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Shorter Communication

Phase equilibria of clathrate hydrates of methyl cyclopentane, methyl cyclohexane, cyclopentane or cyclohexane+carbon dioxide

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In this work, experimental dissociation data for clathrate hydrates of methyl cyclopentane, methyl cyclohexane, cyclopentane or cyclohexane+carbon dioxide are reported at different temperatures. The experimental data were generated using an isochoric pressure-search method. The reliability of this method is examined by generating new dissociation data for clathrate hydrates of methyl cyclopentane+methane and comparing them with the experimental data reported in the literature. The acceptable agreement demonstrates the reliability of the experimental method used in this work. The experimental data for all measured systems are finally compared with the corresponding literature data in the absence of the above mentioned cyclic compounds to identify their promotion effects.

1. Introduction

Gas hydrates, or clathrate hydrates, are a group of nonstoichiometric, icelike crystalline compounds formed through a combination of water and suitably sized “guest” molecule(s) under low-temperatures and elevated pressures (Sloan and Koh, 2008). In clathrate hydrates, water molecules form hydrogen-bonded cagelike structures, encapsulating the guest molecules, which generally consist of low molecular weight gases and organic compounds (Sloan and Koh, 2008). The gas hydrate 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 (Sloan and Koh, 2008). For a molecule to enter a cavity, its size should be smaller than a certain value (Sloan and Koh, 2008). Large molecule guests which can enter only a limited number of large cavities require smaller “help gas” molecules, like methane, carbon dioxide, etc., to mainly fill some smaller cavities sufficiently to stabilize hydrate crystals (Sloan and Koh, 2008). It has been reported that methyl cyclopentane, methyl cyclohexane, cyclopentane and cyclohexane can form clathrate hydrates with a help gas like methane (Sloan and Koh, 2008). However, the information on other help gases is limited.

In this work, dissociation data for clathrate hydrates of methyl cyclopentane, methyl cyclohexane, cyclopentane and cyclohexane with carbon dioxide as help gas are reported in various temperature ranges (Table 1). The experimental data were generated using an isochoric pressure-search method (Mohammadi et al., 2008, 2009; Mohammadi and Richon, 2009; Tohidi et al., 2000). As sufficient gas hydrate dissociation data for the methane+methyl cyclopentane+water system have been reported in the literature, therefore, we first generated and report experimental data for the latter system and compare them with the experimental data reported in the literature (Mehta and Sloan, 1994; Thomas and Behar, 1995; Danesh et al., 1994; Makino et al., 2004) to demonstrate the reliability of the experimental method used in our work. We then report dissociation data for methyl cyclopentane, methyl cyclohexane, cyclopentane and cyclohexane clathrate hydrates with carbon dioxide as help gas. The experimental data for the studied systems are finally compared with some selected experimental data from the literature in the absence of the above mentioned cyclic compounds (Mohammadi et al., 2005; Adisasmito et al., 1991; Jhaveri and Robinson, 1965; Mooijer-van den Heuvel et al., 2001) to identify their hydrate promotion effects.

2. Experimental section

2.1. Chemicals

Table 2 reports the purities and suppliers of the chemicals used in this work.

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Table 1
Dissociation temperature ranges studied in this work for clathrate hydrates of methane+methylcyclopentane and methyl cyclopentane, methyl cyclohexane, cyclopentane or cyclohexane+carbon dioxide.

Clathrate hydrate system	Hydrate dissociation temperature range (K)
Methane+methyl cyclopentane	274.5–285.9
Carbon dioxide+methyl cyclopentane	276.7–279.4
Carbon dioxide+methyl cyclohexane	276.4–280.4
Carbon dioxide+cyclohexane	275.2–278.1
Carbon dioxide+cyclopentane	284.3–291.8

Table 2
Purities and suppliers of chemicals.[a]

Chemical	**Supplier**	**Purity**
Methane	Messer Griesheim	99.995 (volume %)
Carbon dioxide	Air Liquide	99.995 (volume %)
Methyl cyclohexane	Sigma-Aldrich	99+
Methyl cyclopentane	Fluka	99.5
Cyclohexane	Fluka	$\geq$ 99.8
Cyclopentane	Sigma-Aldrich	$\geq$ 99

[a] Deionized water was used in all experiments.

2.2. *Experimental apparatus (Mohammadi and Richon, 2009)*

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. 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 < 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 8 MPa, respectively). Pressure measurement uncertainties are estimated to be < 5 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

2.3. *Experimental method (Mohammadi and Richon, 2009)*

The liquid water+liquid hydrocarbon+hydrate+vapor equilibrium conditions were measured with an isochoric pressure search method (Mohammadi et al., 2008, 2009; Mohammadi and Richon, 2009; Tohidi et al., 2000). The vessel containing liquids (approximately 10% by volume of the vessel was filled by water and 10% by volume by liquid hydrocarbon) 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 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, 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 (Mohammadi et al., 2008, 2009; Mohammadi and Richon, 2009; Ohmura et al., 2004). 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 (Mohammadi et al., 2008, 2009; Mohammadi and Richon, 2009; Ohmura et al., 2004). 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 (Mohammadi et al., 2008, 2009; Mohammadi and Richon, 2009; Ohmura et al., 2004).

3. Results and discussion

All the experimental data are reported in Table 3 and are plotted in Figs. 1 and 2. As mentioned earlier, we first measured the hydrate dissociation conditions for the methane+methyl cyclopentane+water system, for which there is sufficient experimental data in the literature (Mehta and Sloan, 1994; Thomas and Behar, 1995; Danesh et al., 1994; Makino et al., 2004). As can be observed in Fig. 1, the experimental data measured in this work for the latter system are in good agreement with the experimental data reported in the literature (Mehta and Sloan, 1994; Thomas and Behar, 1995; Danesh et al., 1994; Makino et al., 2004) demonstrating the reliability of the experimental method

Table 3
Experimental dissociation data for clathrate hydrates of methane+methyl cyclopentane and methyl cyclopentane, methyl cyclohexane, cyclopentane or cyclohexane+carbon dioxide.

T **(K)**	***p*** **(MPa)**
Methane+methyl cyclopentane clathrate hydrates	
274.5	1.82
276.3	2.29
279.4	3.40
281.7	4.57
283.6	5.82
285.9	7.82
Carbon dioxide+methyl cyclopentane clathrate hydrates	
276.7	1.81
277.4	2.06
279.1	2.49
279.2	2.59
279.4	2.56
Carbon dioxide+methyl cyclohexane clathrate hydrates	
276.4	1.69
277.3	1.89
278.8	2.33
279.5	2.57
280.4	2.91
Carbon dioxide+cyclohexane clathrate hydrates	
275.2	0.95
276.2	1.18
277.3	1.50
278.1	1.81
Carbon dioxide+cyclopentane clathrate hydrates	
284.3	0.35
285.6	0.64
286.9	0.93
288.1	1.20
289.4	1.59
290.7	2.06
291.8	2.52