EXPERIMENTAL DETERMINATION OF METHANE HYDRATE FORMATION IN THE PRESENCE OF AMMONIA

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ABSTRACT

Formation condition data for methane hydrate in ammonia + water and ammonia + water + tetrahydrofunan (THF) systems are very important for the process development and the determination of operation condition for recycling the vent gas of ammonia synthesis using hydrates. This paper focused on the formation conditions of methane hydrate in the presence of $NH_3 + H_2O$ and $NH_3 + H_2O + THF$ system. Equilibrium data of methane hydrate in the temperature, pressure and concentration ranges from 277 to 291 K, 0 to 8 MPa, 1 to 5 % ammonia, were obtained. The experimental results indicate that ammonia has an inhibitive effect on hydrate formation. The higher the concentration of ammonia is, the higher the formation pressure for methane hydrate will be.

Keywords: CH₄ hydrate; THF; ammonia; Measurement, formation

INTRODUCTION

Gas hydrates are non-stoichiometric inclusion compounds formed by a lattice of water molecules, "host", due to strong hydrogen bonds, the host which encage low molecular weight gases or volatile liquids, the guest, in different cavities appropriate conditions under where low temperatures and high pressures favor hydrate formation¹. Although gas hydrates have historically been regarded as a trouble during natural gas transportation because the formed solid hydrate can block pipelines and cause tubing and casing collapse²⁻⁴, the discovery of huge deposits of gas hydrates in deep-sea sediments and in permafrost has sparked interest in gas hydrates as a new energy resource⁵. A cubic meter of hydrate contains about 160 m³ of gas and 0.87 m³ of water at standard temperature and pressure⁶⁻⁷. This relatively high gas density has prompted studies to investigate hydrates as an alternative means to transport and store natural gas⁸⁻¹². When a gas mixture forms hydrate with water partially under certain conditions, the component that can form hydrate more easily will be enriched in hydrate phase, this has been considered as a possible way

to separate gas mixtures through forming hydrate¹³. We need to obtain phase equilibrium data for pure water and aqueous systems containing inhibitors such as electrolytes to avoid the problems associated with the hydrate formation and to exploit the hydrates as an energy resource or to develop new technologies based on hydrates, A number of researchers have been involved in the search for hydrate phase equilibrium data for aqueous systems containing inhibitors¹⁴⁻¹⁹.

This study is a part of an ongoing experimental and computational program dealing with the thermodynamics of gas hydrate formation in ammonia-water systems, and developing a new method to separate and recycle the vent gas of ammonia synthesis by forming / dissociating hydrate. We studied the hydrate-forming conditions of methane in ammonia + water system. The hydrate-forming pressure of methane in ammonia + water system, which we studied is too high to be applied in the industry. THF is miscible in water and forms a structure II hydrate with water at a composition of 1:17 molar ratio²⁰. THF was proved to be a hydrate stabilizer²¹ in many researches that can greatly reduce the required

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hydrate formation pressure and moreover promote the corresponding hydrate formation rate. In this paper the information on the hydrate-forming conditions of methane in ammonia + water + THF system was investigated which might be used for the separation of ammonia plant purge gas mixtures by forming / dissociating hydrate in possible technological applications

Experimental apparatus

A schematic of the apparatus used in this experiment is illustrated in Figure 1. A highpressure cell is immersed in an air bath. The cell was made of stainless steel with a maximum inner volume of 220 ml and separated to 2 parts by a piston assembled in it. Two rectangle viewing 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 pressurized liquid pump was used to transfer pressurized liquid (in this study water and ethylene glycol solution (28 %) is used as pressurized liquid) to the upper part to adjust the piston position and control the pressure. The temperature accuracy is \pm 0.2 K. The pressure sensor made by Shanghai Seaso Digital Technology Co. Ltd. is used for the pressure measurement and the range of the pressure gauge is 0 to 20 MPa with an accuracy of 0.1 %. There is a magnetic stirrer at the bottom of the cell for the mixing of liquid and gas.



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

Materials and preparation of samples

Reagents used in the experiment, including the purity and supplier, are given in Table 1. Distilled water, which was used for preparing the

aqueous	solution	was	boiled	for	half	an	hour	to	
expel the air dissolved in it.									

Table 1 Purity and source of experimental gas or reagent							
Component	Purity / %	Producer					
CH_4	99.99	Beijing AP Beifen Gases Industry Co., Ltd.					
De-ionized	15×10^{6}	Prepared by water					
water	Ω•cm	distillation					
ammonia water	analytically	Guangdong Xilong					
annnonna-water	pure	Chemical Co., Ltd.					
ТИБ	analytically	Beijing Reagents					
1111	pure	Corporation					

Experimental procedure

Firstly, the cell was washed by deionized water and rinsed for three times with the liquid sample used in the study. Then the cell was vacuumized for 30 minutes and the vapor space of the cell was purged with methane for three times to ensure the absence of air in pipeline and cell. After these steps, the liquid sample and the methane were charged into the cell to the desired pressure. Then the air-bath temperature was set to the experimental value. As the temperature of the cell was stabilized, the hydrate formation point was measured by pressure search method¹⁷. The pressure in the cell was raised to 1 MPa higher than the estimated equilibrium pressure by pushing the piston in 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 by a small pressure-step with 0.01 MPa. If a hydrate crystal can remain for 6 h at a given temperature and pressure and will disappear just by reducing the pressure by a maximum of 0.01 MPa, then the system pressure and temperature are taken as the equilibrium hydrate formation condition. The above procedure was repeated at a series of temperature.

Experimental results

Hydrate formation pressures in $NH_3 + H_2O$ system Experiments are firstly conducted with a pure water-methane system to check the results of this study and compare with those from literature. These results are shown in Figure 2 and show a good agreement with those obtained in literature²²⁻



Figure 2 Methane hydrate formation condition in pure water. ■ experimental data; ● cited literature.

Methane hydrate formation data have been measured with ammonia solutions of 1.018, 3.171 and 5.278 %. The data are tabulated in Table 2 in order to demonstrate the inhibitive effect of ammonia on the formation of methane hydrate. The presence of ammonia makes hydrate formation more difficult compared with that in pure water under the same experimental condition. Ammonia shows an inhibitive effect on the formation. The higher the concentration of ammonia is, the higher the formation pressure for methane hydrate will be.

 Table 2 Experimental hydrate formation pressures in ammonia-water system^a

C _{NH3} / %	T/K	P _{exp} . / MPa	P _{cal.} / MPa	ARE
1.018	278.0	4.60	4.49	2.39
	279.0	5.07	5.00	1.38
	280.3	5.78	5.75	0.52
	280.9	6.30	6.14	2.53
3.171	277.0	4.85	4.75	2.06
	278.0	5.38	5.29	1.67
	279.0	5.98	5.91	1.17
	279.9	6.62	6.53	1.35
5.278	276.9	5.43	5.67	4.42
	278.0	6.06	6.41	5.78
	279.0	6.75	7.19	6.52

^aNote: the average relative error (ARE) is defined as: ARE=100 *(|Pcal - Pexp| / Pexp)

For this system, the concentration of ammonia and water in the vapor phase is very small, so the vapor phase is assumed to be pure methane. It is also noticed that in the description of the experimental procedure the quantity of hydrates at equilibrium is negligibly small. Consequently, it is assumed that the concentration of ammonia solution at equilibrium state are identical to the initial concentration injected into the cell. Chen-Guo hydrate model²⁴⁻²⁷ is extended to this methane hydrate system containing ammonia in water. It is shown that the model could be used to predict the formation pressure for methane hydrate.

Hydrate formation pressures in NH3 + H2O + THF system

The formation data of methane hydrate in water + ammonia + THF system are measured at the temperature of 283.7 K to 290.7 K, and ammonia concentration of 0.958, 2.986, 4.977 %, and the results are given in table 3 and showed in figure 4. Adding THF to the ammonia-water solution can reduce the formation pressure of methane hydrate in water + ammonia system dramatically. The reduction of the formation pressure for CH4 hydrate in the presence of THF is attributed to the type change from sI hydrate for CH₄ into sII mixed hydrate for CH₄ and THF. THF is considered to fit the larger cavities and CH₄ enters the smaller ones.



Fig.3 Experimental a hydrate formation pressures in ammonia + water +THF system. ◆ 6 % THF + water; ○ 0.958 % ammonia + 6 % THF + water; ▲ 2.986 % ammonia + 6 % THF + water; ◇ 4.977 % ammonia + 6 % THF + water

The presence of THF makes hydrate-forming easier and it is more suitable for the industrial application compared to making the experimental condition under a low temperature and a high pressure. From the experimental results, it can be expected that the use of THF greatly reduces the operating pressure for separating the vent gas of ammonia synthesis by forming / dissociating , and on the contrary, raises the operating temperature nearly to ambient temperature, which benefits cost reduction of recycling the vent gas.

conclusions

Formation condition data for methane hydrate in ammonia + water system and ammonia + water +THF system were investigated. The present work suggests that measurements of the hydrate formation are essential in the process development and determination of operation condition for recycling the vent gas of ammonia synthesis using hydrate method. The experimental results indicate that ammonia has an inhibitive effect on the hydrate formation. The higher the concentration of ammonia is, the higher the formation pressure for methane hydrate will be. The presence of THF decreases the pressure of hydrate formation significantly.

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