



## Short communication

## Cooperative effect of surfactant addition and gas-inducing agitation on methane hydrate formation rate

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## ABSTRACT

This paper reports experimental measurements of the isothermal and isochoric formation kinetics of methane hydrate in sodium dodecyl sulphate (SDS) solutions of various concentrations with gas-inducing agitation, and the results are compared with those obtained with normal agitation and no agitation. The experiments were conducted at 274 K with initial gas pressure of 10 MPa. At a given SDS concentration, the gas-inducing agitation gave higher hydrate formation rate than normal agitation and no agitation. Gas inducing agitation of deionized water gave a relatively low methane hydrate formation rate, which could be greatly enhanced by adding SDS. The enhanced kinetics can be attributed to increased gas-liquid contact area, with the coalescence of induced gas bubbles being effectively inhibited by SDS at low concentrations.

## 1. Introduction

Gas hydrates are solid, non-stoichiometric compounds of certain small gas molecules and water, which have high gas storage capacity (up to 180 vol gas at STP condition per unit volume of hydrate) [1,2]. As a solid, methane hydrate is a potential alternative to LNG (liquefied natural gas at  $-162\text{ }^{\circ}\text{C}$ ) for cheap and safe storage and transport of natural gas [3], and investigations on gas production from natural gas hydrate have been carried out [4–6]. Gas transportation with hydrates can be economically viable not only at large scale but also at small or medium scale, and the transportation cost with hydrates is 18–24% lower than with LNG transportation [3]. Gas hydrate is also considered safer than LNG against accidental fire, leakage accident, and natural disasters such as earthquake, tsunami, and typhoon and human act disasters such as terrorist attack and military action. These features of gas hydrates make it appealing for gas separation, storage and transport [7]. When it comes to the economic feasibility, the cost of building a gas hydrate-based processing plant is estimated to be approximately a quarter of that of a LNG plant [8–10].

An impediment to advancing the hydrate-based technologies lies in the slow kinetics of gas hydrate formation. Methane gas dissolved marginally in water and the hydrate formation process is exothermic. Heat transfer and mass transfer are therefore considered important factors affecting the gas hydrate formation kinetics. Given that heat removal is well developed at industrial scale, more attention has been paid to mass transfer. Enhancing mass transfer in gas hydrate formation

using mechanical approaches has been extensively investigated with various reactors, including stirring reactors [11–15], bubble tower reactors [16,17], static mixers [18–20], and spraying reactors [17,21,22]. These reactors have varying degrees of success in improving the hydrate formation kinetics.

An alternative way to enhance gas hydrate formation kinetics is to use chemical additives. Kalogerakis et al. [23] found that sodium dodecyl sulphate (SDS) could significantly enhance the formation kinetics of methane hydrate. Zhong and Rogers [24] gave a more quantitative description for the effect of SDS concentration on hydrate formation rate. Since then, understanding surfactant effects on gas hydrate formation has attracted increasingly more interest from researchers throughout the world. More discussion on the role of surfactants in promoting gas hydrate formation can be found elsewhere [25].

In the present work, a combined mechanical and chemical method of promoting methane hydrate formation was tested. This method comprises addition of SDS and gas-inducing agitation. A stirring reactor equipped with gas-inducing impellers was used to generate gas bubbles in aqueous surfactant solutions with recycling of gas from the headspace into the liquid and thus obviating the use of external loop or compressor. A gas-inducing stirring reactor was also used by Linga et al. [26], but in their experiments they used gas mixtures and pure water in the absence of surfactants. The present work demonstrates the cooperative effect of surfactant addition and gas-inducing agitation on promoting methane hydrate formation kinetics, which has important implications for hydrate-based technology development.

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## 2. Material and methods

### 2.1. Materials

The methane used in the present experiments was a research-grade compressed methane gas with high-purity (99.995 vol%, Coregas). The surfactant under test was SDS (98.5% pure, Sigma Aldrich, CAS Number: 151-21-3, Molecular Weight: 288.38 g/mol). Deionized (DI) water (> 18.2 megohm) was used to prepare the surfactant solutions.

### 2.2. Apparatus

A isochoric/isothermal cylindrical high pressure autoclave (Berghof BR-300) made of CrNiMo stainless steel with internal diameter of 68.2 mm and internal height of 94.6 mm was used (see Fig. S1 a schematic drawing of the experimental apparatus). A detailed description about this apparatus can be found elsewhere [27]. A gas entrainment impeller induces gas through an oval-shaped orifice (approximately 13 mm long and 5 mm wide) in the hollow shaft above the liquid surface. The inner diameter of the hollow shaft is 6 mm, the diameter of the holes in the impeller is 4 mm, and the impeller diameter is 39 mm. At a particular rotating speed (the critical speed for gas induction), the local pressure becomes low enough to allow gas to be entrained into the liquid. In general, the higher the stirring speed, the lower the pressure at the tip of the impeller, and the better the dispersion of the gas in the liquid would be. It was observed in our research that a rotating speed of 600 rpm was sufficient for gas inducing.

### 2.3. Experimental procedure and data processing

The high pressure autoclave was cleaned using copious amounts of DI water before each experiment. First, the autoclave enclosed with DI water or SDS solution was immersed in the liquid bath for at least 2 h to achieve a stable liquid temperature ( $274 \pm 0.05$  K). After that, the vacuum pump was used to remove air inside the autoclave before feeding the pressurized methane (see Point A on the pressure-temperature trace shown in Fig. S2) into the autoclave. The agitation speed was 600 rpm. During the period of the methane hydrate formation, the temperature and pressure of the reaction system were monitored and recorded. More details about the experimental procedure can be found elsewhere [27].

Methane hydrates were set to form at 274 K and initial pressure of 10.0 MPa (see Point B in Fig. S2) in the autoclave with 75 g aqueous solution agitated by the gas-inducing stirrer. The stirrer was immersed in the solution. Once the hydrate was formed, the reaction went along the isochoric and isothermal path (Point B to Point C in Fig. S2). The presence of SDS and foams would have no effects on phase equilibrium of methane hydrate [28,29]. Under the experimental pressure of 10.0 MPa, the equilibrium temperature of methane hydrate is 286 K as predicted by CSMHYD [1]. In the present work, the experiments were carried out at 274 K, so the sub-cooling  $\Delta T$  was 12 K. Our calculations suggest that the amount of methane molecules initially loaded in the autoclave cell is sufficient for the complete conversion of water to hydrate.

A sharp decrease in gas pressure indicates the onset of hydrate growth period, and a typical pressure and temperature change versus elapsing time can be found elsewhere [27]. The gas uptake would last for a certain period of time before starting to level off. The cumulative amount of methane gas uptake by the hydrate was calculated following the same method as in our recent work [27], with the change in the volume of methane gas in the headspace taken into account. This change was resulted from the volume expansion associated with the conversion from liquid water to solid hydrate during the hydrate formation.

The hydrate formation rate was defined as the amount of methane gas uptake by the hydrate during the hydrate crystal growth period per

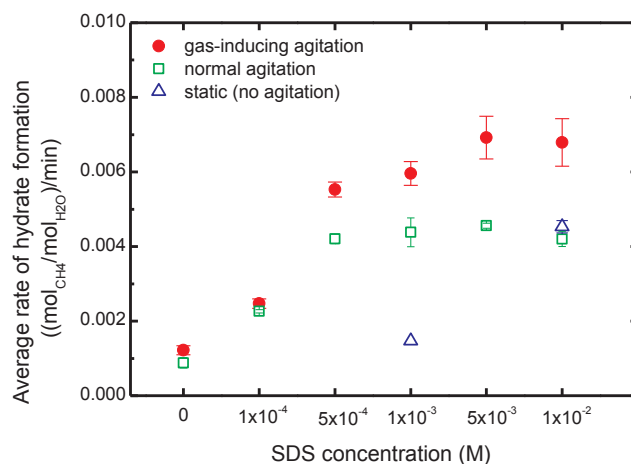


Fig. 1. Influence of SDS concentration on the average rate of methane hydrate formation, with gas-inducing agitation, normal agitation, or under static condition. The formation rate of methane hydrate was calculated using Eq. (1). The error bars associated with the squares represent one standard deviation obtained from 2 independent experiments.

unit time [30]. For simplicity, in the present work the hydrate formation rate ( $r$ ) was calculated using the following expression:

$$r_{\text{exp}} = \Delta n / \Delta t \quad (1)$$

where  $\Delta n$  represents 50% of the measured final methane consumption and  $\Delta t$  is the half-decay time, that is, time lapse from the onset of the gas hydrate growth to 50% of the final methane consumption.

## 3. Results and discussion

The methane hydrate formation experiments with gas-inducing agitation, normal agitation, or no agitation were carried out and the obtained results were compared. The normal agitation was achieved by blocking the holes on the gas-inducing impeller.

Fig. 1 shows that an increase in SDS concentration would steadily increase the methane hydrate formation rate before levelling off at  $5 \times 10^{-3}$  M (1441.9 ppm). Similar observation was made by Okutani et al. [31] who studied the hydrate kinetic in presence of SDS at different concentrations with no agitation and concluded that the most suitable concentration to increase the hydrate formation rate and the final water conversion ratio was 1009.3 ppm ( $= 3.5 \times 10^{-3}$  M). With gas-inducing agitation, in the absence of SDS, the methane hydrate formation rate was approximately 0.0012 (mol<sub>CH4</sub>/g<sub>H2O</sub>)/min, and an increase in SDS concentration from 0 to  $5 \times 10^{-4}$  M led to an approximately 4-fold in the hydrate formation rate. Further increase in SDS concentration results in a small increase in the formation rate. At each SDS concentration tested, gas-inducing agitation gave higher methane hydrate formation rate compared with normal agitation (without gas-inducing), and the difference was larger at SDS concentrations above  $5 \times 10^{-4}$  M (144.2 ppm).

At  $1 \times 10^{-3}$  M (288.4 ppm) SDS, gas-inducing agitation gave a hydrate formation rate of 0.0060 (mol<sub>CH4</sub>/mol<sub>H2O</sub>)/min, approximately 4-fold higher than that under static condition. At  $1 \times 10^{-2}$  M (2883.8 ppm) SDS (slightly above the critical micelle concentration), gas-inducing agitation allowed the formation rate to reach 0.0068 (mol<sub>CH4</sub>/g<sub>H2O</sub>)/min, about 50% higher than that under static condition. Almost the same formation rate was obtained at  $1 \times 10^{-2}$  M SDS with normal agitation and no agitation, implying that at such a high SDS concentration, normal agitation is not needed any more.

Note that gas-inducing agitation with no SDS gave a rather low formation rate whereas addition of SDS at a low concentration (i.e.,  $1 \times 10^{-4}$  M (28.8 ppm) SDS) doubled the formation rate (see Fig. 1). In an attempt to better understand this phenomenon, further investigation

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