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Phase equilibrium and crystallographic structure of clathrate hydrate formed in argon + 2,2-dimethylbutane + water system

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ABSTRACT

This paper reports the four-phase (L_w–H–V–L_g) equilibrium conditions for the structure H hydrates formed in argon + 2,2-dimethylbutane. The experiments were performed at temperatures between 275.6 and 284.3 K, and at pressures between 2.91 and 9.41 MPa. The crystallographic structure of the hydrate was identified to be structure H by powder X-ray diffraction measurements. At a given temperature, the equilibrium pressure of the structure H hydrate formed with argon + 2,2-dimethylbutane was lower than that of the structure II pure argon hydrate. The difference in the equilibrium pressure is 8.1–20.9 MPa in the temperature range of 275.6–284.3 K. Among the system using methane, argon, krypton and xenon, the system using argon shows the highest reduction ratio of equilibrium pressures.

1. Introduction

Argon is one of the most common noble gases like helium. The volumetric composition of argon in the earth's atmosphere is approximately 0.9%. Human beings have used argon widely in their industry because of its safety and low cost. Argon is a noble substance, but it is reported that a clathrate hydrate can be formed with argon [1]. New technologies using hydrates formed with argon may be expected.

Argon gas has also been found on the other planets and satellites, and argon hydrates may be formed there [2,3]. In planetary geoscience, the thermodynamic stabilities of various clathrate hydrates are required for use in the simulation of atmospheric compositions. Argon is one of the main substances on Mars and Pluto and argon hydrate may exist by forming some structures. Though the thermodynamic stability of the pure argon structure II hydrate was used in the studies for conducting simulations of the atmospheric composition, more accurate simulation can be done if there is thermodynamic stability data of the structure H hydrate formed with argon. In the harvest industry, it is reported that fresh-cut peppers subjected to pressurized argon gas maintain water in the peppers due to the formation of argon hydrate [4]. The information about the stabilities of structure H hydrate formed with argon is needed, because some compounds may exist as a guest substance to form the structure H hydrate with argon in fresh peppers.

Clathrate hydrates are ice-like crystalline solid compounds consisting of a network of hydrogen-bonded host water molecules forming cage structures that enclose guest molecules. Depending on the size and shape of the guest substances, water molecules form several different cage structures that interconnect to yield hydrates of different crystallographic structures, such as structure I (sI), structure II (sII), and structure H (sH). The crystal system of the sI and sII hydrates is cubic and that of the sH hydrate is hexagonal. The typical values of the lattice parameters at 100 K are as follows: the *a* axes of sI and sII hydrates are 12 Å and 17.2 Å, and the *a* and *c* axes of sH hydrate are 12 Å and 10 Å [5]. The formation of sH hydrates requires two different guest substances; one is a relatively large molecule guest substance (LMGS), and the other is a small gaseous guest substance, such as methane or xenon. The phase equilibrium conditions of sH hydrates are often milder (*i.e.*, higher temperature and lower pressure) than those of the sI or sII hydrates formed only with small molecule guest substances. The milder phase equilibrium conditions of the sH hydrate formed with argon is advantageous for actual applications. Examples of the applied technologies of the argon sH hydrate are a hydrate-based heat pump [6] and a hydrate engine [7]. Ogawa et al. selected the pair of HFC-32 and cyclopentane as guest substances. HFC-32 is a flammable gas, while argon is an extremely inactive gas. The global warming potential of HFC-32 is also much higher than that of argon. The sH hydrate formed with argon can then be the medium of the

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Table 1
Supplier and purity of the materials used in this study.

Chemical	Supplier	Purity
Argon	Taiyo Nippon Sanso	>99.9999
2,2-Dimethylbutane	Sigma–Aldrich	>99.0

hydrate heat pump and the hydrate engine in terms of safety and low cost of argon gas.

In this study, we targeted argon as a candidate guest gas to form an sH hydrate to be practically applied for the hydrate-related industries because the cost of argon is one-fourth the cost of methane. We selected 2,2-dimethylbutane as the second guest substance used together with argon because the sH hydrates, which have a milder phase equilibrium than the equilibrium of a simple sII hydrate, are often formed with 2,2-dimethylbutane as a LMGS. The phase equilibrium conditions of the sH hydrate formed in methane, krypton or xenon + 2,2-dimethylbutane + water system have previously been reported [8–10]. The equilibrium pressures of these sH hydrates are 10–60% lower than those of the simple methane or xenon sI hydrate and simple Kr sII hydrate. Thus, we expected that the equilibrium pressure of the hydrate formed with argon + 2,2-dimethylbutane would be much lower than that of the simple argon hydrate. The solubility of 2,2-dimethylbutane in water is 8.23×10^{-6} and the solubility of water in 2,2-dimethylbutane is 1.53×10^{-4} at 273.1 K [11]. 2,2-dimethylbutane is not miscible with water and forms a separate phase as a liquid guest substance. In this paper, we demonstrate the formation of a sH hydrate with argon + 2,2-dimethylbutane with four-phase (L_W–H–V–L_g) equilibrium conditions and provide the first phase equilibrium data. The crystallographic structure of this hydrate was identified based on powder X-ray diffraction measurements.

2. Experimental setup and procedure

For the experiments presented in this study, the following chemicals were used: deionized and distilled water; pure argon gas (99.9999% certified purity – Taiyo Nippon Sanso, Co., Ltd., Japan); liquid reagent of 2,2-dimethylbutane (99.0% certified purity – Sigma–Aldrich). The deionized and distilled water was laboratory-made. The conductivity of the deionized and distilled water is lower than 300×10^{-4} s/m at 298 K. The purities and suppliers of the fluid samples are specified in Table 1.

The apparatus for the phase equilibrium measurements and preparing the crystal samples for the powder X-ray diffraction (PXRD) is schematically illustrated in Fig. 1. The test section for the four-phase equilibrium, water-rich liquid (L_W), hydrate (H), argon-rich vapor (V) and 2,2-dimethylbutane (L_g) was a stainless steel cylindrical vessel with the inner volume of 200 cm^3. A magnetically-driven impeller was inserted into the vessel to agitate the liquid phases in the test section. The temperature of the vessel (T) was controlled at a prescribed value using a PID-controlled heater (TM-1, As One Co., Ltd.) and a cooler placed in the bath. A platinum resistance thermistor was inserted into the vessel to measure the temperature in the test section. The pressure in the vessel (p) was measured by a strain-gauge pressure transducer (PHB-A-10MP, Kyowa Electric Co., Ltd.). The estimated uncertainty of the temperature measurements was ±0.1 K for $223 \le T \le 573$ K. The estimated uncertainty of the pressure measurements was ±0.005 MPa for $p \le 10.0$ MPa and for $233 \le T \le 423$ K.

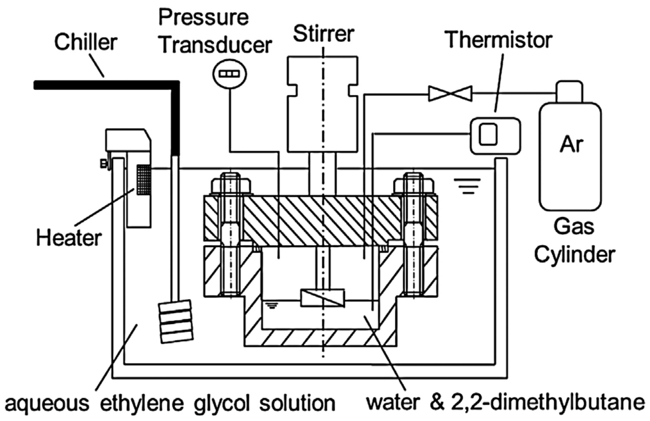

Fig. 1. Schematic of the experimental apparatus.

The present study follows the procedure described by Danesh et al. for measuring the equilibrium temperatures and pressures of the four phases [12]. The vessel was first charged with liquid water and 2,2-dimethylbutane. We used 35 cm^3 of liquid water and 15 cm^3 of 2,2-dimethylbutane to ensure the presence of the two liquid phases. The volume of 2,2-dimethylbutane is 3/7 of water. This amount of 2,2-dimethylbutane is more than twice the stoichiometric composition of the sH hydrate. In this system, the degree of freedom was determined to be 1 from the Gibbs phase rule. The vessel was then placed in the bath. Gaseous argon was supplied from a high-pressure cylinder through a pressure-regulating valve to the vessel after the air in the vessel was evacuated by a vacuum pump. The motor of the magnetically driven impeller was then turned on and the impeller continued to agitate the system through the experimental run at 300 rpm. After p and T were set at the prescribed values within the pressure and temperature range of 3–10 MPa and 278–290 K, respectively, T was decreased to form a hydrate. The hydrate formation in the vessel was detected by the decrease in p. The temperature T was then increased by steps of 0.1 K. At each temperature step, T was maintained until p did not change by 1 kPa within 12 h. By repetition of this incremental temperature increase, a p *versus* T plot diagram for each run was obtained and a four-phase equilibrium condition was determined from the diagram. When the hydrate was dissociated by increasing the temperature in the vessel, the pressure in the vessel increased. When all of the hydrate was completely dissociated, then the increase in the pressure became quite small because of the change in the phase equilibrium of the fluids remaining in the test section. This operation was repeated under different initial conditions to obtain the four-phase equilibrium data over the desired temperature–pressure range.

2.1. *Powder X-ray diffraction*

The hydrate crystal sample for the PXRD measurements was prepared with liquid water, argon gas, and 2,2-dimethylbutane using the same type of apparatus for the phase equilibrium measurements. The amount of water and 2,2-dimethylbutane for the sample is the same as for the equilibrium measurements. The temperature inside the vessel was maintained at 276 K. The pressure was set at 6.0 MPa to avoid forming the simple argon sII hydrate that may form at $p > 12.2$ MPa. Upon hydrate formation, when the pressure decreased to the equilibrium pressure of the sH hydrate formed with argon and 2,2-dimethylbutane, the vessel was recharged with argon gas to 6.0 MPa. This argon charging procedure was repeated until no further pressure reduction was observed. The inside of the vessel was continuously agitated at 300 rpm after the hydrate nucleation. Nearly complete conversion of the water to the hydrate was obtained when no further pressure reduction was observed. After the pressure stabilized, the vessel was subsequently removed from the temperature-controlled bath and immediately immersed in a liquid nitrogen bath. After the temperature in the vessel decreased below 220 K, the vessel was removed from the