



Effect of seawater ions on cyclopentane-methane hydrate phase equilibrium



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ABSTRACT

In present work, phase equilibrium of cyclopentane-methane hydrate formed in different salt solution systems was studied using an orthogonal test method. The target ions including four cations (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) and two anions (Cl^- , SO_4^{2-}) were employed. The experimental results showed that the equilibrium temperature of cyclopentane - methane hydrate decreased when four cations (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) and two anions (Cl^- , SO_4^{2-}) were added. The equilibrium temperature decreased with the increase of ion concentrations. Analysis of variance suggested that cations presented a sequential inhibition effect on hydrate formation as follows: $Mg^{2+} > Ca^{2+} > Na^+ > K^+$, while Cl^- ion had a much stronger hydrate inhibition effect than SO_4^{2-} ion. The hydrate inhibition strength of an ion depended on the charge and radii of ion. The inhibitory effects of ions became intensified with the charge increased and radius decreased. And the radius of ions played a more significant role than charge of ions in altering hydrate phase equilibrium.

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1. Introduction

Clathrate hydrates are non-stoichiometric compounds formed by a lattice of strong hydrogen bonded water, which are composed of host water molecules and guest molecules, such as CH_4 , C_2H_6 , H_2 , CO_2 and so on. Water molecules form the cage-like structures under appropriate thermodynamic conditions [1]. These cages are partially occupied by the guest molecules to stabilize the cage structure of hydrate [2]. Based on the structural characteristics of hydrate, hydrate technology can be proposed in desalination of seawater, which is a novel method with convenient operation and low energy consumption.

Javanmardia et al. [3] analyzed the energy consumption and economy of hydrate-based desalination compared with the other methods. It was found that as long as the suitable hydrate promoter was found, the hydrate-based desalination method was more competitive. The researchers studied hydrate-based desalination

technology with different guest hydrate molecules, such as CH_3CCl_2F , C_2H_4 , CO_2 and cyclopentane (CP) and so on [1,4,5]. Kar-amoddin et al. [1] studied the feasibility of desalination by R141b hydrate formation. The removal percents of dissolved mineral reached 59–70%. Yang et al. [6] investigated the thermodynamic and kinetic characteristics of CO_2 hydrate with C_3H_8 as the co-guest for desalination. Cha et al. [4] proposed a new gas hydrate-based desalination technique by selecting hydrate promoters, CP and cyclohexane (CH), which were insoluble in water. They acted as the secondary hydrate guests to make hydrate formation temperature mild, which could accelerate the hydrate formation and increase energy efficiency of the desalination process. Recently, CP is regarded as an appropriate hydrate promoter, which could lower phase equilibrium temperature of hydrate [2,7–9]. Corak et al. [10] suggested that the formation of simple CP hydrate could be applied to desalination. However, the nucleation rate of simple CP hydrate was so slow that the hydrates started to form when the temperature was lower below 273 K for 24 h [11]. Since the secondary guest substances introduced would guarantee large stabilization energy for the hydrate framework, hydrate nucleation could be achieved easily. Several studies reported the phase equilibrium conditions in CP binary system with different secondary guest substances, such

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as CH₄, CO₂, N₂, H₂, O₂ and so on [12–14]. Comparison of these hydrates, the CP-CH₄ hydrate formation temperature is higher.

With hydrate formation, the seawater is concentrated and the salinity of unreacted seawater is raised. However, the salts have a great influence on the stability of hydrate. Lu et al. [15] investigated the effects of different ionized ions in the salt solution on dissociation conditions of CO₂, CH₄ and C₃H₈ hydrate. It was noticed that the equilibrium temperature of methane hydrate with MgCl₂ was lower than that of methane hydrate with MgSO₄, but not difference between CaCl₂, KCl and NaCl. The experimental results showed that dissociation condition of gas hydrate in electrolyte solution was more determined by anion compared with cation. Sabil et al. [16] compared the effect of salts with different anions and cations on dissociation condition of CO₂-tetrahydrofuran (THF) hydrate. The experimental results did not confirm the conclusion by Lu et al. [15] They found that Mg²⁺ presented the most obvious inhibition while K⁺ had the weakest influence. And among the anions studied, the strength of hydrate inhibition decreased in this order: Br⁻ > Cl⁻ > F⁻. The results showed that the ionic-hydrogen bond strength between ions and water molecules, and the influence of this bond on the surrounding water network were main factors for the inhibition of hydrate by electrolytes. Cha et al. [17] measured the experimental data on methane hydrate phase equilibria in the presence of potassium chloride (KCl), sodium chloride (NaCl), and ammonium chloride (NH₄Cl) using isochoric and high-pressure differential scanning calorimetry (DSC). The experimental results from isochoric method were in good accordance with those from DSC method. The inhibition strength of sodium cation to hydrate was slightly stronger than that of potassium and ammonium cations. Najibi et al. [18] measured the locus of incipient hydrate–liquid water–vapour (H–L_W–V) curve for quaternary systems of methane with aqueous solution of ethylene glycol or methanol and salts such as CaCl₂, NaCl and KCl in wide range of concentrations and pressures. Jager et al. [19] measured the equilibrium data of the quaternary system methane + water + methanol + sodium chloride, and established the inhibiting effect of a mixture of methanol and electrolyte on the hydrate phase equilibria. The dissociation conditions of methane hydrates in the presence of a binary mixture of NaCl, KCl, or CaCl₂ with either ethylene glycol or methanol at different temperatures were also reported [20,21]. Zha et al. [22] obtained the phase equilibrium data of CO₂ hydrate in presence of binary electrolytes aqueous solutions at four different concentrations, which contained NaCl and MgCl₂. Kang et al. [23] found the addition of inhibitor MgCl₂ hindered water molecules in linking hydrogen bonds. This property played an important role in reducing the fugacity of water. Mech et al. [24] investigated the effects of THF and NaCl at various concentrations on the phase equilibrium of methane hydrate. The inhibition effect of NaCl was found to be greater at higher pressure conditions compared to lower pressure conditions. And with an increase on the concentration of NaCl solution, the effect of THF on hydrate formation was diminished. Dholabhai et al. [25] obtained phase equilibrium conditions of CO₂ hydrate in electrolyte solutions containing NaCl, KCl, CaCl₂, or their binary mixtures.

While there are numerous phase equilibrium studies carried out on hydrate equilibrium with single salt system, few data are available for hydrate equilibrium with salt mixture systems. The major chemical ions contained in seawater are chloride, sodium, sulfate, magnesium, calcium and potassium. If these kinds of ions and different concentrations of aqueous salt solution are taken into account, the number of trails is large. At the same time, it will be a very heavy workload for statistical analysis and calculation of a large number of experimental data. In this paper, the effects of cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) and anions (Cl⁻, SO₄²⁻) on the phase equilibria of CP-CH₄ hydrates are studied systematically. In view of

the fact that there are many kinds of ions and different concentrations of aqueous salt solution, the influencing degree of every kind of ion on the phase equilibrium of CP-CH₄ hydrate is analyzed by using orthogonal test method. The experimental data is analyzed by using the analysis of variance.

2. Experiments

2.1. Materials

The materials used are presented in Table 1. All materials were used without further purification or treatment. The deionized water with the resistivity of 18.25 mΩ cm⁻¹ was generated by an ultra-pure water system which was supplied by Nanjing Ultrapure Water Technology Co., Ltd., China. The cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) with different concentrations were obtained by NaCl, KCl, CaCl₂ and MgCl₂, respectively. And the anions (Cl⁻, SO₄²⁻) with different concentrations were originated from NaCl and Na₂SO₄, respectively.

2.2. Experimental apparatus

The experimental apparatus used in this study is shown in Fig. 1. A high pressure reactor was used as the hydrate formation and dissociation reactor. The reactor was made of 316 stainless steel and the effective volume of reactor was of 398 mL. The maximum sustaining pressure was up to 30 MPa. The reactor was immersed in water bath, which had a working temperature range of 258.15 K to 363.15 K. At the front and back of the reactor, two Plexiglas visual windows were installed. A three-paddle helical impeller driven by magnetic system was installed in the reactor. The reactor pressure was controlled by a proportional-integral-derivative (PID) controller through a pressure-regulated valve (Tescom ER3000). The pressure of the reactor was measured by MBS3000 absolute pressure transducer (range of 0–25 MPa) with the accuracy of ±0.02 MPa. The temperatures in the reactor and water bath were measured using Pt1000 thermoprobes (JM6081) with the uncertainty of ±0.05 K. All of the data were automatically recorded every 10 s by a data logger (Agilent 34970A).

2.3. Experimental procedure

An isochoric T-cycle method with step heating technique was employed in determining the phase equilibrium data of CP-CH₄ hydrate. Prior to the experiments, the reactor was successively washed by deionized water and target solution selected in the experiment. Then 220 mL target solution and 5 mL CP was completely filled in the reactor. A small amount of CH₄ was introduced into the reactor, which was flushed at least three times to ensure that there are no traces of the air in the reactor. Then the reactor was pressurized with CH₄ to an approximation of 2.5 MPa. Subsequently, the system was cooled down until the hydrates begin to form in the reactor. Hydrate formation in the reactor was observed through the visual windows. The temperature was slowly rising up with a temperature step of 0.1 K to make a gradual hydrate dissociation until an ignorable amount of hydrate stayed in liquid phase. In order to establish equilibrium adequately, pressure was allowed to remain stable for at least 3h. The changes of temperature and pressure were recorded and depicted in a P-T curve. The intersection point in the P-T diagram was the hydrate phase equilibrium point.

2.4. Analysis of variance

The sum of squares SS_j was calculated by the following equation.

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