

Neutron Powder Diffraction Studies as a Function of Temperature of Structure II Hydrate Formed from a Methane + Ethane Gas Mixture

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Neutron powder diffraction data collected at the high resolution powder diffraction beamlines BT-1 (NIST Center for Neutron Research) and HRPD (JRR-3M) confirmed that a hydrate sample with a gas mixture of 82 mol% CH₄ and 18 mol % C₂H₆ crystallizes as structure II hydrate. The structure has been modeled using rigid-body constraints to describe CH₄ molecules located in the sixteen small polyhedral cavities and a 50/50 mixture of CH₄/C₂H₆ located in the eight large polyhedral cavities of a deuterated host lattice. Data were collected on HRPD at 7, 40, 50, 90, 130, and 180 K and on BT-1 at 10, 40, 70, 100, 130, and 160 K. The thermal expansivity has been calculated from the temperature dependence of the lattice parameters. The data collected at BT-1 allowed for full structural refinement of atomic coordinates and the atomic or molecular displacement parameters. The larger displacement parameters of the guest molecules in the large cages indicate more positional disorder than shown by the guest molecules in the small cages. In all data sets ice was present as a secondary phase.

1 Introduction

The tendency of certain gases to form solid compounds with water has been known for nearly 200 years (Sloan, 1998), but these compounds were largely of academic interest until the oil and gas industry recognized that gas hydrate formation under certain conditions blocks pipelines. This discovery motivated structural studies of hydrates of methane and other gases (Hollander and Jeffrey, 1977; Von Stackelberg, 1949), which revealed them to be clathrates, or 'guest-host' inclusion compounds. The 'host' lattice consists of an ice-like hydrogen-bonded network of water molecules with polyhedral cavities large enough to accommodate a variety of 'guest' molecules.

Most clathrate hydrates crystallize in one of two cubic structures. The unit cell of the Type I structure contains 46 water molecules comprising two pentagonal dodecahedra, with twelve pentagonal faces, and six tetrakaidecahedra, with twelve pentagonal faces and two hexagonal faces. The unit cell of the Type II structure contains 136 water molecules forming sixteen pentagonal dodecahedra and eight tetrakaidecahedra. A hexagonal clathrate hydrate also exists, which requires both large and small guest molecules to stabilize the structure (Ripmeester et al., 1987). More than 50 different gas molecules are known to form clathrate hydrates. Methane (CH₄) or ethane (C₂H₆) alone as the guest gas molecule form structure type I (Sloan, 2000), however, recent studies using Raman and NMR spectroscopic measurements of hydrates formed from binary mixtures of CH₄ and C₂H₆ indicated that for certain compositions the resulting structure was type II (Subramanian, 2000).

Presented in this work, are the structural details of a sample synthesized with a starting gas mixture of CH₄ and C₂H₆, determined from a neutron powder diffraction study at 10 K. Also determined and presented are

structural changes, including the lattice parameters and the atomic displacement parameters, as a function of temperature.

2 Experimental Methods

2.1 Sample Synthesis. Samples of structure II deuterohydrate were grown *in situ* by combining cold, pressurized gas mixture (certified 90.2% methane + 9.8% ethane) with granular D₂O ice "seeds" (Stern et al., 1998) in vanadium sample canisters nested within an outer stainless steel reaction vessel. D₂O seed material was prepared from a gas-free and nearly single-crystal cake of D₂O ice, crushed, ground, and sieved to 180-250 μm grain size. The gas was boosted to initial synthesis pressures (~26 MPa) and admitted quickly to the evacuated seed ice, rather than first cooling the pressurized gas to 250 K in a separate reservoir where unmixing could take place.

2.2 Neutron Powder Diffraction Data Collection. Neutron powder diffraction data were collected on the High Resolution Powder Diffractometer (HRPD) at the JRR-3M research reactor at the Japan Atomic Energy Research Institute (JAERI). The detector bank of the HRPD consists of 64 ³He detectors. The experimental set-up included 6' collimator before the detectors and 12' collimator before the Si (533) focussing monochromator and a take-off angle of 89°. In this configuration HRPD produced a monochromatic beam of neutrons with a 1.164 Å wavelength that was calibrated using silicon powder. Data were collected with constant monitor counts with a step size of 0.05° over the range of 5-160° 2θ. For temperature control a closed-cycle He refrigerator equipped with two temperature sensors was used. Samples in sealed vanadium cans were removed from storage in N₂(l) and immediately attached to the pre-cooled cold-tip of the refrigerator under a glovebag filled with He gas. Diffraction patterns were collected at

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7, 40, 50, 90, 130, 180 and 190 K. Additional sets of neutron powder diffraction data were collected on the BT-1 high-resolution neutron powder diffractometer at the NIST Center for Neutron Research (NCNR) NBSR Reactor. The detector bank of BT-1 consists of 32 ^3He detectors. The experimental set-up included a Cu(311) focusing monochromator with in-pile collimation of $15'$ and a take-off angle of 90° . In this configuration, BT-1 produced a monochromatic beam of neutrons with $\lambda = 1.5402 \text{ \AA}$. Data were collected with constant monitor counts with a step size of 0.05° over the range of $5\text{-}160^\circ 2\theta$. Again for temperature control a closed-cycle He refrigerator equipped with two temperature sensors was used and samples in sealed vanadium cans were removed from storage in $\text{N}_2(\text{l})$ and immediately loaded in the same manner as at JAERI. Diffraction patterns were collected at 10, 40, 70, 100, 130, and 160 K.

2.3 Rietveld Refinements. The General Structure Analysis System (GSAS) (Larson and Von Dreele, 1985) was used for the Rietveld refinements. The background was fit using a radial distribution function. The starting atomic coordinates to model the oxygen-deuterium host network were based on those reported by McMullan and Kvik (1990). The bound coherent scattering lengths, b_c , used were 6.65 fm for C, 6.57 fm for D, -3.74 fm for H, and 5.81 fm for O.

To model the rotational disorder of the CH_4 and C_2H_6 molecules rigid body constraints were used. The rigid bodies were set with CH_4 molecules occupying all sixteen of the pentagonal dodecahedron or small cages and the eight tetrakaidecahedron or large cages were filled with randomly with half C_2H_6 and half CH_4 molecules. For the RBs, translations distances and isotropic mean-square displacements were refined. The extent of deuteration of the host lattice was also determined by refining the H/D fraction for each of the disordered D sites.

3 Results and Discussion

The neutron powder diffraction data collected on the HRPD at JAERI confirmed that the samples synthesized with a resulting gas mixture of 82 mol% CH_4 and 18 mol % C_2H_6 crystallized as a structure type II hydrate. For the data sets collected below 90 K spurious extra peaks were observed that limited the structural information that could be determined from the data. In addition to extra peaks that were not identified the data indicated approximately 14 wt% hexagonal ice was present as a secondary phase. Table 1 summarizes the lattice parameters, wt% ice as a secondary phase, and additional extra peaks as a function of temperature.

Table 1. Refined lattice parameters, wt% ice, and unaccounted for peaks determined from neutron powder diffraction data collected at JAERI as a function of temperature.

Temperature (K)	a (Å),	wt% ice	extra peaks
7	17.102(3)	10	$20.5^\circ 2\theta$
40	17.086(2)	15	$21.4^\circ 2\theta$
50	17.089(3)	16	$21.5^\circ 2\theta$
90	17.107(2)	18	none
130	17.138(3)	16	none
180	17.170(2)	16	none

The neutron powder diffraction data collected on BT-1 at the NIST Center for Neutron Research (NCNR) NBSR Reactor indicated that only the structure type II hydrate and ice were present. The experimental parameters and crystal data are summarized in Table 2. Refined atomic coordinates and isotropic atomic displacement parameters are given in Table 3. The atomic and molecular displacement parameters for the host lattice (D and O atoms) and the small (CH_4) and large (50:50 C_2H_6 : CH_4 mixture) cage guest molecules, respectively, as a function of temperature are shown graphically in Figure 1. The atomic and molecular displacements help to describe the positional disorder found in gas hydrates and Figure 1 shows that the large cage molecule has more positional disorder than the small cage molecule as evidenced by the larger $U(T=0)$ intercept and $U(T)$ behavior of the small cage molecule is similar to that of the atoms in the host lattice. Table 4 summarizes the lattice parameters refined from the NIST data as a function of temperature. Figure 2 shows $\Delta a/a_0$, where a_0 is the lattice parameter at 10 K. The plot shows that the expansion is not linear and has been fit using a second order polynomial.

Table 2. Experimental parameters, crystal data, and refinement details for $\text{CH}_4/\text{C}_2\text{H}_6$ (82:18%) hydrate.

Powder diffraction data collection:	
Wavelength, Å	1.5402
Scan Range (degree 2θ)	5 – 160
Step Size (degree 2θ)	0.05
Temperature, K	10
Instrument	BT-1, NIST
Refinement:	
wR_p	2.89%
R_{exp}	2.06%
Goodness of fit, χ	1.41
Variables:	46
Crystal data	
Color	White
Crystal system	Cubic
Space group	Fd3m
a, Å	17.093(1)
Volume, Å ³	4994.3(6)
Formula	$136\text{D}_2\text{O}\bullet 16(\text{CH}_4)\bullet 4(\text{CH}_4)\bullet 4(\text{C}_2\text{H}_6)$
Formula weight	80.108
Calculated density, g/cm ³	1.036

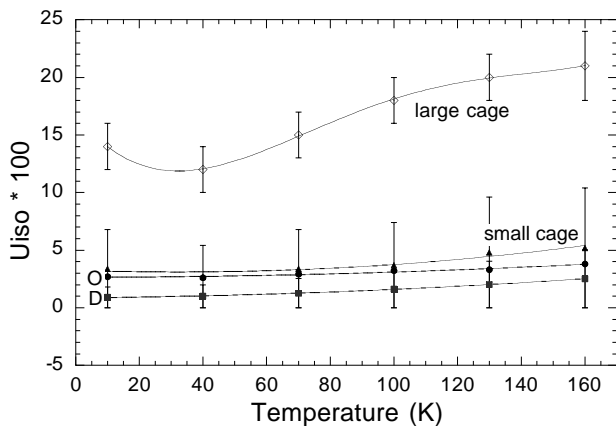


Figure 1. The atomic displacement parameters for the host lattice (D and O atoms) and the large (C_2H_6/CH_4) and small cage (CH_4) guest molecules as a function of temperature

Table 3. Atomic coordinates of CH_4/C_2H_6 (82:18%) hydrate from the Rietveld refinement of neutron powder diffraction data collected at 10 K on the NIST high resolution powder diffractometer (BT-1). Space group $Fd\bar{3}m$, origin at center ($\bar{3}m$), at $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$ from $4\bar{3}m$.

Atom	x	y	z	U_{iso}^* 100
O(1)	0.1822(2)	0.1822(2)	0.3723(4)	0.91(5)
O(2)	0.2187(4)	0.2187(4)	0.2187(4)	0.91(5)
O(3)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.91(5)
D(4)	-0.01646(5)	-0.0196(5)	0.1446(5)	2.7(1)
D(5)	0.1434(4)	0.1434(4)	0.3713(8)	2.7(1)
D(6)	0.1970(6)	0.1970(6)	0.3205(7)	2.7(1)
D(7)	0.2044(6)	0.2044(6)	0.2735(7)	2.7(1)
D(8)	0.1582(7)	0.1582(7)	0.1582(7)	2.7(1)
D(9)	0.1856(7)	0.1856(7)	0.1856(7)	2.7(1)
C(10)	0	0	0	3.4(3)
H(11)	0.1628	-0.01385	0.0607	3.4(3)
H(12)	-0.0534	0.3586	-0.0002	3.4(3)
H(13)	0.0478	0.0326	-0.0281	3.4(3)
H(14)	-0.0107	-0.0546	-0.0323	3.4(3)
C(15)	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	14(2)
H(16)	0.3880	0.3639	0.4370	14(2)
H(17)	0.3215	0.4105	0.3703	14(2)
H(18)	0.4241	0.4067	0.3481	14(2)
H(19)	0.3663	0.3190	0.3445	14(2)
C(20)	0.4049	0.3537	0.4011	14(2)
C(21)	0.3451	0.3963	0.3489	14(2)
H(22)	0.4494	0.3257	0.3640	14(2)
H(23)	0.3006	0.4244	0.3860	14(2)
H(24)	0.4339	0.3994	0.4419	14(2)
H(25)	0.3781	0.4431	0.3126	14(2)
H(26)	0.3719	0.3069	0.4374	14(2)
H(27)	0.3161	0.3506	0.3082	14(2)

Table 4. Lattice parameters refined from neutron powder diffraction data collected at NIST as a function of temperature.

Temperature (K)	a (Å), NIST
10	17.093(1)
40	17.096(2)
70	17.104(2)
100	17.119(2)
130	17.137(2)
160	17.164(2)

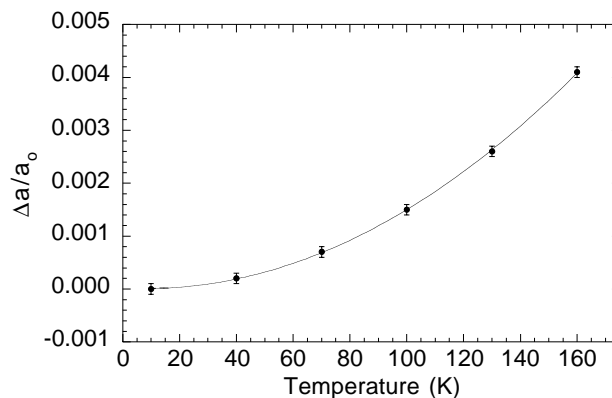


Figure 2. $\Delta a/a_0$ as a function of temperature.

4 Conclusions

Neutron powder diffraction data confirms that hydrate samples synthesized with a resulting gas composition of 82 mol% CH_4 and 18 mol% C_2H_6 crystallize as structure II hydrate. The data collected at BT-1 allowed for full structural refinement of atomic coordinates. The structure has been modeled using rigid-body constraints to describe CH_4 molecules located in the sixteen small polyhedral cavities and a 50/50 mixture of CH_4/C_2H_6 located in the eight large polyhedral cavities of a deuterated host lattice. Refinements on data collected at 10, 40, 70, 100, 130, and 160 K gave lattice parameter and atomic and molecular displacement parameters as a function of temperature. From these results the thermal expansivity has been calculated from the temperature dependence of the lattice parameters. The thermal expansion over this temperature range is twice that of ice Ih (Röttger et al. 1994), and similar to that of other structure II hydrates (Jones et al., 2002, Rondinone et al., 2002, Rawn et al., 2002) The larger atomic displacement parameters of the guest molecules in the large cages indicate more positional disorder than shown by the guest molecules in the small cages. In all data sets ice was present as a secondary phase.

Acknowledgments

Research sponsored by the Laboratory Directed Research and Development Programs of Oak Ridge National Laboratory (ORNL) and Lawrence Livermore National Laboratory (LLNL). We acknowledge the support of the Japan Atomic Energy Research Institute and the National Institute of Standards and Technology, U. S. Department of Commerce, in providing the neutron research facilities used in this work. ORNL is managed by UT-Battelle,

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