Phase Equilibrium for Clathrate Hydrates Formed with Methane + Ethane + Propane Mixtures at Temperatures below the Freezing Point of Water

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This paper reports the three-phase (ice + hydrate + guest-rich vapor) equilibrium pressure−temperature conditions at temperatures (243 to 272) K in the systems of water and each of the following two ternary gas mixtures of methane, ethane, and propane: 90:7:3 molar ratio and 99.48:0.5:0.02 molar ratio. The former is a simulated natural gas (natural-gas composition). The latter has a methane-rich composition that is equal to that of the vapor phase in equilibrium with the clathrate hydrate that has the guest composition of 90:7:3 molar ratio. The pressure ranges of the present measurements in the two systems are (0.233 to 0.711) MPa in the natural-gas-composition gas mixture system and (0.939 to 2.070) MPa in the methane-rich-composition gas mixture system. The measurements were carried out using the batch, isochoric procedure. The measured data were compared with the corresponding predictions using phase equilibrium calculation programs.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bonded water molecules (host molecules) forming cages that enclose the molecules of substances other than water (guest molecules). Hydrocarbons and noble gases are the typical guest substances that form clathrate hydrates with water. A high gas storage capacity, large heat of formation/decomposition, and guest selectivity are the major characteristics of clathrate hydrates. Thus, novel technologies utilizing clathrate hydrates, such as natural gas[1] and hydrogen[2] transportation/storage, heat pump/refrigeration systems,[3] and separation/purification,[4,5] etc., have been proposed. Every clathrate hydrate is thermodynamically stable only at pressures higher than the water + hydrate + gas equilibrium pressure at a given temperature or at temperatures lower than the water + hydrate + gas equilibrium temperature at a given pressure. Therefore, the equilibrium pressure−temperature condition is one of the most important properties for the development of clathrate hydrate-based technologies.

The three-phase equilibrium for clathrate hydrates at temperatures below the freezing point of water (ice (I) + hydrate (H) + guest-rich vapor (V)) is important as related to the idea of transportation/storage of natural gas in the state of clathrate hydrates. The equilibrium pressures at temperatures below the freezing point of water are generally lower than that at temperatures above the freezing point of water, and clathrate hydrates have a “self-preservation effect”[6] at temperatures below the freezing point of water. The self-preservation is the apparent, long-term preservation of hydrate crystals under atmospheric pressure, which is lower than the equilibrium pressure for the hydrate. The technology for the transportation/storage of natural gas in the state of clathrate hydrates at temperatures below the freezing point of water, especially about 253 K, has been developed.[7] For realizing this technology, the accurate three-phase equilibrium conditions at temperatures below the freezing point of water are essential.

If a guest substance is a gas mixture, such as natural gas, the phase equilibrium conditions will depend on the gas compositions. Thus, if we use gas mixtures as guest substances, it will be essential that we know the phase equilibrium conditions corresponding to the gas compositions. On the other hand, if a guest substance is a gas mixture, the vapor-phase composition will not coincide with the guest composition in the hydrate as a result of the preferential uptake of some species from the gas phase into the hydrate. For example, if the guest substance is a methane + ethane + propane gas mixture, propane will selectively occupy the hydrate cavity.[8] Thus, during hydrate formation from a gas mixture in the batch reactor, the vapor-phase and hydrate-phase compositions should continuously change.[9]

For the process design of the continuous production of hydrates from a natural gas, it is important to consider the following two compositions of the gas mixtures. One is the natural-gas composition, that is, the initial vapor-phase composition of the natural gas hydrate formation. The other one is the vapor-phase composition when the clathrate hydrate formation steadily and continuously occurs. In the case of the steady, continuous hydrate formation, the composition of the guests in the produced hydrate should be equal to the feed gas composition. At this time, the composition of the vapor phase in equilibrium with the produced hydrate is different from that of the feed gas and changes into a methane-rich composition because of the preferential uptake of the ethane and propane into the hydrates.[1,9] Therefore, it is important to comprehend the hydrate equilibrium conditions corresponding to these two vapor-phase compositions.

Several studies of the hydrate phase equilibrium conditions for the systems of water + natural gas have already been reported and compiled and reviewed by Sloan and Koh.[10] However, all of these data involved the equilibrium conditions at temperatures above the freezing point of water. No three-phase equilibrium data are available in the mixed gas system at temperatures below the freezing point of water. Calculation/prediction of the phase equilibrium conditions in the systems of water + gas mixture below the freezing point of water using

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Table 1. Composition of the Gas Mixtures

gas mixture	methane	mole fraction of ethane	mole fraction of propane
natural-gas-composition gas mixture	balance	$7.06 \cdot 10^{-2}$	$2.988 \cdot 10^{-2}$
methane-rich-composition gas mixture	balance	$5.07 \cdot 10^{-3}$	$2.03 \cdot 10^{-4}$

the statistical-thermodynamics modeling programs[11−13] is possible, but for a more accurate calculation/prediction, experimental measurements are essential. Therefore, measurements of the systems of gas mixtures at temperatures below the freezing point of water are required.

In this paper, we report the phase equilibrium data for clathrate hydrates formed with two methane + ethane + propane mixtures at temperatures below the freezing point of water. One is a simulated natural gas (natural-gas composition). The other one has a methane-rich composition that is equal to that of the vapor phase in equilibrium with the clathrate hydrate that has the guest composition of a 90:7:3 molar ratio. The determination of the methane-rich composition gas mixture was accomplished by the repetition of (1) assuming the gas mixture composition and (2) substituting these values into statistical-thermodynamics modeling programs[11−13] to predict the hydrate−guest composition, until the predicted hydrate−guest composition agrees with the natural-gas composition gas mixture.

Experimental Section

Materials. The fluid samples used in the experiments were liquid water that was deionized and distilled, and the two ternary gas mixtures of methane, ethane, and propane were from Sumitomo Seika Chemical Co., Ltd., Tokyo. The compositions of the mixtures are listed in Table 1. The deionized and distilled liquid water was made in the laboratory. Ice was formed in a refrigerator from the liquid water.

Apparatus. The main part of the apparatus is the same as that employed in our previous study[14,15] (a stainless steel vessel with a 200 cm^3 inner volume). This vessel is equipped with a magnetic stirrer through its lid to agitate the fluids, ice, and hydrate crystals inside the vessel. The vessel is immersed in a temperature-controlled bath to maintain the temperature inside the vessel, T, at the prescribed level. Two platinum resistance thermometers were inserted into the vessel to measure the temperatures in the upper and lower sections of the vessel. The pressure in the vessel, p, is measured by a strain-gauge pressure transducer (model PHB-A-1MP-F, Kyowa Electric Co., Ltd.; model PHB-A-2MP-F, Kyowa Electric Co., Ltd.) depending on the pressure range. The estimated uncertainty of the temperature measurements was ± 0.1 K. The uncertainty of the pressure measurements was ± 3 kPa for $p < 1.1$ MPa and ± 5 kPa for $p > 1.1$ MPa. The reliability of the measurements using this setup was previously confirmed.[14,15] The vapor-phase composition was measured by a gas chromatograph (model Micro GC 3000A, Agilent Technology Co., Ltd.).

Procedure. The equilibrium conditions were measured using the batch, isochoric procedure, as described by Danesh et al.[16] Each experimental run was begun by charging the vessel with 30 g of a fine-grained ice powder with diameters of (1 to 2) mm. The ice powder was prepared using a pestle and a mortar at a temperature around 220 K. To prevent the charged ice from melting, the vessel was initially cooled to about 263 K in the bath. The vessel containing the ice was then immersed in the temperature-controlled bath. The gas mixture was supplied from a high-pressure cylinder through a pressure-regulating valve into the evacuated vessel until the pressure inside the vessel, p, had increased to the prescribed level. After T and p had stabilized, the in-line valve was closed. T was then decreased to form the hydrate. If the hydrate formation in the vessel was detected by a decrease in p and an increase in T, the temperature of the bath was maintained constant for 8 h, thereby keeping T constant. We then incrementally increased T in steps of 0.2 K. At every temperature step, T was kept constant for (8 to 24) h to achieve a steady equilibrium state in the vessel. In this way, we obtained a $p-T$ diagram for each experimental run, from which we determined the three-phase equilibrium point. If T was increased in the presence of a hydrate, the hydrate partially dissociated, thereby substantially increasing p. After the complete decomposition of the hydrate, only a lower increase in pressure is observed due to the change in the phase equilibria of the solids/fluids in the vessel. Consequently, the point at which the slope of the $p-T$ data plots sharply changes was considered to be the point at which all the hydrate crystals dissociate and, hence, was the three-phase equilibrium point. This operation was repeated under several different initial conditions to obtain the three-phase equilibrium data over the specified temperature range.

Table 2. I + H + V Three-Phase Equilibrium $p-T$ Conditions in a Natural-Gas-Composition Gas Mixture + Water System

T/K	p/MPa	methane	mole fraction of ethane[a]	mole fraction of propane[a]
247.5	0.233	Balance	$6.98 \cdot 10^{-2}$	$2.93 \cdot 10^{-2}$
249.1	0.256	Balance	$6.83 \cdot 10^{-2}$	$2.87 \cdot 10^{-2}$
251.1	0.285	Balance	$7.24 \cdot 10^{-2}$	$3.06 \cdot 10^{-2}$
253.4	0.319	Balance	$6.99 \cdot 10^{-2}$	$2.94 \cdot 10^{-2}$
255.7	0.360	Balance	$7.21 \cdot 10^{-2}$	$3.02 \cdot 10^{-2}$
259.2	0.424	Balance	$7.08 \cdot 10^{-2}$	$2.72 \cdot 10^{-2}$
262.4	0.487	Balance	$7.23 \cdot 10^{-2}$	$3.03 \cdot 10^{-2}$
265.7	0.556	Balance	$7.26 \cdot 10^{-2}$	$3.05 \cdot 10^{-2}$
268.4	0.627	Balance	$7.09 \cdot 10^{-2}$	$2.97 \cdot 10^{-2}$
271.0	0.711	Balance	$7.22 \cdot 10^{-2}$	$3.04 \cdot 10^{-2}$

[a] The final compositions measured by gas chromatography after the hydrate formation/decomposition. Initial mole fractions of ethane and propane are $7.02 \cdot 10^{-2}$ and $2.988 \cdot 10^{-2}$, respectively.

In our previous study[15] on the I + H + V three-phase equilibrium measurements for the systems of water and each of the following guest gases, methane, ethane, propane, or carbon dioxide, in all of the experimental runs for the measurements of the three-phase equilibrium conditions, the pressure did not recover to the initial level after the hydrate formation and decomposition although the temperature did recover to the initial level. This was ascribed to the so-called self-preservation effect. The same phenomenon was observed in the present study. Thus, in the present study, the duration for each temperature step was less than 24 h, similar to the previous study.[15] After the formation/decomposition of the clathrate hydrate, the vapor phase was sampled using an evacuated external cylinder. The composition of the sample was determined by gas chromatography.

Results and Discussion

The $p-T$ data of the I + H + V three-phase equilibrium in the systems containing the natural-gas-composition gas mixture and methane-rich-composition gas mixture are listed in Tables 2 and 3. The data obtained in Tables 2 and 3 are plotted in Figures 1 and 2, respectively.

The final compositions of the ethane and propane measured by the gas chromatograph after the hydrate formation/decomposition in the test vessel are also listed in Tables 2 and 3. As indicated in Tables 2 and 3, in both the systems of water + natural-gas-composition gas mixture and methane-rich-

Table 3. I + H + V Three-Phase Equilibrium *p*−*T* Conditions in a Methane-Rich-Composition Gas Mixture + Water System

T/K	*p*/MPa	methane	mole fraction of ethane[a]	mole fraction of propane[a]
243.7	0.939	Balance	$4.2 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$
244.8	0.979	Balance	$3.5 \cdot 10^{-3}$	$0.8 \cdot 10^{-4}$
248.2	1.094	Balance	$4.4 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$
250.7	1.207	Balance	$4.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$
254.3	1.363	Balance	$5.1 \cdot 10^{-3}$	$2.1 \cdot 10^{-4}$
256.1	1.455	Balance	$4.4 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$
258.7	1.580	Balance	$5.0 \cdot 10^{-3}$	$2.1 \cdot 10^{-4}$
262.0	1.760	Balance	$5.3 \cdot 10^{-3}$	$2.0 \cdot 10^{-4}$
264.0	1.881	Balance	$6.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-4}$
266.9	2.070	Balance	$4.9 \cdot 10^{-3}$	$1.6 \cdot 10^{-4}$

[a] The final compositions measured by gas chromatography after the hydrate formation/decomposition. Initial mole fractions of ethane and propane are $5.07 \cdot 10^{-3}$ and $2.07 \cdot 10^{-4}$, respectively.

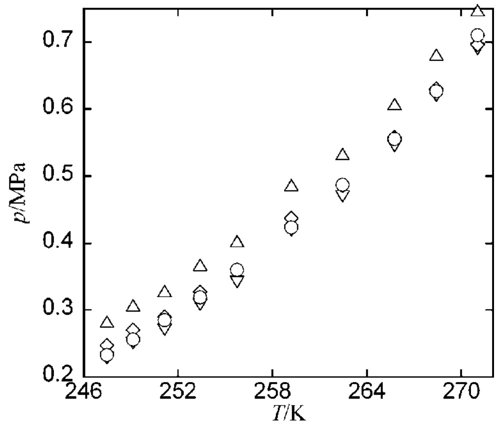

Figure 1. I + H + V three-phase equilibrium *p*−*T* conditions in a natural-gas-composition gas mixture + water system. ○, experimental data obtained in the present study; Δ, prediction by CSMHYD;[11] ▽, prediction by CSMGem;[12,17−20] ◇, prediction by HWHYD.[13]

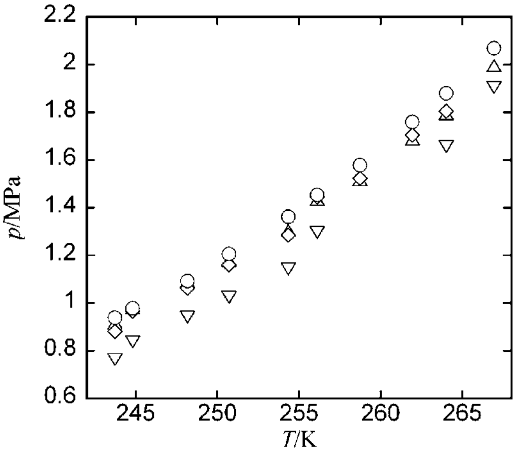

Figure 2. I + H + V three-phase equilibrium *p*−*T* conditions in a methane-rich-composition gas mixture + water system. ○, experimental data obtained in the present study; Δ, prediction by CSMHYD;[11] ▽, prediction by CSMGem;[12,17−20] ◇, prediction by HWHYD.[13]

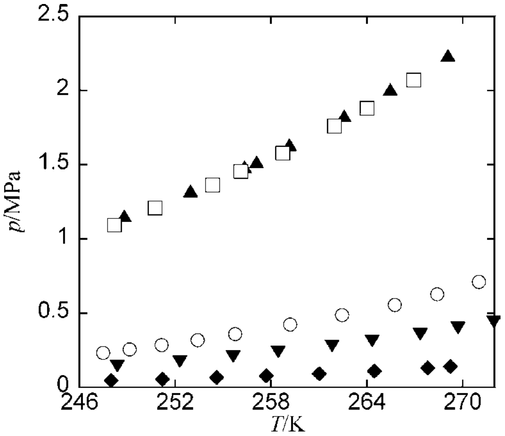

Figure 3. I + H + V three-phase equilibrium *p*−*T* conditions in the systems of water and each of the following guest gases: ○, natural-gas-composition gas mixture; □, methane-rich-composition gas mixture; ▲, methane; ▼,[15] ethane; and ◆,[15] propane.[15]

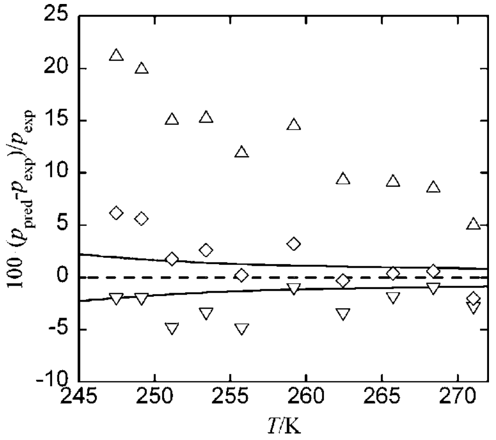

Figure 4. Deviations in the predicted/calculated equilibrium pressure of the phase equilibrium calculation programs in the natural-gas-composition gas mixture system from the experimental data in the present study. Δ, CSMHYD;[11] ▽, CSMGem;[12,17−20] ◇, HWHYD;[13] solid line, the uncertainty of the present measurement.

composition gas mixture, the composition after the formation/decomposition of the clathrate hydrate is not identical to the initial composition in all of the experimental runs. The reason for this difference may be explained as follows. When clathrate hydrates are formed, the vapor-phase composition is not identical to the initial gas composition. In the present study, some portion of the clathrate hydrate remained due to the self-preservation effect as described in the Experimental Section. Thus, the final vapor-phase composition after the formation/decomposition of the clathrate hydrate is not identical to the initial gas composition. Therefore, the *p*−*T* data indicated in Tables 2 and 3 are the three-phase equilibrium conditions corresponding to the respective final vapor-phase composition measured after the hydrate formation/decomposition.

Figure 3 shows a summary of the I + H + V three-phase equilibrium conditions for the systems of water and each of the following guest gases: natural-gas-composition gas mixture, methane-rich-composition gas mixture, methane,[15] ethane,[15] or propane.[15] As indicated in Figure 3, for each of the natural-gas-composition gas mixture and the methane-rich-composition gas mixture, the equilibrium pressures are lower than those of the methane system (that is, these hydrates are more stable than the methane hydrate) and higher than those of the ethane and propane systems (that is, these hydrates are unstable when compared to the ethane and propane hydrates). The equilibrium conditions in the methane-rich-composition gas mixture and the pure methane overlap within the mutual uncertainty of the measurements. However, all of the equilibrium pressures in the system of the methane-rich-composition gas mixture are systematically lower than those of the pure methane system. Figure 3 also indicates that the phase equilibrium conditions in the gas mixtures strongly depend on the gas compositions.

Figures 4 and 5 compare the phase equilibrium data obtained in the present study with the predictions for each of the following

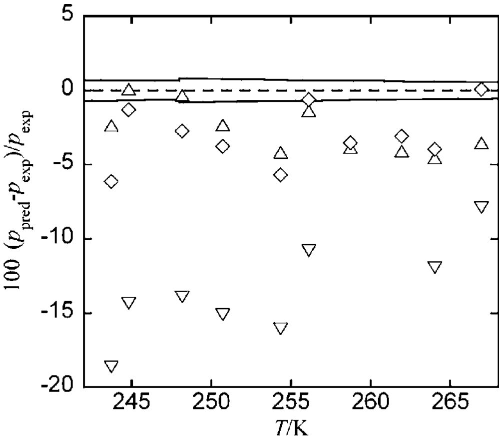

Figure 5. Deviations in the predicted/calculated equilibrium pressure of the phase equilibrium calculation programs in the methane-rich-composition gas mixture from the experimental data in the present study. Δ, CSMHYD;[11] $\triangledown$, CSMGem;[12,17−20] $\diamond$, HWHYD;[13] solid line, the uncertainty of the present measurement.

three phase equilibrium calculation programs: CSMHYD,[11] CSMGem,[12,17−20] and HWHYD.[13] The predicted/calculated equilibrium pressure values indicated in Figures 1, 2, 4, and 5 correspond to the respective final vapor-phase composition and the equilibrium temperature obtained in the present study. Figures 4 and 5 indicate the deviations in the predictions by the phase equilibrium calculation programs from the experimental data obtained in the present study. The definitions of the deviations are $100 \cdot (p_{\mathrm{pred}} - p_{\mathrm{exp}})/p_{\mathrm{exp}}$, where p_{exp} is the experimental equilibrium pressure obtained in this study and p_{pred} is the predicted/calculated equilibrium pressure from the phase equilibrium calculation programs. The uncertainty of the measurements is also indicated in these figures. If the predictions were plotted within the uncertainty of the present measurements, the predictions are consistent with the experimental data obtained in the present study within the uncertainty of the measurements. Figures 1 and 4 indicate that the predictions for the natural-gas-composition gas mixture using the CSMHYD[11] are not consistent with the experimental data obtained in the present study, especially at $T < 260$ K. Also, the predictions from the CSMGem[12,17−20] and HWHYD[13] are not always consistent with the experimental data obtained in the present study. Figures 2 and 5 indicate that the predictions by CSMGem[12,17−20] are not consistent with the data obtained in the present study for the methane-rich-composition gas mixture. The predictions by CSMHYD[11] and HWHYD[13] are somewhat consistent with the experimental data obtained in the present study.

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