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Investigation on Gas Storage in Methane Hydrate

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Abstract: The effect of additives (anionic surfactant sodium dodecyl sulfate (SDS), nonionic surfactant alkyl polysaccharide glycoside (APG), and liquid hydrocarbon cyclopentane (CP)) on hydrate induction time and formation rate, and storage capacity was studied in this work. Micelle surfactant solutions were found to reduce hydrate induction time, increase methane hydrate formation rate and improve methane storage capacity in hydrates. In the presence of surfactant, hydrate could form quickly in a quiescent system and the energy costs of hydrate formation were reduced. The critical micelle concentrations of SDS and APG water solutions were found to be 300×10^{-6} and 500×10^{-6} for methane hydrate formation system respectively. The effect of anionic surfactant (SDS) on methane storage in hydrates is more pronounced compared to a nonionic surfactant (APG). CP also reduced hydrate induction time and improved hydrate formation rate, but could not improve methane storage in hydrates.

Key words: methane hydrate, surfactant, cyclopentane, gas storage

1. Introduction

Natural gas is a kind of clean fuel. As the main component of natural gas is methane whose boiling point is about –162 ℃ under 0.1 MPa, it is difficult to store and transport. There are two main methods for natural gas storage and transport today. One is liquefied natural gas (LNG), and the other is natural gas storage and transport by pipeline, and both the methods are costly. In order to enlarge natural gas consumers in China, economic method for natural gas storage and transport should be found.

Natural gas hydrates are crystalline inclusion compounds composed of water and natural gas. There are three known structures (structure I, structure II and structure H) in which water molecules arrange themselves around guest molecules, depending principally on the molecular size of guest molecules [1,2]. Gas hydrates have drawn much attention today as not only a new natural energy resource but also a new means for natural gas storage and transport.

Natural gas storage in hydrates has been investigated because hydrates store large quantities of natural gas [2]. Gudmundsson *et al.* [3] showed that hydrate could be stored at -15 ℃ under atmospheric pressure for 15 days, retaining almost all the gas. Their study [4] also showed that a substantial cost saving (24%) for the transport of natural gas in hydrates compared to LNG from the northern North Sea to Central Europe. The hydrate formation with additives for the purpose of natural gas storage and transport has been reported recently [2,5–8]. However, industrial applications of hydrate storage processes have been hindered by some problems, such as slow formation rates, unreacted interstitial water as a large percentage of the hydrate mass, the reliability

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of hydrate storage capacity and economy of process scale up.

The main purpose of this work is to investigate the effect of anionic surfactant, nonionic surfactant and liquid hydrocarbon on methane hydrate formation, particularly to investigate their ability of reducing induction time, increasing the formation rate of gas hydrate, improving hydrate storage capacity and reducing energy costs of hydrate formation.

2. Experimental apparatus

Hydrate formation experiments were carried out using a high-pressure system shown in Figure 1. Gas hydrates form in a cylindrical high-pressure stainless steel cell with available volume of about 1000 cm^3. A stainless flange, which has appropriate ports for access to the interior, is used to seal the cell on the top. The cell is designed to operate at pressure up to 20 MPa and temperature in the range of 253–323 K. Jacket coolant of the cell is circulating cooling water with enough ethylene glycol to depress the water's freezing point. The coolant is circulated from a refrigerating bath capable of maintaining the bath temperature within ±0.01 K of the set point to a low temperature capability of 258 K. The cell is enclosed with insulation. Two platinum resistance thermometers were used to measure the experimental temperature, with an accuracy of ±0.01 K. One extends into the bottom of the cell, the other extends into the gas phase at the top. The pressure of the cell was measured using a 10 MPa gauge with an accuracy of ±0.25% of full scale.

A constant pressure regulator can maintain constant pressure of the cell. A mass gas flowmeter was used to measure gas added to the cell during hydrate formation. The flowmeter has a capacity of 0-1 standard liter per minute with an accuracy of ±2% of full scale. There is a data-logger to record parameters in the process of hydrate formation as the function of time.

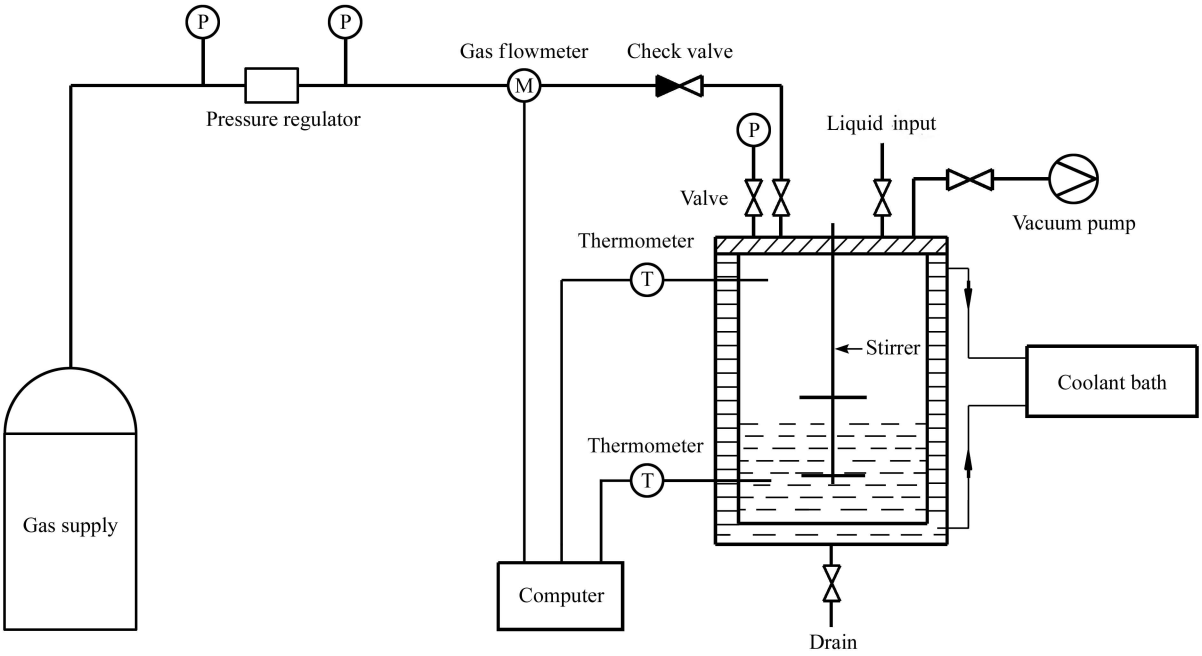

Figure 1. Schematic diagram of experimental apparatus

3. Experimental procedure

One anionic surfactant (SDS), one nonionic surfactant (APG) and one liquid hydrocarbon (CP) were chosen as the hydrate promoters in this work. The pressure of the cell was kept constant during each experimental run. A typical procedure was as follows: the cell was first rinsed with distilled water, and then evacuated by a vacuum pump. Approximately 300 cm^3 water solution was charged into the cell for each experiment. Methane was then injected into the cell up to about 1.0 MPa. The system was cooled to 274.05–277.55 K with a pressure below the methane hydrate formation pressure. Pressure of the cell was then raised to the experimental pressure over a 3–5 min span by flowing hydrocarbon gas into the cell.

The beginning of hydrate formation was judged by the gas consumption, which was shown by a flowmeter. The hydrate formation was considered to be at an end when the methane consumption speed was less than 0.04×10^{-3} m^3/min. Hydrate formation as well as temperature and gas mass flow were recorded and displayed on the data acquisition system.

The test materials used in this work were given in Table 1. The chemicals were not further purified before usage. Surfactants were weighed on an electronic balance with a readability of ±0.1 mg. Distilled water was used in all experiments. Water and CP were weighed on an electronic balance with a readability of ±0.01 g.

Table 1. Test materials

Component	Purity(%)	Supplier
Methane	99.99	Guangzhou Gas Co.
CP	98.4	Meilong Chemical Co.
SDS	≥98	Guangzhou Chemical Reagent Co.
APG	98	Guangzhou Chemical Reagent Co.
Water	Distilled	—

4. Experimental results and discussion

4.1. Effect of additives on hydrate formation induction time

Nucleation of a hydrate crystal requires an excess energy to create a nucleus surface. Since a thermodynamic driving force for nucleation, which can be related to the difference in the chemical potential of the hydrate components in the liquid and hydrate phases at the existing thermodynamic conditions, is necessary to overcome a nucleation barrier, hydrate is nucleated from a solution which is cooled below the equilibrium temperature. Induction time [9] of hydrate formation is mainly dependent on the time of hydrate nucleation.

In the initial work, the ways of reducing induction time of hydrate formation were first studied. Under the conditions of 5.76 MPa and 277.55 K, the experiments of pure water-methane (with 400 rpm stirring velocity and without stirring), water-SDS-methane and water-SDS-CP-methane in a quiescent system were carried out to observe the effect of stirring and additives on hydrate formation induction time. The induction time of pure water-methane hydrate experiment in a quiescent system is more than 28 h, and the induction time of pure water-methane hydrate experiment in a stirring system is about 5 min. The induction time of water-SDS-methane and water-SDS-CP-methane experiments in a quiescent system is 1–1.5 h and 10–20 min, respectively. The experimental results showed that additives reduce the induction time greatly in a quiescent system. The explanation for CP reducing the induction time of hydrate formation was that there was a significant shift in hydrate formation pressures to lower values in the system of methane and CP compared to the system of methane [10].

4.2. Effect of surfactant on hydrate formation rate and storage capacity

Methane storage capacity in hydrates could be calculated by the consumption of methane in the hydrate formation process experiments [11]. It was shown in Figure 2 that the formation rate of methane hydrate and methane storage capacity in hydrates were very small in a stirring pure water system. Surfactant SDS was then added to improve methane formation in a quiescent system. Methane hydrate formation rate and gas storage capacity were improved greatly in the presence of surfactant SDS compared to the hydrate formation in a stirring pure water system.

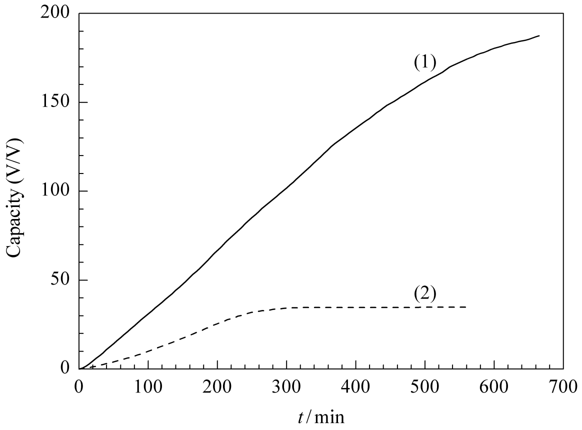

Figure 2. Surfactant increases hydrate formation rate

(1) 300×10^{-6} SDS, (2) Pure water 400 rpm; Reaction conditions: $p = 5.76$ MPa, $T = 277.55$ K

The above experiments showed that hydrate formation could be carried out in a quiescent system in the presence of a surfactant. Hydrate formation in a quiescent system can reduce processing costs as stirring is not needed. The following experiments for gas storage in this work were carried out in the presence of a surfactant in a quiescent system.

Surfactant may alter the mechanism of gas hydrate formation. Hydrates commonly form at the interface between water and gas in a pure water system as the solubility of gas in water is small. Hydrates covered on the gas-water interface block further conversion of water to hydrate. In the presence of surfactant, there are three conditions that contribute to hydrate formation. First, solubility of hydrocarbon gas is improved greatly in the presence of surfactant [12]. Second, there is a layer of water (10–100 nm thick) between water and metal cell surface, whose structure is described as an "ice-like" molecular configuration [13]. Surfactant displaces this tightly held water on metal. Surfactant micelle could form with sufficient surfactant adsorption on the metal surface and solubilize the hydrocarbon gas in contact with the configured water. The "ice-like" water is favored to hydrate formation. Third, the metal surface dissipates the latent heat of hydrate formation quickly by conduction. Hydrate could form both at vapor-water interface and at subsurface of bulk water, and at a high rate in the presence of a surfactant.

Figure 3 was a photograph of the experimental result of hydrate formation. Figure 3(a) showed that the hydrate formation rate and storage capacity were very low over a period of about 20 hours without additives in a stirred system (stirring velocity is about 400 rpm). There was no apparent adsorption or symmetrical packing on the metal cell surface. Hydrate covered on the gas-water interface. Figure 3(b) showed that the hydrate formation rate and storage capacity were large over a period of about 8 h in the presence of 300×10^{-6} SDS in a quiescent system. The dark center shows the bottom of the cell. There were apparent adsorption and symmetrical packing on the metal surface. A possible explanation for the promotion effect on hydrate formation and storage capacity was that the agglomerating hydrate particles moved radially to be adsorbed on the cell walls in a quiescent system with SDS presence. The adsorption of hydrate on the walls prevented the hydrate from hindering further conversion of water to hydrate in the free water.

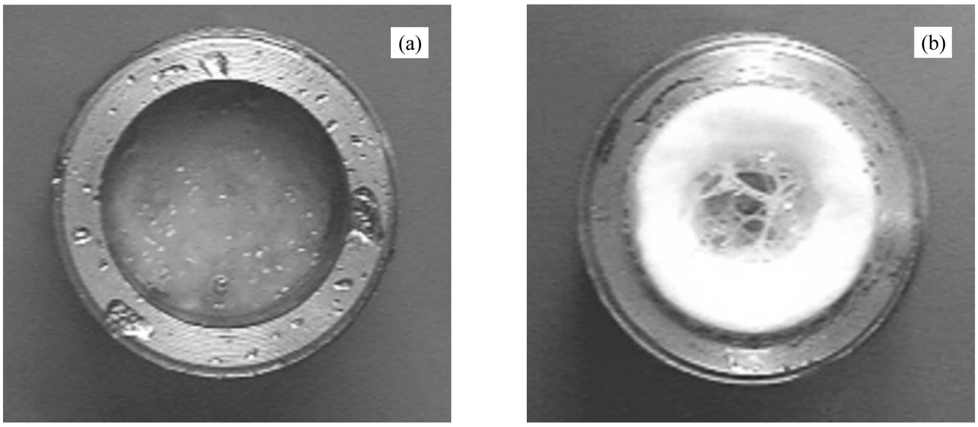

Figure 3. Photograph of experimental result of hydrate formation

(a) Hydrate formation in pure water in a stirred system, (b) Hydrate formation in SDS solutions in a quiescent system

4.3. Critical micelle concentration of surfactants in hydrate formation system

The solubility of methane is small, but it can be improved by adding surfactant [11]. Micelle forms in solutions and its solubility attains a maximal value when surfactant concentration reaches some value. This concentration is defined as the critical micelle concentration. If surfactant concentration in solution exceeds the critical micelle concentration, solubility of gas cannot be further improved [11]. In this work, our main aim is to improve the gas storage capacity in hydrates. So we define that the concentration of surfactant in solutions that gave the highest methane storage capacity in hydrates is the critical micelle concentration.

Figure 4 showed the relation of gas storage capacity in hydrates and surfactant concentration. Gas storage capacity in hydrates first increased sharply, and then dropped a little with the increase of surfactant concentration. This showed that there was the largest storage capacity when the concentrations of surfactant solutions for SDS and APG were about 300×10^{-6} and 500×10^{-6}, respectively. It also showed that the critical micelle concentration of SDS water solutions was 300×10^{-6}, and that of APG was

500×10^{-6} for gas storage in hydrates. The following experiments of methane storage were done under critical micelle concentration water solution.

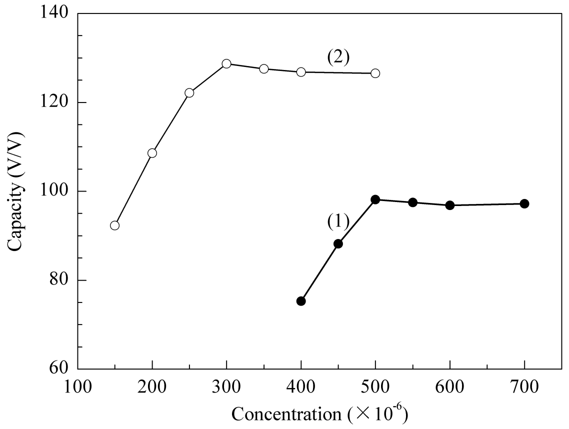

Figure 4. Effect of surfactant concentration on gas storage in hydrate

(1) APG at 275.15 K, (2) SDS at 276.75 K;
Reaction conditions: p = 4.54 MPa

4.4. Methane storage in hydrates

Sixteen methane storage experiments in hydrates were carried out in the presence of additives (SDS, APG, or CP) in a quiescent system. The experimental results were tabulated in Table 2.

The effect of SDS or APG on methane hydrate formation under the conditions of 4.34 MPa and 274.05 K was shown in Figure 5. The hydrate formation rate in aqueous APG solution was almost equal to that in aqueous SDS solution during hydrate formation (0–215 seconds) after hydrate induction time. But the time of hydrate formation in aqueous APG solutions at hydrate growth stage was shorter than that in aqueous SDS solutions. The effect of SDS on methane storage in hydrates was more pronounced compared to APG.

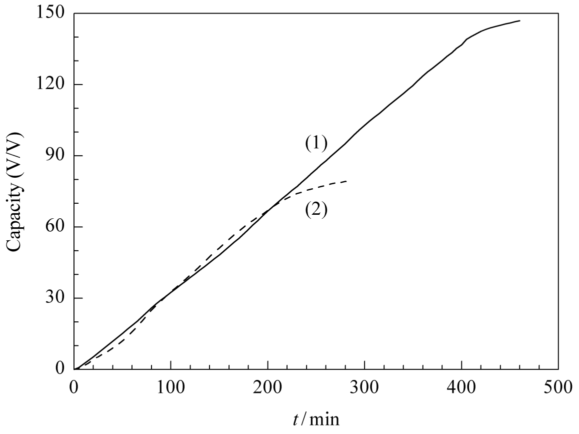

Figure 5. Comparison of the effect of different surfactants on methane hydrate formation

(1) 300×10^{-6} SDS, (2) 500×10^{-6} APG;
Reaction conditions: p = 4.34 MPa, T = 274.05 K

Table 2. Experimental results of methane storage in hydrates

No	Additive	T/K	p/MPa	Experimental time cost (min)	Storage capacity (V/V)
1	SDS	274.05	5.54	330	163
2			4.85	425	154
3			4.34	460	147
4			3.92	765	132
5		277.55	5.76	665	153
6			5.33	705	146
7			4.85	760	113
8	APG	274.05	5.38	455	112
9			4.96	370	101
10			4.34	285	80
11	SDS+CP	274.05	6.18	315	169
12			4.85	340	151
13			3.80	540	129
14		277.55	5.80	480	152
15			5.43	595	149
16			4.85	590	115

Solution concentration: DPG=500×10^{-6}, SDS=300×10^{-6}, CP=1.0%

Figure 6 compared the effect of SDS and SDS+CP on hydrate formation. It showed that use of these additives brought about lower temperature, larger gas storage capacity, and higher hydrate formation rate under the same experimental pressure. It also showed that CP improved the hydrate formation rate, but had no effect on the gas storage capacity in hydrates. That is to say, CP shortened the time costs of hydrate formation. CP can form structure II hydrates [9]. The system of SDS+CP+methane formed a mixture of structure I and structure II hydrates in this work as only 1.0%CP was involved in the experimental system.

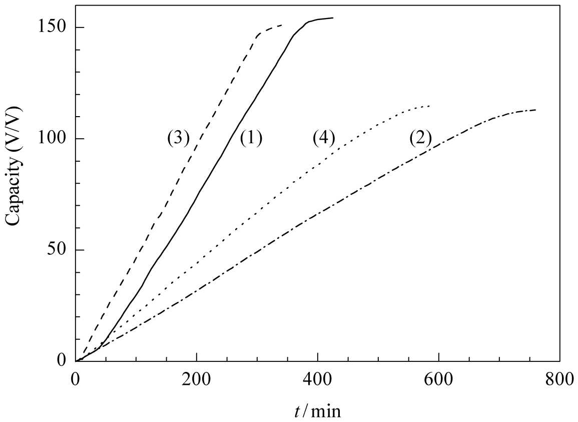

Figure 6. Comparison of the effect of SDS and SDS+CP on methane hydrate formation rate

(1) 300×10^{-6} SDS at 274.05 K, (2) 300×10^{-6} SDS at 277.55 K, (3) 300×10^{-6} SDS+1.0%CP at 274.05 K, (4) 300×10^{-6} SDS+1.0%CP at 277.55 K

5. Conclusions

Anionic surfactant SDS, nonionic surfactant APG, and liquid hydrocarbon CP were used as the methane hydrate formation promoters. The tests showed that the critical micelle concentrations of SDS and APG water solutions were 300×10^{-6} and 500×10^{-6} in hydrate formation system, respectively. It also revealed by the experiments that surfactants SDS and APG reduced the hydrate induction time, improved the hydrate formation rate and gas storage capacity. The effect of APG on hydrate formation is less pronounced compared to SDS. CP could also increase hydrate formation rate and reduce hydrate formation induction time, but could not improve methane storage in the hydrates. The tests also showed that methane hydrate could be formed in a quiescent system in the presence of SDS or APG.

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