THE EFFECT OF SURFACTANT ON THE MORPHOLOGY OF METHANE/PROPANE CLATHRATE HYDRATE CRYSTALS

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ABSTRACT

In the present study the effect of one commercially available anionic surfactant on the formation/dissociation of hydrate from a gas mixture of 90.5 % methane – 9.5% propane mixture was investigated. Surfactants are known to increase gas hydrate formation rate. Memory water was used and the experiments were carried out at three different degrees of undercooling and two different surfactant concentrations. In addition, the effect of the surfactant on storage capacity of gas into hydrate was assessed. The morphology of the growing crystals and the gas consumption were observed during the experiments. The results show that branches of porous fibre-like crystals are formed instead of dendritic crystals in the absence of any additive. Finally, the addition of 2200 ppm of SDS was found to increase the mole consumption for hydrate formation by 4.4 times.

Keywords. Crystal morphology, Surfactant, Gas hydrates, Dendrites, Sodium Dodecyl Sulfate

INTRODUCTION

Storage and transport of natural gas as a solid natural gas hydrate (NGH) is considered an alternative method to liquefied natural gas (LNG) technology (1-6). Compared to LNG, gas hydrates are easier and safer to handle because their explosion potential is significantly less and can be stable at -20°C and 0.1 MPa whereas LNG is stabilized at -160°C and 0.1 MPa. Moreover, depending on the capacity to be stored and the distance to be travelled NGH technology is believed to be economical in certain situations (6). The enhancement of the kinetics of hydrate formation is one area where improvement is needed in order to proceed with the design of relevant facilities. On approach to enhance the kinetics and thus the conversion of gas to hydrate is the use of surfactants.

Kalogerakis et al. [7] observed that surfactant addition did not alter the thermodynamics but it has a large effect on the kinetics of hydrate formation. Karaaslan et al.[8] and Sun et al. [9]

studied the effect of anionic, cationic and nonionic surfactants on the hydrate formation rate and assessed the hydrate storage capacity. Both papers reported that the anionic surfactants are more promising compared to the other two types. Link et al. [10] concluded that Sodium Dodecyl Sulfate (SDS) is one of the best surfactants commercially available to be used for the enhancement of hydrate formation. Daimaru et al. [11] tested three surfactants with sodium sulfonic acid groups in common but different in their carbon chain length (C4, C12, and C18). They observed that the formation rate of xenon hydrate was accelerated at lower range of surfactant concentration up to a point where increase in concentration reduced the formation rate. Another observation made was that C4 or Sodium Butyl Sulfate gave the highest acceleration compared to the other two longer carbon chained surfactants. Okutani et al.[12] also investigated three different types of sodium alkyl sulfates (C12, C14, and C16) and their experimental results show that C12 and C14 can

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increase the formation rate and gas storage capacity equally but the concentration needed for C14 is less than that for C12.

The first mechanism of hydrate growth when surfactant is present in the system was proposed by Kutergin et al.[13] and Mel'nikov et al.[14]. They reported that addition of surfactant to liquid water caused morphological changes in the hydrate film so that the gas-water contact can be continuously maintained until most of the water converted to hydrate. Morphology is concerned with the observation of shapes and sizes of forming hydrate phase boundaries, whose length scales are much larger than molecular structure and much smaller than system dimension. These observations are useful tools to have a better process design for future application of natural gas hydrates [15-17]. Recently, Okutani et al [12] reported qualitative observations of hydrate growth and concluded that it is in qualitative agreement with the description given by Kutergin et al.[13], Mel'nikov et al.[14], Watanabe et al. [18], Zhong and Rogers [19], Gayet et al. [20], and Pang et al.[21]. The above work suggested that the capillary-driven water suction that allows water to flow upward through the porous hydrate layer is responsible for enhanced hydrate formation when surfactant is present in the system.

Another observation made by Okutani et al. [12] is that there is no distinct qualitative difference in hydrate growth behaviour with various surfactant types with different alkyl chain length and the surfactant concentration used (~100ppm - ~ 4000ppm). However, all the previous morphological work done when surfactant is present in the system uses camera or video camera to capture and save images from hydrate formation. Although these images offer a visual observation of the system one may achieve a better understanding of hydrate formation by using a microscope which and a camera to obtain magnified views.

Lee et al. [22] and Kumar et al. [23]) have investigated the morphological changes when water and water-PVP are present in the system using an experimental set up equipped with a microscope. Lee et al. [22] examined morphology of methane – propane – water system without addition of any additives and found that hydrates started to form as thin film at the gas/liquid interface. Hydrate crystals are then observed to grow downwards as dendrites from the thin film into the bulk water. Kumar et al. [23] examined the morphology of the hydrate formed by a methane/propane gas mixture in the presence of poly vinylpyrrolidone (PVP) which is known to inhibit hydrate growth. They observed whiskery type of hydrate crystals at an undercooling of 13.1 K and fibre-type growth at 8.1K of undercooling.

This work is concerned with the effect of sodium alkyl sulfates (C12) concentration and degree of undercooling on dynamics of methane-propane hydrate growth based on morphological observation.

EXPERIMENTAL SECTION

Gas used for the present study was a 90.5/9.5 mol % methane-propane mixture which was already analyzed using gas chromatography (Varian, CP-3800). The surfactant was Sodium Dodecyl Sulfate (SDS) which is anionic surfactant. Water used for the experiments was distilled and deionized. A detailed description of the apparatus is given by Lee et al [22]. The crystallizer consists of three parts: top (stainless steel), middle (polycarbonate called Lexan), and bottom part (stainless steel). The unique design about the crystallizer is the middle part which allows to capture undistorted images of hydrate crystal growth which is shown in Figure 1. A schematic of the apparatus is given in Figure 2. Minor modification were made to the set up reported by Lee et al [22] by installing a digital pressure transmitter (Rosemont) coupled with a data acquisition system (National Instrument). It consists of crystallizer (CR) that is immersed inside a temperature controlled water bath. The temperature of the water bath is being controlled by two external heating/cooling systems. In order to record the picture or video images of hydrate formation, microscope (Nikon, SMZ 1000 with P Plan Apo 1x objectives lens) attached to a CCD video camera (Sony, DXC-390) or microscope (Nikon, SMZ 2T with 0.5 x auxiliary lens) attached to a Nikon D-40 camera were used during experimental run.

The experimental procedures are similar to the other two previous works by Lee et al. [22] and Kumar [23]. Experimental conditions, surfactant type and conditions are summarized in Table 1. The concentration was chosen to be 2200 ppm and 645 ppm(part per million) which is below the CMC (critical micelle concentration) [24,25]. Recent finding by Zhang et al. [26] stated that SDS concentration above 1780 ppm will form solid crystals instead of micelle and according to

Di Profio et al. [25], micelles of SDS will not form in until the concentration reached ~2300ppm. Equilibrium pressure and temperature are calculated using CSMYD software [27].
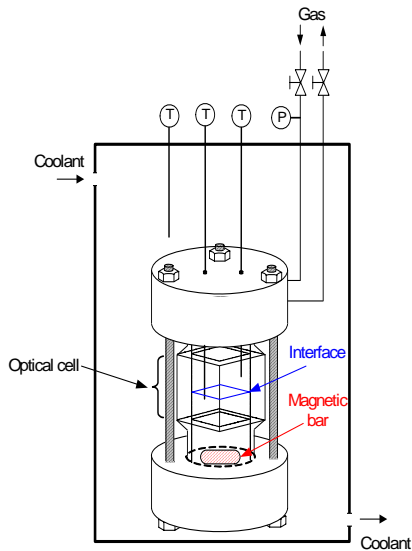

Figure 1. Morphology Apparatus (adapted from Lee et at al. [22]

CR   - Crystallizer
PC   - PC
DAQ - Data Acquisition System
P1 & P2 - Pressure Transmitter
EH   - External Heater
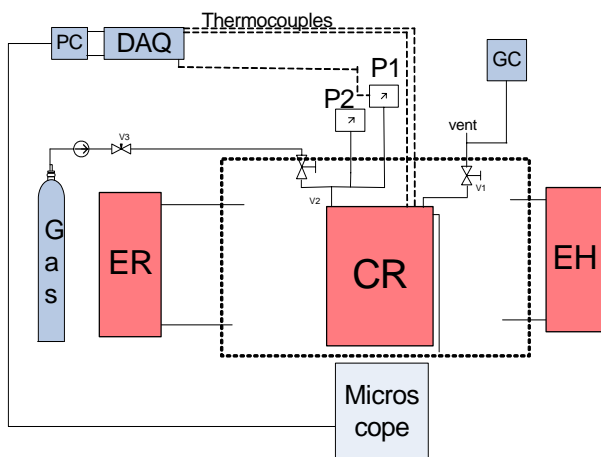ER   - External Refrigerator
GC   - Gas Chromatography

Figure 2. Schematic of the apparatus (adapted from Lee et al. [22]

Each experimental run composed of a 25 cm^3 aqueous phase and a~ 29 cm^3 guest gas phase. Memory water which refers to water that has experience of forming hydrate is used for all morphological experiments in order to reduce induction time.

Exp	Surfactant Conc.	P_{exp}	T_{Eq}	T_{exp}	ΔP
No.	(ppm)	(kPa)	(C)	(C)	(kPa)
A	Water	3200	15.5	2.4	227.5
B	SDS-2200	3200	15.5	2.4	1006.6
C	SDS-2200	2400	13.2	5.2	537.8
D	SDS-2200	1430	8.8	5.2	193.1
E	SDS-645	3200	15.5	2.4	997.7

Table 1. Experimental Conditions

RESULTS AND DISCUSSION

The effect of surfactant on the growth characteristics of methane/propane hydrate crystals in quiescent system was investigated. Experiment A and B were conducted in order to compare the different characteristics of crystal growth with surfactant added into the system. The experiment was done with the same degree of undercooling ($\Delta T = 13.1^oC$). Surfactant is known as promoter for hydrate formation but does not serve as a guest species. Surfactant addition lowers the surface tension of the medium in which it is dissolved, so that it improves the gas to liquid mass transport. Improved mass transport is believed to enable a surfactant to act as a promoter of hydrate formation [10].

Observation of hydrate crystal growth

It was observed that when surfactant is present in the system hydrate crystals were first seen in the vicinity of liquid-gas-solid line and at the tip of a thermocouple touching the water surface. On the other hand in the absence of any additive the hydrates appear as a thin film at the gas/liquid interface [22]. Following nucleation hydrate was seen to grow radially to cover the gas/liquid interface. In addition, as shown in figure 3. branches of fibre-like hydrate crystal were seen to grow towards the bulk water phase unlike a system without any surfactant. In addition, hydrate growth on the wall and the thermocouple tip was also seen with the crystals growing upward. This mode of growth is probably due to the capillary driven mechanism discussed in the introduction. The observed decrease of the level of the gas/water interface was an indication of the continuous consumption of water for hydrate formation. As

mentioned before that addition of surfactant will decrease the surface tension of liquid water which also means lowered the contact angle. Figure 4 shows schematically the gas/liquid interface with and without a surfactant. Due to lowering of the contact angle with the surfactant a film-like interface is created along the wall and below the gas/water//solid line. This film is believed to be the preferred location for nucleation and initiation of hydrate growth.
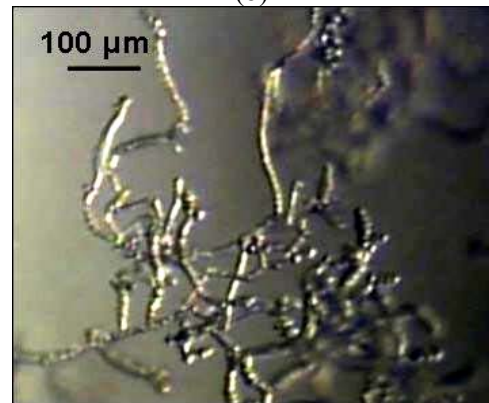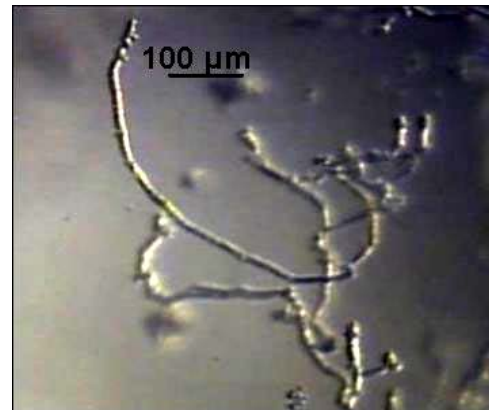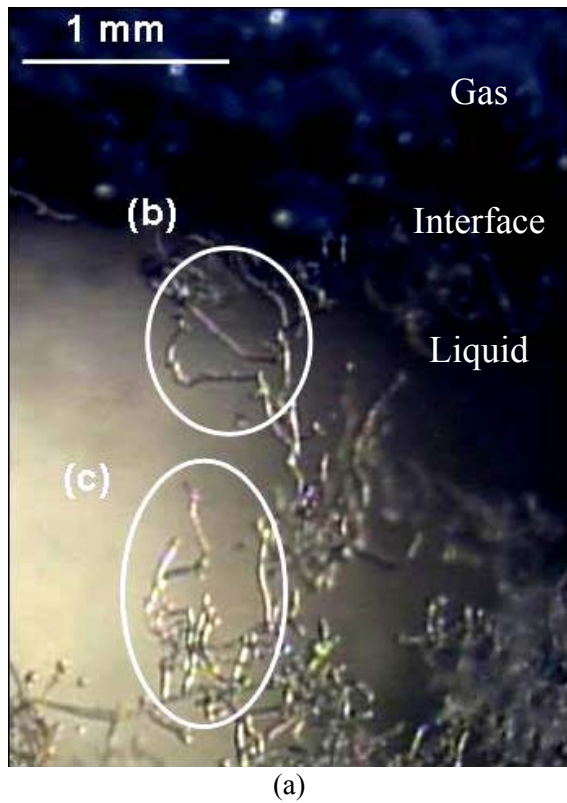

Figure 3. Images of hydrate crystal during hydrate formation with surfactant present in the system (Experiment C). Image (b) and (c) are magnified images from (a).
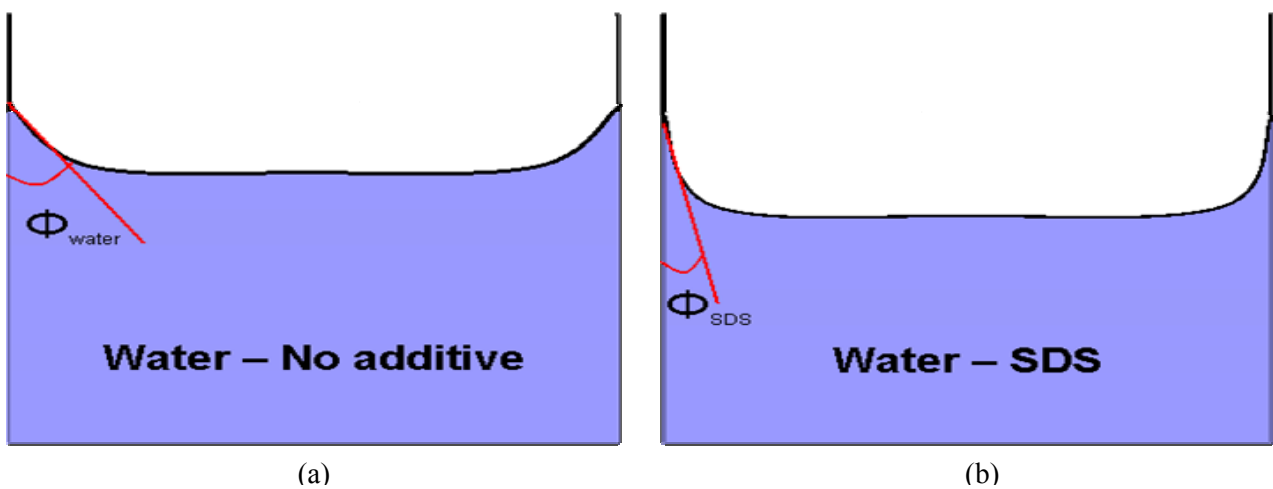

Figure 4. Contact angle comparison of system without additives (a) and with surfactant (b)

Another interesting observation was made when comparing different surfactant concentrations (Experiment B and E). The morphology of growing crystals during both experiments showed similar patterns (in agreement with Okutani et al. [12]), but as concentration increased, the degree of branching increased (Figure 5).

Figure 6 shows the effect of undercooling. At high and medium degrees of undercooling (experiment B and C), similar hydrate crystal growth is observed, but as the degree of undercooling (ΔT) increased, the extent of hydrate crystal increased. At the lowest degree of undercooling (Figure 5c), there is no significant hydrate crystal growth but a thin hydrate layer on the crystallizer wall can still be seen.

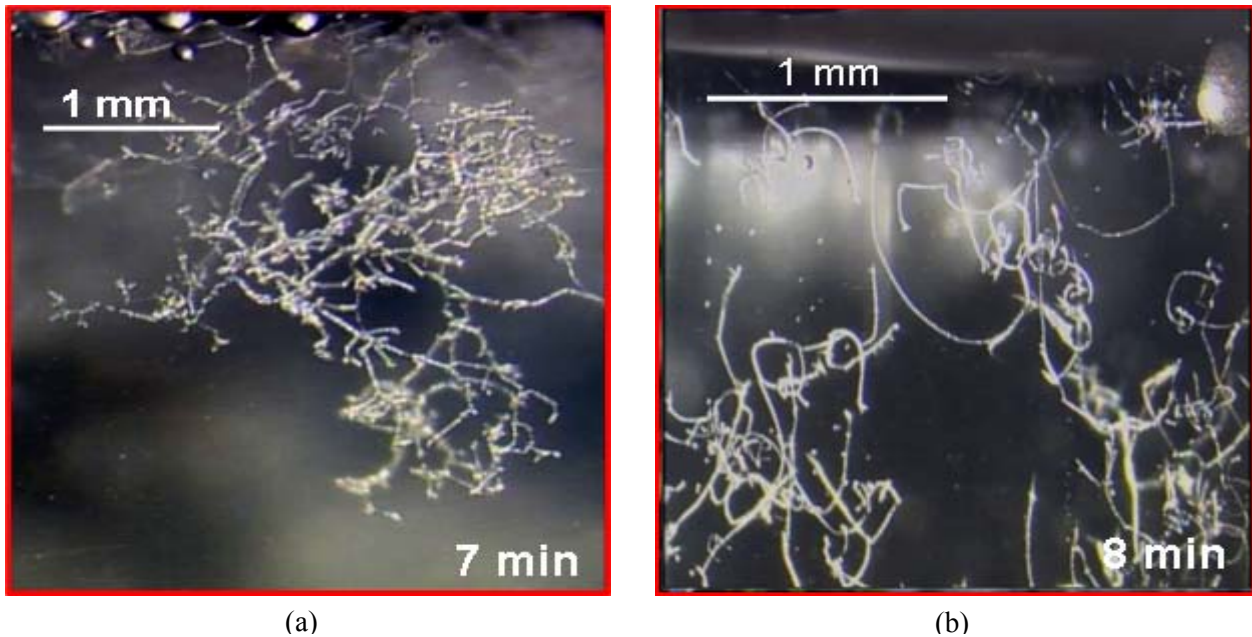(a)   (b)

Figure 5. Hydrate crystal growth at different surfactant concentrations (experiment B and E). Surfactant concentration of 2200 ppm (a) and surfactant concentration of 645 ppm (b).
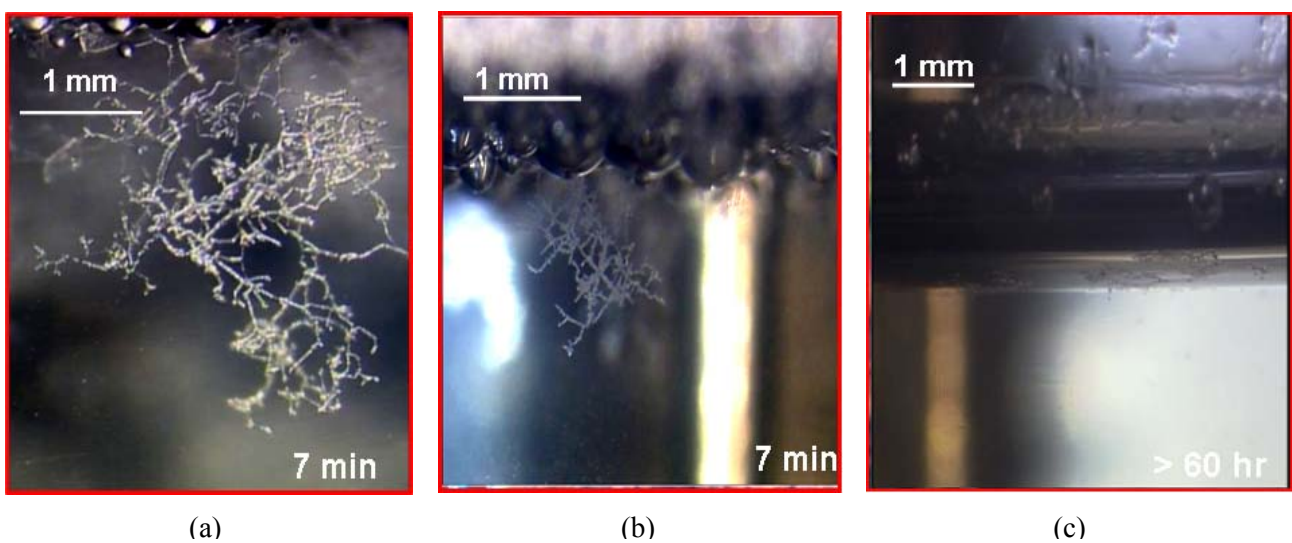

(a)   (b)   (c)

Figure 6. Hydrate crystal growth at different degree of undercooling. $\Delta T = 13.1^{o}K$ (a), $\Delta T = 8.0^{o}K$ (b), and $\Delta T = 3.6^{o}K$ (c)

Effect of surfactant on gas uptake measurement

The moles of methane-propane gas consumed in the crystallizer due to hydrate formation are calculated by using the pressure and temperature data collected with the data acquisition system. In a closed system, the total number of moles in the system will remain constant at any given time. From this data, ratio of moles of gas consumed for hydrate formation in the systems with and without surfactant can be obtained.

Since this study was done in a closed system, the volume of the system at ay given time remains constant ($V_i = V_f$). The ratio of moles of gas consumed for hydrate formation in the system with and without surfactant, ($\frac{\Delta n_s}{\Delta n_w}$), can be determined using the ratio of pressure drops with and without surfactant ($\frac{\Delta P_s}{\Delta P_w}$) as shown in equation (1). ΔP_s and ΔP_w are the total pressure drops due to gas consumed during hydrate formation with and without surfactant present in the system, respectively.

$$\frac{\Delta n_s}{\Delta n_w} = \frac{\dfrac{\Delta P_s . V_s}{Z.R.T_s}}{\dfrac{\Delta P_w . V_w}{Z.R.T_w}} = \frac{\Delta P_s}{\Delta P_w} \qquad (1)$$

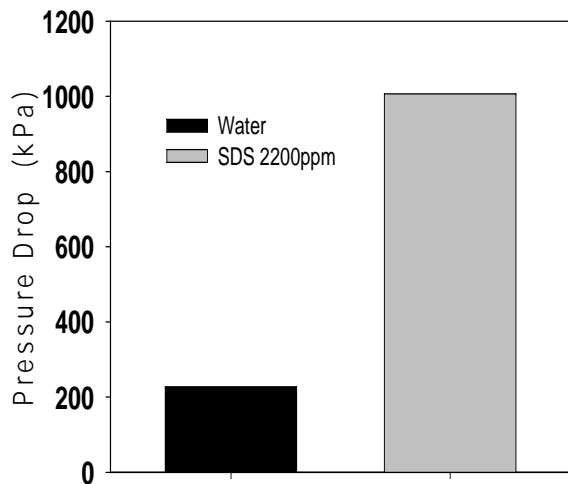z is the compressibility factor calculated by Pitzer's correlation [28].

Figure 7. Pressure drop comparison of system with and without surfactant

As shown in Table 1(experiment A and B) and Figure 7, the ratio of pressure drop for system with and without surfactant is 4.4 which indicate that when surfactant is present, 4.4 times more moles of gas consumed during hydrate formation compare to system without additive.
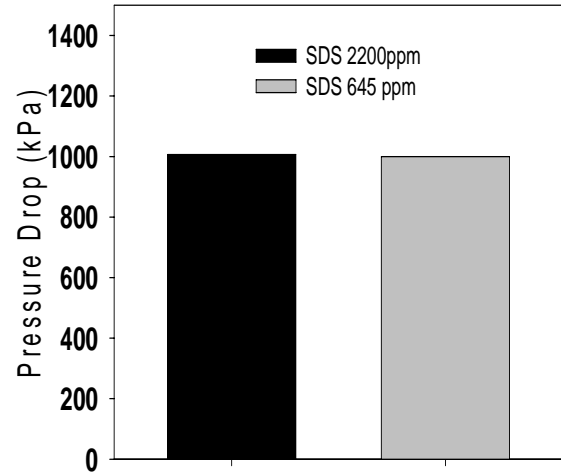

Figure 8. Pressure drop comparison with different surfactant concentration.

Figure 8 shows there is no significant difference in the total moles of gas consumed during hydrate formation which agree with results from Okutani et al [12]. Besides this, his result also showed that the hydrate formation rate based on gas uptake measurement increased with increase in surfactant concentration up to a certain limit. At higher concentrations the hydrate formation rate decreased. It is noted that the surface tension behaves similarly according to Watanabe et al. [18].

The increase observed in the uptake of gas when surfactant is present can be explained by considering the morphological observations during hydrate formation. For hydrate formation without any additives, hydrate will form at the gas-liquid interface as a thin rigid film and cover the gas-liquid interface. This phenomenon will limit or increase the barrier for gas to be adsorbed since gas must pass through the thin hydrate layer to find free water. However, when surfactant is present in the system, porous hydrate is believed to form at the interface of gas-liquid which has the ability to renew the gas-liquid interface through capillary suction of water to flow upward from the bulk liquid to the free surface.

CONCLUSIONS

The dynamics of methane-propane hydrate crystal growth in solution with or without the presence of surfactant (SDS) were studied. The surfactant concentrations used are 2200ppm and 645ppm. When surfactant is present in the system, hydrate formation started to form at the gas-liquid-solid line (sidewall or tip of a thermocouple touching the water surface). This was followed by radial growth along the gas liquid interface. Unlike the system with no surfactant where needle-like dendritic crystals were observed branches of fibre-like crystals were seen when surfactant is present in the system. The degree of branching was found to increase with increasing surfactant concentration. Higher degree of undercooling was found to result in faster growth as expected. In addition, the presence of 2200ppm of SDS surfactant in the liquid phase also promotes the hydrate growth in the system and increases the moles of gas consumed by 4.4 times compared to the system without surfactant.

ACKNOWLEDGEMENT

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