Gas Hydrate Formation for Mixtures of Methane + Helium and Ethane + Helium

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Equilibrium conditions of gas hydrates formed from methane + helium and ethane + helium mixtures are experimentally determined. As the helium concentration in gas mixtures increases, the equilibrium conditions shift to lower temperatures and higher pressures. The experimental data agree with the calculated values from model prediction having the assumption that helium molecules in a hydrate lattice do not contribute to the hydrate stability of gas mixtures. It is suggested that helium rarely contributes to the stability of the gas hydrate at experimental pressures < 10 MPa.

Introduction

Helium is important in the field of superconductivity technology and the thermonuclear industry. Helium is normally produced from natural gases containing hydrocarbons such as methane and ethane by liquefaction. Recently, the feasibility of separating hydrogen from natural gas by hydrate formation has been investigated.[1,2] Gas hydrates are crystalline compounds composed of water and gases in which gas molecules occupy the cavities in a three-dimensional framework consisting of water molecules. While hydrocarbons such as methane and ethane can form gas hydrates, hydrogen normally cannot form hydrogen hydrates because its molecular size is too small to contribute to the hydrate lattice stability except under specific conditions at very high pressure.[3] For the same reason as that for the case of hydrogen, helium normally cannot form helium hydrates. There are no experimental data on gas hydrate equilibria formed from gas mixtures containing helium. In this work, the equilibrium conditions of gas hydrates from mixtures of methane + helium or ethane + helium are experimentally determined to investigate how much pressure is needed to form gas hydrates of a helium-containing gas mixture.

Experimental Section

In this work, equilibrium conditions of gas hydrates formed from helium-containing gas mixtures were determined using two experimental methods: an isochoric method with optical detection and an isothermal method. The schematic diagram of the experimental apparatus having two hydrate cells is shown in Figure 1.

Isochoric Method. The hydrate cell used with the isochoric method is essentially the same as that used by Maekawa and Imai[4] and Maekawa.[5] The hydrate cell has a volume of about 500 mL. Glycol−water coolant whose temperature is controlled by a heater and refrigerator is continuously circulated around the cell. The temperature and pressure inside the cell are measured with two platinum resistance thermometers and a pressure gauge with a semiconductor transducer, respectively. The accuracies of temperature and pressure are ±0.2 K and ±0.05 MPa, respectively. A magnetic stirrer on the bottom of the cell agitates the water. Two glass windows are located on the upper and lower sides for visual observation and optical detection of gas hydrate formation and dissociation.

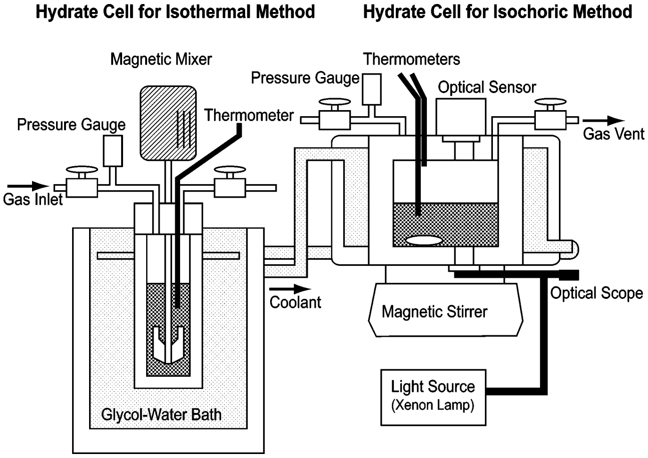

Figure 1. Schematic diagram of the experimental apparatus used in this work.

The optical detection unit, which was used to observe the formation and dissociation of gas hydrate, consists of a light source with a xenon lamp, an optical sensor, and an optical power meter. The light beam from the lamp is introduced into the water through the window on the bottom of the cell. The optical sensor on the upper side measures the intensity of the light penetrating the water. When gas hydrate forms in the cell, the light is scattered by gas hydrate crystals, resulting in a decrease of the light intensity. On the other hand, when gas hydrate dissociates, an increase of the light intensity is observed. Therefore, we can detect the formation and dissociation of gas hydrate inside the cell by measuring the change of light intensity.

One hundred milliliters of distilled water was added into the hydrate cell. After the cell was evacuated, pressurized gas (methane or ethane) was supplied to the cell. Afterward, helium was supplied. The gas mixture in the cell was sampled for the analysis of gas composition. The formation

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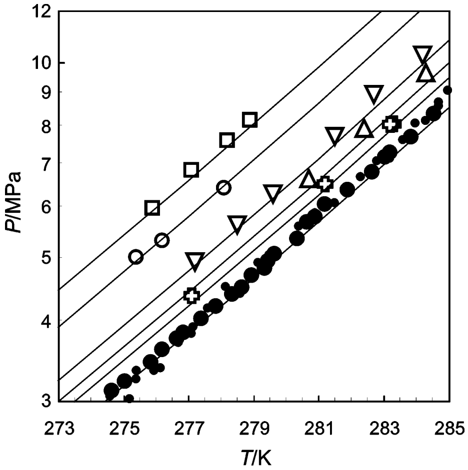

Figure 2. Equilibrium conditions of gas hydrates from methane (1) + helium (2) determined by the isochoric method: ●, pure CH_4; ✙, CH_4 + He ($x_1 = 0.921$); △, CH_4 + He ($x_1 = 0.882$); ▽, CH_4 + He ($x_1 = 0.823$); ○, CH_4 + He ($x_1 = 0.687$); □, CH_4 + He ($x_1 = 0.606$); •, pure CH_4 (compiled by Sloan[10]).

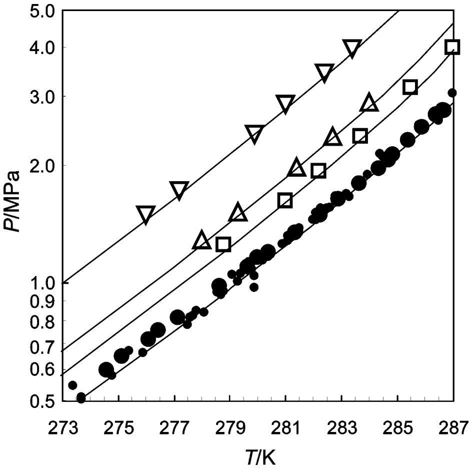

Figure 3. Equilibrium conditions of gas hydrates from ethane (1) + helium (2) determined by the isochoric method: ●, pure C_2H_6; □, C_2H_6 + He ($x_1 = 0.800$); △, C_2H_6 + He ($x_1 = 0.699$); ▽, C_2H_6 + He ($x_1 = 0.473$); •, pure C_2H_6 (compiled by Sloan[10]).

Table 1. Equilibrium Conditions of Gas Hydrates Determined by the Isochoric Method

Methane (1) + Helium (2)			Ethane (1) + Helium (2)		
x_1	T/K	P/MPa	x_1	T/K	P/MPa
0.921	277.1	4.36	0.800	278.8	1.25
	281.2	6.49		281.0	1.62
	283.2	8.02		282.2	1.93
	283.3	8.04		283.7	2.37
0.882	280.7	6.61		285.5	3.16
	282.4	7.91		287.0	4.00
	284.3	9.64	0.699	278.0	1.29
0.823	277.2	4.92		279.3	1.52
	278.5	5.61		281.4	1.98
	279.6	6.26		282.7	2.37
	281.5	7.68		284.0	2.90
	282.7	8.92	0.473	276.0	1.49
	284.2	10.25		277.2	1.72
0.687	275.4	5.00		279.9	2.40
	276.2	5.30		281.0	2.86
	278.1	6.39		282.4	3.44
0.606	275.9	5.95		283.4	3.97
	277.1	6.81			
	278.2	7.57			
	278.9	8.14			

and dissociation of gas hydrate was regulated by changing the temperature inside the hydrate cell. As the temperature was lowered to form gas hydrate, the light intensity detected by the optical sensor sharply decreased when the gas hydrate formed. After gas hydrate formation, the temperature was continuously raised at a rate of 0.25 K per hour. During the heating, the light intensity changed again and recovered the original light intensity when gas hydrate dissociated. The equilibrium condition was determined by measuring the pressure and temperature of gas hydrate dissociation.

Isothermal Method. The other hydrate cell used in the isothermal method is immersed in a glycol−water bath in which temperature is controlled by a heater and refrigerator. This high-pressure stainless steel cell has a volume of about 200 mL. A platinum resistance thermometer and pressure gauge with a semiconductor transducer are connected to the cell to measure the temperature and pressure inside the cell. The accuracies of pressure and temperature are ±0.2 K and ±0.02 MPa, respectively. A magnetic stirring mixer agitates the water in the cell for accelerating the gas hydrate formation.

After 100 mL of water was added into the cell, the cell was placed in a glycol−water bath. Pressurized methane or ethane was supplied from a gas cylinder before helium was supplied. After the temperature was lowered to 273.6 K, gas hydrate formation was induced by increasing the stirring rate of the magnetic mixer. Gas hydrate was formed at a constant temperature with the gas pressure decrease. Gas hydrate continued to form until the gas pressure reached a steady value. The equilibrium pressure in the gas mixture was determined by measuring the pressure at the steady state. At equilibrium, the gas mixture was sampled through the outlet and subjected to the analysis of the gas composition.

Gas Analysis. The gas mixtures used in these experiments were analyzed by two Shimadzu GC-8AIT gas chromatographs. Helium concentration was measured with a MolecularSieve-5A column in an argon carrier, and the concentrations of methane and ethane were measured with a silica gel column in a helium carrier. The accuracy of gas fractions is ±0.005.

Modeling

To evaluate the experimental data, the thermodynamic model based on the clathrate model by van der Waals and Platteeuw[6] was used to predict the equilibrium conditions of gas hydrates from gas mixtures containing helium. According to their model, the phenomenon that gas molecules occupy the cavities of a hydrate lattice can be described as adsorption on a hypothetical empty hydrate lattice. Kihara parameters are normally used for calculating the intermolecular forces between gas and water in a hydrate lattice. In this work, fugacities of gases are calculated using the Soave−Redlich−Kwong equation of state[7] and the binary interaction parameters of methane + helium or ethane + helium mixtures proposed by Schulze.[8] The thermodynamic properties of a hypothetical empty hydrate and the Kihara parameters of methane and ethane proposed by Ballard and Sloan[9] were used in this work. The model assumes that helium does not contribute to the stability of these hydrates. The discrepancies between the experimental and calculated results are evaluated by the following equation

$$\text{AAD} = \frac{1}{N}\sum \frac{|P_{\text{exp}} - P_{\text{calc}}|}{P_{\text{exp}}}$$

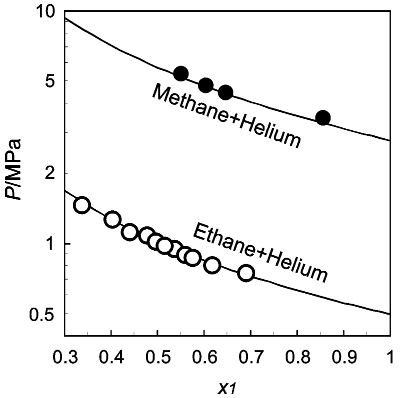

Figure 4. Equilibrium pressures of the gas hydrates from gas mixtures of methane (1) or ethane (1) + helium (2) at a temperature of 273.6 K.

Table 2. Equilibrium Conditions of Gas Hydrates Determined by the Isothermal Method

Methane (1) + Helium (2)			Ethane (1) + Helium (2)		
T/K	x_1	*P*/MPa	*T*/K	x_1	*P*/MPa
273.6	0.857	3.45	273.6	0.692	0.74
	0.648	4.43		0.619	0.80
	0.605	4.75		0.577	0.86
	0.552	5.33		0.561	0.89
				0.539	0.94
				0.538	0.94
				0.517	0.97
				0.498	1.01
				0.479	1.08
				0.442	1.11
				0.405	1.26
				0.339	1.45

where *N* is the number of experimental data points of gas hydrates from helium-containing gas mixtures.

Experimental Results and Discussion

The equilibrium conditions of gas hydrates from five mixtures of methane + helium and three mixtures of ethane + helium were determined by the isochoric method with optical detection. These results are shown in Figures 2 and 3 and Table 1. Some data of pure methane and pure ethane were already reported by Maekawa and Imai.[4] These figures indicate that the equilibrium conditions shift to lower temperature and higher pressure as the helium concentrations in gas mixtures increase. Solid lines indicate the equilibrium conditions predicted by the thermodynamic model if helium molecules in a hydrate lattice do not contribute to the hydrate stability. The discrepancies between the experimental and calculated results for gas mixtures of methane + helium and ethane + helium are obtained to be 0.022 and 0.020 as AAD values, respectively. The experimental data agree with the predicted values, suggesting that helium in gas mixtures has no contribution to the stability of a gas hydrate formed from their mixtures.

Figure 4 and Table 2 show the experimental results of equilibrium conditions at 273.6 K determined by the isothermal method. Gas mixtures with higher helium concentrations require higher equilibrium pressures to form a gas hydrate. The discrepancy between the experimental and calculated results obtained by the isothermal method is 0.018 as the AAD value. Like the results obtained by the isochoric method, the experimental data obtained by the isothermal method agree with the predicted values from the hydrate model having the assumption that helium makes no contribution to the hydrate stability.

Conclusions

In this work, equilibrium conditions of gas hydrates formed from five methane + helium mixtures and three ethane + helium mixtures are experimentally determined by the isochoric method with optical detection, and those formed at a constant temperature of 273.6 K are determined by the isothermal method. As the helium concentration in the gas mixture increases, the equilibrium condition shifts to lower temperature and higher pressure. The experimental data are in good agreement with the predicted values by the thermodynamic model having the assumption that helium molecules in a hydrate lattice do not contribute to the hydrate stability, suggesting the assumption is true for helium-containing mixtures at pressures < 10 MPa.

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