Promotion of CH₄ hydrate generation by various surfactants in quiescent system for renewable energy application

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Abstract. Biogas can be used as a supplement to the consumption gap of natural gas, a propellant for low-carbon and circular economy, as well as an important component in energy security. The storage and transportation of biogas by hydrate method is widely concerned at home and abroad. The main component of biogas is methane. In this paper, two kinds of surfactants, fatty alcohol polyoxyethylene ether (AEO) and fatty alcohol polyoxyethylene ether sodium sulfate (AES), were selected to study the effects of their types and concentrations on the induction time and formation rate of CH₄ hydrate. The results showed that the optimum mass concentrations of AEO and AES in hydrate system were 2.5% and 0.1%, respectively, and the induction time of CH₄ hydrate formation was 63 min and 64 min, respectively. AEO is beneficial to the formation of CH₄ hydrate nuclei, and its promoting mechanism is micelle theory; while AES promotion mechanism is mainly adsorption. The research results are of great significance for the development of rural clean and renewable energy, the prevention of agricultural source pollution, and the consolidation of ecological environment construction.

1. Introduction

Methane hydrate is a kind of ice cage crystal which is composed of methane and water at high temperature and low pressure through intermolecular van der Waals force[1]. Researches show that the gas storage density of methane hydrate can be as high as 180 V/V, so it can be used as a favorite carrier for storing and transporting methane[2]. Taking into the overall comprehension of gas storage density, storage and transportation costs, methane hydrate also has certain economic advantages. Under natural conditions, methane hydrate has low formation rate and small generation amount, which has become an important factor restricting the commercialization of methane hydrate[3].

Zhong[4] investigated the effect of sodium lauryl sulfate (SDS) on the formation of methane hydrate, and proposed that the critical micelle concentration is the key factor for SDS to promote the formation of methane hydrate. The reason is that SDS can form micelles in water solution after it dissolves in water, and the existence of micelles improves the solubility of methane gas. Moraveji[5] investigated the effects of three surfactants, i.e., SDS, cetyltrimethyl ammonium bromide (HTABr) and dow wetting agent (TritonX-405) on methane hydrate formation rate and induction time. The results showed that SDS could promote methane hydrate formation best, while HTABr could shorten the induction time to the maximum extent.

In this paper, the effects of fatty alcohol polyoxyethylene ether (AEO) and fatty alcohol polyoxyethylene ether sodium sulfate (AES) on CH₄ hydrate formation induction time and formation
rate were studied under static conditions, so as to explore the effective way to promote the rapid formation of CH₄ hydrate.

2. Experimental Procedure

Methane hydrate is a crystal formed at low temperature and high pressure[6]. The hydrate formation experimental device is mainly composed of constant temperature water bath, high pressure reactor, temperature and pressure sensors and data acquisition system (as shown in Figure 1). Low temperature water bath can provide low temperature condition for methane hydrate formation, and reactor can provide high pressure environment. The pressure in the reactor can reach the required pressure for methane hydrate formation by injecting gas into the booster pump, and methane hydrate can be generated in the low temperature environment provided by the water bath. The material of the reactor is stainless steel with a mirror on both sides, which can be used to observe the formation of methane hydrate in the reactor.

![Figure 1. Schematic Diagram of Methane Hydrate Formation Experiment](image)

1-constant temperature water bath; 2-high pressure reactor; 3-temperature and pressure sensors; 4-data acquisition system; 5-discharge outlet; 6-booster pump; 7,8-mirror

In the process of experiment, firstly, the reactor was repeatedly washed by deionized water for 5 times, dried, and then purged by nitrogen to remove the air. The hydrated solution prepared was injected into the reactor by the booster pump until the fluid level reached the center line of the mirror, so as to observe the nucleation at the interface. The constant temperature water bath was used to gradually reduce the temperature in the reactor by 0.5°C every 0.5 hours until the nucleation of methane hydrate was observed through the mirror, and the temperature of methane hydrate nucleation under this pressure was recorded. Temperature in the constant temperature water bath was maintained at 3°C, and methane gas was injected into the reactor until it reached 5MPa. With the formation of methane hydrate, the pressure decreased. The data of temperature and pressure was recorded by the data acquisition system. When the system pressure remains constant within 0.5h, the experiment ends.

Addition of effective accelerator can change the formation temperature and pressure conditions of methane hydrate[7]. In the experiments in this paper, phase equilibrium of methane hydrate is obtained by observation.

During the experiments, methane gas volume consumed by methane hydrate is calculated by the following equation[8]:

\[
n_{\text{CH}_4} = \frac{p_0 V_0}{z_0 RT_0} - \frac{p_t V_0}{z_t RT_t} \left(1 - \frac{p_t \Delta VM}{z_t RT_t}\right)
\]

Wherein, \(p_0\) and \(p_t\) are the initial pressure and the pressure at the time \(t\) during experiments, MPa; \(V_0\) is the methane gas volume at initial time, mL; \(T_=276.15K\) (temperature are kept constant during experiments); \(z_0\) and \(z_t\) are gas compression coefficient at initial time and at the time \(t\) during experiments, respectively; \(\Delta V\) is the difference of molar volume between water and methane hydrate, L/mol.
3. Results and Discussion

3.1. Effect of AEO and AES concentration on induction time of CH$_4$ hydrate generation

Formation and growth of methane hydrate can be divided into three stages, i.e., dissolution stage, induction stage and rapid growth stage. Research on methane hydrate formation dynamics mainly focuses on nucleation process, so as to explore the reason of induction, shorten induction time and improve methane hydrate formation rate[9].

Induction time is defined as the period from the time when the temperature drops to the equilibrium temperature of hydrate phase to the beginning of nucleation and heat release. The duration of hydrate formation is defined as the period from the nucleation and heat release of the system to the time when system temperature achieves the same as the experimental temperature. Average induction time is the average value of the induction time of hydrate formation in several parallel experiments. Standard deviation of induction time is used as the reference value to measure the stability of hydrate formation. The smaller the standard deviation, the smaller the randomness of hydrate nucleation. Table 1 lists the average value of the induction time of hydrate formation in several parallel experiments. Standard deviation of induction time was also the smallest. At this time, the randomness of hydrate formation decreased firstly and then increased. When 2.5wt% AEO was added, the induction time of hydrate formation was the shortest, the average induction time was 64.20min, and the standard deviation of induction time was also the smallest. At this time, the randomness of hydrate formation was small. Low concentration of AEO did not reach the mice lle concentration and could not completely dissolve methane in water. At this time, the nucleation of hydrate was less and the induction time was longer. While high mass concentration of AEO made the emulsion to stratification easily, resulting in demulsification, which was not conducive to methane hydrate formation.

**Table 1. Induction Time and Formation Duration of Methane Hydrate Generation**

| Experiment number | Induction time/ min | Average induction time/min | Induction time standard variance | Formation duration/ min | Average duration/ min |
|-------------------|---------------------|-----------------------------|---------------------------------|-------------------------|-----------------------|
| E1                | -                   | -                           | -                               | -                       | -                     |
| E2                | 237, 265, 159, 296, 101 | 211.60                      | 80.03                           | 42, 38, 40, 40, 43      | 40.60                 |
| E3                | 188, 133, 118, 204, 275 | 183.60                      | 62.56                           | 46, 43, 41, 44, 43      | 43.40                 |
| E4                | 102, 135, 64, 128, 175 | 120.80                      | 41.14                           | 42, 48, 39, 42, 48      | 43.80                 |
| E5                | 74, 14, 66, 87, 78    | 64.20                       | 28.90                           | 43, 42, 44, 43, 44      | 43.20                 |
| E6                | 188, 142, 127, 147, 209 | 162.60                      | 34.40                           | 41, 45, 46, 48, 44      | 44.80                 |
| E7                | 89, 88, 82, 105, 96   | 92.00                       | 8.80                            | 52, 34, 38, 43, 45      | 42.40                 |
| E8                | 19, 45, 92, 82, 103   | 68.20                       | 35.09                           | 52, 41, 44, 48, 47      | 46.40                 |
| E9                | 102, 32, 176, 72, 187 | 113.80                      | 66.72                           | 51, 48, 47, 52, 45      | 48.60                 |
| E10               | 392, 102, 192, 76, 166 | 185.60                      | 124.52                          | 38, 52, 41, 47, 46      | 44.80                 |
| E11               | 32, 72, 109, 145, 98  | 91.20                       | 42.22                           | 56, 45, 47, 48, 53      | 49.80                 |
| E12               | 82, 24, 195, 138, 176 | 123.00                      | 70.18                           | 62, 65, 58, 67, 65      | 63.40                 |
| E13               | 315, 435, 636, 462, 515 | 472.60                      | 117.11                          | 99, 72, 66, 75, 87      | 79.80                 |

Effect of AES concentration on methane hydrate formation was studied in experiments E1 and E7 ~ E10. During the experiment, it was found that the hydration system with AES alone had poor stability, easy stratification and low hydrate formation rate. The mechanism of anionic surfactant to promote hydrate formation is mainly adsorption, so the helical 4N anaerobic copper wire with high purity was added to the system while AES was added to promote hydrate formation simultaneously, which increased the adsorption ability of AES on the surface of copper wire and increased hydrate formation rate. Effect of 0.05wt%~0.2wt% AES on the induction time of methane hydrate formation was studied. The results show that there was also an optimal concentration of AES. The shortest
average induction time of 0.1wt% AES hydrate formation was 68.20min, and the standard deviation of
induction time was 35.09. At this time, the randomness of hydration system was low. The emulsifying
capacity of low concentration AES is not as good as that of AEO, and the emulsion is easy to be
layered. Its adsorption capacity on copper wire is not enough, and the nucleation of hydrate is less.
High concentration AES emulsion is not stable enough, easy to settle, and unfavorable to methane
hydrate formation.

3.2. Effect of surfactant type on induction time of CH₄ hydrate generation

Influence of different surfactants on methane hydrate formation under the optimum condition of
mass percentage was studied in experiments E5, E8 and E11. 2wt% is the optimal concentration of
Tween80 obtained by previous studies of the research team[10]. It can be seen that 2.5wt% AEO has the
best promotion effect on the induction time of methane hydrate formation, and it can be found that the
area covered by the temperature rise curve of the hydration system with Tween80 and AEO is larger
than the system with AES, that is to say, the hydrate cold storage capacity of the hydration systems
with Tween80 and AEO system are larger.

3.3. Effect of subcooling temperature on induction time of CH₄ hydrate generation

In chemical reactions, a system reaches a new equilibrium status from turbulent status, which is
promoted by the change of Gibbs free energy of the system. During the formation of methane hydrate,
the change of Gibbs free energy of the system can be described by supercooling degree, which is the
impetus for methane hydrate formation, can lower the phase equilibrium temperature of methane
hydrate. The higher the supercooling degree at initial status and at final status, the easier for methane
hydrate to generate and growth.

Supercooling degree of hydrate is the difference between the experimental temperature and the
phase equilibrium temperature of hydrate. Effects of supercooling degree on methane hydrate
formation were studied in experimental E5, E12 and E13. Supercooling degree has great influence on
hydrate formation. The greater the supercooling degree, the better the promotion effect on methane
hydrate formation. Standard variance of methane hydrate formation induction time in experiment E5 is
the smallest, as shown in Table 1, which indicates that the greater the supercooling degree, the smaller
the randomness of methane hydrate formation. In the process of methane hydrate formation,
temperature is a very important parameter, because the lower the temperature, the weaker the
molecular motion in the methane hydration system, and the water clusters formed by water molecules
are more stable, which promotes the formation and growth of methane hydrate nuclei.

3.4. Effect of surfactant type on generation rate of CH₄ hydrate

According to equations (1) and (2) as shown in follows, the formation rate of methane hydrate with
different concentrations of AEO and AES was calculated. It can be seen that the average formation
rate of methane hydrate with 2.5wt% AEO is the highest, which is 3.97kJ/kg·min. Average formation
rate of methane hydrate with 0.1wt% AES is the lowest, which is 2.70kJ/kg·min.

\[
\Delta H_h = \frac{c_{w2} m_o (T_a - T_f) - c_h m_h (T_h - T_h) - (c_{w1} m_{w1} + c_r m_r) (T_a - T_h) - c_g m_g (T_a - T_h)}{m_h} \tag{1}
\]

\[
\nu_h = \frac{\Delta H_h}{\Delta t} \tag{2}
\]

Wherein, \(\Delta H_h\) is the storage capacity of hydrate per unit mass, kJ·kg⁻¹. \(c_{w2}\) is the specific heat
capacity of warm water, kJ·kg⁻¹·K⁻¹. \(m_{w2}\) is the quality of warm water, kg. \(T_a\) is the temperature of
hydrate after equilibrium, °C. \(T_f\) is the temperature of the initial warm water, °C. \(c_h\) is the specific heat
capacity of the hydrate, kJ·kg⁻¹·K⁻¹. \(m_h\) is the mass of hydrate, kg. \(T_h\) is the decomposition temperature
of hydrate, °C. \(T_b\) is the temperature of the initial hydrate, °C. \(c_{w1}\) is the specific heat capacity of water
produced by hydrate decomposition, kJ·kg⁻¹·K⁻¹. \(m_{w1}\) is the mass of water produced by hydrate
decomposition, kg. \(c_r\) is CH₄ specific heat capacity, kJ·kg⁻¹·K⁻¹. \(m_r\) is CH₄ quality, kg. \(c_g\) is the
specific heat capacity of the glass tube, kJ·kg⁻¹·K⁻¹. \(m_g\) is the quality of the glass tube, kg. \(\nu_h\) is the
average hydrate formation rate, kJ·kg⁻¹·min⁻¹. Δt is the time from the beginning to the end of hydrate formation, min.

Figure 2 shows the photos of methane hydrate generated with 2.5wt% AEO and 0.1wt% AES. The hydrate generated is white, uniform and compact.

![Figure 2. Photos of Methane Hydrate Generated with 2.5wt% AEO and 0.1wt% AES](image)

4. Conclusions

Two kinds of surfactants AEO and AES are used to promote the formation of methane hydrate under static conditions in this paper. The mass concentrations of AEO and AES that are most favorable to shorten the induction time of methane hydrate formation are wt=2.5% and wt=0.1%, respectively. The effect of AES on methane hydrate formation is the worst, although AEO is beneficial to hydrate nucleation. With the increase of AEO mass concentration, the hydrate cold storage capacity firstly increases and then decreases, and the maximum cold storage capacity is 167.74kJ/kg. When 2.5wt% AEO and 0.1wt% AES were added, the cold storage capacity of methane hydrate is 167.74kJ/kg and 122.47kJ/kg, respectively, and the average growth rate of methane hydrate is 3.97 kJ/kg·min and 2.70kJ/kg·min, respectively. Combined with the macroscopic experimental observation, the mechanism of different surfactants promoting methane hydrate formation is analyzed. The mechanism of nonionic surfactant AEO promoting methane hydrate formation is micelle concentration theory, while the mechanism of anionic surfactant AES promoting methane hydrate formation is adsorption.

5. Acknowledgments

This work was financially supported by the Technology Research and Development Program of Suzhou (SNG2018048).

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