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Morphological Studies of Mixed Methane Tetrahydrofuran Hydrates in Saline Water for Energy Storage Application

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Abstract

Solidified natural gas (SNG) in the form of clathrate hydrates has been considered one of the most promising technologies for natural gas storage and transportation because it is safe and economically feasible compared to liquefied natural gas (LNG) and compressed natural gas (CNG). In this direction, we recently observed that mixed methane tetrahydrofuran hydrates had the ability to store a significant amount of methane gas close to ambient temperature conditions. To further improve the economic feasibility of methane gas storage and transportation process, utilization of saline water was recommended. In the present work, we investigate the morphology of mixed CH₄/THF hydrate formation and dissociation in presence of NaCl for the first time. Morphology changes observed during the nucleation, hydrate growth and dissociation of mixed hydrates at two different operating conditions are presented. All the experiments were performed with a stoichiometric concentration of THF (5.56 mol% THF). More over, the gas uptake was also measured and compared with non-salt experiments.

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1. Introduction

The global energy consumption is increasing rapidly and challenging the energy market to satisfy the rising demand. In this direction, natural gas (NG) has been one of the suitable energy sources that can offer high energy density with

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low carbon dioxide emissions compared to gasoline, diesel and other fossil fuels. However, the efficient storage and transportation of NG in a cost effective mode is necessary to cater the growing energy market. Present conventional approaches include pipelines, compressed natural gas (CNG), or liquefied natural gas (LNG) (Gudmundsson et al., 1994; Veluswamy et al., 2016a; Kromah et al., 2003). Regardless of the high energy density of LNG, high pressure (25 MPa at 25 °C) or low temperature (−162 °C at 0.1 MPa) makes the technology undesirable (Casco et al., 2015) for long term storage. Solidified natural gas (SNG) in the form of clathrate hydrates has been considered one of the promising options to store natural gas because it is safe, environment-friendly and economically feasible in comparison to conventional technologies. Clathrate hydrates or gas hydrates are non-stoichiometric crystalline compounds that mimic ice in appearance, formed by water and guest molecules. Guests can be either gas (methane, ethane, carbon Dioxide etc.) or liquid (Tetrahydrofuran, THF; Cyclopentane (CP) etc.) (Sloan and Koh, 2008, Sloan, 2003).

At present, state of the art of SNG technology is dominated by Japanese and Korean activities (Mitsui Engineering & Shipbuilding (MES) along with the operation of demonstration plants with a capacity 600 kg of methane hydrate per day at Chiba and 5000 kg of methane hydrate per day at Yanai power station (Rehder et al., 2012). However, commercialization of the SNG technology was not possible mainly due to challenges in kinetics associated with hydrate formation and the storage of synthesized hydrate pellets at moderate temperature conditions. Recently, it has been reported that THF performed both as a kinetic and thermodynamic promoter for methane hydrate formation and improved the hydrate stability significantly demonstrating the ability to store hydrate pellets at moderate temperatures (−5 to 0 °C) under atmospheric pressure (Veluswamy et al., 2016a, 2016b). Further studies by Kumar et al. (2016a, 2016b) have also supported the rapid production of mixed CH₄/THF hydrate and validated the two-step mechanism of mixed hydrates due to the synergistic effect between CH₄ and THF. The stoichiometric amount of THF (5.56 mol% THF) along with methane forms sII hydrates where large cages are occupied by THF molecules and the small cages are occupied by CH₄ molecules that improve the thermodynamic stability of mixed CH₄/THF sII hydrates significantly compared to pure sI methane hydrates (Kumar et al., 2016; Wu et al., 2016; Seo et al., 2003).

Further, to improve the economic feasibility of SNG technology, it is suggested to substitute the pure water with seawater during hydrate formation. This may enable the commercial realization of the SNG technology with minimal cost. Recently Kumar et al. (2017) reported the hydrate phase equilibrium data of mixed methane-tetrahydrofuran hydrates in saline water (in presence of NaCl). They concluded that mixed CH₄/THF hydrates are very stable even in presence of salt compared to pure methane hydrates showcasing the potential to utilize seawater for SNG technology (Kumar et al., 2017). However, a detailed study of mixed CH₄/THF hydrate formation kinetics along with morphological understanding is required to capitalize on the benefits of using salt water for hydrate formation vide SNG technology. Thus, in the present work, the morphology of mixed CH₄/THF hydrate formation and dissociation in presence of NaCl (THF/ NaCl/Water=5.50/1.1/93.40 mol%) was investigated. Morphology changes observed during the nucleation, hydrate growth and dissociation of mixed hydrates at two starting pressures of 3.0 MPa and 5.0 MPa at 283.15 K are presented. More over, the gas uptake was also measured and compared with binary THF-water system (THF/Water=5.56/94.44 mol%).

2. Experimental Section

The CH₄ gas cylinder of 99.8% purity was purchased from Air Liquide Singapore Pte Ltd. Tetrahydrofuran (THF) of 99.7% purity was obtained from Fisher Chemicals, while NaCl (purity ≥ 99%) was provided by Sigma-Aldrich. Salt water was synthesized artificially by dissolving the calculated amount of NaCl in deionized water (obtained from Elga micromeg deionization apparatus). Experimental setup used was similar to that detailed in Veluswamy et al. (2016a). However, instead of an acrylic column, sapphire column reactor with an inner dia. of 3 cm was used for better clarity of images and to withstand higher experimental pressures. Further, a glass vial of outer diameter 2.23cm (14.74 ml volume) containing the experimental solution was placed inside the sapphire column in order to have better visualization of the formation/dissociation of hydrates. A known volume of experimental solution (4ml) was pipetted into a glass vial. The sapphire column reactor was placed in a water bath which is connected to Polyscience SD15R external refrigerator (ER) through inlet and outlet pipes to maintain the desired reactor temperature. All experiments performed were of the batch type, in a quiescent/unstirred reactor configuration. The reactor pressure was measured using a Rosemount 3051 Pressure Transmitter (PT) supplied by Emerson Proces Management, having an uncertainty of 0.1% and the pressure range of 0–20 MPa. Reactor Temperature was measured by a copper constantan T type thermocouple provided by Omega (uncertainty of 0.1 K). Data Acquisition (DAQ) system supplied by National

Instruments was used to record the temperature and pressure data for every 20 s throughout the experiment. All morphological formation images were captured for every 10 s thorough out the experiment with the help of a microscope. Before pressurizing the system, we purged the sapphire column with methane for few times and then pressurized up to desired pressure.

3. Results and Discussion

Figure 1 presents the gas uptake data along with morphological changes observed during the formation of mixed methane tetrahydrofuran hydrate in a ternary solution of THF/NaCl/Water at 5.0 MPa pressure of methane and 283.15 K temperature. The experimental conditions chosen can result in the formation of structure II hydrates only (Kumar et al., 2017). To effectively understand the hydrate growth, we map the morphology observations to the kinetic data in which each of the morphology images corresponds to a red dot in the gas uptake plot.

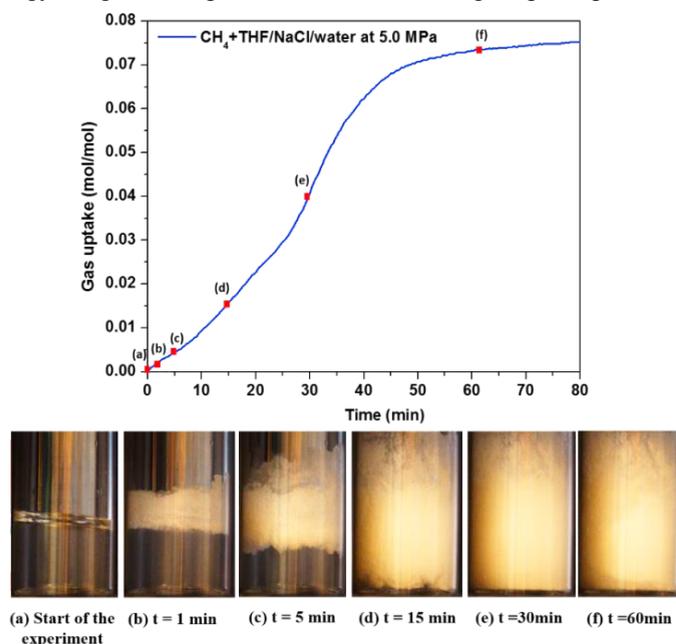


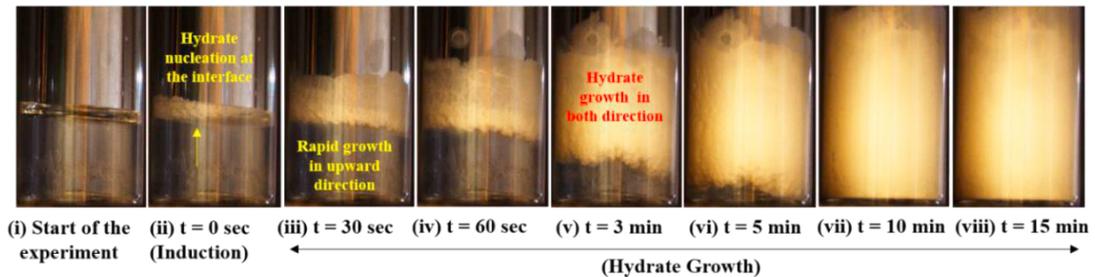
Figure. 1. Gas uptake curve along with morphological images of mixed methane hydrate in a ternary solution of THF/NaCl/ Water (5.50/1.1/93.40 mol%) at 5.0 MPa and 283.15 K. Time zero in the gas uptake curve designates the nucleation point.

As can be seen in figure 1, the morphology images (1a-1d) show extensive hydrate formation in the first 15 min but gas uptake is very less (about 0.01 mol of gas/mol of water). Recently, Veluswamy et al., (2016) have also presented similar kinetic and morphological observations with a binary solution of THF/Water and proposed a two-step mechanism of mixed hydrate formation in presence of stoichiometric THF concentration to explain this behaviour. Further, Kumar et al. (2017) have also validated this mechanism by the synergism of CH₄ and THF. The most characteristic observation during mixed hydrate formation in the presence of salt water is the predominant hydrate growth during the initial stage (after nucleation till about 5 min) which is in an upward direction towards the gas phase rather than downward direction (in the bulk solution). After 15 min of hydrate formation, the hydrate crystals touch the bottom of the vial and cover the entire vial after which considerable methane gas uptake is observed. Formation of the hollow crater was another probable reason attributing to the increased methane uptake after 15 min, as elucidated in the previous study by Veluswamy et al. (2016a).

In order to contrast the morphology differences during the formation of mixed CH₄/THF hydrates, we present the morphology observation carried out using pure deionized water and salt water in figure 2. Figure 2 presents the comparison of morphology images captured during the hydrate formation in a binary THF/Water solution (A) and ternary THF/NaCl/Water solution (B) at the experimental conditions of 5.0 MPa and 283.15 K. From this figure, we observe that both these systems show rapid hydrate formation and fill the glass vial with hydrates in just 15 min after nucleation. From figure 2A and 2B, the hydrate nucleation occurred at the gas/liquid interface in both the systems

(image ii) and the following hydrate growth was in the upward direction (image iii). Further, the hydrate growth at 1 min from nucleation shows that distinct channels exist for pure water system whereas no such distinct channels were observed in the presence of salt. After 5 min, the hydrate touched the bottom of glass vial surface for pure water system. However, in presence of salt [THF/NaCl/water system (B)] the hydrate growth was slow compared to (A). It can be clearly seen that the hydrate formation completely touched the bottom surface of glass vial only after 15 min (B). Further, hydrate growth in upward direction was only observed till 3 min (image v) following which hydrates started growing within the bulk solution. This delay in the hydrate growth is attributed to the presence of salt that inhibits the hydrate growth slightly and thus resulting in lower rate of hydrate formation in salt water in comparison to that of fresh water.

(A) CH₄+THF/water at 5.0 MPa



(B) CH₄+THF/NaCl/water at 5.0 MPa

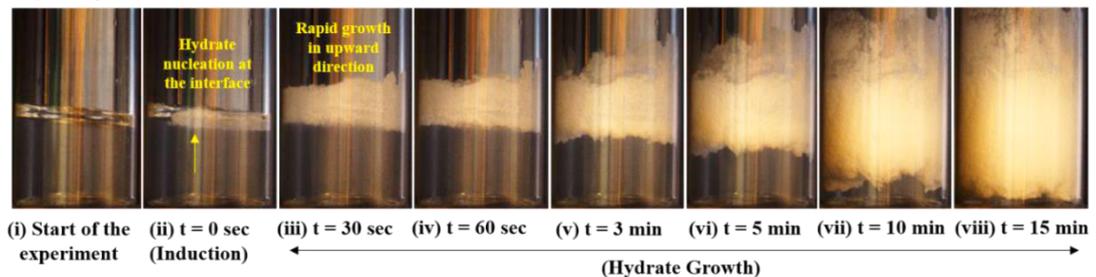


Figure 2. Comparison of the morphology images obtained during mixed methane hydrate formation in a binary solution of THF/Water (5.56/94.40 mol%) and ternary solution THF/NaCl/Water (5.50/1.1/93.40 mol%) at 5.0 MPa and 283.15 K.

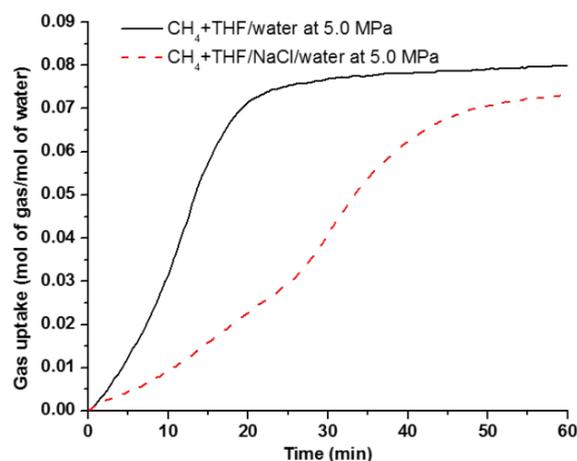
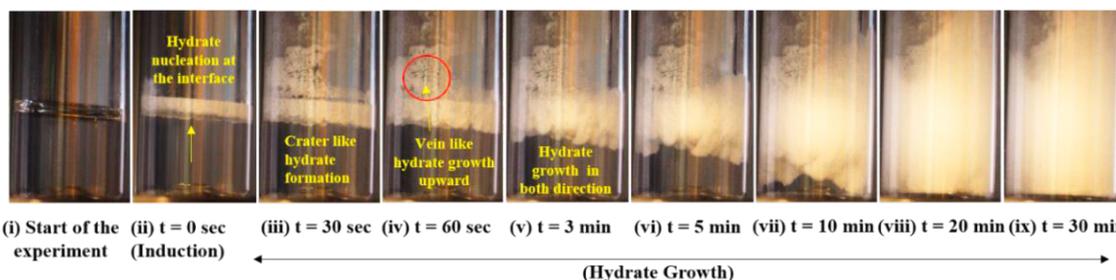


Figure 3. Comparison of gas uptake during mixed methane hydrate formation in a binary solution of THF/Water (5.56/94.40 mol%) and ternary solution THF/NaCl/Water (5.50/1.1/93.40 mol%) at 5.0 MPa and 283.15 K. Time zero in the graph designates the nucleation point.

Figure 3 presents the gas uptake curves for one trial of experiment conducted in a binary solution of THF/Water (5.56/94.40 mol%) and ternary solution THF/NaCl/Water (5.50/1.1/93.40 mol%) at the experimental conditions of 5.0 MPa and 283.15 K. The final gas uptake at 5 MPa was found approximately similar in both the solutions (around

70 mmol gas/mol of water after 60 min). Next, we performed hydrate formation experiments at 3.0 MPa and 283.15 K with a binary solution of THF/Water (5.56/94.40 mol%) and ternary solution THF/NaCl/Water (5.50/1.1/93.40 mol%). Conduction of experiments at 3 MPa infers a lower driving force of hydrate formation ($\Delta P \approx -2.55$ MPa) in comparison to that available at 5.0 MPa ($\Delta P \approx -4.55$ MPa). Figure 4A and 4B presents a series of morphology observations with binary solution of THF/Water and ternary solution THF/NaCl/Water, respectively. As can be seen in morphological images, similar to that observed at 5.0 MPa (higher driving force), the nucleation event with hydrates started first along the gas–liquid interface for both systems at 3.0 MPa.

(A) CH₄+THF/water at 3.0 MPa



(B) CH₄+THF/NaCl/water at 3.0 MPa

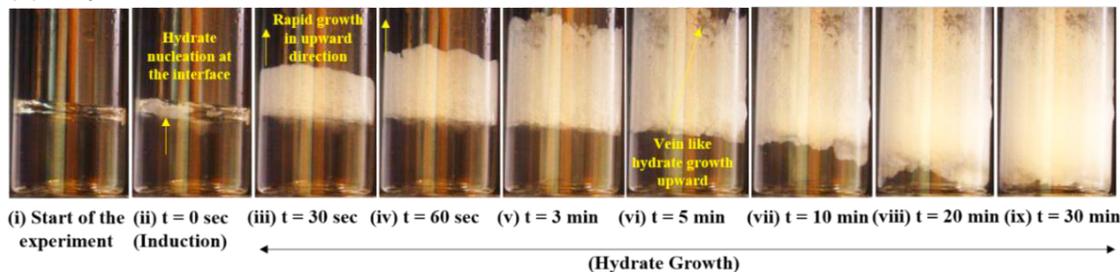


Figure. 4. Comparison of the morphology images obtained during mixed methane hydrate formation in a binary solution of THF/Water (5.56/94.40 mol%) and ternary solution THF/ NaCl/Water (5.50/1.1/93.40 mol%) at 3.0 MPa and 283.15 K.

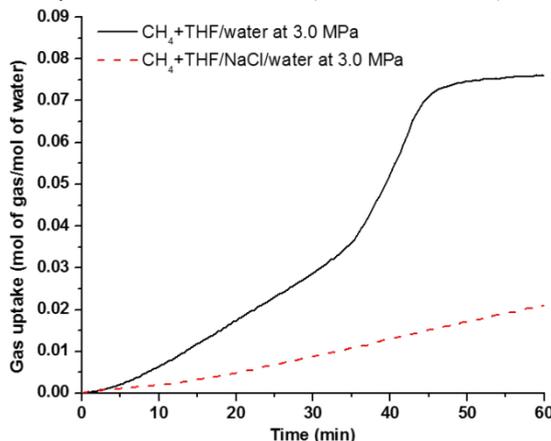


Figure.5. Comparison of gas uptake during the mixed methane hydrate formation in a binary solution of THF/Water (5.56/94.40 mol%) and ternary solution THF/NaCl/Water (5.50/1.1/93.40 mol%) at 3.0 MPa and 283.15 K. Time zero in the graph designates the nucleation point.

At 3.0 MPa, for THF/NaCl/Water solution, hydrates were observed to be significant along the walls of glass vial upward direction above the gas liquid interface (image iii). The pace of the upward growth at 3.0 MPa (lower driving force) was higher than that observed at 5.0 MPa. However, in THF/water solution upward growth is less (vein like growth, images iii-v) and crater like hydrate growth was observed as the hydrates predominantly grew in downward direction (images iv-vi). It was observed that only after 10 min, growth of hydrates into the bulk solution is observed

which cover the entire bulk solution of THF/water in comparison to salts for experiments performed at 3.0 MPa. For the experiments in presence of salt, the hydrates were observed to cover the bottom of the vial only after 30 min at 3.0 MPa. Thus, it is evident that rate of hydrate growth is relatively slow in THF/NaCl/water solution compared to that of THF/water solution. Figure 5 presents the gas uptake curves for one trial of experiment conducted in a binary solution of THF/Water (5.56/94.40 mol%) and ternary solution THF/NaCl/Water (5.50/1.1/93.40 mol%) at the experimental conditions of 3.0 MPa and 283.15 K. As can be seen in figure 5, in the presence of salt, the kinetics of hydrate formation is slow but effect is more severe at 3.0 MPa as compared to 5.0 MPa. But at 3.0 MPa, it is significantly lower compared to no-salt system (reduction of 72.36%). This infers that the kinetics of mixed hydrate formation is significantly affected in presence of salt.

4. Conclusion

SNG technology holds a significant promise for natural gas storage and transportation in the form of clathrate hydrate. Observation of morphology of mixed hydrate formation using ternary solution THF/NaCl/Water at the experimental conditions of 5.0 and 3.0 MPa and 283.15 K was attempted for the first time. Though the salt has the potential to inhibit the hydrate formation, there is no significant drop in methane uptake (gas storage) capacity at moderate pressure of 5.0 MPa and 283.15 K. This study highlights the option to use sea water for mixed methane hydrate formation that can cater to the commercial deployment of SNG technology for stationary natural gas storage applications.

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