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

Alondra Torres Trueba [a], Laura J. Rovetto [a], Louw J. Florusse [a], Maaike C. Kroon [b,*], Cor J. Peters [a,c]

[a] *Delft University of Technology, Faculty of Mechanical, Maritime and Materials Engineering, Department of Process & Energy, Section Process Equipment, Leeghwaterstraat 44, 2628 CA Delft, Netherlands*
[b] *Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Separation Technology Group, Den Dolech 2, 5612 AZ Eindhoven, Netherlands*
[c] *The Petroleum Institute, Chemical Engineering Department, P.O. Box 2533, Abu Dhabi, United Arab Emirates*

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.

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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

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.
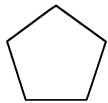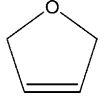
2. Experimental

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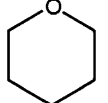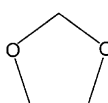
Table 1 lists the different hydrocarbons studied as promoter materials for sII clathrate hydrates and shows the molecular structures. For the liquid phase, double distilled and de-ionized H_2O was used. H_2 was supplied by Hoek Loos with a purity of 99.999 mol%. All the chemicals were used without any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

2.2. Experimental set-up

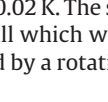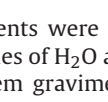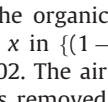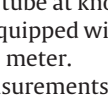The experiments were carried out in a Cailletet apparatus, which is suitable for phase equilibrium measurements within a temperature range of 255–455 K and a pressure range of 0.1–15 MPa. This equipment allows visual observation of the phase transitions and operates according to the synthetic method.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

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	

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 $+ x H_2O\}$ 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

Table 2
Phase equilibrium data (temperature, T, pressure, p and type of phase transition) for single sII organic clathrate hydrates (without H_2). L_1 is the aqueous (water-rich) phase, L_2 is the organic-rich phase and H is the solid (hydrate) phase.

System	T (K)	p (MPa)	Phase transition
H_2O + furan	277.37	2.00	$H-L_1-L_2 \rightarrow L_1-L_2$
5.79 mol% furan	277.33	4.00	
	277.21	8.00	
	277.10	12.01	
	276.95	14.01	
H_2O + 2,5-dihydrofuran	272.00	2.00	$H-L_1-L_2 \rightarrow L_1-L_2$
5.96 mol% 2,5-dihydrofuran	271.88	4.00	
	271.73	8.00	
	271.55	12.01	
	271.44	14.00	
H_2O + tetrahydropyran	272.36	1.91	$H-L_1-L_2 \rightarrow L_1-L_2$
5.44 mol% tetrahydropyran	272.29	6.00	
	272.26	10.00	
	272.26	12.00	
	272.24	14.00	
H_2O + 1,3-dioxolane	270.47	1.99	$H-L_1 \rightarrow L_1$
6.39 mol% 1,3-dioxolane	270.45	2.49	
	270.29	5.99	
	270.08	10.49	
	269.94	13.50	
H_2O + cyclopentane	279.90	2.55	$H-L_1-L_2 \rightarrow L_1-L_2$
5.60 mol% cyclopentane	279.94	5.05	
	280.02	7.55	
	280.00	10.03	
	280.03	12.55	

hydrate phase was present. Then the temperature was elevated in small steps at a rate of 0.1 K per 10 min until the dissociation of the hydrate phase could be observed. Then, the temperature was increased stepwise (every step took much longer than 10 min) until no hydrate crystals were observed. The temperature where the hydrate phase disappeared was taken as the phase transition temperature. The measurements were repeated at lower temperature ramp rates in order to confirm the reliability of the experimental data [28]. It was determined that the temperature difference between appearance and disappearance of the solid phase was ±0.2 K.

This procedure was performed for different pressures, obtaining the clathrate hydrate phase transition conditions at every pressure.

3. Results and discussion

The phase equilibrium measurements of the single sII clathrate hydrates of furan, 2,5-dihydrofuran, tetrahydropyran, 1,3-dioxolane and cyclopentane are reported in Table 2. The data presented in this work correspond to the dissociation curve of the clathrate hydrates i.e., the maximum temperature at which the clathrate hydrate is stable for a given pressure. The systems consisting of H_2O and a water-insoluble organic compound (furan, 2,5-dihydrofuran, tetrahydropyran and cyclopentane) showed a three-phase equilibrium of the nature: aqueous (water-rich) phase (L_1)–organic (organic-rich) phase (L_2)–hydrate phase (H). The system consisting of H_2O and water-soluble organic compound (1,3-dioxolane) displayed a two-phase equilibrium of the nature: aqueous phase (L_1)–hydrate phase (H). Fig. 1 shows graphically the hydrate phase equilibrium of the binary systems.

From Fig. 1 it can be noticed that furan and cyclopentane form the most stable hydrate phases at temperatures above the melting point of H_2O. The other three hydrate phases are less stable than ice. Another interesting fact is that the influence of the pressure on the hydrate dissociation temperature is negligible, as can be observed from the very steep slopes in Fig. 1. This can be explained by the absence of any gaseous compound, due to the incompressibility of the phases of this equilibrium the pressure
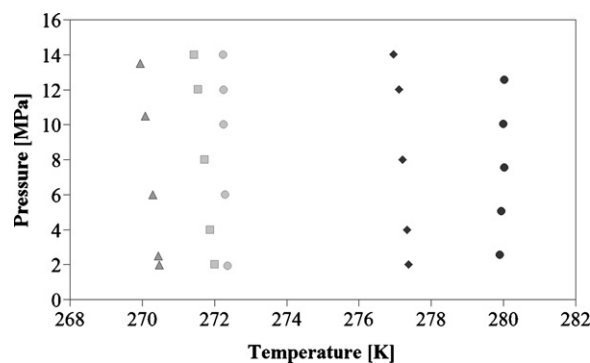

Fig. 1. Phase equilibrium data for the binary systems: H_2O–furan (♦), H_2O–2,5-dihydrofuran (□), H_2O–tetrahydropyran (○), H_2O–1,3-dioxolane (▲) and H_2O–cyclopentane (●).

increases steeply with increasing temperature according to Clapeyron's equation [29]. In Fig. 1, it can be observed that the slopes (dp/dT) of the systems H_2O–1,3-dioxolane, H_2O–2,5-dihydrofuran and H_2O–furan are negative. The reason for this is that the hydrate phase was decomposed to the organic liquid phase and ice before the ice was melted, and that the melting curve of ice has a negative slope.

The phase equilibrium measurements of the mixed sII clathrate hydrates of H_2 and organic compounds are reported in Table 3. The systems consisting of H_2O, H_2 and a water-insoluble organic compound exhibit a four-phase equilibrium of the nature: hydrate phase (H)–aqueous (water-rich) phase (L_1)–organic (organic-rich) phase (L_2)–vapor phase (V). The system consisting of H_2O, H_2 and water-soluble organic compound shows a three-phase equilibrium of the nature: hydrate phase (H)–aqueous phase (L_1)–vapor phase (V). The results are graphically depicted in Fig. 2. For comparison, the previously reported thermodynamic equilibrium conditions of the mixed sII clathrate hydrates of H_2–cyclopentane [23] and H_2–furan [24] were included in Fig. 2, and show good agreement with our data. For illustrative purposes, the thermodynamic equi-

Table 3
Phase equilibrium data (temperature, T, pressure, p and type of phase transition) for mixed sII (H_2 + organic compound) clathrate hydrates. L_1 is the aqueous (water-rich) phase, L_2 is the organic-rich phase, H is the solid (hydrate) phase and V is the vapor phase.

System	T (K)	p (MPa)	Phase transition
H_2O + H_2 + furan	278.44	2.55	$H-L_1-L_2-V \rightarrow L_1-L_2-V$
5.61 mol% furan	279.10	5.05	
	279.95	7.55	
	280.75	10.05	
	281.38	12.55	
H_2O + H_2 + 2,5-dihydrofuran	273.65	2.55	$H-L_1-L_2-V \rightarrow L_1-L_2-V$
5.90 mol% 2,5-dihydrofuran	274.64	5.05	
	275.58	7.55	
	276.40	10.05	
	277.18	12.55	
H_2O + H_2 + 1,3-dioxolane	271.75	2.55	$H-L_1-V \rightarrow L_1-V$
5.62 mol% 1,3-dioxolane	272.71	5.05	
	273.63	7.55	
	274.37	10.05	
	275.07	12.55	
H_2O + H_2 + tetrahydropyran	273.76	2.55	$H-L_1-L_2-V \rightarrow L_1-L_2-V$
6.02 mol% tetrahydropyran	275.03	5.05	
	275.95	7.55	
	276.88	10.05	
	277.71	12.55	
H_2O + H_2 + cyclopentane	280.83	2.50	$H-L_1-L_2-V \rightarrow L_1-L_2-V$
5.60 mol% cyclopentane	281.65	5.00	
	282.64	7.55	
	283.43	10.00	
	284.01	12.50	
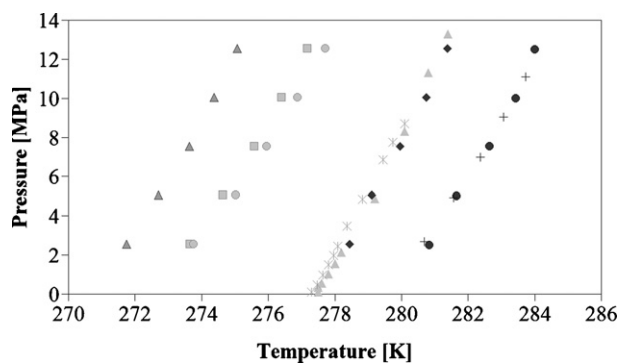
Fig. 2. Phase equilibrium data for the ternary systems in this work: H_2O–H_2–furan (♦), H_2O–H_2–2,5-dihydrofuran (□), H_2O–H_2–tetrahydropyran (○), H_2O–H_2–1,3-dioxolane (▲) and H_2O–H_2–cyclopentane (●). For comparison, also the existing data for H_2O–H_2–furan (*)[24], H_2O–H_2–cyclopentane (+)[23] and H_2O–H_2–THF [30] (△) are presented.

librium conditions of mixed H_2–THF clathrate hydrates [30] were also included in Fig. 2.

From the slopes (dp/dT) in Fig. 2 it can be noticed that the influence of pressure on the hydrate stability is large, which can be explained by the involvement of a gaseous guest molecule (H_2). It is expected that the H_2 molecules occupy the small cavities, while the organic compound occupies the larger cavities. Moreover, Fig. 2 shows that all mixed hydrate phases are more stable than ice at higher pressures. All mixed hydrate phases are also more stable than the corresponding single clathrate hydrates. Thus, the inclusion of H_2 to form a mixed clathrate hydrate increases the stability compared to the single organic clathrate hydrates. The mixed clathrate hydrate also has a much higher stability compared to a pure H_2 sII clathrate hydrate (stable at pressures >200 MPa). Therefore, the organic compounds act as promoter materials.
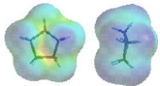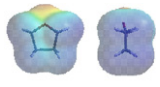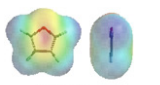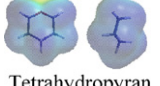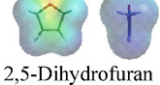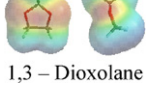
When comparing Figs. 1 and 2, one can observe the same trend with respect to stability of the hydrate phase for the single and mixed clathrate hydrates. This stability increases in the order: 1,3-dioxolane < 2,5-dihydrofuran < tetrahydropyran < furan, THF < cyclopentane. It is expected that the molecular size and geometry of the organic compound determine the stability of the clathrate hydrate. For better understanding, the molecular weight, the van der Waals volume and the dipole moment of the additives are presented in Table 4. All the organic compounds studied fulfilled the size requirement to fit into the larger cavity of the sII clathrate hydrate [1,2,26,31], although tetrahydropyran is rather large for optimal fit. Other differences in hydrate stability most likely result from differences in geometry. For example, it was noticed that 1,3-dioxolane, 2,5-dihydrofuran and furan have similar molecular weight and van der Waals volumes, but their clathrate hydrate stabilities differ significantly from each other. This difference also does not seem to be related to the magnitude of the dipole moment. For example, compounds with similar dipole moments, such as THF and 2,5-dihydrofuran, show significant differences in hydrate stabilities. It can thus be concluded that the molecular geometry of the organic compound has the largest influence on the hydrate stability. The organic compounds with the highest symmetry seem to be able to produce the most stable clathrate hydrates.

The Clausius–Clapeyron equation is used to determine the hydrate dissociation enthalpies (ΔH_{diss}) of the mixed H_2 clathrate hydrates from the phase equilibrium data obtained in this study [32]:

$$\frac{d \ln p}{d(1/T)} = -\frac{\Delta H_{diss}}{zR} \tag{1}$$

Table 4
Physical properties (molecular weight, MW, dipole moment, D, and van der Waals volume, V_{vdW}) of the promoters studied.

Promoter	MW (g mol^{-1})	D (D) [22]	$V_{vdW}{}^a$ (Å)
Cyclopentane	70.1	0.0	94.87
Tetrahydrofuran	72.1	1.75 ± 0.04	85.56
Furan	68.0	0.66 ± 0.01	77.12
Tetrahydropyran	86.1	1.58 ± 0.03	102.3
2,5-Dihydrofuran	70.0	1.63 ± 0.01	81.65
1,3 – Dioxolane	74.0	1.19 ± 0.06	76.27

^a The van der Waals volumes were determined from Spartan® calculations at the Hartree–Fock level.

Table 5
Hydrate dissociation enthalpies (ΔH_{diss}) of the mixed clathrate hydrates of H_2 and water-insoluble organic compounds.

System	ΔH_{diss} (kJ mol^{-1})
H_2O–H_2–furan	343.57
H_2O–H_2–2,5-dihydrofuran	287.26
H_2O–H_2–tetrahydropyran	343.62
H_2O–H_2–cyclopentane	329.23

where p and T are the absolute pressures and temperatures of hydrate equilibrium, R is the universal gas constant, and z is the compressibility factor. According to van der Waals and Platteeuw [33] the application of the Clapeyron equation for the calculation of ΔH_{diss} is thermodynamically acceptable for clathrate hydrates as long as the system is univariant, irrespective of the number of components. In this work the compressibility factor and the stoichiometric ratios of H_2O to guest molecules are assumed to be constant. This may generate inaccuracies caused by volume changes, the non-ideality of the vapor phase and the solubility of the gas in the liquid phase [34,35]. Therefore, the enthalpy data in this report should be taken only as an approximation. The estimated hydrate dissociation enthalpies can then be obtained from the slope of the straight line in a semi-logarithmic plot of the dissociation pressure versus the reciprocal temperature. Table 5 presents the hydrate dissociation enthalpies of the mixed clathrate hydrates of H_2 and water-insoluble organic compounds. The dissociation enthalpies calculated are in the range of values reported for other mixed sII organic clathrate hydrates [36].

4. Conclusions

In this study the phase equilibrium data of several different single and mixed organic hydrate phases with H_2 were determined. It was shown that the addition of H_2 increases the stability of the mixed hydrate phase compared to the corresponding single organic hydrate phase. The mixed H_2 clathrate hydrates are also more stable than pure H_2 clathrate hydrate, indicating that the organic compounds act as promoter materials. The molecular size and geometry of the organic compound most likely determine the stability of the clathrate hydrates, while the dipole moment does not seem to have an apparent influence.

Acknowledgements

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