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Shorter Communication

Phase equilibria of binary clathrate hydrates of nitrogen+cyclopentane/cyclohexane/methyl cyclohexane and ethane+cyclopentane/cyclohexane/methyl cyclohexane

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A B S T R A C T

In this communication, we first report hydrate dissociation conditions for the nitrogen+cyclopentane, cyclohexane or methyl cyclohexane+water and ethane+cyclopentane, cyclohexane or methyl cyclohexane+water systems at various temperatures. The experimental data were generated using an isochoric pressure-search method. The hydrate dissociation data for the aforementioned systems along with the hydrate dissociation data for the methane, carbon dioxide or hydrogen sulfide+cyclopentane, cyclohexane or methyl cyclohexane+water systems collected from the literature are compared with the corresponding literature data in the absence of the aforementioned heavy hydrocarbons in order to study the hydrate promotion effects of cyclopentane, cyclohexane or methyl cyclohexane. It is shown that these effects on ethane simple hydrate are not considerable unlike the corresponding effects on nitrogen, methane, carbon dioxide and hydrogen sulfide simple hydrates.

1. Introduction

Clathrate hydrates (or gas hydrates) are a group of nonstoichiometric, ice-like 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 common gas hydrate crystalline structures are 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 generally require small molecules, like methane, etc., to mainly occupy remaining cavities sufficiently to stabilize hydrate crystals (Sloan and Koh, 2008). The formation of structure H or structure II of some heavy molecules requires the presence of both large and small guest molecules. Large molecules occupy large cavities while small molecules can occupy the remaining cavities (Sloan and Koh, 2008). Oil and gas condensate fluids contain some large guest molecules, so called heavy hydrate formers (HHF), like cyclopentane, cyclohexane, methyl cyclohexane, etc., which can have significant effects on gas hydrate phase equilibria of these fluids (Sloan and Koh, 2008; Mohammadi et al., 2006). However, these HHFs are normally lumped into hydrocarbon groups, i.e., no additional information on HHFs is generally available (Mohammadi et al., 2006). Accurate knowledge of phase equilibria for clathrate hydrates of these HHFs is important in order to predict hydrate stability zones of oil and gas condensate fluids (Sloan and Koh, 2008; Mohammadi et al., 2006). On the other hand, clathrate hydrates forming *s*H have been proposed as a medium for gas storage, especially for the storage of natural gases, due to their higher gas storage capacity in comparison with *s*II and *s*I (Sloan and Koh, 2008; Khokhar et al., 1998). Many efforts have been made to measure hydrate phase equilibria of these HHFs (Sloan and Koh, 2008). In most of cases, methane was used as help gas (Sloan and Koh, 2008). A comprehensive literature review for these HHFs is given by Sloan and Koh (2008). Cyclopentane, cyclohexane and methyl cyclohexane are typical HHFs whose clathrate hydrate phase equilibria have been well studied in the presence of methane (Sloan and Koh, 2008). However, the information on clathrate hydrates of cyclopentane, cyclohexane and methyl cyclohexane in the presence of other gases is limited (Sloan and Koh, 2008). As live oil and gas condensate fluids contain other light components, like ethane, etc.,

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in addition to methane, it is therefore of interest to study phase equilibria of clathrate hydrates of HHFs in the presence of other light hydrate formers.

This work aims at comparing dissociation conditions (liquid water–liquid hydrocarbon–hydrate–vapor (or gas) equilibria) of clathrate hydrates of cyclopentane, cyclohexane or methyl cyclohexane + methane, ethane, carbon dioxide, hydrogen sulfide or nitrogen. We first report hydrate dissociation conditions for the ethane + cyclopentane, cyclohexane or methyl cyclohexane + water and nitrogen + cyclopentane, cyclohexane or methyl cyclohexane + water systems at various temperatures, for which the information is limited. The experimental data were generated using an isochoric pressure-search method (Tohidi et al., 2000; Belandria et al., 2010; Mohammadi and Richon, 2009a, b, c, 2010a, b, c, d). The experimental data for the aforementioned measured systems as well the literature data for the methane, carbon dioxide or hydrogen sulfide + cyclopentane, cyclohexane or methyl cyclohexane + water systems are finally compared with the corresponding literature data in the absence of cyclopentane, cyclohexane or methyl cyclohexane to study the promotion effects of the latter chemicals on simple hydrates of methane, ethane, carbon dioxide, hydrogen sulfide and nitrogen.

2. Experimental section

2.1. Materials

Table 1 reports the purities and suppliers of the materials used in this work. Gases were used as received and liquids were degassed before using.

Two similar apparatuses were used for performing the measurements because of their availability:

2.2. Experimental apparatus-1 (Mohammadi and Richon, 2009a, b, c, 2010a, b, c, d)

Briefly, the main part of the apparatus is a sapphire cylindrical vessel, which can withstand pressures up to 15 MPa. The internal 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 are used to measure temperatures and check for their equality within temperature measurement uncertainty, which is 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 is measured with two DRUCK pressure transducers (Druck, type PTX611 for pressure ranges up to (2.5 and 12) MPa, respectively). Pressure measurement uncertainties are estimated to be less than 5 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

Table 1
Purities and suppliers of materials[a].

Material	Supplier	Purity
Nitrogen	Air Liquide	≥ 99.99 (mole%)
Ethane	Messer Griesheim	99.995 (mole%)
Methyl cyclohexane	Sigma-Aldrich	99+ (%, GC)
Cyclohexane	Fluka	≥ 99.8 (%, GC)
Cyclopentane	Sigma-Aldrich	≥ 99 (%, GC)

[a] Deionized water was used in all experiments.

2.3. Experimental apparatus-2 (Belandria et al., 2010)

Briefly, the main part of the apparatus is a horizontal metallic cylindrical vessel, which can withstand pressures up to 60 MPa. The internal volume of the vessel is 201 cm^3. A "Rushton turbine stirred" mixer was installed in the vessel to agitate the fluids and hydrate crystals inside it. One platinum resistance thermometer (Pt100) inserted into the vessel is used to measure temperature and check for their equality within temperature measurement uncertainty, which is 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 is measured with a DRUCK pressure transducer (Druck, type PTX611 for pressure ranges up to 8 MPa). Pressure measurement uncertainties are estimated to be less than 4 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

2.4. Experimental method

The dissociation conditions were measured with an isochoric pressure search method (Tohidi et al., 2000; Belandria et al., 2010; Mohammadi and Richon, 2009a, b, c, 2010a, b, c, d). The vessel containing liquids (approximately 10% by volume of the vessel was filled with water and 10% by volume with 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 (Belandria et al., 2010; Mohammadi and Richon, 2009a, b, c, 2010a, b, c, d; 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 (Belandria et al., 2010; Mohammadi and Richon, 2009a, b, c, 2010a, b, c, d; 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 (Belandria et al., 2010; Mohammadi and Richon, 2009a, b, c, 2010a, b, c, d; Ohmura et al., 2004). The maximum uncertainties for the hydrate dissociation temperatures and pressures are expected to be ± 0.1 K and ± 0.02 MPa.

3. Results and discussion

All the experimental data are reported in Tables 2 and 3 and are plotted in Figs. 1 and 2. In Figs. 3–5, we have shown similar literature data in the presence of methane, carbon dioxide and hydrogen sulfide, respectively. In all these figures, we have also shown some selected experimental data from the literature in the absence of heavy hydrocarbons studied in this work to identify the hydrate promotion effects of cyclopentane, cyclohexane and methyl cyclohexane. It should be mentioned that hydrate promotion effect means shifting dissociation conditions of simple