

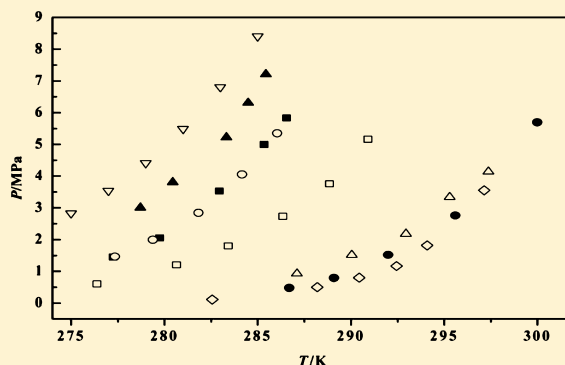
Phase Equilibrium and Dissociation Enthalpies for Hydrates of Various Water-Insoluble Organic Promoters with Methane

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ABSTRACT: Phase equilibrium data were measured for the mixed organic hydrates with methane. The organic compounds studied are cyclopentane, cyclopentyl chloride, cyclopentanone, methylcyclopentane, cyclohexene, tetrahydrothiophene, and trimethylene sulfide, which are water-insoluble. It is found that the organic compounds + methane hydrates are more easily formed than the methane hydrate. Therefore, these organic compounds act as the hydrate formation promoters. The hydrate promotion effectivenesses with methane as a help gas can be summarized in the following order: trimethylene sulfide > cyclopentane > tetrahydrothiophene > cyclopentanone > cyclopentyl chloride and cyclohexene > methylcyclopentane. Trimethylene sulfide has the biggest effect of hydrate promotion among the promoters studied in this work. It may be a promising water-insoluble chemical promoter. It is noted that the promotion effect is heightened with the decrease of the molecular size for the seven compounds. The hydrate dissociation enthalpies were determined via the Clausius–Clapeyron equation based on the different experimental equilibrium data. The absolute value of slope k plays an important role on the $\Delta_{\text{diss}}H_m$.



INTRODUCTION

Natural gas hydrates are crystalline solids consisting of special cages built of hydrogen bonds between water molecules with guest molecules.¹ The guest molecules are commonly gases or organic compounds, which fill the cages and stabilize the hydrate clathrate structure.² Water molecules form the different cages, which combine to form the hydrate of three major crystal structures such as structures I, II, and H.

Gas hydrates as a potential medium have received more and more attention for gas storage and transportation,^{3,4} wastewater treatment,⁵ desalination,⁶ gas separation,^{7–9} solution concentration,¹⁰ and thermal storage air conditioning.¹¹ Nevertheless, the pressure of hydrate formation is generally high. Some chemical additives are used as the promoters to enhance hydrate formation efficiently. Because of the addition of promoter, the hydrate equilibrium pressure is reduced at a given temperature, or the hydrate equilibrium temperature is increased at a given pressure. This is favorable for developing application technologies with the hydrate-based methods. Because water-insoluble chemical additives are easily recycled, they are often used as hydrate promoters, including some heavy hydrocarbons like cyclopentane. Finding suitable water-insoluble chemical additives will be the main challenge for application technologies utilizing hydrates.

Many investigations have indicated that adding some organic promoters can reduce the hydrate equilibrium pressure significantly.^{12–18} Thus, this characteristic may offer an opportunity for various practical applications with the hydrate-based methods. For example, Tsuda et al.¹⁹ inves-

tigated the ability of hydrogen storage in the furan and tetrahydrothiophene hydrates. The amount of hydrogen storage at 275.1 K is about 1.2 mol (hydrogen)/mol (tetrahydrothiophene or furan hydrate) (~0.6 mass fraction) at 41.5 MPa. Mohammadi et al.¹² studied the promotive effects of cyclopentane, methyl cyclohexane and cyclohexane on the binary clathrate hydrates with nitrogen or ethane. Methylcyclopentane and cyclooctane with the help of methane form sH hydrates, which have lower equilibrium pressures than the pure methane sI hydrate.¹³ Trueba et al. investigated the effects of furan, tetrahydropyran, 1,3-dioxolane, cyclopentane, and 2,5-dihydrofuran on the stability of sII clathrate hydrates. It was found that the mixed clathrate hydrate had a much higher stability compared to pure hydrogen sII clathrate hydrate.¹⁴ Kozaki et al.¹⁵ measured the equilibrium pressures in the systems containing liquid water, methane gas, hydrate and water-insoluble (cycloheptane, cycloheptanone, or oxacycloheptane). Structure H hydrates were confirmed by powder X-ray diffraction (PXRD) measurements. Mooijer-van den Heuvel et al. presented the experimental data of gas hydrates in three-phase systems containing carbon dioxide, water, and insoluble additives (cyclohexane, tetrahydropyran, cyclobutanone and methylcyclohexane). In the presence of tetrahydropyran, cyclohexane, and cyclobutanone, sII hydrates were supposed to be formed, while the methylcyclohexane hydrate with carbon

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Table 1. List of Organic Promoters Studied in This Work

Promoter material	Molecular formula	Molecular structure	Supplier & Purity (mass fraction)
Cyclopentane	C_5H_{10}		Chengdu Best Reagent Co., Ltd. >0.99
cyclopentyl chloride	C_5H_9Cl		J&K Scientific Ltd. >0.99
cyclopentanone	C_5H_8O		Sinopharm Chemical Reagent Co., Ltd. ≥ 0.97
Methylcyclopentane	C_6H_{12}		Sinopharm Chemical Reagent Co., Ltd. >0.94
cyclohexene	C_6H_{10}		Sinopharm Chemical Reagent Co., Ltd. ≥ 0.99
tetrahydrothiophene	C_4H_8S		Sinopharm Chemical Reagent Co., Ltd. ≥ 0.99
trimethylene sulfide	C_3H_6S		Tokyo Chemical Industry Co., Ltd. >0.98

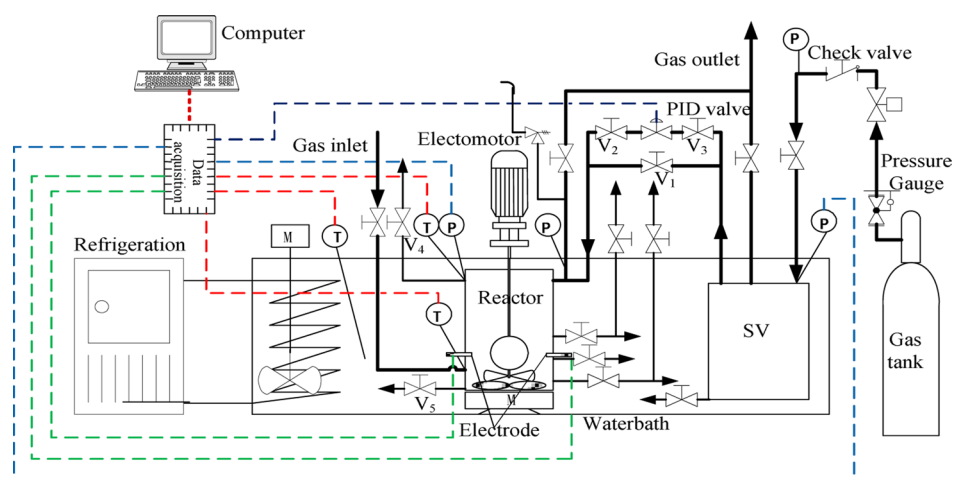


Figure 1. Schematic of experimental apparatus.

dioxide may be either sI or sH hydrate.¹⁶ Takeya et al. reported the four-phase equilibrium conditions in the systems of water + krypton + cyclopentane/cyclopentene/tetrahydropyran. These equilibrium pressures were lowered by at least 4 MPa than those of the krypton hydrate system.¹⁷ Structure II clathrate hydrates were confirmed by PXRD measurements. Imai et al.¹⁸ introduced fluorocyclopentane into the krypton + water system. The equilibrium temperature of fluorocyclopentane hydrate with krypton is higher than that of krypton hydrate system by more than 23 K over the pressure range up to 4.866 MPa.

In this work, the hydrate equilibrium data for water-insoluble organic compounds with methane were measured. The organic compounds are cyclopentane, cyclopentyl chloride, cyclopentanone, methylcyclopentane, cyclohexene, tetrahydrothiophene, and trimethylene sulfide. There are no equilibrium data obtainable for the hydrate systems for these organic compounds with methane except for cyclopentane.^{20,21} Also the promotion effects of the seven cyclic organic promoters were compared. The dissociation enthalpies of organic promoters + methane hydrates were determined on the basis of the experimental phase equilibrium data.

EXPERIMENTAL SECTION

Materials. Table 1 demonstrates the name and molecular structures of the organic promoters used in this work. All organic promoters are poorly soluble in water, and thus these promoters are regarded as insoluble. The deionized water was used as an aqueous phase, which was produced by the ultrapure water system supplied by Nanjing Ultrapure Water Technology Co., Ltd., China. The methane was obtained from Foshan Huate Gas Co., Ltd. with 0.9999 mass fraction certified purity.

Apparatus. The schematic drawing of the experimental apparatus used in this work is shown in Figure 1. A reactor immersed in the water bath with the temperature control system is the core component of the experimental system. The reactor was made of 316 stainless steel, the effective volume is 398 mL, and the maximum working pressure of reactor reaches 30 MPa. The pressure of the reactor was controlled by proportional-integral-derivative (PID) controller through a pressure-regulated valve (Tescom ER3000). Liquid inlet was installed at the bottom of the reactor and gas outlet was installed at the top side-wall of the reactor. Two plexigla windows were equipped at the front and back of the reactor, respectively. The magnetic spin bar was installed at the bottom of the reactor and the three-paddle helical impeller was located at the top of the reactor. Both the magnetic spin bar and the

helical impeller were performed to agitate and mix the reactor contents. Two Pt1000 thermocouples (JM6081) with uncertainties of ± 0.05 K were applied to make the temperature measurements of gas phase and liquid phase in the reactor. In order to precool and meter the volume of the offered gas, a supply vessel (SV, 1.0 L, 30 MPa) was placed in the water bath. In the process of supplying methane, the SV can minimize the temperature perturbation and pressure perturbation of the reactor. MBS3000 absolute pressure transducer (range of 0 to 25 MPa) with the accuracy of ± 0.02 MPa was utilized to measure the pressures of the SV and the reactor. Temperature and pressure data were acquired every 5s using an Agilent model 34970A recording system, which was controlled by the Agilent data acquisition software application BenchLink.

Experimental Procedure. The experimental procedure employed in this work was T-cycle method, which was reliable to determine the equilibrium temperature of hydrate.^{22,23} The experimental apparatus was cleaned by deionized water and evacuated with a vacuum pump. After that, 210 mL of H₂O and 5 mL of organic promoter were introduced into the reactor. Subsequently, the reactor was washed with the methane at least three times to ensure an air-free system. The hydrate phase equilibrium conditions were measured by the desired pressure, and the system temperature was reduced until the hydrate phase appeared. The hydrate formation phenomenon can be observed through the visual windows. Subsequently, the system was gradually heated with each temperature step of 0.1 K until an infinitesimal amount of hydrate was left in the water. The interval time of each heated step was taken at least for one day until no hydrate particles appeared during the gradual heating. At this time, the temperature was determined as the equilibrium point.²⁴ These procedures were performed at the different pressures, and the clathrate hydrate phase-transfer temperature was obtained at every pressure.

RESULTS AND DISCUSSION

The equilibrium hydrate formation conditions of cyclopentane/methane/water mixture are measured and shown in Figure 2. It

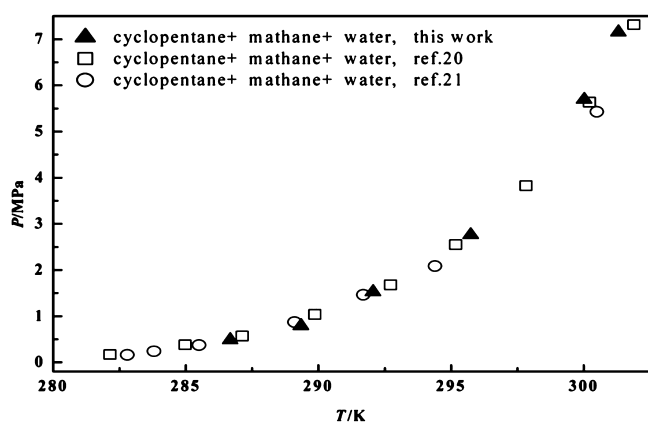


Figure 2. Phase equilibrium curves of cyclopentane–methane hydrate in this work and prior works. \blacktriangle , this work; \square , ref 20; \circ , ref 21.

can be seen from Figure 2 that the experimental data measured in the work are in good agreement with the literature values.^{20,21} This illustrates that our apparatus is reliable. The cyclic organic promoters used in the work are insoluble in water. Thus, the equilibrium hydrate systems containing water, methane, and cyclic organic promoters are the four-phase

equilibrium systems, organic (cyclopentane, cyclopentyl chloride, cyclopentanone, methylcyclopentane, cyclohexene, tetrahydrothiophene or trimethylene sulfide) phase (L_o)–vapor (methane) phase (V)–aqueous (water-rich) phase (L_w)–hydrate phase (H). The equilibrium data measured in this work are tabulated in Table 2 and plotted in Figure 3. It is found that the hydrates can be formed at the lower pressures or higher temperatures on account of the additions of cyclopentane, cyclopentyl chloride, cyclopentanone, methylcyclopentane, cyclohexene, tetrahydrothiophene, or trimethylene sulfide. At a fixed pressure, an additive presenting more excellent promotion ability can result in a higher equilibrium

Table 2. Four-Phase (L_o + V + L_w + H) Equilibrium Data and the Dissociation Enthalpies of Organic Compound + Methane + Water Systems

T/K	P/MPa	$\Delta_{\text{diss}}H_m/\text{kJ}\cdot\text{mol}^{-1}$
Cyclopentane + Methane + Water		
286.70	0.48	131.70
289.10	0.79	130.96
292.00	1.52	129.30
295.60	2.76	126.78
300.00	5.69	121.74
Cyclopentyl Chloride + Methane + Water		
277.25	1.45	97.47
279.75	2.05	96.31
282.95	3.53	93.62
285.35	4.99	91.28
286.55	5.83	90.09
Cyclopentanone + Methane + Water		
276.39	0.60	96.04
280.65	1.20	94.91
283.42	1.80	93.84
286.35	2.73	92.28
288.85	3.76	90.72
290.92	5.16	88.74
Methylcyclopentane + Methane + Water		
278.71	3.01	78.82
280.45	3.81	77.63
283.33	5.22	75.78
284.49	6.31	74.42
285.44	7.21	73.44
Cyclohexene + Methane + Water		
277.35	1.46	95.39
279.39	1.99	94.37
281.83	2.84	92.84
284.17	4.05	90.82
286.05	5.35	88.86
Tetrahydrothiophene + Methane + Water		
287.11	0.93	102.36
290.05	1.52	101.31
292.95	2.18	100.24
295.30	3.34	98.42
297.37	4.14	97.34
Trimethylene Sulfide + Methane + Water		
282.57	0.11	163.14
288.19	0.5	161.94
290.45	0.8	161.09
292.45	1.17	160.07
294.08	1.82	158.54
297.14	3.55	154.10
299.27	5.53	145.78

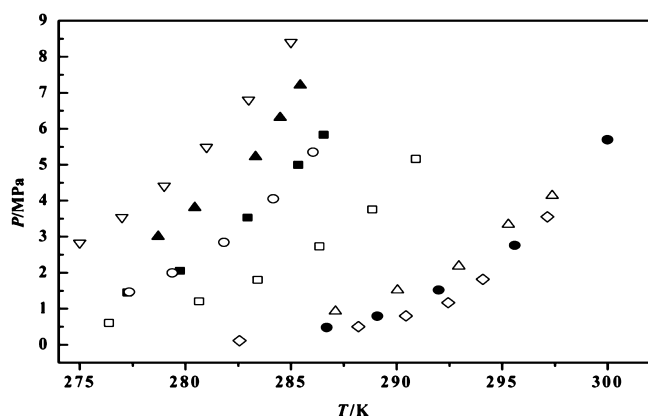
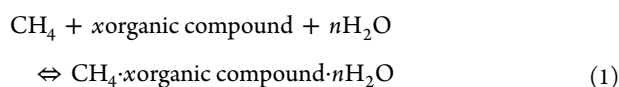


Figure 3. Phase equilibrium curves for the ternary systems in this work: \blacktriangle , $\text{H}_2\text{O}-\text{CH}_4$ -methylcyclopentane; \blacksquare , $\text{H}_2\text{O}-\text{CH}_4$ -cyclopentyl chloride; \circ , $\text{H}_2\text{O}-\text{CH}_4$ -cyclohexene; \square , $\text{H}_2\text{O}-\text{CH}_4$ -cyclopentanone; \triangle , $\text{H}_2\text{O}-\text{CH}_4$ -tetrahydrothiophene; \bullet , $\text{H}_2\text{O}-\text{CH}_4$ -cyclopentane; \diamond , $\text{H}_2\text{O}-\text{CH}_4$ -trimethylene sulfide; ∇ , $\text{H}_2\text{O}-\text{CH}_4$, ref 26.

temperature during the hydrate formation.¹ Therefore, as seen from Figure 3, the promotion effects of the above organic compounds on mixed methane hydrate formation are summarized as trimethylene sulfide > cyclopentane > tetrahydrothiophene > cyclopentanone > cyclopentyl chloride, cyclohexene > methylcyclopentane. Trimethylene sulfide has the biggest effect of hydrate promotion among the promoters studied in this work. It is noted that the promotion effect is heightened with the decrease of the molecular size for the seven compounds. It can be found from our experimental results that the cyclic organic components, which contain less carbon atoms in the ring and have no branched chain, can show a better promoting effect on hydrate formation. Further studies are required to confirm the crystal structures of the hydrates mentioned above and cavity structures of the guest molecules occupied with some advanced analysis techniques, such as nuclear magnetic resonance (NMR), Raman spectroscopy, X-ray diffraction (XRD) etc. It is expected that the molecular size and geometry of the organic compound determine the stability of the clathrate hydrate. The investigation of Trueba et al.²⁵ showed that the molecular geometry of organic compound has the largest influence on the hydrate stability. As seen in Figure 3, the equilibrium pressure of trimethylene sulfide + methane + water system is lower by approximately 7 MPa than that of methylcyclopentane + methane + water system at the same temperature. In other words, equilibrium temperature of trimethylene sulfide + methane + water system is higher by approximately 18 K than that of methylcyclopentane + methane + water system at a given pressure. Figure 3 shows that, at 285 K, the four-phase (L_w-L_o-H-V) equilibrium pressure for the trimethylene sulfide + methane + water system is lower by at least 8.0 MPa than the three-phase (L_w-H-V) equilibrium pressure for the methane + water system.

The hydrate dissociation enthalpies are determined via the Clausius–Clapeyron equation based on the phase equilibrium data.²⁶ The formation and dissociation of the mixed methane hydrates can be shown by the following equations



where x and n are the mole number of organic compound and H_2O in hydrate crystalline, respectively.

$$\frac{d \ln P}{d(1/T)} = \frac{-\Delta_{\text{diss}} H_m}{ZR} \quad (2)$$

where P and T are the absolute pressures and temperatures of hydrate equilibrium; Z is the compressibility factor of the guest gas (CH_4) at each equilibrium P – T condition, and it can be calculated by the Soave–Redlich–Kwong (SRK) equation; R is the universal gas constant ($R = 8.31451 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); and $\Delta_{\text{diss}} H_m$ refers to the enthalpy of dissociation. On the basis of the data of pressure and temperature, the natural logarithms of the pressures ($\ln P$) versus the reciprocals of the temperatures ($1/T$) are shown in Figure 4. The good linear relationships

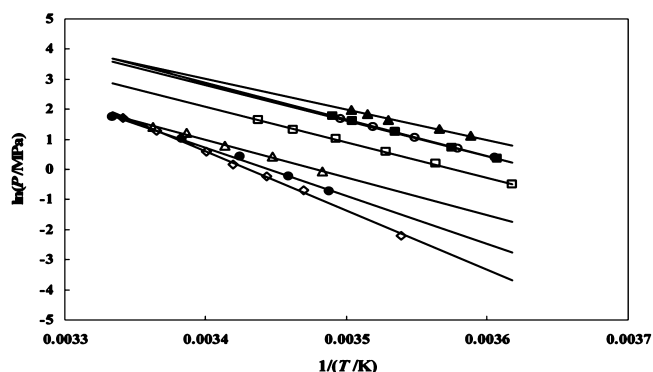


Figure 4. The natural logarithms of the pressures ($\ln P$) versus the reciprocals of the temperatures ($1/T$) along the cyclic organic promoter (L_o)–methane (V)–water (L_w)–hydrate (H) coexistence lines. \blacksquare , cyclopentyl chloride, $k = -12110$, $r = 0.9986$; \bullet , cyclopentane, $k = -15991$, $r = 0.9963$; \square , cyclopentanone, $k = -11712$, $r = 0.9995$; \blacktriangle , methylcyclopentane, $k = -10129$, $r = 0.9958$; \circ , cyclohexene, $k = -11822$, $r = 0.9999$; \triangle , tetrahydrothiophene, $k = -12533$, $r = 0.9959$; \diamond , trimethylene sulfide, $k = -19667$, $r = 0.9983$; $-$, fitting line; k , slope of the fitting line; r , linear correlation coefficient of the fitting line.

(represented by linear correlation coefficients close to 1.0) are seen from $\ln P$ versus $1/T$ for all cyclic organic promoters. Thus, the hydrate dissociation enthalpies can be approximately calculated by the slopes of the straight lines in $\ln P$ versus $1/T$. The slopes of the straight lines in $\ln P$ versus $1/T$ and linear correlation coefficient of the fitting line are tabulated in Table 3. It can be observed from Table 2 and Table 3 that the absolute value of slope k plays a significant role on the value of $\Delta_{\text{diss}} H_m$. The increase of the absolute value of slope k ($|k|$) causes an increase of the $\Delta_{\text{diss}} H_m$.

Table 3. The Slopes of the Straight Lines in the Natural Logarithms of the Pressure ($\ln P$) versus the Reciprocals of the Temperature ($1/T$) and Linear Correlation Coefficient of the Fitting Line

	k/T	r
cyclopentane + methane + water	−15991	0.9963
cyclopentyl chloride + methane + water	−12110	0.9986
cyclopentanone + methane + water	−11712	0.9995
methylcyclopentane + methane + water	−10129	0.9958
cyclohexene + methane + water	−11822	0.9999
tetrahydrothiophene + methane + water	−12533	0.9959
trimethylene sulfide + methane + water	−19667	0.9983

4. CONCLUSION

The hydrate dissociation conditions were reported in the organic promoters (cyclopentane, cyclopentyl chloride, cyclopentanone, methylcyclopentane, cyclohexene, tetrahydrothiophene, or trimethylene sulfide) + methane + water system at the various pressure ranges. All the measurements were carried out using the T-cycle method. The hydrate promotion effects with methane as a help gas can be summarized as trimethylene sulfide > cyclopentane > tetrahydrothiophene > cyclopentanone > cyclopentyl chloride and cyclohexene > methylcyclopentane. Trimethylene sulfide may be a promising water-insoluble chemical promoter. At the pressures (from 0.11 to 5.53) MPa, the equilibrium temperatures were obtained (from 282.57 to 299.27) K in the presence of trimethylene sulfide. It is noted that the promotion effect is heightened with the decrease of the molecular size for the seven compounds. Some feasible physical techniques (e.g., NMR, Raman spectroscopy, or X-ray) will be required in future work to identify the structures of these hydrates and the occupancies of the cavities. The dissociation enthalpies of these hydrates were determined via the Clausius–Clapeyron equation on the basis of the measured phase equilibrium data.

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Notes

The authors declare no competing financial interest.

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