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Clathrate Hydrates of Cyclohexane + Hydrogen Sulfide and Cyclohexane + Methane: Experimental Measurements of Dissociation Conditions

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In this work, experimental hydrate dissociation data for the hydrogen sulfide + cyclohexane + water and methane + cyclohexane + water systems are reported in the temperature ranges of (288.3 to 298.2) K and (274.1 to 292.8) K, respectively. The experimental data were generated using an isochoric pressure search method. The hydrate dissociation data for the methane + 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 cyclohexane reported in the literature to identify the hydrate promotion effects of cyclohexane.

Introduction

Clathrate hydrates or gas hydrates are ice-like solid crystalline compounds, which are formed through a combination of water and small guest molecules, like methane, under low temperatures and elevated pressures.[1] In the clathrate lattice, water molecules form hydrogen-bonded cage-like structures, encapsulating the guest molecule(s).[1] The clathrate hydrate crystalline structures are those of structure I (sI), structure II (sII), and structure H (sH), where each structure is composed of a certain number of cavities formed by water molecules.[1] The formation of structure H and also structure II with some heavy molecules, like normal butane and cyclohexane, requires the presence of two large and small guest molecules. Large molecules occupy large cavities, while small molecules (called a help gas) fill the remaining cavities.[1] It has been reported that cyclohexane can form structure II of clathrate hydrates with a help gas like methane.[1] However, the information on other help gases is limited. To our knowledge, there is no information on clathrate hydrate formation of cyclohexane with hydrogen sulfide as a help gas.

In this work, clathrate hydrate dissociation data for the hydrogen sulfide + cyclohexane + water and the methane + cyclohexane + water systems are reported in the temperature ranges of (288.3 to 298.2) K and (274.1 to 292.8) K, respectively. The experimental data were generated using an isochoric pressure search method.[2,3] As clathrate hydrate dissociation data for the methane + cyclohexane + water system have already been reported in the literature, therefore, we first generated and report some experimental data for the latter system and compare them with some selected experimental data from the literature[4,5] to demonstrate the reliability of the experimental method used in our work. We then report clathrate hydrate dissociation data for the hydrogen sulfide + 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[6−8] and hydrogen sulfide + water[9−12] systems to identify the hydrate promotion effects of cyclohexane.

Table 1. Purities and Suppliers of Materials[a]

material	supplier	purity
hydrogen sulfide	Air Liquide	99.9 (volume %)
methane	Messer Griesheim	99.995 (volume %)
cyclohexane	Fluka	≥ 99.8 % (gas chromatograph, %)

[a] Deionized water was used in all experiments.

Experimental Section

Table 1 reports the purities and suppliers of the materials used.

Figure 1 shows the schematic diagram of the apparatus used in this work.[9] 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 are 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).

The liquid water + liquid hydrocarbon + hydrate + vapor/gas equilibria conditions were measured with an isochoric pressure search method.[2,3] The vessel containing liquids (approximately 10 % of the volume of the vessel was filled by water and 10 % of the volume by 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 the introduction of any liquid and gas. After obtaining temperature and pressure stability (far enough from the hydrate formation region), the valve in the line connecting the vessel and the cylinder was

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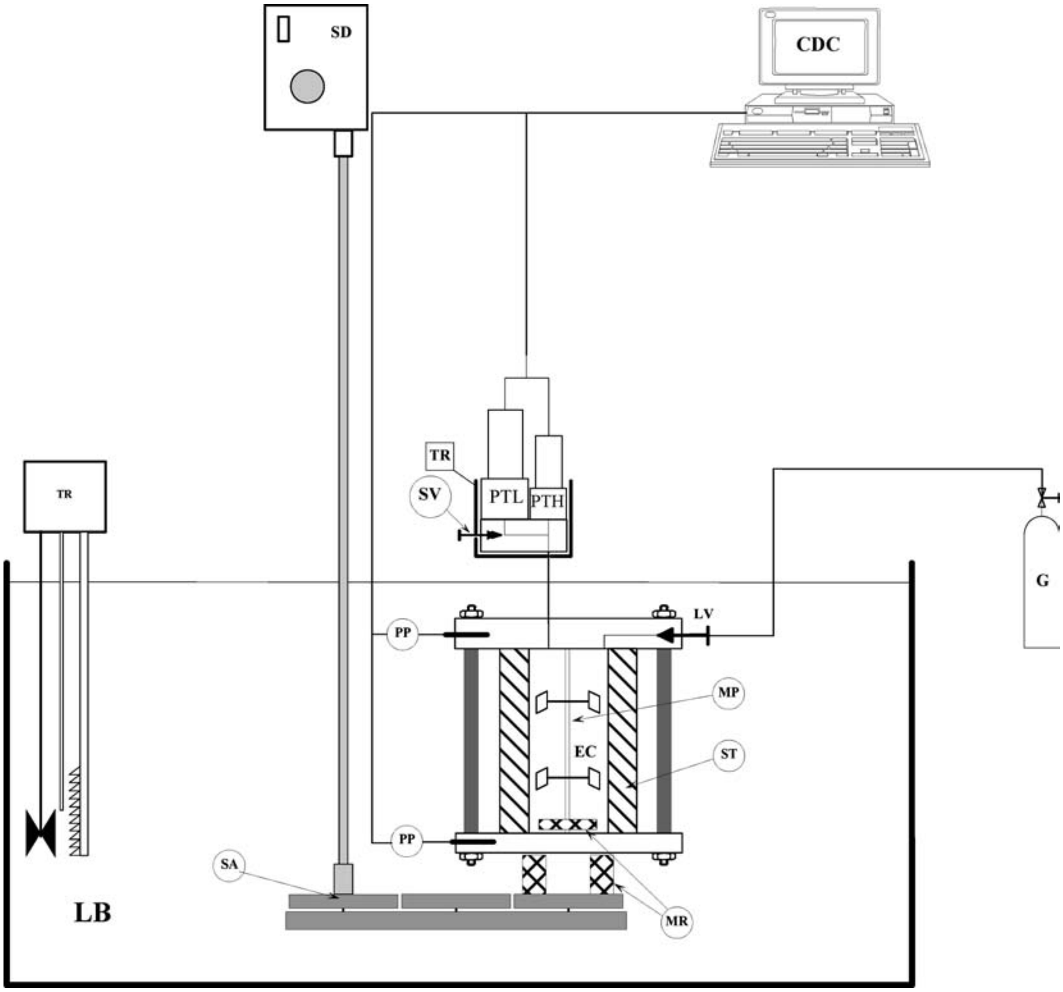

Figure 1. Flow diagram of the experimental setup used to measure hydrate dissociation conditions.[9] Descriptions: CDC, central desktop computer; EC, equilibrium cell; G, gas cylinder; LB, liquid bath; LV, loading valve; MP, multiple propeller; MR, magnetic rod; PP, platinum probe (temperature sensor); 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.

closed. Subsequently, temperature was slowly decreased to form the hydrate. Hydrate formation in the vessel was detected by 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.[2,13] 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.[2,13] Consequently, the point at which the slope of pressure−temperature data plots changes sharply is considered to be the point at which all hydrate crystals have dissociated and hence reported as the dissociation point.[2,13]

Experimental Results

All of the experimental data are reported in Table 2 and are plotted in Figures 2 and 3. As mentioned earlier, we first measured the hydrate dissociation conditions for the methane + cyclohexane + water system. As can be observed in Figure 2, the experimental data measured in this work for the latter system are in acceptable agreement with the experimental data reported in the literature,[4,5] demonstrating the reliability of the experimental method[2,3] used in this work. In Figures 2 and 3, we have shown some selected experimental data from the literature for the methane + water[6−8]

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

T^a	p^b
K	MPa
Methane + Cyclohexane + Water	
274.1	0.651
277.2	1.059
281.7	2.028
286.4	4.078
292.8	10.328
Hydrogen Sulfide + Cyclohexane + Water	
288.3	0.202
289.6	0.240
290.9	0.294
292.1	0.344
293.5	0.440
295.0	0.541
295.6	0.609
296.7	0.721
297.3	0.791
298.2	0.937

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

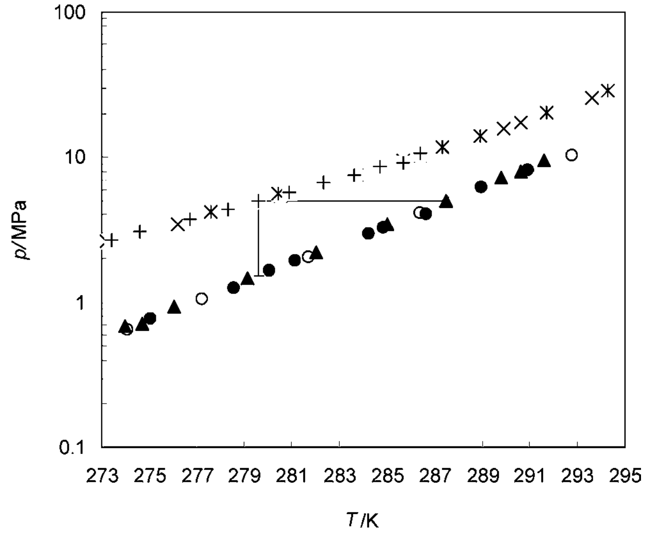

Figure 2. Experimental hydrate dissociation conditions for the methane + cyclohexane + water and methane + water systems. Symbols represent experimental data. Methane + water system: ×, ref 6; +, ref 7; *, ref 8. Methane + cyclohexane + water system: ○, this work; ▲, ref 4; ●, ref 5. Pressure band: 3.5 MPa. Temperature band: 8 K.

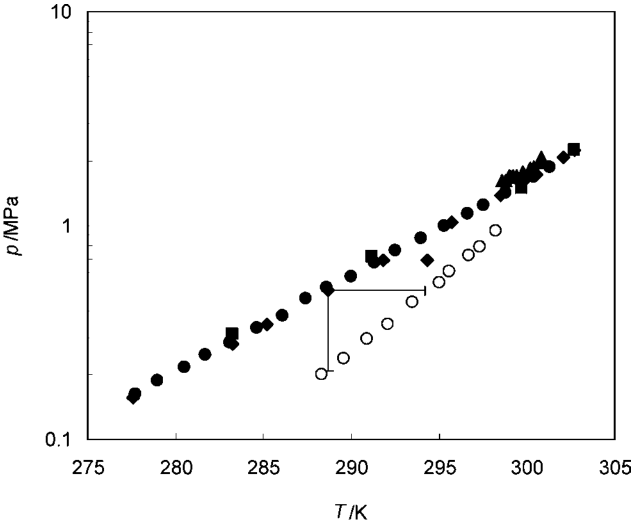

Figure 3. Experimental hydrate dissociation conditions for the hydrogen sulfide + cyclohexane + water and hydrogen sulfide + water systems. Symbols represent experimental data. Hydrogen sulfide + water system: ●, ref 9; ▲, ref 10; ♦, ref 11; ■, ref 12. Hydrogen sulfide + cyclohexane + water system: ○, this work. Pressure band: 0.3 MPa. Temperature band: 5.5 K.

and hydrogen sulfide + water systems,[9−12] respectively, to identify the hydrate promotion effects of cyclohexane. Note that hydrate promotion effect means shifting dissociation conditions of methane or hydrogen sulfide simple hydrates due to the presence of cyclohexane to low pressures and high temperatures. As can be seen in Figure 2, the presence of cyclohexane can increase the hydrate phase dissociation temperature of the methane + water system by approximately 8 K in the temperature range shown in this figure. In other words, it can reduce the hydrate dissociation pressure of the methane + water system by approximately 3.5 MPa at given temperatures, indicating the hydrate promotion effect of cyclohexane is considerable for the methane + water system. In Figure 3, it can be observed that the presence of cyclohexane can reduce the hydrate dissociation pressure of the hydrogen sulfide + water system by approximately 0.3 MPa at given temperatures. In other words, it can increase the hydrate dissociation temperature to approximately 5.5 K at given pressures. This hydrate promotion effect has not been reported for the hydrogen sulfide + cyclohexane + water system and is relatively considerable. Like the clathrate hydrates of cyclohexane + methane, it is likely that the clathrate hydrates of cyclohexane + hydrogen sulfide also form structure II. However, suitable physical techniques (e.g., NMR, Raman spectroscopy, or X-ray) are required for final confirmation.

Conclusions

We reported experimental hydrate dissociation data for the hydrogen sulfide + cyclohexane + water and methane + cyclohexane + water systems in the temperature ranges of (288.3 to 298.2) K and (274.1 to 292.8) K, respectively (Table 2). An isochoric pressure search method[2,3] was used to perform all of the measurements. The measurements were first performed for the methane + cyclohexane + water system, and the comparisons between the experimental data reported in this work and the literature data[4,5] showed acceptable agreement, confirming the reliability of the isochoric pressure search method[2,3] used in our work. We then reported novel hydrate dissociation data for the hydrogen sulfide + cyclohexane + water system, for which there is no information in the literature. The comparison of the hydrate dissociation data for the above-mentioned systems with the corresponding experimental data reported in the literature in the absence of cyclohexane[6−12] showed that the latter compound can reduce hydrate dissociation pressures and therefore can be regarded as a hydrate promoter. The hydrate promotion effects of cyclohexane for the methane + water and hydrogen sulfide + water systems were found generally considerable, especially for the methane + water system (Figures 2 and 3). The financial support of Agence Nationale de la Recherche (ANR) is gratefully acknowledged.

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