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Measurements for the equilibrium conditions of methane hydrate in the presence of cyclopentanone or 4-hydroxy-4-methyl-2-pentanone additives

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ABSTRACT

The equilibrium conditions of methane hydrate in the presence of additives of cyclopentanone (C_5H_8O) or 4-hydroxy-4-methyl-2-pentanone ($C_6H_{12}O_2$, also known as diacetone alcohol) in aqueous solutions were experimentally measured in this study. The hydrate-liquid water-vapor ($H-L_w-V$) three-phase equilibrium conditions were determined by employing the isochoric method within a high pressure cell at low temperature conditions. New experimental results are reported for pressures ranging from 7 to 13 MPa with various concentrations of these additives. It is demonstrated that the cyclopentanone additive has a promotion effect on the formation of methane hydrate, while the other additive of 4-hydroxy-4-methyl-2-pentanone shows an inhibition effect. The structures of methane hydrates with each of the two additives were determined using the Clausius–Clapeyron equation. To simulate the salinity of the seawater environment, this study also measured the hydrate-liquid water-vapor ($H-L_w-V$) three-phase equilibrium temperatures and pressures by adding both additives to brine solution consisted of NaCl at 0.035 mass fraction. In both cases, the additional component of NaCl in the aqueous phase reduces the equilibrium temperature by about 2 K.

1. Introduction

Gas hydrates, naturally found in the permafrost regions or the deep sea around the world, provide huge amount of natural gas energy resources. They are ice-like crystalline molecular complexes that are composed of water and suitably sized guest molecules like methane or carbon dioxide. Gas hydrates usually stably exist under high pressure and low temperature conditions. Water molecules form differently-sized cages through hydrogen bonds into which guest molecules are trapped to stabilize the hydrate structure. There are three main distinct crystalline forms of sI, sII, and sH, depending on the molecular size and structure of the guest molecules. The detailed review of gas hydrate has been presented by Sloan and Koh [1].

Gas hydrates have drawn much attention in various fields. Formation of gas hydrates may cause serious blockage problems at specific temperature and pressure states for oil and gas transportation in pipelines. Thermodynamic inhibitors such as methanol or glycols have been introduced for shifting the hydrate phase boundary in order to prevent the hydrate formation and to maintain flow assurance in pipelines [2–4]. On the other hand, gas hydrates are also used for other applications such as natural gas storage and transportation. For these purposes, formation of gas hydrates is preferred at a relatively lower pressure and higher temperature due to safety and economic concerns. Extensive researches on the screening of appropriate additives with promotion effect in methane hydrate systems have been presented in literature. Those additives include ketone compounds such as cyclobutanone [5], cyclohexanone [6], and acetone [7], all forming sII hydrate structures. Moreover, methane hydrates with sH structure have been reported with additives like cycloheptanone [8] and pinacolone (3,3-dimethyl-2-butanone) [9]. All of those additives demonstrate significant decrease for the methane hydrate dissociation pressure, leading to promotion effect on methane hydrate formation. Zhurko et al. presented their measurements for the decomposition conditions of methane hydrates with various alcohols as additives [10]. In our previous studies, we have also presented our measurement results for the dissociation conditions of methane hydrates with several hydrocarbon additives [11–13].

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Applications of methane hydrates require not only the thermodynamic phase equilibrium data, but also the kinetic information, for example, the induction time on the formation of methane hydrate and its growth rate. Investigations on the kinetic effect of additives for promoting or inhibiting methane hydrate formation are highly needed in basic process design. The thermodynamic phase equilibrium data, however, provide necessary information for kinetic measurements. For example, the subcooling temperature as a driving force in kinetic investigations requires the thermodynamic phase equilibrium data for gas hydrate systems with additives. The motivation of this study is to obtain new experimental phase equilibrium data for methane hydrate in the presence of additives. A cyclic ketone compound, cyclopentanone, and an alkyl ketone compound, 4-hydroxy-4-methyl-2-pentanone, were screened as possible additives for fundamental thermodynamic measurements of methane hydrate dissociation in this study. Phase equilibrium data for methane hydrates with these two additives have not been shown in previous literature. The pressure range in our experiments was from 7 to 13 MPa for both additives. We measured the dissociation temperature of methane hydrate at a specific pressure, where hydrate, liquid water and vapor are in three-phase equilibrium, using the isochoric method. To simulate the salinity of the seawater environment, the dissociation conditions of methane hydrates were also investigated in brine solution consisted of 0.035 mass fraction NaCl in water. These data in brine system are useful for further exploration of methane hydrates from ocean floor. Comparisons of the promotion or inhibition effect are reported between the pure water and brine systems with the same mass fraction of both additives.

2. Experimental

2.1. Materials

Imported methane (grade 4) was purchased from Liu Shiang Company, Taiwan, with a certified purity greater than 99.9 mass%. Cyclopentanone was purchased from Alfa Aesar with purity greater than 99.0 mass%. 4-hydroxy-4-methyl-2-pentanone with purity of 99.0 mass% and sodium chloride with purity greater than 99.5 mass% were purchased from Sigma–Aldrich Company. All chemicals were directly used without further purification. De-ionized water was used in all experiments. The properties and purities of two additives used in this study are listed in the supplementary material.

2.2. Experimental apparatus

The apparatus used in this study for measuring the equilibrium conditions of methane hydrates is the same as that described in our previous studies [11–13]. The main part is the 200 cm^3 equilibrium cell that is made of stainless steel and can bear pressure up to 30 MPa. Three sapphire windows on the top, front, and back sides of the equilibrium cell enable us to monitor the state of the mixture inside the cell. The equilibrium cell is immersed in a water bath with precisely controlled temperature circulator. The bath is equipped with a remote programming controller to program the change of temperature inside the equilibrium cell. A magnetic stirrer is placed at the bottom of the equilibrium cell for mixing the aqueous solution at a speed of 650 rpm. The temperature inside the equilibrium cell is measured by a platinum resistance thermometer (Fluke, 1529), and a pressure gauge (Heise, type PM) is employed to record the pressure. The resolutions for the reading of temperature and pressure are 0.01 K and 0.001 MPa, respectively.

2.3. Experimental method

The isochoric method has been employed in this study to measure the hydrate-liquid water-vapor (H-L_w-V) three-phase equilibrium temperatures and pressures of methane hydrate in the presence of two additives. The experimental procedures for measuring methane hydrate dissociation points are similar to those reported in our previous studies [11–13]. The process diagram for our thermodynamic experiments is presented in Fig. 1. The equilibrium cell was firstly immersed in a water bath equipped with a temperature controlled circulator. This cell was filled with 100 cm^3 solution of water and an additive with a specific concentration. The initial air in the cell was flushed out using

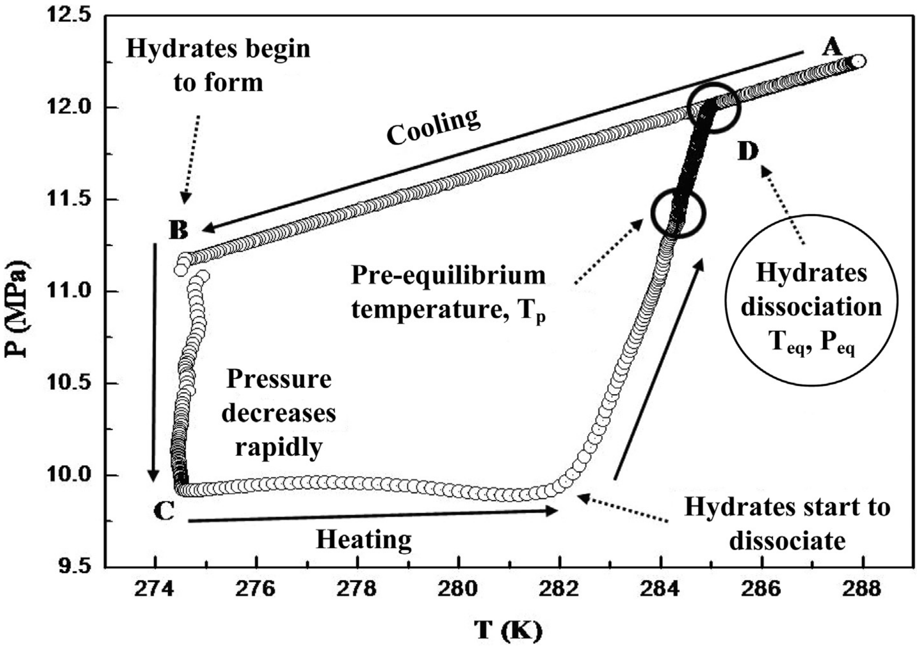

Fig. 1. The schematic illustration of the experimental procedures of this study.