Phase Equilibrium for Structure-H Hydrates Formed with Methane and either Pinacolone (3,3-Dimethyl-2-butanone) or Pinacolyl Alcohol (3,3-Dimethyl-2-butanol)

Ryo Ohmura,* Tsutomu Uchida, Satoshi Takeya, Jiro Nagao, Hideki Minagawa, Takao Ebinuma, and Hideo Narita

Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology (AIST), 2-17-1-2, Tsukisamu-Higashi, Toyohira-ku, Sapporo 062-8517, Japan

The pressure and temperature conditions for the four-phase equilibrium in systems that include structure-H hydrate, methane gas, liquid water, and either 3,3-dimethyl-2-butanone (pinacolone) or 3,3-dimethyl-2-butanol (pinacolyl alcohol) liquid have been measured over the temperature range $T = 273$ K to $T = 281$ K. At a given temperature, the equilibrium pressures of the systems with pinacolone and pinacolyl alcohol are lower by 1.8 MPa and 1.3 MPa, respectively, than those of the structure-I hydrate-forming methane + water system. The equilibrium pressures in the system with pinacolone are roughly equal to those for the system with neohexane, whereas the pressures for the system with pinacolyl alcohol are higher by 0.5 MPa than those with neohexane. This suggests that the hydroxyl functional groups on the large-molecule guest substances can increase the equilibrium pressure in structure-H hydrate-forming systems, whereas the ketone groups can have little influence on the pressure.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of cages built of hydrogen-bonded water molecules that enclose molecules of *guest* substances, that is, some species other than water. Depending on the size and shape of the guest molecules, water molecules form different cages that combine to form the hydrates of the three different crystallographic structures, structures I, II, and H. Among the three hydrates, structure-H hydrate is unique in that it always forms with two different guest substances, with one being a small-molecule guest substance like xenon, hydrogen sulfide, methane, and nitrogen, and the other being a large-molecule guest substance like methylcyclohexane and adamantane that are liquid or solid components of a gas condensate or oil.

Since the discovery of the structure-H hydrate in 1987,[1] considerable efforts have gone into obtaining phase equilibrium data on structure-H hydrate-forming systems, as reviewed by Sloan (Chapter 6 in ref 2) and as seen in more recent phase equilibrium studies.[3−5] In such studies, hydrocarbons such as methylalkanes or methylcycloalkanes have been exclusively targeted as large-molecule guest substances due to the need for safe operation of facilities in the oil and gas industry, with the exception being Hütz and Englezos's study[6] of the system with *tert*-butyl methyl ether. In addition, Ripmeester et al.,[1] Ripmeester and Ratcliffe,[7] and Udachin et al.[8] pointed out that various substances formed by substitutions of methyl groups or hydrogen atoms in some hydrocarbons with atoms or functional groups including Cl, hydroxyl, ether, and ketone groups, as well as the methylalkanes and methylcycloalkanes, could be large-molecule guest substances for structure-H hydrates.

Extension of the phase equilibrium survey to other systems with potential large-molecule guest substances is now demanded because structure-H hydrates have recently aroused additional industrial interest as a material to store and transport natural gas, an idea proposed by Khokhar et al.[9] to reduce the hydrate formation pressure without significant reduction in the gas storage capacity. Following this proposal, thermodynamic properties of structure-H hydrates related to the gas storage/transportation application have been investigated.[10,11] Recently, an experimental study showed a way to continuously form structure-H hydrate crystals using a water spraying technique.[12] For the gas storage/transportation application, methane is the small-molecule guest substance for structure-H hydrates, but the large-molecule guest substances are not limited to hydrocarbons. This study is aimed at obtaining phase equilibrium data for systems with potential large-molecule guest substances for structure-H hydrates, which could be used in the natural gas storage/transportation application. For this purpose, we measured the phase equilibrium conditions of structure-H hydrates with methane and each of two derivatives of neohexane (a well-known large-molecule guest substance for structure-H hydrates[3,6,7,13,14]): pinacolone, which can be viewed as neohexane with two hydrogens replaced by a ketone group, and pinacolyl alcohol, which has a hydroxyl instead of the ketone. Pinacolone is known to form a structure-H hydrate,[1] but its phase equilibrium conditions had not been determined. We also show that pinacolyl alcohol is a large-molecule guest substance for a structure-H hydrate and describe its phase equilibrium conditions.

Experimental Section

Materials. Fluid samples used in the experiments were liquid water deionized and distilled, methane of 99.99 vol % certified purity from Sumitomo Seika Chemicals, Tokyo, pinacolone (3,3-dimethyl-2-butanone) of 99 mass % certified purity from Aldrich Chemical, Milwaukee, WI, pinacolyl alcohol (3,3-dimehtyl-2-butanol) of 99 mass % certified

* Corresponding author. E-mail: r.ohmura@aist.go.jp. Fax: +81 (0)11 857 8971.

10.1021/je034086y CCC: $25.00

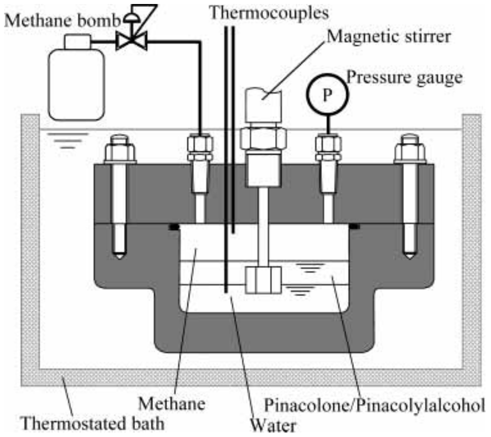

Figure 1. Schematic of the experimental apparatus.

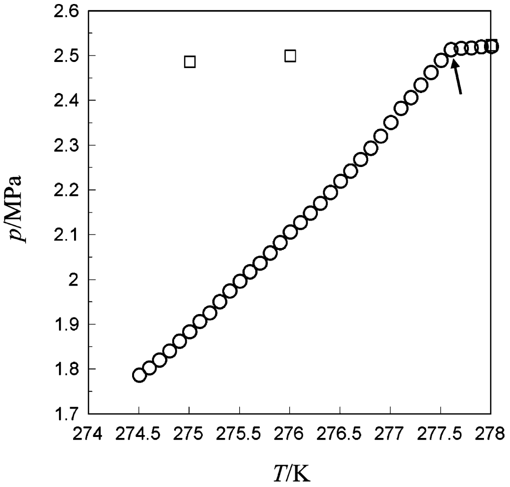

Figure 2. Typical $p-T$ data obtained in an experimental run for determining phase equilibrium conditions in the methane + pinacolyl alcohol + water system. Squares indicate $p-T$ data obtained with decreasing temperature, when the vessel did not contain hydrate crystals. Circles indicate $p-T$ data obtained with increasing temperature, when the vessel initially contained hydrate crystals. The arrow in the figure indicates the point on the curve with an abrupt change in slope, and thus, it marks the disappearance of hydrate crystals during the temperature increase. Thus, four-phase equilibrium is at $p = 2.512$ MPa and $T = 277.6$ K.

Table 1. L_w + H + L_g + V Four-Phase Equilibrium $p-T$ Conditions in the Methane + Neohexane + Water System

T/K	p/MPa
274.3	1.305
276.2	1.623
277.8	1.975
279.6	2.502
280.3	2.720

purity from Aldrich Chemical, and neohexane (2,2-dimethylbutane) of 99 mass % certified purity from Tokyo Kasei Kogyo, Tokyo.

Apparatus. Figure 1 shows the apparatus used to determine the phase equilibrium conditions. A high-pressure vessel that can be charged with liquid water, methane gas, and either pinacolone, pinacolyl alcohol, or neohexane was used as a test section. The vessel is a stainless steel cylinder with inner dimensions of 80-mm diameter and 40-mm height and is equipped with a magnetic stirrer to agitate the fluids and hydrate crystals inside the vessel. The vessel is immersed in a thermostated bath to maintain the temperature inside the vessel T at a prescribed level. The temperatures in the gas and liquid phases are measured with two thermocouples inserted into the vessel. A strain-gauge pressure transducer (model PH-100KB, Kyowa electric) was used to measure the pressure in the vessel p. The estimated uncertainties of the temperature and pressure measurements were ±0.1 K and ±0.016 MPa.

Procedure. The present study generally follows the procedure described by Danesh et al.[15] for measuring the equilibrium temperatures and pressures of the four phases: the water-rich liquid L_w, the hydrate H, the large-molecule guest substance-rich liquid L_g, and the methane-rich gas phase V. In each experimental run, the vessel was first charged with liquid water and each large-molecule guest substance (pinacolone, pinacolyl alcohol, or neohexane). We used 35 cm^3 of liquid water and 25 cm^3 of each large-molecule guest substance to ensure the presence of two liquid phases, in consideration of the mutual solubilities of the large-molecule guest substance and liquid water being a maximum of 10 mass %.[16,17] (Note that the mutual solubilities of pinacolyl alcohol and liquid water are not found in the literature but are presumably similar to those of other hexanol isomers and liquid water that are a maximum of 10 mass %[16]). The vessel containing the liquids was then immersed into the thermostated bath with T set at 283.0 K. The air was purged from the vessel by repeating three times the procedure of pressurization with methane to 1.5 MPa and depressurization to atmospheric pressure. The methane gas was then supplied from the bomb through the pressure regulating valve, thereby setting p at a prescribed level in the range from $p = 1$ MPa to 6 MPa. After T and p stabilized, the valve in the line connecting the vessel and the bomb was shut. We then decreased T in steps of 0.5 to 2 K, keeping each T level for 1 to 2 h. During this procedure, if we detected a decrease in p and an increase in T that indicates hydrate formation, we thereafter kept T constant for 6 h. T was then increased in steps of 0.1 K, keeping each T level for 6 h to allow the liquids and hydrate crystals to equilibrate. The $p-T$ data obtained with this operation give a diagram as shown in Figure 2. When hydrate crystals existed in the vessel, then increasing T by 0.1 K caused the hydrate crystals to partially dissociate, which typically increased p by 0.02−0.05 MPa. In contrast, when no hydrate crystals existed, then the same increase of T caused the much smaller increase in p of typically less than 0.005 MPa. Consequently, the boundary between hydrate existence and nonexistence, which we assume is the four-phase equilibrium point, is the point in the $p-T$ data plots where the slope abruptly changes. By repeating the procedure described above under several different initial pressures, four-phase equilibrium data were obtained over the temperature range between $T = 273$ K and 281 K.

Results and Discussion

The reliability of our experimental method was examined by comparing our resulting L_w + H + L_g + V four-phase equilibrium data obtained in the present measurements for the methane + neohexane + water system to the corresponding data in the literature. The data measured in the present study are tabulated in Table 1. A total of 12 $p-T$ equilibrium data points reported previously for the methane + neohexane + water system[3,6,13,14] were correlated into the form of $p/\mathrm{MPa} = \exp\{a + b/(T/\mathrm{K}) + c \ln(T/\mathrm{K})\}$, where a, b, and c are arbitrary constants, by applying regression analysis. The equilibrium pressure data obtained in the present study or reported in the literature were compared with this fit to the literature data, and then

Table 2. $L_w + H + L_g + V$ Four-Phase Equilibrium $p-T$ Conditions in the Methane + Pinacolone + Water System

T/K	p/MPa
273.7	1.198
275.7	1.545
277.2	1.840
278.7	2.220
280.0	2.573
280.9	2.873

Table 3. $L_w + H + L_g + V$ Four-Phase Equilibrium $p-T$ Conditions in the Methane + Pinacolyl Alcohol + Water System

T/K	p/MPa
273.6	1.568
274.8	1.803
276.1	2.098
277.6	2.512
279.2	3.014
280.4	3.466

the absolute average deviation %AAD was calculated on the basis of the following definition:

$$\%\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{p_i^{\,\mathrm{exp}} - p_i^{\,\mathrm{lit}}}{p_i^{\,\mathrm{exp}}} \times 100\right| \qquad (1)$$

where N is the total number of the experimental data points, p_i^{exp} are the pressure data obtained in the present study or reported in the literature, and p_i^{lit} are the pressure values from the above fit to the data in the literature. The %AAD of the data obtained in the present study and that from the four data sources in the literature[3,6,13,14] were 0.7% and 1.1%, respectively. This analysis indicates that the data measured in the present study are within the scatter of the data reported in the literature, which supports the estimated uncertainties in our measurements.

The $L_w + H + L_g + V$ four-phase equilibrium data obtained for the methane + water + pinacolone system are in Table 2, and the data for the similar system with pinacolyl alcohol are in Table 3. Both data sets are plotted in Figure 3 together with the $L_w + H + L_g + V$ equilibrium data obtained with the present measurements for the methane + neohexane + water system and with the $L_w + H + V$ equilibrium data in the methane + water system reported in the literature.[18,19]

At a given temperature, the equilibrium pressures in the system with pinacolone roughly equal those in the system with neohexane and are lower by 1.8 MPa than those in the methane + water system. The reduction in the equilibrium pressure in the system with pinacolone compared to those in the methane + water system suggests formation of a hydrate different from the structure-I methane hydrate. Furthermore, because pinacolone is known to form a structure-H hydrate with hydrogen sulfide as a small-molecule guest substance,[1] we conclude that the $p-T$ data obtained in the system with pinacolone represent the four-phase equilibrium conditions of liquid water, structure-H hydrate, liquid pinacolone, and methane gas.

Similarly, at a given temperature, the four-phase equilibrium pressures with pinacolyl alcohol are lower by 1.3 MPa than those in the methane + water system. The reduction in the equilibrium pressures in the system with pinacolyl alcohol compared to those in the methane + water system without pinacolyl alcohol indicates the formation of a hydrate different from the structure-I methane hydrate. The crystallographic structure of the hydrate is considered to be structure H, because the molecular size and shape (the dominant factors for a substance to be a large-molecule guest substance for a structure-H hydrate[1,7]) of pinacolyl alcohol are quite similar to those of neohexane and pinacolone. Hence, the $p-T$ data obtained in the system with pinacolyl alcohol likely represent the four-phase equilibrium conditions of water, structure-H hydrate, liquid pinacolyl alcohol, and methane gas. In addition, the system with pinacolyl alcohol has a higher four-phase equilibrium pressure by 0.5 MPa than those of the system with neohexane and pinacolone. This might be due to the hydrophilic nature of the hydroxyl group in the pinacolyl alcohol molecule.

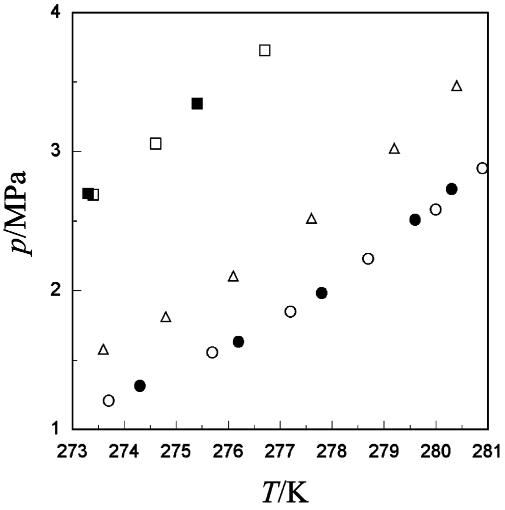

Figure 3. Comparison of the structure-I methane hydrate equilibrium with the four-phase equilibria involving structure-H hydrate that contains methane and large-molecule guest substances: ○, structure H with pinacolone (this work); △, structure H with pinacolyl alcohol (this work); ●, structure H with neohexane (this work); ■, structure-I methane hydrate (de Roo et al.[18]); □, structure-I methane hydrate (Adiasamisto et al.[19]).

Conclusions

The present study reports the first data on the four-phase equilibrium temperature and pressure conditions in the systems of methane and water plus either pinacolone or pinacolyl alcohol. The equilibrium pressures in the systems with either pinacolone or pinacolyl alcohol are lower at least by 1.3 MPa than the equilibrium pressures in the structure-I hydrate-forming methane + water system, which indicates that structure-H hydrates form with pinacolyl alcohol as well as pinacolone as large-molecule guest substances and methane as a small-molecule guest substance. Comparison of the equilibrium pressures of the three structure-H hydrate-forming systems suggests the following: the replacement of a hydrogen on neohexane with a hydroxyl to form pinacolyl alcohol increased the equilibrium pressure of the resulting hydrate system, whereas a similar replacement with a ketone group to form pinacolone did not change the equilibrium pressure.

Acknowledgment

The authors thank Messrs K. Matsushita (Hokkaido Branch, Suzuki Shoko Co., Sapporo, Japan) and J. Itoh (Itoh Keiki Kogyosho, Co., Sapporo, Japan) for their help in the experimental work. The authors also thank Ms. Y. Maeda for her help in preparing the manuscript. Dr. J. A. Ripmeester (National Research Council of Canada), Prof. Y. H. Mori, and Mr. H. Tsuji (Department Mech. Eng., Keio University) are acknowledged for their helpful discussions.

Literature Cited

(1) Ripmeester, J. A.; Tse, J. S.; Ratcliffe, C. I.; Powell, B. M. A New Clathrate Hydrate Structure. *Nature* **1987**, *325*, 135−136.
(2) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*; Marcel Dekker: New York, 1998.
(3) Kang, S. P.; Seo, Y. T.; Lee, H.; Ryu, B.-J. S_H hydrate equilibria of (methane + water + 2-methylbutane + magnesium chloride), (methane + water + 2,2-dimethylbutane + magnesium choloride), and (methane + water + methylcyclohexnae + magnesium chloride). *J. Chem. Thermodyn.* **1999**, *31*, 763−772.
(4) Østergaard, K. K.; Tohidi, B.; Danesh, A.; Burgass, R. W.; Todd, A. C. Equilibirum data and thermodynamic modeling of isopentane and 2,2-dimethylpentane hydrates. *Fluid Phase Equilib.* **2000**, *69*, 101−115.
(5) Sun, Z.-G.; Fan, S.-S.; Guo, K.-H.; Shi, L.; Wang, R. Z. Equilibrium Hydrate Formation Conditions for Methylcyclohexane with Methane and a Ternary Gas Mixture. *Fluid Phase Equilib.* **2002**, *198*, 293−298.
(6) Hütz, U.; Englezos, P. Measurement of Structure H Hydrate Phase Equilibrium and the Effect of Electrolytes. *Fluid Phase Equilib.* **1996**, *117*, 178−185.
(7) Ripmeester, J. A.; Ratcliffe, C. I. Xe-129 NMR Studies of Clathrate Hydrates: New Guests for Structure II and Structure H. *J. Phys. Chem.* **1990**, *94*, 8773−8776.
(8) Udachin, K. A.; Ratcliffe, C. I.; Enright, G. D.; Ripmeester, J. A. Structure H Hydrate: a Single-Crystal Diffraction Study of 2,2-dimethylpentane·5(Xe, H_2S)·34H_2O. *Supramol. Chem.* **1997**, *8*, 173−176.
(9) Khokhar, A. A.; Gudmundson, J. S.; Sloan, E. D., Jr. Gas Storage in Structure H hydrates. *Fluid Phase Equilib.* **1998**, *150−151*, 383−392.
(10) Khokhar, A. A.; Sloan, E. D., Jr.; Gudmundson, J. S. Natural Gas Storage Properties of Structure H Hydrate. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 950−957.
(11) Mooijer-van den Heuvel, M. M.; Peters, C. J.; de Swan Arons, J. Influence of Water-Insoluble Organic Components on the Gas Hydrate Equilibrium Conditions of Methane. *Fluid Phase Equilib.* **2000**, *172*, 73−91.
(12) Ohmura, R.; Kashiwazaki, S.; Shiota, S.; Tsuji, H.; Mori, Y. H. Structure-I and Structure-H Hydrate Formation Using Water Spraying. *Energy Fuels* **2002**, *16*, 1141−1147.
(13) Mehta, A. P.; Sloan, E. D., Jr. Structure H Hydrate Phase Equilibria of Methane + Liquid Hydrocarbon Mixtures. *J. Chem. Eng. Data.* **1993**, *38*, 580−582.
(14) Makogon, T.; Mehta, A. P.; Sloan, E. D., Jr. Structure H and Structure I Hydrate Equilibrium Data for 2,2-Dimethylbutane with Methane and Xenon. *J. Chem. Eng. Data* **1996**, *41*, 315−318.
(15) Danesh, A.; Tohidi, B.; Burgass, R. W.; Todd, A. C. Hydrate Equilibrium Data of Methyl Cyclopentane with Methane or Nitrogen. *Chem. Eng. Res. Des.***1994**, *72*, 197−200.
(16) Stephenson, R.; Stuart, J.; Tabak, M. Mutual Solubility of Water and Aliphatic Alcohol. *J. Chem. Eng. Data* **1984**, *29*, 287−290.
(17) Stephenson, R. Mutual Solubilities: Water-Ketones, Water-Ethers, and Water-Gasoline-Alcohols. *J. Chem. Eng. Data* **1992**, *37*, 80−95.
(18) de Roo, J. L.; Peters, C. J.; Lichtenthaler, R. N.; Diepen, G. A. M. Occurrence of Methane Hydrate in Saturated and Unsaturated Solutions of Sodium Chloride and Water in Dependence of Temperature and Pressure. *AIChE J.* **1983**, *29*, 651−567.
(19) Adiasamisto, S.; Robert, J. F., III; Sloan, E. D., Jr. Hydrates of Carbon Dioxide and Methane Mixtures. *J. Chem. Eng. Data* **1991**, *36*, 68−71.

Received for review April 30, 2003. Accepted June 17, 2003.

JE034086Y