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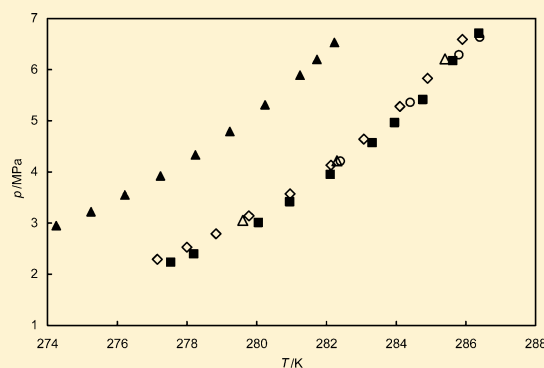
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ABSTRACT: In this communication, experimental hydrate dissociation data for the (methane + cyclooctane + water), (methane + 3,3-dimethyl-1-butene + water), (methane + 2-pentanone + water) and (methane + 3-pentanone + water) systems are reported in the temperature range of (273 to 286) K. Experimental data were generated using an isochoric pressure search method. The experimental hydrate dissociation data for the (methane + 2-pentanone + water) and (methane + 3-pentanone + water) systems are compared to experimental dissociation data for methane hydrate, and it is found that 2-pentanone or 3-pentanone likely shows an inhibition effect on methane clathrate hydrates.



1. INTRODUCTION

Gas hydrates, or clathrate hydrates, are crystalline compounds resembling ice, that are composed of water and small molecules which are generally gases and some volatile liquids, like some “cyclic ethers”, some “ketones”, some “heavy hydrocarbons between C_5 – C_9 ” *etc.* In gas hydrates, small molecules (host) are trapped within cavities composed of hydrogen-bonded water molecules (guest) under low temperatures and relatively high pressures.¹ Gas hydrates are typically composed of three different crystalline structures called structure I (sI), structure II (sII), and structure H (sH) depending on the size and shape of guest molecule(s).¹

Structure H hydrate has a hexagonal space, and, unlike structures I and II, structure H hydrates are required to stabilize two kinds of molecules.^{1,2} Small molecules as help gases, like methane and nitrogen can enter the small and medium cavities and large molecules as structure H former, like methylalkanes and cycloalkanes, enter the large cavity.^{1,2} Gas hydrate promoters as additives to the system (known also as structure H formers) can play a significant role in the reduction of hydrate formation pressure for the hydrate crystallization (formation) processes. To the best of our knowledge, the first structure H hydrate dissociation data were measured for the methane + adamantane + water system by Lederhos *et al.*³ and by Becke *et al.*⁴ for the methane + methylcyclohexane + water system. Later comprehensive studies were made by different researchers which have been well documented by

Sloan and Koh.¹ In recent years, Mohammadi and Richon^{5–9} carried out new studies on structure H hydrates.

Since several water insoluble sH hydrate formers (hydrocarbons) have been already shown to have considerable hydrate inhibition effects,¹ it is worth checking for the effects other alternatives and to obtain accurate knowledge about the corresponding phase diagrams of methane + hydrate promoters. In the present work, we report hydrate dissociation conditions for the (methane + cyclooctane + water), (methane + 3,3-dimethyl-1-butene + water), (methane + 2-pentanone + water), and (methane + 3-pentanone + water) systems, for which the data are either limited or not available in open literature. The experimental data have been generated using an isochoric pressure search method. The latter hydrate dissociation data are compared with the corresponding literature data, in case of availability, to examine the reliability of the experimental method employed in the present work. A comparison is finally made between the aforementioned experimental data and hydrate dissociation data for the methane + water system, reported in the literature, to study the impact of the presence of cyclooctane, 3,3-dimethyl-1-butene, 2-pentanone, and 3-pentanone on methane hydrate dissociation conditions.

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2. EXPERIMENTAL SECTION

2.1. Materials. Table 1 reports the purities and suppliers of the materials used in this work.

Table 1. Purities and Suppliers of Materials Used in This Work

material	supplier	purity/(mole fraction)
methane	Air Product	0.9995
cyclooctane	Merck	> 0.98
3,3-dimethyl-1-butene	Merck	> 0.95
2-pentanone	Merck	> 0.99
3-pentanone	Merck	> 0.99
water		deionized water

2.2. Experimental Apparatus. The schematic diagram of the experimental apparatus used in this work has been already depicted.¹⁰ The main portion of the experimental apparatus is a high pressure equilibrium cell with a 75 cm³ internal volume. This cell is made of 316 stainless steel equipped with double sight glasses. A magnetic stirrer installed in the cell is used to agitate the fluids and hydrate crystals at approximately 500 rpm. The schematic picture of the cell can be found elsewhere.¹⁰ The cell temperature is controlled using an ethanol bath, Julabo FP 50, with an accuracy of 0.1 K.

The pressure of the cell is measured by a pressure transducer within a certitude of ± 0.25 % of full scale, which has been calibrated with a dead weight balance. A Pt100 platinum temperature probe inserted in the inner cell is used to measure the temperature of the system. The accuracy of the temperature measurement is much better than 0.1 K. The data acquisition unit connected to a PC computer is used for recording the system pressure and temperature throughout the experiments.

2.3. Experimental Method. Before the experiment, the equilibrium cell was washed with deionized water and was dried completely. Then, the vacuum pump was turned on and the air inside the reactor was evacuated (down to 0.8 kPa for at least 2 h). The experimental method used in this work is based on an isochoric pressure-search method.^{5–9} This method has already been proven as a reliable technique for the measurement of hydrate dissociation conditions of various systems.^{5–9} To perform the measurements, deionized water and nonaqueous liquid were introduced into the cell (approximately 30% by volume of the vessel is filled with water and nonaqueous liquid), and the pressure of the cell was increased with methane gas to the desired pressure at 298.15 K. Then, the system was cooled (0.2 K/min) to a temperature lower than the expected hydrate dissociation temperature at the desired pressure and was then held constant for a period of time. At this step, the system pressure dropped because of hydrate formation. After the hydrate formation was completed, the cell temperature was then increased in fixed rate insteps of 0.1 K to the ambient temperature. With increasing temperature, the pressure increases. After the complete decomposition of all hydrate, the point at which the slope of the pressure–temperature plot changes sharply is considered as the hydrate dissociation point.^{5–9}

3. EXPERIMENTAL RESULTS

The hydrate dissociation data measured for the (methane + cyclooctane + water), (methane + 3,3-dimethyl-1-butene + water), (methane + 2-pentanone + water), and (methane + 3-

pentanone + water) systems are reported in Tables 2 to 5, respectively.

Table 2. Hydrate Dissociation Conditions for the Methane + Cyclooctane + Water System

T^a /K	P^b /MPa
276.7	2.24
277.3	2.40
279.2	3.01
280.3	3.42
281.6	3.95
282.9	4.57
283.6	4.97
284.4	5.42
285.5	6.18
286.2	6.71

^aTemperature. ^bPressure. The uncertainties for the hydrate dissociation temperatures and pressures are expected to be ± 0.1 K and ± 0.06 MPa, respectively.

Table 3. Hydrate Dissociation Conditions for the Methane + 3,3-Dimethyl-1-butene + Water System

T^a /K	P^b /MPa
276.7	2.20
278.4	2.70
279.9	3.24
281.6	3.95
283.0	4.70
284.1	5.33
285.0	5.95
285.7	6.50

^aTemperature. ^bPressure. The uncertainties for the hydrate dissociation temperatures and pressures are expected to be ± 0.1 K and ± 0.06 MPa, respectively.

Table 4. Hydrate Dissociation Conditions for the Methane + 2-Pentanone + Water System

T^a /K	P^b /MPa
274.0	3.04
274.9	3.33
277.3	4.24
278.8	4.95
279.9	5.53
281.0	6.20
282.2	7.08

^aTemperature. ^bPressure. The uncertainties for the hydrate dissociation temperatures and pressures are expected to be ± 0.1 K and ± 0.06 MPa, respectively.

As noted previously, we first obtained the hydrate dissociation data for (methane + cyclooctane + water) or (methane + 3,3-dimethyl-1-butene + water) systems for which limited information is available in the literature. The results for these two systems and the experimental data reported in the literature,^{11,8,12,13} which show good agreement, are plotted in Figures 1 and 2. In both figures, we have also indicated some selected experimental data from the literature¹⁴ for the methane + water system, to investigate the hydrate promotion effects of the latter large molecules. As can be observe in figures, the presence of these large molecule shifts methane hydrate dissociation conditions to higher temperatures or lower

Table 5. Hydrate Dissociation Conditions for the Methane + 3-Pentanone + Water System

T^a/K	P^b/MPa
277.0	4.14
278.7	4.93
279.9	5.61
280.9	6.21
282.5	7.42
282.6	7.48

^aTemperature. ^bPressure. The uncertainties for the hydrate dissociation temperatures and pressures are expected to be ± 0.1 K and ± 0.06 MPa, respectively.

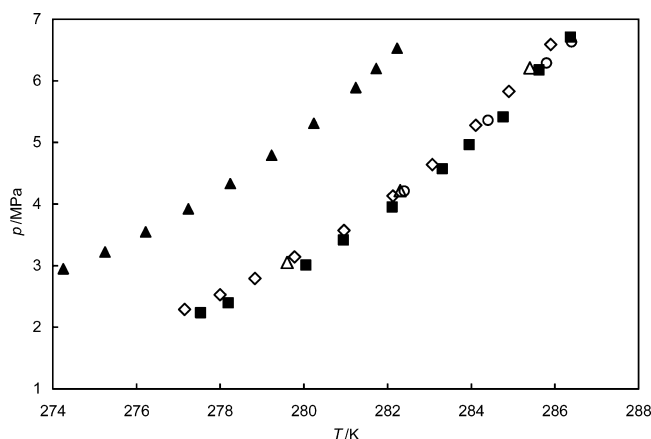


Figure 1. Hydrate dissociation conditions for the methane + cyclooctane + water system. Symbols represent experimental data. Methane + cyclooctane + water system: ■, this work; ◇, ref 11; △, ref 8; ○, ref 12. Methane + water system: ▲, ref 14.

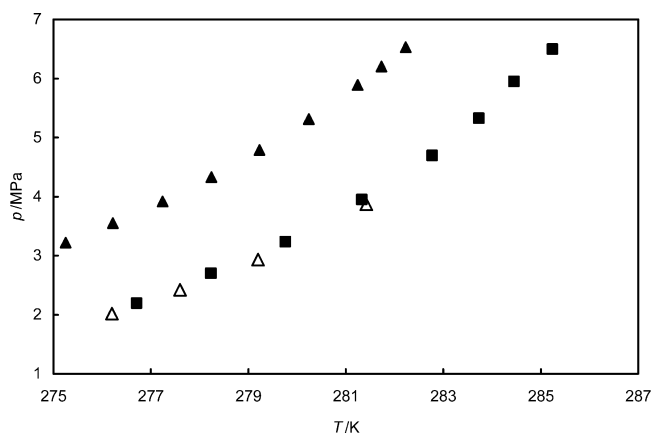


Figure 2. Hydrate dissociation conditions for the methane + 3,3-dimethyl-1-butene + water system. Symbols represent experimental data. Methane + 3,3-dimethyl-1-butene + water system: ■, this work; △, ref 13. Methane + water system: ▲, ref 14.

pressures indicating a hydrate promotion effect. It is known that cyclooctane and 3,3-dimethyl-1-butene form structure H clathrate hydrate with methane as help gas.¹

Considering the above observations, we then measured hydrate dissociation conditions for the (methane + 2-pentanone + water) or (methane + 3-pentanone + water) systems. The results for these two systems are plotted and compared with some selected experiment data¹⁴ from the literature for the methane + water system in Figures 3 and 4.

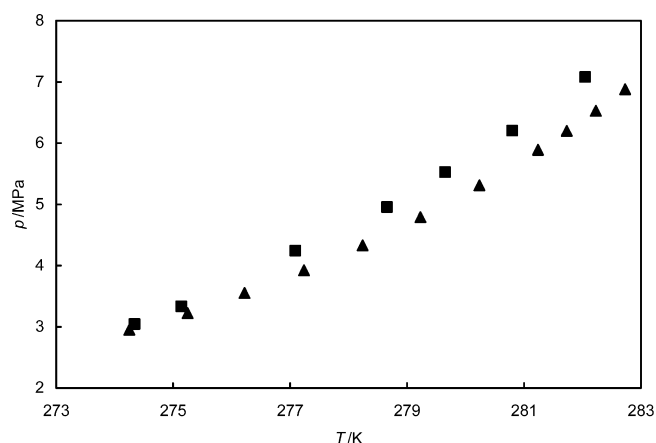


Figure 3. Hydrate dissociation conditions for the methane + 2-pentanone + water system. Symbols represent experimental data. Methane + 2-pentanone + water system: ■, this work. Methane + water system: ▲, ref 14.

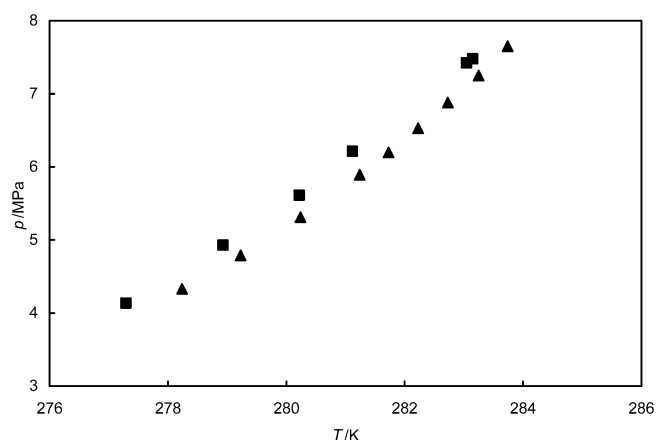


Figure 4. Hydrate dissociation conditions for the methane + 3-pentanone + water system. Symbols represent experimental data. Methane + 3-pentanone + water system: ■, this work. Methane + water system: ▲, ref 14.

The comparison between hydrate dissociation conditions for the (methane + 2-pentanone + water) and (methane + 3-pentanone + water) systems with hydrate dissociation conditions for the methane + water system unexpectedly indicates that the two studied ketones, 2-pentanone and 3-pentanone, likely have inhibition effects on methane clathrate hydrates as the presence of the latter chemicals shifts methane hydrate dissociation conditions to low temperatures or high pressures. The final proof for probable cage occupancy and the stable hydrate structure requires direct measurements by suitable physical techniques. (e.g., solid C13 NMR, X-ray or neutron diffraction techniques, etc.)

4. CONCLUSION

In this contribution, hydrate dissociation data for the (methane + cyclooctane + water), (methane + 3,3-dimethyl-1-butene + water), (methane + 2-pentanone + water), and (methane + 3-pentanone + water) systems were reported (Tables 2 to 5). The data were obtained pursuing an isochoric pressure-search method.^{5–9} The measurements were first performed for the (methane + cyclooctane + water) and (methane + 3,3-dimethyl-1-butene + water) systems. The results were

compared with the experimental data reported in the literature,^{11,8,12,13} and good agreement was observed. We then measured hydrate dissociation data for the (methane + 2-pentanone + water) and (methane + 3-pentanone + water) systems. Comparison of the results for these two systems with hydrate dissociation data for the methane + water¹⁴ system shows that the presence of 2-pentanone or 3-pentanone likely results in the inhibition of methane hydrates.

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Notes

The authors declare no competing financial interest.

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