

Effects of various ionic solutions on the methane hydrate formation kinetics in deep-sea cold seep environments[#]

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ABSTRACT

The study of methane hydrate formation kinetics in various ionic solution systems helps to understand the hydrate formation characteristics in deep-sea cold seep environments, providing insights into methane conversion. The ionic composition and ratio in seawater play an important role in the nucleation and growth of methane hydrate. In this study, we investigated the formation behaviors of methane hydrate in varied ionic solutions and in-situ seawater. It was found that, compared with in pure water system, the inhibition of hydrate formation in the solutions was in the following order: NaCl > seawater > MgCl₂ > CaCl₂ > SrCl₂. The experimental results of this study can provide a reference for further exploration of methane hydrate formation in cold seep environments, and can also contribute to an effective response to the challenge of climate change and the goal of carbon neutrality.

Keywords: methane hydrate, ions, seawater, formation kinetics

1. INTRODUCTION

Methane is the second most important greenhouse gas globally, after carbon dioxide. The global warming potential of methane is 84 times that of carbon dioxide, and the atmospheric concentration of methane reached its highest level in 2020 since systematic monitoring began in 1983 [1][2][3].

Methane hydrates are an important carbon reservoir in the deep ocean. During the methane seepage process in deep-sea cold seep, free gas migrates upward and forms hydrates in the hydrate stability zone, potentially

escaping into the ocean and entering the atmosphere [4][5].

Hydrate formation is subject to thermodynamic conditions, with salt ions playing a crucial role as thermodynamic inhibitors [9]. The formation of methane hydrate in overlying seawater is an important conversion pathway, which is affected by salt ions in seawater. Salt ions can cause partial dissociation of hydrates, it may release large amounts of methane, which will exacerbate the global warming trend. Therefore, it is crucial to investigate the effect of salt ions on the kinetics of methane hydrate formation.

In this study, we used types of main ions in cold seep and in-situ seawater (PC2-R301, which was taken from the Formosa (site F) of the South China Sea) to investigate the effect of ions on methane hydrate formation. Our study focused on the following points: (a) Conducted experiments of induction time for methane hydrate formation, analyzing the influence of ions on methane hydrate nucleation. (b) Calculated the methane consumption in different experimental groups, and analyzed the effect of ions on methane hydrate formation. (c) Observed the morphology of methane hydrate formation in different systems, and analyzed the morphological differences of hydrates in different systems.

2. EXPERIMENTS SECTION

2.1 Experimental set-up

The schematic diagram of the experimental system is shown in Fig. 1. Consists of a hydrate experimental system, a temperature and pressure control system, a data image acquisition system, and CCD image

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acquisition system (data and image acquisition were recorded every 30 s and 90s, respectively). The volume of the high-pressure reactor with a transparent window was 540 cm³, and it was equipped with a stirrer with a range of 60-1200 r/min. The temperature sensor in the middle of the reactor could be accurately measured up to ±0.1 °C, and a pressure sensor with a measurement accuracy of ±0.01 MPa was inserted on top of the reactor.

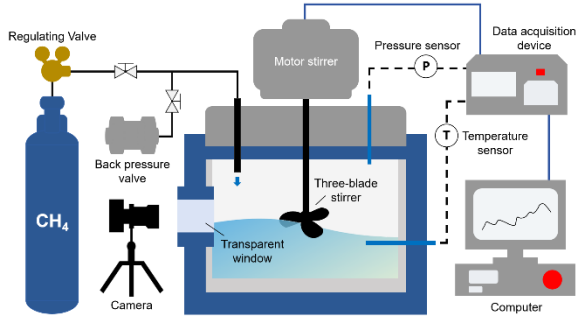


Fig. 1 Schematic diagram of the hydrate formation experimental setup

2.2 Experimental procedure

In this study, the specific steps for evaluating the kinetics of methane hydrates in ion systems were as follows:

1. After the air tightness check was completed, 100 mL of the target solution (with an ionic solution concentration of 3.5wt%) into the reactor, and the system was sealed. Next, methane gas was injected into the reactor and pressurized to 12MPa.
2. Put the reactor into the freezing circulator with the temperature set to 277.15 K, and waited for the temperature of the reactor to stabilize.
3. After the temperature and pressure of the reactor were stabilized respectively. Set the stirrer speed to 500 rpm, and started the data acquisition system for the experiment.

3. RESULT AND DISCUSSION

3.1 Effect of salt ions on the kinetics of methane hydrate formation

Before the start of the experiment, we carried out a cation test on the in-situ seawater, as shown in Fig. 2(a). Fig. 2(b) shows the induction time of methane hydrate in different salt ion systems. It is observed that the average induction time of methane hydrate in the NaCl system was the longest (405 min), which was about 6.6 times that of the pure water system (61 min). It indicated that this system had a strong inhibition effect on the formation of hydrate. The induction time of MgCl₂ and CaCl₂ systems was similar.

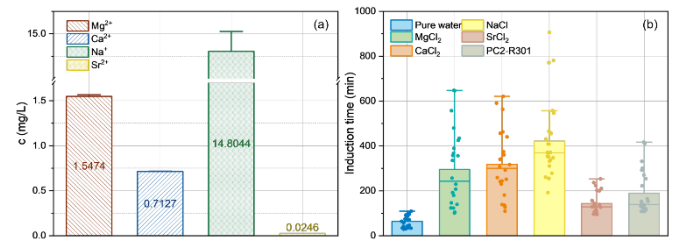


Fig. 2 (a) Ion concentration in seawater; (b) Comparison of the average induction time for methane hydrate formation in different systems

Fig. 3 shows the gas consumption of methane hydrate in different systems. There is an exact inhibition of hydrate formation by salt ions [7]. Both the ionic system and the in-situ seawater system showed an inhibitory effect on methane hydrate formation. It can be seen that in the early stage of hydrate nucleation, the change in the slope of the gas consumption curves of all systems showed a similar trend of rapid growth followed by slow growth. When methane hydrate formation started, the gas consumption rate increased rapidly and the gas consumption curves of each system almost overlapped (0-30 min). Then, as the reaction progressed, the gas consumption curves of each system gradually showed significant differences. The most significant inhibition of methane hydrate formation was observed for NaCl, which had the lowest gas consumption in this system and the curves stabilized after 400 min. The gas consumption curves of the MgCl₂ and CaCl₂ systems were almost the same, indicating that these two systems inhibited methane hydrate formation to a similar extent under the experimental conditions in this study. By calculating the methane consumption of the different systems during methane hydrate formation, we found that the order of the strength of the inhibition effect on hydrate formation was as follows: NaCl > in-situ seawater > MgCl₂ > CaCl₂ > SrCl₂, which was in agreement with the strength of ionic inhibition as shown by the experiments of Huang et al [8]. It may be due to the ions concentration during the hydrate formation can be more obviously increased due to the water converted to hydrate. Ion density may lead to a substantial increase, hindering the continued replenishment of water for hydrate growth [6][10]. Thereby, methane hydrate growth has been inhibited, and the formation of methane hydrate in the ionic system was inhibited compared to the pure water, and the gas consumption during the formation process was reduced accordingly.

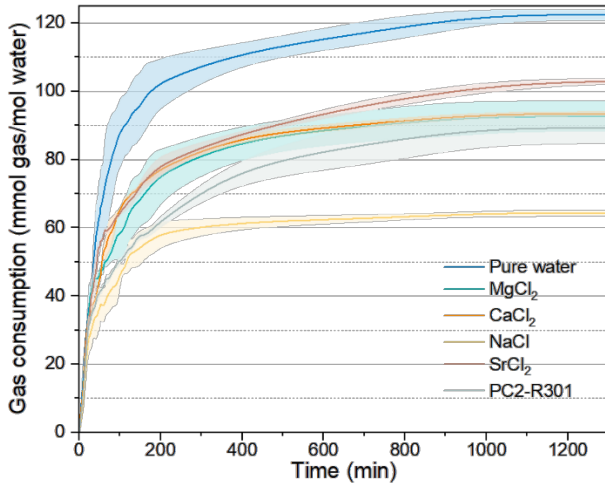


Fig. 3 Gas consumption profiles in different systems during a 1300-min period after methane hydrate nucleation

3.2 Comparison of methane hydrate morphological analysis for different ions

The hydrate growth behavior is closely related to the occurrence of mass transfer resistance during hydrate formation, which involves complex interactions between gas, liquid, and solid hydrates [12][13][14]. Fig. 4 shows the morphological changes of hydrate formation. At the 5th minute, except for the gas-liquid interface of the NaCl system where no obvious flocculent hydrate appeared, all the other experimental systems showed hydrates. Until the 20th minute when obvious hydrates appeared in all the systems, and the hydrates grew downwards with a gradual increase in thickness. At the 50th minute of methane hydrate formation, the hydrate propagates upward toward the gas phase. Next, it started to grow rapidly in both up and down directions and formed a fine hydrate layer, which covered the sapphire window. The blocky hydrate attached to the viewing window solidified with time and showed no further significant changes in the subsequent synthesis process, stabilized at the 50th minute. After the completion of hydrate generation, hydrates of pure water, ion (NaCl as a representative due to the hydrate of the ionic system presents a similar morphology), and seawater (PC2-R301) were selected for comparative observation on morphology in Fig. 4 (a)-(c). There were significant differences in morphology between the methane hydrate in the ionic and seawater and pure water systems. The hydrate surface of the pure water system was relatively smooth with a small amount of ice particles attached to the surface, and the hydrate particles were transparent, with good light transmittance. The ionic and seawater systems have the

common point that the hydrate is a dense powdery particle, the generated hydrate is dense and the surface is rough. The difference between the two lay in that seawater had a small number of ice particles on the surface, while the surface of the hydrate in the ionic system whether the ice particles was not obvious. It may be due to salt ions in hydrate crystal gaps during hydrate formation, which makes it more difficult to build a connection between the hydrate grains and leads to the formation of a loose hydrate structure [8]. Therefore, morphological studies of hydrates from different systems need to improve the experiments even further to better explain the reasons for the differences in the morphology of ions on hydrates as well as the mechanism of action.

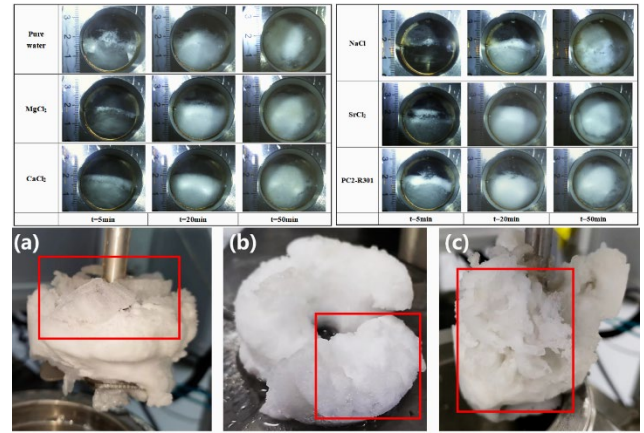


Fig. 4 Morphology of the hydrate generation process. (a) pure water system; (b) ionic system; (c) in-situ seawater system

4. CONCLUSIONS

In this study, we investigated the effect of different ionic systems as well as in-situ seawater on methane hydrate formation under the same pressure and temperature found in cold seep environments. The key conclusions are summarized as follows:

- 1) Ions significantly prolonged the induction time of hydrate generation. Na^+ had the strongest inhibition ability on methane hydrate nucleation, followed by in-situ seawater.
- 2) By calculating the methane gas consumption, we found that the order of inhibition effect on methane hydrate formation was as follows: $\text{Na}^+ > \text{in-situ seawater} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$.
- 3) Compared with pure water and in-situ seawater, the methane hydrate generated under the ionic system was denser and thicker with a rougher surface.

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