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Equilibrium Data of Sulfur Dioxide and Methyl Mercaptan Clathrate Hydrates

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ABSTRACT: In this communication, we report dissociation pressures for sulfur dioxide clathrate hydrates in the temperature range of (279.9 to 285.2) K and for clathrate hydrates of methyl mercaptan in the temperature range of (283.4 to 285.0) K. The experimental data were measured using an isochoric pressure-search method. It is shown that the dissociation pressure of sulfur dioxide clathrate hydrates is higher than the dissociation pressure of methyl mercaptan clathrate hydrates in the temperature ranges studied in our work.

INTRODUCTION

Clathrate hydrates, or gas hydrates, are solid crystalline compounds stabilized by the inclusion of suitably sized guest molecule(s) inside cavities, of different sizes, formed by water molecules through hydrogen bonding.[1,2] The common clathrate hydrate crystalline structures are 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 large (and medium, in case of structure H) and small cavities formed by water molecules.[1,2] It is believed that sulfur dioxide and methyl mercaptan (or methanethiol) can form a structure I clathrate hydrate.[1,2] Currently, very limited information is available in the literature for the latter clathrate hydrates.[1,2] In 1829, it was shown that sulfur dioxide forms clathrate hydrates.[1,2] Later, in 1887, it was proven that methyl mercaptan also forms clathrate hydrates.[1,2] There are few sets of experimental data on phase boundaries of sulfur dioxide clathrate hydrates: Bakhuis Roozeboom,[3] Tamman and Krige,[4] and van Berkum and Diepen[5] reported three different liquid water−hydrate−liquid sulfur dioxide phase boundaries. In addition, van Berkum and Diepen[5] studied the inconsistencies among the literature data.[3−5] Bakhuis Roozeboom,[3] Tamman and Krige,[4] von Stackelberg,[6] von Stackelberg and Müller,[7] Davidson,[2] and Chinworth and Katz[8] reported few experimental data on the liquid water−hydrate−vapor sulfur dioxide phase boundary. No further work on investigating the reliability of the latter experimental data has been reported yet. However, Tamman and Krige[4] showed that their experimental data are in good agreement with the experimental data of Bakhuis Roozeboom,[3] which has been reported graphically by Davidson.[2] To our knowledge, Bakhuis Roozeboom[3] and Tamman and Krige[4] reported the ice−hydrate−vapor sulfur dioxide phase boundaries. Again, Tamman and Krige[4] showed that their experimental data are in good agreement with the experimental data of Bakhuis Roozeboom,[3] which has been reported graphically by Davidson.[2] von Stackelberg,[6] von Stackelberg and Müller,[7] and later Davidson[2] reported very few experimental data on the liquid water−hydrate−vapor methyl mercaptan phase boundary. Again, no further work on investigating the reliability of the latter experimental data has been reported yet. The National Institute of Standards and Technology (NIST)[9] has recently developed a gas hydrate database reporting only the experimental data of von Stackelberg[6] and von Stackelberg and Müller[7] for the liquid water−hydrate−vapor methyl mercaptan phase boundary, while the experimental data of von Stackelberg[6] and von Stackelberg and Müller[7] for the liquid water−hydrate−vapor sulfur dioxide phase boundary and the experimental data of van Berkum and Diepen[5] for the liquid water−hydrate−liquid sulfur dioxide phase boundary are reported. Figure 1 shows all of the literature data for the liquid water−hydrate−vapor phase boundary of sulfur dioxide and methyl mercaptan clathrate hydrates. As can be seen, the literature data are not generally in good agreement with each other. The above literature review therefore warrants new phase equilibria measurements for sulfur dioxide and methyl mercaptan clathrate hydrates.

This work aims at studying the liquid water + hydrate + vapor equilibrium conditions of sulfur dioxide and methyl mercaptan clathrate hydrates. A previously reported experimental apparatus,[10,11] which takes advantages of an isochoric pressure-search method,[10−12] has been used for performing the measurements. The dissociation pressures were measured for sulfur dioxide clathrate hydrates in the temperature range of (279.9 to 285.2) K and for clathrate hydrates of methyl mercaptan in the temperature range of (283.4 to 285.0) K. The dissociation data of sulfur dioxide and methyl mercaptan clathrate hydrates are finally compared with the hydrate dissociation data of hydrogen sulfide and carbonyl sulfide reported in the literature.[10]

EXPERIMENTAL SECTION

Table 1 reports the purities and supplies of the chemicals used in this work.

A description of the experimental setup used in this study is given elsewhere.[10,11] 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

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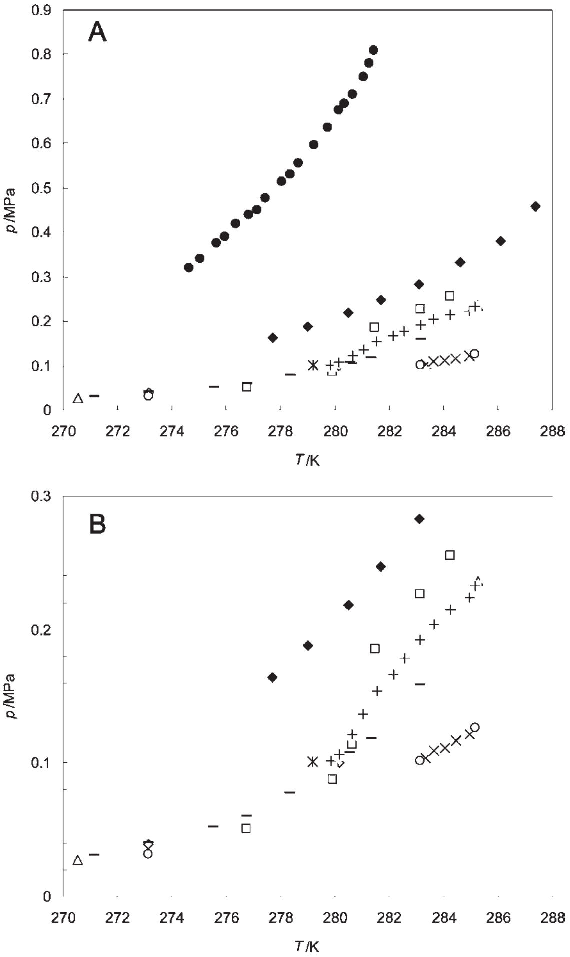

Figure 1. (A) Experimental liquid water + hydrate + vapor equilibrium conditions for clathrate hydrates of carbonyl sulfide, hydrogen sulfide, sulfur dioxide, or methyl mercaptan in the presence of water. Symbols represent experimental data. Carbonyl sulfide clathrate hydrates: ●, ref 10. Hydrogen sulfide clathrate hydrates: ♦, ref 10. Sulfur dioxide clathrate hydrates: —, ref 4; □, ref 8; +, this work; ◇, ref 6, 7; △, ref 2 (the experimental data of ref 3 have not been shown but have been reported graphically in ref 2). Methyl mercaptan clathrate hydrates: ○, ref 2; ×, this work; ∗, ref 6, 7. (B) Experimental liquid water + hydrate + vapor equilibrium conditions for clathrate hydrates of hydrogen sulfide, sulfur dioxide, or methyl mercaptan in the presence of water (different zoom). Symbols represent experimental data. Hydrogen sulfide clathrate hydrates: ♦, ref 10. Sulfur dioxide clathrate hydrates: —, ref 4; □, ref 8; +, this work; ◇, ref 6, 7; △, ref 2 (the experimental data of ref 3 have not been shown but have been reported graphically in ref 2). Methyl mercaptan clathrate hydrates: ○, ref 2; ×, this work; ∗, ref 6, 7.

Table 1. Purities and Suppliers of Chemicals[a]

chemical	supplier	purity (mole fraction)
sulfur dioxide	Air Liquide	0.99
methyl mercaptan	Aldrich	0.995+

[a] Deionized water was used in all experiments.

installed in the vessel to agitate the fluids and hydrate crystals inside it. 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 a Druck pressure transducer (Druck, type PTX611 for pressures up to 2.5 MPa). Pressure measurement uncertainty is 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 + hydrate + vapor equilibrium conditions were measured with an isochoric pressure-search method.[10−12] The reliability of this method has already been examined and reported in ref 10. The vessel containing water (approximately 10 % by volume of the vessel was filled by water) 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 water 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, the temperature was slowly decreased to form the hydrate. Hydrate formation in the vessel was detected by the 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 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.[10,11,13] 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 temperature change of the fluids in the vessel.[10,11,13] 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.[10,11,13]

■ EXPERIMENTAL RESULTS

All experimental dissociation data measured in this work are reported in Table 2 and are plotted in Figure 1. This figure also shows the experimental data reported in the literature for sulfur dioxide, methyl mercaptan, carbonyl sulfide, and hydrogen sulfide clathrate hydrates. As can be observed, the few experimental data reported by von Stackelberg and Müller[6,7] and Davidson[2] for methyl mercaptan clathrate hydrates are not in agreement with each other. However, our experimental data are in better agreement with the experimental data of Davidson.[2] On the other hand, the few experimental data reported by Tamman and Krige,[4] von Stackelberg,[6] von Stackelberg and Müller,[7] Davidson,[2] and Chinworth and Katz[8] for sulfur dioxide clathrate hydrates are generally in disagreement. Our experimental data do not match any of the latter experimental data. On the other hand, it is of interest to compare the dissociation data of methyl mercaptan and sulfur dioxide clathrate hydrates with the hydrate dissociation data of carbonyl sulfide and hydrogen sulfide reported in the litearture.[10] As can be seen in Figure 1, the equilibrium data for sulfur dioxide, methyl mercaptan, carbonyl sulfide, and hydrogen sulfide clathrate hydrates show that the studied dissociation temperatures of the aforementioned clathrate hydrates at given pressures can be summarized as carbonyl sulfide > hydrogen sulfide > sulfur dioxide > methyl mercaptan. It should finally be mentioned that it is likely that other mercaptan

Table 2. Experimental Dissociation Data for Sulfur Dioxide and Methyl Mercaptan Clathrate Hydrates

T/K	p/MPa
Sulfur Dioxide Clathrate Hydrates	
279.9	0.101
280.2	0.106
280.7	0.122
281.1	0.137
281.6	0.154
282.2	0.166
282.6	0.178
283.2	0.193
283.7	0.204
284.3	0.215
285.0	0.224
285.2	0.233
Methyl Mercaptan Clathrate Hydrates	
283.4	0.103
283.7	0.109
284.1	0.111
284.5	0.117
285.0	0.122

compounds can form clathrate hydrates at low pressures (most likely below atmospheric pressure). It is expected that the presence of a light hydrate former such as methane (called help gas) may be required to stabilize the clathrate hydrates of some heavy mercaptans. This, however, requires further investigation.

CONCLUSIONS

In this work, we have come to the following conclusions.

1. We report a literature review on the equilibrium conditions of sulfur dioxide and methyl mercaptan clathrate hydrates. It was shown that the liquid water + hydrate + vapor equilibrium data for sulfur dioxide[2−4,6−8] and methyl mercaptan[2,6,7] clathrate hydrates reported in the literature are not generally in good agreement with each other.

2. We report experimental liquid water + hydrate + vapor equilibrium data for sulfur dioxide clathrate hydrates in the temperature range of (279.9 to 285.2) K and for clathrate hydrates of methyl mercaptan in the temperature range of (283.4 to 285.0) K, which were measured using an isochoric pressure-search method.[10−12]

3. The comparison among the experimental liquid water + hydrate + vapor equilibrium data for sulfur dioxide, methyl mercaptan, carbonyl sulfide, and hydrogen sulfide clathrate hydrates shows that the dissociation temperatures of the aforementioned clathrate hydrates at given pressures can be summarized as follows: carbonyl sulfide > hydrogen sulfide > sulfur dioxide > methyl mercaptan.

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