

MORPHOLOGY OF CARBON DIOXIDE HYDRATE WITH MIXED ADDITIVE OF TETRAHYDROFURAN(THF) AND SODIUM DODECYL SULFATE(SDS)

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ABSTRACT

Gas hydrate, as an effective method for Carbon dioxide (CO₂) capture, is facing the problem of the slow kinetics associated with hydrate formation. Adding promoters such as tetrahydrofuran(THF) and sodium dodecyl sulfate(SDS) has become a good solution to promote the formation. In this paper, the formation process of CO₂ hydrate in the presence of 5.56mol% THF with and without 500ppm SDS has been studied combined with morphology. The experiments are carried at the temperature from 279K to 283K and the pressure of 3Mpa. The results show that the combination of THF and SDS has a better effect than adding THF alone. And it provides morphological changes during the formation process. When $\Delta T \leq 10K$, the hydrates with needle-like morphology are observed and when $\Delta T > 10K$, there are dendrite-like crystals.

Keywords: CO₂ capture, hydrate, promoter, formation morphology

1. INTRODUCTION

Carbon dioxide capture and storage (CCS) is an advanced technology that reduces carbon dioxide emissions into the atmosphere. Hydrate based CO₂ capture and storage technology is currently considered as a promising and economical CCS technology. To effectively use hydrate technology in CCS, it is necessary to solve the problem of the slow kinetics associated with hydrate formation. Previous studies found that stirring[1] and additives have a good effect in solving this problem. However, stirring is difficult to use in large-scale production, so additives become a better choice and have been widely studied. Thermodynamic promoters can participate in hydrate formation by shift

the phase equilibrium curve to higher temperatures and lower pressures than that of pure CO₂ hydrate, such as tetrahydrofuran (THF), propane, cyclopentane and so on. Delahaye et al. reported that at 280K, a 78.9% decrease of CO₂ pressure is experimentally observed if the solution contains 3.8 wt% of THF[2]. Another additive named kinetic promoters (also known as surfactants), can enhance the hydrate formation kinetics by changing the interfacial properties of gas-liquid without affecting the phase equilibrium curve. Sodium dodecyl sulfate (SDS), a commonly used surfactant, had significant effect in increasing the rate of CH₄ hydrate formation and decreasing the induction time. But in some studies, the addition of THF[3] or SDS[4] alone to CO₂ is not as good as the CH₄ experiment. The combination of additives THF(1mol%)+SDS(0.3 wt%) is very effective in promoting CO₂ hydrate growth at 2.7Mpa and 275K[5]. While THF(5mol%)+SDS (0.05 wt%) solution presented a reduction of time for induction and a increase of CO₂ storage capacity than pure water at 3.0Mpa and 274.15K[6]. The synergy effect of THF and SDS seems to improve the kinetics of CO₂ hydrate formation better.

The growth characteristics including the crystal sizes and shapes related to the hydrate formation kinetics. Morphology observation plays an important role in understanding the growth of hydrate crystal. Previous studies revealed that the crystal morphology depended on the thermodynamic condition, with skeletal plates polyhedron-like[7], Dendrites-like[8] or needle-like[9] shapes in the liquid phase.

Until now, few studies on morphology of CO₂ hydrate in the presence of mixed additives were found. Therefore, this study reports the promotion effect of THF and SDS on the formation of CO₂ hydrate in a static

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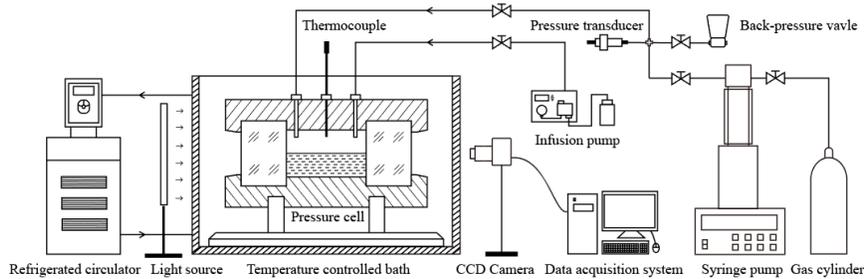


Fig 1 Experimental facilities

state in combination with morphology for analysis the kinetic of hydrate formation.

2. EXPERIMENT

2.1 Experimental apparatus

The experimental facilities are shown in Fig 1. A high-pressure cell has two glass vertical windows that can endure a maximum pressure of 20 Mpa to observe the progress of the experiment. The images were captured at regular time intervals using a CCD camera (model MD091CU-SY from XIMEA, German) with a resolution of 3312×2496 pixels. And there is a uniform light source as a backlight behind the cell. A thermocouple with an accuracy of 0.1K and a pressure transducer with an accuracy of ± 25 kPa were used. A high-precision infusion pump (model LC-3060, China) and a syringe pump (ISCO, Model500D, USA) injects liquid and gas respectively. A refrigerated circulator (JULABO, model300F, Germany) cools the cell to keep the required temperature.

2.2 Experimental Material and methods

Industrial production CO₂ (99.9% purity, Dalian Special Gases Co., Ltd., China) and deionized water were used. Industrial production CO₂ (99.9% purity, Dalian Special Gases Co., Ltd., China) and deionized water were used as the materials. Moreover, the additives in our experiments are THF (99.9% purity, Sinopharm Chemical Reagent Co., Ltd., China) and SDS (99.9% purity, Tianjing Bodi Chemical Holding Co., Ltd., China). About 18 ml solution made up in advance is poured to the half of the cell by using the high-precision infusion pump with 2ml/min. We inject CO₂ used in the experiment to the cell and evacuate it third times, to make certain that the air in the cell is all relaxed. The pressure P is then increased to 3Mpa for 2h to ensure that the liquid sufficiently dissolves the CO₂ at 291K and then close the intake valve. The temperature is then reduced to the desired temperature by the refrigerated circulator.

3. RESULTS AND DISCUSSION

3.1 Hydrate formation processes

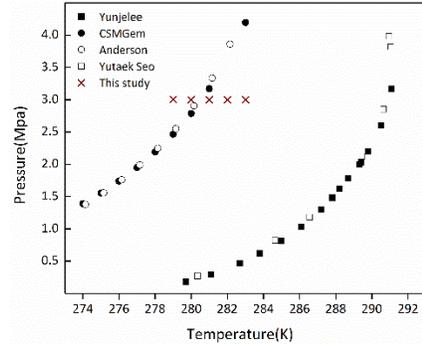


Fig 2 CO₂ equilibrium curves in pure water and THF

Fig 2 shows the CO₂ equilibrium curves in pure water (using CSMGem software[10] and by Anderson[11]), CO₂+THF(5.56mol%) by Yunjelee[12], CO₂+THF(5mol%) by Yutaek Seo[13] and the condition chosen for this study. It demonstrated that SDS has no effect on the equilibrium curve[5], so the curve with THF is used instead of THF+SDS. The concentration of THF used in this study is 5.56mol%[14]. The experimental conditions and the subcooling ($\Delta T = T_{\text{exp}} - T_{\text{eq}}$) are summarized in Table 1.

Table 1 The experimental conditions

Solution	P _{exp}	T _{exp}	ΔT	Induction time
THF5.56mol% + SDS500ppm	3Mpa	279K	12K	25.3min
		280K	11K	23min
		281K	10K	22.8min
		282K	9K	31.8min
THF5.56mol%		283K	8K	25.2min
THF5.56mol%		283K	12K	-

The reaction curve (typical P and T changes with time) of experiment (279K, 3Mpa, THF5.56mol%+SDS500ppm) is shown in Fig3. After about 2h for CO₂ dissolution, the reactor was cooled by water bath to induce hydrate formation (from the point A), and temperature and pressure in the vessel begin to decrease. At the point B (2.57Mpa, 280.72K), the temperature and pressure suddenly rise to point C because the hydrate formation begin, and then decrease. CO₂ clathrate hydrate has the structure sl,

and THF can form a type of sII hydrate under normal pressure.

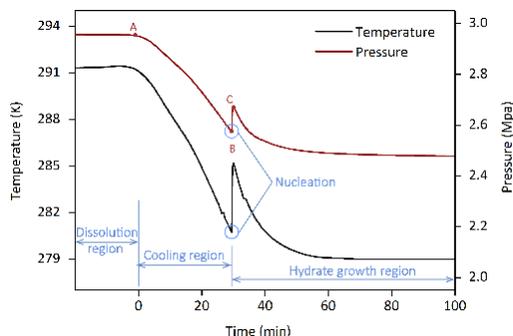


Fig 3 Reaction curve (279K, 3Mpa, THF5.56mol%+SDS500ppm)

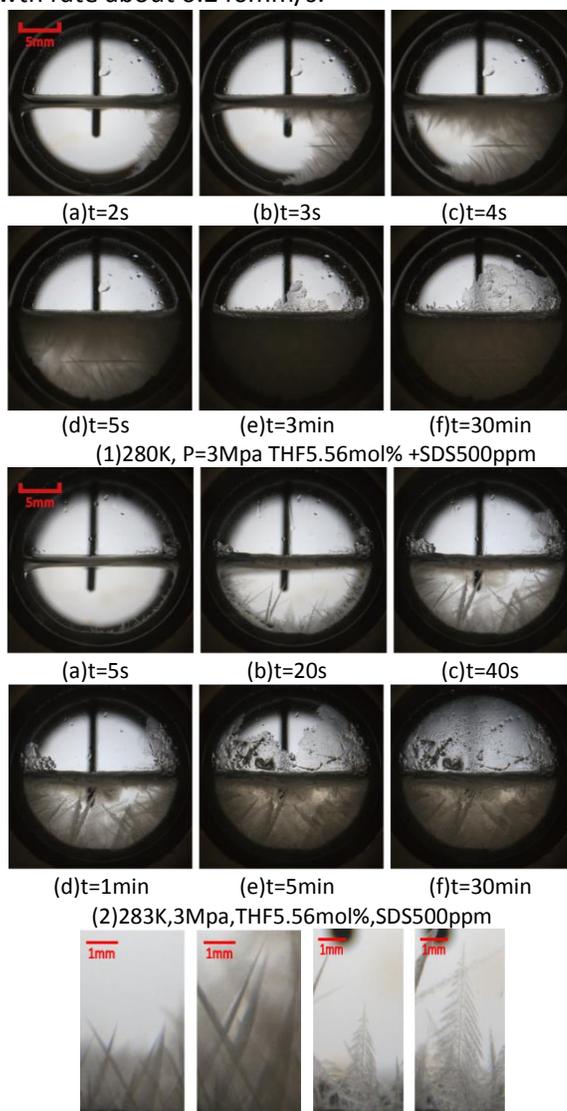
In the experiment, THF is more likely to nucleate to form hydrates, providing nucleation for the formation of CO₂ hydrate, thus shortening the induction time and reducing the phase equilibrium pressure of CO₂ hydrate. When THF hydrate is formed, the temperature and pressure increase simultaneously (this is due to the increase in volume and crystallization exotherm when THF hydrate is formed), and when CO₂ hydrate is formed, the temperature rises and the pressure drops (this is due to the consumption of gas and the crystallization exotherm). Due to increase in temperature, CO₂ in the liquid phase becomes gaseous (pressure increase), and the transition is faster than hydrate formation, so the pressure and temperature appear to increase at the point B at the same time. The inflection point (C) indicates that CO₂ molecules can be trapped in the hydrate cage after consuming THF, and thus the pressure continuously reduces. Finally, the temperature and pressure of the reaction remain the constant for a long time. In addition, since a large amount of CO₂ dissolving in the reaction before the reaction is involved in the hydrate formation, the pressure curve may not have a sudden drop at the point B seen in the previous literatures.

Under the same working conditions (283K, 3Mpa, THF5.56mol%), hydrate formation was observed within 30 min in the presence of SDS, but there is no hydrate formation in 2h without SDS (with 5 replicate experiments).The results prove the synergy effect of THF and SDS has a better effect in improving the CO₂ hydrate formation mentioned in the introduction.

3.2 Growth Morphology

The Fig4(1-2) shows the morphology of hydrate growth at 280K and 283K respectively. Considering that the temperature of the metal wall surface may be lower and there is greater subcooling, and the CO₂ was dissolved in the liquid phase before the experiment,

hydrate formation was first observed at the bottom edge of the reactor, and then there are hydrates formation near the meniscus formed by the gas-liquid-metal three phases. Followed by nucleation, the hydrate is formed then grows to form a hydrate film on the gas side along the gas-liquid interface in the radial direction, at the same time, the hydrate in the liquid phase grows rapidly. Through observation of a series of hydrate forms, we obtained two forms of hydrate crystals in liquid water in this experiment: needles Fig4(3) and branches Fig4(4). The growth rate of the crystal increases as the increase of subcooling, and the number density of crystal also increases. When $\Delta T=10K, 11K, 12K$, the dense hydrates with needle-like morphology, filling the liquid phase in 10s with the growth rate about 3.457mm/s. And when $\Delta T=9K, 10K$, there are dendrite-like crystals with a relatively slow growth rate about 0.246mm/s.



(3) Needle-like crystals (4) Dendrite-like crystals
Fig 4 Morphological changes during the formation process

In addition, it can be observed in the experiment that hydrates grow up along the window glass. This may be due to the formation of a porous hydrate layer in the presence of SDS which continuously draws the solution into the porous hydrate layer on the wall under the capillary force, thereby maintaining hydrate formation in the layer. This phenomenon is called the capillary drive mechanism, which has been observed in the literature of the Okutani[15] studying on the effects of surfactant additives on the formation of a clathrate hydrate.

4. CONCLUSIONS

In this experiment, the hydrate formation processes at 3Mpa, $8K < \Delta T < 12K$, in presence of THF (5.56mol%) and SDS (500ppm) are studied with the image acquisitions of hydrate morphology. It is demonstrated that the mixed additive of THF and SDS alter the harsh conditions of low temperature and high pressure required for the formation of CO₂ hydrates in pure water. It also has a better effect than adding THF alone.

This work also records the morphology of the hydrate formation process. Since CO₂ dissolved in the liquid phase in advance, hydrate is first formed in the liquid phase. It reveals that morphology in the liquid phase varies according to the thermodynamic conditions. When $\Delta T \leq 10K$, the hydrates with needle-like morphology are observed and when $\Delta T > 10K$, there are dendrite-like crystals. And the growth rate of the crystal increases as the increase of subcooling, and the number density of crystal also increases.

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