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Gas Hydrate Phase Equilibrium Data of Cyclohexane and Cyclopentane

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Four-phase (liquid water + hydrate + liquid hydrocarbon + vapor) equilibrium data are reported for structure II hydrates of methane + cyclohexane or cyclopentane and a ternary mixture gas (methane = 91.96 mol %, ethane = 5.13 mol %, propane = 2.91 mol %) + cyclohexane in the pressure range (0.165 to 9.486) MPa and the temperature range (273.83 to 301.90) K. The equilibrium pressures of the experimental systems of methane + cyclohexane or cyclopentane are concededly lower than that of the system of pure methane at a given temperature. The presence of cyclohexane inhibits hydrate formation, rather than promoting it, at higher temperatures in the test system of the ternary mixture gas + cyclohexane.

Introduction

Clathrate hydrates are icelike crystalline inclusion compounds formed by hydrogen-bonding of water molecules in the presence of molecules such as methane, ethane, or propane. The most well-known hydrate structures are those of structure I and structure II. Comprehensive treatises on hydrates have been reviewed by Sloan.[1] In the oil and gas industry, *n*-butane was formerly regarded as the largest hydrate-forming compound and anything larger than that as a nonhydrate-former. There are other compounds in reservoir fluids, which are intermediate/heavy hydrocarbon compounds heavier than *n*-butane, which can form structure II or structure H gas hydrates with their effective van der Waals' diameters. The structure H hydrate was first discovered by Ripmeester et al.[2] The structure H hydrate has larger cavities than any cavities of structure I and structure II, and is capable of forming hydrates with molecules from five to eight carbon atoms long such as methylcyclohexane and 2-methylbutane, in the presence of smaller help guest molecules such as methane or carbon dioxide. Equilibrium data for the structure H hydrate have been recently reported.[3−7]

Ripmeester et al. suggested that cyclopentane can form structure II gas hydrates without a help gas to fill small cavities and stabilize the structure.[8] And in our laboratory the equilibrium data of cyclopentane were measured.[9] Cyclohexane can also form a structure II hydrate with a help gas such as methane.[8] Tohidi et al. studied the equilibrium of cyclohexane, cyclopentane, and neopentane gas hydrates with methane or nitrogen.[10,11]

Three series of hydrate equilibrium experiments of cyclohexane and cyclopentane with methane, or a ternary mixture gas, have been performed in this laboratory. The measurements are performed in the pressure range (0.165 to 9.486) MPa and the temperature range (273.83 to 301.90) K.

Experimental Apparatus

The experimental apparatus and procedures used for obtaining the equilibrium data were described in detail by Sun et al.[12] They were described briefly here. The equilibrium cell was a "full view" sapphire variable-volume cell with a movable piston. The cell consisted of a sapphire tube sealed at the top end with a stainless steel flange. The cell contents were mixed with a stirrer and a circulating pump. The stirring was achieved by the rotation of a helix with four blades. The cell pressure was measured using a TF01 400A absolute pressure transducer (0−40 MPa) of accuracy about ±0.06% of the scale (i.e. 24 kPa). The cell temperature was measured using platinum resistance thermometers with an accuracy of ±0.1 K. The cell volume was adjusted with a movable piston. The signals of pressure, temperature, and volume were acquired with a data acquisition system driven by a personal computer. The cell pressure, cell temperature, cell volume, air bath temperature, flow, and stirring velocity data from the acquisition system were saved at preset sampling intervals on a computer hard disk. A gas sample from the sapphire cell was analyzed on a HP6890 gas chromatograph to ensure the absence of air.

Experimental Procedure

The test fluids used in this work are described in Table 1. The gas mixtures were made from research-grade pure gas. The cell was rinsed with distilled water two times and evacuated with a vacuum pump. The cell was initially charged with approximately 12.5 g of distilled water. An excess amount of liquid hydrocarbon was used in order to ensure the presence of a hydrocarbon-rich liquid phase in all tests. Water and liquid hydrocarbon were weighed on an electronic balance with a readability of ±0.1 mg. The test fluids of methane + cyclohexane or cyclopentane were comprised of three components (1, methane; 2, water; 3,

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Table 1. Test Fluids Used in This Work

component	purity/composition	supplier
methane	99.9%	Guangzhou Gas Co.
the gas mixture	91.96 mol % methane, 5.13 mol % ethane, 2.91 mol % propane	Fushan Kede Gas Co.
cyclohexane	⩾98%	Shanghai Chemical Reagent Co.
cyclopentane	98.4%	Meilong Chemical Co.
water		distilled

Table 2. Equilibrium Conditions of Methane and Cyclohexane

T/K	P/MPa	T/K	P/MPa
291.58	9.486	282.02	2.212
290.63	8.021	279.14	1.463
289.82	7.282	276.06	0.938
287.47	4.961	274.68	0.713
285.03	3.436	273.97	0.684

Table 3. Equilibrium Conditions of Methane and Cyclopentane

T/K	P/MPa	T/K	P/MPa
301.90	7.312	289.87	1.033
300.22	5.636	287.13	0.568
297.83	3.824	284.98	0.380
295.18	2.547	282.15	0.165
292.72	1.678		

cyclohexane or cyclopentane) and four phases (vapor, water, liquid hydrocarbon, and hydrate). According to the Gibbs phase rule, there is only one degree of freedom for the systems of methane + cyclohexane or cyclopentane. Therefore, the equilibrium conditions at a given temperature do not depend on the mixture composition in the test system of methane + cyclohexane or cyclopentane.

The hydrate equilibrium was established using the "pressure search" procedure at a fixed temperature.[12,13] The presence of hydrates in the cell was discovered visually in the equilibrium cell. The cell's temperature was lowered to form hydrates with the cell contents being mixed. Once the solution in the cell reached the desired temperature, the pressure of the cell was raised to a pressure exceeding the estimated equilibrium pressure by about 1.0 MPa in order to reduce the induction time. A large amount of hydrates were observed, and then the pressure was decreased by moving the cell piston to decompose the hydrates. The procedure was repeated two times for each experimental run. The hydrates were formed, and the equilibrium pressure was established using the pressure search method. The temperature and pressure were considered as the equilibrium conditions when a small quantity of the hydrate crystals remained stable for 3-4 h. Once the equilibrium conditions were established, the system pressure of the cell was lowered by 50 kPa to confirm that all hydrates decomposed. A different temperature was subsequently selected, and the procedure was repeated to obtain another hydrate equilibrium condition.

Results and Discussion

The isothermal pressure search method was used to determine the hydrate phase equilibrium conditions for the system of methane + cyclohexane or cyclopentane, and the ternary mixture gas + cyclohexane. The experimental hydrate equilibrium conditions were tabulated in Tables 2−4. The data were also plotted in Figures 1−4. The solid lines shown in the figures were drawn by "visual fit" to clarify the trends of the experimental data.

Figure 1 shows hydrate equilibrium conditions for the methane + cyclohexane system. The hydrate formed in the presence of cyclohexane is of structure II, compared to those of pure methane that formed structure I. Figure 1 shows there is a significant shift (more than 2 MPa) in hydrate formation pressures to lower pressures at any temperatures, due to the presence of cyclohexane. And the equilibrium pressures of the experimental system show a large difference at higher temperatures.

Table 4. Equilibrium Conditions of the Mixture and Cyclohexane[a]

T/K	P/MPa	T/K	P/MPa
289.08	6.278	279.95	1.657
285.86	3.842	277.68	1.107
284.13	3.036	275.69	0.883
283.19	2.506	273.83	0.614
282.20	2.238		

[a] Feed composition (mole %): methane = 2.18, ethane = 0.12, propane = 0.07, cyclohexane = 7.84, water = 89.79.

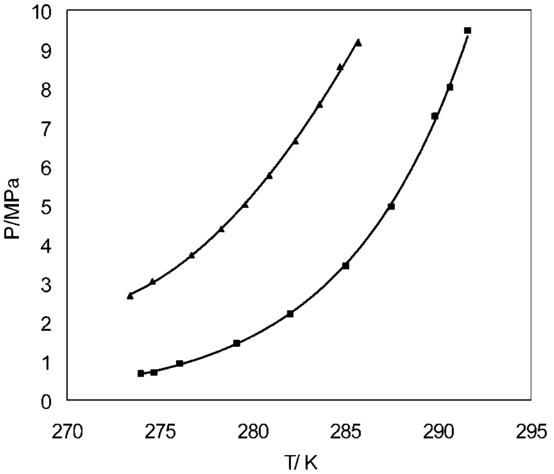

Figure 1. Hydrate dissociation conditions of methane, and methane + cyclohexane: (▲) methane;[1] (■) methane + cyclohexane; (—) visual fit.

Figure 2 presents hydrate equilibrium data of the methane + cyclopentane system. This system also formed a structure II hydrate. However, the shift phenomenon of equilibrium pressures was similar to that of the methane + cyclohexane system, which had a larger shift of the hydrate phase boundary than that of methane + cyclohexane.

Figure 3 presents hydrate formation conditions for the ternary mixture gas + cyclohexane. The results showed that the hydrate equilibrium pressures of the ternary mixture gas + cyclohexane were higher than those of the ternary mixture gas alone at higher temperatures (about 283 K). That is to say, the presence of cyclohexane was inhibiting hydrate formation, rather than promoting it, at higher temperatures. A possible explanation for the inhibition of the hydrate phase boundary at higher temperatures was that the mixture formed an sII hydrate at higher temperatures, with cyclohexane present as an inhibitor.

Figure 4 compares the equilibrium data of methane + cyclohexane and the ternary mixture gas + cyclohexane. The equilibrium data of methane + cyclohexane in this work agreed with those of Tohidi et al.[10] at lower temper-

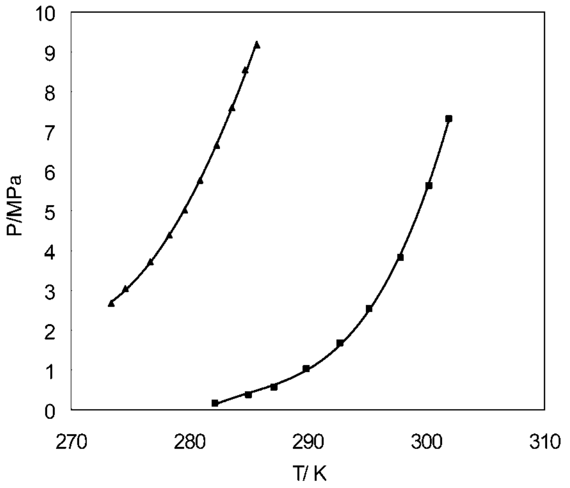

Figure 2. Hydrate dissociation conditions of methane, and methane + cyclopentane: (▲) methane;[1] (■) methane + cyclopentane; (—) visual fit.

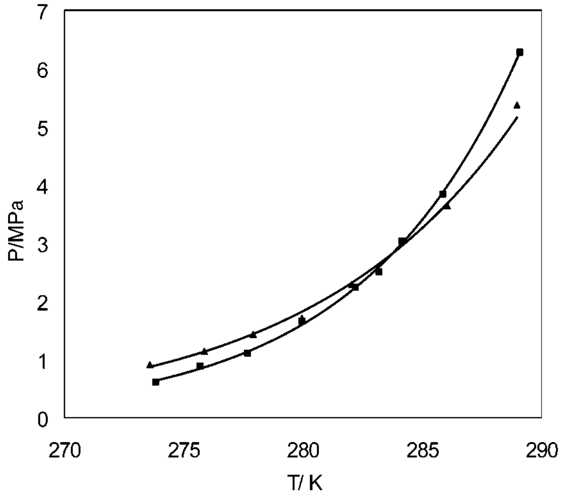

Figure 3. Hydrate dissociation conditions of the mixture of methane + ethane + propane, and the mixture of methane + ethane + propane + cyclohexane: (▲) methane + ethane + propane; (■) methane + ethane + propane + cyclohexane; (—) visual fit.

atures (about 282 K) but were a little higher at higher temperatures (The hydrate phase boundary shifted about 0.3 MPa at 290 K). It was very interesting that the equilibrium data of the ternary mixture gas + cyclohexane were in accordance with those of the methane + cyclohexane system in this work. Ethane, propane, and cyclohexane all enter only the large cavities of the structure II hydrate. It is possible that the presence of cyclohexane affects how ethane and propane fill the hydrate cavities. It is necessary to confirm how the gases ethane, propane, and cyclohexane enter the large cavities of structure II by measurements using suitable physical techniques.

Conclusions

Two structure II formers, that is, cyclohexane and cyclopentane, have been studied in this work. Experimental hydrate equilibrium conditions for the system methane + cyclohexane or cyclopentane, and the ternary mixture gas + cyclohexane, have been studied and reported. The methane + cyclohexane or + cyclopentane systems show that a structure II hydrate forms, compared to forming a structure I hydrate with pure methane. The experimental results for the ternary mixture gas + cyclohexane show that the intermediate hydrocarbon compound is a hydrate promoter at lower temperatures but an inhibitor at higher temperatures. The data are obtained in the pressure range (0.165 to 9.486) MPa and the temperature range (273.83 to 301.90) K using a variable-volume sapphire cell.

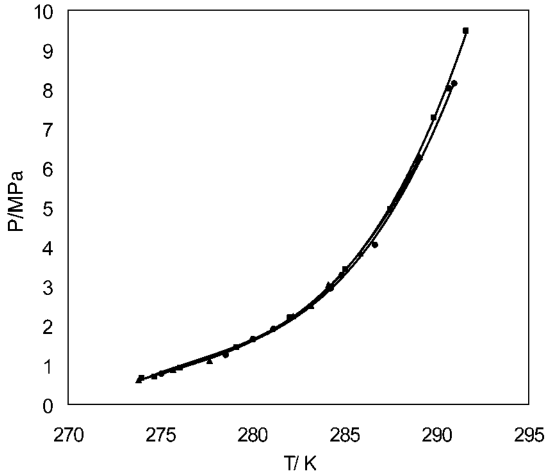

Figure 4. Comparison of hydrate equilibrium data of methane + cyclohexane and the ternary mixture gas + cyclohexane: (▲) methane + ethane + propane + cyclohexane; (■) methane + cyclohexane; (●) methane + cyclohexane;[12] (—) visual fit.

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