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Phase equilibrium measurements of structure II clathrate hydrates of hydrogen with various promoters

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ABSTRACT

Phase equilibrium measurements of single and mixed organic clathrate hydrates with hydrogen were determined within a pressure range of 2.0–14.0 MPa. The organic compounds studied were furan, 2,5-dihydrofuran, tetrahydropyran, 1,3-dioxolane and cyclopentane. These organic compounds are known to form structure II clathrate hydrates with water. It was found that the addition of hydrogen to form a mixed clathrate hydrate increases the stability compared to the single organic clathrate hydrates. Moreover, the mixed clathrate hydrate also has a much higher stability compared to a pure hydrogen structure II clathrate hydrate. Therefore, the organic compounds act as promoter materials. The stabilities of the single and mixed organic clathrate hydrates with hydrogen showed the following trend in increasing order: 1,3-dioxolane < 2,5-dihydrofuran < tetrahydropyran < furan < cyclopentane, indicating that both size and geometry of the organic compound determine the stability of the clathrate hydrates.

1. Introduction

Clathrate hydrates are a class of crystalline inclusion compounds, where one or more types of guest molecules are trapped inside a host material. The host material is water (H_2O) and consists of an ice-like lattice with well-defined cages [1]. The guest molecules are typically gases or volatile organic compounds, which fill the cages and stabilize the hydrate structure [2]. Depending on the size and properties of the guest molecules, clathrate hydrates occur in three different crystal structures: (i) structure I (sI), (ii) structure II (sII) and (iii) structure H (sH). Each structure is characterized by cages with different sizes and geometry.

In 1999, the first experimental reports of clathrate hydrates with hydrogen (H_2) as guest molecules stored within the cavities were published [3,4]. Since then, these materials have been attracting particular interest due to their potential for H_2 storage. H_2 clathrate hydrates are safer, cost less, and can be produced more efficiently, faster and with higher reversibility [5] compared to other potential H_2 storage materials including metal hydrides, carbon nanotubes, etc. [6]. However, the low storage capacity and the extreme conditions necessary for the formation and stabilization of H_2 clathrate hydrates have limited their development for technological applications [7]. The major scientific and technological challenges are therefore to increase the storage capacity and to stabilize the material at more practical conditions (close to ambient conditions).

Single H_2 clathrate hydrates show a sII configuration, where 136 H_2O molecules form sixteen small cavities (5^{12}) and eight large cavities ($5^{12}6^4$) [1]. With a double H_2 occupancy of all sixteen small cavities, and quadruple occupancy of the large cavities, the maximum H_2 storage capacity of this sII clathrate hydrate is 5.0 wt%. However this maximum capacity has been reported only at extremely high pressures in excess of 200 MPa [8].

The addition of a second type of guest molecule, a so-called promoter, was found to reduce the formation pressure by two orders of magnitude. For example, the addition of tetrahydrofuran (THF) to form sII H_2 clathrate hydrate resulted in the formation of a mixed sII THF–H_2 clathrate hydrate that was stable at pressures as low as 5 MPa at 280 K [9]. However, the addition of a promoter significantly reduces the H_2 storage capacity of the clathrate hydrate. The addition of THF, for example, reduces the maximum H_2 storage capacity to only 1.1 wt% [10]. In a controversial report, Lee et al. [11] claimed that the H_2 storage capacity of the mixed THF–H_2

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clathrate hydrate could be increased up to 4.0 wt% at 12 MPa and 270 K by tuning its composition. Nevertheless, further studies suggested the unfeasibility of reaching this storage capacity at the conditions tested [10,12]. Recently, Sugahara et al. [13] reported the possibility of reproducing the tuning effect by a new method of hydrate formation from ice and solid THF. Using this method the H_2 storage capacity of the mixed THF–H_2 clathrate hydrate can be increased to 3.4 wt% at 70 MPa and 255 K [13]. Although the pressure and temperature conditions reported by Sugahara et al. [13] to stabilize these materials are still far from practical, the results highlight the importance of the promoter on the stability of the hydrate phase.

Several studies have been performed in order to determine the role of the promoter molecule on the stability conditions of clathrate hydrates of methane (CH_4) [2,14–16], carbon dioxide (CO_2) [17–19] and propane (C_3H_8) [20–22], among others. However, the role of the promoter in systems involving H_2 is still not clearly understood. Phase equilibrium measurements of mixed organic sII clathrate hydrates with H_2 are scarce [23,24] because most of the research has been focused on THF–H_2 clathrate hydrates. Consequently, from the practical and scientific point of view the search for H_2 clathrate hydrates with increased storage capacity at more practical conditions is a priority, and a suitable promoter molecule could play an important role in the development of such material.

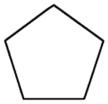
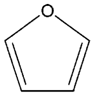
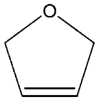
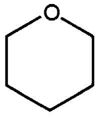
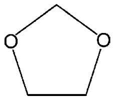
In the present work the effect of five organic compounds on the stability of mixed sII (promoter–H_2) clathrate hydrates was studied. The additives studied are: furan, 2,5-dihydrofuran, tetrahydropyran, 1,3-dioxolane and cyclopentane. These organic compounds are known to form single sII clathrate hydrates [25,26] and consequently are suitable to form mixed sII (promoter–H_2) clathrate hydrates. The hydrate phase equilibrium conditions (p, T data) of the ternary systems $H_2O + H_2$ + 1,3-dioxolane, $H_2O + H_2$ + 2,5-dihydrofuran, $H_2O + H_2$ + tetrahydropyran and of the binary systems H_2O + 2,5-dihydrofuran, H_2O + tetrahydropyran and H_2O + furan up to pressures of 14.0 MPa, have never been measured before and they may help to elucidate the factors dictating the stability trend of the mixed sII H_2 clathrate hydrates.

2. Experimental

2.1. Materials

Table 1 lists the different hydrocarbons studied as promoter materials for sII clathrate hydrates and shows the molecular structures. For the liquid phase, double distilled and de-ionized H_2O was used. H_2 was supplied by Hoek Loos with a purity of 99.999 mol%. All the chemicals were used without any further purification.

Table 1
List of promoter materials studied in this work.

Promoter material	Molecular structure
Cyclopentane C_5H_{10} CAS [287-92-3] Fluka	
Furan C_4H_4O CAS [110-00-9] Fluka	
2,5-Dihydrofuran C_4H_6O CAS [1708-29-8] Sigma–Aldrich	
Tetrahydropyran $C_5H_{10}O$ CAS [142-68-7] Sigma–Aldrich	
1,3-Dioxolane $C_3H_6O_2$ CAS [646-06-0] Sigma–Aldrich	

2.2. Experimental set-up

The experiments were carried out in a Cailletet apparatus, which is suitable for phase equilibrium measurements within a temperature range of 255–455 K and a pressure range of 0.1–15 MPa. This equipment allows visual observation of the phase transitions and operates according to the synthetic method. Details of the Cailletet apparatus can be found elsewhere [27].

A sample of known fixed composition was sealed into the closed top of the Cailletet tube. The open bottom-end of the tube was immersed in mercury contained in an autoclave connected to a high-pressure hydraulic system applying oil as pressure medium. The pressure was measured with a dead weight pressure balance with an accuracy of 0.03% of the reading. The Cailletet tube was jacketed and ethanol was used as coolant fluid. The temperature of the sample was kept constant by circulating the coolant fluid with the help of a thermostatic bath (Lauda), which was capable to maintain the coolant fluid at the desired temperature with an accuracy better than ±0.01 K. A platinum resistance thermometer (Pt-100) located as close as possible to the sample, recorded the temperature of the coolant fluid with a maximum error of 0.02 K. The sample inside the tube was stirred by a stainless steel ball which was moved up and down by two button magnets activated by a rotating disc mounted on a stirring motor.

2.3. Experimental procedure

The phase equilibrium measurements were carried out with samples of known composition. Samples of H_2O and organic compounds were prepared by dosing them gravimetrically into the Cailletet tube in such a way that the concentration in the clathrate hydrate lattice would be as close as possible to the stoichiometric concentration (5.6 mol%). This is the concentration where all the larger cavities are occupied by the organic compound. The maximum error in the mole fraction x in $\{(1-x)$ organic compound $+ xH_2O\}$ is estimated to be 0.002. The air dissolved in the H_2O + organic compound mixture was removed by freezing and melting the sample several times and degassing under high vacuum. The H_2 (for the mixed clathrate hydrate measurements) was dosed volumetrically into the Cailletet tube at known temperature and pressure via a gas rack apparatus equipped with a high vacuum turbo pump and an ionization vacuum meter.

The hydrate phase equilibrium measurements were carried out by fixing the pressure and cooling down the sample until the