

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231272657>

Experimental Measurement and Thermodynamic Modeling of Hydrate-Phase Equilibria for the Ternary $C_2H_6 + NaCl + Water$ and $C_3H_8 + NaCl + Water$ Mixtures in Silica Gel Pores

ARTICLE in ENERGY & FUELS · OCTOBER 2010

Impact Factor: 2.79 · DOI: 10.1021/ef101181u

CITATIONS

3

READS

16

2 AUTHORS, INCLUDING:



Yongwon Seo

Ulsan National Institute of Science and Tech...

55 PUBLICATIONS 1,062 CITATIONS

SEE PROFILE

Experimental Measurement and Thermodynamic Modeling of Hydrate-Phase Equilibria for the Ternary $C_2H_6 + NaCl + \text{Water}$ and $C_3H_8 + NaCl + \text{Water}$ Mixtures in Silica Gel Pores

Seungmin Lee and Yongwon Seo*

Department of Chemical Engineering, Changwon National University, 9 Sarim-dong, Uichang-gu, Changwon-si, Gyeongnam 641-773, Republic of Korea

Received September 1, 2010. Revised Manuscript Received October 5, 2010

We measured hydrate-phase equilibria for the ternary $C_2H_6 + NaCl$ (3 wt %) + water and $C_3H_8 + NaCl$ (3 wt %) + water mixtures in silica gel pores of nominal 6.0, 15.0, and 30.0 nm diameters. We also measured hydrate-phase equilibria for the ternary $C_2H_6 + NaCl + \text{water}$ and $C_3H_8 + NaCl + \text{water}$ mixtures in nominal 30.0 nm silica gel pores at two different NaCl concentrations of 3 and 10 wt %. The combined effect of pores and electrolytes shifted three-phase H–L_W–V equilibrium lines to a higher pressure region for any given temperature depending upon NaCl concentrations and pore sizes. The experimentally measured hydrate-phase equilibria were compared to the calculated results based on the van der Waals and Platteeuw model. The activity of water within silica gel pores saturated with the aqueous electrolyte solutions was expressed by adopting a Pitzer model for electrolyte solutions and a correction term for the capillary effect. With the values for a hydrate–water interfacial tension (σ_{HW}) of $39 \pm 2 \text{ mJ/m}^2$ for C_2H_6 hydrate and $45 \pm 1 \text{ mJ/m}^2$ for C_3H_8 hydrate, the calculation values were in good agreement with the experimental values. The structure of each C_2H_6 and C_3H_8 hydrate formed in silica gel pores saturated with NaCl solutions was found to be identical to that of each C_2H_6 and C_3H_8 hydrate in the pure bulk state through nuclear magnetic resonance spectroscopy.

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.¹ Gas hydrates occur naturally under permafrost regions and within deep ocean sediments. Naturally occurring gas hydrates have great potential as an energy source in the future because of their huge quantities and wide geographical distribution. Each volume of natural gas hydrate can contain as much as 164 volumes of gas at standard temperature and pressure conditions.¹ The natural gas hydrates generally consist of a mixture of hydrocarbons, such as CH_4 , C_2H_6 , and C_3H_8 , and non-hydrocarbons, such as hydrogen sulfide, carbon dioxide, and nitrogen. Each of these components has their own structural characteristics and hydrate-phase equilibrium conditions. CH_4 , a major component of natural gas hydrate, and C_2H_6 are known to form sI hydrate and need a relatively higher pressure for gas hydrate formation, whereas C_3H_8 forms sII hydrate at a much lower pressure.¹

Oceanic gas hydrates are commonly found in sand or clay-type sediments. The capillary inhibition of hydrate stability in narrow pores, such as fine-grained silts, muds, and clays, has previously been considered to possibly explain differences between predicted and actual hydrate stability zones in ocean

sediments, while the equilibrium pressure for hydrate dissociation and the thermodynamic properties in large pores of coarse-grained sand sediment are nearly identical to those in the pure bulk water phase.^{2,3} Another key factor in considering gas hydrate stability in the ocean sediment is the inhibition effect of electrolytes dissolved in seawater. Therefore, it is crucial to consider the combined inhibition effects of both pores and electrolytes to predict an accurate gas hydrate stability zone in the ocean sediment. In most cases, C_2H_6 and C_3H_8 are the second and third major components of natural gas hydrates, respectively, although their compositions are dependent upon the origin (biogenic or thermogenic) and location of reservoirs. Despite the importance and urgency of experimental data, no research on the hydrate-phase equilibria for the $C_2H_6 + NaCl + \text{water}$ and $C_3H_8 + NaCl + \text{water}$ mixtures in narrow pores has been reported, even though numerous investigations separately covering either pore or electrolyte effects have been conducted by many researchers^{4–13} and, recently, some limited studies concerning the combined effects of both pores and electrolytes

(2) Clennell, M. B.; Hovland, M.; Booth, J. S.; Henry, P.; Winters, W. J. *J. Geophys. Res.* **1999**, *104*, 22985–23003.

(3) Henry, P.; Thomas, M.; Clennell, M. B. *J. Geophys. Res.* **1999**, *104*, 23005–23022.

(4) Handa, Y. P.; Stupin, D. J. *Phys. Chem.* **1992**, *96*, 8599–8603.

(5) Seo, Y.; Lee, H.; Uchida, T. *Langmuir* **2002**, *18*, 9164–9170.

(6) Smith, D. H.; Wilder, J. W.; Seshadri, K. *AIChE J.* **2002**, *48*, 393–400.

(7) Uchida, T.; Ebinuma, T.; Takeya, S.; Nagao, J.; Narita, H. *J. Phys. Chem. B* **2002**, *106*, 820–826.

(8) Anderson, R.; Llamedo, M.; Tohidi, B.; Burgass, R. W. *J. Phys. Chem. B* **2003**, *107*, 3507–3514.

(9) Kang, S. P.; Lee, J. W.; Ryu, H. J. *Fluid Phase Equilib.* **2008**, *274*, 68–72.

(10) Seo, Y.; Lee, S.; Cha, I.; Lee, J. D.; Lee, H. *J. Phys. Chem. B* **2009**, *113*, 5487–5492.

(11) Patil, S. L. M.S. Thesis, University of Alaska—Fairbanks, Fairbanks, AK, 1987.

*To whom correspondence should be addressed. Telephone: +82-55-213-3757. Fax: +82-55-283-6465. E-mail: yseo@changwon.ac.kr.

(1) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008.

Table 1. Physical Properties of Silica Gel Samples^a

sample	6.0 nm SG	15.0 nm SG	30.0 nm SG
mean particle diameter (μm)	(33–74)	(33–74)	(40–75)
mean pore diameter (nm)	6.8 (6.0)	14.6 (15.0)	30.5 (30.0)
maximum pore diameter (nm)	12.9	22.6	56.6
pore volume (cm^3/g)	0.84 (0.75)	1.13 (1.15)	0.84
surface area (m^2/g)	497 (480)	308 (300)	111 (100)

^a Values in parentheses are vendor data.

on the stability of simple and mixed gas hydrates appear in the literature.^{14–16}

In this work, we present the precise nature and characteristics of pore C_2H_6 and C_3H_8 hydrates in the presence of electrolytes through hydrate-phase equilibrium measurement and nuclear magnetic resonance (NMR) analysis. First, hydrate-phase equilibria for the ternary $\text{C}_2\text{H}_6 + \text{NaCl}$ (3 wt %) + water and $\text{C}_3\text{H}_8 + \text{NaCl}$ (3 wt %) + water mixtures in silica gel pores of nominal 6.0, 15.0, and 30.0 nm diameters were measured to check the effect of the pore size. Second, hydrate-phase equilibria for the ternary $\text{C}_2\text{H}_6 + \text{NaCl}$ + water and $\text{C}_3\text{H}_8 + \text{NaCl}$ + water mixtures in silica gel pores of a nominal 30.0 nm diameter at two different NaCl concentrations (3 and 10 wt %) were measured to confirm the effect of salinity. Experimental results were compared to the predicted values obtained from a more adequate and refined model, which accounts for the presence of geometrical constraints and electrolytes. Finally, NMR spectroscopy was used to analyze the structural characteristics of each C_2H_6 and C_3H_8 hydrate formed in silica gel pores saturated with NaCl solution.

2. Experimental Section

2.1. Material. 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%, respectively. Silica gels of nominal pore diameters of 6.0 nm (6.0 nm SG) and 15.0 nm (15.0 nm SG) were purchased from Aldrich (St. Louis, MO). Silica gels of nominal pore diameters of 30.0 nm (30.0 nm SG) were purchased from Silicycle (Quebec City, Quebec, Canada). All materials were used without further treatment. The properties of silica gels having three different pore diameters were measured by ASAP 2420 (Micromeritics, Norcross, GA) and presented in Table 1. Figure 1 shows the pore-size distribution and cumulative pore-size distribution of a nominal 6.0 nm silica gel sample. As shown in Figure 1, the maximum pore diameter of each silica gel sample was determined as the pore diameter corresponding to a 99.5% value of each final cumulative pore volume. Hereafter, for clarity, the silica gel sample will be expressed as the maximum diameter (nominal diameter) in the text: 12.9 (6.0), 22.6 (15.0), and 56.6 (30.0) nm.

2.2. Apparatus and Procedure. To prepare the pore-saturated silica gels, some amount of dried silica gel powder was placed in a bottle and an amount of electrolyte solution identical to the pore volume of silica gel was added to the powder. After mixing, 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 electrolyte solution.

The experimental apparatus for hydrate-phase equilibria was specially designed to accurately measure the hydrate dissociation

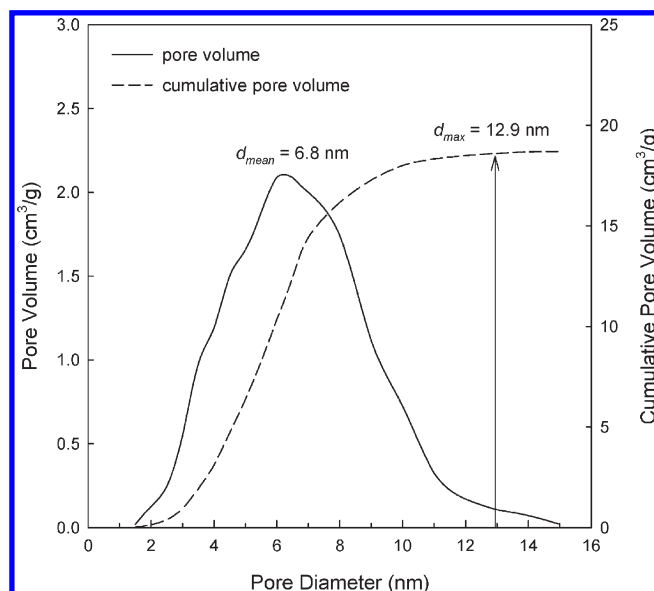


Figure 1. Pore-size distribution and cumulative pore-size distribution of nominal 6.0 nm silica gel.

pressures and temperatures. The equilibrium cell was made of 316 stainless steel and had an internal volume of about 150 cm^3 . The experiment for hydrate-phase equilibrium measurements began by charging the equilibrium cell with about 80 cm^3 of silica gels containing electrolyte solution. After the equilibrium cell was pressurized to the desired pressure with C_2H_6 (or C_3H_8) gas, the whole main system was slowly cooled to a temperature lower than the expected equilibrium temperature. When pressure depression because of hydrate formation reached a steady-state condition, the cell temperature was increased in 0.3 K steps of 2 h equilibrium time for samples of all pore sizes used in this study, which was confirmed to be sufficient by checking the pressure (P) versus time (t) curves for each step.

The equilibrium pressure and temperature of the three phases [hydrate (H)–water-rich liquid (L_W)–vapor (V)] in the silica gel pores should be determined by considering the pore-size distribution of the silica gels. For the pure gas hydrates with a single guest, the dissociation equilibrium point in silica gel pores was chosen as the inflection point of the pressure (P) versus temperature (T) heating curve, which corresponds to the equilibrium dissociation point in the pores of the mean diameter (d_mean) of the silica gels, as indicated by Anderson et al.⁸ and Seo et al.¹⁰ However, for the gas hydrates made from electrolyte solutions, the inflection point of the P versus T heating curve does not correspond to the initial electrolyte concentration. Gas hydrates formed in pores of mean diameter will be in equilibrium with an electrolyte solution of higher concentration than the initial concentration because hydrate lattices exclude electrolytes, resulting in an increase in the electrolyte concentration of the liquid water phase in the H– L_W –V equilibrium. Therefore, for systems with an electrolyte present, the electrolyte concentration in the liquid water phase becomes equal to the initial conditions only at the point of final pore hydrate dissociation, i.e., maximum pore diameter (d_max). Figure 2 shows one example of the P versus T heating curve for the $\text{C}_2\text{H}_6 + \text{NaCl}$ (3 wt %) + water mixture in 22.6 (15.0) nm silica gel pores. To accurately account for pore-size distribution and initial electrolyte concentration, the hydrate dissociation equilibrium point in silica gel pores was chosen in the present study as the final pore hydrate dissociation point that corresponds to the hydrate dissociation at d_max .

To measure structural characteristics of the C_2H_6 and C_3H_8 gas hydrates formed in silica gel pores saturated with electrolyte solution, a Bruker 400 MHz solid-state NMR spectrometer that belongs to the Korea Basic Science Institute (KBSI) was used in this study. The NMR spectra were recorded at 243 K by placing

(12) Dholabhai, P. D.; Englezos, P.; Kalogerakis, N.; Bishnoi, P. R. *Can. J. Chem. Eng.* **1991**, *69*, 800–805.

(13) Tohidi, B.; Burgass, B. W.; Danesh, A.; Todd, A. C. *Society of Petroleum Engineers (SPE) Offshore European Conference*; 1993; SPE Paper 26701.

(14) Østergaard, K. K.; Anderson, R.; Llamado, M.; Tohidi, B. *Terra Nova* **2002**, *14*, 307–312.

(15) Seo, Y.; Lee, H. J. *Phys. Chem. B* **2003**, *107*, 889–894.

(16) Lee, S.; Seo, Y. *Langmuir* **2010**, *26*, 9742–9748.

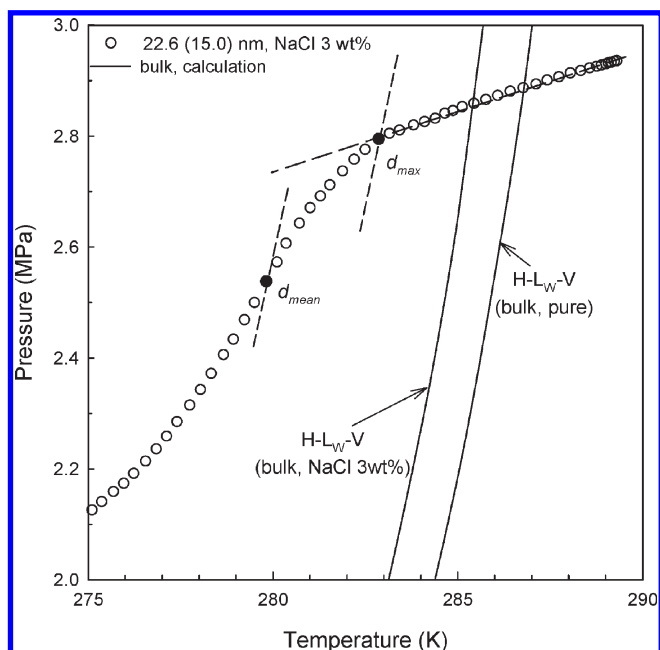


Figure 2. P versus T heating curve for the $C_2H_6 + NaCl$ (3 wt %) + water mixtures in 22.6 (15.0) nm silica gel pores.

the hydrate samples within a 4 mm outer diameter Zr rotor that was loaded into the variable-temperature (VT) probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at about 2–4 kHz. The pulse length of 2 μs and pulse repetition delay of 10 s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 μs 90° pulses were used. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. The hydrate samples for NMR analysis were prepared with the same apparatus as that used for hydrate-phase equilibrium measurement. When gas hydrate formation was completed, the formed gas hydrates were finely powdered in the liquid nitrogen vessel and sampled into Zr rotor immersed in liquid nitrogen to prevent any gas hydrate dissociation. A more detailed description of the experimental apparatus and procedure was given in previous papers.^{7,10,16}

3. Thermodynamic Modeling

The equilibrium criteria of the hydrate-forming mixture are based on the equality of fugacities of the specified component i in all phases that coexist simultaneously

$$\hat{f}_i^H = \hat{f}_i^L = \hat{f}_i^V (=f_w^1) \quad (1)$$

where H stands for the hydrate phase, L stands for the water-rich liquid phase, V stands for the vapor phase, and I stands for the ice phase. It can be reasonably assumed that electrolytes are completely excluded from the hydrate lattice and remain only in the liquid phase.

The chemical potential difference between the empty hydrate and filled hydrate phases, $\Delta\mu_w^{MT-H} (= \mu_w^{MT} - \mu_w^H)$, is generally derived from statistical mechanics in the van der Waals and Platteau model¹⁷

$$\Delta\mu_w^{MT-H} = \mu_w^{MT} - \mu_w^H = -RT \sum_m v_m \ln(1 - \sum_j \theta_{mj}) \quad (2)$$

(17) van der Waals, J. H.; Platteau, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1–58.

where μ_w^{MT} is the chemical potential of water in the hypothetical empty hydrate lattice, v_m is the number of cavities of type m per water molecule in the hydrate phase, and θ_{mj} is the fraction of cavities of type m occupied by the molecules of component j .

Holder et al.¹⁸ suggested the method to simplify the chemical potential difference between the empty hydrate and the reference state as follows:

$$\frac{\Delta\mu_w^{MT-L}}{RT} = \frac{\Delta\mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{MT-I} + \Delta h_w^{fus}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{MT-I} + \Delta v_w^{fus}}{RT} dP - \ln a_w \quad (3)$$

where T_0 is 273.15 K, the normal melting point of water, $\Delta\mu_w^0$ is the chemical potential difference between the empty hydrate and water at T_0 and zero absolute pressure, Δh_w^{MT-I} and Δv_w^{MT-I} are the molar difference in enthalpy and volume between the empty hydrate and ice, respectively, Δh_w^{fus} and Δv_w^{fus} are the molar difference in enthalpy and volume between ice and liquid water, respectively, and a_w is the activity of water.

The decrease of water activity in silica gel pores filled with electrolyte solution can be expressed as^{3,15,19}

$$\ln a_w = \ln a_w^{EL} - \frac{FV_L \cos \theta \sigma_{HW}}{rRT} \quad (4)$$

where a_w^{EL} is activity of water in electrolyte solution, F is the shape factor, a function of the curvature of the hydrate–liquid interface, V_L is the molar volume of pure water, θ is the wetting angle between water and hydrate phases, σ_{HW} is the interfacial tension between hydrate and liquid water phases, and r is the pore radius. In the present study $F=1$ was used for hydrate dissociation in narrow pores.

The activity of water in electrolyte solution is given as

$$\ln a_w^{EL} = -\frac{M_w v m}{1000} \phi \quad (5)$$

where M_w stands for the molecular weight of water, m stands for the molality of the electrolyte, v stands for the number of ions that the electrolytes dissociate, and ϕ stands for the osmotic coefficient. The osmotic coefficient was calculated from the model of Pitzer.²⁰

Combining and solving the above equations determines the values of H–L_w–V equilibrium pressure and temperature for the pore radius and electrolyte concentration. The fugacities of supercooled water and all components in the vapor phase were calculated using Soave–Redlich–Kwong (SRK) equation of state incorporated with the modified Huron–Vidal second-order mixing rule.^{21,22} The optimized Kihara potential parameters used in this study and more details of the model description were given in our previous papers.^{7,10,15,16}

4. Results and Discussion

Three-phase H–L_w–V equilibria for the ternary $C_2H_6 + NaCl$ (3 wt %) + water mixtures in 12.9 (6.0), 22.6 (15.0), and 56.6 (30.0) nm silica gel pores and for the ternary $C_2H_6 + NaCl$ + water mixtures in 56.6 (30.0) nm silica gel pores at the

(18) Holder, G. D.; Corbin, G.; Papadopoulos, K. D. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 282–286.

(19) Llamado, M.; Anderson, R.; Tohidi, B. *Am. Mineral.* **2004**, *89*, 1264–1270.

(20) Pitzer, K. S.; Mayorga, G. J. *Phys. Chem.* **1973**, *77*, 2300–2308.

(21) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.

(22) Dahl, S.; Michelsen, M. L. *AIChE J.* **1990**, *36*, 1829–1836.

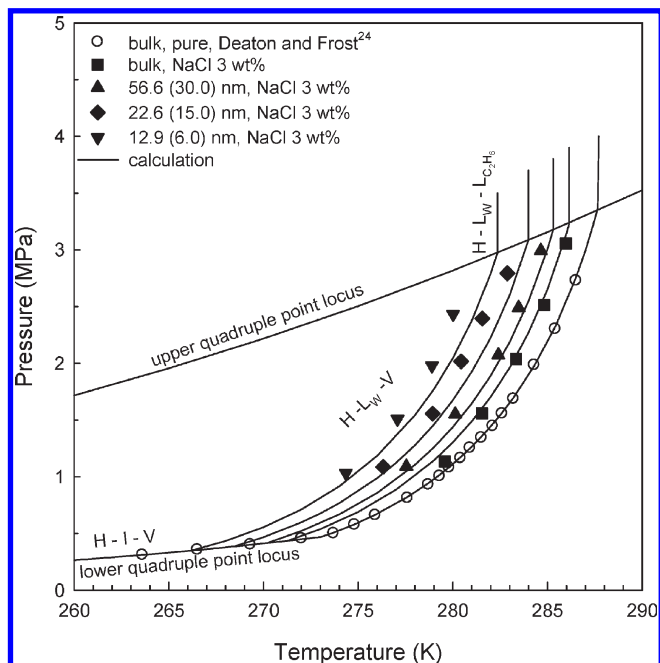


Figure 3. Hydrate-phase equilibria of the ternary $C_2H_6 + NaCl$ (3 wt %) + water mixtures in silica gel pores.

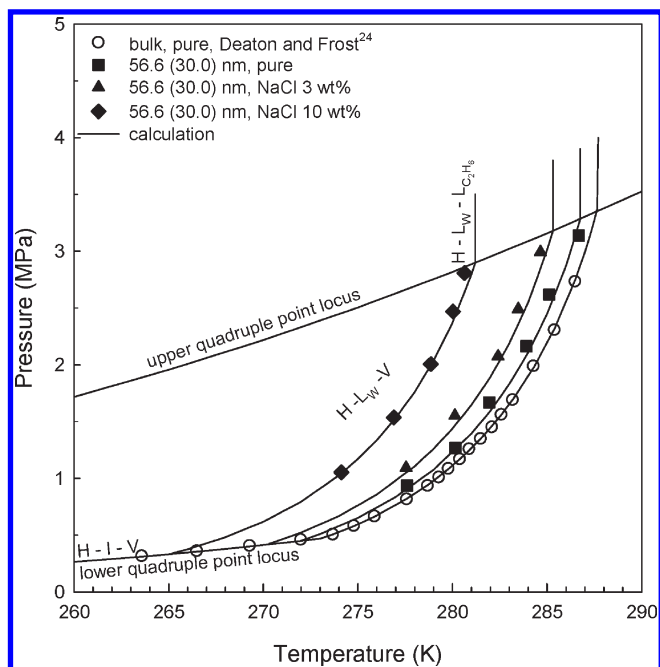


Figure 4. Hydrate-phase equilibria of the ternary $C_2H_6 + NaCl$ + water mixtures in 56.6 (30.0) nm silica gel pores.

$NaCl$ concentrations of 3 and 10 wt % were experimentally measured and presented along with model calculations in Figures 3 and 4. The equilibrium dissociation pressure and temperature data for C_2H_6 hydrates were listed in Table 2. In the same way, three-phase $H-L_W-V$ equilibria for the ternary $C_3H_8 + NaCl$ (3 wt %) + water mixtures in 12.9 (6.0), 22.6 (15.0), and 56.6 (30.0) nm silica gel pores and for the ternary $C_3H_8 + NaCl$ + water mixtures in 56.6 (30.0) nm silica gel pores at the $NaCl$ concentrations of 3 and 10 wt % were experimentally measured and presented along with model calculations in Figures 5 and 6. The equilibrium dissociation pressure and temperature data for C_3H_8 hydrates were listed in Table 3. The

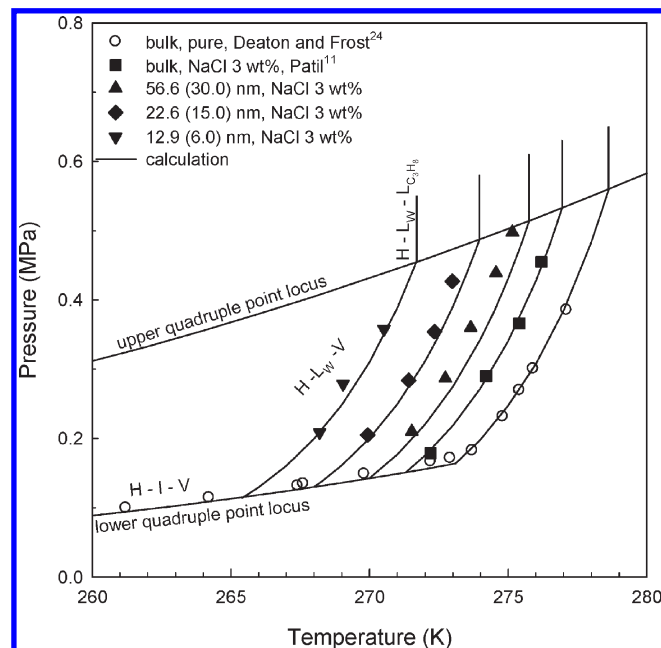


Figure 5. Hydrate-phase equilibria of the ternary $C_3H_8 + NaCl$ (3 wt %) + water mixtures in silica gel pores.

Table 2. Hydrate-Phase Equilibrium Data for the $C_2H_6 + NaCl$ + Water Mixtures in Silica Gel Pores

$C_2H_6 + NaCl$ (3 wt %) + Water Mixtures							
12.9 (6.0) nm		22.6 (15.0) nm		56.6 (30.0) nm		bulk	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
274.35	1.033	276.32	1.087	277.55	1.091	279.57	1.136
277.08	1.51	278.93	1.556	280.13	1.553	281.54	1.559
278.90	1.979	280.43	2.017	282.41	2.073	283.33	2.038
280.01	2.434	281.55	2.394	283.48	2.49	284.83	2.515
		282.88	2.794	284.65	2.993	285.96	3.056
$C_2H_6 + NaCl$ + Water Mixtures in 56.6 (30.0) nm							
pure		$NaCl$ (3 wt %)		$NaCl$ (10 wt %)			
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)		
277.60	0.937	277.55	1.091	274.12	1.052		
280.14	1.267	280.13	1.553	276.90	1.536		
281.94	1.668	282.41	2.073	278.85	2.006		
283.90	2.164	283.48	2.49	280.03	2.47		
285.11	2.618	284.65	2.993	280.64	2.808		
286.67	3.137						

presence of either geometrical constraints or electrolytes resulted in hydrate inhibition, which means that hydrate dissociation occurs at a higher pressure for any given temperature or at a lower temperature for any given pressure when compared to either bulk or pure conditions. As can be seen in Figures 3–6, the $H-L_W-V$ equilibrium lines were shifted more to the inhibition region as the pore size decreased and electrolyte concentration increased. It should also be noted that the combined inhibition effects of both pores and electrolytes that closely simulated real marine sediments were also confirmed through examining the shift of experimentally measured $H-L_W-V$ curves to the inhibition region.

Inside the pores, water activity is depressed by the partial ordering and bonding of water molecules with hydrophilic pore surfaces.² The depression of water activity because of the presence of geometrical constraints causes a depression of the

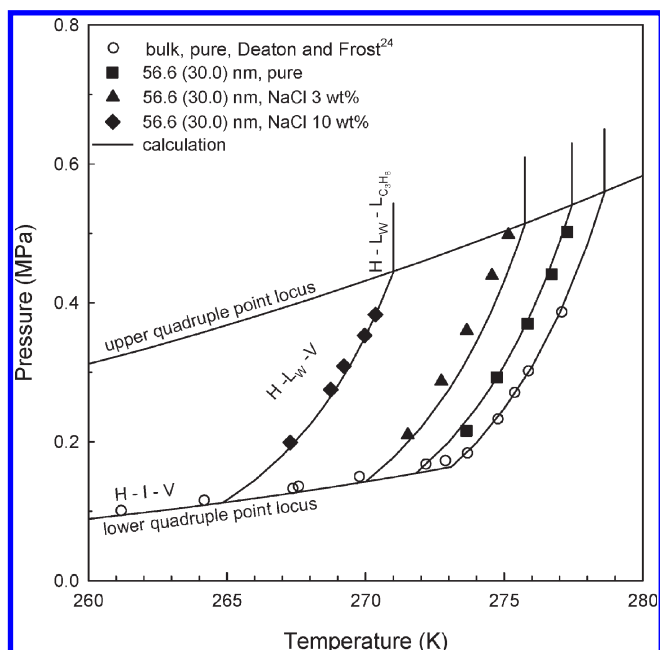


Figure 6. Hydrate-phase equilibria of the ternary $C_3H_8 + NaCl +$ water mixtures in 56.6 (30.0) nm silica gel pores.

Table 3. Hydrate-Phase Equilibrium Data for the $C_3H_8 + NaCl +$ Water Mixtures in Silica Gel Pores

$C_3H_8 + NaCl$ (3 wt %) + Water Mixtures					
12.9 (6.0) nm		22.6 (15.0) nm		56.6 (30.0) nm	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
268.20	0.209	269.94	0.205	271.52	0.21
269.05	0.279	271.41	0.284	272.73	0.287
270.53	0.358	272.34	0.354	273.65	0.36
		272.98	0.427	274.56	0.439
				275.15	0.498
$C_3H_8 + NaCl +$ Water Mixtures in 56.6 (30.0) nm					
pure		NaCl (3 wt %)		NaCl (10 wt %)	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
273.64	0.216	271.52	0.21	267.28	0.199
274.73	0.293	272.73	0.287	268.75	0.275
275.85	0.37	273.65	0.36	269.22	0.309
276.72	0.441	274.56	0.439	269.97	0.353
277.28	0.502	275.15	0.498	270.36	0.383

freezing point of water and hydrate inhibition, which are also observed in the mixtures containing thermodynamic inhibitors, such as electrolytes and alcohols. Therefore, it is generally accepted that the effect of pores on water activity is considered to be equivalent to a change in water activity caused by electrolytes.⁴ In the solid-solution model, equilibrium conditions of hydrates are directly affected by the water activity. As the water activity decreases, the hydrates need higher pressure for stability at a specified temperature, indicating hydrate inhibition. Therefore, the presence of both geometrical constraints and electrolytes can equivalently lead to hydrate inhibition induced by the depression of water activity.

In the present study, it can be reasonably assumed that the wetting angle (θ) between the water and hydrate phases is 0° because silica gel pores were first completely saturated with NaCl solution and, in the $H-L_W-V$ equilibrium state, the pores were filled with only the hydrate and aqueous liquid

Table 4. % AAD between the Experimental and Calculated Values

system	pore size (nm)	% AAD
$C_2H_6 + NaCl$ (3 wt %) + water	12.9 (6.0)	10.8
	22.6 (15.0)	9.1
	56.6 (30.0)	4.8
	bulk	3.4
system	NaCl (wt %)	% AAD
$C_2H_6 + NaCl +$ water in 56.6 (30.0) nm	pure	3.8
	3	4.8
	10	2.6
system	pore size (nm)	% AAD
$C_3H_8 + NaCl$ (3 wt %) + water	12.9 (6.0)	4.2
	22.6 (15.0)	5.4
	56.6 (30.0)	9.8
	bulk	2.2
system	NaCl (wt %)	% AAD
$C_3H_8 + NaCl +$ water in 56.6 (30.0) nm	pure	3.1
	3	9.8
	10	2.6

phases. In particular, the value of the interfacial tension between hydrate and liquid water phases (σ_{HW}) is an essential prerequisite to predict hydrate dissociation equilibrium pressure at a specified temperature in silica gel pores. Recently, Seo et al.¹⁰ presented the values of σ_{HW} for C_2H_6 and C_3H_8 hydrates, which were obtained from fitting their experimental data by the Gibbs–Thomson equation: 39 ± 2 mJ/m² for C_2H_6 hydrate and 45 ± 1 mJ/m² for C_3H_8 hydrate. Using these values of the hydrate–water interfacial tension, the predicted $H-L_W-V$ equilibrium values were generally in good agreement with the experimental values in all experimental ranges. As shown in Figures 3–6, the present thermodynamic model accounting for both the capillary effect and electrolyte inhibition turned out to be reliable in both quantitative and qualitative manners, and for reference, the percent average absolute deviations (% AADs) between experimental and calculated $H-L_W-V$ values are listed in Table 4.

In the pure bulk state, the $H-L_W-V$ equilibrium dissociation point can be accurately determined by the intersection between hydrate dissociation and thermal expansion lines because an abrupt change in the slope of these two lines is observed on the P versus T heating curve. However, because of pore-size distribution, hydrates in pores dissociate over a range of temperatures, as shown in Figure 2. Therefore, there must be inherent uncertainty in determining $H-L_W-V$ equilibrium data in silica gel pores saturated with electrolyte solutions when compared to that in the pure bulk state, even though the pore-size distribution and initial electrolyte concentration were thoroughly taken into consideration in equilibrium measurement. In particular, the systems with combined effects of both pore and salt have generally larger % AADs than the systems with single effects of either pore or salt, as shown in Table 4.

Because of experimental difficulties in measuring hydrate (H)–ice (I)–vapor (V) and hydrate (H)–water-rich liquid (L_W)– C_2H_6 (or C_3H_8)-rich liquid [$L_{C_2H_6}$ (or $L_{C_3H_8}$)] phase equilibria, the experimental measurement of the ternary $C_2H_6 + NaCl +$ water and $C_3H_8 + NaCl +$ water mixtures in silica gel pores were restricted to the $H-L_W-V$ phase boundary. However, the model calculation could be extended to two different three-phase boundaries of $H-I-V$ and $H-L_W-L_{C_2H_6}$ (or $L_{C_3H_8}$). The upper quadruple points (Q_2), where two $H-L_W-V$

Table 5. Calculated Lower and Upper Quadruple Points

system	pore size (nm)	Q ₁		Q ₂	
		T (K)	P (MPa)	T (K)	P (MPa)
C ₂ H ₆ + NaCl (3 wt %) + water	12.9 (6.0)	266.2	0.349	282.35	2.971
	22.6 (15.0)	268.5	0.390	284.0	3.088
	56.6 (30.0)	270.3	0.424	285.3	3.178
	bulk	271.3	0.438	286.15	3.234
system	NaCl (wt %)	Q ₁		Q ₂	
		T (K)	P (MPa)	T (K)	P (MPa)
C ₂ H ₆ + NaCl + water in 56.6 (30.0) nm	pure	271.9	0.446	286.75	3.280
	3	270.3	0.424	285.3	3.178
	10	265.2	0.341	281.2	2.897
system	pore size (nm)	Q ₁		Q ₂	
		T (K)	P (MPa)	T (K)	P (MPa)
C ₃ H ₈ + NaCl (3 wt %) + water	12.9 (6.0)	265.4	0.114	271.7	0.456
	22.6 (15.0)	268.0	0.130	273.96	0.487
	56.6 (30.0)	270.0	0.143	275.75	0.513
	bulk	271.3	0.151	276.94	0.532
system	NaCl (wt %)	Q ₁		Q ₂	
		T (K)	P (MPa)	T (K)	P (MPa)
C ₃ H ₈ + NaCl + water in 56.6 (30.0) nm	pure	271.8	0.154	277.44	0.540
	3	270.0	0.143	275.75	0.513
	10	264.85	0.113	271.0	0.444

and H–L_W–L_{C₂H₆} (or L_{C₃H₈}) phase boundaries intersect and, thus, four phases [H, L_W, L_{C₂H₆} (or L_{C₃H₈}), and V] coexist, were located very closely along the saturation vapor pressure curve of C₂H₆ (or C₃H₈). The lower quadruple points (Q₁), where two H–L_W–V and H–I–V phase boundaries intersect and, thus, four phases (H, I, L_W, and V) coexist, appears generally adjacent to the corresponding melting point of ice. It should be noted that, for the prediction of the H–I–V equilibrium line, the interfacial tension between the ice and hydrate phases (σ_{IH}) was assumed to be 0 for C₂H₆ and C₃H₈ hydrates. The calculated upper and lower quadruple points of the ternary C₂H₆ + NaCl + water and C₃H₈ + NaCl + water mixtures in silica gel pores were listed in Table 5.

In the present study, a ¹³C MAS NMR experiment was conducted to investigate the structural characteristics of C₂H₆ and C₃H₈ hydrates because NMR spectroscopy has been recognized as a powerful tool for the structure identification and hydrate composition.²³ In particular, the cage-dependent ¹³C NMR chemical shifts for the captured guest molecules can be used to determine structure types of the formed gas hydrates. Figure 7 shows the ¹³C MAS NMR spectra of C₂H₆ hydrates in the pure bulk state and in 56.6 (30.0) nm pores saturated with NaCl (3 wt %) solution. C₂H₆ hydrate in the pure bulk state, known to form sI, showed only one resonance peak at 7.3 ppm, which can be assigned to C₂H₆ molecules captured only in large 5¹²6² cages of sI. For C₂H₆ hydrate, small 5¹² cages of sI are left vacant because of the molecular size of C₂H₆. C₂H₆ hydrate in 56.6 (30.0) nm pores saturated with NaCl (3 wt %) solution also showed one resonance peak at 7.3 ppm, which indicates no structural transition. On the other hand, Figure 8 demonstrates the ¹³C MAS NMR spectra of C₃H₈ hydrates in the pure bulk state

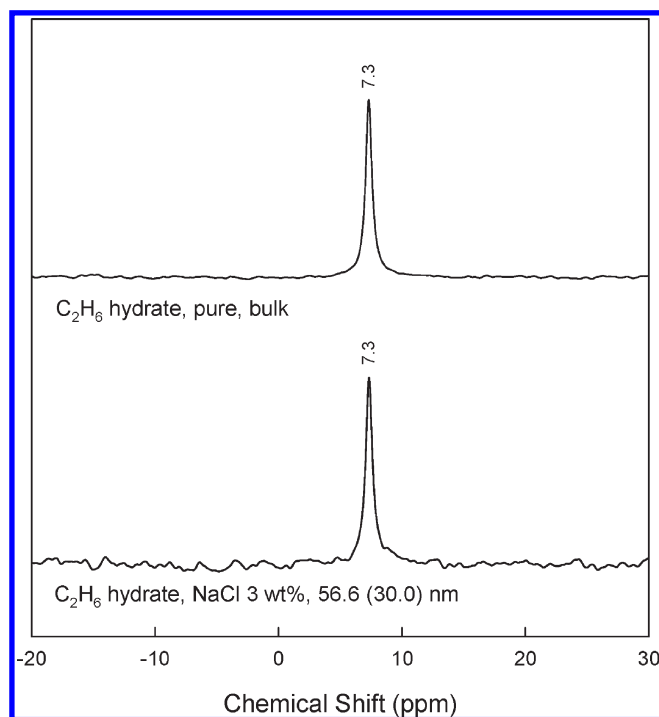


Figure 7. ¹³C NMR spectra of the C₂H₆ hydrates in the pure bulk state and in 56.6 (30.0) nm pores saturated with NaCl (3 wt %) solution.

and in 56.6 (30.0) nm pores saturated with NaCl (3 wt %) solution. For the C₃H₈ hydrate in the pure bulk state, known to form sII, C₃H₈ molecules enclathrated only in the large 5¹²6⁴ cages of sII were identified by two distinct resonance peaks, one from –CH₂– (at 16.4 ppm) and the other from CH₃– (at 17.2 ppm). C₃H₈ hydrate in 56.6 (30.0) nm pores saturated with NaCl (3 wt %) solution also presented two

(23) Ripmeester, J.; Ratcliffe, C. J. *Struct. Chem.* **1999**, *40*, 654–662.

(24) Deaton, W. M.; Frost, E. M. U.S. Bureau of Mines, Monograph 8, 1946.

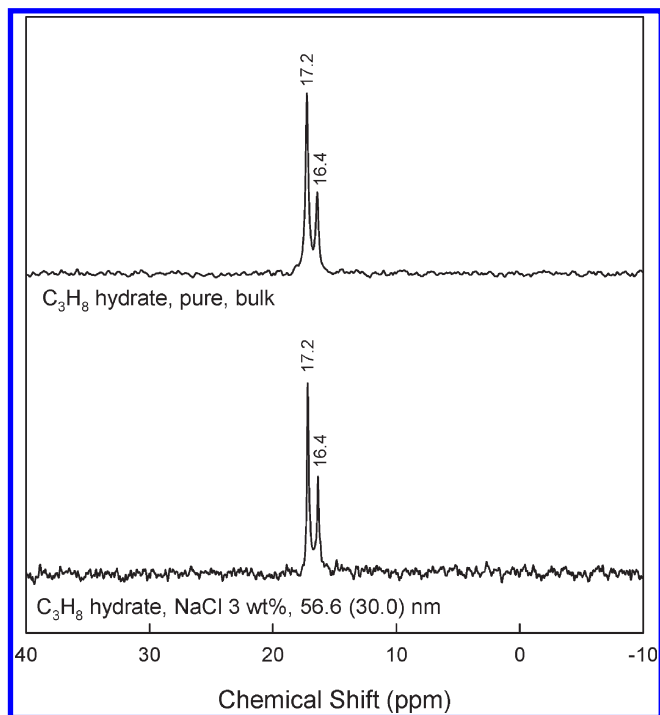


Figure 8. ^{13}C NMR spectra of the C_3H_8 hydrates in the pure bulk state and in 56.6 (30.0) nm pores saturated with NaCl (3 wt %) solution.

distinct resonance peaks at the same chemical shifts as those of C_3H_8 hydrate in the pure bulk state, which also suggests no structural transition. Seo et al.⁷ reported that, from ^{13}C MAS NMR spectra, the structure of CH_4 hydrates formed in silica gel pores of nominal 6.0, 15.0, and 30.0 nm diameters was the same as that of the bulk CH_4 hydrate without any structural transition and, more importantly, the hydration numbers of the pore CH_4 hydrates were identical to that of bulk CH_4 hydrate within experimental error range. In the present study, from the results of the ^{13}C NMR spectra, it can be concluded that the presence of both geometrical constraints and electrolytes does not lead to any structural transition of each C_2H_6 and C_3H_8 hydrate, even though it can noticeably shift the

$\text{H-L}_\text{W}\text{-V}$ equilibrium lines of each C_2H_6 and C_3H_8 hydrate to the inhibition region.

5. Conclusions

The combined inhibition effects of pores and electrolytes were confirmed by measuring hydrate-phase equilibria for the ternary C_2H_6 (or C_3H_8) + NaCl (3 wt %) + water mixtures in 12.9 (6.0), 22.6 (15.0), and 56.6 (30.0) nm silica gel pores and for the ternary C_2H_6 (or C_3H_8) + NaCl + water mixtures in 56.6 (30.0) nm silica gel pores at the NaCl concentrations of 3 and 10 wt %. $\text{H-L}_\text{W}\text{-V}$ equilibrium lines were shifted more toward a higher pressure region for any given temperature as pore sizes decreased and NaCl concentrations increased. The experimentally measured hydrate-phase equilibria were compared to the predicted values based on the van der Waals and Platteeuw model. To estimate the depression of water activity within silica gel pores saturated with the aqueous electrolyte solutions, additional terms accounting for inhibition by both the capillary effect and electrolytes were incorporated into the model. Using the values of hydrate–water interfacial tension (σ_{HW}) of 39 ± 2 mJ/m² for C_2H_6 hydrate and 45 ± 1 mJ/m² for C_3H_8 hydrate, the calculation values were in good agreement with the experimental values. From the ^{13}C NMR spectra, it was confirmed that the structure of each C_2H_6 and C_3H_8 hydrate was not affected by the presence of both geometrical constraints and electrolytes. Thermodynamic and spectroscopic results obtained in this study could be used to understand the fundamental phase behavior and structural characteristics of pore hydrates and, thus, could be useful in various fields, such as exploration and exploitation of natural gas hydrates in marine sediments and sequestration of carbon dioxide into the natural gas hydrate layer.

Acknowledgment. This work was supported by the Human Resources Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) Grant funded by the Korea Government Ministry of Knowledge Economy (20104010100060) and also supported by the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Knowledge Economy of Korea. We thank Mrs. S. H. Kim and Dr. O. H. Han [Korea Basic Science Institute (KBSI)] for their support with respect to NMR measurements.