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Effect of kinetic hydrate inhibitor and liquid hydrocarbon on the heterogeneous segregation and deposition of gas hydrate particles

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Abstract−Segregation and deposition of hydrate particles observed in flowloop experiments are required to be investigated more thoroughly to understand the hydrate plugging mechanism in offshore flowlines. We used natural gas as gas phase and selected three different systems as liquid phase, which are pure water only, kinetic hydrate inhibitor added aqueous solution, and water+decane mixture, respectively. Hydrate formation process including onset and growth was studied by measuring the pressure, temperature, and torque changes in high-pressure autoclave. The obtained results suggest that poly-vinyl caprolactam (PVCap) solution shows elongated growth period than pure water until distinct torque change is observed, which also indicates the suppressing effect of PVCap on the growth of hydrate crystals. However, the presence of decane as continuous liquid phase enhances the deposition of hydrate particles on the wall. The torque change with conversion to hydrate used in this study is found to be useful to classify the hydrate formation process into three different regions.

Keywords: Gas Hydrates, Particle Agglomeration, Kinetic Hydrate Inhibitor, Flow Assurance, Offshore Gas Fields

INTRODUCTION

Gas hydrates have been a serious concern in the oil and gas industry because the formation of gas hydrates in offshore flowlines can cause blockages, leading to costly production stoppage and complex remediation works [1,2]. To avoid hydrate formation in offshore flowlines transporting hydrocarbons, thermodynamic hydrate inhibitors (THIs), such as methanol and glycol, have been commonly used to shift the hydrate equilibrium curve outside the flowline operation conditions [1]. As the energy industry moves to deeper and colder regions to produce hydrocarbons, this conventional method is facing difficulties such as large injection volume and high cost. Recent trends for avoiding hydrates, thus, have been moving from complete prevention toward risk management, which is allowing hydrate formation in flowlines but delaying nucleation or avoiding agglomeration of hydrate particles forming blockage [1].

Kinetic hydrate inhibitors (KHIs) are water-soluble polymers that delay the formation of hydrate crystals, and these include homo- and copolymers of the N-vinyl pyrrolidone and N-vinyl caprolactam. KHIs have been applied in field operations successfully and their performance has been evaluated by measuring the hydrate induction time in autoclave cells, rocking cell, and flow loop [3-5]. Spectroscopic observation using NMR and Raman spectroscopies suggests the possibility of structure dependency of KHI performance such that KHIs may have difficulty in preventing structure I hydrates [4]. The technical drawback of using KHIs is they become ineffective at subcoolings higher than 14 °C [3-5]. Interaction between other chemicals such as corrosion inhibitor may also affect the performance of KHIs. Efforts have focused on improving its performance by incorporating various functional groups or developing novel KHIs based on anti-free protein [6,7]. However, its effect on the agglomeration and deposition of hydrate particles has not been studied thoroughly. Previous works suggest that PVP would increase the energy barrier to form hydrate nuclei while PVCap may adsorb to the surface of hydrate crystals [8,9]. In this study, we decided to use PVCap as its performance is known to be better than PVP.

During the development of offshore gas wells, the presence of liquid hydrocarbons would affect the agglomeration and deposition of hydrate particles as well since the liquid hydrocarbon will mix with the aqueous phase and either one of the phases will form a dispersed phase in a continuous phase. The effect of liquid hydrocarbon on the deposition process of hydrate particles needs to be investigated. Recent studies suggest that the hydrate particles will be segregated from the continuous phase before their deposition into the wall. The heterogeneous segregation of hydrate particles and their deposition on pipe wall would be central to understanding the mechanism of hydrate blockage formation. There have been numerous studies to study the nucleation, growth, and agglomeration of hydrate particles with various scenarios for the blockage formation [10-14]. However, there still exists unrevealed nature of the blockage formation of hydrate particles; thus, more diverse approaches and data accumulations are required for better understanding of the hydrate blockage mechanism.

Torque measurement in the autoclave can be a simple and useful approach to investigate hydrate particle growth and deposition in the laboratory scale measurements [15,16]. This study focuses on the torque monitoring of three systems: (1) gas+water for pipelines transporting natural gas with condensed water, (2) gas+0.5 wt%

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PVCap solution for flowlines transporting natural gas and kinetic hydrate inhibitor (KHI) added water, and (3) gas+water+decane for flowlines transporting natural gas and condensate with low water cut. This approach would provide important information on the roles of condensate and KHI for growth, segregation, and deposition of hydrate particles.

EXPERIMENTS

A synthetic natural gas composed of 90.0 mol% CH_4, 6.0 mol% C_2H_6, 3.0 mol% C_3H_8, and 1.0 mol% $n\text{-}C_4H_{10}$ was supplied by Special Gas (Korea). Decane was purchased from Sigma-Aldrich. Deionized water and PVCap (MW≈5000, purity 98.0 wt%) were used without further purification.

A high pressure autoclave, equipped with magnet stirrer coupling and hydrofoil impeller, was used in this study. The liquid of total 120 mL was loaded in the autoclave cell with an internal volume of 300 cm^3. Then, synthetic natural gas was injected into the cell until pressure reached the desired value. For the water+decane mixture, 100 mL decane was mixed with 20 mL water. For KHI added aqueous system, 0.5 wt% PVCap solution was prepared using deionized water. The constant cooling method was adopted in this work. The reactor was cooled to the desired temperature within an hour while mixing at 600 rpm. While cooling the fluids, pressure, temperature, and torque data were continuously monitored. After the experiments were completed with the magnet stirrer coupling, additional experiments were carried out using a magnet spin bar and optical camera to visually observe hydrate formation.

A total of five experiments were performed in pure water as a baseline experiment and to obtain the average hydrate onset time without any additives in the aqueous phase. Another five experiments were carried out for 0.5 wt% PVCap solution to investigate the hydrate formation characteristics such as subcooling temperature, hydrate onset time, and conversion of water to hydrate. Then five more experiments were repeated for water+decane mixture. The conversion of water to hydrates was calculated from the difference between the measured pressure during experiment and the extrapolated pressure assuming no hydrate was formed [17]. The extrapolated pressure was calculated by a volume-temperature flash with thermodynamic software, Multiflash, as suggested by Hemmingsen et al. We note that the system containing anti-agglomerant is not the scope of this work because there would be little change of torque during hydrate formation in the presence of anti-agglomerant.

RESULTS AND DISCUSSION

Hydrate formation in pure water was first investigated. Fig. 1 shows the pressure and temperature changes during the constant cooling process. Hydrate formation is indicated by the pressure reduction as shown in Fig. 1 where the solid line represents the calculated pressure assuming no hydrate formation. Due to gas consumption during the hydrate formation, measured pressure is less than the calculated pressure assuming no hydrate. The moles of gas consumed during hydrate formation were calculated from the pressure difference between the measurement moment and calculated pressure assuming no hydrates. Thus,

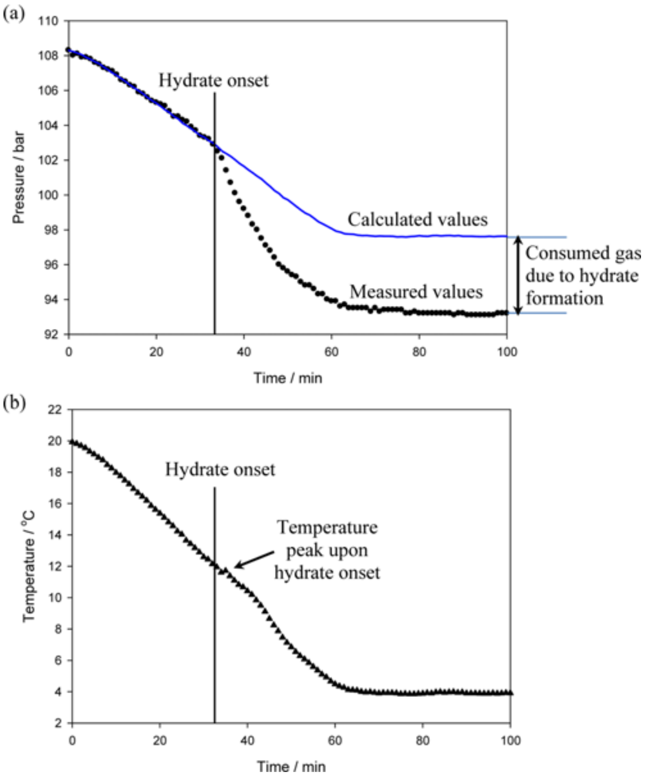

Fig. 1. Pressure and temperature changes during the cooling of water+decane mixture. Solid line indicates calculated results for pressure assuming no hydrate formation.

$$\Delta n_{H,t} = \left(\frac{P_{cal}V_{cell}}{zRT}\right)_t - \left(\frac{P_{exp}V_{cell}}{zRT}\right)_t$$

where, $\Delta n_{H,t}$ is the moles of gas consumed for hydrate formation at a given time, P_{cal} is the calculated pressure assuming no hydrate. P_{exp} is the measured pressure, V_{cell} is the volume of gas phase, z is the compressibility factor calculated using Peng-Robinson equation of state. Once confirming the hydrate formation, hydrate onset time was calculated from the time difference between the hydrate onset and the time when the temperature became lower than the hydrate equilibrium temperature. Similarly, subcooling temperature was also determined from the definition of $\Delta T_{sub}=T_{eq}-T_{onset}$. The obtained average value of hydrate onset time and subcooling temperature for each system is tabulated in Table 1. The standard deviation is also presented inside brackets. In addition, the conversion ratio of

Table 1. Subcooling temperature, hydrate onset time, and conversion to hydrate of each system

System	T_{eq} (°C)	T_{onset} (°C)	ΔT_{sub} (°C)	t_{onset} (min)	x_{hyd}
Water only	20.3	14.7	5.6 (±1.4)	23.2 (±2.6)	0.14
0.5 wt% PVCap	22.1	6.5	15.6 (±0.3)	72.5 (±5.3)	0.22
Decane+Water	17.3	11.6	5.7 (±0.7)	21.3 (±2.5)	0.31

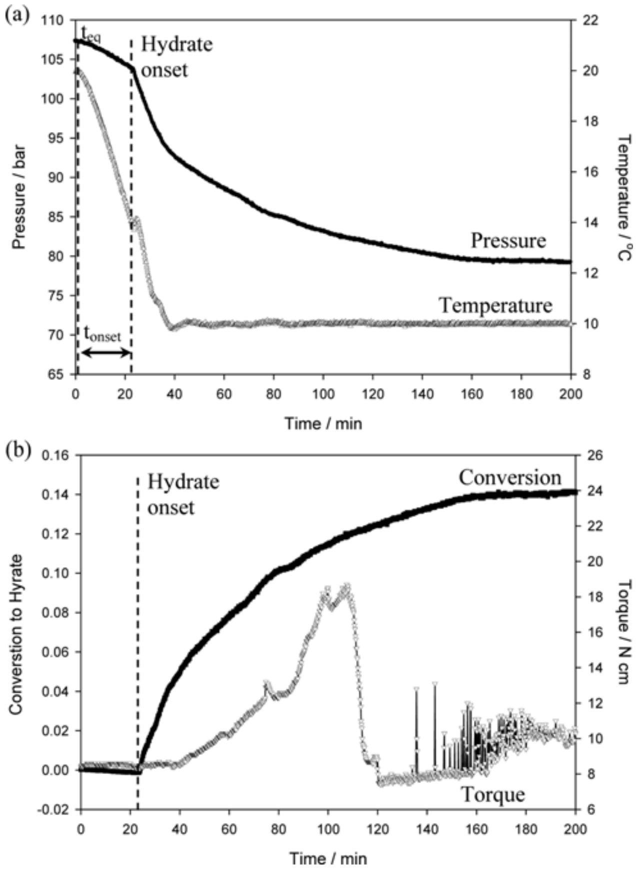

Fig. 2. Hydrate formation process in pure water. (a) Pressure and temperature profiles, and (b) conversion of water to hydrate with torque change during the constant cooling process.

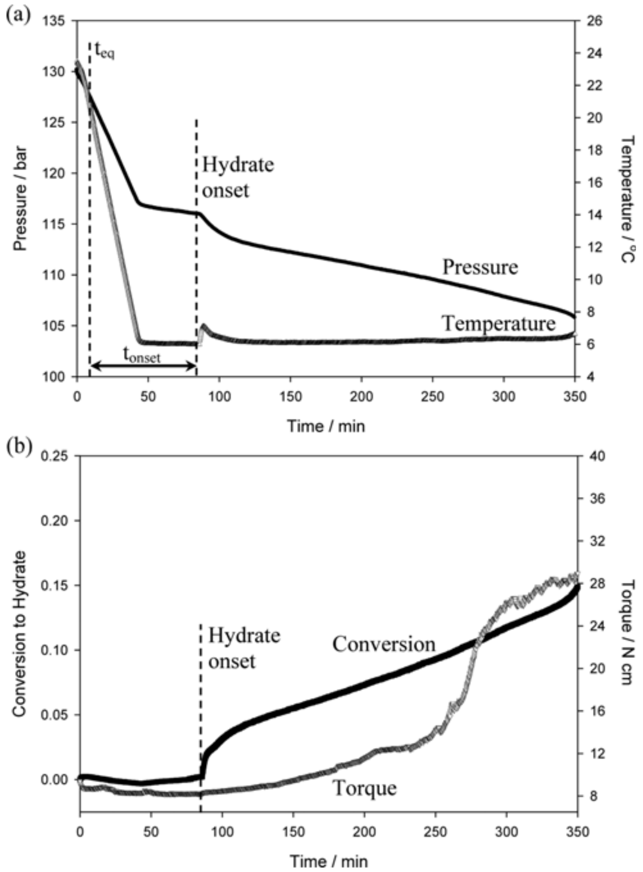

Fig. 3. Hydrate formation process in 0.5 wt% PVCap solution. (a) Pressure and temperature profiles, and (b) conversion of water to hydrate with torque change during the constant cooling process.

water to hydrate is also calculated from the consumed amount of gas with the hydration number of 6.5.

Fig. 2(a) shows typical pressure and temperature changes when hydrates form from pure water and natural gas. From the gas composition used in this study, the equilibrium temperature of hydrate is predicted to be 20.1 °C at 104 bar, but the hydrate onset appears at 14.5 °C when the pressure becomes 104 bar, resulting subcooling temperature, ΔT_{sub}, 5.6 °C and hydrate onset time 23.2 min. The standard deviation of subcooling and hydrate onset time was 1.4 °C and 2.6 min, respectively. When hydrate forms from pure water without any additives, hydrate crystals form and grow into particles. Eventually they agglomerate into bigger hydrate chunks before segregating from the aqueous phase. Fig. 2(b) shows a typical hydrate formation curve along with corresponding torque changes when hydrate forms from pure water. The conversion to hydrate indicates the amount of water converted to hydrate. It shows steep increase at the beginning, and then the growth rate decreases gradually before reaching a plateau at the final stage. The torque starts to increase 17 min after the hydrate onset when the conversion to hydrate reaches 0.05. It reaches a maximum value of 19 N cm, but reduces 10 N cm with severe fluctuation when conversion to hydrate becomes more than 0.13. This indicates that the agglomerated hydrate particles in aqueous phase become a restriction of the rotating stirrer, but once the conversion increases more than 0.13 they form a thin film on the autoclave wall or rotate together with stirrer, leading to the fluctuation of torque.

When PVCap is added to the aqueous phase, it is expected that the hydrate onset time will be delayed and the growth rate will be reduced from our previous works. Again, the hydrate onset was significantly delayed for 72.5 min and subcooling temperature was increased to 15.6 °C in the presence of 0.5 wt% PVCap as seen in Fig. 3(a). The standard deviation of hydrate onset time was 5.3 min, leading to the relative standard deviation of 7%. Fig. 3(b) shows slow increase of the conversion to hydrate at early stage of hydrate formation. It takes about two-times longer before reaching the conversion to hydrate of 0.14. This indicates that PVCap suppresses the hydrate growth as well as their nucleation [18]. For 0.5 wt% PVCap solution hydrate onset time was 72.5 min, but the significant torque change appeared about 40 min after the onset, which is twice longer than in pure water. The torque shows maximum value of 28 N cm, then the stirrer stops rotating due to restriction on the autoclave wall. We are performing more experiments to investigate the effect of adding PVCap in aqueous phase on the torque changes during hydrate formation at various concentrations of PVCap.

Fig. 4(a) shows temperature and pressure changes with time during hydrate formation for water+decane mixture. The average onset temperature was 5.7 °C and the average onset time was 21.3 min. The standard deviation of hydrate onset time was 2.5 min, leading to the relative standard deviation of 12%. The obtained results under

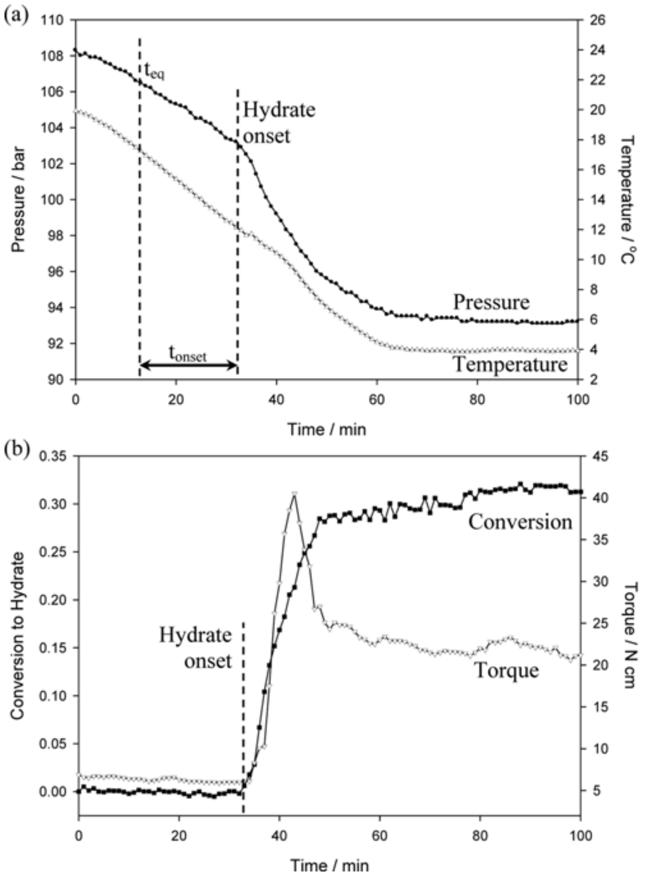

Fig. 4. Hydrate formation process in water+decane mixture. (a) Pressure and temperature profiles, and (b) conversion of water to hydrate with torque change during the constant cooling process.

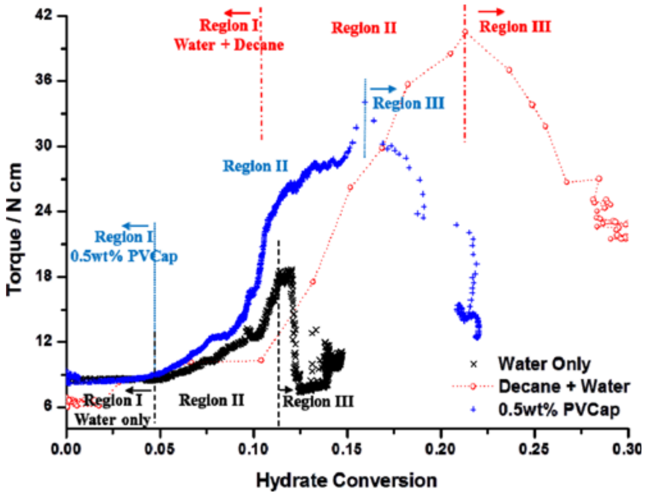

Fig. 5. Torque versus conversion to hydrate during the hydrate formation of pure water, 0.5 wt% PVCap solution, water+decane mixture.

the same conditions for pure water indicate that hydrate formation in the presence of liquid hydrocarbon, decane in this work, is very similar to that of pure water. Fig. 4(b) shows torque changes with time along with conversion to hydrate. Rapid increase of conversion to hydrate is observed in Fig. 4(b), where it takes only 20 min before reaching plateau. Hydrate onset time of water+decane mixture was 21 min and the torque increased rapidly just after the onset. There was no delayed increase of the torque that was observed in pure water and 0.5 wt% PVCap solution. Conversion to hydrate maintains stable when the torque peaks the maximum and then becomes stable at around 22 N cm. These results suggest that hydrate onset and growth is faster for water+decane mixture than in pure water, as free water droplets are well dispersed in decane phase as the volume ratio of water to decane is 0.17.

To examine the torque change by the conversion to hydrate, the torque data were plotted with the conversion to hydrate as shown in Fig. 5. Joshi et al. [19] recently reported a study on hydrate plug formation with a 4” flow loop. They classified the hydrate formation process into three different regions with the diagram of pressure difference versus conversion to hydrate: homogeneous region, heterogeneous segregation region, and plug with stationary bed region, respectively. For the studied systems in this work, the above three regions can be found in Fig. 5. For pure water, the first region is from the hydrate onset to where the torque started to increase. The torque did not change from the hydrate onset to the conversion of 0.05, considering that the hydrate particles are homogeneously dispersed in the water (region I). After the conversion value of 0.05, the torque started to rise gradually until the conversion of 0.10, then it shows fast growth from the conversion of 0.10 to 0.12, implying that the hydrate phase starts to be segregated from water phase (region II). The torque drastically fell just after the conversion of 0.12 and kept fluctuating as hydrate particles seemed to deposit on the wall (region III). In the case of PVCap solution, the first transition from region I to II is 0.05, and the maximum torque appears at the conversion of 0.15, leading to region III. Overall trend of the torque change for PVCap solution is similar to pure water, indicating that there is no significant effect of PVCap on torque change during the hydrate formation. It is envisaged that PVCap only suppresses the growth of hydrate crystals, resulting in slowed conversion to hydrate rather than working on agglomeration of hydrate particles. For water +decane mixture, the torque becomes slightly higher upon hydrate onset (region I) and rapidly increases to the maximum value of 40 N cm. This fast increase of the torque since the conversion of 0.10 indicates that fast segregation of hydrate particles happens (region II). When the conversion approaches 0.21, the torque decreases and maintains at around 22 N·cm (region III). Note that decane is the continuous phase and thus the stirrer stoppage would be caused by the growth and deposition of hydrate particles on the wall.

We visually observed the hydrate onset and growth period through the optical camera in order to understand the difference between the pure water and water+decane mixture. Fig. 6 shows snapshots of pure water and water+decane mixture taken during the hydrate formation process. Stirring with magnet spin bar was stopped temporarily while taking snapshots. For pure water (Fig. 6(a), top) hydrate forms and grows as sphere-shaped particles at 8 min after the onset (Fig. 6(b)), and then start to be agglomerated with each other before forming slush-like liquid phase, as seen in the picture taken at 300 min after the onset. In contrast, for water+decane mixture (Fig. 6(a), bottom) hydrate forms in free water droplets suspended in decane phase, then deposition of hydrate-containing water droplets happens on the wall as seen in the picture taken at 2 min after the onset. The

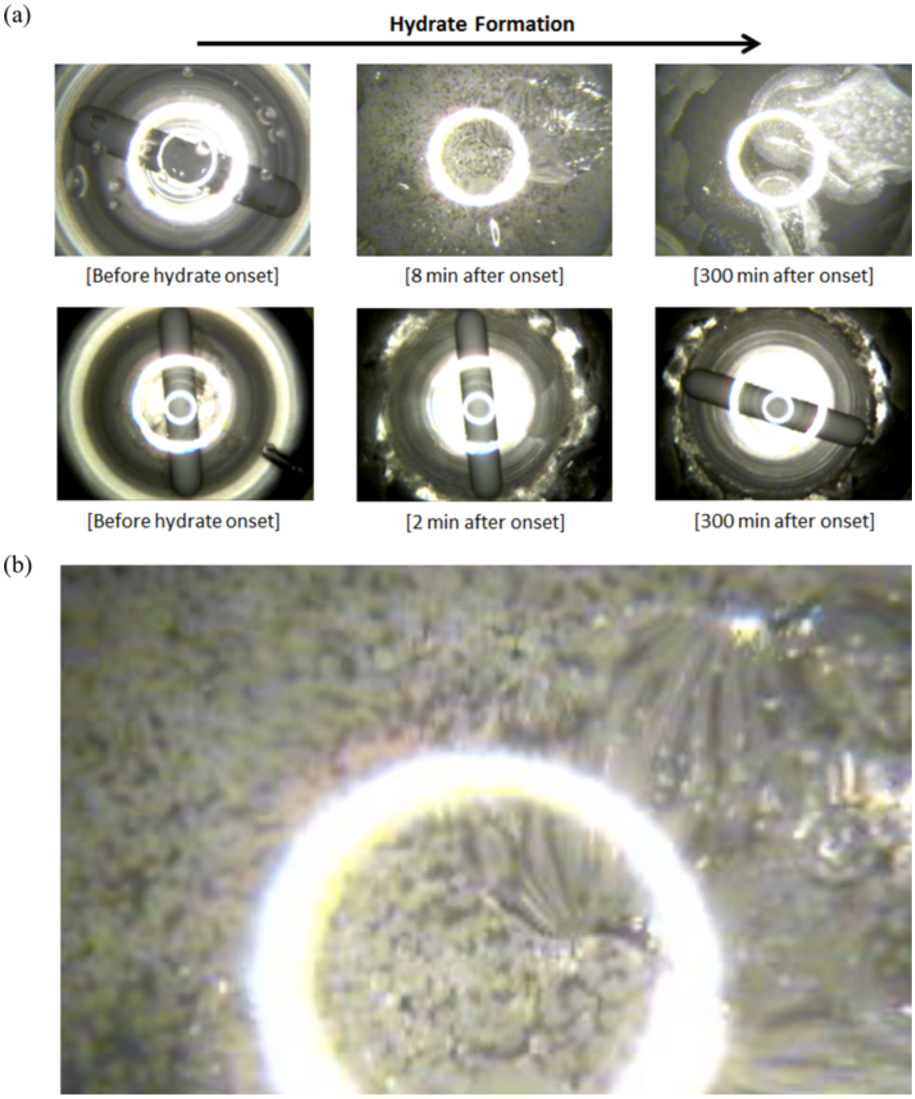

Fig. 6. The snapshots of visually observed hydrate formation process: pure water (Top) and water+decane mixture (bottom), (b) Images of hydrate particles 8 min after hydrate onset in pure water.

thickness of the deposition on wall slowly increases as hydrate formation proceeds. These images confirmed that the hydrate deposition on the wall is quite susceptible when hydrates form on water droplets dispersed in liquid decane phase.

From this observation, it can be considered that the different torque change trends in Fig. 5 are due to different nature of hydrate growth and deposition. For pure water, hydrate particles are formed and suspended in aqueous phase and torque change is affected by heterogeneous segregation of hydrate particles, which are still flowable while mixing. However, for decane+water mixture, hydrates form on the already suspended water droplets in decane phase and torque change is mainly affected by the deposition of hydrate particles. The deposited hydrate particles seem to be sticky and unmovable, resulting in high torque value of the rotating impeller. According to previous works [12,20-22], the adhesion force between hydrate and surface material becomes stronger than the force between hydrate particles when hydrate forms in water droplets on surface material such as stainless steel. The obtained results in this work agree well with the previous works and suggest that the torque measurement can be one of the options to study the formation process of hydrates in different liquid systems. However, more experimental data and a plausible model to describe the hydrate formation process are required to quantify the effect of flow parameters such as water-cut and flow speed. Further experiments and modeling works are on-going in the laboratory.

CONCLUSION

The hydrate formation process for three different systems--pure water, PVCap solution, water+decane mixture--was investigated by monitoring the torque while stirring the fluids inside an autoclave. The torque changes with time for pure water showed that the hydrate formation process could be classified into three different regions and the result was agreeable with the previous study with flow loop. PVCap solution showed a similar pattern of torque changes over hydrate conversion to pure water, where the torque increases due to heterogeneous segregation of hydrate particles from aqueous phase. The growth rate of hydrates was reduced due to suppressing effect of PVCap. On the other hand, for water+decane mixture, segregation and subsequent deposition of hydrate particles result in rapid increase of torque. This result implies that flow parameters such as water cut and flow regime would be important factors to understand the segregation and deposition of hydrate particles in offshore flowlines.

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