THF를 포함하는 다중객체 시스템의 하이드레이트 상평형

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Hydrate phase equilibria of multiple - guest systems containing THF

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Introduction

Clathrate compounds are crystalline materials formed by a physical interaction between host molecules and relatively light guest molecules. There are various cavites capable of entrapping guest molecules in an open network of host molecules composing a crystalline framework. Depending on the chemical properties of the host molecules, clathrate compounds can be divided into two categories: aqueous and nonaqueous. Clathrate compounds in which the host molecules are water of deuterium oxide belong the aqueous clathrates. This kind of inclusion compound is specifically called a clathrate hydrate or simply gas hydrate. Gas-phase guest molecules generally form nonaqueous clathrates with phenolic compounds such as hydroquinone, phenol, and simple substituted phenols.

Three-phase (hydrate-liquid water-vapor) equilibrium dissociation conditions for simple and mixed hydrates of carbon dioxide, methane, and THF were measured. Equilibrium dissociation pressures were affected by concentration of added THF. THF was used as a hydrate promoter to increase the hydrate stability: that is, the hydrate promoter THF showed a striking decrease of the equilibrium pressure at a temperature. New thermodynamic model was suggested for describing the hydrate promoter.

The CO_2+CH_4+THF mixed hydrate system would be investigated. Unruh and Katz reported the first phase equilibrium data for CO_2+CH_4 mixed hydrate system and determined vapor phase concentrations indirectly [1]. Seo et al. in 2001 measured multiple-phase hydrate equilibrium of the ternary CO_2+CH_4+water mixed hydrate system [4]. In the present work, the isobaric equilibrium conditions of the carbon dioxide and methane mixture that 3 mol% THF made the hydrate forming temperature and pressure higher was added were measured to identify the hydrate - forming stable region. The composition of CO_2 and CH_4 gas was changed in about 20, 40, 60 and 80 mol%. Additionally the CH_4+THF mixed system was measured. The CO_2+THF mixed hydrate system was also investigated by Kim et al. in 2000 [6]. Nevertheless, The CH_4+THF mixed hydrate system was not investigated without only 3mol% THF mixed hydrate system.[7]

Experimental Section

Apparatus The apparatus was constructed to measure the gas hydrate dissociation pressures and analyze the equilibrium compositions of vapor via on-line gas chromatography. The apparatus consisted of two major parts; preparation of gas mixture section and equilibrium dissociation pressure and temperature measurement section. An equilibrium cell was made of 316 stainless steel and its internal volume was about 50 cm^3. Two sapphire sight glasses were equipped at the front and back of the cell, and allowed visual observation of phase transitions. The cell contents were agitated by a magnetic spin bar that was coupled with an immersion magnet placed under the cell in the bath. The bath contained about 30 L of a liquid mixture of ethylene glycol and water, which was controlled by an externally circulating refrigerator/heater.

For the measurement of vapor compositions at a given equilibrium condition, sampling valve having sampling loop volume of about 0.5 mL respectively was installed and connected to a gas chromatography on-line through a high-pressure metering pump. The gas chromatography used a thermal conductivity detector (TCD) and a Porapak Q packed column. A vapor-sampling valve that has a calibrated loop volume of 4.8827 mL was used to perform the calibration for CO_2 and CH_4. After the cell was pressurized with CO_2 or CH_4 at a fixed pressure, gas in the loop was injected into the gas chromatography to obtain the curve for moles vs. peak areas. The calibration curve for each gas was fitted to a linear equation, which showed minor deviations from linearity.

CO_2 and CH_4 gas mixture was made using a couple of D series micro-syringe pumps. CO_2 was charged with known amount of moles using syringe pump, then CH_4 was charged with needed amount of moles for desired gas composition by another pump. The charged gas mixture was gathered in a reservoir, and then analyzed using a gas chromatography for confirmation.

Procedure After the equilibrium cell was well cleaned, overall inner parts were evacuated with vacuum pump. An amount of approximately 35 cm^3 of the aqueous solutions containing hydrocarbons was initially charged into the evacuated equilibrium cell. The air in the cell was eliminated with flushing of gas mixture several times and the pressure was first adjusted to a desired pressure with gas mixture. The cell temperature was kept constant as a temperature just above that at which gas hydrates formed. Clathrate nucleation was then induced by agitation of magnetic spin bar with immersed magnet in bath. When gas hydrates were formed and the system pressure reached a steady state, external heater was used to increase the system temperature at a rate of 1 to 2 K per hour to a condition where the hydrate phase was dissociated and in coexistence with liquid and vapor phases. The nucleation and dissociation steps were repeated at least twice in order to remove the hysteresis phenomenon. When the amount of minute crystals existed and system temperature were kept constant at least for 8 to 10 hour after the system pressure was stabilized, the pressure was considered a hydrate dissociation pressure at the specific temperature. The existence of crystal was confirmed by visual observation.

For the measurement of the equilibrium composition, the experiment was more carefully carried out. It should be noticed that the best condition for the measurement of the equilibrium compositions could be obtained when the amount of hydrates was relatively small in liquid water. Thus, the nucleation and dissociation process for the analysis of composition is nearly similar to that of the measurement of dissociation pressures. When the system temperature and pressure was in equilibrium condition, the vapor phase was analyzed three times though the gas chromatograph. The reported equilibrium composition of the vapor phase was taken as the average value.

Thermodynamic model

In a system with N substances from which Nc are the hydrate-forming components, thermodynamic equilibrium is established among the vapor (V), liquid (L), and hydrate (H) phases. At the equilibrium condition of H-L-V phases,

$$\hat{f}^{V}_{i} = \hat{f}^{L}_{i}, \quad i = 1, \cdots, N \qquad (1)$$

and

$$\hat{f}^{V}_{j} = \hat{f}^{L}_{j}, \quad j = 1, \cdots, Nc \qquad (2)$$

Water is also included in this fugacity relationship. Given temperature, overall composition of the mixture, and expressions for the fugacities of each component in each phase, equation 1 and 2 is solved to obtain the pressure where hydrate first forms and to determine the proportions and compositions of each coexisting phase. In this study, the Soave-Redlich-Kwong equation of state [2] incorporated with a modified version of the Huron-Vidal mixing rule [3] was used.

Cubic equation of state incorporated with various mixing rule have been not only applied in low-pressure vapor-liquid equilibrium (VLE) calculations, but also used for estimating the high-pressure phase equilibria.

Results and Discussion

In Figure 2, The three phases HLV equilibria of the CO_2+CH_4+THF+water system were determined at several different ratio of CO_2 and CH_4 in the condition of 3 mol% THF. The mixed hydrates formed over the wide temperature and pressure ranges of 275-300 K and 15-200 bar largely depending on the gas-phase compositions.

THF itself is a guest species to water. THF forms S_{II} hydrate in which the THF molecules occupy only the larger cages. According to the experimental data of H-L phase equilibrium of THF it was found that about 5.56 mol% THF have the strongest promotion effect on its hydrate. In this study reasonably 3 mol% THF hydrate system was operated.

The effect of THF on CH_4 hydrate and CO_2 hydrate system in proportion to the increase of amount of THF added was obtained (Fig 3, Fig 4). The former showed the effect of THF in spirit of a small amount of THF. In the latter CO_2+THF+water system showed unpredicted results to make a curve when THF added.

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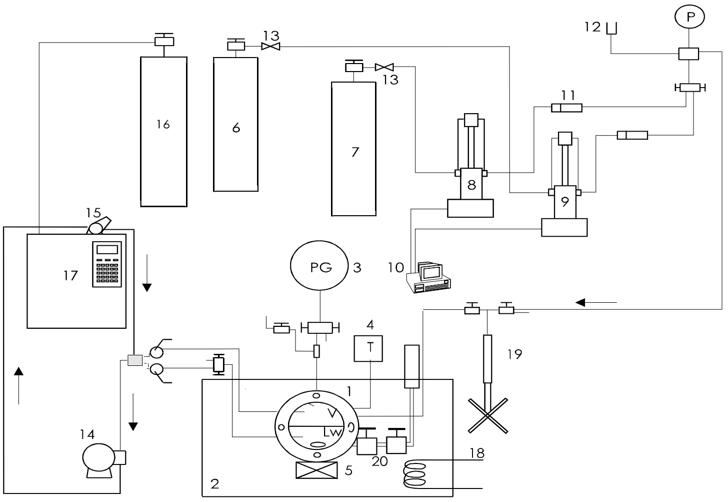

Figure 1. Schematic diagram of the experimental apparatus used in this work: 1. Equilibrium cell ; 2. Water bath ;3. Pressure gauge ;4.Thermocouple ;5. Magnetic stirrer ;6. CO2 sylinder ; 7. CH4 cylinder ;8 , 9. Syringe pump ;10. Multi controller; 11. Check valve; 12. Rupture disc ;13. Line filter ;14. High pressure pump ;15. Sampling valve ;16. Helium gas ;17. Gas Chromatograph ;18. External heat exchanger ;19. High pressure pump ;20. Sampling port

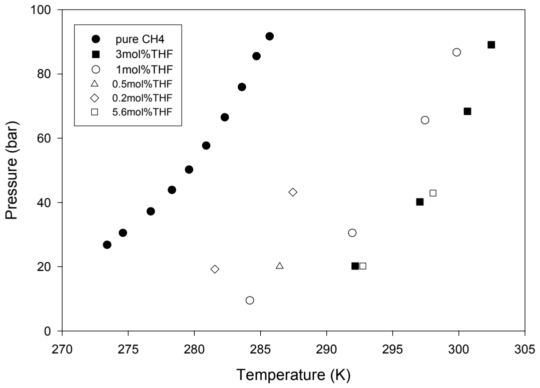

Figure 2. Hydrate phase equilibria of methane, THF, and water system

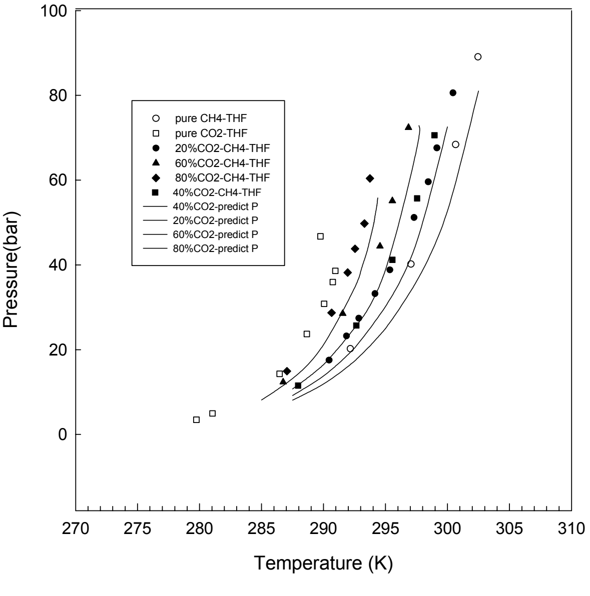

Figure 3. Hydrate phase equilibria of carbon dioxide, methane, THF (3mol%), and water system

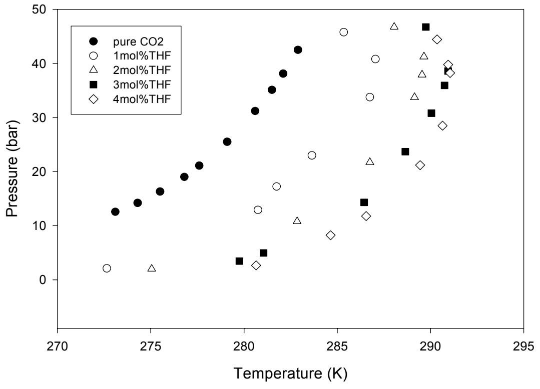

Figure 4. Hydrate phase equilibria of carbon dioxide, THF, and water system