ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment:	Crystal structures of methanol-water and methanol-ammonia compounds	**Local Contact:**	K. S. Knight
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Introduction: The water - methanol system is of great importance in biological and industrial chemistry [1] (particularly the oil industry where it is used as a clathrate inhibitor in pipelines), and is also of interest to cosmochemists studying ice grain reactions in the interstellar medium and the source of carbon in comets and other primitive solar nebula materials [2]. Moreover, methanol may be an important constituent of aqueous cryovolcanic solutions (along with ammonia) on the icy moons of our solar system [3]. In the methanol-water system there exists a single binary compound, methanol monohydrate ($CH_3OH.H_2O$), and in the methanol-ammonia system there exists a mono-ammoniate ($CH_3OH.NH_3$) and a hemi-ammoniate ($CH_3OH.½NH_3$). X-ray powder diffraction has been used previously [4,5] to determine that methanol monohydrate is tetragonal (a = 4.660(1), c = 13.813(5) at 80 K), but the structure remains unknown and nothing is known at all regarding the ammoniates.

We proposed to collect powder neutron diffraction patterns from all three compounds suitable for ab initio structure determination. Having been awarded two of the three days required, we decided to focus solely on methanol monohydrate.

Sample preparation: A solution of 1:1 molar stoichiometry was prepared from deuterated methanol and heavy water at room temperature. The solution was flash frozen to a glass in a liquid-N_2-cooled steel cryomortar, ground to a powder and transferred to a pre-prepared aluminium-framed slab can, which was held in a shallow plastic dish of liquid nitrogen whilst the powder sample was prepared and loaded. The back window of the slab can was quickly screwed into place and the centre-stick / slab-can assembly was moved (in a L-N_2 dewar) to an Orange cryostat where the sample was equilibrated at 160 K for ~ 20 hours to allow devitrification. The cryostat was positioned on the HRPD beamline; a brief inspection of the diffraction pattern at ~ 90 K revealed Bragg reflexions, indicating that the glass had devitrified, and none of the observed reflexions could be attributed to either ice Ih or α-methanol. However, all lines in the 90 K data were reasonably well indexed with the unit cell reported by Nakayama *et al.* [4].

Data collection: The sample temperature was reduced to 4.2 K and data were collected in the backscattering (2θ = 168°), 90°, and low angle (2θ = 35°) detector banks over the time-of-flight range 30 – 130ms. The data were integrated at 4.2 K for four hours (150 μAhr), after which shorter integration times were used (10 μA hr, or ~15 minutes) whilst warming back to 160 K in 10 K increments, with 5 minutes of thermal equilibration at each point. A second 4 hour data set was acquired at 160 K, and a second run of shorter counts were made upon cooling, again at 10 K intervals, but interleaved between the warming data. The cooling was ended when the sample temperature reached 15 K, and 4 hour data sets were then collected at 20 K intervals from 50 – 130 K.

Results: The structure of deuterated methanol monohydrate was solved by *ab initio* methods, using the FOX software package, and refined to Rp = 2.35 % in GSAS. The crystal is orthorhombic, space-group $Cmc2_1$ (Z = 4) with unit cell dimensions a = 4.649100(24) Å, b = 14.084637(67) Å, c = 4.693577(10) Å, V = 307.340(2) Å^3 at 160 K and a = 4.66319(6) Å, b = 13.61287(22) Å, c = 4.637841(26) Å, V = 294.408(4) Å^3 at 4.2 K The structure consists of water – water chains, linked by an ordered hydrogen bond, extending along the c-axis, which cross link methanol - water chains with disordered hydrogen bonds along the a-axis. These perpendicular water - water and methanol - water chains form sheets which are stacked parallel to the b-axis and which interact only through weaker contacts between the methyl hydrogens and hydroxyl oxygens of neighboring sheets. Details of the structure solution are presented elsewhere [6].

Data collected between 4.2 K and 160 K (twice on warming and once on cooling) yield the thermal expansivity of methanol monohydrate. The volume thermal expansion coefficient, α_V, is positive and normally behaved at all temperatures although it is very large, being 527 x10^{-6} K^{-1} at 160 K – almost six times larger than ice Ih at the same temperature. The greater part of this expansion occurs along the axis perpendicular to the h-bonded sheets.

References:

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