EFFECTS OF ADDITIVES ON CARBON DIOXIDE HYDRATE FORMATION

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ABSTRACT

In this paper, the effect of additives on CO_2 hydrate formation is investigated in a high-pressure test cell surrounded by a thermostated coolant bath. An agitator is configured inside the cell. The characteristics of CO_2 gas hydrate formation with additives SDS, THF and mixture of both were discussed. It was found that, in a quiescent system with single SDS，hydrate could form rapidly and the induction time of hydrates formation was reduced, while THF shows no improvement effect on CO_2 hydrate formation. However, the mixture of SDS and THF can promote the hydrate formation rate considerably, and large amount of hydrates formed. In a stirring system with mixture additives, hydrates can form completely about 100 minutes early than that in the quiescent system.

Keywords：carbon dioxide, gas hydrate, additive, formation rate

INTRODUCTION

The fast development of economy and urban commerce makes a sharp increase of the air conditioner use, which lead to the imbalance of the electrical power use. Especially in summer, the air conditioner takes 25%-30% of the national electrical power with focusing on the day time when lots of electricity is consumed. The policy of time-interval power price and encouragement of using night dip electricity will promote the development of cool storage technology. At present, the media of cool storage are mainly water, ice, salt solution, etc. Using gas hydrate as cool storage media in a chemical way is a new technology which overcomes the weaknesses such as low efficiency using ice, low density of cool storage using water, low efficiency of heat exchanging and easy-aging using salt solution and so on[1]. Some researches focus the gas hydrate cool storage media on normal refrigerants, such as R11, R12 and R21 as well as the alternative refrigerant R134a，R141b, but little attention to the natural refrigerant carbon dioxide(R744). Carbon dioxide gas hydrate can be used as cool storage media with more than 500kJ/kg dissolution enthalpy comparing to 334kJ/kg and 344kJ/kg for R11, R141b respectively. More over, carbon dioxide is a kind of environment -friendly working fluid[2].

Carbon dioxide gas hydrate ($CO_2 \cdot nH_2O$) is a nonstoichiometric clathrate compound which formed under proper temperature and pressure condition. The process of hydrate formation is a slowly crystallized procedure characterized with long induction time, large supercooled degree and slow growth. To successfully make use of cool storage technic with carbon dioxide gas hydrate, it must be formed fast and uniformly to get a high density of cool storage and easy to flow in the pipeline. Currently, the common ways to improve gas hydrate formation are stirring, additive adding and making use of ultrasonic and magnetic field, and so on[3,4]. In this work, an experimental study of carbon dioxide gas hydrate formation has been conducted in a high-pressure reactor. The characteristics of CO_2 gas hydrate formation with additives SDS, THF and mixture of both were discussed.

EXPERIMENTAL APPARATUS AND PROCEDURE
Experimental Apparatus
The schematic diagram of the apparatus is given in Fig.1. The established experimental setup

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mainly consists of:1) a high pressure test cell where the hydrates are produced; 2) a thermostated coolant bath which can remove the reaction heat and keep the low temperature condition inside the reactor;3) gas supply system which supplies CO_2 gas and maintain high pressure; 4) data acquisition system.

The cell is a stainless steel cylinder with inner available volume of 680 cm^3. It is designed to operate at pressures under 20MPa and temperatures in the range of 253-303 K. The reactor is equipped with a stirrer driven by a permanent-magnetic motor with feasible adjustment. The platinum resistance thermometer was used to measure the reaction temperature with an accuracy of $\pm$0.01K. The pressure in the cell was continuously measured by a 10MPa digital pressure transducer which is installed on the top of the cell. The 4-20mA output signal is recorded on a computer.

A mass gas flowmeter (model D07-11M/ZM, Peking Jianzhong Instruments, Inc.) was used to measure the amount of gas supplied to the cell during hydrate formation. The flowmeter has a capacity of 0-1000 sccm, with an accuracy within 2% of full scale and a repeatability of within 0.2% of the flow rate. The temperature and pressure of the cell as well as outputs from the mass gas flowmeter in the process of hydrate formation were recorded and displayed on-line through a data acquisition system as a function of time.
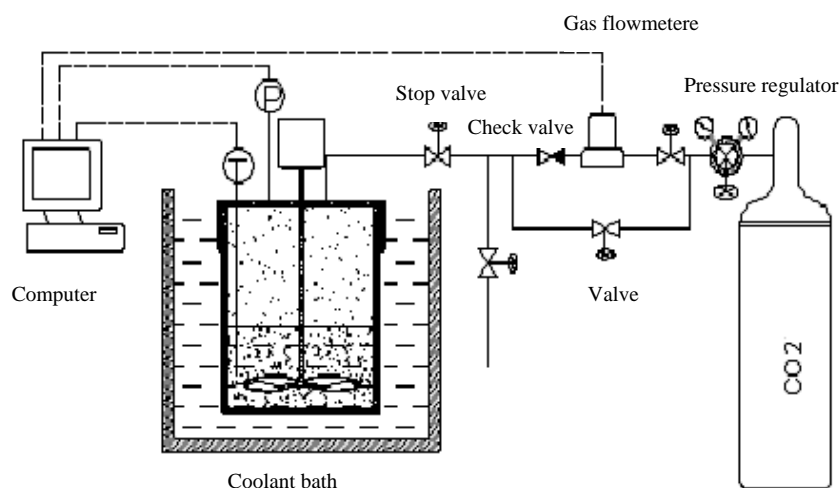

Figure 1 Experimental apparatus

Table 1. Experimental materials

materials	Purity	source
CO_2	99.99%	Shanghai Pujiang Special gases Co.,Ltd
sodium dodecyl sulfate, SDS	≥98%	Shanghai Aibi Chemistry Preparation Co.,Ltd
tetrahydrofuran ,THF	≥99%	Shanghai Lingfeng Chemistry Preparation Co.,Ltd

Materials Used

The test materials used in this work were summarized in Table 1. Distilled water produced in the laboratory was used in all experiments. Sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF) were used as promoters for gas hydrate formation.

Experimental Procedure

The experimental set-up is designed to work as a closed system (the gas pressure decreases when hydrate forms) or as an open isobaric system (fresh gas is injected to keep the gas pressure constant during hydrate formation). In this study, the experiments were designed to conduct at a closed system to observe the effect of additives on the hydrate formation.

A typical procedure was as follows. The cell was rinsed with distilled water three times and approximately 200 cm^3 of the water solution was charged into the cell for each experiment. The gas space of the cell was purged three times with CO_2 gas to ensure the absence of air. The CO2 gas was then injected into the cell up to a pressure of ~4.0MPa. The solution becomes saturated after several hours at environmental temperature. The pressure of the cell was adjusted at a prescribed value of ~3.5MPa and put in the water bath that has been cooled at a set temperature of about 273.65K with a pressure decrease with the decrease of temperature in certain time. Then hydrate formation started and it was tracked through monitored temperatures and pressures continuously displayed on-line through a data acquisition system and recorded on the computer. After complete reaction, taking out the cell at environmental temperature to dissolute the hydrate and release the CO_2.

RESULTS AND DISCUSSION

SDS is an effective surfactant for natural gas hydrate formation [5]. It shows that the surfactant can effectively reduce the interfacial tension of gas-liquid contact and accelerate the rate of gas hydrate formation. THF is one of water-soluble polymers which can form SII hydrate. THF was additionally used as a hydrate promoter that can greatly reduce the required hydrate formation pressure and enhance the corresponding kinetic rate[6]. Anthony Delahaye [7] reported that the dissolution enthalpy of CO_2 hydrate formed with THF is roughly two times higher than that of without THF. Furthermore, the gas-water surface was increased and continuously refreshed by stirring. It can reduce the induction time and increase the driving force of heat and mass transfer that can keep a high reaction rate.

Effect of Single Component Additive
Fig.2 represents the effect of SDS or THF on CO_2 hydrates formation rate in a quiescent system. The formation rate of hydrates can be described by the gas pressure drop in certain time($\triangle P/\triangle t$). The experiments were conducted at a initial pressure of 3.5Mpa and temperature of 0.5 ℃. The result shows that the solution with 0.3%SDS surfactant resulted in a larger pressure drop($\triangle P/\triangle t$) than pure water. However, the hydrate formation rate is slow after 400mins and much CO_2 gas still

remained in the cell after long reaction time (about 1400mins). But the solution with 4% THF shows no effect on CO_2 hydrate formation.
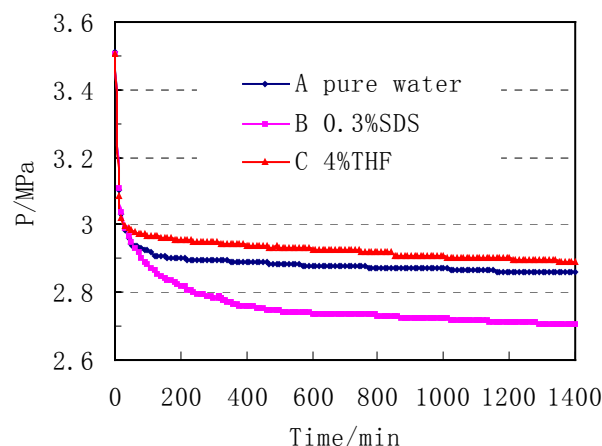

Figure 2 Effect of SDS/THF on hydrate formation

Effect of Mixed Additives
Fig3. shows the effect of mixed additives of SDS and THF on the process of hydrate formation in quiescent/ stirring system. It van be seen that, hydrate formation with mixed additives of SDS and THF is improved effectively and the formation rate is greatly increased. In the stirring system (200r/min), hydrate formation took less about 100mins to access the stage of quick reaction, so as to shorten the whole reaction time. Comparing to the experiment D and E, in the stage of quick reaction, the pressure decreased at almost the same slope, but the temperature rising amplitude with stirring was smaller because stirring can accelerate the heat transfer rate.

Table 2. Experimental conditions and tem. rise

NO.	System Condition	Tem. peak /℃	Time of Tem. rising/min
A	pure water, quiescent	1.6	52
B	0.3%SDS, quiescent	3.1	300
C	4%THF, quiescent	NO	-
D	0.3%SDS+4%THF, quiescent	3.0	750
E	0.3%SDS+4%THF,stirring	2.1	650

Tab.2 shows the temperature peak values at different experiment condition. The phenomena of temperature suddenly rising represents large amount of CO_2 hydrate formed. The higher of reaction rate makes the larger of reaction heat that resulted the temperature rise because the reaction heat cannot be removed at once by coolant bath.
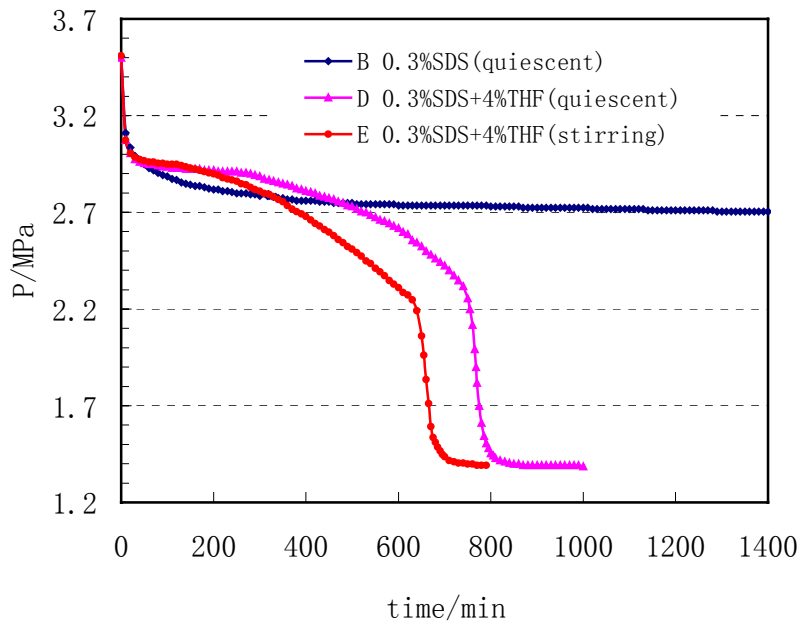
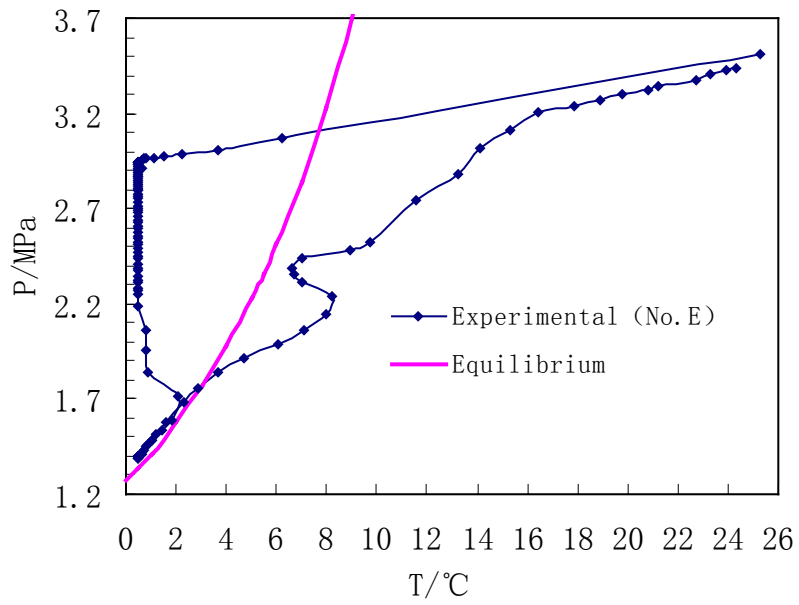Figure 3 Effect of mixed SDS and THF on hydrate formation

Figure 4 P-T curves of CO_2 hydrate formation and dissolution [8]
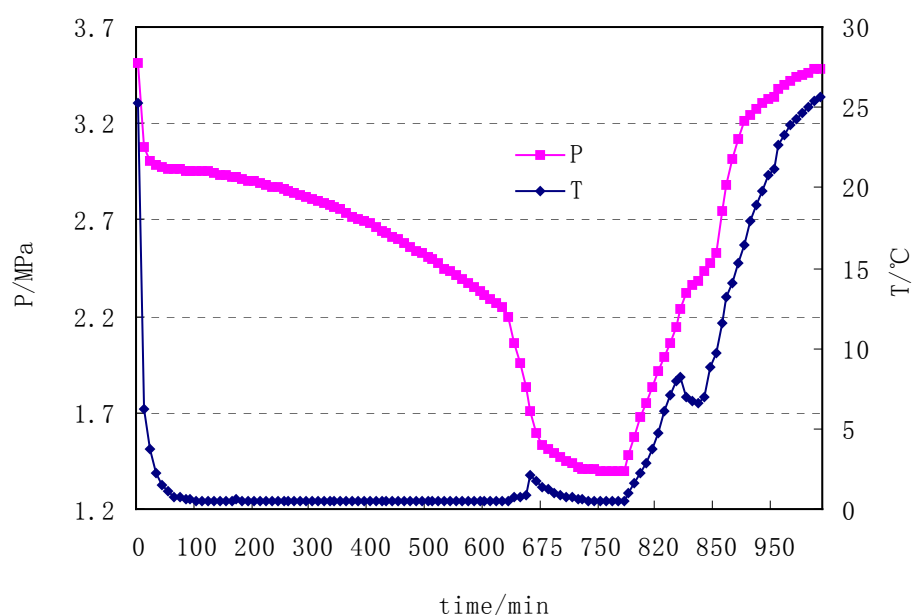
Figure5 CO_2 hydrate formation and dissolution (experiment E)

Formation and Dissolution of CO_2 Hydrates

Fig.4 and Fig.5 shows the hydrates formation and dissolution process. In the stage of CO_2 dissolving, the gas pressure declined slowly. After the nucleation inducted, the pressure dropped sharply that resulted in a temperature rising suddenly. The more hydrate formed, the more heat was released. The results show that, hydrate formation with mixed surfactants permitted a very close approach to the equilibrium pressure at the end of experiment (about 800mins), which represents that large amounts of CO_2 was stored in the hydrate. Finally, the hydrate decomposed at environmental temperature. In Fig.4 and Fig.5, the temperature shows a suddenly drop during hydrate decomposition for this is a heat-absorbing process. The phenomena also illustrated that hydrate formation with mixed THF and SDS has a large decomposition enthalpy.

CONCLUSION

In a quiescent system, the formation rate of CO_2 hydrate can be accelerated and the induction time can be shortened with single additive SDS，but most of CO_2 still remain in gas space of the cell. While single THF shows no little effect on CO_2 hydrate formation.

However, the mixture of SDS and THF can promote the hydrate formation rate considerably,

and large amount of hydrates formed. In a stirring system with mixture additives, hydrates can form completely about 100 minutes earlier than that in the quiescent system because stirring can accelerate the heat and mass transferring. The results showed that mixture additive of SDS and THF was effective for CO_2 hydrate formation and it has larger dissolution enthalpy, which is very useful for the application of cool storage with CO_2 hydrate.

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