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Clathrate hydrate dissociation conditions and structure of the methane + cyclopentane + trimethylene sulfide hydrate in NaCl aqueous solution

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ABSTRACT

In present work, the phase equilibrium of methane + cyclopentane (CP) + timethylene sulfide (TMS) hydrate were measured in NaCl solution at the temperature range from 286.42 to 303.77 K and the pressure varying from 1.16 to 12.49 MPa. The experimental data were measured with an isochoric T-cycle method. The phase equilibrium pressure of organic compounds (V_{CP}:V_{TMS} = 4:1) + CH_4 hydrate increases with the temperature and the NaCl concentration. When the temperature was higher, the effect of temperature and NaCl concentration on the phase equilibrium pressure was more remarkable. The dissociation enthalpies of organic compounds (V_{CP}:V_{TMS} = 4:1) + CH_4 hydrate in 3.5, 5.0, 7.0, 10% (mass fraction) NaCl solution were calculated through the Clausius–Clapeyron equation based on the phase equilibrium data. The dissociation enthalpy decreases with the increase of either the temperature or the NaCl concentration. The crystal structure of organic compounds (V_{CP}:V_{TMS} = 4:1) + CH_4 hydrate was determined by using Raman spectroscopy. Methane was present only in the small sII cavity, cyclopentane and timethylene sulfide were all in the large sII cavities.

1. Introduction

Clathrate hydrates are non-stoichiometric, icelike crystals formed by water and guest molecules under low temperature and high pressure [1]. Hydrogen bonding between water molecules forms cavities and the guest molecules are encapsulated in the cavities, such as gases and organic compounds. Typical gas molecules include methane (CH_4), carbon dioxide (CO_2), ethane (C_2H_6) and propane (C_3H_8) etc [2]. Empty hydrate lattice is like a high efficiency gas reservoir, one cubic meter of hydrate can hold approximately 160–180 m^3 of natural gas [3]. So natural gas hydrates (NGHs) formed in permafrost regions and in deep oceanic sediment have been considered to be a potential strategic energy resource [4,5].

Some methods of NGHs production have been presented, such as (1) depressurization [6–9], to reduce the reservoir pressure below the decomposition pressure of hydrate; (2) thermal stimulation [10–13], to produce gas from hydrates by increasing the reservoir temperature of the gas hydrate above the equilibrium temperature; (3) inhibitor injection [14,15], to inject chemicals such as glycol or methanol to change the phase equilibrium; (4) CO_2 replacement [16,17], to replace the methane molecules with the carbon dioxide molecules in the hydrate structure. However, each of these methods has its own advantages and disadvantages. The heat required to dissociate hydrates of thermal stimulation only accounts for 10% of the calorific value of the natural gas produced [18]. However, the heat injected into reservoir can spread to not only the NGHs zone, but also the surrounding zone where there may not be natural gas hydrates. Therefore, the heat loss is considered to be the major disadvantage [19]. The method of inhibitor injection may be effective but a large number of these expensive chemical additives are required to ensure hydrate decomposition and gas production. At the same time, the pollution of the environment caused by chemical inhibitor injection may be another weakness. In order to enhance the energy efficiency of

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thermal stimulation, we proposed a novel technology to prepare hot brine in-situ seafloor by hydrate formation for NGHs exploitation in marine sediment [20]. A hydrate forming agent is injected into an apparatus installed in-situ seafloor, in which the hydrates form rapidly under the condition of temperature and pressure on the seafloor. During the formation of hydrates, the water in the apparatus is gradually consumed and heat is released by hydrate formation. So the salinity and the temperature of residual seawater are raised. Thus, the hot residual seawater is injected into NGHs reservoirs for NGHs dissociation. This technology combines the advantages of thermal stimulation and inhibitor injection, and heat losses also reduce.

Selecting out suitable hydrate forming agent plays an important role in this technology. The hydrate forming agent should form hydrate rapidly under the submarine pressure and the certain salinity ($\geq$3.5% wt) condition. Besides, it would be insoluble in water, nontoxic or low toxic to the environment and easily recycled in use. The hydrate formation enthalpy should be as high as the heat of the residual brine [21]. Some water-insoluble hydrate forming agents like cyclohexane, cyclopentane (CP), methlcyclohexane, etc. were found to raise hydrate formation temperature [22]. Matsumoto et al. [23] investigated phase equilibrium of the mixed hydrate composed of methane and fluorocyclopentane, chlorocyclopentane, or bromocylopentane. The equilibrium pressure of each hydrate mixture is lower than that of the simple methane hydrate. Especially, the methane + floorocyclopentane hydrate has the lowest equilibrium pressure among three mixed hydrate. Trueba et al. [24] found that the stability of the mixed organic clathrate hydrates with hydrogen could be enhanced compared to the pure one. The stabilities of the mixed organic clathrate hydrates with hydrogen could be summarized in the following order: cyclopentane > furan > tetrahydropyran > 2,5-dihydrofuran > 1,3-dioxolane. Mohammadi et al. [25] reported hydrate formation conditions for two systems: the carbon dioxide + cyclooctane/cycloheptane + water and the methane + cyclooctane/cycloheptane + water. And the results indicated that both cyclooctane and cycloheptane can reduce the formation pressure of carbon dioxide or methane hydrates. The phase equilibrium of CH_4 + c-C_5H_9Br mixed hydrate was measured and the cage occupancy of guest species was clarified by Raman spectroscopy [26]. c-C_5H_9Br occupied the $5^{12}6^8$-cages of s-H hydrates with the support of CH_4 occupying the 5^{12}- and $4^35^66^3$-cages. Ripmeester et al. [27] reported the thermodynamic equilibrium of water + trimethylene sulphide/ethanethiol/dimethyl sulphide system, and indicated that the hydrates formed by cyclic sulphides and dimethyl sulphide behaved higher equilibrium temperature than the hydrates formed by the corresponding ethers. Zylyftari et al. [28] measured the equilibrium temperature and cumulative dissociation heat of cyclopentane hydrate in brine system using micro-differential scanning calorimeter. Salako et al. [29] investigated the effect of NaCl on adsorption of sodium dodecyl sulfate (SDS) at CP hydrate-water interface. The adsorption of DS^- ions is responsible for accelerated enclathration even with a salt in solutions. Our previous data demonstrated that the hydrate promotion effectivenesses with methane can be ranged as follows: trimethylene sulfide > cyclopentane > tetrahydrothiophene > cyclopentanone > cyclopentyl chloride and cyclohexene > methylcyclopentane [30]. Trimethylene sulfide (TMS) can form the hydrates at the lower pressure and higher temperature in pure water and release larger amounts of heat. And there were a few studies on the equilibrium data of binary hydrates of cyclopentane with gas [31,32].

In the present study, trimethylene sulfide and cyclopentane were adopted as hydrate forming agents. The four-phase (gas phase, aqueous, organic phase and hydrate) equilibrium curves of the CH_4+ CP + TMS mixed hydrate system were measured in 3.5, 5.0, 7.0, 10% (mass fraction) NaCl solution. The formation/dissociation enthalpies of CH_4 + CP + TMS hydrates in NaCl solution were determined based on the corresponding phase equilibrium data. The structure of CH_4 + CP + TMS mixed hydrate was identified by using Raman spectroscopy.

2. Experimental section

2.1. Materials

The chemicals used are presented in Table 1. The deionized water was used with the resistivity of 18.25 mΩ cm^{-1}, which was produced by an ultra-pure water system supplied by Nanjing Ultrapure Water Technology Co., Ltd., China. All chemicals used in this work were not repurified.

2.2. Experimental apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. This experimental apparatus is used to measure the data on mixed hydrate phase equilibrium. The apparatus mainly consisted of a stainless steel reactor, which is immersed in a temperature-controlled water bath. The maximum effective volume and working pressure of reactor are 398 mL and 30 MPa, respectively. There are two circular visual windows made of Plexiglas on the front and back of the reactor. The formation of hydrate in the reactor can be observed through the visual windows. The magnetic stirring bar placed at the bottom of the reactor or the magnetically driven three-paddle helical impeller placed on the top of the reactor is used to agitated contents in the reactor. The pressure of the reactor is controlled by proportional–integral–derivative (PID) controller through a pressure-regulated valve (Tescom ER3000). The pressure of the reactor is measured by MBS3000 absolute pressure transducer (range of 0–25 MPa) with the accuracy of ±0.02 MPa. The temperature in the reactor is measured using a Pt1000 thermoprobe (JM6081) with the uncertainty of ±0.05 K. All of the data are recorded every 10 s by a data logger (Agilent 34970A).

2.3. Experimental procedure

The hydrate formation conditions were measured using the T-cycle method which was reliable to determine the phase equilibrium data [33,34]. The reactor was successively washed by the deionized water and the NaCl solution used in the experiment. Then, the reactor was evacuated with a vacuum pump. Next, liquid phase including 210 mL of NaCl solution and 5 mL of organic promoter was successively introduced into the reactor. Subsequently, the reactor was flushed with the methane at least three times to ensure the absence of air. The reactor was pressured by methane to a desired value. Then the system temperature decreased until the hydrate phase began to form in the reactor. The hydrate formation phenomenon can be observed through the visual windows. Next, the temperature of system was gradually increased with each temperature step of 0.1 K until an infinitesimal amount of hydrate left in the liquid phase. After each temperature increase, pressure was allowed to equilibrate and to remain stable for at least 3 h. The temperature where the hydrate phase disappeared was taken as the equilibrium point [24]. These procedures were conducted at the different pressures to obtain the phase equilibrium conditions.

2.4. Raman spectroscopy procedure

To synthetise mixed hydrate sample, the liquid including 50 mL of NaCl solution and 3 mL of organic promoter was charged to the