Theoretical Study of the Influence of Seeding on the Dynamics of Propane Hydrate Nuclei Formation in Pure and Sea Water

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Abstract. The effect of the addition of a propane hydrate seed on the dynamics of nucleation in propane solutions based on pure or seawater is considered within the framework of the molecular dynamics method. The time dependencies of the number of long-lived hydrogen bonds and the number of $5^{12}$ and $5^{16}6$ cavities formed were calculated. It was shown that presence of the seed leads to the immediate increase in the number of "stable" hydrogen bonds and the growth of hydrate nuclei, which can significantly reduce the induction time of hydrate formation in industrial use and, consequently, enhance the efficiency of the hydrate method of seawater desalination.

1. Introduction

Classic clathrate hydrates are inclusion compounds [1], which crystal lattice consists of water molecules and contains the structural cavities filled with non-ionic gases or light liquids. Hydrate formation is the promising technology for desalination of seawater, since at a relatively low pressure the temperature of hydrate formation can be higher than that of ice formation. In both cases, during desalination, a crystalline substance, the salt content of which is insignificant, and brine are obtained.

The nucleation process is stochastic, the number of attempts were made to reduce the induction time, for example, by using microbubbles, ultrasound, localized undercooling by decompressing liquid propane, increasing the gas-liquid interface area through the use of stirring, bubble or spray columns, fixed bed of quartz sand, glass droplets or a variable reactor volume [2]. The increase of the interfacial area is associated with the transition from homogeneous to heterogeneous nucleation. Modeling of large systems [3] shown that homogeneous nucleation induction time reaches microsecond scale, but the presence of structural defects leads to heterogeneous nucleation, which is energetically favorable [4]. The heterogeneous type is often realized in practice, however due to its complexity it is rarely studied in theoretical studies [5].

The induction time decreases with an increase in the hydrophilicity of an ice-like substrate and an increase in the induction time when a strongly hydrophobic substrate is used [6,7]. Thus, until now the issue of heterogeneous hydrate formation remains poorly understood, and the use of seed hydrate powder for desalination of seawater using hydrate method has practically not been considered. Perspective of using propane hydrates in this case is associated with the accelerated kinetics of hydrate formation, when propane acts as helper gas [8] in systems containing silica sand.
The aim of this work is to study the dynamics of nucleation in solutions of propane hydrate seed and sea salt in water with propane using the molecular dynamics method and own software package for analyzing the short-range order of water and gas molecules.

2. Methods
The study was conducted using the LAMMPS software package [9]. The TIP4P/Ice water model is chosen due to its accuracy in reproduction of the melting point of ice in comparison to other potentials [10]. The potential parameters for propane and sea salt ions are given in [11] and [12], respectively. Water molecules were considered rigid, gas molecules were considered as single particles. Salt concentration corresponded to seawater, the number of propane molecules corresponded to 50% filling of large cavities of the cubic structure II (sII) if the entire water becomes hydrate.

Composition of systems: “water + gas” - 1200 H$_2$O + 35 C$_3$H$_8$ + 43 H$_2$O in seed (connected small and large cavities); “water + gas + sea salt” - 1200 H$_2$O + 35 C$_3$H$_8$ + 12 Na$^+$ and 12 Cl$^-$; “seed + water + gas + sea salt” - 1157 H$_2$O + 35 C$_3$H$_8$ + 12 Na$^+$ and 12 Cl$^-$ + 43 H$_2$O in seed. Other ions were not considered due to the insignificant concentration in our case. The starting structures were constructed by multiple parallel transfer of water molecule and random distribution of gas molecules and salt ions in the resulting liquid volume. Equilibration was made in an NVT ensemble at 270 K and 1 bar for 1 ns. Hydrate seeds were considered rigid during equilibration. The main calculations were carried out in an NPT ensemble at $T = 270$ K and $P = 1, 10$ and 1000 bar with 1 fs timestep. System pressure and temperature were controlled by Nose-Hoover barostat and thermostat [13,14]. Long-range electrostatic interaction was calculated using the PPPM method [15].

The geometric criterion of hydrogen bond (H-bond) was chosen as in our works [16,17]: length $d_{O-O} < 3.2$ Å, mutual orientation angle $\alpha_{OH-O} \leq 30^\circ$. Long-lived H-bonds are those that existed for more than 2 ns. Filled and empty cavities were identified as voids in the H-bond network with the certain number of water molecules, H-bonds and polygons forming these cavities.

3. Results and discussion

![Figure 1](image1.png)

**Figure 1.** The number of long-lived H-bonds in (left) “water + gas”, “seed + water + gas” and (right) “water + gas + sea salt”, “seed + water + gas + sea salt” systems at 270 K.

Fig. 1 shows the time dependence of long-lived H-bond number: presence of salt ions has no significant effect when the hydrate nuclei are forming. This may be due to the low concentration of propane, i.e. the larger number of free water molecules are involved in salt hydration [18]. Thus, the presence of salt ions does not affect the kinetics of nucleation. In seedless systems the number of long-lived H-bonds both increases and decreases to the initial state with time, i.e. no confident growth of the solid phase is observed (induction time is going on). The presence of seed leads to an increase in the long-lived H-bond number that indicates structure solidification and induction time absence. This increase at 270 K and 1 bar is justified by the low propane hydrate formation pressure ($\sim 1.55$ bar [1]).
Fig. 2. The number of cavities corresponding to large cavities $5^{12}6^4$ of the sII structure formed over time in the systems (left) “water + gas”, “seed + water + gas” and (right) “water + gas + sea salt”, “seed + water + gas + sea salt” at 270 K. The data are averaged for each nanosecond of simulation.

Fig. 2 shows the time dependence of large cavity number formed. Note that all large cavities are filled by the propane, i.e. empty large cavities were not formed. The number of large cavities slightly increases with time in pure water solutions and the presence of a seed stabilizes the structure of water around that leads to the fluctuations of large cavity number around 3–5 pieces depending on the pressure. In seedless models, this number fluctuates around 0–1 pieces. Seawater systems act similarly that indicates weak quantitative effect of salt ions on the water environment of propane molecules. The formation of nucleation centers (and the subsequent growth of the hydrate) may be evidenced by the formation of small cavities, since propane does not fill them (unlike methane hydrate [19]), whereas spontaneous formation is energetically disadvantageous.

Fig. 3. The number of cavities corresponding to small cavities $5^4$ of the sII structure formed over time in the systems (left) “water + gas”, “seed + water + gas” and (right) “water + gas + sea salt”, “seed + water + gas + sea salt” at 270 K. The data are averaged for each nanosecond of simulation.

Fig. 3 shows the time dependence of the number of small cavities formed. Small cavities are not forming or their lifetime is less than 1 ns in seedless systems. On the other hand, addition of seed leads to an increase of small cavity number in pure water, while no stable growth is observed in seawater. The results presented in fig. 2 and fig. 3 for seedless models are in qualitative agreement with the results of [20,21] taking into account the difference in thermodynamic conditions. Theoretical TIP4P/Ice model works [22-24] shows that the size of methane hydrate critical nucleus is about 16 - 24 cavities. In this work, nucleus size reaches a value of 8-9 cavities, however, it is rather stable and slowly grows.
4. Conclusions
This work shows the advantage of using a seed in order to reduce the hydrate formation induction time that could be used for seawater desalination. The number of long-lived hydrogen bonds, small and large cavities formed during the simulation of propane solutions based on pure and sea water in the presence/absence of hydrate seed were calculated. In the absence of seed only large cavities of the sII structure filled with propane are spontaneously formed in the solution, but not the full-fledged sII hydrate nuclei (both small + large cavities). The presence of a nanometer seed led to the growth of a stable nucleus of propane hydrate that is clearly pronounced in a salt-free solution. If a larger seed is used, a higher rate of cavity formation on its surface can be expected.

The formation of empty small cavities in this case could explain the accelerated growth of hydrate of binary gas mixtures of propane and those gases which are capable of filling small cavities and have higher hydrate formation pressure, for example, hydrogen.

5. References
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