ISIS Experimental Report

Rutherford Appleton Laboratory

RB Number: 720010

Date of Report: 7 July 2008

Title of Experiment: Crystal structures of methanol mono-ammoniate ($CD_3OD{\cdot}ND_3$) and methanol hemi-ammoniate ($2CD_3OD{\cdot}ND_3$)

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Date of Experiment: 26-29/04/2008

Introduction: The ammonia-methanol system represents an interesting counterpoint to the water-methanol system, which is of great importance in biological and industrial chemistry and has been the subject of many experimental and computational studies. By contrast, the only known study of phase relations in the ammonia-methanol system is that of Kargel (1992). Although this binary system has received almost no attention, the interaction between ammonia and methanol, both in the liquid and solid state, provides a simple archetypal system for understanding weak hydrogen bonding. Methanol and ammonia may also be important constituents of aqueous cryovolcanic solutions on the icy moons of our solar system.

Two binary compounds exist in the methanol-ammonia system, a mono-ammoniate ($CH_3OH{\cdot}NH_3$) and a hemi-ammoniate ($2CH_3OH{\cdot}NH_3$): the structure of neither ammoniate is known; there have been no X-ray studies to indicate the symmetry or unit cell dimensions. However, both phases have melting points significantly higher than the monohydrate, and this might indicate a fully three-dimensional hydrogen bonded network, rather than the 2D network in methanol monohydrate (Fortes, 2006).

Sample preparation: Deuterated ammonia was condensed into an evacuated glass bulb immersed in a dry-ice cooled acetone bath at ~ 210 K. The liquid condensate was weighed, and the appropriate quantity of deuterated methanol was pipetted into the bulb to form solutions of 1:1 and 2:1 molar stoichiometry for the mono- and hemi-ammoniates, respectively. The 2:1 solution was left immersed in the cold acetone bath for ~30 minutes prior to sample loading, and whitish crystals (which we believe to be the mono-ammoniate) precipitated. These were melted prior to loading, although some microscopic seeds may have persisted. The solutions were decanted into a liquid-N_2-cooled steel cryomortar, each forming a toffee-like substance. Nitrogen was poured directly onto the sample causing it to become a brittle solid, which was ground to a coarse powder very easily. The 2:1 powder was transferred immediately into a pre-prepared aluminium-framed slab-can (10mm deep), which was held in a shallow plastic dish of liquid nitrogen whilst the 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 OC100 Orange cryostat where the sample was equilibrated initially at 100 K. The 1:1 powder was stored in a plastic container immersed in liquid nitrogen for ~ 24 hours before the start of the diffraction experiment

Data collection: Diffraction patterns were collected in the 30-130ms t-o-f window from both 2:1 and 1:1 mixtures during warming from 100 K to 180 K. At 180 K, data were collected from both specimens in the 30-130ms window (450 μAhr) and 100-200ms window (100 μAhr). The sample temperatures were subsequently reduced to 4.2 K and the high-temperature data collection was reproduced, with the exception that no data was collected from the 2:1 specimen in the 100-200ms window.

Results: The diffraction patterns of both specimens were new, neither containing any Bragg peaks from either α- or β-methanol, or from solid ammonia phase I. The mono-ammoniate patterns were indexed very quickly with an orthorhombic unit cell of dimensions a = 11.2105 Å, b = 7.7457 Å , c = 7.6799 Å, and V = 666.87 $Å^3$ (Z = 8) at 180 K using DICVOL06. Analysis of the absences revealed that the most likely space-group is Pbca, and the structure was indeed solved in this spacegroup during the experiment using the FOX software package. Details of the structure solution will be presented elsewhere.

The 2:1 mixture proved to contain a significant quantity of methanol mono-ammoniate, which may be due to the presence of microscopic seed crystals in the mother liquor (see sample prep). Once the mono-ammoniate peaks were subtracted from the data it was possible to obtain an extremely high FOM indexing of the residual hemi-ammoniate Bragg peaks with an orthorhombic unit cell of dimensions a = 12.9026 Å, b = 8.9689 Å , c = 4.7921 Å, V = 554.56 $Å^3$ (Z = 4) at 180 K. The most likely spacegroup is Pnma; structure solution is ongoing.

An additional phase was identified in the 100 K (warming) data collected from the 1:1 mixture, which subsequently was replaced by the mono-ammoniate phase described above. This phase was indexed with a monoclinic unit cell of dimensions a = 6.8215 Å, b = 6.4819 Å , c = 3.9842 Å, β = 108.4746°, V = 167.09 $Å^3$, which corresponds closely to the volume expected for Z =2. We suspect that this is a metastable phase formed by rapid quenching, but further work is required to understand crystallisation kinetics in this system.

Preliminary analysis show that both phases exhibit much more isotropic thermal expansion than methanol monohydrate, which is in agreement with the difference in hydrogen bonding between the hydrate and ammoniates.

References:

Kargel, J. S. (1992) *Icarus* **100**(2), 556-574.

Fortes, A. D. (2006) *Chem. Phys. Lett.* **431**, 283-288.