



The 8th International Conference on Applied Energy – ICAE2016

Molecular Dynamics Simulation and Experimental Study on the Growth of Methane Hydrate in Presence of Methanol and Sodium Chloride

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Abstract

The plugging of processing and transportation lines by gas hydrate formation is a challenging problem for safe exploitation of oil and gas. The existence of water soluble third component (like methanol and sodium chloride) in the aqueous phase influence the gas hydrate formation thermodynamically also possibly affects the kinetics of hydrate growth. Inorganic salt and organic molecule (alcohols) at high concentration in the aqueous phase have been used as thermodynamic inhibitors to effectively prevent the hydrate formation. This study utilizes molecular dynamics as well as an experimental method to investigate the mechanism of the hydrate formation and the effect of additives. The MD simulation showed that at moderate temperature and pressure, a low concentration (1 wt %) of methanol and NaCl enhances methane hydrate growth kinetics. Significant numbers of methanol molecules were observed inside the gas hydrate cages whereas Na⁺/Cl⁻ ions leach out during hydrate formation.

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Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.

Keywords: Gas Hydrates; Experiments; Molecular Dynamics Simulation; Methanol; Sodium Chloride.

1. Introduction

The Clathrate hydrates or gas hydrates have potential applications in gas storage and transportation, clean energy production, water desalination, deep sea carbon dioxide sequestration, gas separation and

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purification.[1–5] Gas hydrate forms through proper coordination of guest-host molecule mostly due to the hydrophobic interaction between the guest (methane, ethane, etc.) and the host (water) molecules.[2,6,7] The requirement of low temperature and high pressure for hydrate formation is frequently encountered in oil and gas production and transportation pipelines. The growth of unwanted hydrates in the pipelines may lead to partial or complete blockage of processing pipelines, thus resulting in the safety hazards which may result in significant financial losses.[3,8–11] Therefore, the flow assurance protocol requires prevention of the gas hydrate formation by introducing a suitable amount of thermodynamic inhibitors like methanol and ethylene glycol in flow stream (as high as 40 %). These thermodynamic inhibitors prevent hydrate formation by shifting the phase boundary and thus making it impossible for gas hydrate crystals to nucleate and grow at a particular temperature and pressure condition. [3,12] However a recent study suggests that these thermodynamic inhibitors may affect the kinetics of hydrate growth at low dosage and specific temperature and pressure conditions. [11,13–17]

McLaurin et al. 2014 showed the catalyzing effect of the small concentrations of methanol (and other additives) on gas hydrate formation kinetics at sub-freezing temperatures and moderate to high pressures.[17] Further, it is likely that due to mass transfer limitation at large scale these results may vary when compared to the small experimental setup being used by McLaurin et al. 2014. Additionally, an interesting phenomenon revealed that alcohols (like methanol) and other functional water-soluble compounds may also act as a guest and participate inside cages during clathration of the help gas. Small molecules similar to methanol, may potentially occupy the hydrate cages if the nearby cages are stabilized by hydrophobic gasses like methane.[2,12,17] Hence, the size and nature of additive molecules, the extent of their hydrophobic or hydrophilic interactions with host molecules, the concentration, temperature and pressure conditions are determining factors for the final outcome.

In the present investigation, we report a detailed and comparative MD simulations as well as experimental studies on the formation of methane hydrates in sodium chloride and methanol solutions at various concentrations.

2. Computational details and simulation procedure

The three-component systems comprised of additive, methane and water was used in MD simulation such that all components have a random distribution in entire simulation box. NaCl (contains Na^+ and Cl^- ion) and methanol were used as additive. Three independent systems were prepared so that the first (NaCl) and second (methanol) system contain 1 % weight fraction (with respect to water) of NaCl and methanol respectively. Third system (Pure water) contains no additive and it is used as datum system. Total 11000 water molecule was used for each system. The number of methane was 650, which were above solubility limit. [7] To overcome the time lag of initial nucleation, one seed supercell (perfect methane hydrate crystal) comprising two unit cell ($2 \times 1 \times 1$) of methane hydrate was inserted in the system.[7,18,19] MD simulation was done using single precision GROMACS (version 4.6.3) software package.[20] Rigid TIP4P/Ice water model was used for water.[21] While for methane united atom model was used. [22] Methanol and NaCl potential parameter were taken from OPLS all-atom force field database.[23,24] Computational detail and simulation procedure were similar to the one reported in our previous work. [7] NPT simulation at 270.0 K and 10.0 MPa was performed for each system. [7]

3. Experimental details and procedure

Materials, methods and apparatus: Methane gas having a purity of 99.95 % was supplied by Vadilal Gases Pvt. Ltd., India. HPLC grade methanol, RANKEM, India and sodium chloride extrapure, 99.5 %

purity, S.D. fine-chemicals Ltd., India were used without any further treatment. Double deionized water was used to conduct all the experiments. The apparatus consists of a 250 cm³ SS-316 stirred crystallizer (CR) fitted with a stirrer. It was connected to a temperature-controlled external refrigerator (ER) (Julabo F34). A pressure transducer (Wika, range 0–16 MPa) and a temperature detector (RTD, Pt-100) were employed for data acquisition during hydrate formation. Hydrate formation experiments were conducted in batch mode under stirred condition (400 rpm) with a fixed amount of water (80 cm³). The pressure drop data and the temperature inside the reactor were acquired by the system (Micro Technics; every 5s) coupled with a computer. Details about the position of safety valve, vent, supply vessel, data acquisition unit etc. are as shown in Figure 1. CR was purged with methane gas multiple times before final pressurization at 274.15 K. All the experiments are repeated multiple times to calculate the standard error; the mole consumption plots are provided with standard error bar. The plots showing moles of consumption of methane gas per mole of water are average of the best three experimental runs.

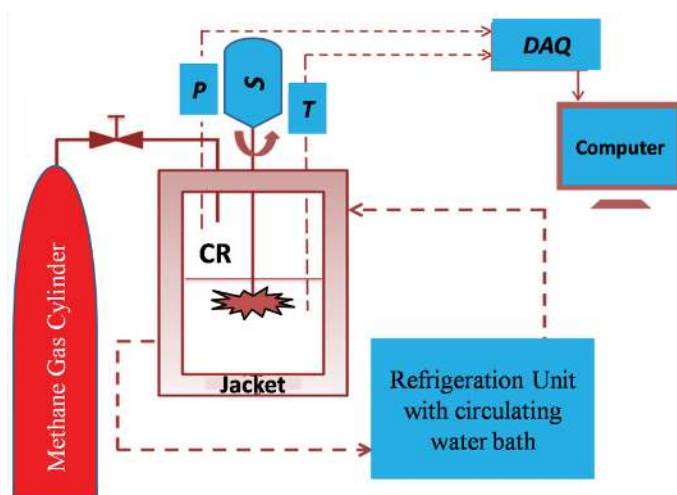


Fig. 1. Schematic of a stirred tank reactor used for methane hydrate formation. Where P is Pressure Transducer; CR is Crystallizer; DAQ is Data Acquisition System; S is Stirrer and T is Thermocouple.

Hydrate formation: A fixed quantity of deionized water (80 cm³) and/or additives 1 wt % NaCl and 1 wt % methanol are used in the crystallizer (CR). On reaching an experimental temperature of the CR (274.15 K), it is pressurized by the methane gas to a pre-determined experimental pressure (6 MPa). Gas uptake measurements were initiated at this stage (274.15 K gas uptake measurements were carried out in batch mode and the drop in the reactor pressure was used to calculate the gas consumption during hydrate formation). Calculation of the amount of gas consumed during hydrate formation was done using Pitzer's correlation. [7,25] The total number of moles of gas that was consumed in the hydrate formation process at any given time is the difference between the number of moles of gas present in the gas phase of the CR at time $t = 0$. The number of moles of gas present in the gas phase of the CR at time $t = t$. The same is given by the following equation:[26]

$$(\Delta n_{H,\downarrow})_t = V_{CR} \left[\frac{P}{zRT} \right]_0 - V_{CR} \left[\frac{P}{zRT} \right]_t \quad (1)$$

Where z is the compressibility factor calculated by using Pitzer's correlation [25], VCR is the volume of the gas phase inside the crystallizer and P and T are the pressure and temperature of the crystallizer respectively.

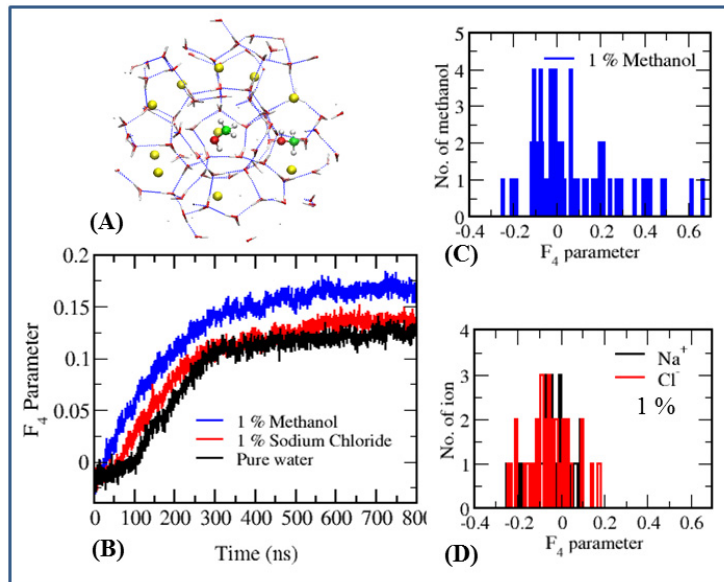


Fig. 2. (A) Showing methanol trapped inside the cage; yellow is methane; ball and stick model is methanol; red line model is water and water molecule connected by hydrogen bonding (shown in blue line) (B) F_4 parameter of water for all systems during simulation. (C) and (D) are an F_4 parameter of water around methanol and NaCl ions respectively for only water molecules those come under 0.6 nm from each additive molecule at the end of the simulation.

4. Molecular dynamics simulation results

All three systems were subjected to multiple independent runs. Four body structural order parameter (F_4) of whole system water molecule was calculated as shown Figure 2(B).[27] It was observed that both the systems with additives show higher growth rate compared to the pure water system. Among all the systems, the highest growth rate was observed with 1 wt% methanol-water mixture. Further, F_4 parameter of water molecules in proximity with additive molecules (under 0.6 nm) was calculated for identifying the presence of additives trapped inside the cages. F_4 parameter higher than 0.2 signifies that additive molecule is present inside the hydrate cages or probably it adsorbed at the hydrate-amorphous water interface; while lower F_4 parameter suggests the presence of amorphous water around additives (no solid crystals). Figure 2 (C, D), shows that many methanol molecules have higher F_4 parameter in comparison with NaCl ions. As shown in Figure 2(A) shows one of the identified methanol molecules which trapped in the large cages of resulting SI hydrate. The NaCl system does not show such observation and at no instance, NaCl ions were found close to host water. It can be said that NaCl ions tend to leach out during crystallization. Figure 3 shows the snapshot of additive systems at the end of the simulation. The overall MD results suggest faster hydrate growth kinetics in presence of 1wt% methanol in the system, while no significant difference in hydrate growth kinetics was observed with 1wt% NaCl compared to the pure water system.

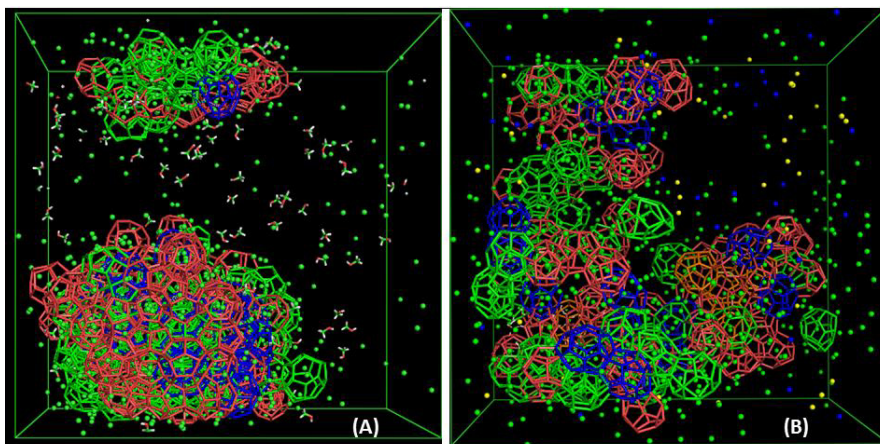


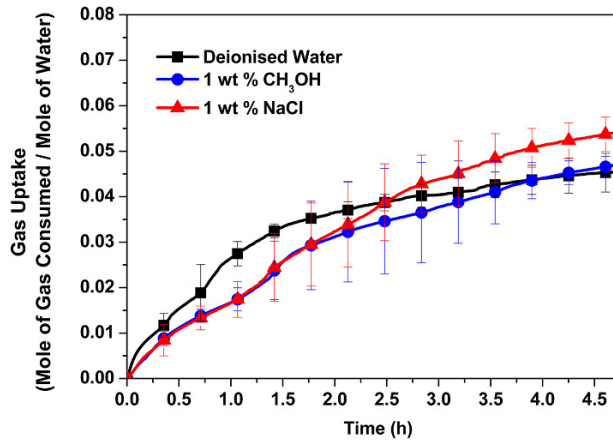
Fig. 3. Snapshots at the end of the simulation; (A) 1 % methanol system and (B) 1 % NaCl system. Component representation: Methanol is in stick model, methane is a green sphere, sodium is a blue sphere, chloride is a yellow sphere and water is hidden. Cage representation: Red is 5^{12} cages, green are $5^{12}6^2$ cages and blue are $5^{12}6^3$ cages.

5. Experimental results

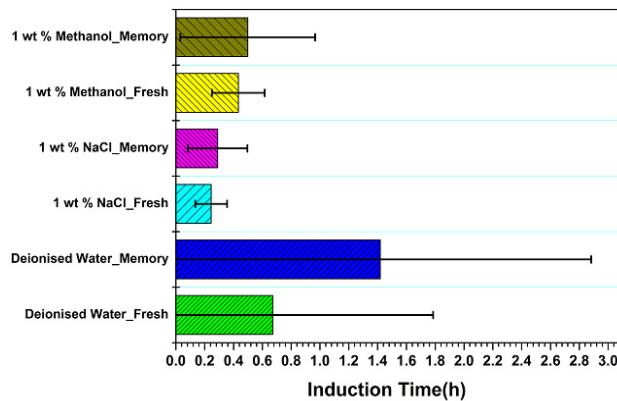
The experimental observations of methane hydrate formation and induction time are shown in Figure 4. Figure 4(A) shows the comparative hydrate growth (immediately after hydrate nucleation) under stirred condition and above freezing temperature using three systems; 1 wt % NaCl, 1 wt % methanol, and deionized water. The methane gas consumption experiments are carried out in order to have better understanding and comparison with the molecular dynamics simulation experiments during methane hydrate formation. The gas uptake calculations (moles of consumption of methane gas per mole of water) are shown with the initiation of the gas hydrate nucleation. The time zero in the graph corresponds to the first nucleation point. The temperature and initial pressure were fixed at 274.15 K and 6.0 MPa. Figure 4(a) reveals that there is no significant difference in the initial rates of hydrate growth during the formation of methane hydrates. All the three systems showed the formation of methane hydrates with water having highest formation rate up to 2.5 hours after nucleation when sodium chloride surpassed it. Hydrate growth is found to exceed in the case of sodium chloride than pure water after 2.5 hours of nucleation. Sodium chloride and methanol systems showed similar rates initially but a notable difference is observed after 1.5 h of nucleation with sodium chloride showing better growth kinetics compared to methanol. Similarly, methanol system showed enhanced formation after 4.25 h with methanol showing better growth kinetics compared to pure water. The experimental results support the observations made from molecular dynamics simulation studies that additives such as methanol and sodium chloride can also act as kinetic hydrate promoters when used in small concentrations. The increased hydrate growth in the presence of thermodynamic inhibitors may be explained on the basis of i) solubility of hydrate forming gasses, ii) change in interfacial tension iii) change in hydrate morphology.

Figure 4(B) shows the induction time of all the three systems with fresh and memory runs. It is evident that the induction time decreased when sodium chloride and methanol are incorporated; the sodium chloride having a more pronounced effect. The reduced induction time may be attributed to the rapid dissolution of the methane molecules and their interaction with the locally available water molecules at

low concentrations. It is well known that sodium chloride when dissolved in water dissociated into sodium and chlorine ions. Upon hydration, these ions keep a lot of water molecules engaged. Therefore, the gas to free water molecule ratio may increase drastically at the local level and hence lead to the reduced induction times. Similarly, reduced induction times are evidenced in the case of methanol system which may also be attributed to the small size of methane molecules and the increased gas to free water molecule ratio in the local environment. More induction time is evident in methanol system compared to the sodium chloride which may be attributed to the strong hydrogen bonding between methanol-methanol, methanol-water and methanol-water-methanol molecules which may affect the mobility as well as the availability of the free water molecules in the local environment.



(a)



(b)

Fig. 4. Experimental results showing (a) moles of methane gas consumption per moles of water for hydrate growth measured for pure water, 1 wt % concentration of NaCl and 1 wt % concentration of methanol in a stirred tank reactor and (b) the induction time. Time zero in the graph corresponds to the nucleation point.

6. Conclusions

We have investigated the effect of low concentrations of thermodynamic inhibitors (1wt %) on the formation kinetics of methane hydrate in aqueous sodium chloride and methanol solutions through molecular dynamics simulations and its validation by experimental gas uptake laboratory measurements. In MD simulation, it was observed that in presence of 1wt% thermodynamic additives the kinetics of hydrate growth was better compared to growth from pure water. Methanol shows slightly higher kinetics compared to other two systems. It was also identified that a very small amount of methanol may occupy the hydrate cages and possibly promotes hydrate growth at low concentration. NaCl, however, leach out into liquid phase upon crystallization of hydrate crystals. During experiments, initially, a faster kinetics of hydrate formation was observed in pure water than 1 wt % NaCl and 1 wt % methanol systems but only after 2.5 h the kinetics of hydrate formation in NaCl system surpassed to that of water and methanol systems. A similar but slower observation was found in the case of methanol system when compared to the pure water system. Overall, from experimental results, it may be concluded that the MD simulation calculations of the three systems provided a comparable projection of the hydrate kinetics at low concentrations of additive.

7. Copyright

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Acknowledgements

Authors gratefully acknowledge the financial support received for this work from Council of Scientific and Industrial Research (CSIR) under the 12th five-year plan: Project Code-CSC0102. NC acknowledge the Senior Research Fellowship (SRF) received from CSIR and computational support from CSIR-4PI, Bangalore, India.

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Biography

Nilesh Choudhary is a Ph.D. student in Chemical Engineering Science at CSIR-National Chemical Laboratory, Pune, India. He is working on gas hydrate using molecular dynamics simulation and density functional theory. He has developed various simulation protocols and post-processing algorithms for gas hydrate formation and decomposition studies in Molecular simulation. He is exploring the effect of additive during gas hydrate formation and decomposition.