

Formation Behaviours of Mixed Gas Hydrates Including Olefin Compounds

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It requires high energy and cost to separate specific components from alkane + alkene mixtures, especially for mixtures with similar physical properties. Although some studies have reported hydrate-based processes to replace existing separation/recovery technologies in petroleum refining and petrochemical fields, as the latter are too costly due to their high energy consumption, they mainly focused on macroscopic results regarding stability regions at various concentrations of gas mixtures. In this study, three-phase (liquid-vapour-hydrate) equilibria for (CH₄ + C₂H₄) and (C₂H₆ + C₂H₄) gas mixtures with various compositions were investigated. ¹³C solid-state NMR spectroscopy was also used in order to obtain quantitative information of the guest behaviours of mixed components after the hydrate formation. Experimental and calculated results obtained in this study can provide useful information when applying a hydrate-based process to separate or recover a specific component from gas mixtures having similar physical properties such as (C₂H₆ + C₂H₄).

1. Introduction

Gas hydrates are crystalline solid compounds that form with the enclathration of guest species into three-dimensional lattice frameworks of hydrogen-bonded water (host) molecules (Sloan and Koh, 2008). Crystal structures, mainly determined by the molecular size of accommodated guest species, can be categorized into three classes, structure-I (sI), structure-II (sII), and structure-H (sH). Each structure of the sI and sII hydrates has two types of cavities per unit structure (Mak and McMullan, 1965; McMullan and Jeffrey, 1965), while the sH hydrate has three types of cavities (Ripmeester et al., 1987). Furthermore, a second guest substance (so-called "help-gas") that will occupy small and middle cavities is necessary to stabilize the sH hydrate. Since Sir Humphrey Davy found chlorine hydrate in 1810, more than 120 guest species that form gas hydrates have been identified (Sloan and Koh, 2008).

In engineering areas, gas hydrates were initially recognized as a hazardous material causing blockage problems in oil and gas pipelines (Hammerschmidt, 1934). In this regard, hydrocarbons of C1 and C2 compounds, occurring widely in petroleum and natural gas processes, have been intensively investigated at first (Jhaveri and Robinson, 1965). Many researchers have also measured hydrate-phase equilibria of various systems including methane and ethane to identify hydrate-forming conditions where gas hydrates can form and exist stably (Kang et al., 2001a). With the collected hydrate-phase equilibrium data, the blockage problem can be prevented by operating oil and gas pipelines at non-forming conditions. Moreover, hydrate-phase equilibria of some olefin compounds were also measured (Sugahara et al., 2003). In addition to macroscopic investigations of the phase equilibrium, microscopic analyses have been adopted to obtain occupational behaviours and quantitative information on guest species. Sum et al. (1997) reported cavity occupancies and hydration numbers of various hydrate systems including methane and propane, calculated by means of Raman spectroscopy with a statistical thermodynamic equation. Ripmeester et al. used ¹H and ¹³C NMR spectroscopy to find cavity occupancies of guest species and crystal structures (Ripmeester and Ratcliffe, 1990). Recently, Sugahara et al. (2000) reported stability

boundaries and cage occupancy of an ethylene hydrate system. They showed characteristic “S-shape” behavior in the pressure-temperature projection around the critical points, and used a laser Raman spectroscopic analysis to identify cavity occupation of ethylene molecules in small cavities of the sl hydrate and to examine the pressure dependence of bonding motions of ethylene molecules (Sugahara et al., 2003).

Because gas hydrates can hold a large volume of gases in small units of a solid structure, they have been applied to storage media and separation/recovery technology through synthesis with a variety of gas mixtures (Lee et al., 2003). For example, separating CO₂ from flue gas with a hydrate-based process is a well-known application (Kang et al., 2001b). Recently, research on other light-gas mixtures such as (H₂ + CH₄) and (C₁ + C₂) has been performed. Ma et al. measured the hydrate formation behaviours of (CH₄ + C₂H₄) and (CH₄ + C₃H₆) gas mixtures and applied a modelling equation to represent the experimental data to obtain fundamental data for separation of specific components from alkane + alkene gas mixtures. In addition, they also measured the two-phase (vapor and hydrate phases) equilibria for (H₂ + CH₄), (H₂ + N₂ + CH₄), and (CH₄ + C₂H₄) gas mixtures in the absence and presence of a well-known thermodynamic promoter, tetrahydrofuran (THF) (Ma et al., 2008).

Although some studies have reported hydrate-based processes to replace existing separation/recovery technologies in petroleum refining and petrochemical fields, as the latter are too costly due to their high energy consumption, they focused on macroscopic results mainly regarding stability regions at various concentrations of gas mixtures. In this report, three-phase (liquid-vapour-hydrate) equilibria for (CH₄ + C₂H₄) and (C₂H₆ + C₂H₄) gas mixtures with various compositions were investigated. In addition, ¹³C solid-state NMR spectroscopy was used in order to obtain quantitative information of the guest behaviours of mixed components after the hydrate formation. Experimental and calculated results obtained in this study can provide useful information to develop a hydrate-based process in application to separation/recovery of a specific olefin component from gas mixtures having similar physical properties.

2. Experimental Methods

CH₄, C₂H₆, C₂H₄, and gas mixtures at various concentrations were supplied by Daemyoung Special Gas Co. (Korea). Pure CH₄, C₂H₆, and C₂H₄ gases have nominal purity of 99.95, 99.5, and 99.5 mol%, respectively. Gas mixtures of (CH₄ + C₂H₄) with concentrations referred to as 10 mol%, 30 mol%, 50 mol%, 70 mol%, and 90 mol% C₂H₄ have nominal concentrations of 10.0 mol%, 30.0 mol%, 50.0 mol%, 70.0 mol%, and 90.0 mol% C₂H₄, respectively. In addition, gas mixtures of (C₂H₆ + C₂H₄) with concentrations referred to as 20 mol%, 40 mol%, 60 mol%, and 80 mol% C₂H₄ have nominal concentrations of 20.0 mol%, 40.0 mol%, 60.0 mol%, and 80.0 mol% C₂H₄, respectively. These gases were used with HPLC grade water, supplied by Sigma-Aldrich Chemical Co. with a nominal purity of 99.99 mol %, to form gas hydrates. All the materials were used without further purification or treatment.

The same high-pressure cell and procedures as described in our previous reports were used to measure pressure-temperature dissociation equilibrium curves and to prepare hydrate samples for spectroscopic analysis (Lee et al., 2010; Lee and Kang, 2012). The experiments for hydrate-phase equilibrium measurements began with charging of the high-pressure cell (internal volume of approximately 350 cm³, maximum working pressure of 15.0 MPa) with 20.0 g of HPLC grade water and stoichiometric amounts of the chemical compounds. The cell was then purged sufficiently by methane so as to remove the remaining air in the system. After the cell was pressurized to the desired pressure with methane, it was cooled from room temperature to a sufficiently low temperature to form hydrates with a cooling rate of 1.5 K/h. When the drop in pressure due to hydrate formation reached a steady state, the cell temperature was increased stepwise by 0.1 K and was maintained for 1 h to reach thermal equilibrium. During the cooling and heating cycles, the temperature and pressure of the cell were logged using a K-type thermocouple and a Heise digital pressure transducer (DXD series) at intervals of 10 s. To check the reproducibility, the above P-T cycles were performed three times to obtain a hydrate-phase equilibrium point. For structural and microscopic investigations, a Bruker DSX400 NMR spectrometer at the Korea Basic Science Institute was used. ¹³C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were obtained at 240.0 K by packing the hydrate samples within a 4 mm o.d. zirconium rotor. All ¹³C NMR spectra were collected at a Larmor frequency of 100.6 MHz with MAS at 9 kHz. A contact pulse length of 2 ms and a pulse repetition delay of 10 s under proton decoupling were employed with radio frequency field strengths of 50 kHz on both proton and carbon channels. The downfield carbon resonance peak of adamantane, assigned as a chemical shift of 38.3 ppm at 300.0 K, was used as an external chemical shift reference.

3. Results and Discussion

Figure 1 shows hydrate-phase equilibria for the ($\text{CH}_4 + \text{C}_2\text{H}_4$) gas mixture with various concentrations along with the equilibrium curves for pure methane and pure ethylene hydrates. As shown in the figure, because pure ethylene hydrate has milder formation conditions than pure methane hydrate (that is, it requires higher temperature at a given pressure, or lower pressure at a given temperature to form), the equilibrium curves of the ($\text{CH}_4 + \text{C}_2\text{H}_4$) gas mixture shift to the right-hand side as the concentration of ethylene in the mixed gas increases. However, it should be noted that the equilibrium curves change drastically up to 50 mol% of ethylene in the mixture, while they do not change significantly at ethylene concentrations of 70 and 90 mol%. In addition, considering that none of the equilibrium curves obtained in this study showed inflection, and that the critical point of ethylene is 282.4 K and 5.04 MPa, the obtained equilibria are regarded as being representative of three phases of liquid water, hydrate, and vapour.

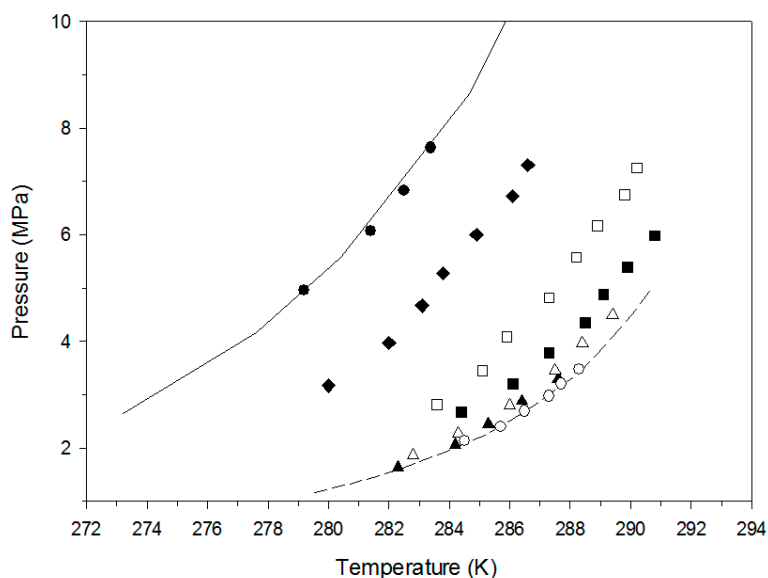


Figure 1: Hydrate-phase equilibrium curves for binary ($\text{CH}_4 + \text{C}_2\text{H}_4$) hydrates at the following gas compositions: ●, pure CH_4 ; ◆, 90% $\text{CH}_4 + 10\%$ C_2H_4 ; □, 70% $\text{CH}_4 + 30\%$ C_2H_4 ; ■, 50% $\text{CH}_4 + 50\%$ C_2H_4 ; △, 30% $\text{CH}_4 + 70\%$ C_2H_4 ; ▲, 10% $\text{CH}_4 + 90\%$ C_2H_4 ; ○, pure C_2H_4 . Literature values for pure CH_4 (Jhaveri and Robinson, 1965) and pure C_2H_4 (Sugahara et al., 2000) are also plotted as solid and dashed lines respectively for comparison with experimental data.

In contrast to distinct phase equilibria depending on gas compositions attributed to different physical properties of two components for the ($\text{CH}_4 + \text{C}_2\text{H}_4$) mixture, the collected hydrate-phase equilibria of the ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) gas mixture were very similar regardless of the gas compositions (Figure 2). Although the equilibrium curves nearly overlapped, pure ethane hydrate has milder equilibrium conditions than pure ethylene hydrate, and the equilibrium curves at various compositions lie between them. Equilibrium curves for pure ethane hydrate are thought to indicate milder formation conditions, because ethylene molecules, having larger molecular size (5.5 Å in diameter) than ethane (5.3 Å), require higher driving force (for example, larger force or pressure at a given temperature) to be accommodated into hydrate cavities. However, two equilibrium curves for pure ethane and pure ethylene hydrates are almost overlapped at around 285 K, and the stability trend is reversed at temperature higher than 285 K. Because the formation conditions of pure ethane and pure ethylene hydrates are very similar, those of the mixed gas also showed little difference regardless of gas compositions. The two components have no significant difference in physical properties such as molecular size, and hence are not distinguishable in the aspect of enclathration into hydrate cavities.

To investigate the molecular behaviours of each gas component, low-temperature solid-state ^{13}C NMR spectra of hydrate samples were collected at 240 K. Then, the obtained NMR spectra were used to calculate cage occupancies for ($\text{CH}_4 + \text{C}_2\text{H}_4$) mixed gas hydrates (Figure 3). Cage occupancies of CH_4 are

found to decrease in accordance with increased C_2H_4 compositions, as observed in the NMR signals. Particularly, occupancy of methane in large cavities drops rapidly up to an ethylene concentration of 50 mol%, and then shows little change with a value of around 0.10. Such occupancy changes support the observed shifts of equilibrium curves. In addition, only methane can occupy small cavities up to an ethylene concentration of 50 mol%. However, ethylene and methane molecules compete with each other to occupy small cavities at ethylene concentrations higher than 50 mol%. In this figure, the total occupancies for small and large cavities are plotted as solid and dotted lines for reference. As shown in the figure, the total occupancy for large cavities is obtained as 0.99, while the value for small cavities is increased at higher ethylene concentrations (0.76 for 70 or 90 mol%) as compared to at lower concentrations (0.60 for 10 mol%). The smaller driving force at lower ethylene concentrations is thought to contribute to this cavity occupancy, because binary gas hydrates at lower ethylene concentrations have more challenging formation conditions (that is, higher pressure at a given temperature).

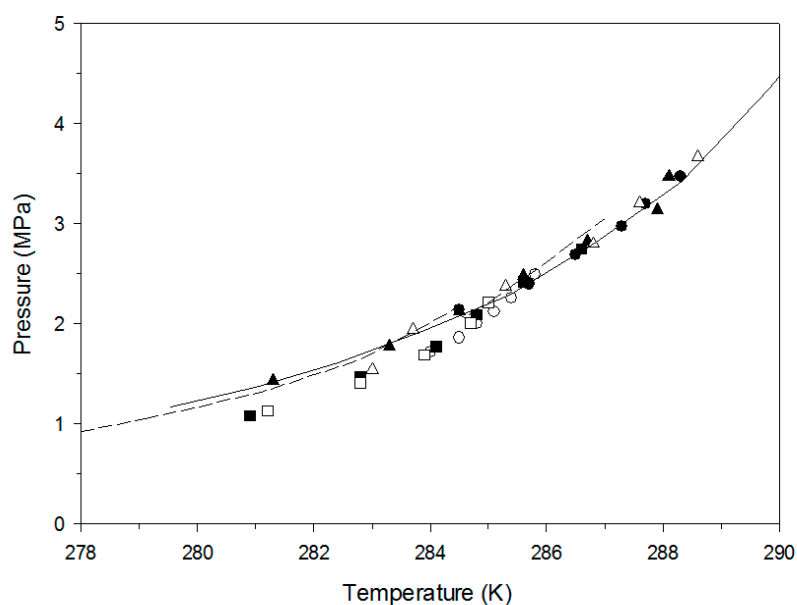


Figure 2: Hydrate-phase equilibrium curves for binary ($C_2H_6 + C_2H_4$) hydrates at the following gas compositions: ●, pure C_2H_4 ; □, 20% $C_2H_6 + 80\%$ C_2H_4 ; ■, 40% $C_2H_6 + 60\%$ C_2H_4 ; △, 60% $C_2H_6 + 40\%$ C_2H_4 ; ▲, 80% $C_2H_6 + 20\%$ C_2H_4 ; ○, pure C_2H_6 . Literature values for pure C_2H_6 (Roberts et al., 1940) and pure C_2H_4 (Sugahara et al., 2000) are also plotted as dashed and solid lines respectively for comparison with experimental data.

Cavity occupancies for both components of the ($C_2H_6 + C_2H_4$) gas mixture calculated with peak areas of the obtained NMR spectra are plotted in Figure 4. As shown in the figure, small cavity occupancy only by ethylene molecules remained constant, while large cavity occupancy of ethylene molecules linearly increased with increased concentration. Large cavity occupancy is linearly related with gas composition, because the two guest species, having indistinguishable physical properties, compete with each other. In the figure, total occupancies for small and large cavities are also plotted, and the values are constant at 0.60 and 0.99, respectively. Similar phase equilibria regardless of ($C_2H_6 + C_2H_4$) composition are thought to contribute to a constant driving force for preparing hydrate samples, which leads to constant cavity occupancies.

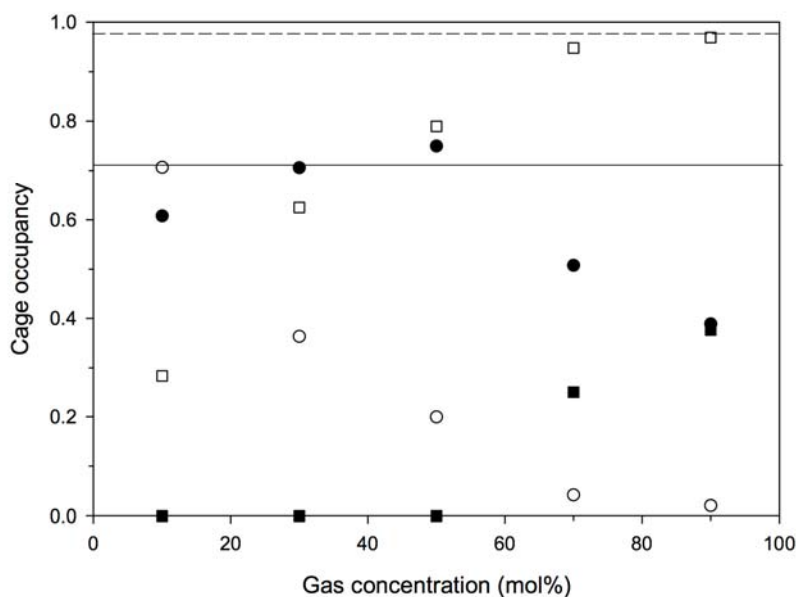


Figure 3: Cage occupancies for CH_4 and C_2H_4 molecules of binary ($\text{CH}_4 + \text{C}_2\text{H}_4$) hydrates at various gas compositions: ●, small cavity occupancy of CH_4 ; ○, large cavity occupancy of CH_4 ; ■, small cavity occupancy of C_2H_4 ; □, large cavity occupancy of C_2H_4 . Solid and dashed lines represent total small (0.71) and large (0.99) cavity occupancies by both guest species, respectively.

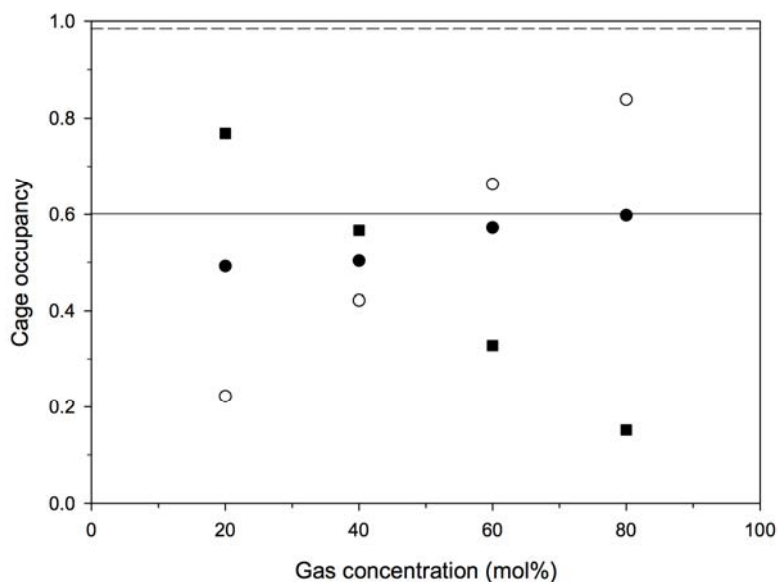


Figure 4: Cage occupancies for C_2H_6 and C_2H_4 molecules of binary ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) hydrates at various gas compositions: ●, small cavity occupancy of C_2H_4 ; ○, large cavity occupancy of C_2H_4 ; ■, large cavity occupancy of C_2H_6 . Solid and dashed lines represent total small (0.60) and large (0.99) cavity occupancies by both guest species, respectively.

4. Conclusions

In this investigation, three-phase equilibria for binary ($\text{CH}_4 + \text{C}_2\text{H}_4$) and ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) gas hydrates were measured with various gas compositions to identify stability regions of binary (alkane + alkene) gas hydrates. Hydrate-phase equilibria of the binary ($\text{CH}_4 + \text{C}_2\text{H}_4$) hydrate show a significant change according to compositional change due to the distinct physical properties of the two guest species, such as molecular size. However, the phase equilibrium curves were not shifted linearly because of easier hydrate formation and small cavity occupation of ethylene molecules. On the contrary, three-phase equilibria for binary ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) hydrates show little difference due to the similar physical properties of the two guest species. In addition to macroscopic equilibrium measurements, solid-state ^{13}C NMR spectra for hydrate samples were collected to identify cavity occupancies of the guest components as well as the hydrate structure. For the binary ($\text{CH}_4 + \text{C}_2\text{H}_4$) hydrate, large cavity occupancy of ethylene molecules increased non-linearly in accordance with increased ethylene concentration, which supports the observed non-linear shifts of equilibrium curves. Meanwhile, large cavity occupancy of ethylene molecules from the ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) gas mixtures increased linearly according to increased ethylene concentration, attributed to linear change of its distribution or density. Results obtained experimentally and calculated can provide quantitative information to evaluate a hydrate-based process for separation/recovery of specific components from (alkane + olefin) gas mixtures.

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