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## Methane Hydrate Crystal Growth At the Gas/Liquid Interface in the Presence of Sodium Dodecyl Sulfate

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### Abstract

This study reports the visual observation made of the formation and growth of clathrate hydrate on the surface boundary of a Sodium Dodecyl Sulfate (SDS) aqueous solution droplet and surrounding methane gas. The experimental temperature range was from 276 K to 282 K, under the pressure of 7.8 MPa, at pure water,  $w_{\text{SDS}} = 10$  ppm and  $w_{\text{SDS}} = 100$  ppm, where  $w_{\text{SDS}}$  denotes the mass fraction of SDS in the aqueous solution. At pure water and  $w_{\text{SDS}} = 10$  ppm, the hydrate crystals were initially observed at the droplet surface, and followed by lateral growth at the droplet surface. However, at  $w_{\text{SDS}} = 100$  ppm, it was observed that hydrate growth behavior greatly changed compared to pure water system. At  $w_{\text{SDS}} = 100$  ppm and  $\Delta T_{\text{sub}} < 6.0$  K, the structure of the droplet was not maintained and hydrate crystals grew horizontally on to the stage. We defined the subcooling,  $\Delta T_{\text{sub}}$ , the difference between the system temperature and the equilibrium temperature of methane hydrate as driving force index for crystal growth. At  $w_{\text{SDS}} = 100$  ppm and  $\Delta T_{\text{sub}} \geq 6.0$  K, the hydrate grew perpendicularly to the stage. At  $w_{\text{SDS}} = 100$  ppm and each  $\Delta T_{\text{sub}}$ , the amount of hydrate produced increased compared to pure water system.

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### 1. Introduction

Clathrate hydrates (hereafter hydrates) are crystalline solids composed of hydrogen-bonded cage-forming water molecules called the “host” and enclose different molecules called “guests” within those cages. Hydrates are usually stable at low temperature and high pressure conditions. It is generally known that hydrates have several properties, such as, high gas-storage capacity, large heat of formation and decomposition, and guest substance selectivity. These properties enable hydrates to be applied to various industrial technologies, for example, transportation and storage of natural gas [1,2], the ocean and ground sequestration of CO<sub>2</sub> [3, 4, 5], developing highly efficient heat pump and refrigeration [6], and gas separation [7]. Therefore, the promotion of the hydrates is important to develop various industry technologies.

On the other hand, it is generally known that hydrates cause a serious problem in flow assurance of oil and gas pipeline. It was reported that the formed hydrates plug the oil and gas pipeline due to the conditions of low temperature and high pressure [8]. Therefore, it is necessary to prevent hydrate formation for flow assurance of oil and gas pipeline. To solve the problem, the usage of surfactants has garnered wide attention. It is reported that surfactants have two different effects on hydrate formation. One is

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the promotion of hydrate formation, while the other is the prevention of the hydrate agglomeration. Watanabe et al. [9] reported that surfactants such as Sodium dodecyl sulfate (SDS) increase water-to-hydrate conversion ratio. Aman et al. [10] measured the adhesion forces between the two hydrate particles and reported that the adhesion force decrease by adding the surfactant. As above, surfactants have two effects – prevention of hydrate agglomeration and promotion of hydrates – though their relations are not fully understood. To clarify the two effects, it is necessary to understand the physical mechanism of hydrate formation in surfactant systems.

To realize valuable hydrate applications, we acknowledge that the need for a more comprehensive understanding of hydrate growth behavior and hydrate crystal morphology is important. Here, hydrate crystal morphology denotes the crystal size and shape. Knowledge of the hydrate crystal morphologies provided the effective process including hydrate transportation, dehydration, and hydrate decomposition.

In recent years, there has been substantial progress in studies on the morphology of hydrate crystals formed at the guest-water interface in surfactant systems. Mitarai et al. [11] observed the hydrates growth and hydrate crystal morphology at the interface between water and cyclopentane dissolved in the surfactant (liquid/liquid interface). They reported that the amount of the hydrate crystals increased and crystal size was larger than in the system without surfactant because the hydrate crystals detached from the interface.

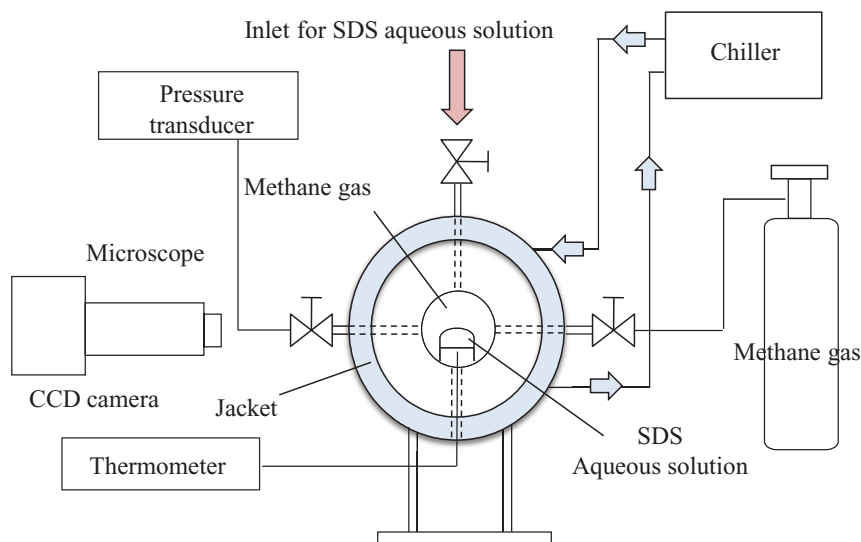
To solve the problem of pipeline plugging, as the hydrate guest substance are mostly in gaseous form, it is important to observe the hydrate at the gas/liquid interface with a surfactant added.

In this study, we used SDS as the surfactant because that is commonly used in industries and one of the most commercially available surfactants. To clarify the mechanism that surfactant effects on the hydrate, we report visual observations of hydrate growth behavior and crystal morphology at the interface between methane gas and SDS aqueous solution.

## 2. Experimental Section

The fluid sample used in the experiments was methane (99.99 vol %, Takachiho Chemical Industrial Co.). SDS aqueous solution was prepared by dissolving SDS of solid reagent (99.0 mass%, Aldrich Chemical Co.) into distilled water and set for two different concentration,  $w_{\text{SDS}} = 10$  ppm and  $w_{\text{SDS}} = 100$  ppm, where  $w_{\text{SDS}}$  denotes the mass fraction of SDS aqueous solution.

Fig. 1 shows the schematic diagram of the experimental apparatus used in this study. The test cell is a cylindrical vessel made of stainless steel. The inner space of the test cell functions to hold the test gas and hydrate crystals is 25 mm in diameter and 20 mm in axial length. Test cell temperature is controlled by circulating ethylene glycol aqueous solution in the jacket covering the test cell. A droplet of SDS aqueous solution was placed on the Teflon stage in the test section. Teflon stage size is 6 mm or 13 mm in diameter. The air was then replaced with the methane gas from the gas cylinder to the test cell valve by repeating the pressurization and depressurization of the cell. The pressure of inside the test cell,  $P$  was measured by a strain gauge pressure sensor with an uncertainty of  $\pm 0.02$  MPa. The droplet temperature on the Teflon stage,  $T$  was measured by Pt-resistance thermometer with an uncertainty of  $\pm 0.2$  K inserted just below the Teflon stage. As a precaution, it was confirmed that the temperature of the droplet and Teflon stage were equal by measuring the droplet temperature with inserting Pt-resistance thermometer into the droplet.



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