

Measurements for the dissociation conditions of methane hydrate in the presence of 2,5-dihydrofuran and 3,4-dihydro-2H-pyran

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ABSTRACT

This study reports the equilibrium conditions for the dissociation of methane hydrate in the presence of cyclic ethers of 2,5-dihydrofuran (C₄H₆O) and 3,4-dihydro-2H-pyran (C₅H₈O) as additives. For the water-soluble additive of 2,5-dihydrofuran, the hydrate–liquid water–vapor (H–Lw–V) three-phase equilibrium conditions were measured using the isochoric method in the pressures ranging from 6 to 12 MPa and temperatures ranging from 291 to 300 K. For the water-insoluble additive of 3,4-dihydro-2H-pyran, the hydrate–liquid water–liquid additive–vapor (H–Lw–La–V) four-phase equilibrium conditions were measured in the same pressure range with temperature range from 296 to 300 K. The experimental results show that both additives have significant promotion effects on the formation of methane hydrates. At a specific pressure, the maximum increase in methane hydrate equilibrium temperature is approximately 13 K for both additives. In order to simulate the seawater environment, this study also measured the methane hydrate dissociation conditions by adding these two additives to a brine system with 0.035 mass fraction NaCl. The equilibrium temperature at an isobar of the brine system shows a decrease of 1–2 K for both additives in comparison to that of the pure aqueous system.

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1. Introduction

Gas hydrates are ice-like solids that are composed of water and small-diameter guest molecules (for example, methane or carbon dioxide). Water molecules construct cages through the molecular interaction force of hydrogen bonds which can trap guest molecules of different sizes. These cages are grouped into three major distinct crystalline types of structure I (sI), II (sII), and H (sH). Gas hydrates naturally exist at high pressure and low temperature, and can be found in the deep sea or the permafrost regions.

Besides the traditional flow assurance concern in oil and gas industry, gas hydrates are generally considered as an emerging energy resource. Extensive research has been presented in literature. For example, studies of gas hydrate to solve the pipeline blockage have been reported. One approach is to add chemicals into the pipelines to prevent the formation of gas hydrates. Basic thermodynamic data are required for the studies on inhibiting the formation of hydrates in pipelines and keeping hydrocarbons in hydrate-free zone and the corresponding *P–T* conditions. Additives such as electrolytes, methanol, ethylene glycol can be used as the inhibitors for the formation of methane hydrates [1–4].

On the other hand, the techniques of forming gas hydrates can also be used in gas storage and transportation [5–7]. Sequestration of carbon dioxide by replacing methane molecules in hydrates is another research of great interest [8]. Various additives are considered as inhibitors or promoters for the formation of gas hydrates. There are currently growing reports of thermodynamic phase equilibrium data and kinetic studies of gas hydrate systems with various additives [9]. The additive of cyclic hydrocarbon compounds in gas hydrate of carbon dioxide [10,11]. Tetra-*n*-butyl ammonium bromide (TBAB) has been used as an additive for methane hydrate [12,13]. Other typical additives for methane hydrate include cyclopentane (CP) [14,15], sodium dodecyl sulfate (SDS) [16,17], tetrahydrofuran (THF) [18,19]. In our previous studies, we have reported that 2-methyl-2-propanol is a promoter for methane hydrate formation [20]. The equilibrium temperature for the dissociation of methane hydrate increases by 5 K with 2-methyl-2-propanol additive. We have also depicted that 1,3,5-trioxane is another good methane hydrate promoter [21]. The increase in equilibrium temperature at a given pressure is up to 13 K. The additive of oxolan-2-yl methanol, however, has an inhibitory effect on the formation of methane hydrate reducing the equilibrium temperature by 5 K [21].

Further investigation of additives for promoting or inhibiting methane hydrate formation is still needed to provide basic engineering design information. It is indicated that 2,5-dihydrofuran itself can form hydrate with water molecules [9]. To our knowledge,

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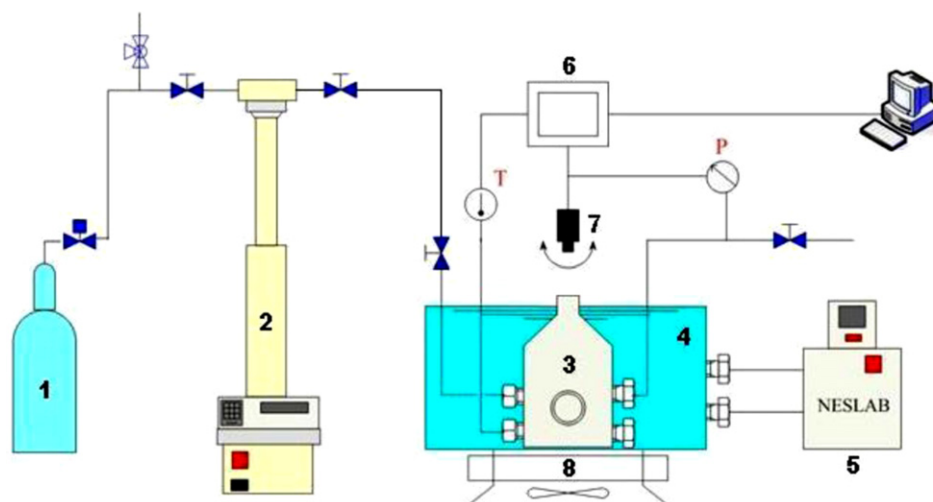


Fig. 1. A schematic illustration of the experimental setup of this study.

no literature data for the thermodynamic three-phase (H–Lw–V) equilibrium with 2,5-dihydrofuran additive has been presented. The motivation of this study is to provide new phase equilibrium data for methane hydrate dissociation with this additive. This study also investigates the other water-insoluble additive of 3,4-dihydro-2H-pyran to obtain new thermodynamic four-phase (H–Lw–La–V) equilibrium data. The isochoric experimental method has been employed in this investigation. To model the seawater condition, our phase equilibrium measurements have also been conducted in brine solution with 0.035 mass fraction NaCl aqueous solution. The concentration range of 2,5-dihydrofuran in our measurement was with mass fraction from 0.025 to 0.15 in aqueous solution, and with mass fraction from 0.025 to 0.10 in brine system. The pressure range in our study was from 6 to 12 MPa. The same pressure range was investigated for the other additive of water-insoluble 3,4-dihydro-2H-pyran for both pure water and brine systems.

2. Experimental

2.1. Materials

The aqueous samples in the experiments consisted of deionized water with additives of 2,5-dihydrofuran and 3,4-dihydro-2H-pyran. The purity of 2,5-dihydrofuran (Aldrich) has been confirmed as greater than 99% through our gas chromatograph test. 3,4-Dihydro-2H-pyran was purchased from Alfa Aesar with certified purity of 99%. Methane was purchased from Air Product with purity of 99.9%. The chemicals were directly used in our experiments without further purification.

2.2. Experimental apparatus

The experimental apparatus of this study for measuring the dissociation conditions of methane hydrates with additives has been described in our previous publications [20,21]. A schematic illustration of our experimental setup is shown in Fig. 1. The equilibrium cell is a cylindrical vessel made of stainless steel with a volume of 200 cm³. This vessel has three sapphire windows that can bear pressures up to 30 MPa. The equilibrium cell was immersed in a water bath with precisely controlled temperature circulator (Neslab RTE equipped with a remote programming controller). The aqueous solution with hydrate was agitated by a magnetic stirrer at the bottom of the equilibrium cell with a speed of 650 rpm.

Data of temperature and pressure inside the equilibrium cell were measured by a platinum resistance thermometer (Fluke, 1529) and a pressure gauge (Heise, type PM), respectively. The resolutions for temperature and pressure readings are ± 0.01 K and ± 0.001 MPa, respectively.

2.3. Experimental method

This study employs the isochoric method to measure the equilibrium temperatures and pressures for the dissociation of methane hydrates with 2,5-dihydrofuran and 3,4-dihydro-2H-pyran additives. The equilibrium cell was immersed in a water bath equipped with temperature controlled circulator. Firstly, 100 ml of aqueous solution with additive at a specific concentration was placed into the equilibrium cell. The cell was continuously flushed with methane to purge air. After the degas process, methane was delivered into the equilibrium cell through an ISCO pump (D series, 260D) at a desired pressure. The magnetic stirrer was set at 650 rpm to keep mixing the system until a stable condition in the equilibrium cell was reached. The temperature of the water bath circulator was then decreased using a programmable controller. The temperature in the equilibrium cell decreased gradually and methane hydrates started to form where a rapid pressure drop in the equilibrium cell was observed. The temperature was maintained at this point for about 2 h to keep the formation of methane hydrates. The temperature in the equilibrium cell was then increased to a point slightly below the dissociation temperature of methane hydrate. The solution was kept at this point for 330 min. In the final stage, the temperature in the equilibrium cell was increased at a very slow rate 0.05 K h⁻¹ in order to obtain the thermodynamic equilibrium condition for methane hydrate dissociation. After the methane hydrate was completely dissociated, the measured curve of pressure against temperature during the continuous heating process coincided with that of the initial cooling steps. The dissociation temperature and pressure data were determined from the measured *P–T* curve where a sharp slope change during the final heating process was observed. These are reported as the equilibrium data for methane hydrate dissociation. The dissociation conditions of methane hydrate were measured at various initial pressures and concentrations of the additive. The reproducibility of the equilibrium temperature and pressure was confirmed by repeated measurements in this study. The uncertainty for our temperature and pressure measurements is estimated as 0.1 K and 0.02 MPa, respectively.

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