Equilibrium Data of Methyl Cyclohexane + Hydrogen Sulfide and Methyl Cyclohexane + Methane Clathrate Hydrates

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In this work, experimental hydrate dissociation data for the hydrogen sulfide + methyl cyclohexane + water and methane + methyl cyclohexane + water systems are reported in the temperature ranges of (286.6 to 297.1) K and (274.2 to 290.4) K, respectively. The experimental data were generated using an isochoric pressure-search method. The hydrate dissociation data for the methane + methyl cyclohexane + water system are compared with some selected experimental data from the literature, and the acceptable agreement demonstrates the reliability of the experimental method used in this work. The experimental data for both measured systems are finally compared with the corresponding experimental data in the absence of methyl cyclohexane reported in the literature to identify the hydrate promotion effects of methyl cyclohexane.

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1. Introduction

Gas hydrates (or clathrate hydrates) are icelike solid crystalline compounds, which are formed through a combination of water and small guest molecules like methane, nitrogen, etc.[1] In the clathrate lattice, water molecules form hydrogen-bonded cagelike structures, encapsulating the guest molecule(s).[1] The gas hydrate crystalline structures are generally those of structure I (*s*I), structure II (*s*II), and structure H (*s*H), where each structure is composed of a certain number of cavities formed by water molecules.[1] The formation of structure H requires the presence of two large and small guest molecules. Large molecules occupy large cavities, while small molecule(s) (called help gas) fill the remaining cavities.[1] It has been reported that methyl cyclohexane can form structure H of clathrate hydrates with a help gas such as methane.[1] However, information on other help gases is limited.[1] To our knowledge, there is no information on clathrate hydrate formation of methyl cyclohexane with hydrogen sulfide as a help gas.

In this work, gas hydrate dissociation data for the hydrogen sulfide + methyl cyclohexane + water and the methane + methyl cyclohexane + water systems are reported in the temperature ranges of (286.6 to 297.1) K and (274.2 to 290.4) K, respectively. The experimental data were generated using an isochoric pressure-search method.[2,3] As gas hydrate dissociation data for the methane + methyl cyclohexane + water system have already been reported in the literature, therefore, we first generated and report experimental data for the latter system and compare them with some selected experimental data from the literature[4−9] to demonstrate the reliability of the experimental method[2,3] used in our work. We then report hydrate dissociation data for the hydrogen sulfide + methyl cyclohexane + water system. The experimental data for the studied systems are finally compared with some selected experimental data from the literature for the methane + water[10−12] and hydrogen sulfide + water[13−16] systems to study the hydrate promotion effects of methyl cyclohexane.

Table 1. Purities and Suppliers of Chemicals[a]

chemical	supplier	purity, %
hydrogen sulfide	Air Liquide	99.9 (by volume)
methane	Messer Griesheim	99.995 (by volume)
methyl cyclohexane	Sigma-Aldrich	99+ (GC)

[a] Deionized water was used in all experiments.

2. Experimental Section

2.1. Chemicals. Table 1 reports the purities and suppliers of the chemicals used in this work.

2.2. Experimental Apparatus. Figure 1 shows the schematic diagram of the apparatus used in this work.[16] Briefly, the main part of the apparatus is a sapphire cylindrical vessel, which can withstand pressures higher than 10 MPa. The volume of the vessel is 33.1 cm^3. A stirrer was installed in the vessel to agitate the fluids and hydrate crystals inside it. The stirrer and all metallic parts of the apparatus (flanges, etc.) were made of stainless steel. Two platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperatures and check for equality of temperatures within temperature measurement uncertainties, which is estimated to be less than 0.1 K. This temperature uncertainty estimation comes from calibration against a 25 Ω reference platinum resistance thermometer. The pressure in the vessel was measured with two DRUCK pressure transducers (Druck, type PTX611 for pressure ranges up to (2.5 and 12) MPa, respectively). Pressure measurement uncertainties are estimated to be less than 5 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

2.3. Experimental Method. The liquid water + liquid hydrocarbon + hydrate + gas/vapor equilibria conditions were measured with an isochoric pressure search method.[2,3] The vessel containing liquids (approximately 10 % by volume of the vessel was filled by water and 10 % by volume by methyl cyclohexane) was immersed into the temperature-controlled bath, and the gas was supplied from a cylinder through a pressure-regulating valve into the vessel. Note that the vessel was evacuated before introducing any liquid and gas. After obtaining temperature and pressure stability (far enough from the hydrate formation region), the valve in the line connecting

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10.1021/je900368z CCC: $40.75

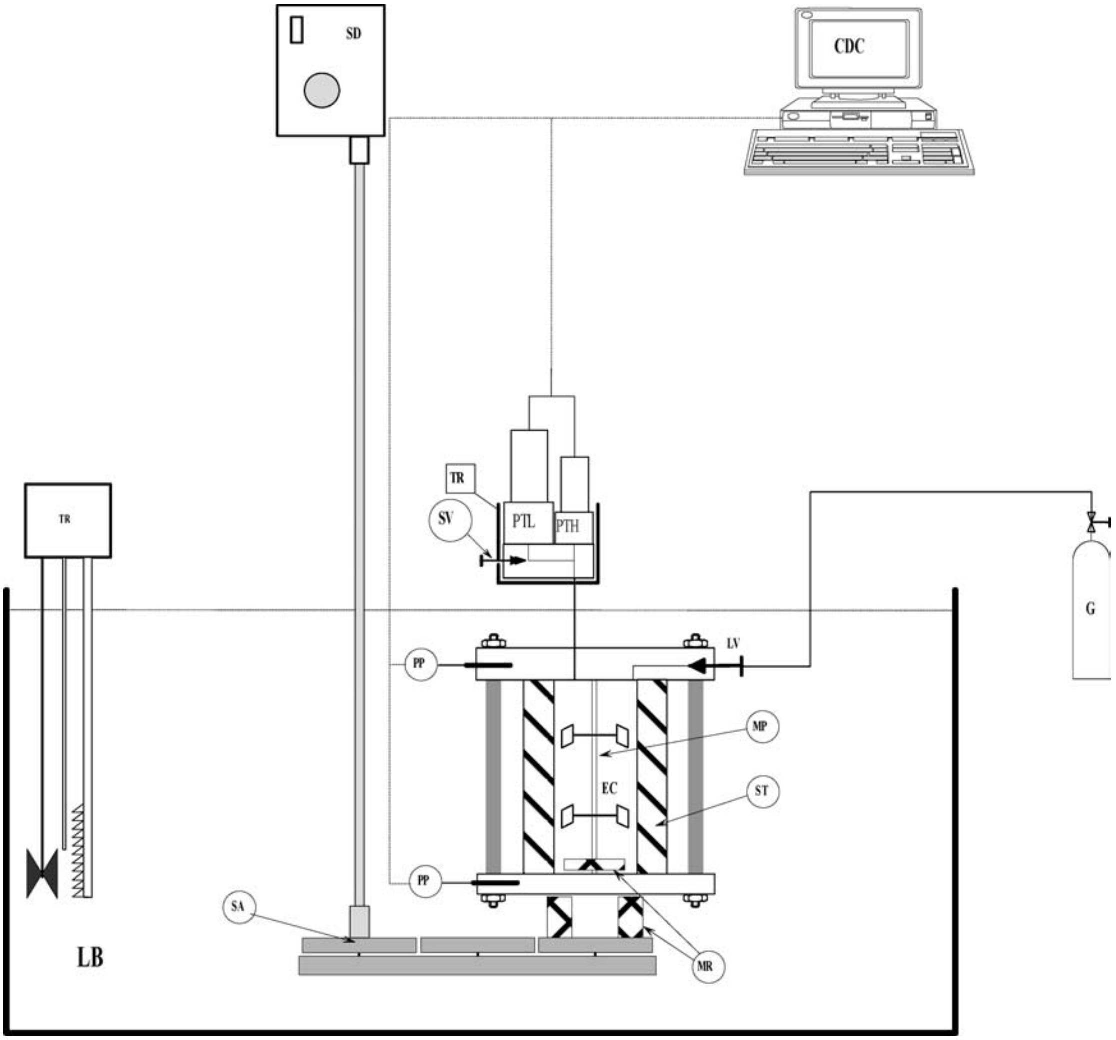

Figure 1. Flow diagram of the experimental setup used to measure hydrate dissociation conditions.[16] Descriptions: CDC, Central Desktop Computer; EC, Equilibrium Cell; G, Gas Cylinder; LB, Liquid Bath; LV, Loading Valve; MP, Multiple Propeller; MR, Magnetic Rod; PP, Platinum Probe (Temperature Sensor); PT, Pressure Transducer (L, Low Pressure; and H, High Pressure); SA, Stirring Assembly; SD, Stirring Device with variable speed motor; ST, Sapphire Tube; SV, Separation Valve; TR, Temperature Controller.

the vessel and the cylinder was closed. Subsequently, temperature was slowly decreased to form the hydrate. Hydrate formation in the vessel was detected by a pressure drop. The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was kept constant for 4 h to achieve an equilibrium state in the vessel. In this way, a pressure−temperature diagram was obtained for each experimental run, from which we determined the hydrate dissociation point (Figure 2).[2,17] If the temperature is increased in the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. If the temperature is increased outside the hydrate region, only a smaller increase in the pressure is observed as a result of the change in the phase equilibria of the fluids in the vessel.[2,17] Consequently, the point at which the slope of the pressure−temperature data plots changes sharply is considered to be the point at which all hydrate crystals have dissociated and hence is reported as the dissociation point.[2,17]

3. Experimental Results

All the experimental data are reported in Table 2 and are plotted in Figures 3 and 4. As mentioned earlier, we first measured the hydrate dissociation conditions for the methane + methyl cyclohexane + water system. As can be observed in

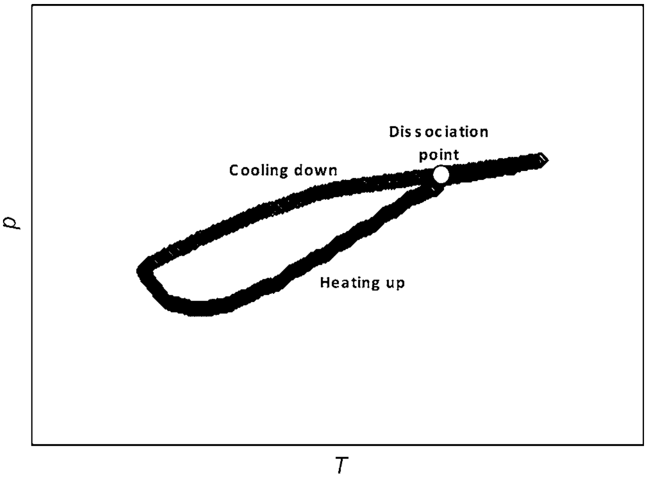

Figure 2. Typical pressure−temperature diagram for estimating the hydrate dissociation point.[2]

Figure 3, the experimental data measured in this work for the latter system are in acceptable agreement with the experimental data reported in the literature[4−9] demonstrating the reliability of the experimental method[2,3] used in our work. In both figures, we have shown some selected experimental data from the

Table 2. Experimental Hydrate Dissociation Data for the Methane + Methyl Cyclohexane + Water and Hydrogen Sulfide + Methyl Cyclohexane + Water Systems

T/K[a]	p/MPa[b]
methane + methyl cyclohexane + water system	
274.2	1.48
278.2	2.33
282.6	4.12
287.1	7.38
290.4	11.30
hydrogen sulfide + methyl cyclohexane + water system	
286.6	0.255
287.7	0.289
288.4	0.315
290.0	0.385
290.8	0.425
291.9	0.481
293.1	0.566
293.6	0.593
294.8	0.699
296.0	0.816
297.1	0.945

[a] Uncertainty on temperatures through calibrated platinum resistance thermometers is estimated to be less than 0.1 K. [b] Uncertainty on pressures through the calibrated pressure transducer is estimated to be less than 5 kPa.

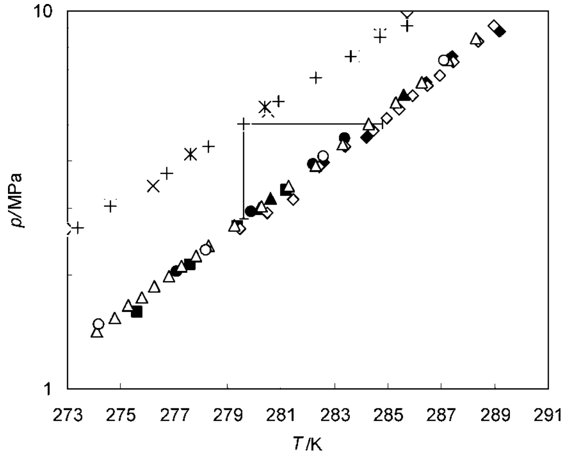

Figure 3. Experimental hydrate dissociation conditions for the methane + methyl cyclohexane + water and methane + water systems. Symbols represent experimental data. Methane + water system: ×, ref 10; +, ref 11; *, ref 12. Methane + methyl cyclohexane + water system: ○, this work; ■, ref 4; ▲, ref 5; ◆, ref 6; ●, ref 7; ◇, ref 8; △, ref 9. Pressure band: 2.2 MPa. Temperature band: 5.2 K.

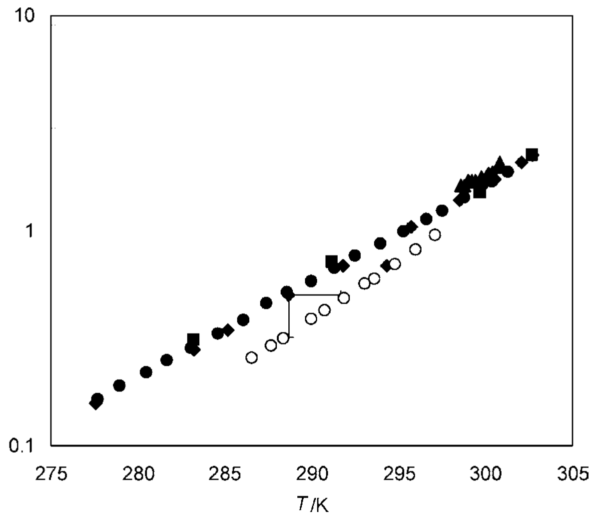

Figure 4. Experimental hydrate dissociation conditions for the hydrogen sulfide + methyl cyclohexane + water and hydrogen sulfide + water systems. Symbols represent experimental data. Hydrogen sulfide + water system: ●, ref 16; ■, ref 15; ◆, ref 14; ▲, ref 13. Hydrogen sulfide + methyl cyclohexane + water system: ○, this work. Pressure band: 0.18 MPa. Temperature band: 3 K.

literature for the methane + water[10−12] and hydrogen sulfide + water systems,[13−16] respectively, to study the hydrate promotion effects of methyl cyclohexane. It should be mentioned that hydrate promotion effect means shifting dissociation conditions of methane or hydrogen sulfide hydrates due to the presence of methyl cyclohexane in the system to low pressures/high temperatures.[1] As can be seen in Figure 3, the presence of methyl cyclohexane can increase the hydrate phase dissociation temperature of the methane + water system by approximately 5.2 K at given pressures in the temperature ranges shown in this figure. In other words, it can reduce the hydrate dissociation pressure of the methane + water system by approximately 2.2 MPa at given temperatures, indicating the promotion effect of methyl cyclohexane is considerable for the methane + water system. In Figure 4, it can be observed that the presence of methyl cyclohexane can reduce the hydrate dissociation pressure of the hydrogen sulfide + water system by approximately 0.18 MPa at given temperatures. In other words, it can increase the hydrate dissociation temperature by approximately 3 K at given pressures. Although, this hydrate promotion effect has not already been reported for the hydrogen sulfide + methyl cyclohexane + water system, it is not very considerable.

In Figures 3 and 4, the slope of the logarithm of hydrate dissociation pressure versus temperature changes when methyl cyclohexane exists in the system indicating a change in clathrate hydrate structure due to the presence of methyl cyclohexane.[1] It is well-known that the clathrate hydrates of methyl cyclohexane + methane form sH.[1] It is likely the methyl cyclohexane + hydrogen sulfide clathrate hydrates also form sH. However, the final proof for the stable hydrate structure and also the exact compositions of the latter clathrate hydrate at various temperatures require direct measurements by suitable physical techniques (e.g., NMR, X-ray, or Raman spectroscopy).

4. Conclusions

We reported hydrate dissociation data for the hydrogen sulfide + methyl cyclohexane + water and methane + methyl cyclohexane + water systems in the temperature ranges of (286.6 to 297.1) K and (274.2 to 290.4) K, respectively. An isochoric pressure-search method[2,3] was used to perform all the measurements. The measurements were first performed for the methane + methyl cyclohexane + water system, and the comparisons between the experimental data measured in this work and the literature data[4−9] showed acceptable agreement confirming the reliability of the isochoric pressure-search method[2,3] used in this work. We then reported novel hydrate dissociation data for the hydrogen sulfide + methyl cyclohexane + water system, for which there is no information in the literature. The comparison of the hydrate dissociation data for the above-mentioned ternary systems with the experimental data reported in the literature for the binary systems of methane + water[10−12] and hydrogen sulfide + water[13−15] showed that methyl cyclohexane can reduce hydrate dissociation pressures. Although the promotion effect of methyl cyclohexane on the methane + water system is not ignorable, it is not very considerable on the hydrogen sulfide + water system.

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Received for review April 21, 2009. Accepted July 22, 2009. The financial support of Agence Nationale de la Recherche (ANR) is gratefully acknowledged.

JE900368Z