Equilibrium Data of Carbonyl Sulfide and Hydrogen Sulfide Clathrate Hydrates

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In this communication, we report equilibrium data for carbonyl sulfide and hydrogen sulfide clathrate hydrates in the temperature ranges of (274.7 to 281.5) K and (277.7 to 301.3) K, respectively. The experimental data were measured using an isochoric pressure search method. The new equilibrium data for hydrogen sulfide clathrate hydrates are compared with the experimental data reported in the literature, and the acceptable agreements demonstrate the reliability of the experimental method used in this work.

Introduction

Petroleum fluids are normally saturated/produced with water. One serious problem that can cause equipment blockage as well as operational, safety, and economical problems is formation of gas hydrates. Gas hydrates (or clathrate hydrates) are solid ice-like crystalline compounds, which are formed from the combination of water and small guest molecules. The most common gas hydrate structures are those of structure I (*s*I) and structure II (*s*II), where each structure is composed of a certain number of large and small cavities formed by water molecules.[1] In a gas hydrate molecule, the guests are trapped inside the cavities. Comprehensive studies have been made on hydrate phase equilibria of hydrocarbons.[1] Production, transportation, and processing of sour petroleum fluids have increased the interest in gas hydrate phase equilibria of acid gases and sulfur species. The information on hydrate phase equilibria of acid gases and sulfur species is also important when studying acid gas capture and sequestration by gas hydrates.

Carbonyl sulfide is a suitably sized guest molecule, which is believed to form mostly structure I gas hydrate.[1,2] Indeed, very limited information is available in the literature for this clathrate hydrate.[1,2] To the best of our knowledge, there is no phase equilibrium data for carbonyl sulfide clathrate hydrates. On the other hand, few sets of phase equilibrium data for hydrogen sulfide clathrate hydrates have been reported in the literature.[1,3−5]

In this work, we report equilibrium data of carbonyl sulfide and hydrogen sulfide clathrate hydrates. The experimental technique is similar to our previous experimental works,[6,7] which take advantage of an isochoric pressure search method.[6−8] The dissociation pressures have been measured for carbonyl sulfide hydrates in the temperature range of (274.7 to 281.5) K and for hydrates of hydrogen sulfide in the temperature range of (277.7 to 301.3) K. The dissociation data of hydrogen sulfide hydrates are compared with the experimental data reported in the literature,[3−5] and the acceptable agreements demonstrate the reliability of the experimental method used in this work.

Experimental Section

Table 1 reports the purities and suppliers of the chemicals used in this work. Figure 1 shows the schematic picture of the apparatus used in our study. Briefly, the main part of the

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Table 1. Purities and Suppliers of Materials[a]

chemical	supplier	purity (mole fraction)
carbonyl sulfide	air liquide	0.99
hydrogen sulfide	air liquide	0.999

[a] Deionized water was used in all experiments.

apparatus is a sapphire cylindrical vessel, which can withstand pressures higher than 10 MPa. The volume of the vessel is 33.1 cm³. A stirrer was installed in the vessel to agitate the fluid and hydrate crystals inside it. Two platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperature 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 careful 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 8) MPa, respectively). Pressure measurement uncertainties are estimated to be less than 5 kPa, as a result of careful calibration against a dead weight balance (Desgranges and Huot, model 520).

The liquid water + hydrate + vapor equilibrium conditions were measured with an isochoric pressure search method.[6−8] The vessel containing pure water (approximately 15 % by volume of the vessel was filled by water) was immersed into the temperature-controlled bath, and the gas was supplied from a high-pressure 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 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, temperature was kept constant with sufficient time to achieve a steady 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.[6,7,9] 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
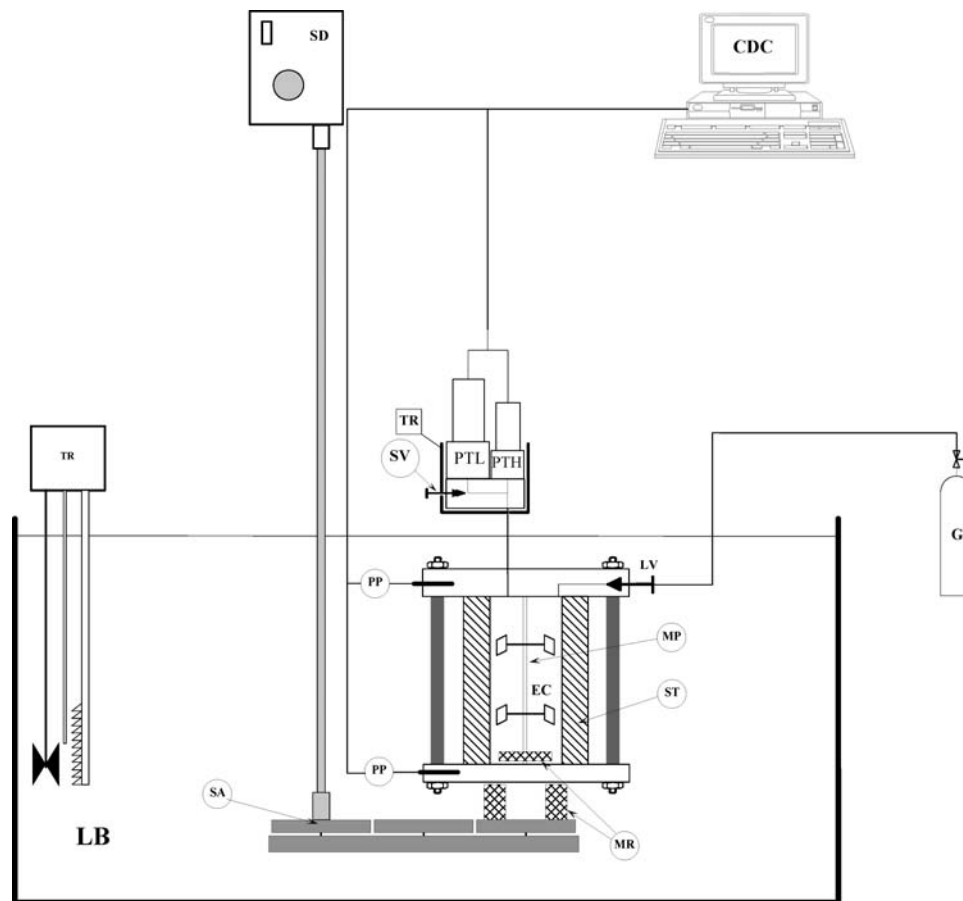
Figure 1. Flow diagram of the experimental setup used to measure hydrate dissociation points.[10] Descriptions: CDC, Central Desktop Computer; EC, Equilibrium Cell; G, Gas Cylinder; LB, Liquid Bath; LV, Loading Valve; MP, Multiple Propeller; MR, Magnetic Rod; PP, Platinum Probe (Temperature Sensor); 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.

observed as a result of the change in the phase equilibria of the fluids in the vessel.[6,7,9] 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.[6,7,9]

Results and Discussion

We first started our measurements with hydrogen sulfide to check the compatibility of the materials used in our apparatus with corrosion. The new equilibrium data of hydrogen sulfide clathrate hydrates are reported in Table 2 and are plotted in Figure 2. This figure also shows the selected experimental data reported in the literature.[3–5] As can be observed, the agreements are generally acceptable demonstrating the reliability of the experimental method used in this work. However, it should be mentioned that the experimental data reported in refs 3 and 4 are the most reliable among the experimental data previously reported in the literature.

Table 3 reports estimated dissociation conditions of carbonyl sulfide clathrate hydrates in the presence of pure water. These data are also plotted in Figure 2. It should be mentioned that COS hydrolysis in the presence of water is an important factor that should be considered in the COS + water (or any aqueous solution) phase equilibria studies. Hydrolysis of COS can be expressed by the following equation[10]

$$COS + H_2O \rightarrow H_2S + CO_2 \qquad (1)$$

Table 2. Experimental Dissociation Data for Hydrogen Sulfide Clathrate Hydrates

T/K^a	p/MPa^b
277.7	0.164
279.0	0.188
280.5	0.218
281.7	0.247
283.1	0.283
284.6	0.332
286.1	0.380
287.4	0.458
288.6	0.514
290.0	0.578
291.3	0.672
292.5	0.764
294.0	0.865
295.3	0.988
296.6	1.131
297.5	1.237
298.8	1.425
300.4	1.692
301.3	1.861

^{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 transducer is estimated to be less than 5 kPa.

A recent gas chromatography study has confirmed that the rate of H_2S and CO_2 productions due to COS hydrolysis at temperatures below 288.15 K is very low over any time.[10] Having this in mind, we can safely assume that the COS clathrate hydrates formed in this work are, at least, very rich of COS. However, final proof for the stable hydrate structure at
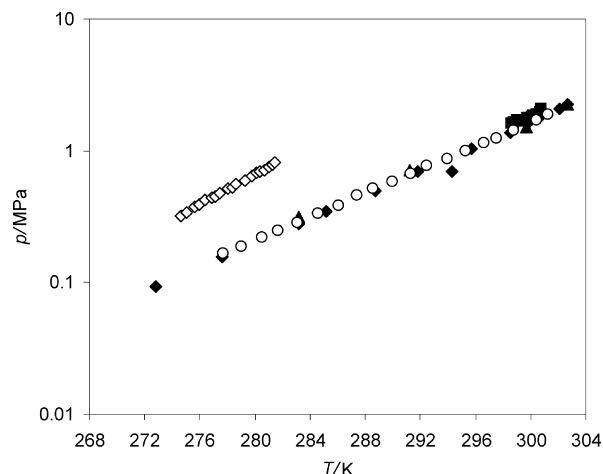
Figure 2. Experimental dissociation conditions of carbonyl sulfide and hydrogen sulfide clathrate hydrates in the presence of pure water. $\diamond$, Experimental dissociation data of COS hydrates, this work; $\bigcirc$, Experimental dissociation data of H_2S hydrates, this work; $\blacktriangle$, Experimental dissociation data of H_2S hydrates, literature;[3] $\blacklozenge$, Experimental dissociation data of H_2S hydrates, literature;[4] $\blacksquare$, Experimental dissociation data of H_2S hydrates, literature.[5]

Table 3. Experimental Dissociation Data for Carbonyl Sulfide Clathrate Hydrates

T/K^a	p/MPa^b
274.7	0.320
275.1	0.341
275.7	0.375
276.0	0.390
276.4	0.420
276.9	0.440
277.2	0.451
277.5	0.476
278.1	0.514
278.4	0.530
278.7	0.555
279.3	0.596
279.8	0.635
280.2	0.675
280.4	0.690
280.7	0.712
281.1	0.750
281.3	0.781
281.5	0.810

[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 transducer is estimated to be less than 5 kPa.

various temperatures and also compositions of COS clathrate hydrates requires direct measurements by suitable physical techniques (e.g., NMR, X-ray, or Raman spectroscopy). The comparison between the experimental hydrate dissociation data for carbonyl sulfide and hydrogen sulfide in Figure 2 shows that the dissociation temperature of carbonyl sulfide clathrate hydrates is lower than the dissociation temperature of hydrogen sulfide clathrate hydrates at given pressures.

Conclusions

We reported experimental hydrate dissociation data for carbonyl sulfide in the temperature range of (274.7 to 281.5) K and for hydrogen sulfide in the temperature range of (277.7 to 301.3) K. The experimental data were measured using an isochoric pressure search method.[6−8] The new dissociation data of hydrogen sulfide clathrate hydrates were generally in acceptable agreement with the experimental data reported in the litearture.[3−5] This study showed that the dissociation temperature of carbonyl sulfide clathrate hydrates is lower than the dissociation temperature of hydrogen sulfide clathrate hydrates at given pressures.

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