



Research on surfactants effect gas hydrate phase properties and energy storage

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ABSTRACT

This paper deals with the effects of a surfactant additive on the formation of methane hydrate in water system with and without sodium dodecyl sulfate (SDS). The properties of sodium dodecyl sulfate are listed. The results manifested that the presence of SDS could not only accelerate the hydrate formation process, but also increase the partition coefficient of methane between hydrate and vapor drastically. The paper then describes our experimental observations of the hydrate formation from methane, to show how the hydrate formation behaviors are affected by the additives of chamber partially filled with a quiescent pool of water (pure water or an aqueous SDS solution) to compensate for the gas consumption due to the hydrate formation, thereby maintaining a constant pressure inside the chamber. The results revealed that the addition of SDS not only on the liquid-pool surface but also on the chamber walls above the level of the pool surface, leaving the bulk of the liquid pool free from hydrate crystals. An excessive addition of SDS beyond the solubility was found to cause a decrease in the rate of hydrate formation but an increase in the final level of the water-to-hydrate conversion.

Key words: sodium dodecyl sulfate; methane hydrate; biochemical materials; formation

INTRODUCTION

Gas hydrates (or clathrates) are group ice-like crystalline compounds, which form through a combination of water and suitably sized 'guest' molecules under low temperature and elevated pressure conditions. Within the clathrate lattice, water molecules form a network of hydrogen-bonded cage-like structures, enclosing the guest molecules, which generally comprise of low-molecular diameter gases (e.g., methane, ethane, propane, carbon dioxide (CO₂), etc. [1]. The gas molecules occupy these cavities and a solid gas hydrate formed. There are three known type of hydrate crystal structure. Structure I, structure II and structure H, which was described in detail by Sloan [2]. These structures are formed by different combinations of crystalline cavities, with different sizes depending on guest molecules. The actual gas storage density depends on the gas occupation fraction in the hydrate and the particular crystallographic structure of the hydrate [3].

Gas hydrate can form naturally on Earth or as a result of manmade conditions. Naturally occurring gas hydrate in sediments (permafrost regions and subsea sediments) can be a potential natural gas resource [4]. Natural gas hydrates offer a largely unexploited means of energy recovery and transportation and they could play a significant role in past and future climate changes [5]. Compared to pure gas samples at standard temperature and atmospheric pressure, the same volume of gas hydrate contains more than 150 times the volume of gas. Hydrate decomposition under seafloor may result in subset landslides, therefore, methane escape that would seriously impact global climate. Therefore, the possible effect of hydrate dissociation on the geo-mechanical properties of sediments has become an environmental concern. Furthermore, marine gas hydrate could pose hazards to deepwater drilling and production, considering the increasing number of oil and gas fields that are being developed in deepwater and onshore arctic environments [6, 7]. Hydrate equilibrium data were available to determine the depressurization pressure, found to be 1.5 MPa at 0°C.

The total depressurization time was unknown due to the unavailability of a plug dissociation model [8]. The pipeline pressure was gradually reduced to 1.38 MPa, a pressure slightly below the equilibrium pressure, to cause hydrate dissociation without the formation of ice. Twenty-three days were required to completely clear the hydrate blockage. The pipeline was restarted successfully after it was fully inhibited by MEG [9]. Overall, the remediation cost about US\$3 million without counting lost production. Non-delivery penalty costs, equipment repair and strained vendor-buyer relationships also resulted. Fortunately, the presence of an extra intake valve in the manifold and the immediate availability of FPSO vessel reduced expenses. However, the loss of 6-8 weeks of production was by far the largest expense in remediation.

In order to make recovery of natural gas from hydrates commercially viable, the hydrates must be dissociated in situ or transported to the factory and then recovery [10]. So as to get these hydrates or make hydrate recovery as a gas, the drilling engineering must be used to explore and develop. The dissociation rate, which depends on the T-P conditions and other environmental conditions, is an essential parameter to evaluate the gas recovery from the hydrate layer. Especially the drilling fluids properties are playing a very important role for hydrate dissociation [11]. There has been little information on the effect of the fluids for hydrates dissociation. So as to control the risk of gas hydrate, or clathrate hydrate, formation, in the oil and gas industry, it is common to add thermodynamic inhibitors (e.g., methanol, glycol)[12] or surfactants (e.g., sodium dodecyl sulfate) to the fluids system (which may consist of saline formation water)[13].

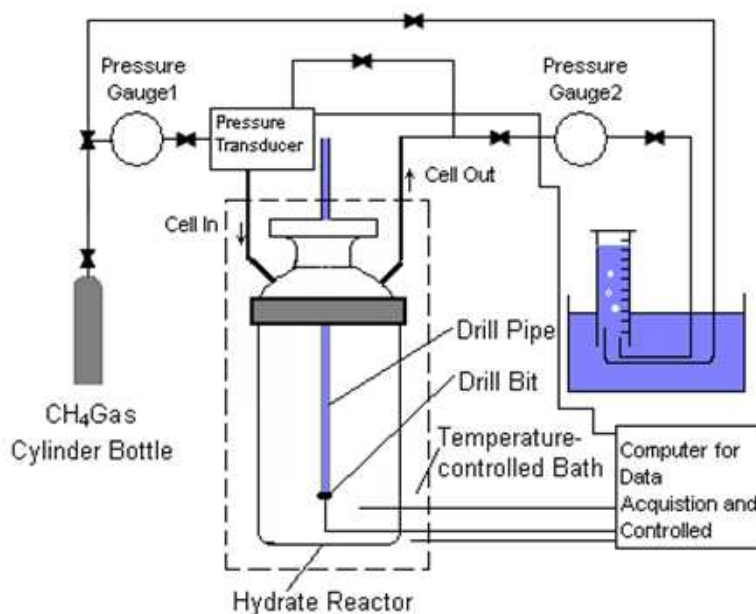


Fig.1: Schematic of experimental apparatus

EXPERIMENT SECTION

Figure 1 shows the schematic of the experimental apparatus of gas hydrate formation and micro-drilling system. The hydrate was artificial in cylindrical cell that can work under high pressure up to 40MPa. The pressure of the cell is controlled by the pressure transducers which were fixed in the cell in and out, which can simulate the overburden pressure of the seafloor. The cell was submerged in a temperature-controlled air bath, which controls the experimental temperature to simulate thermal environment of sediments housing gas hydrates, normally within a temperature range -7 to 50°C .

A pressure transducer was used to measure the system pressure in the vessel that is monitored by a pressure transducer (accuracy of 0.02MPa), and the temperature distribution in an axial direction of the vessel was measured by a PRT to an accuracy of 0.1°C . A mechanical stirrer that is fixed to the drill bit with adjustable rotation speed (from 0 to 1200 R/min) is used to agitate the test fluids. The torque required driving the stirrer and drilling process at a constant speed is measured and related to the viscosity of the system. This temperature, pressure and torque data were transmitted into a personal computer through a recorder collection and controlled board and were recorded in a data file simultaneously and continuously. Pure methane gas was supplied with from a cylinder bottle in the reactor before hydrate formation. An inverted cylinder was used to restore and measure evolved gas from the reactor during hydrate dissociation test. Hydrate formation is detected by a drop in the system pressure (in addition to increase in temperature and torque applied to the stirrer). The set-up can be used to study hydrate induction time (in this study, in the presence of low

dosage hydrate and scale inhibitors), formation rates, volume of hydrate formed, relative transportability of the slurry and hydrate blockage (seize-up of the stirring blades). The experiments for measuring the hydrate formation of with or without surfactant were separately performed.

EXPERIMENT MATERIALS

In this experiment, the main materials were used are Sodium dodecyl sulfate and methane. Table 1 lists the properties of Sodium Dodecyl Sulfate.

Table1 The properties of Sodium Dodecyl Sulfate

mp	204-207 °C (lit.)
density	1.03 g/mL at 20 °C
Fp	>100°C
Storage temp.	Store at RT.
solubility	H ₂ O: 0.1 M, clear to nearly clear, colorless to slightly yellow
Water Solubility	ca. 150 g/L (20 °C)
Merck	14,8636
BRN	3599286
CAS Database Reference	151-21-3(CAS DataBase Reference)
EPA Substance Registry System	Sulfuric acid monododecyl ester sodium salt(151-21-3)

HYDRATE PHASE MESAURMENT

Since most pipeline natural gases contain propane and higher hydrocarbons that are stable sII formers, pipeline hydrates are always assumed be structure II. Gas processing usually removes ethane, propane and higher hydrocarbons before gas is transported for burning. We studied one such natural gas with a composition (given in Figure 2) similar to that of a gas in a Middle East pipeline. Figure 2 shows a pressure-temperature diagram of the natural gas hydrate. The predictions suggest a structural transition in this hydrate from sII to sI with an increase in pressure. The pipeline pressure temperature profiles for the startup and design conditions, shown in Figure 1, suggested the formation of sII and sI, respectively. To investigate this possibility, the hydrate structure was measured using Raman spectroscopy. A high-pressure cell was charged with a small amount of distilled water and pressurized with the natural gas to 3.55 MPa. Hydrates were annealed before heating to 0.5°C. A hydrate Raman spectrum, shown in bottom half of Figure 2, indicates the hydrate was sII. The same procedure was repeated at a pressure of 30.7 MPa. After hydrates were aged at 0°C, hydrates were dissociated and crystallized again at 13°C. The Raman spectrum of these hydrates, shown in the top part of Figure 3, is a sI spectrum. While there is a small shift in the peak positions, a significant change in peak areas indicates a structural transition from structure II (bottom spectrum) to structure I (top spectrum) at a pressure between 3.55 and 30.7 MPa. This is the first measurement of structural transition in a natural gas with small amounts of propane and butanes. In the future, the realization of such structural transitions may not be unusual for any gas with the heavier components removed.

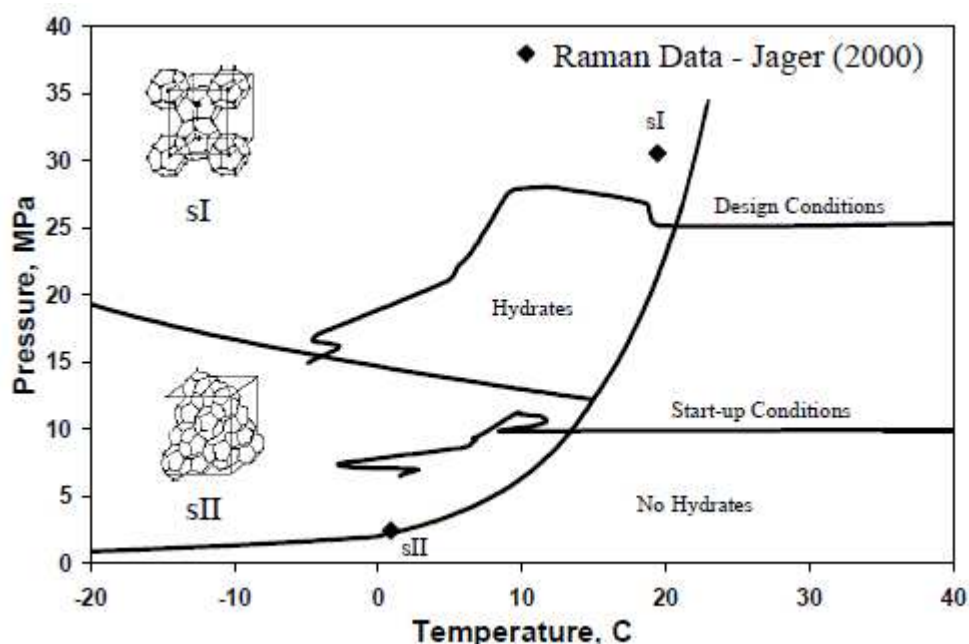


Fig.2: Predicted natural gas hydrate PT diagram showing hydrate stability boundary.

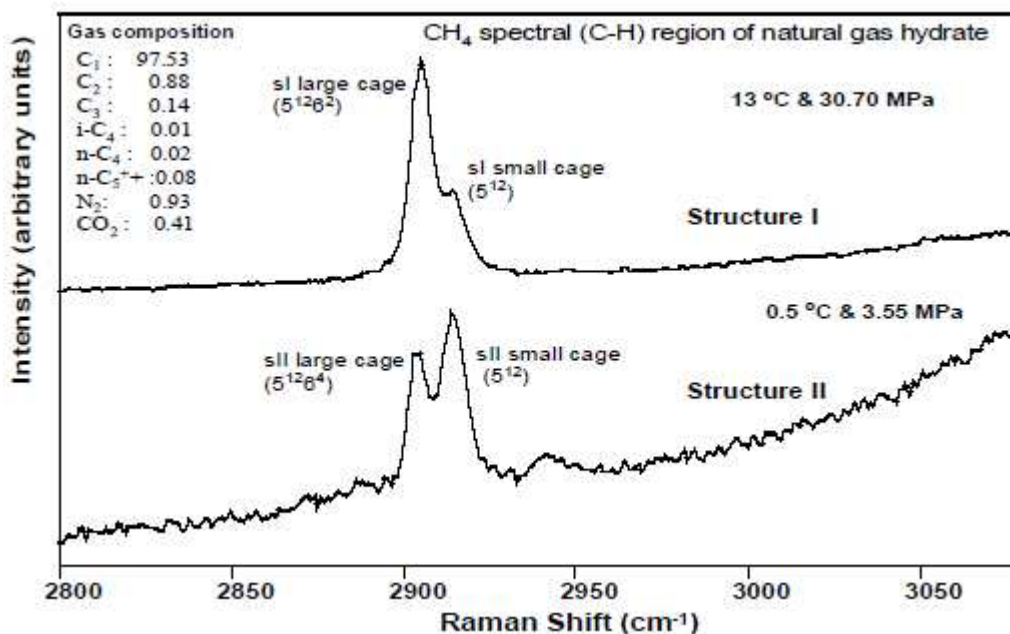


Fig.3:Raman spectra of natural gas hydrate

The above result shows that sI formation in natural gas systems is possible. Any natural gas that has a sufficiently low (< 0.5%) concentration of propane and butanes can form sI at high pressure. Beyond the incipient formation pressure, sI can be the prevalent structure, as sII hydrate formation strips the gas phase of the heavier hydrocarbons. The time required for complete melting of hydrate blockage is very sensitive to hydrate structure. Figure 3 shows the predicted gas evolution during plug dissociation in a 0.6 m diameter pipeline, as a function of time for both sI and sII. Hydrate dissociation is carried out by two sided depressurization to atmospheric conditions and is complete when the gas evolution stops. Plug dissociation time is predicted to be 370 hours for sII but only 284 hours for sI hydrate. Thus, 25 % more time (approximately 4 days in the present example) will be unnecessarily spent in remediation if an incorrect structure is assumed. Current experiments in this laboratory confirm these predictions for smaller diameter pipes.

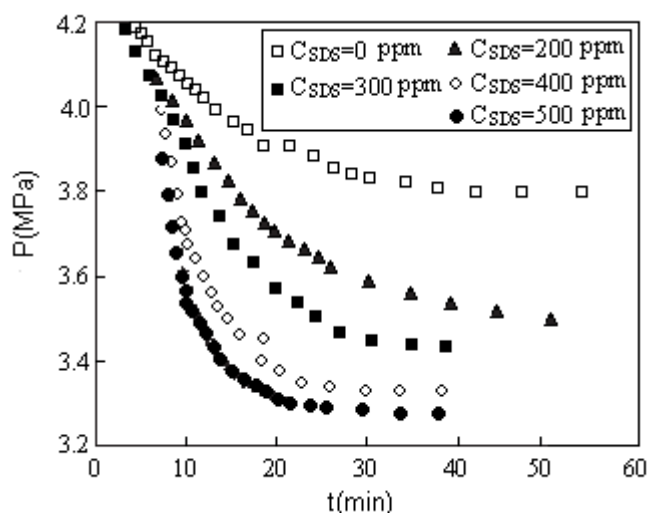


Fig.4:The Profile of methane with SDS aqueous solution (274.15K)

The hydrate formation experiments were conducted at 274.15K with methane and pure water or SDS aqueous solution. The measured pressure profiles were depicted in Figure 3. The results of the experiments showed that the formation rate of gas consumed increases with the concentration of SDS in aqueous solution. Surfactants do not promote the formation of hydrates but either accelerate their onset or modify them to increase the agglomeration tendency. The SDS concentration of was carried from experiment to experiment over the range up to 500ppm. At a concentration as high as 300ppm or above, we noted that during the induction time before the inception of the hydrate formation, that solution forming a pool in the test chamber was no longer clear but lightly opaque and that fine precipitate particles

were sparsely sprinkled over the bottom of the chamber.

RESULTS AND DISCUSSION

It is clear that the formation rate and the quantity of gas consumed increases with the concentration of SDS in aqueous solution; the highest formation rate reaches at 500 ppm. The fact is that the presence of SDS increases the formation rate and storage capacity. The results of both the pressure drop and the partition coefficient of ethylene between hydrate phase and vapor phase were increased remarkably by adding SDS to water. Theoretically, as a kinetic promoter, SDS cannot dramatically influence the initial hydrate formation conditions thermodynamically because its concentration is very small. However, when large quantity of hydrate is formed, SDS might have effect on the water-hydrate equilibrium behavior. At first, as it has been widely proved, the presence of SDS increases the fraction of water converted into hydrate. For the closed systems concerned in this work, the increase of the quantity of the hydrate phase will certainly increase the pressure drop and influence the partitions of gas components between water and hydrate. Secondly, with the proceeding of hydrate formation, SDS will be condensed in the residual aqueous solution and its concentration might become high enough to influence phase equilibrium conditions. Thirdly, when with the presence of SDS in water, a large number of SDS micelles with gas molecules solubilized in them are formed in solution. Each micelle may become a nucleation center. Therefore, unlike the formation of hydrate from pure water occurs only in the gas/water interface, a number of small hydrate particles forms subsurface of the bulk water. When hydrate particles move above the surface of water, the SDS molecules might be adsorbed to the surface of hydrate particles with their hydrocarbon tail towards gas phase. The adsorption of SDS molecules in the surface of hydrate particles will lower the surface free energy and resist the agglomeration among the hydrate particles. Hence, hydrate formed from SDS aqueous solution is in the form of fine powder as has been observed. There are sufficient spaces among the hydrate particles to guarantee a perfect gas/hydrate contact and make vapor-hydrate equilibrium could be established more easily and the composition of hydrate phase is more uniform. On the contrary, when without the presence of SDS, hydrate formation rate is very low and the formed hydrate is in the form of bigger block. Because the composition of gas phase changes with the proceeding of hydrate formation, the composition of hydrate formed will also change with time. As the diffusion of gas molecules among the cavities of hydrate is very difficult, the composition of the hydrate block might not be uniform. Additionally, as ethylene molecules could be solubilized in SDS micelles more easily than methane molecules, ethylene molecules may be enclosed into the hydrate lattice preferentially. That might be one reason why the presence of SDS can increase the partition coefficient of ethylene between hydrate and vapor. It is of significance that adding SDS can increase both hydrate formation rate and partition coefficient of ethylene between hydrate and vapor (Zhang, 2005).

The behavior of macroscopic hydrate phase growth observed here is generally in qualitative agreement with the descriptions given by Kutergin *et al.* (1992), Mel'nikov *et al.* (1998), and Zhong and Rogers (2000) on their observations with hydrocarbon guests and SDS, and, on the other hand, it is much different from such hydrate formation behavior at a quiescent interface between the methane gas and surfactant-free water that Ho *et al.* (2002) reported.

CONCLUSION

The methane hydrate equilibrium data was measured for methane in cases with and without the presence of SDS in aqueous. The results showed that the formation rate and partition coefficients of methane could be increased remarkably by adding the SDS. The particular SDS concentration in an aqueous phase, characteristic of the hydrate-forming behavior, is the solubility, instead of the critical micelle concentration, above which SDS forms a hydrated solid in the aqueous phase. The solubility at the hydrate-forming condition (279K and 0.401MPa) is only slightly lower than the critical micelle concentration in a laboratory-air condition (293K and 0.101MPa). The rate of hydrate formation is maximized at an SDS concentration slightly below the solubility. The water-to-hydrate conversion ratio or the gas storage capacity of a hydrate-forming reactor initially charged with a prescribed amount of water, has a peak at an SDS concentration nearly half of the solubility. The ratio has a minimum as the concentration approaches the solubility, and then tends to increase with a further increase in the concentration exceeding the solubility.

Acknowledgement

The financial support received from the National Natural Science Foundation of China (41174159) is gratefully acknowledged.

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