

Phase Equilibrium Characteristics of Methane Hydrate Formation in the Deep Sea

Yanyan Huang^{1,2}, Jing-Chun Feng^{1,2,*}, Pian Li¹, Mingrui zhang¹, Liwei Sun^{1,2}, Si Zhang^{1,3}, Zhifeng Yang^{1,2}

1 Institute of Environmental and Ecological Engineering, Guangdong University of Technology, Guangzhou, 510006, P. R. China

2 Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou, 511458, P. R. China

3 South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, P. R. China

ABSTRACT

Hydrate phase equilibrium in the most important foundation for other hydrate, especially for marine environment condition. In this study, a three-phase liquid water-hydrate-vapor equilibrium conditions for methane hydrate in aqueous solutions of NaCl + CaCl₂/MgCl₂/SrCl₂ mixture with a salinity of 34.5 in the temperature and pressure range of 283.65 – 288.85 K and 8.84 – 13.2 MPa have reported using a temperature search method. The ion categories, ion concentrations, temperature and pressure range were determined based on the situ conditions of haima cold seep. And the in situ concentrations of Mg²⁺, Ca²⁺, Sr²⁺ in haima cold seep were 1000 mg/L, 300 mg/L, 8 mg/L, respectively. Comparison of ions in the same ionic conditions with different ionic concentrations at the same salinity revealed that methane hydrate phase equilibrium in high salinity containing Ca²⁺, Mg²⁺ ion is mainly affected by salinity while the influence of cation concentration can be ignored, however, it is clearly observed that the inhibitory effect of Sr²⁺ on hydrate phase equilibrium increases with increasing cation concentration at a salinity of 34.5. This may be because Sr²⁺ has the smallest electron density and the smallest electrostatic force to interact with water molecules when intruding into the hydrogen bonding network within the water molecule, and has the weakest inhibitory effect on the hydrate. The inhibition effect of Sr²⁺ concentration on hydrate was more significant than Ca²⁺, Mg²⁺ at the same salinity.

Keywords: gas hydrate, hydrate inhibitors, phase equilibrium, seawater ions

1. INTRODUCTION

Cold seep is leakage pathway created by gravitational and tectonic forces, that is a specific geological phenomenon of a cryogenic fluid rich in methane and other hydrocarbons that lead to a series of geochemical reactions when it enters the seabed, and ultimately some of the methane may into water column and even enter the atmosphere(1, 2). It was reported that methane released from the seafloor accounts for 5~10% of the current global methane emissions to the atmosphere(3). As methane is a potential greenhouse gas to the global warming, it is significant to understand the balance between current and geological time of methane production, migration and emission on the seafloor(4). Therefore, understanding the ultimate fate of methane is critical, and is an important part of the global budget. The formation of methane hydrate on the seafloor during methane leakage is an important way to capture and fix methane. However, Phase equilibrium characteristic is the prerequisite to determine whether methane can form hydrate after leaking from the seabed. According to the survey, the salinity of "haima" cold seep is 34.5 and contains Ca²⁺, Mg²⁺, Sr²⁺, Na⁺, K⁺ and so on, in which the concentrations of Mg²⁺, Ca²⁺, Sr²⁺ are 1000mg/L, 300mg/L, 8mg/L respectively. In the experiment, the effects of ion concentration on hydrate phase equilibrium are studied systematically based on in situ salinity and ion concentration in "haima" cold seep. This will help to provide a reference for deep-sea carbon sequestration capacity.

2. MATERIAL AND METHODS

Hydrate forming gas (CH_4) used in this work were bought from Zhongshan Yigas CO, Ltd. The used water was deionized and had $> 18.2 \text{ M}\Omega$ of electric resistivity. The materials used in this study were presented in Table 1. All materials were used without further purification or treatment. The weight of salts was measured using a high

precision analytical balance to an accuracy of $\pm 0.0001\text{g}$. Nine groups of mixed salt solutions with different concentrations were made-up in the laboratory in table 2. All solutions were adjusted to a salinity of 34.5 with sodium chloride. An isochoric T-cycle method with step heating technique was employed in determining the phase equilibrium data of methane hydrate in the study.

Table 1 Specifications of the materials used in the experiments

Chemical Name	Molecular formula	Supplier	Purity
Sodium chloride	NaCl	Guangzhou Yankexin Biotechnology Co., Ltd.	99.9%
Calcium chloride	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	Guangzhou Yankexin Biotechnology Co., Ltd.	99.9%
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Guangzhou Yankexin Biotechnology Co., Ltd.	99.9%
Strontium chloride	SrCl_2	Guangzhou Yankexin Biotechnology Co., Ltd.	99.9%

Table 2 salts solution made-in the laboratory

number	Ionic category	Concentration(mg/L)
blank	Pure water	
1		1000
2	Ca^{2+}	300
3		8
4		1000
5	Mg^{2+}	300
6		8
7		1000
8	Sr^{2+}	300
9		8

* All solutions were adjusted to a salinity of 34.5 with sodium chloride

3. RESULTS

Fig 1, Fig 2, Fig3 show the phase equilibrium data of methane hydrate in aqueous solution with a salinity of 34.5 was adjusted with NaCl, where the concentration gradients of MgCl_2 , CaCl_2 , and SrCl_2 were 1000 mg/L, 300 mg/L, 8 mg/L. The 3.45wt% salt containing CaCl_2 , MgCl_2 , and SrCl_2 plays an important role of a hydrate inhibitor to block or delay hydrate formation. The average temperature decrease is about 1.8 K compared to the methane + water system at same pressure. And it also can be seen that the phase equilibrium conditions of methane hydrate in an aqueous mixture of inhibitors NaCl + CaCl_2 / MgCl_2 / SrCl_2 is more harsh for hydrate phase equilibrium conditions of methane system than NaCl aqueous solutions with a salinity of 34.5. In addition, it also seems that methane hydrate equilibrium in a salinity 34.5 solution containing 1000mg/L, 300mg/L, 8mg/L Ca

is change and the change is rough agreement with each other(Fig1). Moreover, the same phenomenon was observed for the three concentrations of Mg^{2+} (Fig2). This indicates that methane hydrate phase equilibrium in high salinity containing Ca^{2+} , Mg^{2+} ion is mainly affected by salinity while the influence of cation concentration can be ignored. However, it is clearly observed that the inhibitory effect of Sr^{2+} on hydrate phase equilibrium increases with increasing cation concentration at a salinity of 34.5(Fig3).

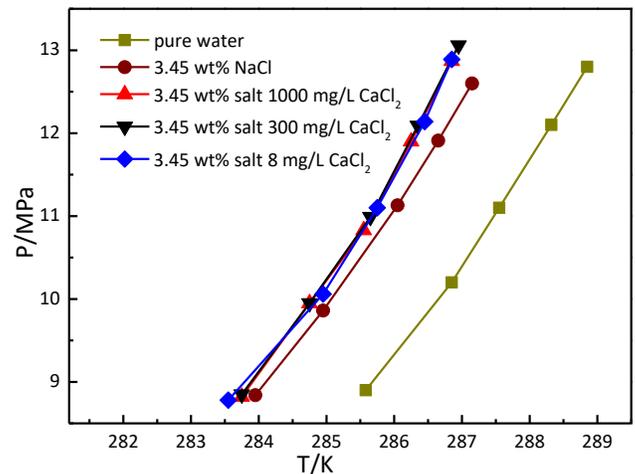


Fig. 1 phase equilibrium diagrams for methane hydrates in aqueous solution with a salinity of 34.5 contains different concentrations of Ca^{2+} .

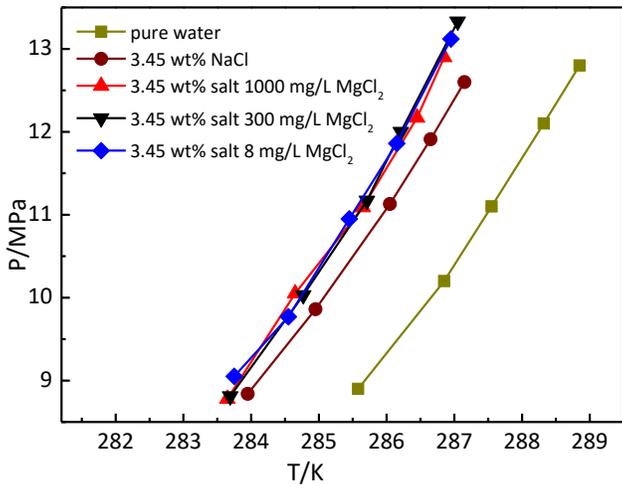


Fig. 2 phase equilibrium diagrams for methane hydrates in aqueous solution with a salinity of 34.5 contains different concentrations of Mg^{2+} .

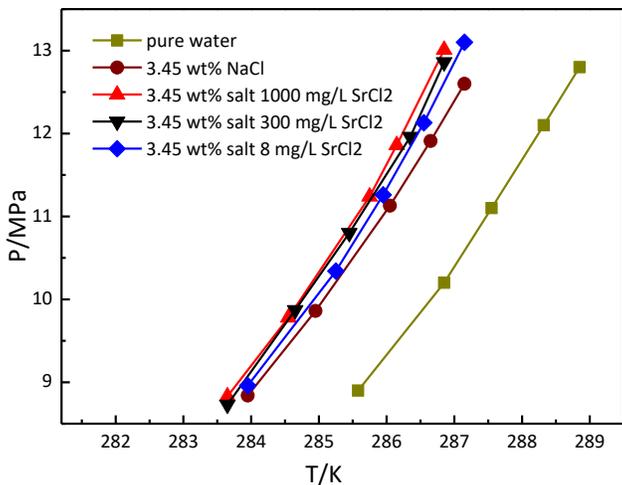


Fig. 3 phase equilibrium diagrams for methane hydrates in aqueous solution with a salinity of 34.5 contains different concentrations of Sr^{2+} .

4. DISCUSSION

When salts are added to water, the ions dissolved in water and interacted with the dipoles of water molecules. The interaction between water and hydrate guest molecules was weaker than that between water and salt ions. It reduces the concentration of the host water through a called "salting-out" and the addition of inhibitor salts hindered the connecting hydrogen bonds of water molecules(5). This property played an important

role in decreasing the fugacity of water. This in turn reduces the interaction between the guest and host water and ultimately prevents the formation of hydrate. The strength of ionic dipole bond between cations and water molecules is relevant to inhibit the formation of hydrates. The intensity of ionic dipole bond increased as cation concentration. This is to say, the formation of methane hydrate becomes more difficult at high ionic concentrations.

This suggests that the inhibition of methane hydrate by Ca^{2+} , Mg^{2+} , Sr^{2+} is greater than that by Na^{+} . The results appear to confirm Sabil(6) assertion that the inhibitor effect increases with increasing charge on the cation. One possible explanation for the phenomenon is that, the strong dipole interaction between water and salt ions disturbs the structure of water lattice around the clathrate hydrate guest molecules, thus inhibits the formation of hydrate. The strength of the salt ion-dipole bond between cations and water molecule may be related to the degree of inhibition of hydrate formation. The intensity of ion-dipole bond decreased with ionic radius, and increased as the charge z of the cation(6). Therefore, the cations with smaller ionic radius and higher charge were expected to have a stronger interaction with water molecules, which inhibited the methane hydrate formation more effectively. Because Ca^{2+} , Mg^{2+} and Sr^{2+} had +2 charge, and Na^{+} +1 charge, it was proved that the cation with higher charge has stronger hydrate inhibition. So an aqueous mixture of inhibitors $NaCl + CaCl_2/MgCl_2/SrCl_2$ had a more marked inhibition effect on the formation of methane hydrate than $NaCl$ aqueous solutions.

Methane hydrate phase equilibrium in high salinity containing Ca^{2+} , Mg^{2+} ion is mainly affected by salinity while the influence of cation concentration can be ignored. However, it is clearly observed that the inhibitory effect of Sr^{2+} on hydrate phase equilibrium increases with increasing cation concentration at a salinity of 34.5. The tendency of the effect of cation (Ca^{2+} , Mg^{2+} , Sr^{2+}) on the phase equilibrium of gas hydrate is not the same. The radius of Mg^{2+} , Ca^{2+} , and Sr^{2+} are 0.72Å, 0.99 Å and 1.13 Å, respectively, and they have same charge. Therefore, Sr^{2+} has the smallest electron density and the smallest electrostatic force to interact with water molecules when intruding into the hydrogen bonding network within the water molecule, and has the weakest inhibitory effect on the hydrate(7). The inhibition effect of Sr^{2+} concentration on hydrate was more significant than Ca^{2+} , Mg^{2+} at the same salinity. So at the same salinity, ions with weaker inhibition of

hydrate showed more significant differences in the inhibition of hydrate by ion concentration.

5. CONCLUSIONS

Phase equilibrium conditions of methane hydrate in an aqueous mixture of inhibitors NaCl + CaCl₂/MgCl₂/SrCl₂ is more harsh for hydrate phase equilibrium conditions of methane system than NaCl aqueous solutions with a salinity of 34.5. The strength of the salt ion-dipole bond between cations and water molecule may be related to the degree of inhibition of hydrate formation. The intensity of ion-dipole bond decreased with ionic radius, and increased as the charge z of the cation. Ca²⁺, Mg²⁺, Sr²⁺ have stronger inhibition effect on methane hydrate than Na⁺ at same salinity.

Sr²⁺ has the smallest electron density and the smallest electrostatic force to interact with water molecules when intruding into the hydrogen bonding network within the water molecule, and has the weakest inhibitory effect on the hydrate. Therefore, The inhibition effect of Sr²⁺ concentration on hydrate was more significant than Ca²⁺, Mg²⁺ at the same salinity.

ACKNOWLEDGEMENT

REFERENCE

- [1] Boetius A, Wenzhoefer F. Seafloor oxygen consumption fuelled by methane from cold seeps. *Nature Geoscience*. 2013;6(9):725-34.
- [2] Suess E. Marine cold seeps and their manifestations: geological control, biogeochemical criteria and environmental conditions. *International Journal Of Earth Sciences*. 2014;103(7):1889-916.
- [3] Etiope G, Milkov AV. A new estimate of global methane flux from onshore and shallow submarine mud volcanoes to the atmosphere. *Environmental Geology*. 2004;46(8):997-1002.
- [4] Kvenvolden KA, Rogers BW. Gaia's breath - global methane exhalations. *Marine And Petroleum Geology*. 2005;22(4):579-90.
- [5] Priya T, Mohanta VL, Mishra BK. Performance evaluation of zirconium oxychloride for reduction of hydrophobic fractions of natural organic matter. *Separation And Purification Technology*. 2017;174:104-8.
- [6] Sabil KM, Roman VR, Witkamp GJ, Peters CJ. Experimental observations on the competing effect of tetrahydrofuran and an electrolyte and the strength of hydrate inhibition among metal halides in mixed CO₂

hydrate equilibria. *Journal Of hemical Thermodynamics*. 2010;42(3):400-8.

- [7] Xiao C, Wibisono N, Adidharma H. Dialkylimidazolium halide ionic liquids as dual function inhibitors for methane hydrate. *Chemical Engineering Science*. 2010;65(10):3080-7.