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Article

A Molecular Dynamics Study of the Influence of Low-Dosage Methanol on Hydrate Formation in Seawater and Pure Water Metastable Solutions of Methane

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Abstract: The behavior of low concentrations of methanol (0.5 and 1.0 wt% of water) as a promoter for hydrate formation in seawater or pure water metastable solutions of methane was investigated using the classical molecular dynamics method at moderate temperature and pressure. The influence of methanol on the dynamics of the re-arrangement of the hydrogen bond network in seawater and pure water solutions of methane was studied by calculating order parameters of the tetrahedral environment and intermolecular torsion angles for water molecules, as well as by calculating the number of hydrogen bonds, hydrate and hydrate-like cavities. It was found that hydrate nucleation can be considered a collective process in which the rate of hydrate growth is faster in systems with low concentrations of methanol and confident hydrate growth begins earlier in a metastable solution without sea salt with a small amount of methanol than in systems without methanol.

Keywords: gas hydrates; nucleation mechanism; seawater; intramolecular hydrogen bonds; computer simulation

1. Introduction

The development of offshore oil and gas fields located far from the coastline is currently intensifying, which makes the ocean an even more important source of vital resources for humanity [1,2]. Exploration and utilization of such fields require different approaches and technical solutions due to the more severe conditions at greater depths than those used in modern offshore development. High pressure and low water temperature on the seabed are conducive to the formation of clathrate hydrates [3] of simplest hydrocarbons, such as methane, etc., which in turn creates additional challenges for deep-sea drilling. Due to the formation of hydrates under these circumstances, almost any gas released during drilling or other operations can lead to rapid plugging of the well or blocking of free access. Hydrate decomposition can also result in the formation of large quantities of gas, disrupting the operation of the installations. Thus, there are significant risks in the development and operation of deep-water oil and gas wells associated with the formation of hydrates. This requires the ability to control the process [4,5].

Despite these problems, a distinctive feature of gas hydrates is the high content of gas in their structure, which can be used for gas storage (including natural gas, carbon dioxide and hydrogen) and transportation purposes, seawater desalination, and other applications. However, the slow kinetics of hydrate formation remains a major challenge for the large-scale use of hydrates; it highly depends on the temperature and pressure, the ratio of the components and the presence of promoters or inhibitors. Many mechanical, chemical and other types of promoters affecting the thermodynamics and kinetics of the hydrate formation process have been proposed [6] to solve this problem.

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The most common chemical promoters are tetrahydrofuran (THF), cyclopentane, quaternary salts and sodium dodecyl sulfate (SDS). At the same time, methanol is often considered as an inhibitor that increases pressure and reduces the temperature of hydrate formation [7]. However, previous work [8] has shown that thermodynamic inhibitors can act as catalysts for hydrate formation; methanol creates a film at the interface, which significantly accelerates gas absorption into the condensed phase by reducing the interfacial free energy barrier and breaking hydrogen bonds [9]. This decrease in energy reduces the nucleation barrier and induction time [10].

Thus, methanol can be considered as a surfactant for two-phase systems [11,12]. The most effective methanol concentration varies depending on the type of gas, the degree of subcooling of the system, and other conditions. For example, for methane, the optimal concentration of methanol is 5 wt%. For a mixture of carbon dioxide and nitrogen, it is 1 wt% [12]. It has been shown that even a small amount of methanol, 0.016 wt%, increases the rate of propane absorption and reduces the initial pressure required for producing hydrate from ice [13]. In this case, the effect is most pronounced in aerosol systems [14], where the ratio of surface area to volume is maximized and hydrate growth occurs at a sub-second timescale, as well as in systems where the layer of water suitable for dissolving methane is thin [8]. The experimental contribution to a study on the effect of methanol in volume [15] revealed that the addition 1 wt% of methanol to the reactor accelerates the formation of methane hydrate at very late stages (after several hours). The theoretical contribution to this study showed a slight increase in the rate of hydrate growth from a homogeneous water-methane solution with 1 wt% methanol from the beginning of the simulation.

Reducing the hydrate formation pressure is also important. An increase in the methane concentration [16] and a decrease in the formation pressure [17] down to atmospheric pressure [18] can be achieved using the nano-confinement effect or foam [19]. In the works [20,21], the possibility of formation of O_2, Ar, N_2 and CO hydrates from a solid solution at pressures below the hydrate formation pressure has been shown. A supersaturated methane solution at a certain gas concentration can transform into hydrate-like structures at moderate temperature and pressure [22]. The growth of hydrate structures is associated with a high gas content in the aqueous phase and the large entropy contribution of guest molecules located in the hydrate lattice is associated with the free energy of the hydrate phase. This contribution is enough to transform the hydrogen bond network of the liquid solution into that of the hydrate, leading to the formation of both fluctuating and stable hydrate cavities.

Because of its simplicity and availability, methanol can serve to break down natural gas hydrates in marine and permafrost environments, extract natural gas, and promote the formation of carbon dioxide hydrate for disposal at sea (so-called CH_4-CO_2 swapping). Under such conditions, the properties of methanol are comparable to those of other widely used surface-active chemicals, such as methionine and SDS [12,23]. Therefore, it is important to determine the kinetic properties of methanol in order to develop an effective inhibition method [24], including in seawater. A thermodynamic description of the influence of low-molecular-weight alcohols on gas dissolution [9] and hydrate formation acceleration [11,25] has been described, but the mechanism by which methanol influences the process of hydrate formation is still poorly understood.

The main aim of this work is to study the influence of methanol molecules on the kinetics of methane gas hydrate formation and the concomitant rearrangement of the network of hydrogen bonds of the water molecules that form the crystalline structure of the hydrate.

2. Computational Methods

The MD method (LAMMPS software package [26]) was used in this study. Using the PackMol package [27] a series of models of homogeneous aqueous solutions was created, consisting of 3600 water molecules, 250 methane molecules, 36 Na^+Cl^- ion pairs (the concentration of sea salt in seawater) and 0, 10 and 20 methanol molecules, which corresponds to 0, 0.5 and 1.0 wt% methanol in relation to water molecules only. The initial positions and rotational angles of the molecules in all model systems were randomly determined, which made it possible to achieve a uniform distribution throughout the volume. Generated structures and LAMMPS input scripts are presented in Supplementary Materials.

It is important to note that the initial system created in this way is supersaturated. Usually, supersaturation created for example by high pressure [6] is considered as a driving force for the hydrate formation. However, in our system, it exceeds the experimentally observed values. Nevertheless, the mechanisms of hydrate formation studied remain the same as in experimentally achievable cases.

To reduce stochasticity in hydrate formation, a series of three models with different initial particle distributions in space were created for each methanol concentration and sea salt concentration. The results presented are the averages of the results from each series.

Water molecules were described by the TIP4P/Ice potential [28], which has a melting line for ice that is very close to the experimental data. Depending on the calculation method the TIP4P/Ice model melting point could be varied from 268(2) to 272(6) K [29], however according to [29] it is reasonable to assume this point is 269.1 K. All other molecules were described using the OPLS-UA model [30].

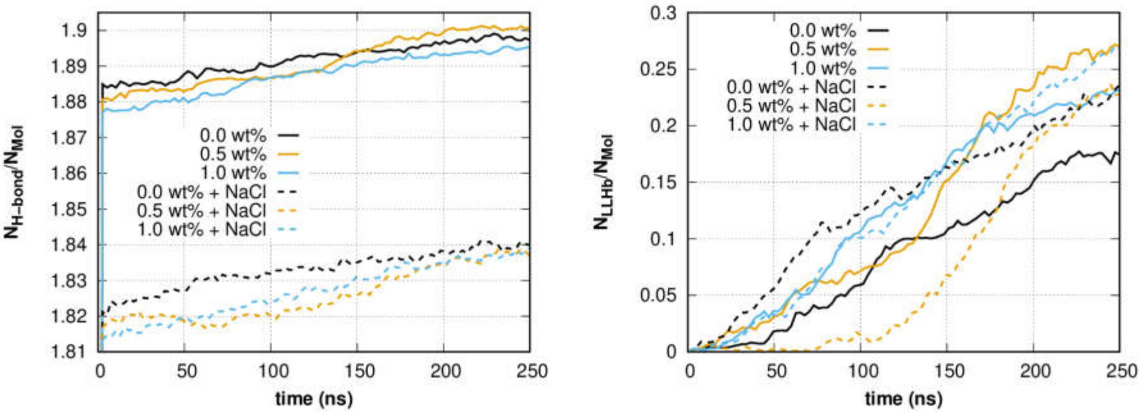
In our previous work [22] we have observed methane hydrate formation at 270K and 1bar. In this work we have chosen the same conditions except for pressure due to the presence of sea salt, whereigher value of pressure should not inhibit the hydrate growth. Thus, all the simulations were performed at 270 K and 5 bar in the NPT ensemble with a 2 fs timestep. This temperature selection should prevent the I_h ice formation. Thermostat and barostat [31, 32] dumping parameters were chosen to be 300 and 3000 fs, respectively. The selected temperature corresponds to the liquid phase and is close to the melting point [33]. A more detailed description of the calculation procedure can be found in our previous work [22].

To analyze the structure of the solution, the number of hydrogen bonds was calculated using the geometric criterion ($R_{OO} \leq 3.2$ Å and $\angle HOH \leq 30°$ [34]), tetrahedrality order parameter F_3 ($F_{3\_crystal} \approx 0$ and $F_{3\_liquid} \approx 0.1$ [35]) and torsion angle order parameter F_4 ($F_{4\_ice} \approx -0.4$, $F_{4\_liquid} \approx -0.04$ and $F_{4\_hydrate} \approx 0.7$ [36]). Hydrogen bonds that existed for more than 1 ns were considered long-lived. To study the early stages of hydrate formation, a search for methane hydrate cavities (5^{12} and $5^{12}6^2$) and topologically similar cavities ($5^{12}6^3$, $5^{12}6^4$, $4^15^{10}6^2$, $4^15^{10}6^3$, $4^15^{10}6^4$) was carried out by searching for polygons formed by four, five, or six water molecules connected by hydrogen bonds. This could be divided into a few steps: (i) build a hydrogen bond network graph; (ii) search for closed polygons; (iii) search for common edges in order to build the polygon connectivity graph; (iv) search for closed polyhedral structures using the connectivity graph; (v) check for guest molecule occupation. This algorithm, implemented in our own software, allows us to find the cavities discussed above.

3. Results and Discussion

To understand the effect of methanol on the structure of the solution at moderate temperatures and pressures, the dynamics of the rearrangement of hydrogen bonding networks in methane solutions based on pure water and seawater was studied.

Figure 1a shows the series-averaged number of hydrogen bonds ($N_{H\text{-}bond}$) normalized to the number of molecules (N_{Mol}) as a function of time at moderate temperature and pressure (non-averaged values are given in Supplementary Figure S1a,b). An increase in the $N_{H\text{-}bond}/N_{Mol}$ ratio indicates a crystal-like ordering of the hydrogen bond network, because crystalline phases of water and hydrates have $N_{H\text{-}bond}/N_{Mol} = 2$. The addition of sea salt reduces this ratio by several percent, as the sodium and chlorine ions are able to orient neighboring water molecules towards themselves, reducing the total number of available hydrogen bonds for water molecule formation. In the systems based on pure water without methanol, growth occurs faster during the first 150 ns, after which systems containing 0.5 wt% show faster growth rates. In the systems with sea salt, the increase in the number of hydrogen bonds occurs most actively without methanol during the first 200 ns. After that the rate of increase in the number of hydrogen bonds becomes higher for the systems containing methanol.



(**a**) (**b**)

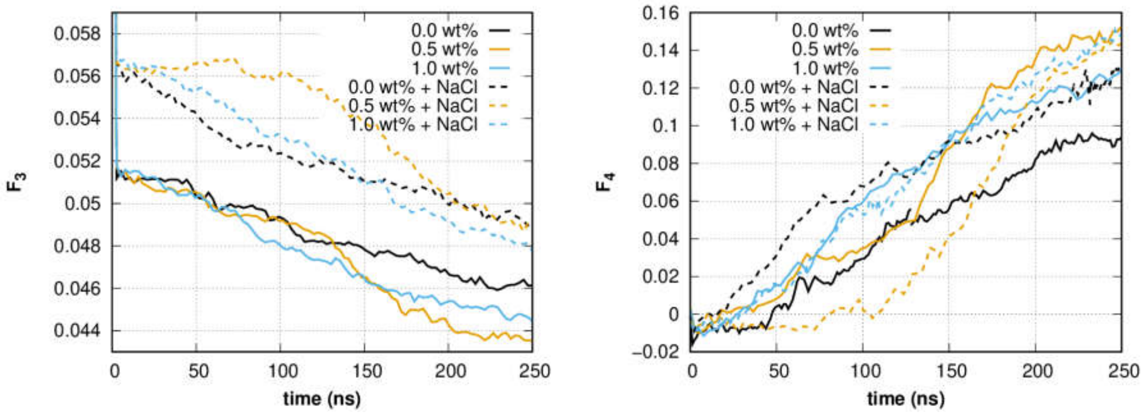
Figure 1. Time dependence of the averaged values of the normalized numbers of (**a**) hydrogen bonds $N_{H\text{-}bond}/N_{Mol}$ and (**b**) long-lived hydrogen bonds N_{LLHb}/N_{Mol} in pure water and seawater-based solutions.

The growth of solid structures at moderate temperature and pressure in solution is evidenced by the formation of long-lived hydrogen bonds. Figure 1b shows the time dependence of the series-averaged number of these bonds (N_{LLHb}) normalized to N_{Mol} (non-averaged values are given in Supplementary Figure S1c,d). The main difference between Figure 1a and 1b is that, in the systems based on pure water, the rate of formation of solid structures in the presence of methanol is significantly higher than without it. However, in seawater, a small amount of methanol slows the rate of solidification of the solution during the first 100 ns, but further simulation shows an increase and that exceeds the growth rate of solid structures. Adding more methanol inhibits the formation of hydrates at temperatures above 0 °C [37,38].

Despite the faster initial increase in the number of hydrogen bonds in the methanol-free systems based on pure water and seawater, faster short-range tetrahedral ordering of the water molecules (F_3) does not occur in the methanol-free systems based on pure water at moderate temperature and pressure (Figure 2a, non-averaged values are given in Supplementary Figure S2a,b). The tendency towards greater ordering sharpens after 50 ns in pure water and after 150 ns in the seawater systems with methanol. Tetrahedral ordering is more pronounced in systems with 0.5 wt% methanol, followed by 1.0 wt%.

The presence of sea salt initially disrupts the hydrogen bond network by ~0.06, but over time this difference decreases slightly. In this case, the pattern of the ordering is similar. Due to the presence in the solution of both gas (with an insufficient amount for the transition of the entire system to the hydrate phase) and methanol, these order parameter values do not reach the reference ones.

The series-averaged order parameter F_4 (Figure 2b, non-averaged values are given in Supplementary Figure S2c,d) behaves similarly to F_3. However, for all systems, the initial values correspond to the reference value for liquid water. The values of F_4 do not reach the reference value of the hydrate because of the small amount of dissolved methane, as in the case of F_3. Over time, the behavior of methanol as a promoter can be seen in all systems.



(**a**) (**b**)

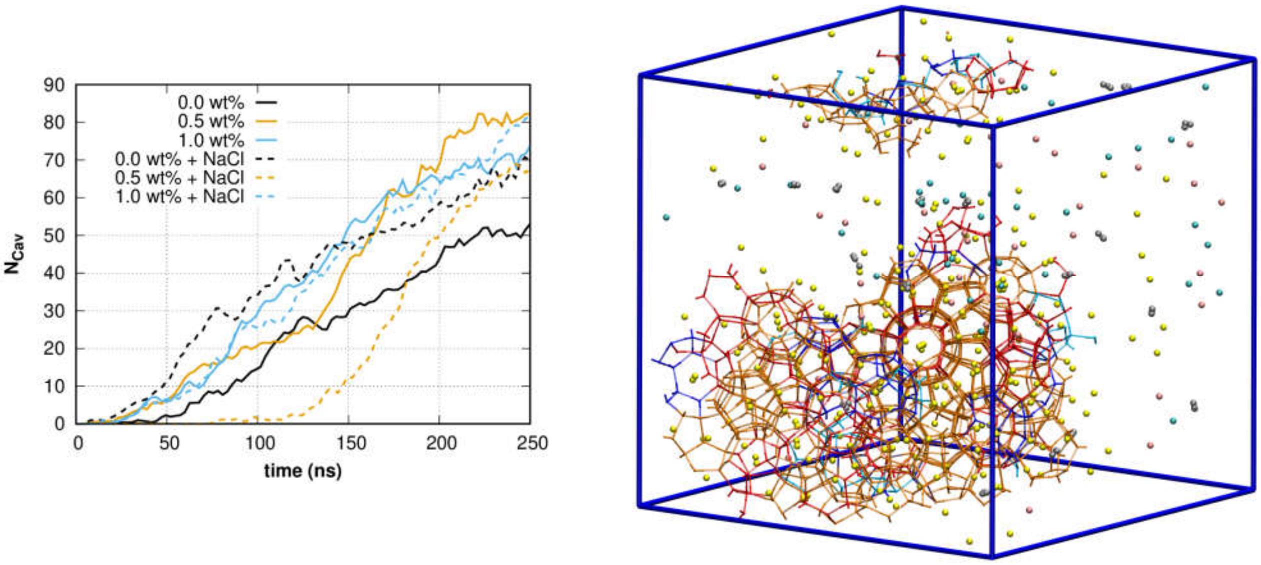
Figure 2. Time dependence of the averaged values of the order parameters (a) F3 and (b) F4 in methane solutions based on pure water and seawater.

The presence of salt in systems without methanol leads to faster ordering of the system at moderate temperature and pressure. However, the effect of NaCl as a promoter has been shown at lower salt concentrations in other works [15,39–41]. Analysis of these works and comparison with the current work show that the amount of dissolved gas is important for the manifestation of the promoting effect. NaCl appears to have such a significant promoting effect in this study due to its much lower concentration of gas.

In general, an increase in the value of F_4 and a decrease in F_3 indicate the formation of hydrate-like structures. The most indicative parameter describing the hydrate-likeness of the resulting structure is the time dependence of the series-averaged number of hydrate cavities (N_{Cav}) filled with methane, which is shown in Figure 3a. (Non-averaged values are given in Supplementary Figure S3a,b.) The number of empty cages for all models and runs does exceed 2 cavities during this stage of hydrate formation, when an amorphous hydrate is formed [41]. Figure 3a shows that the presence of methanol in methane solution in non-marine water results in an increase in the number of cavities by 40-60%, while in seawater the increase is 0-15%, depending on the concentration of methanol. The addition of salt to the methanol-free systems results in an increase in the number of cavities by ~40%. This is further evidence that salt promotes hydrate formation. In the systems containing methanol, the addition of sea salts results in a reduction in cavity number by ~20% at 0.5 wt% of methanol and an increase by ~12% at 1 wt%. The systems with 0.5 wt% and 1 wt % of methanol form the largest number of cavities over the course of the simulation, suggesting the presence of promoting properties at moderate temperature and pressure. The induction times in our type of system are ~40, 20 and 23 ns for the pure water-based systems with methanol concentration growth and ~18, 24 and 113 ns for the seawater-based systems. The presence of methanol in the pure water-based systems shows a statistical reduction in the induction time.

Figure 3b shows an example of a hydrate-like structure formed in the system with 1 wt% methanol and sea salt. The formation of cavities that are unusual for a hydrate with a certain structure is quite typical of the process of hydrate formation during the amorphous hydrate stage (polycrystal [43]), which explains the presence of $5^{12}6^3$ and $5^{12}6^4$ cavities.

Despite its indicative nature, the N_{Cav} parameter is the least sensitive to changes occurring in the system. For example, the parameter F_4 or the number of hydrogen bonds begins to change much earlier than the detection time of the first cavities, indicating a collective rearrangement of the hydrogen bond network prior to the onset of hydrate formation [22,43].



(**a**) (**b**)

Figure 3. (**a**) Time dependence of the average number of cavities N_{Cav} in solutions based on pure and seawater. (**b**) Spatial distribution of cavities: 5^{12} (*orange*), $5^{12}6^2$ (*red*), $5^{12}6^3$ and $5^{12}6^4$ (*blue*), as well as topologically similar cavities (*light blue*), Na^+ ions (*cyan*), Cl^- ions (*pink*), and methanol (*gray*).

The presence of methanol, on average, reduces the induction time for pure water solutions and results in slightly higher hydrate growth rates for all types of water in long-term simulations. This increase in hydrate growth rate is consistent with the results of [15]. However, the presence of sea salt can make methanol ineffective in the initial stages at 0.5 wt%, while sea salt itself acts as a weak promoter in systems of this type.

The nature of the methanol promoting effect could be associated with higher methane diffusion caused by the presence of methanol [45,46]. A decrease in induction time may be due to earlier formation of hydrate nuclei caused by an increase in the local methane concentration due to accelerated diffusion of methane molecules.

Our results are in qualitative agreement with the results of other studies [47,48], which showed a decrease in hydrate nucleation stochasticity with the addition of methanol. However, in this case, we can discuss an average reduction in induction time in solutions containing methanol based on pure water under moderate temperatures and pressures.

5. Conclusions

We carried out a study on the influence of low concentrations of methanol on the process of formation of methane hydrates from a metastable supersaturated solution based on seawater and pure water under moderate temperature and pressure conditions. This process was characterized by calculating the number of normal and long-lived hydrogen bonds, and order parameters. The number of different hydrate and hydrate-like cavities characteristic of the early stages of hydrate formation was also studied. It was shown that the hydrate growth process in this case is collective, and the presence of methanol and sea salt could increase the number of cavities formed over the certain time during this process in agreement with previous studies [49,50]. In the presence of methanol without sea salt, a decrease in induction time is also observed. The observed here hydrate formation promoting properties of NaCl are associated with a low concentration of dissolved methane, in contrast to other studies. The promoting properties of methanol do not appear immediately, but only at a later stage, when the residual methane concentration in the liquid phase becomes low, requiring more time for the transport of methane to the hydrate surface. This process is limited by diffusion, which can be affected by methanol disrupting the network of hydrogen bonds.

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The obtained results are fundamental for understanding the effect of methanol on the properties of the hydrogen bond network in seawater and the hydrate formation process. These results can be taken into account when developing technologies based on gas hydrates and seawater, e.g. the methane extraction and the carbon dioxide utilization. This work is essential for studying the mechanism of hydrate formation under moderate conditions discovered in experiments, where a homogeneous supersaturated gas phase is created.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: Time dependence of the the normalized numbers of (a,b) hydrogen bonds $N_{H\text{-}bond}/N_{Mol}$ and (c,d) long-lived hydrogen bonds N_{LLHb}/N_{Mol} in (a,c) pure and (b,d) seawater-based solutions.; Figure S2: Time dependence of the order parameters (a,b) F_3 and (c,d) F_4 in methane solutions based on (a,c) pure and (b,d) sea water.; Figure S3: Time dependence of the number of cavities N_{Cav} in solutions based on (a) pure and (b) sea water.

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