EFFECT OF SDS AND THF ON FORMATION OF METHANE-CONTAINING HYDRATES IN PURE WATER

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ABSTRACT

Gas hydrate formation generally involves gas dissolution, formation of nuclei and growth of new nucleus. On condition of synthesizing experiments without agitation, the formation of hydrate nuclei is comparatively difficult and needs an induction period which is considerably uncertain and random. Some additives such as surfactant sodium dodecyl sulfate (SDS) can increase the formation rate and reduce the induction time. A hydrate formation and mini drilling experimental system was used to carry on methane hydrate formation experiments with small quantity of SDS and SDS- tetrahydrofuran(THF) in deionized water. The reactor is a high pressure cell (40Mpa) made of titanium alloy with 4 transparent windows and an inner volume of about 2.8 liters. The effect of SDS and THF hydrate on the formation rate and amount of methane hydrate was studied by comparative testing and analyzing the collected data of temperature and pressure. According to the results of the tests, the formation rate of methane hydrate in the SDS-THF solution was faster than that in the SDS solution. As a water-soluble hydrate former, THF hydrate nucleation may be benefit of methane hydrate nucleation. A small amount of SDS and THF could dramatically promote the formation of methane hydrate in the pure water, and rapidly increase the amount of methane hydrate too. Therefore, a great deal of time for experiment was saved, which established a good basis for the coming mini drilling and drilling fluid experiments.

Keywords: methane hydrate, formation rate, SDS, THF, mechanism

INTRODUCTION

Gas hydrate is ice-like compound with cage structure, made of water and hydrocarbon The formation of gas hydrate includes gas dissolution, formation of nuclei and growth of new nucleus. There exists two steps, induction and growth of hydrate formation[1]. But in pure water, because the mixing of gas and liquid mostly happens in the interface of gas and liquid, the induction time of gas hydrate growing is long, the speed of hydrate growing is slow, and the density of gas storage in hydrate is low. So it is needed to use some methods to accelerate the growth of gas hydrate.

Magnetic stirring apparatus are often used which advance the interaction of water and gas and increase the hydrate growing speed with the help of the stepless speed adjusting stir[2]. But there are some problems exiting in the magnetic stirring system, such as increasing the consume of energy, the rate of hydrate phase and water phase lower than 5% for maintaining the certain stirring speed[3]. Some researchers applied water spraying

into a guest–gas phase as a practical means of rapid hydrate formation[4]. Among the techniques to increase the hydrate formation rate and the storage capacity of gas in the hydrate, the additives as a promoter were often used. If an additive for instance THF is added to the water/methane system, a hydrate of sII may form at a pressure that is 30%, or even less, of the pressure required for the formation of sI methane hydrate. Some surfactants including SDS and biosurfactants were reported to have effects on hydrate formation rate and hydrate induction time[5-7]. According to the researches of Zhang C.S et al.[8-10], little anion surfactant, such as SDS and THF, can apparently improve the hydrate growing speed, which decreases the research cost and improves the experiment efficiency. At the same time, the real environment can be simulated better with the magnetic stirring system, and this is helpful to research the dynamics of hydrate growing[11]. So the effect of these two kind hydrate accelerants on the hydrate growing was studied through the contrast tests in the lab.

EXPERIMENTS

Experimental apparatus and material

The schematic of the experiment system is as following fig.1. There are six parts in the system: (1) programmable temperature apparatus, providing the temperature environment for hydrate growing and dissociation, (2) autoclave, made of titanium alloy with 4 transparent windows for videos and an inner volume of about 2.8 liters, used for hydrate growing and dissociation and micro-drilling in the simulating sediments, working pressure high up to 50MPa, (3) an alarming system for gas leakage, (4) gas resource, providing gas for the hydrate formation, (5) pressure control panel, including high pressure control, an air compressor and a vacuum pump, (6) data acquisition and control system and micro-imaging system, acquiring and processing the experiment data, and observing the hydrate growing and dissociation and the change during the micro-drilling of the simulating sediments. This system is not only used to research on the hydrate forming and dissociation, but also research odrilling control, low-temperature drilling fluids, the physics and mechanics properties. In addition, this system can also provide the high-pressure and low-temperature environment which can be extended to be applied to other research fields.
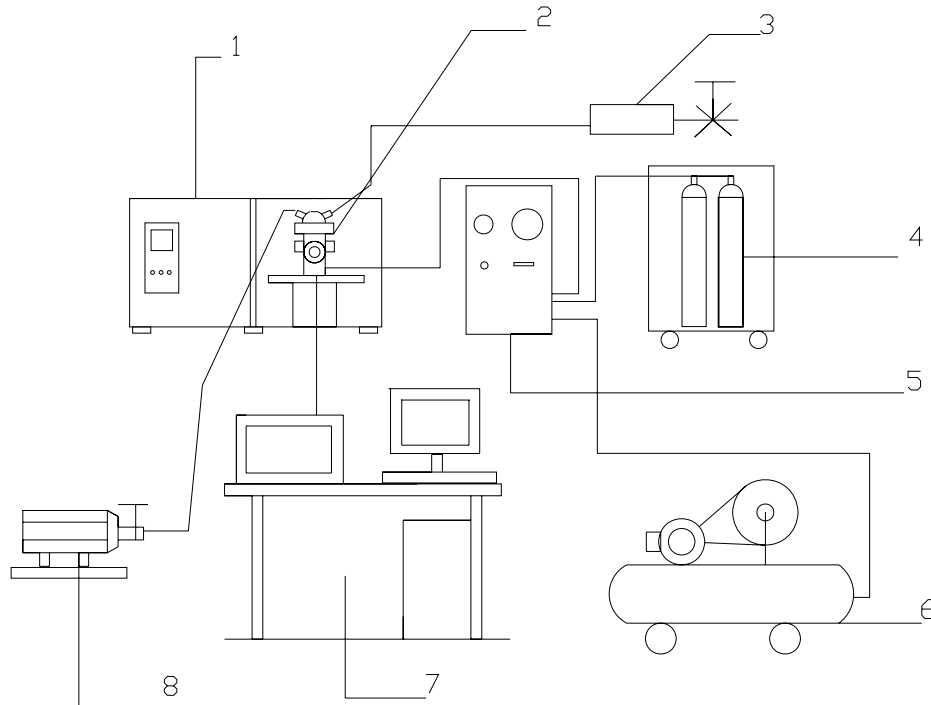

Fig. 1 Schematic diagram of hydrate formation and mini drilling experimental system
1. programmable temperature apparatus; 2.autoclave; 3.alarming system; 4.gas resource; 5.pressure control panel;
6.air compressor; 7.data acquisition system; 8.vacuum pump

Methane with a purity of 99.99% is provided by Wuhan Hong Sheng Industry Gas Corporation. Deionized distilled water is used. The SDS surfactant is provided by Guoyao Group chemical agent Corporation, and THF is provided by Shanghai chemical agent Corporation, and both are analytical purity.

Experimental procedure

Firstly, connecting all parts according to fig.1, and checking the leak tightness of valves, gas pipelines and the autoclave. Then the distilled water was used to clean the autoclave and high pipeline through the pressure control system. Three experiments have been done, which using the deionized distilled water, the deionized distilled water and SDS(0.04wt%), and the deionized distilled water with SDS(0.04wt%) and THF(0.04wt%), respectively. The volume of each solutions was same, and the liquid level in the autoclave was on the center of the lower left transparent window, which is easy for the observation of the experiment changes.

After the solution was injected into the autoclave, the vacuum pump was opened to make the autoclave vacuum. And methane was injected into the autoclave through the valve of the gas supply till the pressure reached 8MPa. Wait till the pressure in the autoclave became stable, closed the needle valves in the pressure control system, and put the autoclave for almost 12 hours in order to mix the gas and solution sufficiently. After that, the programmable temperature apparatus started to cool the autoclave. At the same time, the temperature of solution, free gas in the autoclave, environment outside and the pressure in the autoclave were collected through the data acquisition and control system. The hydrate growing and decomposing were observed through the micro-imaging system. The changes in the interface between solution and gas were mostly focused on in the experiments.

The hydrate forming was deemed to end till the temperature and pressure in the autoclave were still stable in about 1 hour. Then, the relief valve was opened, releasing the residual gas to drop the pressure to normal atmosphere, and lastly the autoclave was opened to observe the hydrate in it. For gas hydrate was quickly decomposed under normal atmosphere, the process of opening

autoclave to observe hydrate must be as quickly as possible.

EXPERIMENTAL RESULTS AND DISCUSSION

Results of the formation experiments

Fig.2 a, b and c show the temperature and pressure evolution during the methane hydrate formation in pure water, pure water/SDS and pure water/SDS/THF system respectively. There are 3 temperature sensors in the experimental system, which measures the temperature of solution(T1), gaseous phase(T2) and environment outside(T3) respectively. Since the formation of hydrate is a process of exothermal reaction, when the rate of hydrate formation is so rapid that the heat can't release in time, this would cause the temperature of liquid phase (T1) increase quickly, and at meantime, the pressure decreases as methane is consumed. In combination with the observation of micro-imaging system(Fig 3), we can judge the rate and acuteness of methane hydrate formation.

From Fig. 2a, we can see that the curves of pressure and temperature are flat gradient in the pure water system. The formation of hydrate began at the time of about 550min, and at time 600min, the reaction almost ended. It can be inferred that in the pure water system, the inducement of hydrate formation needs a long time, while the formation process lasted for a comparatively short time. When the autoclave was opened after the formation, we can see that there was only a small amount of hydrate floating above the water(Fig 4a). On the contrary, in the system of pure water/SDS and pure water/SDS/THF, the pressure dropped more significantly, and this indicates that the reaction of hydrate formation was very acute. It seems that the formation may have begun when the system was still in the beginning of the experiment, and the formation rate remained high during the whole formation process. Among the three experiments, the system of pure water/SDS/THF had the highest rate of formation. When the experiment almost finished, the declination of pressue is very distinct. Consequently, almost all the water in pure water/SDS and pure water/SDS/THF system had been transformed into hydrate, as showing in Fig.4b and Fig.4c, which is to say, SDS and THF can increase the amount of methane hydrate too.
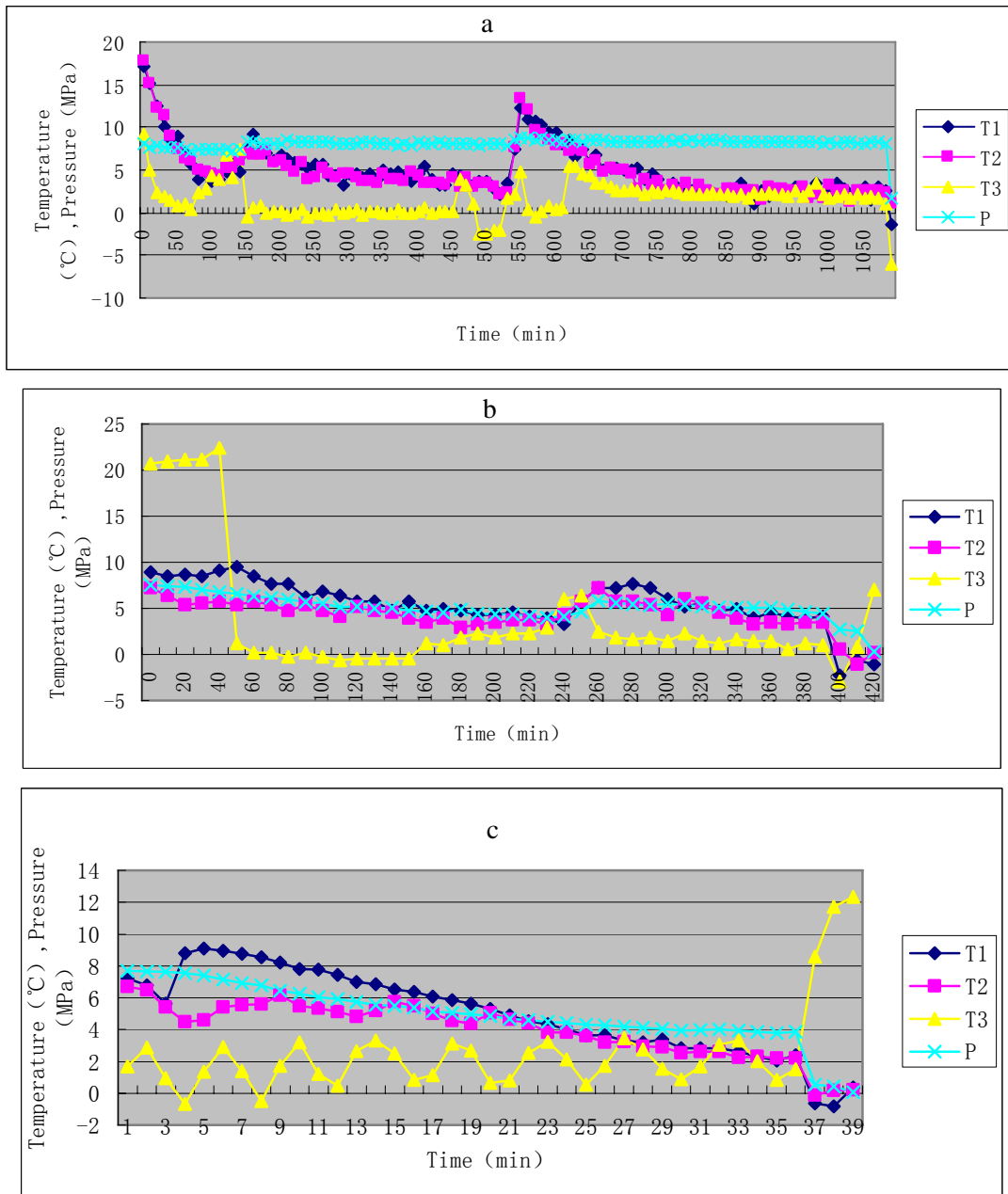
Fig. 2. a. b. and c. are temperature and pressure evolution during methane hydrate formation in (1) pure water system, (2)pure water/SDS, and (3) pure water/SDS/THF system respectively
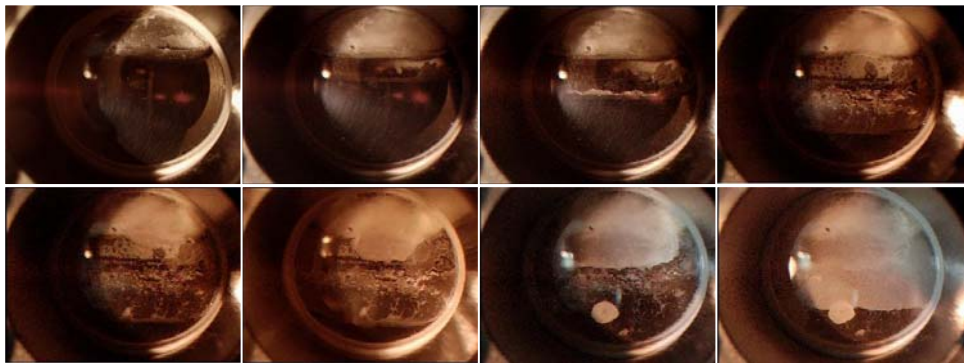

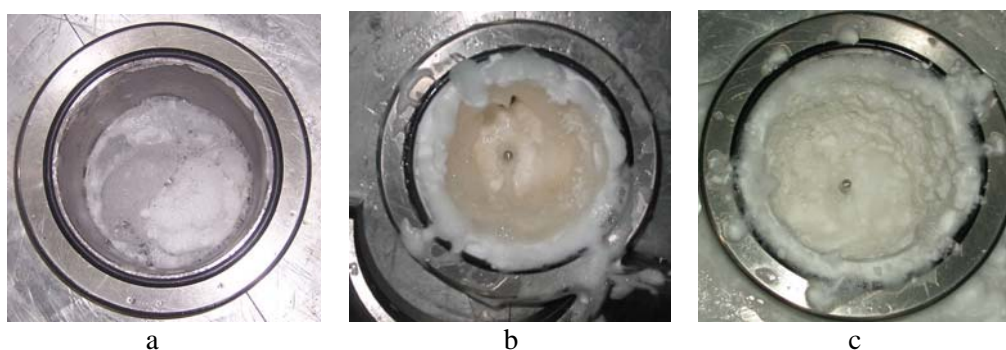Fig.3 Observation of hydrate formation process in the water+methane+SDS system

<p align="center">a   b   c</p>

Fig. 4 From left to right are the methane hydrate formed in the three experiments

Analysis of effect mechanism concerning with SDS and THF

It can be seen from Fig.3 and Fig.4 that the hydrate formation mainly occur at the gas-fluid interface in the system of pure water, the reason is that the insulation effect of the further contact between gas and fluid produced by the hydrate formed on this interface, can prevent the water and gas from continuing to form, and reduce the rate of water translation. However, in the systems with SDS, when other experiment conditions (pressure, temperature and water injection amounts) were the same, the hydrate formed with a great amount and centralized upon the wall of the autoclave, which caused a hollow column figure in the center of autoclave(Fig.4b and Fig.4c). It showed that the hydrate masses on the wall of the reactor during the process of formation. The reason for the occurrence of the above-mentioned phenomena is that SDS absorbs metal surface more easily than water, the film made of SDS replaces the one made of water on metal surface. This film similar to glacial structure can exist in water and has a rapid reaction with gas and crystal cores come into being, therefore, the rate of hydrate formation can be increased. And as water-soluble hydrate former, THF hydrate nucleation may be benefit of methane hydrate nucleation and thus causes the system of pure water/SDS/THF had the higher rate of formation than that of pure water/SDS.

Some scholars[12] considered that the main reason why surfactants could increase the rate of hydrate formation was that the surfactants might reduce the surface tension of gas-fluid interface, and make gas diffuse in water easily. However, when reaction happens in static system with SDS, this point of view can hardly explain the above-mentioned phenomena. In addition, hydrate formed in the system with SDS equably absorbs the whole wall of the autoclave and there is little of static water in hydrate. Contrarily, hydrate formed in the system with no SDS piles at the bottom of reactor, and there is a large amount of static water in hydrate. Hereby, Zhong Y. et al.[6] put forward a process of hydrate formation with surfactants: (1) hydrate crystal cores form in water, and buoyancy makes them move up to the gas-fluid interface, (2) collective crystal cores transfer to metal-solution-gas three phase interface rapidly, (3) hydrate formed is absorbed by the wall of reactor along with reaction carrying on and water surface descending, (4) when gas is taking reaction with free water, static water absorbed in porous hydrate on the metal wall continuously has reaction with free gas rapidly and new hydrate forms, therefore, hydrate particle grows rapidly along the wall of autoclave. However, in this process, How the THF hydrate influence the methane hydrate nucleation and the kinetic process of methane hydrate particles on gas-fluid interface transferring to metal-solution-gas three phase interface, can not be rationally explained at present, it needs further researches.

CONCLUSION

Adding a little SDS and THF can help to form hydrate rapidly in static system, to shorten the induction time of hydrate formation, and to avoid some problems caused by using magnetic stirring system. Therefore, it can greatly save the time of experiments, and provide some good conditions for minitype drilling experiments. The rate of hydrate formation in mixed external active reagents (SDS+THF) solution, is higher than in the one with no surfactant and with SDS because HF hydrate nucleation is benefit of methane hydrate nucleation. Further researches are needed for the mechanism with regard to surfactants how to promote the

formation of gas hydrate. In addition, in order to find a better accelerant for the formation of hydrate, there should be further studies of the effects of other types of external active reagents on promoting hydrate formation.

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