Phase Equilibrium of the Carbon Dioxide and Methane Hydrate in Silica Gel Pores and Thermodynamic Prediction

Seong-Pil Kang*

Abstract

Hydrate phase equilibrium for the binary CO2+water and CH4+water mixtures in silica gel pore of nominal 6, 30, and 100 nm were measured and compared with the calculated results based on van der Waals and Platteeuw model. At a specific temperature three-phase hydrate-water-vapor (HLV) equilibrium curves for pore hydrates were shifted to the higher-pressure condition depending on pore sizes when compared with those of bulk hydrates. Notably, hydrate phase equilibria for the case of 100 nominal nm pore size were nearly identical with those of bulk hydrates. The activities of water in porous silica gels were modified to account for capillary effect, and the calculation results were generally in good agreement with the experimental data.

Key words

gas hydrate, equilibrium, silica gel, pores, carbon dioxide, methane

1. Introduction

Clathrate hydrates (or gas hydrates) are a kind of inclusion compounds which are formed by physically stable interactions between water and relatively small guest molecules entrapped in the cavities of a three dimensional lattice-like structure built by water molecules under low temperature and high pressure conditions. These kind of non-stoichiometric crystalline compounds are divided into three distinct structures, I, II and H, which differ in cavity size and shape. CO2 and CH4 are known to form the structure I hydrate.

Nomenclature

\( f \): fugacity, MPa
\( R \): gas constant, J/mol ⋅ K
\( \theta \): contact angle, °
\( v \): number of cavities of type m per water molecule in the hydrate phase
\( \Delta \mu \): chemical potential difference between the empty hydrate and filled hydrate phase

\( V \): vapor
\( H \): hydrate
\( L \): liquid
\( I \): ice
\( w \): water
\( MT \): empty
\( fus \): fusion(melting or dissociation)

* Gasification Research Center, Korea Institute of Energy Research (KIER)
E-mail : spkang@kier.re.kr  Tel : 0429860-3475  Fax : 0429860-3097
2. Experimental Procedure

CO$_2$ gas used for the present study was supplied by World Gas (Korea) and had a stated purity of 99.9 mol%, CH$_4$ gas with a minimum purity of 99.995 mol% was supplied by Matheson Gas Products Co, and deionized water produced by a Millipore purifier was used. As a porous material, spherical silica gels of nominal pore diameter 6 nm, 30 nm, and 100 nm were selected and purchased from Aldrich (6 nm) and Silicycle (30 nm and 100 nm), respectively. All the materials were used without further treatment. The properties of silica gels having three different pore diameters were measure by nitrogen adsorption/desorption experiments with ASAP 2400 (Micrometrics) and listed in Table 1.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>6nm SG</th>
<th>30nm SG</th>
<th>100nm SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean particle diameter (nm)</td>
<td>150 to 250</td>
<td>40 to 75</td>
<td>40 to 75</td>
</tr>
<tr>
<td>mean pore diameter (nm)</td>
<td>5.51</td>
<td>30.1</td>
<td>94.5</td>
</tr>
<tr>
<td>specific pore volume (m$^3$/kg)</td>
<td>8.4x10$^{-4}$</td>
<td>8.4x10$^{-4}$</td>
<td>8.3x10$^{-4}$</td>
</tr>
<tr>
<td>specific surface area (m$^2$/kg)</td>
<td>586x10$^2$</td>
<td>94.9x10$^2$</td>
<td>42.4x10$^2$</td>
</tr>
</tbody>
</table>

The used silica gels were first dried at 373 K for 24 h before water sorption. The, the pore saturated silica gels were prepared by placing these dried silica gels in a

![Fig. 1 Schematic illustration of the equilibrium experimental setup](image-url)
desiccator containing degassed water, evacuating the desiccator, and allowing more than 3 days in order to establish the solid–vapor equilibrium. The total amount of sorbed water in the silica gel pores was confirmed by measuring the mass of silica gels before and after saturation and was found to be almost identical with the pore volume of each silica gel. The pressure–temperature dissociation equilibrium curves for CO₂ and CH₄ hydrates formed in silica gel pores were determined using a high-pressure cell with accompanying experimental setup (Fig. 1). The apparatus was specifically constructed to measure accurately the hydrate dissociation pressures and temperatures. The experimental setup consisted of an equilibrium reactor and a buffer cell, both made of 316 stainless steel (maximum working pressure of 15 MPa).

The equilibrium reactor had an internal volume of about 350 cm³. The experiment for hydrate phase equilibrium measurements starts with charging the equilibrium cell with about 250 cm³ of silica gels containing pore water. After the cell was pressurized to a desired pressure with CO₂ or CH₄, the whole main system was slowly cooled to 263 K. When pressure depression owing to hydrate formation reached the steady-state condition, the cell temperature was increased at a rate of about 0.1 K/h. The nucleation and dissociation steps were repeated at least two times in order to reduce hysteresis phenomenon. While the experiment was performed, the temperature and pressure of the equilibrium cell was gathered by data acquisition system. The equilibrium pressure and temperature of three phases (HLV) were determined by tracing the PT profiles from hydrate formation to dissociation.

3. Thermodynamic Model

The equilibrium criteria of the hydrate–forming mixture (CO₂+water or CH₄+water) are based on the equality of fugacities of the specified component i in all phases which coexist simultaneously

\[
\dot{f}_i^H = \dot{f}_i^L = \dot{f}_i^V = \dot{f}_i^I
\]  

(1)

where \( H \) stands for the hydrate phase, \( L \) for the water–rich liquid phase, \( V \) for the vapor phase, and \( I \) for the ice phase. From the author’s previous works, the final equilibrium equation is derived as follows

\[
\begin{align*}
\frac{\Delta \mu_i^\infty}{RT_i} &= -\int_{T_0}^T \frac{\Delta h_i^{\infty+} + \Delta h_i^{\infty-}}{RT} \, dT + \\
&+ \int_0^P \frac{\Delta v_i^{\infty+} + \Delta v_i^{\infty-}}{RT} \, dP + \sum_{m} \nu_m \ln(1 - \sum_{\alpha} \theta_{\alpha}) - ln(\gamma_{\alpha+})
\end{align*}
\]  

(2)
In the present study, it is assumed that the pores of silica gels were completely saturated with water, and thus, in the HLV equilibrium, the pores are completely filled with liquid water and hydrate in equilibrium with bulk gas. The decrease of water activity in porous silica gels mainly due to capillary effect occurring by the presence of geometrical constraints, that a cylindrical pore and solid–phase dissociation (i.e. melting or hydrate dissociation) are assumed, can be modified, thus the last term of (2) is expressed as(9),(10)

\[ \ln a_p = \ln a(\gamma_{W}) - \frac{F v_{L} \cos \theta}{RT} \]  

(3)

where \(v_L\) is the molar volume of pure water, \(\theta\) is the wetting angle between water and hydrate phase, HW is the interfacial tension between hydrate and water phase, \(r\) is the pore radius, and \(F\) is the shape factor of the hydrate–water interfacial curvature. Solving (2) and (3) will determine the three–phase HLV equilibrium conditions for pores of radius \(r\). The right side of (3) moves the equilibrium conditions to higher pressures and lower temperatures when compared with those of bulk hydrates.

4. Results and Discussion

Three–phase HLV equilibria of \(CO_2\) and \(CH_4\) hydrates in silica gel pores with nominal pore diameters of 6, 30, and 100 nm were measured. Model prediction results were also presented along with the experimental data in Fig. 2 and 3 for \(CO_2\)+water and \(CH_4\)+water mixture, respectively. All HLV equilibrium lines of each hydrate in silica gel pores were shifted to the lower temperature and higher pressure region when compared with those of bulk hydrates. This inhibition behavior can appear similarly for melting point depression of ice in small pores. As clearly seen in figures, the measured data showed in a good agreement with those of Anderson et al.(11) previously reported data but largely deviated from those of Smith et al. In case of 30 and 100 nm silica gel pores, the measured equilibrium pressures in this study was generally in agreement with those of Seo et al., and Uchida et al, even though their experimental method is controversial. On the other hand, the difference of the equilibrium dissociation pressures between this study and Seo et al, was significant at smaller silica gel pore of 6 nm nominal pore diameter. It was also shown that the equilibrium pressure shifts were found to be larger as the pore size decreases at constant temperature, and the equilibrium pressure shifts become larger as temperature increases at constant pore size.

In silica gel pores, the chemical potential of components had been affected by a consequence of molecular interactions at the hydrophilic pore wall surfaces, and the energy required maintaining capillary equilibrium. Partial ordering and bonding of water molecules with pore surfaces let down water activity, therefore decrease of water activity needs higher pressure at a specific temperature and lower temperature. This phenomenon is also observed in the mixtures containing inhibitors such as salts and alcohols which cause a depression in the freezing point of water thereby reducing its activity.
Even we carefully introduced water to silica gel pores, a significant part of water in the wall of confined spaces would be existed as bound water. All of the To get a solution of predicted equilibrium pressure to (2) at a proposed initial guessed temperature, the only remaining property is now the interfacial tension between hydrate and liquid water, \( \sigma_{HW} \). Uchida et al. presented the values of \( \sigma_{HW} \) from fitting their experimental data by the Gibbs–Thompson equation for CO\(_2\) and CH\(_4\) hydrates, but the estimated values (0.017 J/m\(^2\) for CH\(_4\) and 0.014 J/m\(^2\) for CO\(_2\) hydrate) did not produce good agreement to experimental data. Recently, Anderson et al. presented more sophisticatedly estimated values from experimental data for hydrate dissociation condition (0.032 J/m\(^2\) for CH\(_4\) and 0.030 J/m\(^2\) for CO\(_2\) hydrate). We employed our previously used ones including the latter two interfacial tension values, All of the parameter values in this model were given in the previous papers.

To confirm the formation of gas hydrate in silica gel pores, the FE–SEM was adopted, and shown in Fig. 4. Ex situ FE–SEM observation of porous silica gel particle shows the wave–like surface, which is guessed owing to hydrate formation in pores. It seems that the confined water among spherical silica gel particles does not occur, although water added to silica gels were controlled not to exceed the adequately absorbed only to inside the pores of particles. This could be a great merit to handle hydrate easily when it is applied to gas transport/storage method. Comparing to bulk hydrate, it seems easier to handle particles than sticky and massive hydrates. Further research will be continued to investigate this method.

Acknowledgement

This work was supported by Ministry of Commerce, Industry and Energy (MOCIE) through Electric Power Industry Technology Evaluation & Planning Center (ETEP).

References

(9) Henry P, Thomas M, Cennell MB, Formation of natural gas hydrates in marine sediments 2. thermodynamic


강성필

1994년 고려대학교 화학공학과 공학사
1996년 한국과학기술원 화학공학과 공학석사
2000년 한국과학기술원 화학공학과 공학박사

현재 한국에너지기술연구원 가스화연구센터 산업연구원
E-mail : spkang@kier.re.kr