



Structural and thermodynamic characteristics of sH 2,2-dimethylbutane-methane deuterohydrate



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ABSTRACT

The structural features of mixed 2,2-dimethylbutane-methane deuterohydrate and 2,2-dimethylbutane-methane hydrogenated hydrate were studied by low-temperature powder X-ray diffractometer, and the thermodynamic properties of the two hydrates were investigated by studying their dissociation pressures within the temperature range of 277.05 to 283.85 K. The results obtained show that 2,2-dimethylbutane-methane deuterated hydrate and hydrogenated hydrate are the same in structure type (sH) and space group ($P6/mmm$), and the lattice constants and unit cell volume of the deuterohydrate are marginally larger than those of hydrogenated hydrate. The 2,2-dimethylbutane-methane deuterohydrate is thermodynamically more stable than 2,2-dimethylbutane-methane hydrogenated hydrate.

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1. Introduction

Gas hydrates are crystalline solid compounds, in which water molecules form cages via the hydrogen-bond and guest molecules are enclosed in the cages. There are three common types of hydrate structures including structure I (sI), structure II (sII) and structure H (sH), mostly dependent on the size and type of guest molecules [1]. The formation pressure can also affect the structural characteristics of gas hydrate in not only cage occupancy [2] but also structure type, especially at super high pressure of \sim GPa [3]. The sH gas hydrate was reported for the first time in 1987 [4], and it has been found that the large cages of sH hydrate can accommodate hydrocarbons containing 5–8 carbon atoms with the help of small molecule such as methane or carbon dioxide. In a sH hydrate, large cages are filled with the guest molecules with relatively large size, while medium and small cages are occupied with small guest molecules [5,6]. Different from sI and sII hydrates which have cubic structure, sH hydrate is hexagonal. A unit cell of sH hydrate consists of 34 H₂O molecules which form 3 small cages (5^{12}), 2 medium size cages ($4^35^66^3$) and 1 large cage ($5^{12}6^8$) [7] as shown in figure 1. The 2,2-dimethylbutane (or neohexane) has been reported as a sH hydrate former [8–10], and its structural and thermodynamic properties have been studied [8–11]. The investigation of 2,2-dimethylbutane-methane hydrate have revealed that the large

cages are occupied almost 100% by 2,2-dimethylbutane, while 79% of small cages and 88% of medium cages by methane [10]. Because sH hydrate has been identified as a promising material for gas storage [12] and gas separation of flue gas [13], a better understanding of its structural and thermodynamic characteristics will help in developing it as an energy material.

Neutron Scattering is a powerful tool in studying the formation mechanism [14,15] and crystal structure [16] of gas hydrates. As a well applied approach in neutron studies of gas hydrate, a certain percentage of deuterated water (heavy water) is introduced to substitute for light water to achieve a better scattering contrast. The isotope effects of H/D (hydrogen/deuterium) on water ice have been found to result in lattice expansion. In addition, the melting point of D₂O ice shifts to higher temperature region by 3.8 K as compared with H₂O ice [17]. To our knowledge, systematic studies of the isotope effect of H/D on structural and thermodynamic properties of gas hydrate are still few. Currently there are almost no structural information and stability conditions of deuterohydrate available [18]. To fill this knowledge gap, we investigated the structural and thermodynamic properties of 2,2-dimethylbutane-methane deuterohydrate. Here we report the results obtained.

2. Experimental

The provenance and mass fraction purity of the chemicals used in this research are listed in table 1. The hydrate samples studied in this research were synthesized in a 100 cm³ pressure cell. The

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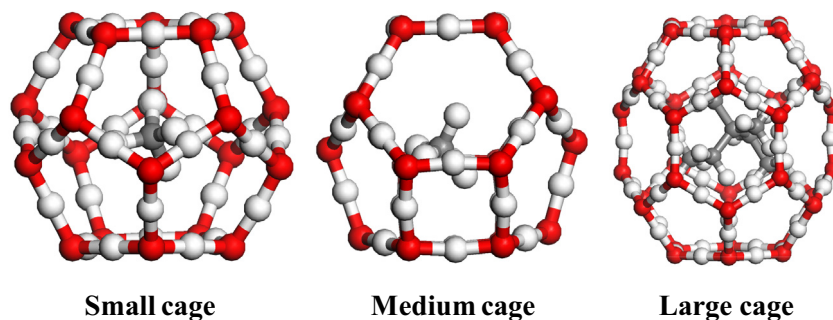


FIGURE 1. Three types of cages that construct sH gas hydrate.

TABLE 1

Provenance and mass fraction purity of the chemicals used in the study.

Chemical name	Source	Purification method	Final mass fraction purity
2,2-Dimethylbutane	Alar Aesar Chemical Co. Ltd.	None	0.95
Methane	Haikeyuanchang Practical Gas Co.	None	0.9999
Deuterium oxide	J&K Scientific Ltd.	None	0.998

powdered ice was well mixed with 2,2-dimethylbutane in the pre-cooled cell, and then the cell was sealed, vacuum applied and finally charged with CH₄ gas. The pressure cell was placed in a water-glycol bath. During reaction, the cell temperature was cycled between 258 and 276 K, generally at each state temperature being maintained for ~24 h. The conversion was thought almost complete when no significant pressure drop was observed after a cycle ended at $T = 276$ K. In order to compare the structural characteristics of 2,2-dimethylbutane-methane deuterohydrate and hydrogenated hydrate, the two hydrate samples were prepared in the same pressure cell to ensure that they experienced exactly the same reaction conditions. The hydrate samples prepared were recovered for further study while the pressure cell remained in the liquid nitrogen bath.

The low-temperature powder X-ray diffraction (PXRD) measurement was performed on a Bruker D8 X-ray diffractometer, which is equipped with a solid state detector LynxEye and Cu K α radiation ($\lambda = 0.15406$ nm). The sample was scanned at a step width of 0.02° in the 2θ range of 10.0 to 55.0° under the conditions of 40 kV and 40 mA. Through each measurement, the temperature of the sample holder was kept at $T = (123 \pm 1)$ K to prevent hydrate dissociation.

The thermodynamic behaviour of 2,2-dimethylbutane-methane deuterohydrate was investigated using an *in situ* system as shown in figure 2. Two thermocouples (with the precision of $T = \pm 0.1$ K)

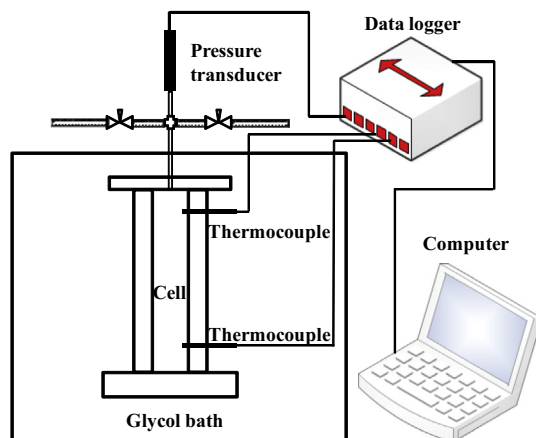


FIGURE 2. Experimental setup for studying the thermodynamic property of gas hydrate.

were installed, to detect the temperatures in the hydrate sample and gas phase, respectively. A pressure transducer (with a precision of $\pm 0.1\%$ of full scale) was used for monitoring the pressure change in the cell. The hydrate sample, which was prepared as discussed previously, was placed in the pre-cooled pressure cell. Vacuum was applied to the sealed pressure cell and then 1.5 MPa methane gas was introduced at $T = 276$ K. The temperature of the cell, which was controlled by a water-glycol bath, was increased by increments of $T = 1$ K. The pressure was taken as an equilibrium pressure at a specific temperature after no pressure increase, which resulted in by hydrate dissociation, and no temperature difference between the two thermocouples was observed for ~12 h. For sH gas hydrate, large guest molecules (2,2-dimethylbutane for this research) can only enter the large cages, and small guest molecules (methane for this research) can only occupy the small and medium cages. The large guest molecule is liquid with a low vapour pressure (less than 0.6% of full pressure in our current research), so the gas phase is overwhelmingly composed of methane gas. Using this behaviour of sH gas hydrate, its thermodynamic properties can be investigated by simply dissociating a previously synthesized sH hydrate sample. This method is easily applied to the investigation of sH hydrate stability [7,8,11]. To avoid dissociating excess hydrate to obtain one equilibrium point, we re-pressurized the sample with methane gas. This does not create a significant difference in the final result, because the gas phase is overwhelmingly composed of methane gas.

Moreover, when a gas hydrate is pressurized with a different gas from that of its guest composition, it will dissociate along its phase line while no disturbing action is applied [19]. As a result, the method described above can be used in pursuing the stability condition of the gas hydrate studied in this research, and this has been verified by the results obtained.

3. Results and discussion

Figure 3 shows the PXRD results obtained on 2,2-dimethylbutane-methane deuterohydrate and 2,2-dimethylbutane-methane hydrogenated hydrate. It can be seen that no significant shift in peak positions between the two hydrates can be observed. The results obtained were explained with Rietveld refinement. As no significant difference was identified between the refined results and experimental results, the results of refinement are reliable.

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