

Effects of surfactant micelles and surfactant-coated nanospheres on methane hydrate growth pattern



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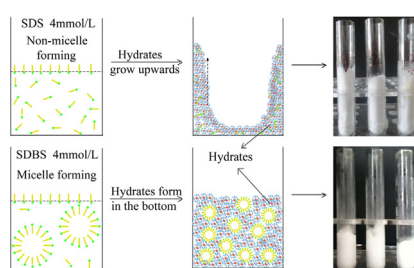
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HIGHLIGHTS

- SDS led to the upward methane hydrate growth on the reactor side-wall.
- SDBS micelles were conducive to the hydrate formation in the bulk of solution.
- SDS adsorbed on polystyrene nanospheres acts like micelles in hydrate formation.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfactants have been reported to promote the gas hydrate formation by changing the hydrate formation pattern. In this work, methane hydrate formation was carried out in glass tubes to study the effects of the existence of surfactant micelles on methane hydrate growth pattern. For comparison, surfactants could and could not form micelles at hydrate formation temperature were used, which were sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS), respectively. SDS led to obvious upward hydrate growth on the reactor sidewall (cover factors 2.8–3.7), while SDBS resulted in obviously less extent of upward hydrate growth (cover factors 1.8–2.6) due to the micelle effect. When SDS-coated polystyrene nanospheres were used, SDS existed in the reaction solution in the form of mimic micelles and consequently much less extent of upward hydrate growth was achieved (cover factors 1.8–2.3). When SDBS was used together with SDS at non-micelle forming condition, prominent upward hydrate growth was obtained (cover factors 2.7–3.3).

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1. Introduction

Natural gas hydrates, formed by water and natural gas molecules (Sloan and Koh, 2007a), have aroused great attention during the past decades due to the significant potential in natural gas storage and transportation (Gudmundsson et al., 1994, 1995; Mori,

2003). How to shorten the induction period and accelerate the hydrate growth have been the research focus, because the long induction period and slow hydrate growth are not conducive to the application of natural gas hydrates (Zhong and Rogers, 2000).

Surfactants, such as SDS, have been reported with effective promotion to gas hydrate formation (Ganji et al., 2007; Ando et al., 2012; Lo et al., 2012; Du et al., 2014; Veluswamy et al., 2015a, 2015b) because surfactants could change the hydrate formation pattern (Zhong and Rogers, 2000; Gayet et al., 2005; Watanabe et al., 2005a; Okutani et al., 2008; Zhang et al., 2007a; Yoslim et al.,

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2010). In the unstirred gas/liquid system without surfactants, gas hydrates initially formed as a thin hydrate film at the gas/liquid interface (Sloan and Koh, 2007b; Kashchiev and Firoozabadi, 2002) and then grew downwards as dendrites (Lee et al., 2006). However, the hydrate film isolated the liquid phase from the gas phase and therefore led to slow hydrate formation (Mori and Mochizuki, 1996). While in the SDS solution system, according to Zhong and Rogers (2000), hydrates initially formed as particles by the gas dissolved in the SDS micelles and the water associated on the micelle surface. Afterwards, the hydrate particles would be adsorbed on the reactor sidewall, resulting in the formation of concentric hydrate layers held by the reactor sidewall. As a result, the hydrate film that isolated the gas phase from the liquid phase was removed and therefore rapid hydrate formation was achieved. However, this hypothesis was also disputed by several researchers (Watanabe et al., 2005a, 2005b; Zhang et al., 2007a; Di Profio et al., 2007; Zhang et al., 2007b), because no micelles were detected at the SDS concentration reported by Zhong and Rogers (2000) and no efficient promotion was observed although with the existence of surfactant micelles.

Another phenomenon about the hydrate formation with surfactants was that hydrates initially formed on the reactor sidewall and then grew upwards under capillary effects (Gayet et al., 2005; Watanabe et al., 2005a, 2005b; Okutani et al., 2008; Zhang et al., 2007a; Yoslim et al., 2010). Gayet et al. (2005) reported that surfactants could prevent the aggregation of hydrate particles at gas/liquid interface and hydrates primarily formed on reactor sidewall as porous structures. Then the surfactant solution could be sucked up to the hydrate surface through the porous structure under capillary force. Watanabe et al. (2005a, 2005b) reported that the reactor sidewall would be splashed with surfactant solution when charging the solution into reactor, leading to solution films adhered on the sidewall. Therefore, hydrate formation initially took place on the reactor sidewall with the solution films, resulting in the formation of hydrate films on reactor sidewall. Although many researchers have reported the upward hydrate growth on the reactor sidewall, the reasons that cause the upward hydrate growth still remain poorly understood.

In our previous study (Wang et al., 2015a), the wettability of reactor sidewall with surfactant solution (revealed by the contact angle) was found to affect methane hydrate growth pattern. SDS solution, with good wettability, led to obvious upward hydrate growth on the reactor sidewall, while SDBS solution resulted in the hydrates formed mainly in the reactor bottom due to the poor wettability. However, when a glass layer, which showed good wettability with surfactant solution, was installed in the reactor, a certain extent of upward hydrate growth was also obtained in methane hydrate formation with SDBS solution. Then in our other previous study (Wang et al., 2015b), direction controlled methane hydrate growth on the reactor sidewall was achieved through changing the hydrophilicity and hydrophobicity of hydrate growth surface.

In this work, to further study the methane hydrate growth pattern in the presence of surfactants, methane hydrate formation was carried out in glass reactors, which showed very good wettability with reaction solutions, therefore, the effects of wettability could be avoided. To understand the effects of surfactant micelles on methane hydrate growth, both SDS and SDBS were used, because SDS and SDBS showed similar molecular structures and SDBS could form micelles at hydrate formation conditions while SDS could not.

2. Experimental section

2.1. Materials

Sodium dodecyl sulfate (SDS, AR) and sodium dodecyl benzene sulfonate (SDBS, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Styrene (St, AR) was provided by Tianjin Guangcheng Chemical Reagent Co., Ltd. (Tianjin, China). Ammonium persulfate (APS, AR) was purchased from Hengxing Chemical Reagent Co., Ltd. (Tianjin, China). Methane and nitrogen with purities of 99.99% were provided by Heli Gas Co., Ltd. (Qingdao, China). The deionized water used in this work was laboratory-made and the conductivity was $1.1 \pm 0.1 \mu\text{s}/\text{cm}$ (298.15 K). The molecular structures of the surfactants are shown in Fig. 1.

2.2. Preparation of the mimic micelles of SDS

In this work, to clear the effects of surfactant micelles on methane hydrate growth pattern, SDS-coated nanospheres were prepared and used in methane hydrate formation. With SDS molecules fixed on the surface of polystyrene nanospheres, SDS-coated nanospheres showed similar structures as SDS micelles, as shown in Fig. 2. Therefore, the SDS-coated nanospheres were also called mimic micelles of SDS (M-micelle-SDS).

The mimic micelles of SDS were prepared by fixing the surfactant molecules on the surface of polystyrene nanospheres, which was achieved through emulsion polymerization with SDS as emulsifier, styrene as monomer and ammonium persulfate as initiator. The recipes and conditions of emulsion polymerization are shown in Table 1. The details of emulsion polymerization and the characterizations of M-micelle-SDS were provided in our previous study (Wang and Fang, 2014).

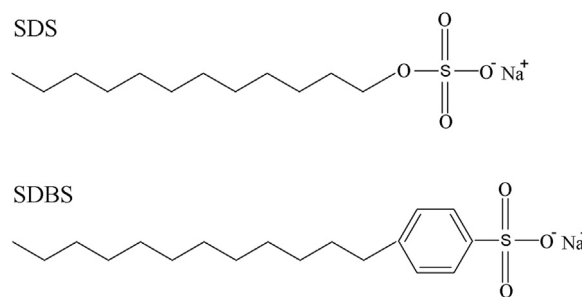


Fig. 1. Molecular structures of the surfactants used in this work.

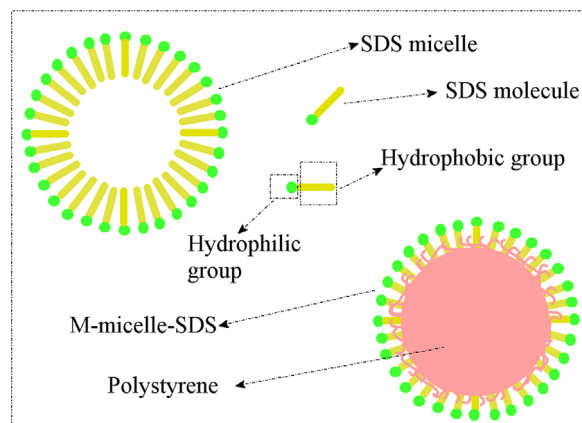


Fig. 2. Schematic diagram of the structures of SDS micelle and M-micelle-SDS.

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