

Hydrate phase equilibrium and dissociation enthalpies for tetrahydrothiophene and different gas systems

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ABSTRACT

The phase equilibrium data of hydrate formation in tetrahydrothiophene (THT) and different gases (including CH₄, H₂, CO₂, and IGCC syngas (40 mol% CO₂/60 mol% H₂)) were measured in this work. The results show that the addition of THT remarkably reduces the CH₄, H₂, CO₂, and IGCC syngas hydrate formation conditions. Besides, for H₂, CO₂, and IGCC syngas, THT's effect in reducing hydrate formation conditions is slightly less than that in the system containing CP or 5.6 mol% THF. However, for the CH₄ gas, the hydrate formation conditions curve obtained from the system containing THT, 5.6 mol% THF and CP are almost similar. In addition, since THT is a water-insoluble promoter, the results proved that its molar fractions can not affect the hydrate formation conditions. Based on the phase equilibrium data we obtained, the dissociation enthalpies of hydrate formation in these systems were also determined via the Clausius-Clapeyron equation and its modified style. The hydrate dissociation enthalpies for THT + CH₄, THT + H₂, THT + CO₂, and THT + IGCC syngas are within 102.2 - 115.26 kJ•mol⁻¹, 312.01 - 315.94 kJ•mol⁻¹, 149.93 - 213.40 kJ•mol⁻¹ and 160.19 - 181.02 kJ•mol⁻¹, respectively.

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1. Introduction

Gas hydrates are non-stoichiometric cage-like crystals composed of water and guest molecules under high-pressure and low-temperature conditions [1], in which guest molecules such as small gas molecules and some organic compounds are encapsulated in hydrate cages through van der Waals interaction [2]. This can ensure that the solid hydrate has high thermodynamic stability. Normally, gas hydrates exist in three main structures, named structure I (sI), structure II (sII), and structure H (sH). It is noted that the hydrate structure formed in the system depends on several aspects, such as the size of guest molecules, the system's temperature, and pressure, etc. [3]

It is well known that over the past several decades, gas hydrate has been considered as a potential material to be used in energy and environmental fields, including carbon dioxide (CO₂) capture and storage [4], gas (methane, hydrogen, etc.) storage and transportation [5], and cold energy storage and transportation [6]. Although considerable developments have been achieved for these techniques, the harsh condition of gas hydrate formation limits

their industrial application. Typically, in the pure water system, low temperatures and high pressures are needed in the formation of gas hydrates. Simultaneously, a relatively low hydrate formation kinetic and gas storage capacity are presented. Therefore, reducing the hydrate formation conditions is considered a long-term focus of research in these techniques.

Adding thermodynamic promoters have been proved to be an effective way to reduce hydrate formation conditions. By occupying some of the hydrate cages, thermodynamic promoters typically result in hydrate structure change, thereby significantly reducing the hydrate formation conditions. Widely used thermodynamic promoters include Tetrahydrofuran (THF) [7, 8], tetra-n-butyl ammonium bromide (TBAB), and cyclopentane (CP) [9]. For example, Zhang et al. [10] determined the CH₄ and H₂/CH₄ mixed gas hydrate formation conditions in the system with or without THF. It was found that the addition of THF significantly reduce the hydrate formation conditions, by up to 96.7% for CH₄ system and 96.6% for 35 mol% H₂ + 65 mol% CH₄ system at 277.7 K. Li et al. [11] measured the phase equilibrium of hydrate formation in the CH₄ + TBAB + H₂O ternary system with the TBAB mass fraction from 0.05 to 0.385. They found that relative to the CH₄ + H₂O system, the equilibrium pressures decrease by 52–96% at a specified temperature in the presence of TBAB. Sun et al. [12] obtained the hydrate formation conditions of CH₄ + cyclopentane and CH₄ + cy-

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cyclohexane systems. The results showed that both cyclopentane and cyclohexane significantly reduce the equilibrium pressure of CH₄ hydrates formation and cyclopentane is a more efficient promoter relative to cyclohexane. Specifically, at 282.1 K, compared to CH₄ hydrate formation condition obtained in pure water (~6.5 MPa), the equilibrium pressure of CH₄ hydrate formation in the presence of cyclopentane and cyclohexane reduce to 0.16 MPa and 2.21 MPa, respectively.

Tetrahydrothiophene (THT) is a new promising thermodynamic hydrate formation promoter that was developed recently. With a structure similar with to THF, THT can also only occupy the large cages of sII hydrates. THT has many advantages such as low price, being harmless to humans, and being easy to recycle. Additionally, to detect gas leakage, THT is usually used as an additive in city gas due to its noticeable smell. Tsuda et al. [13] tentatively measured the phase equilibrium of hydrate formation in the THT + H₂ and furan + H₂ systems. They found that the addition of THT can significantly reduce the H₂ hydrate formation conditions from >400 MPa to 3.88 MPa at 277.2 K, which means the equilibrium pressure was reduced more than 99% at this temperature after adding THT. Besides, they presented that the hydrate formation rate obtained in presence of THT is much faster than that in the system containing THF. Lv et al. [14] determined the hydrate formation conditions and hydrate dissociation enthalpies for the THT + CH₄ and six other systems. Their results proved that the promotion effect of those organic compounds is heightened with the decrease of the molecular size. To the best of my knowledge, up to now, only these two hydrate studies are conducted in the presence of THT and no more experimental data is available in the literature. Especially, it is well known that the dissociation enthalpy of gas hydrates is a basic parameter in the field of economic and energy consumption evaluation. To industrialize and optimize these hydrate-based techniques, it is necessary to obtain these parameters.

In this work, the phase equilibrium of hydrate formation in THT+CH₄, THT+H₂, THT+ CO₂, and THT+ IGCC syngas systems were measured by the classical “T-cycle” method [15]. Simultaneously, Based on these data, we obtained the dissociation enthalpies of hydrates formed in these systems by using the Clausius–Clapeyron equation and its modified style. The results can provide the basic parameters for the hydrate formation in the system containing THT, thereby benefiting hydrate-based techniques.

2. Experimental

2.1. Materials

Methane with a purity of 99.9% was supplied by Guangdong Huate Gas Co., Ltd., China. Hydrogen with a purity of 99.999% and IGCC syngas with a composition of 40 mol% CO₂ and 60 mol% H₂ and purity of 99.999% were obtained from Foshan Sanshui Deli Messer Gas Co., Ltd., China. Carbon dioxide with a purity of 99.999% was supplied by Guangzhou Shengying Gas Co., Ltd., China. An analytical-grade Tetrahydrothiophene with a purity of 99.0% was supplied by Shanghai Mecklin Co., Ltd., China. The deionized water with a resistivity of 18.25 mΩ·cm⁻¹ was produced in our laboratory by an ultrapure water system which is purchased from Nanjing EPED Co., Ltd., China. The experimental materials are shown in Table 1.

2.2. Experimental apparatus

Fig. 1 shows a schematic of the experimental apparatus used in this study. The reactor is made of 316 stainless steel with an effective volume of 120.0 ml. The maximum working pressure of the

reactors is 10.0 MPa. Each reactor is equipped with viewing windows on the front and back sides to observe the morphology of hydrate formation. The liquids are mixed by magnetic stirrers underneath the reactors. The hydrate formation temperature is controlled by a XT5218 water bath with an accuracy of ± 0.1 K (248.15 - 323.15 K). A thermocouple (Pt100) with an uncertainty of ± 0.1 K and a pressure transducer (Trafag NAT8251) with an accuracy of ± 0.01 MPa (0–25.0 MPa) are installed to measure the temperature and pressure of the hydrate formation, respectively. The thermocouples and pressure transmitter are calibrated with mercury thermometers and precision pressure gauges, respectively. Data of the temperature and pressure are collected every 8 s using an Agilent 34970A system.

2.3. Procedure

In this work, the “T-cycle” method is used to determine the hydrate formation conditions [15]. Briefly, before the experiment, the reactor should be washed thoroughly with deionized water at least three times and then dried. 30 ml of the liquids is then injected into the reactor. After that, the reactor is sealed and evacuated by a vacuum pump to ensure the air-free. Subsequently, the reactor is immersed in the water bath. After the temperature stabilizes, fill the reactor with gas to reach the required pressure and wait at least 12 h. Simultaneously, the liquid is mixed constantly by a magnetic stirrer at 500 r/min to accelerate the gas dissolution. After the pressure remains at a constant value for 2 h, decreasing the system temperature slowly to form the hydrates. After a large amount of hydrates formed, the temperature increases gradually with the step of 0.2 K until the last particle of gas hydrates disappeared. Typically, the condition of this point is considered to be the phase equilibrium point of hydrate formation. The typical process of “T-cycle” is shown in Fig. 2. In Fig. 2, the condition of point d is the phase equilibrium point of hydrate formation.

3. Results and discussion

3.1. Phase equilibrium determination

The phase equilibrium of CH₄ hydrate formation in the system containing 1.0 mol% and 5.6 mol% THT was measured within the temperature range of 288.3 K to 301.0 K. It should be noted that the mole fraction of THT mentioned in this work is the initial mole fraction of THT in the liquid phase (THT + H₂O). The results are shown in Fig. 3. From Fig. 3, it can be found that relative to pure CH₄ hydrate formation, the addition of THT can significantly reduce the hydrate formation conditions. For example, at the temperature of 288.3 K, the pressure requirement of CH₄ hydrate formation is larger than 11.0 MPa. However, only 0.95 MPa is needed for CH₄ hydrate formation in the presence of THT. It is worth mentioning that the results obtained in this work are in good agreement with the work conducted by Lv et al. [14] This proved that the method used in this work is reliable. Besides, Fig. 3 shows that the CH₄ hydrate formation conditions obtained from the system containing 1.0 mol% THT are almost consistent with those obtained from 5.6 mol% THT. This is due to the fact that THT is a water-insoluble promoter and the amount of THT used cannot affect the hydrate formation conditions. In addition, Fig. 3 presents that relative to CH₄ hydrate formation in the presence of 1.07 mol% THF, lower hydrate formation conditions are observed from the system containing THT. Taking 293.0 K as an example, the pressure requirement of CH₄ hydrate formation in 1.0 mol% THF solution is about 3.55 MPa, while this value is approximately 2.03 MPa in the presence of 1.0 mol% THT molar fractions. Meanwhile, we find that the curve of CH₄ hydrate formation conditions obtained in the

Table 1
The experimental materials.

Materials	Formula	CAS number	Provided by	Purity ^a
Methane	CH ₄	74–82–8	Guangdong Huate Gas Co., Ltd.	99.9%
Hydrogen	H ₂	1333–74–0	Foshan Sanshui Deli Messer Gas Co., Ltd.	99.999%
IGCC syngas(40 mol% CO ₂ + 60 mol% H ₂)	N/A	N/A	Foshan Sanshui Deli Messer Gas Co., Ltd.	99.999%
Carbon dioxide	CO ₂	124–38–9	Guangzhou Shengying Gas Co., Ltd.	99.999%
Tetrahydrothiophene	C ₄ H ₈ S	110–01–0	Shanghai Mecklin Co., Ltd.	99.0%
Deionized water	H ₂ O	7732–18–5	This laboratory	18.25 mΩ·cm ⁻¹

^a Reported by the suppliers.

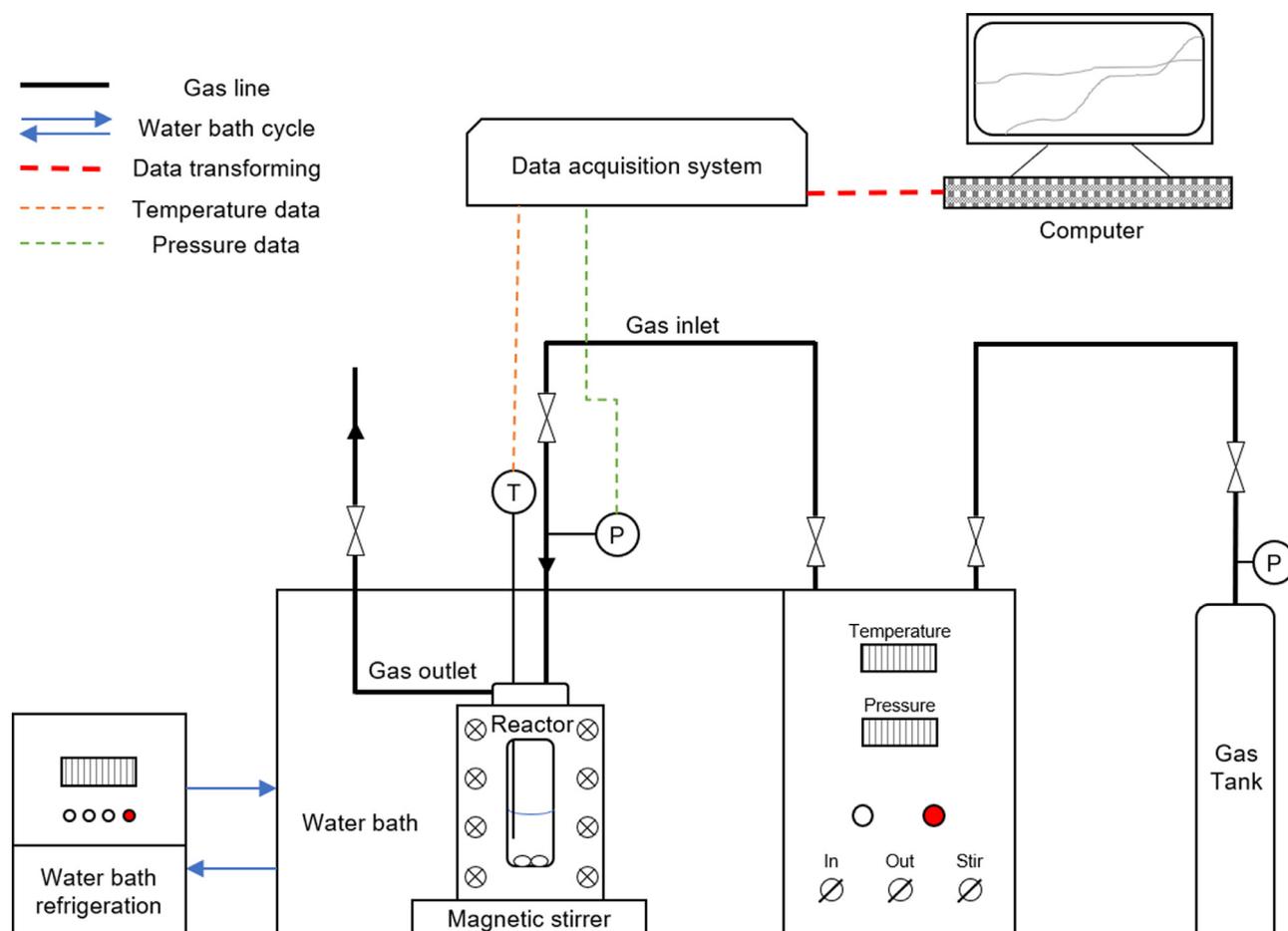


Fig. 1. Schematic of the experimental apparatus.

presence of CP or THF ≥ 3.0 mol% is consistent with that obtained from the system containing THT. This implies that THT is comparable to the system with CP or THF ≥ 3.0 mol% in terms of reducing CH₄ hydrate formation conditions. The initial molar ratio of liquid and gas phase and phase equilibrium data for each experiments are summarized in Table 2.

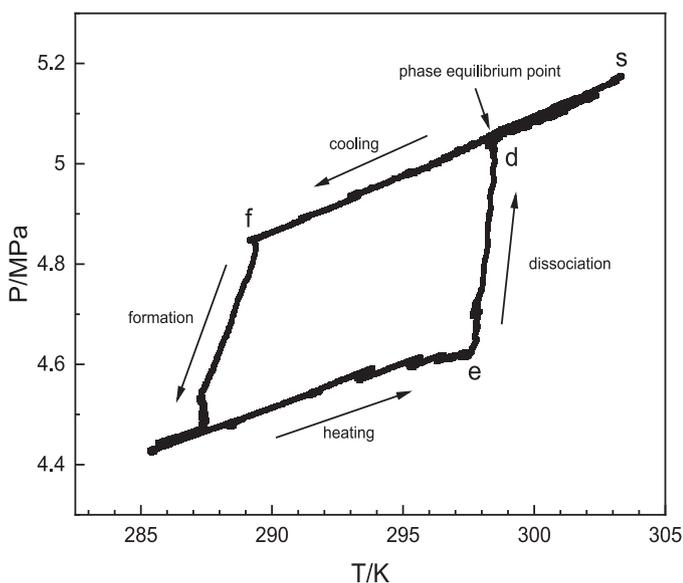
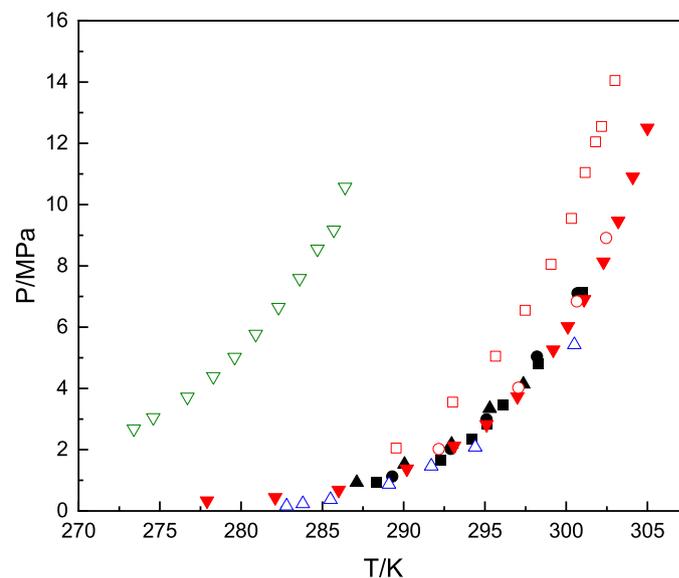
From the studies of CH₄ hydrate formation, we confirm that the molar fractions of THT cannot affect the hydrate formation conditions when above 1.0 mol%. Hence, only one molar fraction is adopted in the following studies. Fig. 4 shows the H₂ hydrate formation conditions in the presence of 5.6 mol% THT within 276.1–278.6 K. It can be found that relative to pure H₂ hydrate formation conditions, ~ 430 MPa at 278 K [21], THT can also greatly reduce H₂ hydrate formation conditions, ~ 6 MPa at 278 K. However, from Fig. 4, we can find that the phase equilibrium curve of H₂ hydrate formation in the presence of THT is consistent with that acquired from the 2.4 mol% THF system. Besides, Fig. 4 shows that among the promoters mentioned above(THT, THF, CP), CP is the most ef-

ficient promoter in reducing H₂ hydrate formation conditions. This means that from the view point of thermodynamic, CP is a more promising promoter for hydrate-based H₂ storage. The specific data of curves presented in Fig. 4 are shown in Table 2.

The phase equilibrium of hydrate formation in the IGCC syngas (40 mol% CO₂/60 mol% H₂) + 5.6 mol% THT system within 280.7–287.9 K is shown in Fig. 5. Obviously, the addition of THT also can significantly reduce the IGCC syngas hydrate formation conditions. For example, at the pressure of approximately 6.5 MPa, the formation temperature of pure IGCC syngas hydrate is about 275 K, while the same value of IGCC syngas hydrate in the system containing THT is about 288 K. Meanwhile, Fig. 5 shows the effect of THT in reducing IGCC syngas hydrate formation is similar with that in 3.0 mol% THF solution, but slightly worse than that in CP or 5.6 mol% THF solution. Actually, the IGCC syngas hydrate formation conditions curve obtained from the system containing 5.6 mol% THF and CP are almost similar. The specific data of curves presented in Fig. 5 are shown in Table 2.

Table 2Hydrate phase equilibrium data and the dissociation enthalpies for THT+CH₄+H₂O, THT+H₂+H₂O, THT+IGCC syngas+H₂O, and THT+CO₂+H₂O systems.

System	T/K	P/MPa	Initial liquid-gas mole ratios	ΔH_m /kJ•mol ⁻¹	ΔH_{m-mod} /kJ•mol ⁻¹
1.0 mol%THT+CH ₄ +H ₂ O	289.3	1.12	45.27:1	115.26	N/A
	292.9	2.03	25.29:1	113.00	N/A
	295.1	2.99	17.30:1	110.74	N/A
	298.2	5.04	10.37:1	106.50	N/A
	300.7	7.11	7.41:1	103.05	N/A
5.6 mol%THT+CH ₄ +H ₂ O	288.3	0.95	45.36:1	114.78	N/A
	292.3	1.67	26.16:1	112.97	N/A
	294.2	2.34	18.79:1	111.36	N/A
	295.1	2.83	15.59:1	110.22	N/A
	296.1	3.48	12.72:1	108.78	N/A
	298.3	4.79	9.31:1	106.15	N/A
	301.0	7.15	6.29:1	102.20	N/A
5.6 mol%THT+H ₂ +H ₂ O	276.1	0.88	46.90:1	N/A	N/A
	276.2	1.25	33.03:1	N/A	N/A
	276.4	2.38	17.36:1	N/A	N/A
	277.3	4.51	9.19:1	312.01	N/A
	278.0	6.05	6.87:1	313.72	N/A
	278.6	7.91	5.26:1	315.94	N/A
5.6 mol%THT+IGCC syngas+H ₂ O	280.7	0.83	43.48:1	184.36	181.02
	282.9	1.69	22.14:1	182.34	176.70
	284.2	2.47	15.61:1	180.63	172.84
	287.1	5.03	7.78:1	175.76	163.96
	287.9	6.37	6.17:1	173.58	160.19
5.6 mol%THT+CO ₂ +H ₂ O	287.4	1.46	22.06:1	227.87	213.40
	288.9	2.49	13.48:1	209.86	190.20
	289.5	3.15	10.75:1	197.45	176.30
	290.0	3.73	9.24:1	185.57	162.71
	290.4	4.31	8.17:1	172.42	149.93

**Fig. 2.** P-T diagram of a "T-cycle" process in 1.0 mol% THT + CH₄ + Water system.**Fig. 3.** CH₄ hydrate phase equilibrium data for: ■ 1.0 mol% THT, this work; ● 5.6 mol% THT, this work; ▲ 0.6 mol% THT, [14]; □ 1.07 mol% THF, [16]; ○ 3.0 mol% THF, [17]; ▼ 5.56 mol% THF, [18]; △ CP, [19]; ▽ pure water, [20].

The phase equilibrium of hydrate formation in the 5.6 mol% THT+CO₂ system with a temperature range of 287.4–290.4 K was also measured in this work and the result is shown in Fig. 6. Similar to the others gas system, THT presents a noticeable effect on reducing gas hydrate formation conditions. Compared to CO₂ hydrate formation in the pure water system, the hydrate formation temperature at 2.49 MPa increases from 279.0 K to 288.9 K in the presence of THT. Besides, it can be seen from Fig. 6 that THT's effect in reducing CO₂ hydrate formation conditions is better than that in 1.56 mol% THF solution, but less than that in the system containing CP or 5.6 mol% THF. The specific data of curves presented in Fig. 6 are shown in Table 2.

3.2. Dissociation enthalpy of hydrates with the presence of THT

Dissociation enthalpy is an important parameter in developing production schemes of hydrate-based techniques. Typically, two methods are adopted to obtain the hydrate dissociation enthalpies: (1) direct calorimetric measurement; (2) indirect determination via the Clapeyron or Clausius-Clapeyron equation which greatly depends on the accuracy of hydrate phase equilibrium data. In this work, due to the disgusting smell of THT, we adopted the second method to determine the hydrate dissociation enthalpies. It is noted that to ensure the accuracy of the hydrate dissociation en-

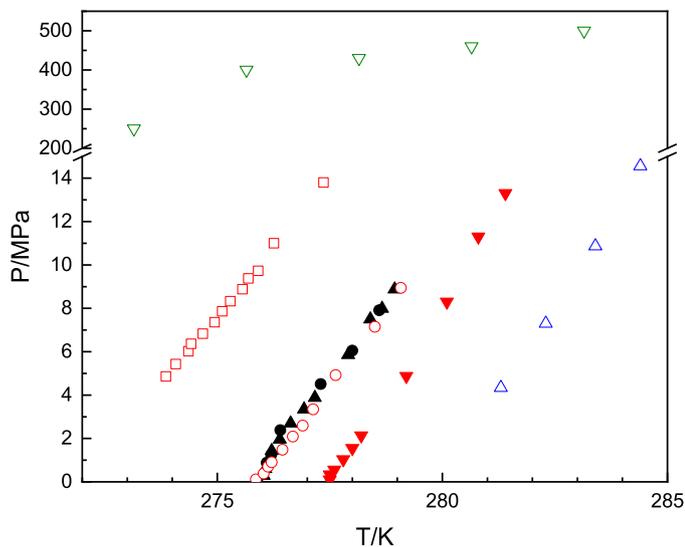


Fig. 4. H₂ hydrate phase equilibrium data of H₂ for: ● THT, this work; ▲ THT, [13]; □ 1.0 mol% THF, [22]; ○ 2.4 mol% THF, [22]; ▼ 5.6 mol% THF, [23]; △ CP, [17]; ▽ pure water, [21].

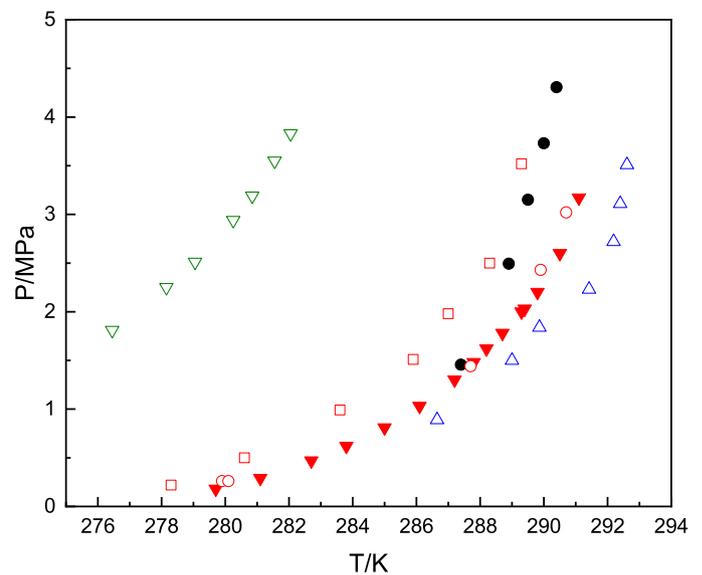


Fig. 6. CO₂ hydrate phase equilibrium data for: ● THT, this work; □ 1.56 mol% THF, [28]; ○ 2.99 mol% THF, [28]; ▼ 5.6 mol% THF, [18]; △ CP, [29]; ▽ pure water, [30].

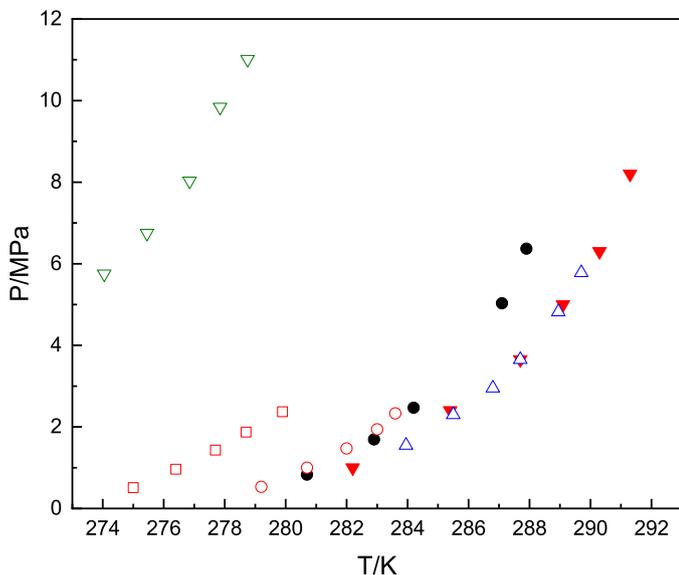
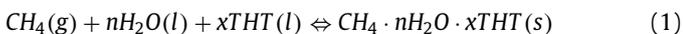


Fig. 5. IGCC syngas hydrate phase equilibrium data for: ● THT, this work; □ 1.0 mol% THF, [24]; ○ 3.0 mol% THF, [24]; ▼ 5.6 mol% THF, [25]; △ CP, [26]; ▽ pure water, [27].

thalpies, the solubility of the gas in water needs to be considered, especially for systems containing CO₂.

It is well known that the formation and dissociation process of the hydrate can be progressed as the following equation



Where x and n are the mole number of THT and H₂O in the hydrate crystal formed.

For the single sparingly soluble gas such as CH₄ or H₂ mentioned above, according to a first-order approximation, the hydrate dissociation enthalpy above 273.15 K can be calculated via the Clausius–Clapeyron equation, where the univariant slope of the line of $\ln P$ (MPa) vs $1/T$ (K) should be determined based on the phase equilibrium data, as shown in Eq. (2)

$$\frac{d \ln(P)}{d \left(\frac{1}{T}\right)} = \frac{-\Delta H_m}{ZR} \quad (2)$$

where P and T are the pressure and temperature of the hydrate phase equilibrium point; ΔH_m is the molar hydrate dissociation enthalpy; Z is the compression factor of the guest gas at the phase equilibrium of hydrate formation conditions, which can be determined by the Peng–Robinson (P–R) equation or the Soave–Redlich–Kwong (S–R–K) equation; R ($R = 8.31451 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the universal gas constant.

For the system containing in-soluble gas such as IGCC syngas and CO₂ mentioned above, by considering the solubility of the gas in water, an improved Clausius–Clapeyron model should be used to calculate the hydrate dissociation enthalpy [31]. The modified Clausius–Clapeyron model can be progressed as follows:

$$\frac{d \ln(P)}{d \left(\frac{1}{T}\right)} = -\frac{\Delta H_m + nx\Delta H_s}{ZR \left(1 - \frac{nx}{1-x}\right) - n \frac{P\Delta v}{T}} \quad (3)$$

where x is the molar fraction of CO₂ dissolved in the solution; y is the molar fraction of CO₂ in the gas phase; Δv is the molar volume change between the liquid phase and hydrate ($\Delta v = 3.4 \text{ cm}^3/\text{mol}$ obtained from the data from Yoon et al. [32]); n is the hydrate number, which is obtained from the literature [33]. The solution data of CO₂ can be found in the literature [34].

ΔH_s is the dissolution enthalpy of the gas, which can be predicted via the Henry constant H_{21} [35]

$$\frac{\partial \ln(H_{21})}{\partial \left(\frac{1}{T}\right)} = \frac{\Delta H_s}{R} \quad (4)$$

According to Carroll et al. [36], Henry's constant of CO₂ in water can be calculated by the following polynomial:

$$\ln(H_{21}) = -6.8346 + 1.2817 \times \frac{10^4}{T} - 3.7668 \times \frac{10^6}{T^2} + 2.997 \times \frac{10^8}{T^3} \quad (5)$$

where H_{21} is in MPa and T is in K.

From Eq. (4) and Eq. (5), ΔH_s can be described as Eq.(6):

$$\Delta H_s = 106.56 - 6.2634 \times 10^4 T^{-1} + 7.475 \times 10^6 T^{-2} \quad (6)$$

The P - T data of THT + CH₄, THT + IGCC syngas, and THT + CO₂ systems in this work are replotted as $(\ln P)$ versus $(1/T)$ in Fig. 7. As can be seen from Fig. 7, $(\ln P)$ versus $(1/T)$ show good linear relations under these three systems. However, for the THT + H₂ system, the linear relationship between $(\ln P)$ and $(1/T)$ shows a deviation when the pressure is lower than 3.0 MPa. Fortunately, at the conditions above 3 MPa, $(\ln P)$ versus $(1/T)$ exhibits a very good linear relation, as shown in Fig. 8. Therefore, in this work, by combining the data obtained by Tsuda et al. [13], we obtained the

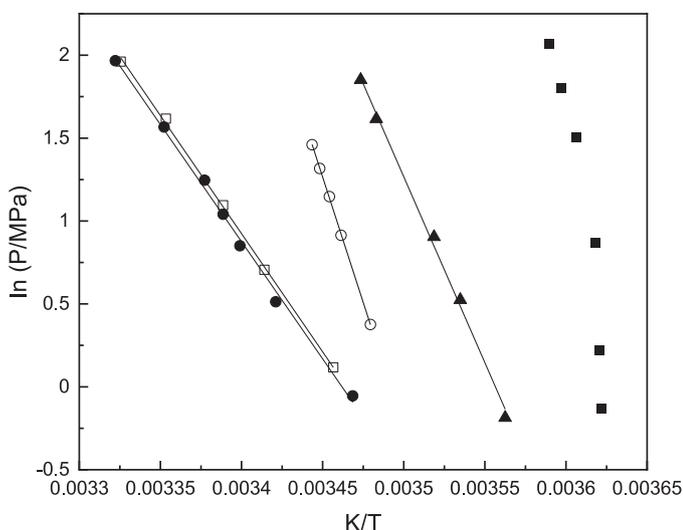


Fig. 7. The natural logarithms of the pressures ($\ln P$) versus the reciprocals of the temperatures ($1/T$) along the phase coexistence lines: \square 1.0 mol% THT + CH_4 , $k = -14,249$, $r = 0.9996$; \bullet 5.6 mol% THT + CH_4 , $k = -14,132$, $r = 0.9981$; \blacktriangle THT + IGCC syngas, $k = -22,431$, $r = 0.9985$; \blacksquare THT + H_2 ; \circ THT + CO_2 , $k = -30,242$, $r = 0.9999$. k , slope of the fitting line; r , linear correlation coefficient of the fitting line.

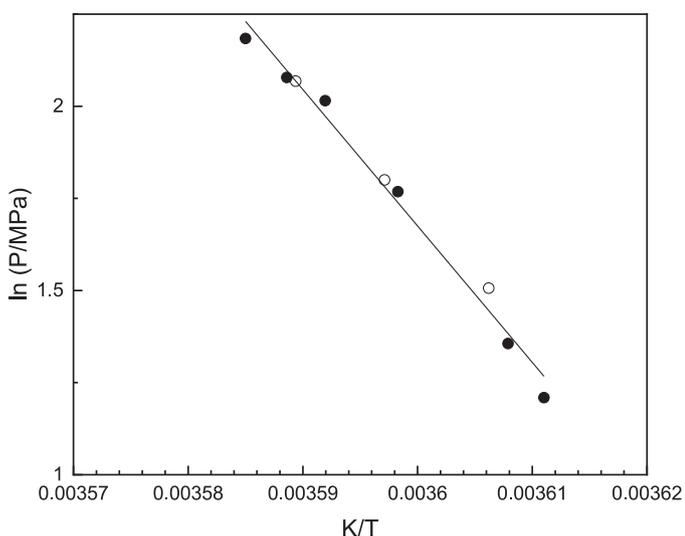


Fig. 8. The natural logarithms of the pressures ($\ln P$) versus the reciprocals of the temperatures ($1/T$) along the phase coexistence lines: \circ THT + H_2 , this work; \bullet THT + H_2 , [14]. $k = -37,023$, $r = 0.9931$. k , the slope of the fitting line; r , linear correlation coefficient of the fitting line.

hydrate dissociation enthalpy for THT + H_2 system at the pressure above 3.0 MPa. For the pressure lower than 3.0 MPa, further research is needed to determine the hydrates dissociation enthalpy by using direct calorimetric measurement.

For CH_4 hydrate formation in the presence of 1.0 mol% and 5.6 mol% THT, the slopes k in Fig. 7 are $-14,249$ with a linear correlation coefficient of 0.9996 and $-14,132$ with a linear correlation coefficient of 0.9981, respectively. The dissociation enthalpies of hydrate formed in these two systems can be calculated by Eq. (2), which are listed in Table 2. As can be seen in Table 2, the hydrate dissociation enthalpies for THT + CH_4 systems are within 102.2 - 115.26 $\text{kJ}\cdot\text{mol}^{-1}$. Besides, Table 2 shows there is only a very slight difference in the dissociation enthalpies obtained from these two systems. Actually, the result in section (3.1) proved that the concentration of THT above 1.0 mol% cannot affect the phase equilibrium of the CH_4 hydrate formation. Naturally, based on Eq. (2),

its concentration also cannot affect the hydrate dissociation enthalpies. It is worth mentioning that the dissociation enthalpy of THT + CH_4 hydrates obtained in this work is approximately 10% higher than that obtained by Lv et al. [15] This may be because that the THT concentration used in Lv's work is only 0.6 mol% which is much lower than that used in this work. Actually, it is well known that for some promoters such as THF, gas may occupy some of the large cages of sII at low promoter mole fractions. Undoubtedly, this may affect the hydrate dissociation enthalpies.

For THT + IGCC syngas and THT + CO_2 systems, the slopes k and linear correlation coefficient are $-22,431$ and 0.9985 and $-30,242$ and 0.9999, respectively. Since CO_2 is a water-soluble gas, the improved Clausius - Clapeyron model (Eq. (3)) is used to calculate the hydrate dissociation enthalpies, $\Delta H_{m-\text{mod}}$. Meanwhile, we obtained the hydrate dissociation enthalpies, ΔH_m using the original Clausius-Clapeyron equation (Eq. (2)) for comparison. The results are displayed in Table 2. In Table 2, it can be found that hydrate dissociation enthalpies are within 160.19-181.02 $\text{kJ}\cdot\text{mol}^{-1}$ for THT + IGCC syngas system, and within 149.9 -213.40 $\text{kJ}\cdot\text{mol}^{-1}$ for THT + CO_2 system. Besides, Table 2 shows that relative to the results obtained by Eq. (3), the hydrate dissociation enthalpies, ΔH_m , acquired by Eq. (2) decrease by approximately 1.8 to 7.7% for THT + IGCC syngas system and 6.4 to 13.0% for THT + CO_2 system, respectively. This indicates that for the system containing water-soluble gas, it is necessary to consider the dissolution enthalpy of the gas when calculating the hydrate dissociation enthalpy.

For the THT + H_2 system, at the pressure above 3.00 MPa, the slope k in Fig. 8 is $-37,023$ with a linear correlation coefficient of 0.9931. From Eq. (2), we can obtain the hydrate dissociation enthalpies, which are summarized in Table 2. It can be found that the hydrate dissociation enthalpies of hydrate formed in the THT + H_2 system are within 312.01 - 315.94 $\text{kJ}\cdot\text{mol}^{-1}$.

4. Conclusion

The phase equilibrium of hydrate formation in THT+ CH_4 , THT+ H_2 , THT+IGCC syngas(40 mol% CO_2 /60 mol% H_2), and THT+ CO_2 systems were determined using "T-cycle" method in this work. The results show that THT can significantly reduce the CH_4 , H_2 , IGCC syngas, and CO_2 hydrate formation conditions. Besides, for H_2 , CO_2 , and IGCC syngas, THT's effect in reducing hydrate formation conditions is slightly less than that in the system containing CP or 5.6 mol% THF. However, for the CH_4 gas, the hydrate formation conditions curve obtained from the system containing THT, 5.6 mol% THF and CP are almost similar. In addition, this work confirms that due to its water-insoluble properties, THT molar fractions cannot affect the hydrate formation conditions. By combining the phase equilibrium data we obtained and the Clausius-Clapeyron equation and its modified style, the dissociation enthalpies of hydrate formation in these systems were also determined. The results show that the hydrate dissociation enthalpies for THT+ CH_4 , THT+ H_2 , THT+IGCC syngas, and THT+ CO_2 are within 102.20-115.26 $\text{kJ}\cdot\text{mol}^{-1}$, 312.01-315.94 $\text{kJ}\cdot\text{mol}^{-1}$, 160.19-181.02 $\text{kJ}\cdot\text{mol}^{-1}$, and 149.93-213.40 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

Availability of data and materials

Virtually all data are provided within the paper and references, and if any data not provided can be obtained from the author.

Declaration of Competing Interest

The authors declare that they have no competing interests.

CRediT authorship contribution statement

Wen-Zhe Yi: Data curation, Investigation, Methodology, Software, Writing – original draft. **Xiao-Sen Li:** Supervision, Validation, Writing – review & editing. **Yi-Song Yu:** Conceptualization, Supervision, Validation, Writing – review & editing. **Zhao-Yang Chen:** Supervision, Validation, Writing – review & editing.

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