Effect of ions on Methane Hydrate Phase Equilibrium in Deep-Water Environment of "Haima" Cold Seep

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ABSTRACT

The mechanism researches on seabed methane fate are a critical part to reveal the global methane budget. Hydrate formation by natural gas bubbles in the course of seepage is an essential way for methane capture and fixation. Nevertheless, the hydrate phase equilibrium characteristics that affect the stability of hydrate formation during the bubble ebullition process are unclear. "Haima" cold seep is a typical active methane seeping environment associated with abundant methane hydrate, which necessitates unveiling the stability of methane hydrate formation. This work investigated the hydrate phase equilibrium conditions based on the in-situ water depth and practical ion categories and salinity. The results show that the strength of inhibition of methane hydrate in chloride salts of 3.45wt% salinity was in the order of $Mg^{2+} > Na^+ > Ca^{2+} > K^+$, $Mg^{2+} > Ca^{2+} > Mn^{2+} > Ba^{2+}$. The mechanism of different ions categories effect on hydrate equilibria can be elucidated by the difference of charge and radius of the ions. Hydrate phase transition enthalpies was calculated by the Clausius-Clapeyron equation. The response law of hydrate phase transition enthalpy was almost consistent with the phase equilibrium change. This work have important reference value for the mechanism exploration about how hydrate formation characteristic is influenced by ions in "Haima" cold seep environment.

Keywords: gas hydrate, phase equilibrium, seawater ions, cold seep

1. INTRODUCTION

With the increasing demand for energy, natural gas hydrate (NGH) have gained widespread attention as a potential new strategic energy. NGH, a caged ice-like solid compound with CH_4 as the main gas component, is stable in special conditions of high pressure and low temperature and is a major form of global unconventional natural gas [1]. NGH exploitation is an effective way to obtain natural gas, but it may lead to a series of environment problems, such as seawater acidification, geological damage, global warming, et al [2]. Therefore, the ecological environment problems have been receiving extensive attention. Cold seep is a geological phenomenon that the fluid rich in methane and other hydrocarbons overflows from the seabed sediment interface, provides a basis for the decomposition and leakage of natural gas hydrate. A large number of cold seeps formed by methane escape from the seafloor have been found in major seas around the world. The seeped CH_4 can be converted into viscous gas hydrate and can be sequestrated in the deep-sea environment [3]. The prerequisite for hydrate formation depends on the hydrate phase equilibrium condition, which directly determines the stable existence of NGHs, and can also affect their formation kinetics [4]. Hydrate phase equilibrium refers to the temperature and pressure conditions of gas-liquid-hydrate three-phase conversion equilibrium, generally influenced by ion categories, ion concentrations, gas components, porous media [5]. Studies on the characteristics of hydrate phase equilibrium in cold seep area are scarce. In this work, the phase equilibrium characteristics of NGH formation in the salt solution condition from the deep-sea "Haima" cold seep was investigated. The in-situ seawater sample was acquired from "Haima" cold seep and the experimental samples were prepared according to the seawater salinity and contained cations. Based on the in-situ composition, the effects of cation categories on methane equilibrium were examined. It should be mentioned that although the contents of Na^+, Mg^{2+}, Ca^{2+}, K^+, Mn^{2+}, Ba^{2+} in the collected seawater samples are limited. Higher those cation content might exist in deep marine sediments or in other marine environments. It is necessary to study the effect of those cations on methane hydrate phase equilibrium, which could provide references for the other environments.

2. MATERIAL AND METHODS

Fig.1 shows the phase equilibrium measuring apparatus used in this work. Hydrate forming gas (CH_4) used in this work were supplied by Zhongshan Yigas CO, Ltd. The bottom water was obtained from 1350 m depth in the area of "Haima" cold seep by our team, which contains cation Na^+, Mg^{2+}, Ca^{2+}, K^+, Mn^{2+}, Ba^{2+} and the salinity of 3.45wt%. All chemicals were used as received from Yankexin Biotechnology Co., Ltd. The used water was deionized and the electric resistivity > 18.2 MΩ. An isochoric T-cycle method with step heating technique was employed in determining the phase equilibrium data of methane hydrate in the study.
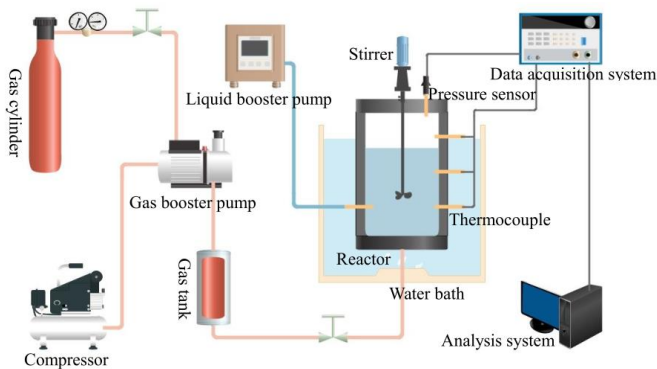

Fig. 1 Schematic diagram of the experimental apparatus

3. RESULTS AND DISCUSSION

3.1 Effect of salt category on methane hydrate phase equilibrium condition

Salt is a common thermodynamic inhibitor. Adding salt will reduce hydrate stability and make hydrate formation more difficult. Fig.1 and Fig.2 show the phase equilibrium condition of methane hydrate in four common salt aqueous solutions and different divalent ion salt solution with a salinity of 3.45wt%, respectively. The P-T curves of CH_4 hydrate formed in salt solutions were significantly shifted to the left than that in pure water. This is to say, the presence of 3.45 wt% salts played an important role of a hydrate inhibitor to block or delay hydrate formation, which can be mainly attributable to the decrease in water activity [6]. This is because the Coulomb force between ions and water molecules is stronger than the van der Waals force between water and gas molecules when compared to the hydrogen bond between water molecules. This leaded to the aggregation of a large number of water molecules around the ions and resulted in the decrease in water activity.

In the meanwhile, it is quite clear from Fig. 1 that the common salts inhibition effect on methane hydrate is in the order of $Mg^{2+} > Na^+ > Ca^{2+} > K^+$ at salinity of 3.45wt%. The result is consistent with the experimental results of Li et al [7]. Fig. 2 shows the inhibitory effect of divalent ion on methane hydrate is $Mg^{2+} > Ca^{2+} > Mn^{2+} > Ba^{2+}$. The inhibition mechanism of ion categories on hydrate formation mainly stems from the dipole force on water molecules. The stronger interaction between water with salt ions interferes with the organization of the water lattice around the clathrate hydrate guest molecule and inhibits hydrate formation [8]. The strength of the salt ion-dipole bond between the cation and water molecules may correlate with the degree of inhibition of hydrate formation. Generally, the strength of the dipole force increases with increased ionic charge and decreased radius, in which the effect is commonly stronger for anions than that of cations. Table 1 shows the radius of each cation that can explain the strength of the inhibitory effect of divalent cations on methane hydrate phase equilibrium. Although the concentration of those cations in the detected in-situ seawater environment was relatively low, higher cations content might exist in deep marine sediments or in other marine environments. The regulation about those cations affecting hydrate phase equilibrium obtained in this study could provide reference for the other marine environments.
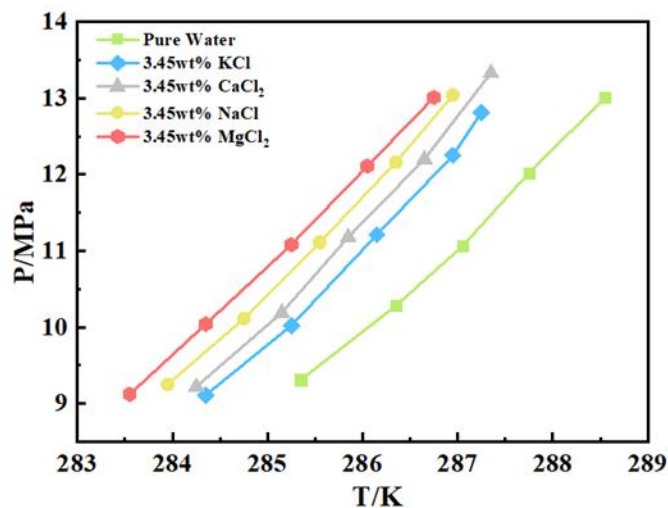

Fig. 2 Phase equilibrium conditions of CH_4 hydrate in 3.45wt% four common salt solutions.

Table 1 Ionic radii

Ion	Ionic radii(Å)
Na^+	1.02
Mg^{2+}	0.72
Ca^{2+}	1
Ba^{2+}	1.35

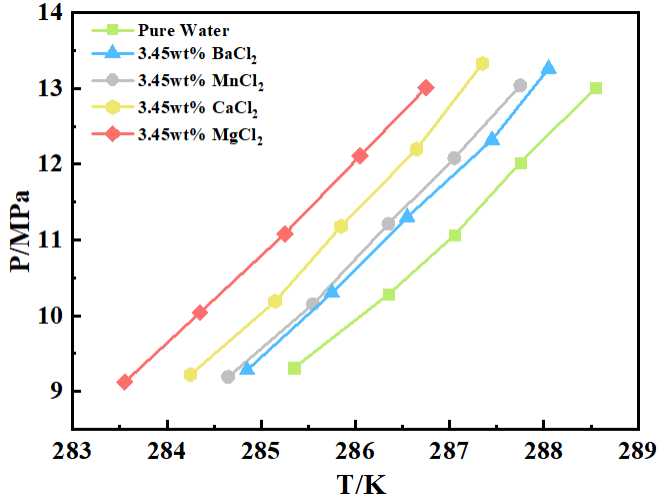|	
Mn^{2+}	0.83
K$^+$	1.38
Cl$^-$	1.81

Fig. 2 Phase equilibrium conditions of CH$_4$ hydrate in 3.45wt% different divalent ion salt solution.

3.2 Methane hydrate phase transition enthalpy

The hydrate phase transition enthalpy reflects heat change in the formation/decomposition of 1 mol hydrate. In this work, the enthalpy of hydrate decomposition was calculated by the Clausius-Clapeyron equation [9]:

$$\frac{d\ln P}{d\,1/T} = \frac{-\Delta H}{zR}$$

The hydrate phase transition enthalpy can be calculated by linear fitting with $\ln P$ as the ordinate and $1/T$ as the abscissa shown in Fig. 3 and Fig. 4. It can be found that the value of $\ln P$ and $1/T$ have a good linear relationship, indicating the reliability of the experimental data. As shown in Table 2, the calculated phase transition enthalpy of CH$_4$ hydrate in pure water and salt solution. Compared with the deionized water system measured in the experiment, the hydrate enthalpy in the salt solution system decreased [10]. Moreover, the higher is the inhibition effect of cations, the lower will be the hydrate formation. If the amount of hydrate formation is lower under the same conditions, the amount of heat required to dissociate that particular piece of hydrate will likewise be lower. Therefore, the hydrate phase transition enthalpy is significant and is linked to salt inhibition strength. From Fig.3 and Fig. 4, we can see the hydrate phase transition enthalpy is high for the methane hydrate in pure water. And the hydrate phase transition enthalpy in 3.45wt% chloride salt

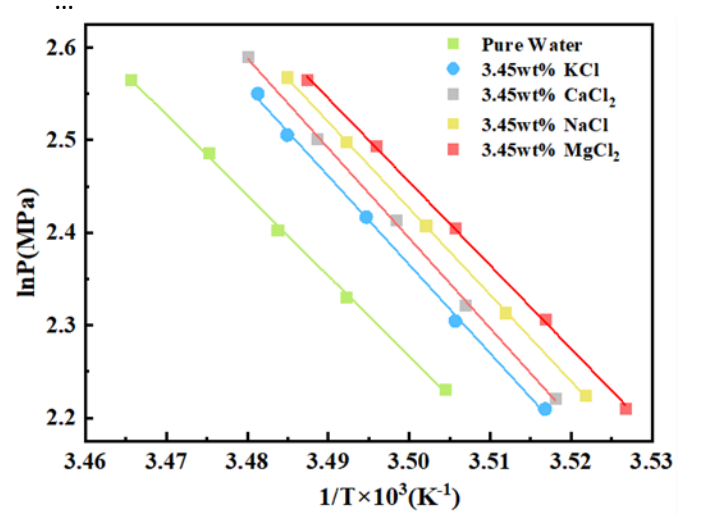system follows the order is consistent with its inhibitory effect on methane hydrate.

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Fig. 3 $\ln P$ and $1/T$ fitting relationship of hydrate equilibrium under 3.45wt% salt solution.
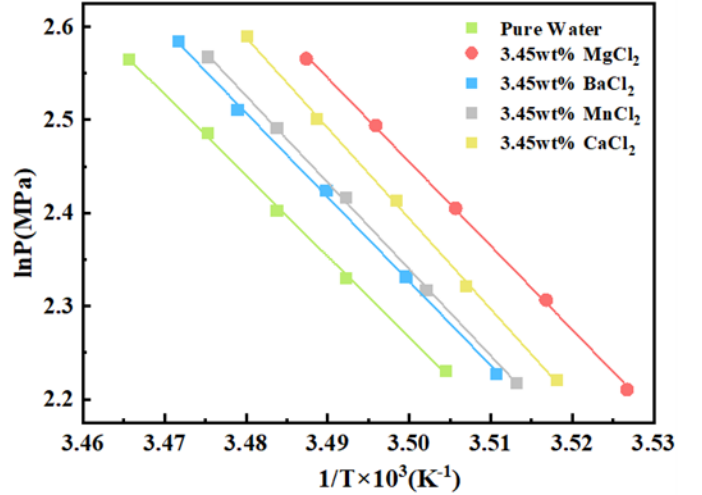

Fig. 4 $\ln P$ and $1/T$ fitting relationship of hydrate equilibrium under 3.45wt% salt solution.

Table 2 Hydrate phase transition enthalpies calculated by the Clausius−Clapeyron

Sysystem	T/K	P/Mpa	R^2	Z	$\triangle H(kJ/mol)$
Pure Water	285.35-288.55	9.31-13.01	0.9989	0.8123-0.830	58.754-60.107
NaCl	283.95-286.95	9.25-13.04	0.9999	0.8076-0.8282	56.720-58.320
KCl	284.35-287.25	9.11-12.81	0.9986	0.8093-0.8309	57.421-59.140
$MnCl_2$	284.65-287.75	9.19-13.01	0.9995	0.8099-0.8307	57.634-59.243
$MgCl_2$	283.55-286.75	9.12-13.01	0.9995	0.8071-0.8288	56.152-68.150
$CaCl_2$	284.25-287.35	9.22-13.33	0.9992	0.8079-0.8293	57.298-59.028
$BaCl_2$	284.85-288.05	9.28-13.26	0.9989	0.8101-0.8301	57.887-59.391

4. CONCLUSIONS

In this work, the effect of six cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Ba^{2+}) on methane hydrate phase equilibrium were investigated based on in-situ "Haima" cold seep environment. The results show that the inhibition effect of ions on CH_4 hydrate formation is as following sequence of Mg^{2+} > Na^+ > Ca^{2+} > K^+ and Mg^{2+} > Ca^{2+} > Mn^{2+} > Ba^{2+}. It is found that the effect of ions on the phase equilibrium of CH_4 hydrate increases with the decrease of radius, in which Ions disrupt the crystal lattice of water molecules by weakening their hydrogen bonds. Ions with smaller ionic radii have higher charge densities, which results in stronger electrostatic connections and weaker hydrogen bonding interactions between water molecules and ions. hydrate phase transition enthalpy in 3.45 wt% salt solution is significantly higher than that in pure water. This work have important reference value for the mechanism exploration about how hydrate formation conditions in "Haima" cold seep.

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