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Equilibrium of Hydrogen + Cyclopentane and Carbon Dioxide + Cyclopentane Binary Hydrates[†]

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Cyclopentane (CP) forms sII hydrates, in which CP only occupies the large cavities. Small gas molecules such as hydrogen and carbon dioxide can be encaged in the small cavities. However, there are no reported data on the equilibrium conditions of CP + H_2 and CP + CO_2 binary hydrates, which are essential to developing CO_2 capturing or H_2 enriching processes. In this study, the dissociation temperature of CP + H_2 hydrate pressures ranging from (2.7 to 11.1) MPa and CP + CO_2 hydrates at pressures of (0.89 to 3.51) MPa was measured by using a high-pressure MicroDSC.

Introduction

Gas hydrates are crystalline compounds in which small molecules such as methane, nitrogen, carbon dioxide, hydrogen, etc. stabilize the cavities formed by hydrogen-bonded water molecules.[1,2] The equilibrium condition of gas hydrates is predominately determined by the nature of hydrate formers; e.g., the dissociation pressure is 300 MPa for H_2 hydrates[3] and 2.91 MPa for CO_2 hydrates[1] at 280 K, indicating that CO_2 preferably occupies the water cavities at the lower pressure. Therefore, it is possible to remove CO_2 from the H_2 + CO_2 mixture by hydrate formation.

The concentration of CO_2 in the precombustion stream after gasification is around (20 to 40) v/v % with a typical total pressure of (2.5 to 5) MPa.[4] Having a large enough driving force for CO_2 removal in the hydrate form is related to reducing the equilibrium pressure of CO_2 hydrates. To reduce the equilibrium pressure of CO_2 hydrates, one approach is to reduce the crystallization temperature, but it increases the operating cost due to further cooling. Another option is to add a small amount of organic compounds such as tetrahydrofuran (THF),[5] tetrabutylammonium bromide (TBAB),[6] and cyclopentane (CP).

Cyclopentane (CP) is known to form sII hydrates with a melting point higher than that of THF hydrates at atmospheric pressure.[7,8] Many studies have reported the dissociation conditions of binary hydrates of THF with different gases, such as H_2,[9,10] CO_2,[5] CH_4,[11] etc. However, there were a few studies on the equilibrium data of binary hydrates of CP with a gas,[12–14] and no equilibrium data are available for the binary hydrates of CP with hydrogen and CO_2. The equilibrium condition of these binary hydrates is important in designing the CO_2 capturing processes of precombustion. In this work, the dissociation temperatures of CP + H_2 hydrates in a pressure range of (2.7 to 11.1) MPa and those of CP + CO_2 hydrates in a pressure range of (0.89 to 3.51) MPa are presented.

Experimental Section

Materials. Cyclopentane with a certified purity of > 95 % was purchased from Sigma-Aldrich. H_2 was supplied by Labelmaster with a purity of 99 %, and CO_2 was obtained from T. W. Smith with a minimum purity of 99 %. All chemicals were used as received without further purification. Deionized water was produced in our laboratory with a resistivity of 17 $m\Omega \cdot cm^{-1}$.

Apparatus. Figure 1 shows the schematic diagram of the experimental setup to measure the dissociation temperatures of hydrates using a high-pressure MicroDSCVII (SETARAM). The principle of this technology was described in detail by Le Parlouër et al.[15] This high-pressure differential scanning calorimetry is less time-consuming compared to the classical PVT technique. Several studies have indicated that this technique is accurate enough to determine the equilibrium conditions of gas hydrates.[15–17]

Dalmazzone et al.[17] compared the dissociation temperature of methane hydrates by using a classical thermodynamic method (PVT) and a calorimetric method (DSC), and they concluded that PVT and DSC results are in good agreement with data available in the literature.

The high-pressure cells with a volume of 0.33 cm^3 are made of hastelloy, and they can be operated up to 40 MPa and at temperatures between (233.2 and 393.2) K. The uncertainty of temperature measurement stated by the manufacturer is ± 0.02 K. The MicroDSC was calibrated with *n*-decane (274.51 K), water (273.15 K), and naphtalane (353.38 K). The pressure of the sample cell is measured by using an ITS-5 M pressure transducer (ONEhalf20, (0 to 34.47) MPa) with the uncertainty of ± 0.05 MPa. The temperature, heat flow, and pressure of the sample cell are sampled by the SETSOFT interface. The onset temperature of the endothermic peak is taken as the dissociation temperature or the melting point.

Procedures. About 0.01 cm^3 DI water and 0.015 cm^3 CP were charged to the sample cell, followed by purging the gas phase with the test gas (H_2 or CO_2) twice. For the CP + water system, the dissociation conditions were measured at 0.1 MPa air. The sample cell was then pressurized with the test gas to a desired pressure. The cells were cooled down to 242.6 K and then heated up to 274.3 K for CP + water and CP + H_2 + water systems and 281.3 K for the CP + CO_2 + water system. The CP + water and CP + H_2 + water systems were held at 274.3 K for 2 h and then heated up to 293.2 K. The CP + CO_2 + water system was kept at 281.3 K for 0.5 h and then heated

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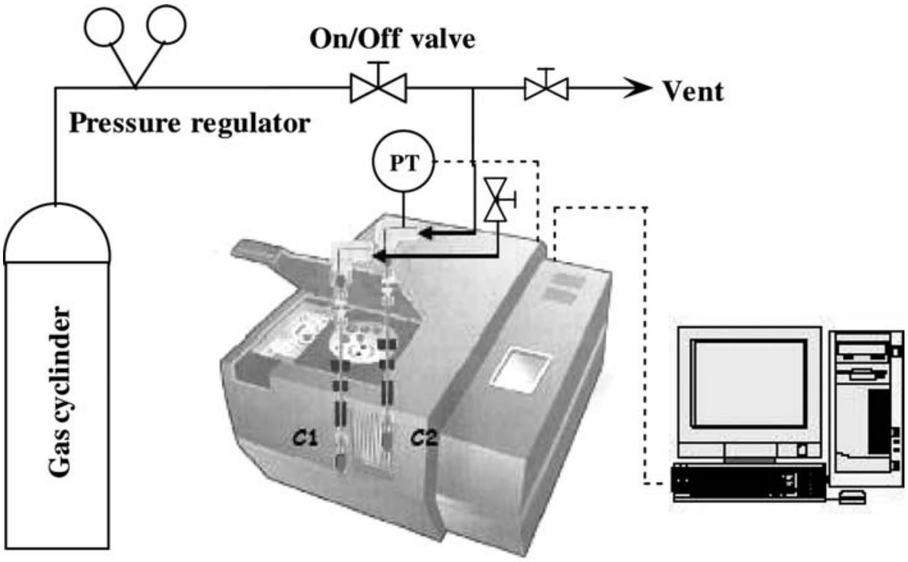

Figure 1. Schematic diagram of the experimental setup (modified from Parlouër[15]).

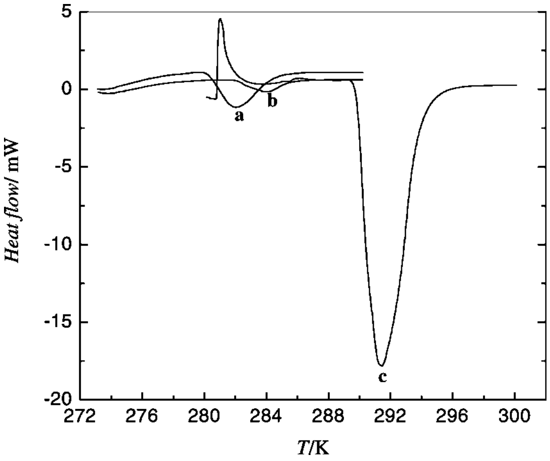

Figure 2. Thermograph of CP + water, CP + water + H_2, and CP + water + CO_2 hydrates: a, CP + water; b, CP + water + H_2, P = 4.94 MPa; c, CP + water + CO_2, P = 1.84 MPa.

Table 1. Dissociation Temperatures of CP + H_2 at Different Pressures

T/K	P/MPa (± 0.05 MPa)
280.68 ± 0.01	2.70
281.56 ± 0.01	4.94
282.36 ± 0.02	7.00
283.07 ± 0.01	9.04
283.72 ± 0.02	11.09

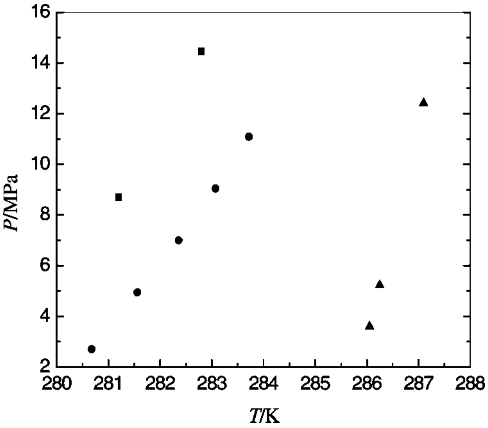

Figure 3. Dissociation conditions for H_2 binary hydrates: ■, THF + H_2, weight fraction of THF = 0.1907;[9] ●, CP + H_2; ▲, TBAB + H_2, weight fraction of TBAB = 0.43.[6]

Table 2. Dissociation Temperatures of CP + CO_2 at Different Pressures

T/K	P/MPa (± 0.05 MPa)
286.65 ± 0.16	0.89
289.00 ± 0.01	1.50
289.86 ± 0.10	1.84
291.42 ± 0.10	2.23
292.19 ± 0.04	2.72
292.40 ± 0.09	3.11
292.61 ± 0.13	3.51

up to 303.2 K. The measurement at each data point was repeated three times, and the average value with the precision of measurement was reported in this work.

Results and Discussions

A typical DSC thermograph of the CP + water + gas (H_2 or CO_2) system is given in Figure 2 where the heating curves for three different hydrates are presented. Curve a is the heating curve for the CP hydrate, while curves b and c are representing the heating curves for the CP + H_2 and CP + CO_2 hydrates. In curve c, there is an exothermic peak, which indicates the formation of hydrates from the unconverted water before the dissociation of the CP + CO_2 hydrates.

Melting Point of Ice and CP Hydrates. The melting point of ice is (273.69, 273.46, and 273.01) K at a heating rate of 0.25 $K \cdot min^{-1}$, 0.5 $K \cdot min^{-1}$, and 1 $K \cdot min^{-1}$, respectively. The heating rate of 1 $K \cdot min^{-1}$ was used in this work to determine the dissociation temperature of hydrates since the ice melting point at this rate is the closest to 273.15 K. The difference between the melting point reported here and the literature value is due to the systematic or gross error. The small difference may be noted with the real temperature due to the thermal gradient and the time for the heat to cross the cell wall and the detector, although the measurement is carried out in the sample.

Figure 2 shows that the melting point of CP hydrates is (280.17 ± 0.16) K at atmospheric pressure. Werezak[8] reported the melting point of CP hydrates is 280.85 K, which is 0.63 K higher than the quadruple point temperature (280.22 K) of the CP + water system.[18] This quadruple point temperature determined by PVT measurements can be more reliable than

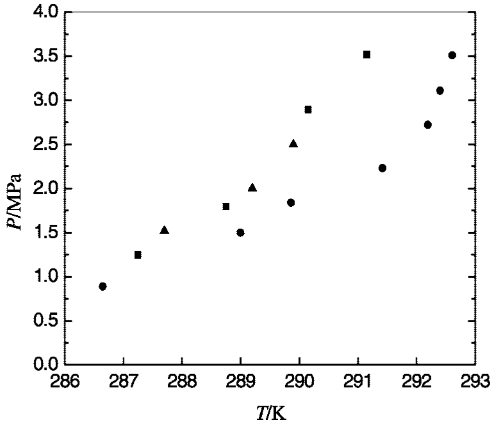

Figure 4. Dissociation conditions for CO_2 binary hydrates: ■, THF + CO_2, weight fraction of THF = 0.1097;[5] ●, CP + H_2; ▲, TBAB + CO_2, weight fraction of TBAB = 0.427.[6]

the reported melting point because no detail of apparatuses and procedures was presented by Werezak.[8] The quadruple point temperature is almost identical to the melting point, like a very small difference between the ice melting point and the triple point of water. The melting point of CP hydrates (280.17 K) presented here is very close to the reported quadruple point temperature (280.22 K), suggesting that the heating rate of 1 $K \cdot min^{-1}$ is sufficient for determining the dissociation temperature of hydrates in our MicroDSC.

CP + H_2 Hydrates. The dissociation temperature of CP + H_2 hydrates at pressures between (2.7 and 11.1) MPa is summarized in Table 1, and the results are also plotted in Figure 3. The dissociation temperature of CP + H_2 hydrates is lower than that of TBAB + H_2 hydrates[6] but higher than that of THF + H_2 hydrates.[9] This trend coincides with the melting point of THF hydrates, CP hydrates, and TBAB semiclathrate hydrates.

CP + CO_2 Hydrates. The dissociation temperature of CP + CO_2 at pressures of (0.89 to 3.51) MPa is listed in Table 2, and the results are also plotted in Figure 4. The dissociation temperature of CP + CO_2 is a little higher than that of TBAB + CO_2 and THF + CO_2 hydrates[5,6] at the same pressures, while the dissociation temperature of TBAB + CO_2 is close to that of THF + CO_2 hydrates. The effect of THF, CP, and TBAB on the equilibrium conditions of CO_2 binary hydrates does not follow the order of the melting point of THF hydrates, CP hydrates, and TBAB semiclathrate hydrates. One possible explanation is that the high concentration of dissolved CO_2 in aqueous phase has a significant effect on the activity of THF and TBAB.

Conclusion

The dissociation temperatures of CP + H_2 hydrates in a pressure range of (2.7 to 11.1) MPa and those of CP + CO_2 hydrates at pressures of (0.89 to 3.51) MPa were determined by using a high-pressure MicroDSC. The dissociation temperatures of H_2 binary hydrates with other hydrate promoters are strongly dependent on the nature of the promoters. However, the dissociation temperature of CO_2 binary hydrates is less affected by the property of the other hydrate promoters.

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