# ISIS Experimental Report

## Rutherford Appleton Laboratory

| | |
|---|---|
| **RB Number:** | **20047** |
| **Date of Report:** | 06/2005 |

| | | | |
|---|---|---|---|
| **Title of Experiment:** | The structure and thermal expansivity of $D_2SO_4 \cdot 6\frac{1}{2}H_2O$ and $D_2SO_4 \cdot 8D_2O$. | **Local Contact:** | K. S. Knight |
| **Principal Proposer: Affiliation:** | A. D. Fortes | **Instrument:** | **HRPD** |
| **Experimental Team:** | I. G. Wood, L. Vočadlo, and H. E. Brand | **Date of Experiment:** | 23-26/05/05 |

**Introduction.** The sulfuric acid – water system is of great interest, not least from a crystal chemical point of view, but also because it plays a role in the formation of aerosols in the terrestrial stratosphere (e.g., Bertram *et al.* 1996), and is likely to be of relevance to understanding acidic groundwaters on Mars. Moreover, it has been suggested that water-rich $H_2SO_4$ hydrates are significant rock-forming minerals in the crust of Jupiter's icy moon Europa (e.g., Pappalardo and Barr 2003, Carlson 2004).

At the water-rich end of the $H_2O – H_2SO_4$ phase diagram, there are two solid hydrates; a hemitriskaidecahydrate ($H_2SO_4 \cdot 6\frac{1}{2}H_2O$) and a purported octahydrate ($H_2SO_4 \cdot 8H_2O$). The existence of the former is well established, whereas there has been some dispute in the literature as to whether or not the higher hydrate may in fact be a 9-, 9½-, or 10-hydrate (Beyer *et al.* 2003).

The only structural data for these two hydrates are from the single-crystal X-ray diffraction studies of Mootz and Merschenz-Quack (1987). Given that Mootz and Merschenz-Quack assumed a stoichiometry of $H_2SO_4 \cdot 8H_2O$ when this may not be the case indicates that the structure solution could be incorrect. More recently, Hirsch and Ojamäe (2004) carried out a density functional theory (DFT) study of these two sulfuric acid hydrates in an attempt to locate the hydrogen atoms in the structures.

The aim of this investigation was to collect high quality powder neutron diffraction data from the two higher hydrates in order to confirm existing structural models. We also examined a composition corresponding to sulfuric acid trihydrate, for which no diffraction data exists in the literature.

**Experimental.** Reagent grade $D_2SO_4$ (Aldrich, 98 wt. %, 99 at. % D) was diluted with $D_2O$ (Aldrich, 99 at. % D) to form solutions with the requisite stoichiometries (1:9, 1: 6½, and 1:3). For each composition, approximately 3 $cm^3$ of solution was pipetted into a standard vanadium sample canister (i.d. 10 mm) along with 0.15 g of silica wool to aid the crystallisation of a fine powder: unlike previous workers, we did not use $BaSO_4$ to promote nucleation. The sample can was sealed, attached to a centre stick, and then dipped in liquid nitrogen before the assembly was loaded into an OC50 cryostat (pre-cooled to 125 K) mounted on the HRPD beamline. Initially the sample formed an amorphous substance; subsequent warming above the glass transition caused the sample to crystallise. The 1:9 composition formed a two phase mixture containing Bragg peaks that could be indexed with the 'octahydrate' unit cell of Mootz & Merschenz-Quack (1987), and very weak peaks due to minor ice Ih. The 1:6½ mixture exhibited only Bragg peaks that could be indexed with the 6½-hydrate unit cell of Mootz & Merschenz-Quack (1987), and the 1:3 mixture crystallised single-phase sulfuric acid tetrahydrate: the sulfuric acid rich residue presumably persisting as a glass.

**Data collection.** From the 1:9 composition, a low-noise data set (253 µAhr) was collected in the backscattering (2θ = 168°) and 90° banks of HRPD at 178 K using the normal 30-130 millisecond time-of-flight window. The sample was then cooled to 4.2 K and another low noise data set was collected (351 µAhr). From the 1:6½ composition, low noise data sets were collected at 4.2 K using the double-width t-o-f window, 30-230 ms (120 µAhr) in backscattering and at 90°, and in the normal 30-130 ms window (435 µAhr) in the backscattering, 90° and

low-angle (2θ = 30°) detector banks. From the tetrahydrate, low noise data sets were collected at 217 K (129 µAhr in backscatter and at 90) and at 4.2 K (263 µAhr). In addition, observations were made during cooling; counting for 3.9 µAhr between 144-133 K, 3.5 µAhr between 100-90 K, and 3.1 µAhr between 75-60 K.

**Results.**
*Sulfuric acid 'octahydrate'.* The observed diffraction patterns agree with the proposed unit cell (space-group $I\bar{4}2d$, $a = b = 7.4342(2)$ Å, $c = 21.3734(5)$ Å at 4.2 K); analysis of the data is continuing.
*Sulfuric acid hemitriskaidecahydrate.* The observed diffraction patterns agree with the proposed unit cell (space group $Cm$, $a = 6.25189(9)$ Å $b = 26.8068(3)$ Å, $c = 5.90786(5)$ Å, $\beta = 112.190(1)°$ at 4.2 K); analysis of the data is continuing.
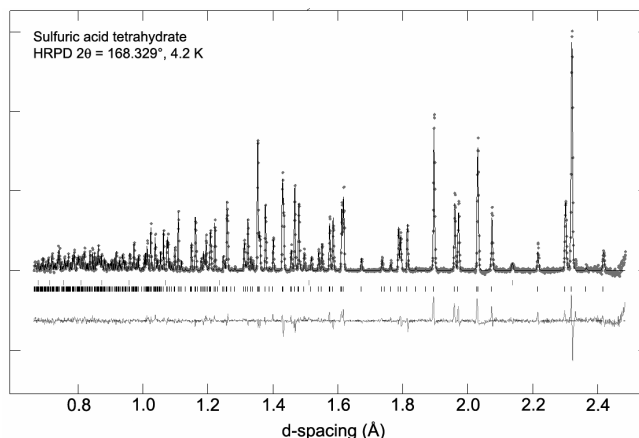


Fig. 1. Rietveld refinement of the $D_2SO_4 \cdot 4D_2O$ data collected in the backscattering banks of HRPD. Lower tick marks are for the tetrahydrate, upper tick marks are for vanadium.

*Sulfuric acid tetrahydrate.* The diffraction patterns at 217 K and 4.2 K (Fig. 1, above) were very well fitted with the existing structural model for $D_2SO_4 \cdot 4D_2O$ from the X-ray work of Kjällman & Olovsson (1972); analysis confirms that the structure consists of $SO_4^{2-}$ and $D_2O_5^+$ ions, the latter having a symmetrical hydrogen bond. The unit-cell dimensions as a function of temperature from the shorter runs show that the c-axis has a much larger thermal expansivity than the a-axis, and that the expansivity of the a-axis becomes anomalously small as the melting point is approached.

**References.**

Bertram *et al.* (1996) J. Phys. Chem. **100**, 2376.
Beyer *et al.* (2003) J. Phys. Chem. A **107**, 2025.
Carlson (2004) Workshop on Europa's Icy Shell: Past, Present, and Future, February 6-8, 2004, Houston, Texas, abstract no.7031.
Hirsch and Ojamäe (2004) Acta Cryst. B**60**, 179.
Kjällman & Olovsson (1972) Acta Cryst. B **28**, 1692.
Mootz and Merschenz-Quack (1987) Z. Naturforsch. B **42**, 1231.
Pappalardo and Barr (2003) American Astronomical Society, DPS meeting **35**, #06.05