High-Energy X-ray Scattering Study of UO_2SO_4 Solution

S. Skanthakumar,[1] J. Neuefeind,[2] J. C. Sullivan,[1] L. Soderholm[1]
[1] *Chemistry Division, Argonne National Laboratory, Argonne, IL, U.S.A.*
[2] *HASYLAB at DESY, Hamburg, Germany*

The fate and transport of uranium(VI) in groundwater is dependent on its speciation. Present as the dioxo ion, UO_2^{2+}, the coordination is complicated by the formation of binary and higher order complexes, the details of which are strongly influenced by the identity and concentration of dissolved anions, as well as the solution pH and Eh. The sulfate ion, SO_4^{2-}, prevalent in groundwater, is a complexing ion that can significantly affect the formation of complex aggregates. Equilibrium analyses can be used to estimate the presence and relative concentrations of various uranyl sulfate aggregates, but little has been done to verify these calculations. EXAFS measurements have been previously reported which provide important metrical information.[1] We have undertaken high-energy scattering experiments to try to extend the quantitative understanding of uranyl sulfate aggregation in solution.

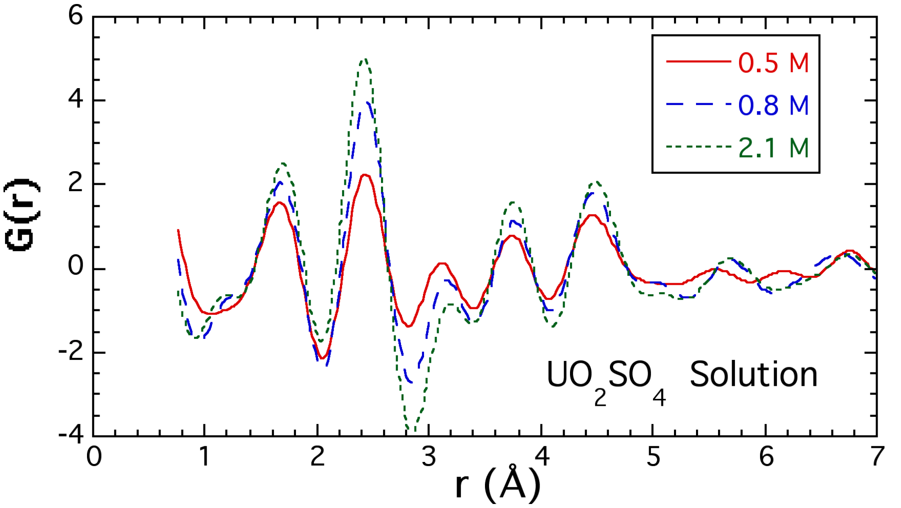

FIG. 1. Pair distribution functions for UO2SO4 solutions with different concentrations. The contribution from water has been removed.

High-energy x-ray scattering data were collected at room temperature on the BESSRC beamline 11-ID-C, which is equipped with a Si(311) monochromator. The incident energy of 115.2 keV was selected, which has an energy resolution of 0.8 keV (FWHM) in our setup. In order to reach high momentum transfers, the sample was placed at the regular analyzer position of the spectrometer,[2] but no analyzer was used in this experiment. The distance between sample and detector was 659 mm. Momentum transfers Q up to 40 $Å^{-1}$ can be measured in this configuration. A single-element Ge detector was used to remove the higher-order harmonics and fluorescence signal. Samples with various concentrations of UO_2SO_4 were loaded into 3 mm capillary tubes in the Actinide Facility at the Chemistry Division, ANL, and triply encapsulated before transport to the APS. Empty and water-filled capillary tubes were measured to obtain the background and water contributions to the observed data. The background was removed, and the data analyzed using standard techniques.[3]

The pair distribution functions, after the removal of solvent and background contributions, are compared in Fig. 1. The compared spectra were obtained from three samples with uranyl sulfate concentrations of 0.5, 0.8, and 2.1 M. Whereas these data all show peaks at 1.7, 2.4, 3.1, 3.8, 4.5 Å, their relative intensities appear to change significantly with changing concentration. The distances of 1.7 and 2.4 are typical of uranyl ion,[4] whereas the distance at 3.1 is the S atom. The more distance peaks at 3.8 and 4.5 Å are consistent with the U-U interactions that signal aggregation. A comparison of these data with those simulated from thermodynamic calculations is expected to yield significant insight into the formation and concentration dependence of uranyl sulfate aggregates in solution.

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References

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[3] See, for example, *Local Structure from Diffraction*, eds. S. J. L. Billinge and M. F. Thorpe (Plenum Press, New York, 1998).

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