfuric acid was determined by titration with standardized NaOH solution (Aldrich) in a separate experiment as described in the literature.¹⁴ The X-ray powder diffraction pattern determined for the $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ was found to be in agreement with published data.¹⁵

Scattering Measurements. High-energy X-ray scattering experiments (HES) were conducted at beamline 11-ID-C¹⁶ at the Advanced Photon Source in top-up mode with a constant storage ring current of 100 mA. The energy of the monochromatic X-rays employed for the angle-dispersive scattering experiments was 115 keV. Samples were enclosed in thin-walled (0.01 mm) silica tubes with a 3 mm outer diameter (Glas Müller). Data were collected in the region $0.3 \text{ \AA} < Q < 35 \text{ \AA}^{-1}$, with $Q = (4\pi/\lambda) \sin \theta$. The scattered X-ray intensity from the UO_2SO_4 solution is compared to the scattering from a $\text{UO}_2(\text{ClO}_4)_2$ solution in Figure 1. The data were corrected for detector dead-time, background (empty container), polarization, and tangential detector movement, normalized to a cross section per formula unit, and extrapolated to $Q = 0$ using standard procedures.¹⁷ The result is the structure factor $S(Q)$.

Data Treatment. The X-ray structure factor $S(Q)$ is related to the pair distribution function $g(r)$ by a Fourier–Bessel transform:

$$\rho[g(r) - 1] = \frac{1}{(2\pi)^3} \int 4\pi Q^2 [S(Q) - 1] \frac{\sin(Qr)}{Qr} dQ$$

A pair distribution function is a measure to the probability of finding a neighboring atom at a certain distance r compared to a random distribution, and ρ is the number density. The momentum transfer ranges up to 15 \AA^{-1} , and a Lorch window function¹⁸ have been used for the transform. A scattering experiment with X-rays is a weighted average of the partial structure factors between all atoms present in the sample, with the weight depending on the number of electrons in the atoms, and therefore, it is biased toward the heavier atoms.¹⁹ To emphasize ion pairing in the UO_2SO_4 solution, we construct the difference structure factor between a UO_2SO_4 and a $\text{UO}_2(\text{ClO}_4)_2$ solution. The perchlorate ion is accepted to be noncoordinating to uranyl.²⁰ All contributions to the total structure factor that occur in both solutions, such as water–water correlations, cancel to a first approximation in the difference spectrum. To account for a possible change of the water structure induced by the presence of perchlorate or sulfate, the difference structure factor between a LiClO_4 and a Li_2SO_4 solution was determined and subtracted from the obtained difference. The derived structure factors are shown in Figure 2.

The structure of the uranyl–sulfate ion pair can be described in terms of a few parameters. The distance between the uranium atom and the sulfur atom is determined by the UOS angle φ (cf. Figure 3) and the UO and the OS bond lengths. If $\varphi \neq 180^\circ$, then the dihedral angle δ between the UOS and the OSO plane determines the distance between the uranium and the other three oxygen atoms of the sulfate group. A deviation of the OSO bond angle β within the sulfate ion from the tetrahedral angle is possible. However, if sulfate is bound in monodentate coordination, then the 3-fold symmetry should be retained; that is, all angles between the bound and the three free oxygen atoms should be the same and all angles between the non-uranyl-bound oxygens should be the same. All the UO and OS bond-length distributions are assumed to be Gaussian. The angular distributions are constructed as Gaussian cosine distributions to avoid singularity problems at angles close to 180° . The dihedral angle distribution needs to reflect the 3-fold symmetry of the problem. Therefore, a distribution of the form

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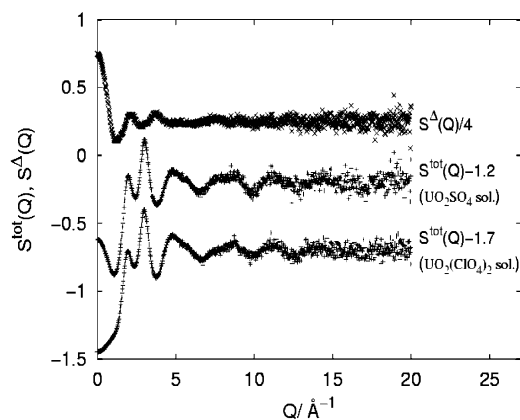


Figure 2. Structure factors derived from the X-ray intensities in Figure 1. The difference between the sulfate and perchlorate structure factor is easily seen, especially at low Q .

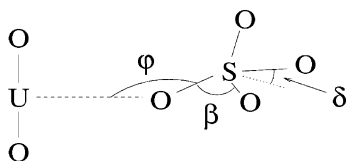


Figure 3. Parameter used to describe the structure of the uranyl-sulfate ion pair.

$$V(\delta) = \{ \exp[-(\delta - \delta_0)^2/(2\sigma^2)] + \exp[-(\delta - \delta_0 - 120^\circ)^2/(2\sigma^2)] + \exp[-(\delta - \delta_0 + 120^\circ)^2/(2\sigma^2)] \}$$

has been chosen. In general the parametrization of the problem is quite similar to the one chosen in ref 21. The parameters are visualized in Figure 3. The ratio α of uranium in ion pairs to total uranium completes the parametrization.

Results

The difference-pair distribution obtained by Fourier-Bessel transform from the difference structure factor in Figure 2 is shown in Figure 4. This distribution, which represents the difference between the uranyl coordination environment in the sulfate and the perchlorate solutions, shows two distinct features centered at 2.4 and about 4 Å. The 2.4 Å feature is characteristic of a shift in peak position that occurs when subtracting a peak from one spectrum from a peak at lower r from another spectrum. This region in r is characteristic of the first uranyl coordination shell. The change is due to the partial replacement of water molecules in the solvation shell in the perchlorate solution by an oxygen originating from the coordinating sulfate. The distance between uranium and a sulfate oxygen is expected to be smaller than the distance to the water oxygen that it replaces. The feature at around 4 Å is a group of three peaks, with maxima at 3.67, 4.23, and 4.83 Å. The distance of 3.67 Å is characteristic of monodentate sulfate coordination whereas a U-S distance of about 3.1 Å is expected for bidentate-sulfate coordination. There is no sign of a correlation at such a distance, and therefore, there is no detectable bidentate

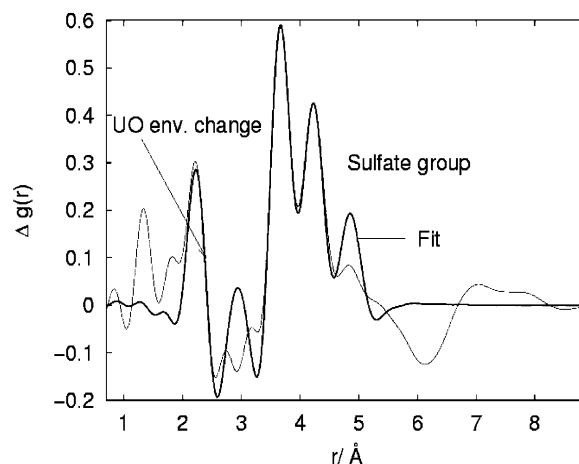


Figure 4. Difference-pair distribution function between the sulfate and perchlorate solutions. The fit of the structural model of the uranyl-sulfate ion pair is shown with the thicker line.

Table 1. Values of the Fit Parameter Used to Describe the Uranyl-Sulfate Ion Pairs As Described in the Text^a

param	value
paired ion ratio α	0.61
$\angle \text{UOS } \varphi_0$	143°
σ_φ	<1°
$\angle \text{UOSO } \delta_0$	0 ^f
σ_δ	14°
$\angle (\text{U}-)\text{OSO } \beta_0$	114°
$r_{\text{UO}(\text{H}_2\text{O})} - r_{\text{UO}(\text{SO}_4)}$	0.017 Å
$r_{\text{SO}(-\text{U})}$	1.49 Å ^f
$r_{\text{SO}(+\text{U})}$	1.44 Å ^f
σ_β	0 ^f
σ_r	0.04 Å ^f

^a Fixed parameters are marked with a superscript "f".

sulfate coordination. Table 1 summarizes the parameters obtained from a fit of the distance and bond angle distributions as outlined above.

Discussion

Table 2 summarizes the published structural parameters for selected uranyl sulfates. The first eight of these are chosen because they do not contain any other anions especially hydroxide. Several trends appear from all these structures. The UOS angle with which the sulfate bonds to the uranyl ion is significantly smaller than 180°, and the average angle in each crystal varies between 139 and 146° with a grand average of 143°. The SO distance to the oxygen bound to the UO_2^{2+} ion is longer than the SO distances to nonbonded oxygens by an average of 0.043 Å. The uranium-oxygen distance of the remaining coordinated waters are considerably longer than the uranium to sulfate oxygen distance. A comparison with the UOS angle determined in this work reveals the equality of this angle in solution and in the crystalline phases. This is a significant finding because the crystals are different from the solution on several counts. First, the sulfate ions are bridging in all eight of the crystal structures. The crystalline phase appears to retain only one or two water molecules in the UO_2^{2+} solvation shell, which rules out hydrogen bonding between the sulfate and solvation-shell water as an explanation for the bent UOS angle. Obviously, there are no symmetry constraints imposed by a

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Table 2. Bond Distances and Angles (Å, deg) in Various Crystalline Uranyl Sulfates^a

compd	$r_{\text{UO}(\text{H}_2\text{O})}$	$r_{\text{UO}(\text{SO}_4)}$	N_{SO_4}	$r_{\text{US}(\text{md})}$	$r_{\text{US}(\text{bd})}$	$r_{\text{SO}(-\text{U})}$	$r_{\text{SO}(+\text{U})}$	$\angle\text{UOS}$	refs
$(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2$	2.516	2.361	4	3.642		1.493	1.460	141	25
$\text{UO}_2\text{SO}_4(\text{H}_2\text{O})_{3.5}$	2.429	2.364	3	3.678		1.482	1.434	145	26
$\text{UO}_2\text{SO}_4(\text{H}_2\text{O})_{2.5}$	2.448	2.368	3	3.658		1.467	1.434	144	27
$\text{UO}_2\text{SO}_4(\text{H}_2\text{O})_{3.5}$	2.399	2.358	3	3.681		1.469	1.446	147	28
$\text{K}_2\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2$	2.517	2.352	4	3.634		1.516	1.471	139	29
$\text{MgUO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_{11}$	2.425	2.350	4	3.627		1.478	1.451	142	30
$\text{Mn}_2\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_5$	2.461	2.347	4	3.687		1.497	1.443	146	31
$\text{UO}_2(\text{HSO}_4)_2(\text{H}_2\text{O})_5$	2.459	2.360	4	3.648		1.480	1.399	142	32
average	2.457(39)	2.358(7)		3.657(21)		1.485(15)	1.442(20)	143(3)	
$\text{K}_4\text{UO}_2(\text{SO}_4)_3$		2.375	3 + 1	3.689	3.07	1.472	1.484	146	33
$\text{KNa}_5[\text{UO}_2(\text{SO}_4)_4](\text{H}_2\text{O})$		2.344	3 + 1	3.600	3.090	1.502	1.460	138	34
$\text{Na}_6[\text{UO}_2(\text{SO}_4)_4](\text{H}_2\text{O})$		2.320	3 + 1	3.597	3.101	1.497	1.461	140	35
$\text{Na}_{10}[\text{UO}_2(\text{SO}_4)_4](\text{SO}_4)_2(\text{H}_2\text{O})_3$		2.304	3 + 1	3.629	3.091	1.505	1.450	144	36

^a The notation $N_{\text{SO}_4} = 4$ means four monodentate-sulfate ions bound to uranyl, $N_{\text{SO}_4} = 3$ means three monodentate-sulfate bound to uranyl, and $N_{\text{SO}_4} = 3 + 1$ means three monodentate- and one bidentate-sulfate bound to uranyl.

lattice in the case of a solution. Therefore, a bond angle of about 143° appears to be an intrinsic property of uranyl–sulfate bonding. Furthermore, the thermal parameter for the bond angle determined herein is small and the width of the US peak in the pair distribution function is determined by the experimental resolution. This is an indication for covalent character to the UOS bonds. A further indication is the above-mentioned distortion of the sulfate ion in the crystalline phase, which indicates that the S–O bond that is pointing toward the uranyl ion increases its single-bond character, relative to the S–O bonds pointing away from the uranyl group. This makes an interaction of the uranyl ion with the free electron pair of the oxygen atom a likely explanation for the observed nonlinear U–O–S bond. Quantum mechanical calculations could quantify this hypothesis. Published calculations⁸ are not helpful in this regard because they assume bidentate sulfate coordination, which is not observed here.

The remaining four crystal structures presented in Table 2 do contain one bidentate sulfate together with three monodentate-coordinated sulfates/uranyl ion. The US distance for the bidentate sulfate ions is 3.07–3.11 Å. No peak appears in our data at this distance. Therefore, we conclude that, for our solution, the sulfate coordination is purely monodentate. Moll et al.¹ do report a peak at 3.1 Å in their EXAFS data of uranyl sulfate solutions; however, their experimental conditions differ from ours in that they have $\text{SO}_4^{2-}/\text{UO}_2^{2+}$ ratios larger than 10, higher pH values, and lower uranium concentrations. In an additional experiment, we obtained EXAFS data for solutions bridging our experimental conditions with those of Moll et al.¹ A figure showing the Fourier transform of the k^3 -weighted EXAFS amplitude is deposited as Supporting Information. The data are consistent with those presented by Moll et al. and appear to change in the region $2.5 \text{ \AA} < r' < 3.5 \text{ \AA}$ upon introduction of a large excess of sulfate but not upon dilution of the uranyl solution. The result of these experiments indicates that the coordination mode may change if sulfate is present in large excess.

The fitting results indicate a preference for a configuration in which the in-plane oxygen of the sulfate points away from the uranyl ion ($\delta_0 = 0$). Structures with $\delta_0 = 60$ give a different pattern of U–O distances at $r > 4 \text{ \AA}$. The disorder

parameter of the OSO bond angle and the UOSO dihedral angle are correlated. That is why σ_β has been kept at zero and all disorder has been ascribed to rotation about the dihedral angle. The misfit of the peak at 4.8 Å (experimental peak is broader than the fitted distribution function) indicates a larger disorder for the oxygen pointing away from the uranyl ion. The distortion of the SO sulfate bond length has not been refined but rather taken as the average of the crystal structures listed in Table 2. The (U–)OSO β angle determines the exact position of the UO peak at 4.23 Å and can therefore be determined from the fit. Its deviation from the tetrahedral angle (114° rather than 109.47°) appears to be real. The difference between the UO distance in coordinating water and sulfate oxygens found in solution is small compared to the values found in the solid state. A possible explanation is that the replacement of water by sulfate is far less complete in solution. That is, the degree of ion pairing α is considerably below unity. Using the same equilibrium constants as used by Moll et al.¹ yields a degree of ion pairing of 80%. The $\text{HSO}_4^-/\text{SO}_4^{2-}$ equilibrium can lower that value to a minor extent. Discrepancies between fit and data remain in the region $r > 5.5 \text{ \AA}$, around 3 Å, and around 1.4 Å. The correlations at $r > 5.5 \text{ \AA}$ and the region around 3 Å—the position of the main O–O peak in water—are likely to be caused by the influence of the dissolved ions on the water structure. Leberman and Soper²² measured the effect of ions on the water structure for a sulfate compared to a chloride solution. The solutes interacting with the water structure relevant in this case are the perchlorate, the free sulfate, and the free uranyl ion as well as the uncharged uranyl–sulfate ion pair. The water-structure-related contributions most likely extend below the sulfate peaks and may be responsible for the small value of a , the bound-sulfate ratio. They are not expected to produce any sharp peaks, however, since the pair distribution function of water varies slowly with r in this region.²³ The feature around 1.4 Å is introduced by the difference between the free and bound sulfate ion structure. The binding of sulfate to uranyl may introduce further changes into the uranyl ion structure such as changing the strength of the uranium–water or the uranium–uranyl

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oxygen interactions. Inclusion of parameters to describe these effects does not seem warranted, however.

In theoretical treatments,²⁴ the ion-pairing process is often subdivided in three steps, formation of a solvent-separated ion pair and formation of the contact ion pair and dehydration of the ion pair. The last step is expected, as two charged

particles are replaced by a neutral particle, which does not require solvation. The liberation of water in the last step contributes strongly to the entropy of the overall process. There is no indication of a dehydration process of the ion pair for the uranyl–sulfate system. Dehydration would be expected to be visible as a strong negative peak in the pair distribution function change around 2.4 Å, which is not present.

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Supporting Information Available: An additional figure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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