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Phase Equilibrium for Structure H Hydrates Formed with Methane plus Cycloheptane, Cycloheptanone, or Oxacycloheptane

Takahiro Kozaki,[†] Tatsuhiko Taguchi,[†] Satoshi Takeya,[‡] and Ryo Ohmura*,[†]

Department of Mechanical Engineering, Keio University, Yokohama 223-8522, Japan, and National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

Pressure and temperature conditions for the four-phase equilibrium in systems that include liquid water, structure H hydrate, methane gas, and liquid hydrocarbon substances (cycloheptane, cycloheptanone, or oxacycloheptane) were measured over the temperature range (273.5 to 284.1) K. The measurements indicate that, at 274 K, the equilibrium pressures of the systems with cycloheptane, cycloheptanone, and oxacycloheptane were lower by (1.6, 1.3, and 1.5) MPa, respectively, than those of the structure I methane hydrates in equilibrium with liquid water and methane vapor. Powder X-ray diffraction measurements of the formed hydrate samples confirmed structure H hydrates.

1. Introduction

Clathrate hydrates are crystalline solid compounds consisting of a network of hydrogen-bonded 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 structure, such as structures I, II, and H.[1] Among the three hydrate structures, structure H hydrates are unique because they can only form with two different guest substances: one is a small molecule guest substance, such as methane and krypton (these can also form simple structure I or II hydrates), and the other is a relatively large molecule guest substance, such as methylcyclohexane and neohexane. The latter substance will be denoted as a large molecule guest substance (LMGS).

The phase equilibrium for hydrate-forming systems depends on the guest substances. For example, both methane and ethane form structure I hydrates, but the equilibrium pressures of pure methane and pure ethane hydrates at 273.2 K are (2.6 and 0.5) MPa, respectively. Structure H hydrates often form under thermodynamic conditions that are milder (i.e., lower equilibrium pressure at a given temperature) than those of structure I and II hydrates that form exclusively with small molecule guest substances.

Gas hydrates offer attractive characteristics for high-density gas-storage media. The amount of a guest gas stored in 1 m^3 of a hydrate may be over 160 m^3 at standard pressure and temperature. Specifically, hydrates may be utilized to store and transport natural gas and hydrogen. The crystallographic structure of a hydrate formed from natural gas may be structure I, II, or H, depending on the composition of the natural gas and the pressure−temperature conditions of the system. An LMGS may be added to the system of natural gas and water to ensure the formation of a structure H hydrate, thereby lowering the phase equilibrium conditions. Therefore, the measurement of the phase equilibrium conditions for structure H hydrates and the identification of an effective LMGS to reduce the hydrate equilibrium pressure without significantly reducing the natural gas storage capacity should contribute to the development of an efficient hydrate-based energy storage/transportation technology.[2–6]

A large number of phase equilibrium data have been reported for various LMGS's that form structure H hydrates together with methane. Among such LMGS's, 1,1-dimethylcyclohexane is the most effective LMGS, followed by 2,2,3,3-tetramethylbutane and 2,2,3-trimethylbutane, in reducing the equilibrium pressures of structure H hydrates.[7–14] Significant pressure reduction is also observed with cycloheptane. (The literature data are summarized in Figure S1 in Supporting Information.) Many studies have also considered derivatives of methylcyclohexane and methylbutane, such as ketones, alcohols, and ethers. On the other hand, only one set of phase equilibrium data of a structure H hydrate-forming system with cycloheptane is available, and no literature data exist on the derivatives of cycloheptane.

Equilibrium properties for favorable LMGS's to be utilized in the hydrate-based technology are obviously important, such as the equilibrium pressure and temperature for hydrate formation. Also of importance is the solubility of LMGS in liquid water because higher hydrate formation rates can be obtained with higher water solubility of LMGS's, as noted in previous studies.[4–6] Thus, in the present study, water-soluble derivatives of cycloheptane, cycloheptanone, and oxacycloheptane are selected and tested as potential effective LMGS's by measuring the phase equilibrium data of structure H hydrates. Powder X-ray diffraction (PXRD) measurements are also presented in the characterization of the hydrate structure.

2. Experimental Setup and Procedure

Fluid samples used in the measurements were distilled deionized liquid water, methane gas (0.9999 mass fraction basis certified purity from Takachiho Chemical, Japan), cycloheptane, cycloheptanone, and oxacycloheptane (all cyclo compounds were 0.98 mass fraction basis purity from Tokyo Kasei Industrial).

The apparatus for phase equilibrium measurements was the same as that employed in our previous study.[15] The test cell for the four-phase equilibrium, water-rich liquid (L_w) + hydrate

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* Corresponding author. E-mail: rohmura@mech.keio.ac.jp.
[†] Keio University.
[‡] National Institute of Advanced Industrial Science and Technology.

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(H) + methane-rich vapor (V) + LMGS (L_g) measurements was a stainless steel cylindrical vessel with inner dimensions of 50 mm in diameter and 120 mm in height. In the vessel, a magnetic stirrer provided agitation to the fluid at 400 rpm. Two platinum resistance thermometers were inserted into the vessel to measure the gas and liquid temperatures. The pressure in the vessel (*P*) was measured with a strain-gauge pressure transducer (model PHB-A-5MP Kyowa Electric, Japan). The vessel was immersed in a bath filled with aqueous ethylene glycol solution. The temperature of the vessel (*T*) was controlled at a prescribed value by the use of a proportional−integral−derivative controlled heater and cooler set in the bath. The estimated uncertainty of the temperature measurements was ± 0.1 K, and that of the pressure measurements was ± 0.015 MPa.

The four-phase equilibrium conditions were measured by a batch isochoric procedure described by Danesh et al.[16] We started each run by placing 30 g of water and 5 g of LMGS in the vessel, which was then immersed in the bath. Methane gas was supplied from a high-pressure cylinder through the pressure-regulating valve after the air in the vessel was evacuated by a vacuum pump. After *P* and *T* were set at prescribed values in the range of (1.388 to 5.0) MPa and (273.5 to 284.1) K, respectively, *T* was decreased to form hydrates. When the hydrate formation in the vessel was detected by a *P* decrease and *T* increase, the temperature of the bath was held constant. After a steady state was achieved in the vessel, the pressure was recorded. *T* was then incrementally increased in steps of 0.1 K. At each temperature step, *T* was maintained for 10 h until *P* stabilized. By repetition of this incremental temperature increase, a *P* versus *T* plot for each run was obtained and the four-phase equilibrium condition determined from the diagram.

When the hydrate was dissociated by increasing the temperature in the vessel, the pressure increased to the equilibrium state. If all of the hydrate was entirely dissociated by incrementing the temperature, then the increase in the pressure was significantly changed, as the pressure increased only from the fluid expansion in the vessel. Consequently, the intersection in the changes of slope in the *P*−*T* trace was identified as the four-phase equilibrium point. This operation was repeated at different initial conditions to obtain the four-phase equilibrium data over the desired temperature−pressure range.

Powder X-ray Diffraction. Hydrate crystal samples for the PXRD measurements were prepared with liquid water, methane gas, and liquid LMGS using the hydrate-forming apparatus.[17,18] The amount of liquid samples were the same as those for the phase equilibrium measurements. The pressure and temperature were set at 2.5 MPa and 273.6 K, respectively, slightly below the conditions for the simple methane hydrate formation.

Upon hydrate formation and reduced pressure in the system, the line connecting the test cell and the high-pressure methane cylinder was opened to keep the pressure constant. Agitation in the vessel was continuous at 400 rpm after hydrate nucleation. This procedure was continued until no further pressure reduction was observed. At that point, the vessel was subsequently removed from the temperature-controlled bath and immediately immersed in a liquid nitrogen bath. After *T* decreased below 160 K, the vessel was removed from the liquid nitrogen pool and quickly disassembled at room temperature before the temperature of the hydrate sample increased to 170 K. Then, the lower part of the vessel containing the hydrate sample was again placed in a liquid nitrogen pool, and hydrate samples were taken out of the vessel. Each prepared sample was stored in a container that was kept below 90 K to be later subjected to PXRD measurements.

Table 1. Four-Phase (L_w + H + L_g + V) Equilibrium Pressure of Structure H Hydrate-Forming System with Water + Methane + LMGS

	T/K	*P*/MPa	*T*/K	*P*/MPa
cycloheptane	273.8	1.388	279.0	2.590
	274.1	1.434	280.7	3.198
	275.3	1.659	282.5	4.015
	276.9	2.010	284.1	4.903
cycloheptanone	273.5	1.463	278.9	2.779
	274.4	1.612	280.4	3.260
	275.7	1.885	282.4	4.152
	276.9	2.171	283.6	4.782
oxacycloheptane	273.6	1.424	278.9	2.684
	274.6	1.612	280.6	3.306
	276.1	1.926	282.4	4.062
	277.4	2.238	283.5	4.692

For the PXRD measurements, the hydrate samples were finely powdered in a liquid nitrogen atmosphere at a temperature below 100 K. The fine-powdered hydrate samples were top-loaded on a Cu-specimen holder. The PXRD measurements were done using Cu Kα radiation by parallel beam optics (40 kV, 40 mA; Rigaku model Ultima III) in the $\theta/2\theta$ step scan mode with a step width of 0.02° at 93 K. The unit cell parameters were determined by a full-pattern fitting method using the RIETAN-2000 program.[19]

3. Results and Discussion

The four-phase (L_w + H + L_g + V) equilibrium data obtained in the system water + methane + LMGS (cycloheptane, cycloheptanone, or oxacycloheptane) are tabulated in Table 1 and plotted in Figure 1. The equilibrium data of the simple methane hydrate (water + methane) is also shown in Figure 1. At 274 K, the equilibrium pressure of the systems with cycloheptane, cycloheptanone, and oxacycloheptane are lower by (1.6, 1.3, and 1.5) MPa, respectively, than those of the structure I methane hydrate. The data in the water + methane + cycloheptane system measured by Thomas and Behar[14] is also included in Figure 3. The difference between our data and the data measured by Thomas and Behar is approximately 0.3 MPa and 0.4 K. It is unclear if the data by Thomas and Behar and the present study agree within experimental error because the uncertainty of the measurements by Thomas and Behar was not clearly stated. The equilibrium pressure in the water + methane + cycloheptane system is the lowest among the three LMGS's tested in the present study.

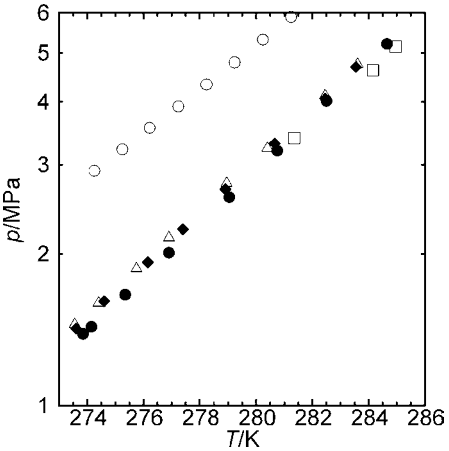

Figure 1. *P*−*T* diagram with the data in this work and prior works. ●, four-phase (L_w−H−L_g−V) equilibrium conditions in the system of water + methane + cycloheptane; △, cycloheptanone; ◆, oxacycloheptane; ○, ref 10; □, ref 14.

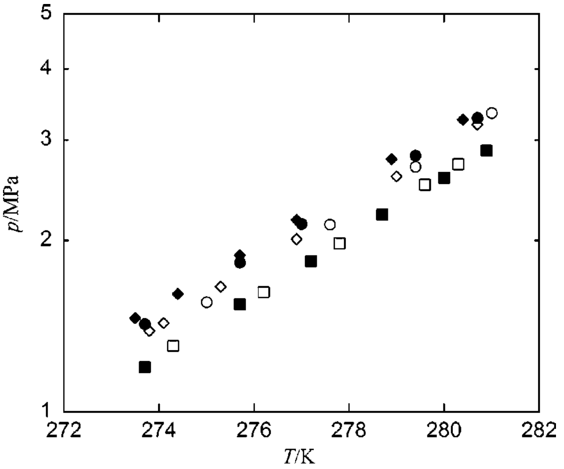

Figure 2. Equilibrium conditions of structure H hydrate-forming systems. Equilibrium data for LMGS's with or without a carbonyl group plotted for comparison. ○, methylcyclohexane; ●, methylcyclohexanone; □, neohexane; ■, pinacolone; ◇, cycloheptane; ◆, cycloheptanone.

The crystallographic structure of the hydrates in the three systems measured in the present study was identified by PXRD measurements. (The PXRD patterns are shown in Figure S2 in Supporting Information.) On the basis of the PXRD measurements, all hydrate samples were identified to be structure H. The lattice constants of cycloheptane hydrate were determined to be $a = 1.220$ nm and $c = 0.996$ nm, for cycloheptanone $a = 1.219$ nm and $c = 0.996$ nm, and for oxacycloheptane hydrate $a = 1.218$ nm and $c = 0.998$ nm.

The solubilities (mole fraction) of cycloheptane and cycloheptanone in water are reported to be $5.5 \cdot 10^{-6}$ at 298.3 K and $5.9 \cdot 10^{-3}$ at 293.0 K, respectively.[20,21] The solubility of oxacycloheptane is unavailable. The solubility of cycloheptanone is 3 orders of magnitude greater than that of cycloheptane. Generally, the chemical potential of water in an aqueous phase is decreased when LMGS's dissolve in water. The difference between the phase equilibrium pressures of the cycloheptane system and that of the cyclohepanone system is about 0.2 MPa, at a given temperature. This difference of the phase equilibria in the cycloheptane and cycloheptanone systems is at least, in part, ascribed to the decrease in the water chemical potential in the aqueous phase due to the dissolution of the LMGS's.

The phase equilibrium conditions of structure H hydrate-forming systems with water + methane + LMGS's reported in the literature and in this work are summarized in terms of functional groups in LMGS's. Ohmura et al.[12] reported the phase equilibrium of structure H hydrate systems with LMGS's having carbonyl groups. Figure 2 shows the equilibrium conditions of LMGS's with or without carbonyl groups. These data indicate that phase equilibrium conditions in the systems with LMGS's each having carbonyl groups are at lower temperatures and higher pressures than those in the systems with LMGS's analogues without the carbonyl groups. On the other hand, as shown in Figure 3 for ether substitute cyclic compounds, the ether analogues do not follow the same trend as the carbonyl-substituted compounds, that is, the phase equilibrium condition is observed to be either higher (oxacycloheptane) or lower (3-methyltetrahydropyran) than their respective hydrocarbon (cycloheptane and methycyclohexane). Measurements for other substituted compounds are needed to better define a trend in the phase equilibrium boundary based on the functional groups in the LMGS's.

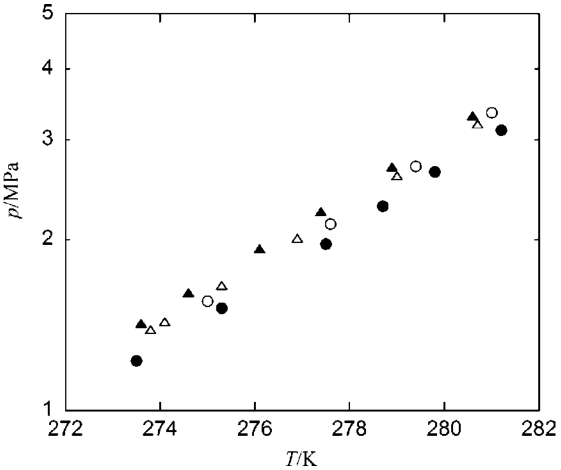

Figure 3. Equilibrium conditions of structure H hydrate-forming systems. Equilibrium data for LMGS's with or without an ether group plotted for comparison. ○, methylcyclohexane; ●, 3-methyltetrahydropyran; △, cycloheptane; ▲, oxacycloheptane.

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Supporting Information Available:

Equilibrium data in literature for structure H hydrate systems with methane (Figure S1) and powder X-ray diffraction patterns (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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