Molecular dynamics simulation of the effects of different salts on methane hydrate formation: an analysis of NaCl, KCl and CaCl₂

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Abstract. The formation of hydrates in seawater is of great significance for hydrate prevention and control and seawater desalination. Molecular dynamics simulations were performed to investigate the spontaneous methane hydrate formation in 3.5wt % (seawater salinity) NaCl, 3.5wt % KCl and 3.5wt % CaCl₂ solution, respectively. Results indicated that salt inhibited the formation of hydrates, and the strength of inhibition followed the sequence of 3.5wt % CaCl₂ > 3.5wt % NaCl > 3.5wt % KCl. Salt inhibited nucleation and growth of hydrates by suppressing methane dissolution and reducing the number of tetrahedral water molecules in the methane hydration layer. It was observed that Na⁺, K⁺ and Cl⁻ can replace the water molecules in the hydrate cage to participate in the formation of the cage. Compared with the pure water system and KCl system with a fast hydrate growth rate, the randomness of hydrate crystallization was smaller in the NaCl system and CaCl₂ system with slow hydrate growth rate.

1. Introduction
Hydrates are crystalline solid compounds composed of polyhedral water cages connected by hydrogen bonds and the gas molecules in the cages, the most common of which include methane, carbon dioxide, and hydrogen [1]. In nature, hydrates are found primarily in the sea floor and permafrost. Natural gas hydrates are considered a very promising energy source for cleanliness and large reserves. It is estimated that global natural gas hydrates contain twice as much carbon as all conventional fossil fuels combined. Hydrates are easily formed at high pressures and low temperatures and can be generated in pipelines and blowout preventers, posing significant challenges and losses to the safe production of oil and gas. In addition, hydrates are relevant to a variety of scientific research and industrial applications, such as seawater desalination [2], carbon dioxide sequestration, and the storage of hydrogen and natural gas. Due to the structural characteristics of hydrates, compared with other methods, using hydrates for desalination has certain advantages in terms of energy consumption and economic feasibility. Inorganic salts can change the phase equilibrium conditions for hydrate formation, making hydrates to be formed at lower temperatures or higher pressures. In the oil and gas industry, inorganic salts are often used as thermodynamic inhibitors forhydrate control. The main thermodynamic inhibitors are NaCl, KCl and CaCl₂, which are similar to the salts commonly found in seawater. Both prevention of hydrates and the desalination of seawater using hydrates involve the action of inorganic salts on hydrates.
A lot of experimental work has been done on the effect of inorganic salts on hydrates, but the microscopic interactions between ions and hydrates are difficult to be observed by conventional experimental means. Molecular dynamics (MD) simulation technique is a powerful tool for studying hydrates at the microscopic scale and has been used to understand the effects of salt on hydrate growth and decomposition [3-5]. However, there are few studies on the spontaneous nucleation and growth of hydrates in solutions containing salt, which is closely related to seawater desalination and hydrate prevention and control in the environment. Accordingly, in this paper, we used MD to comparatively investigate the spontaneous nucleation and growth of methane hydrates in the presence of three typical inorganic salts: NaCl, KCl and CaCl₂, respectively.

2. Simulation details
The initial system was a two-phase model with the sizes of 50×50×50 Å³, which consisted of solution phase and methane gas phase (bubble). The solution phase contained 3487 water molecules and ions, and the methane gas phase contained 550 methane molecules. Three models containing NaCl, KCl and CaCl₂ were established based on the type of salt in solution, respectively. The mass concentration of salt was set to 3.5wt % (similar to the concentration of NaCl in seawater). As shown in Figure 1, which is a schematic representation of the KCl system, ions were randomly distributed in the aqueous solution. A salt-free system was available as a control group (0 wt%). MD simulations were performed using the Gromacs package [6]. The TIP4P/Ice model [7] was used for water, OPLS-AA model [8] was used for methane, and the force fields for ions were taken from ref [9]. Periodic boundary was used in all three spatial directions. Lennard-Jones interactions were calculated with a cutoff of 10 Å, and long-range electrostatic interactions were calculated using the particle mesh Ewald summation method. Geometric combining rules were used for the Lennard-Jones cross-terms. The fastest descent method was used to minimize the energy of the system structure before the start of the simulation. Then, the system will be equilibrated for 2 ns in the NPT ensemble (300K, 650bar) to eliminate internal stress. All formal simulations were performed in the NPT ensemble (250K, 650bar) with a simulation time of 1500 ns and a time step of 1 fs. Each system was run twice, run1 and run2. Temperature and pressure were controlled by the Nose-Hoover thermostat and the Parrinello-Rahman barostat, respectively.

3. Results and discussion
3.1. Inhibitory effect of salt on hydrate nucleation and growth
3.1.1. Hydrate formation process. As shown in Figure 2, the process of spontaneous nucleation and growth of methane hydrates in the presence of salt was presented using NaCl run1 as an example. The method of Guo et al. (FSICA) was used to identify complete hydration cages [10]. The criteria for
determining the existence of hydrogen bonds between two water molecules are: the distance between the oxygen atoms is less than 3.5, and there is an O-O-H angle less than 30°. As the simulation proceeded, the methane bubble began to dissolve, and the first isolated 512 cage appeared at 169 ns, which was unstable and collapsed within 1 ns. Then, isolated hydrate cages and clusters consisting of several interconnected hydrate cages in solution kept appearing and disappearing. At 400 ns, a cluster consisting of four 512 cages was generated in a place where dissolved methane was dense, as shown in Figure 2(a). This cluster survived and grew into an initial hydrate nucleus. Then, hydrates rapidly grew around the methane bubble, and the ions were expelled in Figure 2(b). Hydrate growth consumed methane and liquid water in the system, and the bubble became smaller, as shown in Figure 2(c). Eventually, most of the water in the system was converted to hydrates, and the ions were forced to be distributed in the liquid water channels between the hydrates.

Figure 2. Snapshots of NaCl run1. The white, blue, and cyan balls are methane, sodium, and chloride ions, respectively. The red rods are hydrates and the iceblue blocks are liquid water.

3.1.2. Analysis of order parameter \( F_4 \) and hydrogen bond. For a comparative description of the evolution of hydrates in different systems, we used the four-body structural order parameter \( F_4 \) [11], which is defined as follows:

\[
F_4 = \frac{1}{n} \sum_{i=1}^{n} \cos 3\phi_i
\]

where \( n \) is the number of other water molecules within 3.5 Å radius of a water molecule, and \( \phi_i \) is the dihedral angle formed by H-O... O-H in the water molecule pair consisting of this water molecule and its i-th surrounding water molecule, where the two hydrogen atoms are the most distant (outermost hydrogens) in the water molecule pair. The \( F_4 \) values for ice, liquid water, and hydrate are −0.4, −0.04, and 0.7, respectively. Figure 3 showed the evolution of hydrates in different systems. According to the change of \( F_4 \), the growth of hydrate can be divided into three stages. The first stage was the induction stage, where \( F_4 \) fluctuated smoothly, methane gas dissolved, and a small amount of hydrate cages were formed. The second stage was the rapid growth stage of hydrate, where \( F_4 \) increased rapidly, and a stable hydrate nucleus appeared, which accelerated the hydrate formation. The methane and water molecules in the solution were consumed, and the ion concentration increased accordingly. The third stage was the slow growth stage of hydrate, where the increase of \( F_4 \) became slower until it fluctuated smoothly and a large amount of hydrates were generated. Ions inhibited the formation of hydrates during the induction stage, and the induction time of the salt-containing system was significantly longer than that of the control group. The average induction times for the NaCl, KCl and CaCl\(_2\) systems were 500 ns, 180 ns and 550 ns, respectively, while that of the control group was only 100ns. Compared with the NaCl and KCl systems, the induction time of the two simulations of the CaCl\(_2\) system was quite different. This was due to the stronger inhibitory effect of CaCl\(_2\) on hydrates, and the uncertainty of hydrate nucleation increased. It can be seen from the slope of the curve of \( F_4 \) during the rapid growth of hydrate that the growth rate of hydrate in the NaCl and CaCl\(_2\) system was significantly lower than that in the KCl system and the control group. Because of ion hydration, the hydration layer was formed around ions, as shown in Figure 4(a), with a wave peak at
2.5 Å to 3.4 Å around the ion. Based on the height of the first peak, it can be seen that the hydration capacity of the cations is arranged as follows: Ca$^{2+}$ > Na$^+$ > K$^+$, which was consistent with the induction time of hydrate. It showed that the hydration of ions is an essential factor in inhibiting the formation of hydrates.

3.1.3. Analysis of methane hydration layer and dissolved methane. Ion hydration affected the orientation of water molecules within the methane hydration layer, which was defined as the angle between the water dipole and the direction of ion-carbon atom. As shown in Figure 4(b), the orientation distribution of water molecules in the first 100ns of all simulations, and the orientation distribution of hydrate water molecules in the control group in the last 100ns was calculated. In hydrates, the probability curve of the orientation distribution of water molecules around methane peaked around 60° and 120° and 120° and troughed around 95°. The probability value of the orientation distribution of water molecules around methane in the control group around the peak was slightly higher than that of the salt-containing system, and the opposite was at the trough. The above analysis showed that ions inhibit the orientation of water molecules around methane from changing in a direction that is conducive to the formation of hydrates.

Figure 3. Evolution of (a) F$_4$ and (b) hydrogen bond number.

Figure 4. (a) Radial distribution function of oxygen atoms in water around ions. (b) Orientation distribution of water molecules around methane.

Around the dissolved methane, there is a network of tetrahedral water molecules in a structure similar to the hydrate structure and favorable to hydrate formation (Figure 5(a) inset). Compared with the control group, the tetrahedral water molecules in the salt-containing system were reduced by up to 5%, and the KCl system has more tetrahedral water molecules than CaCl$_2$ and NaCl systems. Ions affected not only the structure of the water molecule network around methane but also its dissolution. It was seen in Figure 5(b), less methane was dissolved in the salt-containing system than in the control group during the induction stage. Because the hydration capacity of ions and the ability to bind water molecules were stronger than methane molecules. Furthermore, the inhibitory effect of 3.5wt% CaCl$_2$
on methane dissolution was stronger than 3.5wt% NaCl and 3.5wt% KCl. The reduction of tetrahedral water molecules and dissolved methane was detrimental to the nucleation of hydrate at the induction stage and decreased the growth rate of hydrate at the growth stage.

Figure 5. (a) Proportion of tetrahedral water molecules around methane in the first 100ns. (b) Evolution of dissolved methane overtime in the first 200ns. The red dashed lines represent hydrogen bonds; the solid green line is part of a tetrahedral structure.

3.2. Effects of ions on hydrate structure

3.2.1. Ions involved in cage formation. As shown in Figure 2, some ions were distributed at the hydrate growth interface during hydrate formation. Next, we explored the effects of ions on the hydrate structure. Using hydrates to desalinate seawater is a potentially essential method, and the salinity is an essential indicator for evaluating the seawater conversion. In the simulation, it was found that the hydrate was not completely salt-free, and some ions would replace the water molecules in the hydrate cage to participate in the hydrate formation. In Figure 6, Na\(^+\) and Cl\(^-\) were involved in the formation of 512 and 4251062 cages, respectively, and these ions were called cage ions. However, not all kinds of salt ions can participate in the formation of hydrate cages. In this study, we observed Na\(^+\), Cl\(^-\) and K\(^+\) in the cage structure, but no Ca\(^{2+}\). A potential explanation for this phenomenon is that Ca\(^{2+}\) has strong hydration capacity and a small hydration radius (Figure 4), and its hydrate layer structure is incompatible with the hydrate structure.

Figure 6. Schematic diagram of cage with ion. (a) A 512 cage with s Na\(^+\). (b) A 4251062 cage with Cl\(^-\).

According to the distribution location cage ions can be divided into two categories: cage ion at the hydrate growth interface and cage ion within the hydrate. The cage ion at the hydrate growth interface appeared after the induction stage and mainly during the slow growth stage, when there was less liquid water in the system and most of the ions were dispersed at the hydrate growth interface in Figure 2(c). Cage ions at the hydrate growth interface were involved in the formation of only one cage and may leave the cage. The departure of the ion can alter the surrounding water structure and cause disintegration of the cage, indicating that the cage formed by ions and water molecules at the interface is unstable. On the other hand, this also reflects the inhibitory effect of salt ions on hydrates. The cage
ions within the hydrate were involved in the formation of multiple hydrate cages at the same time acting as a connection point. Compared with the hydrate growth interface, there was no free water inside the hydrate, and the water molecule network structure was more stable, so the cage ion can exist stably for a long time. Statistics found that these cage ions all appeared during the rapid growth stage. The cage ions inside the hydrate were formed when the cage ions at the hydrate growth interface were encapsulated into the hydrate by the rapidly growing hydrate around it. In the rapid growth stage, there was less cage ion within the hydrate hydrates due to fewer ions involved in hydrate cage formation at the hydrate interface. However, the cage ion within hydrates can coexist stably with the hydrate structure, so it is a key factor influencing the salinity of hydrates. Considering the process of ions entering the hydrate, in the macro experiment, timely supplementation of fresh seawater to avoid the appearance of high-concentration seawater may be able to reduce the salinity of hydrate.

3.2.2. Effect of salt on the crystallinity of hydrate. In the simulation, the spontaneously formed hydrate was not the common standard sI \((5_{12}^{12}+5_{12}^{1262})\) or sII \((5_{12}^{12}+5_{12}^{1264})\) hydrate, but an amorphous hydrate composed of a variety of cages. Amorphous hydrates contain cage structures belonging to sI or sII type hydrates. These structures are called crystalline hydrates and water molecules that make up these structures are crystalline water molecules. The ratio of crystal water molecules to the water molecules constituting hydrate is the crystallinity. The variation in hydrate crystallinity in different saline systems was calculated by using the method of Jacobson et al [12]. As shown in Figure 7, the change in hydrate crystallinity can be divided into two stages. In the early stage of hydrate growth, hydrate clusters containing sI and sII hydrate cages appeared when the number of water molecules in the hydrate was small, and the hydrate cages were mainly stable \(5_{12}^{12}\) and \(5_{12}^{1262}\) cages, and the crystallinity increased rapidly. As hydrates grew, the types of hydrate cages increased, and cages that do not belong to sI and sII hydrates were formed, such as \(5_{12}^{1263}\), \(4_{5}^{10}6_{2}\) and \(4_{5}^{10}6_{3}\) cages, etc. The number of water molecules in hydrate increased, the proportion of crystal water molecules decreased, and the crystallinity fluctuated sharply or decreased. It was found that the crystallinity difference between the two simulations in the control group and the KCl system was 9% and 4%, respectively, while the crystallinity difference between the two simulations in the NaCl and CaCl\(_2\) systems was approximately 1%. This was attributed to the slower growth of hydrates in the latter two systems reducing the uncertainty of hydrate crystallization.

4. Conclusions
Molecular dynamics simulation technique was employed to investigate the spontaneous formation of methane hydrates in different salt solutions: 3.5 wt% NaCl, 3.5 wt% KCl and 3.5 wt% CaCl\(_2\). The presence of salt increased the induction time of hydrate and slowed its growth. The strength of inhibition was as follows: 3.5 wt% CaCl\(_2\)>3.5 wt% NaCl>3.5 wt% KCl. As a result of ion hydration, the number of hydrogen bonds and dissolved methane in the salt solution decreased. In addition, salt ions affected the orientation distribution of water molecules in the methane hydration layer and

![Figure 7. Evolution of hydrate crystallinity.](image)
reduced the number of tetrahedral water molecules, which was not conducive to hydrate formation. It has been found that hydrates were not completely salt-free and that Na⁺, Cl⁻ and K⁺ could replace water molecules in the formation of hydrate cages. In the salt-free system and the KCl system where the hydrate growth rate is fast, the uncertainty of the hydrate crystallinity is greater than that of the NaCl and CaCl₂ systems where the hydrate growth rate is slower.

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