

Experimental study of separation of ammonia synthesis vent gas by hydrate formation

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Abstract: Thermodynamic data on methane hydrate formation in the presence of ammonia are very important for upgrading of ammonia synthesis vent gas using hydrate formation. This paper is focused on the formation conditions of methane hydrate in the presence of ammonia and the effects of gas-liquid ratio and temperature on the separation of vent gas by hydrate formation. Equilibrium data for methane hydrate within an ammonia mole concentration range from 1% to 5 % were obtained. The experimental results indicated that ammonia has an inhibitive effect on hydrate formation. The higher the ammonia concentration, the higher is the pressure required for methane hydrate formation would be. The primary experimental results showed that when volume ratio of gas to liquid was 80:1 and temperature was 283.15 K, total mole fraction of (H_2+N_2) in gas phase could reach 96.9 %.

Key words: CH_4 hydrate, ammonia, THF, thermodynamics, separation

1 Introduction

Only about 20% of the hydrogen and nitrogen reacts on the first pass through the Haber process, and the unreacted hydrogen and nitrogen is recycled after removal of the ammonia product. Continuous recycling of the unreacted H_2 and N_2 is part of the normal process. Inert gases like argon and methane build up in the recycling process, and have to be removed out as "Vent gas" to keep the conversion efficiency high.

A typical vent gas composition from the Haber process is 65% hydrogen, 23% nitrogen, 9% methane and 2.4% argon (mole fraction). Normal industrial procedure is for the bulk of the hydrogen in the vent gas to be recovered by membrane filtration and the residual hydrogen and methane along with the inert nitrogen and argon is burnt for process heat, unless it is economic to recover the argon as an industrial gas.

If a proportion of the inert gases (argon and methane), can be removed from the vent gas, the remaining H_2 and N_2 can be fed back into the recycled gas stream to be reacted again. Using hydrate formation to reduce the concentrations of both Ar and CH_4 offers an opportunity to recycle more of the hydrogen and nitrogen, and perhaps to recover argon and methane efficiently.

Gas hydrates are non-stoichiometric compounds formed by low-molecular-weight gases and water at low temperature and high pressure (Sloan, 1990). In the oil and gas industry hydrates have historically been regarded as an obstacle as methane hydrate can block gas pipelines and cause tubing and casing expand/burst during natural gas transportation

(Hammerschmidt, 1934; Chatti et al, 2005; Makogon, 1965). One m^3 of solid methane hydrate typically contains 167 m^3 of gas at standard temperature and pressure (STP) (Englezos, 1993; Lee et al, 2003), which may perhaps lead to its consideration as an alternative means to transport and store natural gas (Lee et al, 2003; Rovetto et al, 2006; Strobel et al, 2006; Florusse et al, 2004; Makogon, 1981). Because different gases form hydrates under different pressures at a given temperature, hydrate formation has been considered as a possible way to separate gas mixtures (Kim et al, 2007). When a gas mixture form a hydrate with water under specific conditions, the components that can form hydrate more easily will be enriched in the hydrate phase. For new technologies based on hydrates to be developed, for example, avoiding the problems associated with hydrate formation and using the hydrates as an energy resource, the phase equilibrium data in pure water and aqueous systems containing inhibitors such as electrolytes should be acquired. A number of researchers have been involved in the work of hydrate thermodynamics concerning aqueous systems with inhibitors (Sun et al, 2007; Ng and Robinson, 1985; Song and Kobayashi, 1989; Dholabhai and Bishnoi, 1994; Clarke et al, 2004; Zhang et al, 2004).

This study is a part of an ongoing experimental and computational program on hydrate formation in ammonia-water systems. A new method of separating and recycling the vent gas of ammonia synthesis by forming/dissociating hydrate is investigated. We studied the hydrate-forming conditions of methane in (NH_3+H_2O) system and found that the hydrate-forming pressure of methane is too high to be practically applicable. Tetrahydrofuran (THF) is miscible with water and could form structure II hydrate at a molar THF to H_2O ratio of 1:17 (Mahmoodaghdam and Bishnoi, 2002). THF is proved to be a hydrate stabilizer (Hashimoto

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and Murayama, 2006). It can greatly lower the hydrate-forming pressure and increase the corresponding hydrate formation rate. The hydrate-forming condition of methane in ($\text{NH}_3+\text{H}_2\text{O}+\text{THF}$) system was investigated in this paper, which might be a guide for separation of exhaust gas mixture of ammonia plant by forming and then dissociating hydrate.

2 Experimental apparatus

A schematic diagram of the apparatus used in this experiment is illustrated in Fig. 1. A high-pressure cell was immersed in an air bath. The cell was made of stainless steel with an inner volume of 220 mL separated to two parts by a piston. Two rectangle observation windows were fixed at the front and back of the lower section of the cell. The piston can be moved up/down to change the pressure in the cell. A manual pressure liquid pump was used to transfer pressurized liquid (ethylene glycol solution with a mass fraction of 28% ethylene glycol) to the upper part to adjust the piston position and control the pressure. The accuracy of temperature measurement was ± 0.1 K. A pressure sensor made by Shanghai Seaso Digital Technology Co., Ltd. was used for the measurement of pressure. The range of the pressure gauge was from 0 to 20 MPa with an accuracy of 0.1%. There was a magnetic stirrer at the bottom of the cell for blending liquid and gas.

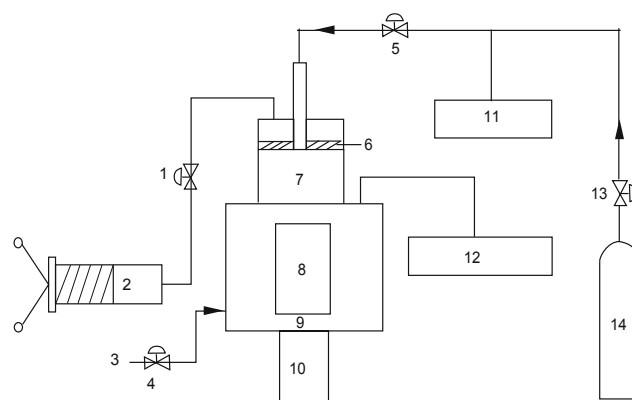


Fig. 1 Schematic diagram of the experimental apparatus
1,4,5,13-valve; 2-manual pressure liquid pump; 3-inlet/outlet for liquid; 6-piston; 7-reaction vessel; 8-glass window; 9-magnetic stirrer; 10-electromotor; 11-pressure sensor; 12-temperature sensor; 14- CH_4 gas cylinder

3 Materials and preparation of samples

Reagents used in the experiment, including the purity and supplier, are given in Table 1. Distilled water used for preparing the aqueous solution was boiled for half an hour to expel the dissolved air.

Table 1 Purity and supplier of the gas or reagent used in experiment

Components	Purity	Producer
CH_4	99.99%	Beijing AP Beifen Gases Industry Co., Ltd., China
Ar	99.99%	Beijing AP Beifen Gases Industry Co., Ltd., China
N_2	99.99%	Beijing AP Beifen Gases Industry Co., Ltd., China
H_2	99.99%	Beijing AP Beifen Gases Industry Co., Ltd., China
Deionized water	$15 \times 10^6 \Omega \cdot \text{cm}$	Prepared by water distillation (SZ-93, Shanghai Yarong Biochemistry Instrument Factory, China)
Ammonia-water	Analytical pure	Guangdong Xilong Chemical Co., Ltd., China
THF	Analytical pure	Beijing Reagents Corporation, China

4 Experimental procedures

4.1 Measurement of methane hydrate-forming conditions

First, the cell was washed by de-ionized water and rinsed three times with the liquid sample used in experiment. Then, the cell was evacuated for 30 minutes and purged with methane three times to ensure the absence of air in the pipeline and cell. After that, the liquid sample and methane were charged into the cell until the designated pressure was reached. Then the air-bath temperature was set to a designated value. When the temperature of the cell was stable, the hydrate formation point was measured by the

pressure-searching method (Song and Kobayashi, 1989). The pressure in the cell was raised to 1 MPa higher than the estimated equilibrium pressure by pushing the piston with the pump. When hydrate crystals could be seen, the pressure was reduced gradually to make the hydrate crystals decompose slowly. When all the hydrate crystals disappeared, the pressure of the system was elevated again with a small pressure-step of 0.01 MPa. If a hydrate crystal could remain for 6 hrs at a given temperature and pressure and would disappear when the pressure was reduced by a maximum of 0.01 MPa, then the pressure and temperature of the system were taken as the equilibrium hydrate formation conditions. The above procedures were repeated at a series of temperature.

4.2 Upgrading of ammonia synthesis vent gas by hydrate formation

First, a hydrogen, nitrogen, methane and argon gas mixture was prepared with a composition typical of ammonia synthesis vent gas (see Table 4). The reaction vessel and pipeline were rinsed three times with liquid sample and the gas mixture, respectively, and a specific amount of liquid and gas mixture were injected into the vessel. The temperature was set to a designated value through the air-bath. The reaction started as soon as the stirrer began to work. The stirring velocity and vapor pressure must be kept invariable in the entire reaction process. When the pressure of vapor did not change with time, the reaction could be regarded as terminated. At this time the vapor sample was taken out and its composition was measured by gas chromatography (GC). Then the temperature of the air bath was set to 268.15 K and kept for 1 hour, and the vapor was released at once, and the vessel was evacuated again. Then, the temperature was set to a higher value to ensure the gas hydrate dissociated completely, and the gas sample of the hydrate phase was taken out. The composition of hydrate was measured with GC.

5 Experimental results

5.1 Methane hydrate formation pressures

Experiments were firstly conducted with a pure water-methane system, and these results are listed in Table 2 and shown in Fig. 2. The results showed good agreement with literature (Devarakonda et al, 1999; Thakore and Holder, 1987).

Table 2 Methane hydrate equilibrium conditions

T, K	P_{exp}, MPa	P_{ref}, MPa	Reference
278.2	4.49	4.50	Devarakonda et al, 1999
279.1	4.85		
279.2		4.90	Devarakonda et al, 1999
280.4	5.54		
280.9		5.77	Thakore and Holder, 1987
281.1	6.00		
281.2		6.1	Devarakonda et al, 1999
282.3		6.65	Thakore and Holder, 1987

Methane hydrate formation data were measured with (NH₃+H₂O) system and (NH₃+H₂O+THF) system. The data are listed in Table 3 and shown in Fig. 3. It was obvious that the presence of ammonia made hydrate formation more difficult compared with that in pure water (Table 2) under

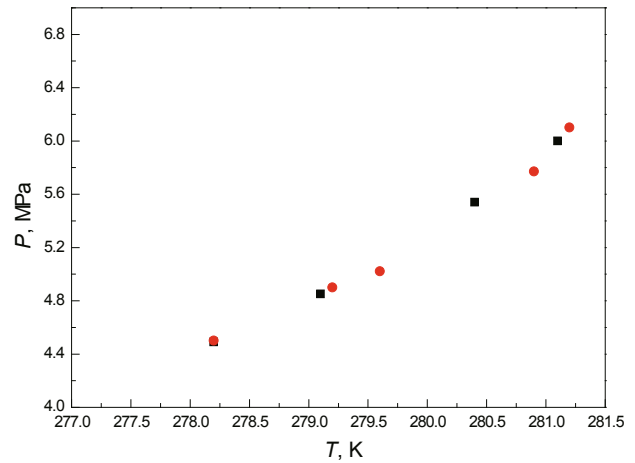


Fig. 2 Pressure-temperature phase equilibrium of methane hydrate formation in pure water
 ■ experimental data; ● data from literature (Devarakonda et al, 1999; Thakore and Holder, 1987)

the same conditions. Ammonia acted as an inhibitor in the process of hydrate formation. The higher the concentration of ammonia was, the higher the pressure for methane hydrate formation would be. However, the hydrate-forming pressure would be lower greatly in the presence of THF, making it possible in an industrial application for separation of vent gas of ammonia synthesis by hydrate formation.

For these systems, the concentrations of ammonia and water in the vapor phase were all very small, so the vapor phase was assumed to be pure methane. It was also found that the quantity of hydrates at equilibrium was negligibly small. Consequently, it was assumed that the concentration of ammonia solution at equilibrium state was identical to the initial concentration injected into the cell. Chen-Guo hydrate model (Chen and Guo, 1998) was extended to calculate the pressure of methane hydrate formation in the presence of ammonia. It demonstrated that the model could be applied to these systems.

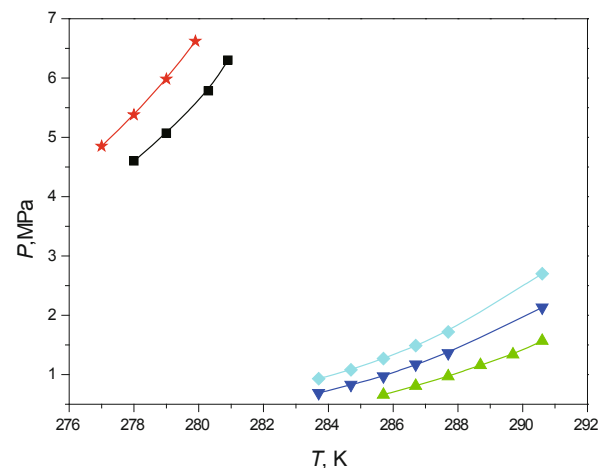


Fig. 3 Pressure-temperature phase equilibrium of methane hydrate formation in the presence of ammonia
 ★ 3.17%NH₃+H₂O; ■ 1.02%NH₃+H₂O; ◆ 4.98%NH₃+5.70%THF+H₂O;
 ▼ 2.99 %NH₃+5.82%THF+H₂O; ▲ THF+H₂O

Table 3 Methane hydrate formation pressures in the presence of ammonia

System	T, K	P, MPa	System	T, K	P, MPa
1.018%NH ₃ +water	278.0	4.60	3.171%NH ₃ +water	277.0	4.85
	279.0	5.07		278.0	5.38
	280.3	5.78		279.0	5.98
	280.9	6.30		279.9	6.62
5.278%NH ₃ +water	276.9	5.43			
	278.0	6.06			
	279.0	6.75			
6.000%THF+water	285.7	0.66	0.958%NH ₃ +5.943%THF+water	283.7	0.53
	286.7	0.81		284.7	0.65
	287.7	0.97		285.7	0.77
	288.7	1.16		286.7	0.91
	289.7	1.34		287.7	1.09
	290.6	1.57		290.6	1.75
2.986%NH ₃ +5.821%THF+water	283.6	0.69	4.977%NH ₃ +5.701%THF+water	283.7	0.93
	284.7	0.83		284.7	1.08
	285.7	0.97		285.7	1.27
	286.7	1.17		286.7	1.49
	287.7	1.36		287.7	1.72
	290.6	2.13		290.6	2.70

5.2 Primary experimental results of gas-liquid ratio and temperature on separation of ammonia synthesis vent gas by hydrate formation

The compositions of the gas mixture used in the experiment are listed in Table 4. The separation reaction was carried out under a pressure of 8 MPa. The effects of gas-liquid ratio and temperature on the separation were investigated. The compositions of equilibrium vapor phase are listed in Table 5.

The results showed that the ammonia synthesis vent gas could be separated effectively by hydrate formation. The total mole fraction of (H₂+N₂) in the equilibrium vapor was more than 92% and the fraction of H₂ was up to or even more than

Table 4 Compositions of gas mixture in experiment

Gas	H ₂	N ₂	CH ₄	Ar
Mole fraction, %	65.4	23.4	8.7	2.5

70%. The temperature influenced the reaction greatly. The higher the temperature was, the greater the recovery percent of H₂ would be. When the volume ratio of gas to liquid was 80:1 and the temperature was 283.15 K, the total mole fraction of (H₂+N₂) reached a maximum of 96.9%.

Table 5 Compositions of equilibrium vapor phase at 8 MPa

Volume ratio of gas to liquid	T, K	H ₂ , %	Ar, %	N ₂ , %	CH ₄ , %
110	278.15	69.8	1.9	22.3	5.9
	279.15	71.1	1.9	22.0	5.0
	280.15	73.5	1.6	20.7	4.2
	281.15	73.5	1.7	20.8	4.0
	283.15	76.7	1.3	19.2	2.8
100	278.15	71.4	1.9	20.9	5.8
	279.15	71.8	1.8	21.5	4.9
	280.15	73.6	1.7	20.6	4.1
	281.15	75.2	1.7	20.1	3.1
	283.15	77.3	1.3	18.8	2.6
80	278.15	73.6	1.6	20.8	4.0
	279.15	76.6	1.5	19.4	2.5
	280.15	77.4	1.3	18.6	2.7
	281.15	77.6	1.3	18.7	2.4
	283.15	79.4	1.1	17.5	2.0

6 Conclusions

Formation conditions for methane hydrate in the presence of ammonia and THF were investigated. The experimental results indicate that ammonia has an inhibitive effect on the hydrate formation. More ammonia in water would result in a higher pressure for methane to form hydrate. The calculated results showed that the Chen-Guo hydrate model fitted these systems well. The presence of THF could decrease the pressure of hydrate formation significantly, making hydrate available in industrial application of recycling the ammonia synthesis vent gas. The present work proved that this new method could be used to separate this gas mixture effectively, and the best operation conditions obtained for the simulated vent gas mixture was that volume ratio of gas to liquid 80:1 and temperature 283.15 K, then the total mole fraction of (H₂+N₂) in the gas phase could reach 96.9%.

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