Chemical Engineering Science 65 (2010) 3356–3361

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Shorter Communication

Clathrate hydrate dissociation conditions for the methane+cycloheptane/cyclooctane+water and carbon dioxide+cycloheptane/cyclooctane+water systems

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ARTICLE INFO

Article history:
Received 24 December 2009
Accepted 13 February 2010
Available online 19 February 2010

Keywords:
Gas hydrate
Cycloheptane
Cyclooctane
Methane
Carbon dioxide

ABSTRACT

In this communication, we report hydrate dissociation conditions for the methane+cycloheptane/cyclooctane+water and carbon dioxide+cycloheptane/cyclooctane+water systems. The experimental data were generated using an isochoric pressure-search method. The dissociation data for clathrate hydrates of cycloheptane or cyclooctane+methane are successfully compared with the literature data demonstrating the reliability of the literature data and the experimental method used in our work. The experimental data for all measured systems are finally compared with the corresponding literature data in the absence of cycloheptane or cyclooctane to study the hydrate promotion effects of the latter two chemicals.

1. Introduction

Clathrate hydrates (or gas hydrates) are a group of non-stoichiometric, 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 molecule(s), which generally consist of low molecular diameter gases and organic compounds (Sloan and Koh, 2008). The gas hydrate structures are generally 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 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 small “help gas” molecules, like methane, etc. to mainly fill some smaller cavities sufficiently to stabilize hydrate crystals (Sloan and Koh, 2008). The formation of structure II with heavy molecules or structure H generally requires the presence of large and small guest molecules. Large molecule occupies large cavities while small molecule (called help gas) fills the remaining cavities (Sloan and Koh, 2008). It has been proven that cycloheptane and cyclooctane form structure H of clathrate hydrates with the presence of methane as help gas (Sloan and Koh, 2008). However, the information on other help gases is limited (Sloan and Koh, 2008). To our knowledge, there is no information on possible clathrate hydrate formation of cycloheptane or cyclooctane with carbon dioxide as potential help gas.

In this work, hydrate dissociation pressures for the methane+cycloheptane/cyclooctane+water and carbon dioxide+cycloheptane/cyclooctane+water systems are reported in various temperature ranges (Table 1). The experimental data were generated using an isochoric pressure-search method (Tohidi et al., 2000; Mohammadi and Richon, 2009a–g; Mohammadi, 2009). We first generated and report some dissociation data for clathrate hydrates of cycloheptane or cyclooctane+methane and compare them with the experimental data reported in the literature (Thomas and Behar, 1994; Makino et al., 2004) to demonstrate the reliability of the experimental method used in our work (Tohidi et al., 2000; Mohammadi and Richon, 2009a–g; Mohammadi, 2009) and consequently the literature data. We then report hydrate dissociation data for the carbon dioxide+cycloheptane/cyclooctane+water systems. The experimental data for the aforementioned systems are finally compared with the corresponding literature data in the absence of cycloheptane or cyclooctane (Mohammadi et al., 2005; Adisasmito et al., 1991; Jhaveri and Robinson, 1965; Mooijer-van den Heuvel et al., 2001) to study the hydrate promotion effects of the latter chemicals.

2. Experimental section

2.1. Materials

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

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doi:10.1016/j.ces.2010.02.027

Table 1
Hydrate dissociation temperature ranges studied in this work.

System	Hydrate dissociation temperature range (K)
Methane+cycloheptane+water	275.4–290.1
Methane+cyclooctane+water	274.8–288.8
Carbon dioxide+cycloheptane+water	278.2–281.7
Carbon dioxide+cyclooctane+water	278.5–281.2

Table 2
Purities and suppliers of materials.[a]

Material	Supplier	Purity
Methane	Messer Griesheim	99.995 (mole%)
Carbon dioxide	Air Liquid	99.995 (mole%)
Cycloheptane	Aldrich chemistry	98 (%,GC)
Cyclooctane	Aldrich chemistry	99+(%,GC)

[a] Deionized water was used in all experiments.

2.2. *Experimental apparatus (Belandria et al., 2010)*

Briefly, the main part of the apparatus is a horizontal cylindrical vessel, which can withstand pressures higher than 60 MPa. The volume of the vessel is 200 cm^3. A “Rushton turbine stirred” mixer was installed in the vessel to agitate the fluids and hydrate crystals inside it. The stirrer and all parts of the apparatus were made of stainless steel. One platinum resistance thermometer (Pt100) inserted into the vessel was used to measure temperature and check for equality of temperature within temperature measurement uncertainty, 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 a DRUCK pressure transducers (Druck, type PTX611 for pressure ranges up to 8 MPa). Pressure measurement uncertainty is estimated to be <5 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

2.3. *Experimental method*

The dissociation conditions were measured with an isochoric pressure search method (Tohidi et al., 2000; Mohammadi and Richon, 2009a–g; Mohammadi, 2009). The vessel containing liquids (approximately 10% by volume of the vessel was filled by water and 10% by volume by heavy 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 introducing 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 the hydrate dissociation point was determined (Mohammadi and Richon, 2009a–g; Mohammadi, 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 temperature change of the fluids in the vessel (Mohammadi and Richon, 2009a–g; Mohammadi, 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 and Richon, 2009a–g; Mohammadi, 2009; Ohmura et al., 2004).

3. Results and discussion

All the experimental data are reported in Tables 3 and 4 and are plotted in Figs. 1–6. As mentioned earlier, we first measured the dissociation conditions for clathrate hydrates of cycloheptane

Table 3
Experimental hydrate dissociation data for the methane+cycloheptane+water and methane+cyclooctane+water systems.

T (K)	*p* (MPa)
Methane+cycloheptane+water	
275.4	1.58
277.7	2.11
279.1	2.50
280.9	3.13
282.6	3.86
285.8	5.78
288.2	7.78
290.1	10.00
Methane+cyclooctane+water	
274.8	1.77
279.6	3.05
282.3	4.22
285.4	6.21
288.8	9.53

Table 4
Experimental hydrate dissociation data for the carbon dioxide+cycloheptane+water and carbon dioxide+cyclooctane+water systems.

T (K)	*p* (MPa)
Carbon dioxide+cycloheptane+water	
278.2	2.29
278.6	2.40
279.3	2.61
280.0	2.87
280.1	2.87
281.2	3.31
281.3	3.52
281.5	3.52
281.7	3.69
Carbon dioxide+cyclooctane+water	
278.5	2.32
278.9	2.45
279.5	2.65
280.1	2.85
280.8	3.14
281.2	3.31