

Phase Equilibria of Ethane and Propane Hydrates in Porous Silica Gels

Yongwon Seo¹, Seungmin Lee¹, Inuk Cha¹, Ju Dong Lee², Seong-Pil Kang³

¹Department of Chemical Engineering, Changwon National University, 9 Sarim-dong, Changwon, Gyeongnam 641-773, Korea

²Advanced Energy Resource Development Team, Korea Institute of Industrial Technology, 1274 Jisa-dong, Gangseo-gu, Busan 618-230, Korea

³Clean Fossil Energy Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Korea

In the present study, we examined the active role of porous silica gels when used as natural gas storage and transportation media. We adopted the dispersed water in silica gel pores to substantially enhance active surface for contacting and encaging gas molecules. The three-phase hydrate (H) – water-rich liquid (L_w) – vapor (V) equilibria for the binary C_2H_6 + water and C_3H_8 + water mixtures in silica gel pores of nominal diameters 6.0, 15.0, and 100.0 nm were measured. At specified temperatures the hydrate stability region is shifted to the higher pressure region depending on pore size when compared with those of bulk hydrates. Through application of the Gibbs-Thomson relationship to experimental data, we determined the value of 39 ± 2 mJ/m² and 45 ± 1 mJ/m² for C_2H_6 hydrate – water and C_3H_8 hydrate – water interfacial tensions, respectively. The overall results given in this study could be quite useful in various fields such as exploitation of natural gas hydrate and transportation of natural gas.

1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds formed when “guest” molecules of suitable size and shape are incorporated in the well-defined cages in the “host” lattice made up of hydrogen-bonded water molecules. These compounds exist in three distinct structures, structure I (sI), structure II (sII) and structure H (sH), which contain differently sized and shaped cages. The sI and sII hydrates consist of two types of cages, while the sH hydrate consists of three types of cages (Sloan and Koh, 2007). Large masses of natural gas hydrates exist both on-shore buried under the permafrost and off-shore buried under the oceanic and deep lake sediments. Naturally occurring gas hydrates in the earth, which contain mostly CH_4 , are regarded as future energy resources. Recent investigations suggest the possibility of sequestering carbon dioxide produced from fossil fuel-fired power plants and industry as gas hydrates in the deep ocean or in the natural gas hydrate layer to prevent further release into the atmosphere. Since each volume of gas hydrate can contain as much as 170 volumes of gas at standard temperature and pressure conditions, gas hydrate can also be applied to natural gas

storage and transportation (Sloan and Koh, 2007). Even though all the applications above are related to gas hydrate formation in porous media, only a few limited works focusing on CH_4 and CO_2 hydrates were published in the literature (Handa and Stupin, 1992; Seshadri et al., 2001; Seo et al., 2002; Anderson et al., 2003)

When gas hydrates directly form from bulk water or powdered ice, the conversion of water or ice to hydrate is not so high because of the quite limited surface area of the host media. Therefore, we adopted the dispersed water in silica gel pores to substantially enhance active surface for contacting gas molecules when porous silica gels were used as natural gas storage and transportation media. In the present study, the hydrate phase equilibria of binary C_2H_6 + water and C_3H_8 + water mixtures were measured in 6.0, 15.0, and 100.0 nm silica gel pores to thoroughly examine the effect of geometrical constraints on hydrate phase equilibria. C_2H_6 and C_3H_8 are the second and third major components of natural gas, respectively. However, the accurate and systematic approach to the hydrate phase equilibria for the binary C_2H_6 + water and C_3H_8 + water mixtures in porous media have rarely been reported by other researchers. In this study, we attempted to examine the more precise nature and unique pattern of pore effects on C_2H_6 and C_3H_8 hydrate equilibria in silica gel pores of various diameters (6.0, 15.0, and 100.0 nm).

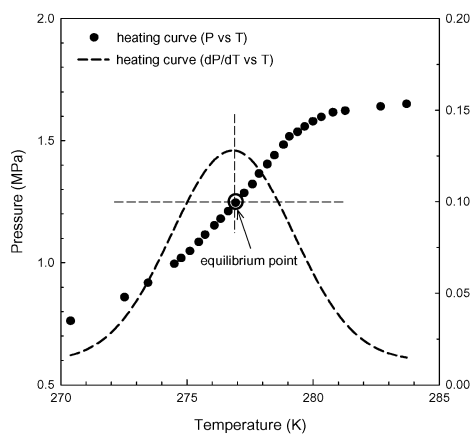


Figure 1. P - T trace for determination of H - L_V - V equilibrium point of C_2H_6 hydrate in 15.0 nm SG.

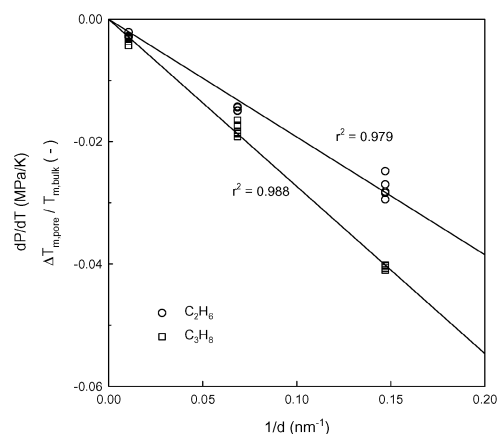


Figure 2. Plot of the reciprocal pore diameter ($1/d$) versus $\Delta T_{m,pore} / T_{m,bulk}$ for C_2H_6 and C_3H_8 hydrates in silica gel pores.

2. Experimental

The C_2H_6 and C_3H_8 gases used for the present study were supplied by Union Special Gas (Korea) and had a stated purity of 99.9 and 99.7 mol %, respectively. Silica gels of nominal pore diameters 6.0 nm (6.0 nm SG) and 15.0 nm (15.0 nm SG) were purchased from Aldrich (USA). Silica gel of nominal pore diameter 100.0 nm (100.0 SG) was purchased from Silicycle (Canada). All materials were used without further treatment. The properties of silica gels having four different pore diameters were measured by

ASAP 2420 and Autopore IV 9520 (Micromeritics, USA) and listed in Table 1. For hydrate phase equilibrium measurement, the silica gels were first dried at 393 K for 24 h before water sorption. Some amount of dried silica gel powder was placed in a bottle and an amount of water identical with the pore volume of silica gel was added to the powder. After being mixed, the bottle was sealed off with a cap to prevent water evaporation. Then, the bottle was vibrated with an ultrasonic wave at 293.15 K for 24 h to completely fill the pores with water. A more detailed explanation of the method was given in the previous paper (Seo et al., 2002).

The equilibrium cell was made of 316 stainless steel and had an internal volume of about 150 cm³. The experiment for hydrate-phase equilibrium measurements began by charging the equilibrium cell with about 80 cm³ of silica gels containing pore water. After the equilibrium cell was pressurized to the desired pressure with C₂H₆ or C₃H₈, the whole main system was slowly cooled to a temperature lower than the expected equilibrium one. When pressure depression due to hydrate formation reached a steady-state condition, the cell temperature was increased in 0.3 K steps, with sufficient time. The equilibrium pressure and temperature of the three phases (hydrate (H) – water-rich liquid (L_w) – vapor (V)) were determined by considering the pore-size distribution of the silica gels used. Unlike the bulk hydrate, in the case of hydrates in porous silica gels, it becomes very difficult to determine the unique equilibrium dissociation point in the *P-T* profile. In the present study, to overcome this inherent difficulty, the dissociation equilibrium point in porous silica gels was chosen as the inflection point of *P* versus *T* curve, which corresponds to the extremum point of the *dP/dT* versus *T* curve (Figure 1). As indicated by Anderson et al. (2003), the inflection point of the heating curve (*P* versus *T*) corresponds to the equilibrium dissociation point in the pores of the mean diameter of the silica gels used. A strong resemblance between the heating curve (*dP/dT* versus *T*) and pore-size distribution curve guarantees the validity of this method for determining the equilibrium dissociation point in silica gels with broad pore-size distributions.

Table 1. Physical properties of silica gel samples

sample	6.0 nm SG	15.0 nm SG	100.0 nm SG
mean particle diameter (μm)	(33-74)	(33-74)	(40-75)
mean pore diameter (nm)	6.8 (6.0)	14.6 (15.0)	94.5 (100.0)
pore volume (cm ³ /g)	0.84 (0.75)	1.13 (1.15)	0.83 (-)
surface area (m ² /g)	497 (480)	308 (300)	42.4 (50)

*Values in the parenthesis are vendor data.

3. Results and Discussion

In the present study, the pores of silica gels were first completely saturated with water, and upon reaching the H – L_w – V equilibrium, the pores were filled with only hydrate and liquid water. Therefore, it is assumed that the wetting angle (θ) is 0°. Even though the operative interface of the hydrate and liquid water phases is very important in understanding the pore effect on hydrate formation/dissociation and thermodynamic modeling of pore hydrate equilibrium, no data for the C₂H₆ hydrate – water and C₃H₈ hydrate – water interfacial tensions (σ_{HW}) have been reported in the literature.

To relate the dissociation temperature depression (from bulk conditions) with the pore size of silica gels at a given pressure, the Gibbs-Thomson equation was used in this study. According to this relationship, the temperature depression of hydrate dissociation in a cylindrical pore, $\Delta T_{m,pore}$, relative to the bulk dissociation temperature, $T_{m,bulk}$, is defined as (Clennell et al., 1999)

$$\frac{\Delta T_{m,pore}}{T_{m,bulk}} = - \left(\frac{\sigma_{HW} \cos \theta}{\rho_h \Delta H_{h,d} r} \right) \quad (1)$$

or, in terms of pore diameter,

$$\frac{\Delta T_{m,pore}}{T_{m,bulk}} = - \left(\frac{2 \sigma_{HW} \cos \theta}{\rho_h \Delta H_{h,d} d} \right) \quad (2)$$

where $\Delta T_{m,pore}$ is the difference between the pore ($T_{m,pore}$) and bulk dissociation temperature, $T_{m,bulk}$, at a specified pressure, ρ_h the hydrate density, $\Delta H_{h,d}$ the hydrate dissociation enthalpy, r the pore radius, and d the pore diameter.

As shown in Figure 2, the interfacial tension between the hydrate and water can be estimated from the slope of the plot of the reciprocal pore diameter ($1/d$) versus $\Delta T_{m,pore} / T_{m,bulk}$ for hydrate dissociation in silica gel pores. Handa (1986) reported $\Delta H_{h,d}$ values of 71.8 kJ/mol for C₂H₆ hydrate and 129.2 kJ/mol for C₃H₈ hydrate through calorimetric studies. For C₂H₆ hydrate, assuming the hydration number is 7.67 (C₂H₆•7.67H₂O), which yields a hydrate density of 969 kg/m³, and hydrate dissociation enthalpy is 71.8 kJ/mol, and applying these values to eq (1) or eq (2), an average value for C₂H₆ hydrate – water interfacial tension of 39 ± 2 mJ/m² was obtained from the slope of data in Figure 2. For C₃H₈ hydrate, assuming the hydration number is 17.0 (C₃H₈•17.0H₂O), which gives a hydrate density of 898 kg/m³, and hydrate dissociation enthalpy is 129.2 kJ/mol, and applying these values to eq (1) or eq (2), an average value for C₃H₈ hydrate – water interfacial tension of 45 ± 1 mJ/m² was obtained from the slope of data in Figure 2.

To the best of our knowledge, the value for C₂H₆ hydrate – water interfacial tension was obtained for the first time in this work. This value is a little larger than those of the ice – water interfacial tension, 32 ± 2 mJ/m², CH₄ hydrate – water interfacial tension, 32 ± 1 mJ/m², and CO₂ hydrate – water interfacial tension, 30 ± 1 mJ/m² (Uchida et al., 2002; Anderson et al., 2003). The value for C₃H₈ hydrate – water interfacial tension obtained in this work is slightly smaller than that of Uchida et al. (2002), 50 ± 2 mJ/m². However,

Uchida et al. (2002) used the mixed gas of 91.2 % C_3H_8 , 6.7% CH_4 , and 2.1% C_2H_6 to determine the value for C_3H_8 hydrate – water interfacial tension.

The three-phase H – L_W – V equilibria of C_2H_6 and C_3H_8 hydrates confined in silica gel pores with nominal diameters of 6.0, 15.0, and 100.0 nm were measured between lower and upper quadruple point temperatures. The hydrate equilibrium data of the binary C_2H_6 + water mixtures were presented in Figure 3. Figure 3 also includes the hydrate equilibrium data obtained by Zhang et al. (2002) for 6.0 and 15.0 nm pores, which showed a similar trend. At specified temperatures, the H – L_W – V lines of C_2H_6 hydrates in silica gel pores were shifted to a higher pressure region depending on pore size when compared with that of bulk hydrate.

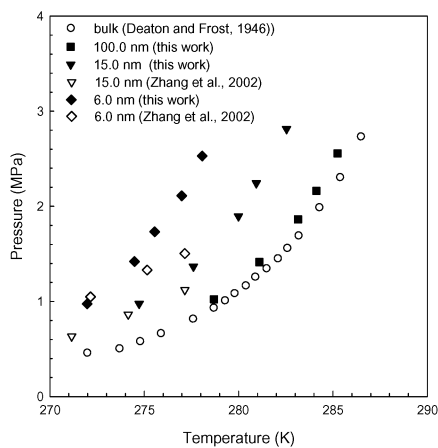


Figure 3. Hydrate phase equilibria of the binary C_2H_6 + water mixtures in silica gel pores.

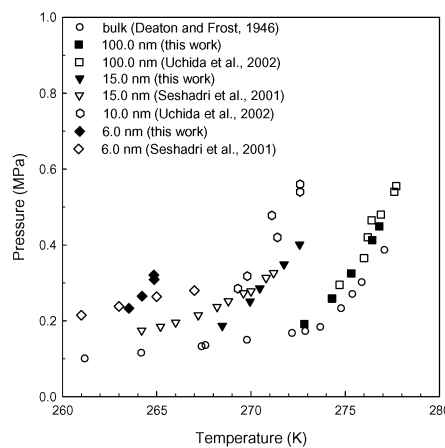


Figure 4. Hydrate phase equilibria of the binary C_3H_8 + water mixtures in silica gel pores.

In addition, hydrate equilibrium data of the binary C_3H_8 + water mixtures were presented in Figure 4. For a close comparison, the pore hydrate data reported in the literature were all included in Figure 4: Uchida et al. (2002) for 10.0 and 100.0 nm pores and Seshadri et al. (2001) for 6.0 and 15.0 nm pores. The present experimental data were in good agreement with those of Uchida et al. (2002), but largely deviated from those of Seshadri et al. (2001), even though Uchida et al. (2002) used Vycor porous glass beads and a mixed gas of 91.2% C_3H_8 , 6.7% CH_4 , and 2.1% C_2H_6 .

In the present study, we examined the effect of pore size on the hydrate phase equilibria to utilize porous silica gels, which can yield an enhanced surface area for contacting gas molecules, as natural gas storage and transportation media. The optimum pore size for natural gas storage and transportation should be determined by considering both the larger surface area at smaller pore sizes and smaller pressure shift at larger pore sizes. From the experimental results, it was found that silica gels with pore diameter over 30.0 nm gave only very slight pressure shift at a specified temperature and, thus, could be a good candidate for natural gas storage and transportation.

4. Conclusions

Three-phase H – L_w – V equilibria of C₂H₆ and C₃H₈ hydrates confined in silica gel pores with nominal diameters of 6.0, 15.0, and 100.0 nm were measured. Decrease in water activity due to geometrical constraints caused pore hydrates to form at much higher pressure at a specified temperature. Through the Gibbs-Thomson equation for dissociation within the cylindrical pores, the C₂H₆ hydrate – water interfacial tension (σ_{HW}) of 39 ± 2 mJ/m² and the C₃H₈ hydrate – water interfacial tension (σ_{HW}) of 45 ± 1 mJ/m² were obtained. The values of hydrate – water interfacial tension and thermodynamic results obtained in this study could be used for understanding the fundamental phase behavior and thermodynamic models of gas hydrates in pores, and, thus, could be quite useful in various fields, such as exploitation of natural gas hydrate in marine sediments and sequestration of carbon dioxide into the deep ocean.

5. Acknowledgement

The authors would like to acknowledge funding from the Korea Ministry of Knowledge Economy (MKE) through “Energy Technology Innovation Program”.

6. References

- Anderson R., Llamedo M., Tohidi, B. and Burgass, R.W., 2003, Experimental measurement of methane and carbon dioxide clathrate hydrate equilibria in mesoporous silica, *J. Phys. Chem. B*, 107, 3507-3514.
- Clennell M.B., Hovland M., Booth, J.S., Henry, P. and Williams, J.W., 1999, Formation of natural gas hydrates in marine sediments 1. Conceptual model of gas hydrate growth conditioned by host sediment properties, *J. Geophys. Res.* 104, 22985.
- Deaton W.M. and Frost E.M. Jr., 1946, Gas hydrates and their relation to the operation of natural-gas pipe lines, U.S. Bur. Mines Monogr. 8, 101.
- Handa Y.P., 1986, Compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of methane, ethane, and propane, and enthalpy of dissociation of isobutene hydrate, as determined by a heat-flow calorimeter, *J. Chem. Thermodyn.* 18, 915-921.
- Handa Y.P. and Stupin D., 1992, Thermodynamic properties and dissociation characteristics of methane and propane hydrates in 70-A-radius silica gel pores, *J. Phys. Chem.* 96, 8599.
- Seo Y., Lee H. and Uchida T., 2002, Methane and carbon dioxide hydrate phase behavior in small porous silica gels: Three-phase equilibrium determination and thermodynamic modeling, *Langmuir* 18, 9164-9170.
- Seshadri K., Wilder J.W. and Smith D.H., 2001, Measurement of equilibrium pressure and temperatures for propane hydrate in silica gels with different pore-size distributions, *J. Phys. Chem. B* 105, 2627.
- Sloan E.D. and Koh, C.A., 2008, *Clathrate Hydrates of Natural Gases*. 3rd Ed.; CRC Press: Boca Raton.
- Zhang W., Wilder J.W. and Smith D.H., 2002, Interpretation of ethane hydrate equilibrium data for porous media involving hydrate-ice equilibria, *AIChE J.* 48, 2324-2331.