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Phase Behavior and Spectroscopic Analysis of the Pure and Mixed Hydrates in Porous Media

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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 termed as structure I, II, and H [1].

There are worldwide occurrences of natural gas hydrates, both on-shore buried under the permafrost and off-shore buried under the oceanic and deep lake sediments. Natural gas hydrates are usually found dispersed in pores of coarse-grained sediments. Since each volume of hydrate can contain as much as 170 volumes of gas at standard temperature and pressure conditions, naturally occurring gas hydrates in the earth containing mostly CH₄ are regarded as future energy resources [1]. Recent investigations consider the possibility of sequestering industrially produced carbon dioxide as crystalline gas hydrates in the deep ocean to prevent further release into the atmosphere as greenhouse gas. Since these natural phenomena of hydrate formation/substitution occur in deep ocean sediments, it becomes essential to consider the complicated effects of both porous media and electrolytes on the formation of simple and mixed hydrates. However, any research work on simple and mixed hydrates containing electrolytes in porous media has not yet appeared in the literature, even though numerous investigations covering separately either porous medium or electrolyte effect have been found from various sources [1-3]. In the present study, hydrate phase equilibria for the ternary CH₄ + NaCl + water and CO₂ + NaCl + water mixtures in 15.0 nm silica gel pores and for the ternary CH₄ + CO₂ + water mixtures of various CO₂ vapor compositions (20, 40, 60 and 80 mol %) in silica gel pores of nominal diameters 6.0, 15.0 and 30.0 nm were measured and compared with the calculated results based on van der Waals and Platteuw model. In addition, the ¹³C NMR spectra were examined to identify hydrate structures formed in silica gel pores.

Experimental Section

Materials

The carbon dioxide and methane with a minimum purity of 99.9 mol % were supplied by World Gas Co. (Korea). The CH₄ + CO₂ gas mixtures (20, 40, 60, 80 mol% CO₂) were supplied by World Gas (Korea) and their compositions were checked again. The water with ultra high purity was supplied from Merck Co. (Germany). Silica gels of nominal diameter 6.0 nm (6.0 nm SG) and 15.0 nm (15.0 nm SG) was purchased from Aldrich Co. (USA) and 30.0 nm silica gel (30.0 nm SG) from Silicycle Co. (Canada). All materials were used without further treatment.

Apparatus and procedure

A schematic diagram and detailed description of the experimental apparatus for hydrate phase equilibria is given in the previous paper [4]. The experiment for hydrate-phase equilibrium measurements began by charging the equilibrium cell with about 25 cm³ of silica gels containing pore water. After the equilibrium cell was pressurized to a desired pressure with gas, the whole main system was slowly cooled to 263 K. When pressure depression due to hydrate formation reached a steady-state condition, the cell temperature was increased at a rate of about 0.1 K/hr. The nucleation and

dissociation steps were repeated at least two times in order to reduce hysteresis phenomenon. The equilibrium pressure and temperature was determined by tracing P-T profiles from hydrate formation to dissociation. Unlike the bulk hydrate, in case of hydrates in porous media there is a gradual change of slope around the final hydrate dissociation point due to the pore-size distribution. Therefore, it is very difficult to determine the unique equilibrium dissociation point in porous media. The accurate dissociation equilibrium point in porous media was determined as the cross point between the maximum inclination line and complete dissociation line. As indicated by Uchida et al [3], the unique point corresponds to the dissociation in the pores of the mean diameter of used silica gels.

Thermodynamic Model

The statistical thermodynamic model for hydrate phase was developed by van der Waals and Platteeuw [5], which related the chemical potential of water in the hydrate phase to that in hypothetical empty hydrate lattice. The fractional occupancy of guest molecules in hydrate cavity is given by classical adsorption theory represented by Langmuir's isotherm. It contains the potential interaction between a host water molecules and a encaged guest gas molecule in each cage with the assumption that the lattice cavity is spherically symmetric. The Kihara core pair potential was used to calculate the guest-water interaction. The Kihara core pair potential was used to calculate the guest-water interaction. The Kihara parameters for each guest species are obtained by fitting the expression in chemical potential differences of water.

$$\Delta\mu_w^H = \mu_w^{MT} - \mu_w^H = -RT \sum_i v_i \ln \left(1 - \sum_k \theta_{ki} \right) \quad (1)$$

$$\frac{\Delta\mu_w^H}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^T \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta v_w}{RT} dP - \ln a_w \quad (2)$$

where v_i is the number of type i cages per water molecule, and θ_{ik} is the fractional occupancy of type i cages with type k guest molecules. Δh_w and Δv_w are the enthalpy and volume differences between the hypothetical empty hydrate cage and pure ice or liquid water phases. The RKS-EOS incorporated with the MHV second order (MHV2) mixing rule was used to determine the corresponding fugacity. Any appropriate excess Gibbs energy model for the VLE calculations can be used for the Huron-Vidal mixing rules. In the present study, we used only the modified UNIFAC group-contribution model with the interaction parameters given elsewhere [6].

The fugacity coefficient of water, ϕ_w , in the aqueous electrolyte liquid phase is given by the model of Aasberg-Petersen et al.[7]

$$\ln \phi_w = \ln \phi_w^{EOS} + \ln \gamma_w^{EL} \quad (3)$$

The first term for normal contribution can be calculated from SRK-EOS and the second term for electrolyte contribution from the Pitzer model [8]

The decrease of water activity in silica gel pores due to capillary effect occurring by the presence of geometrical constraints can be expressed as [9]

$$\ln a_w = \ln a_w^{EL} - \frac{V_L \cdot 2 \cos \theta \cdot \sigma_{HW}}{rRT} \quad (4)$$

where V_L is the molar volume of pure water, θ the wetting angle between hydrate and liquid water phases, σ_{HW} the interfacial tension between hydrate and liquid water phases, and r the pore radius.

Results and Discussion

Three-phase H-L_w-V equilibria for the ternary CH₄ + NaCl + water and CO₂ + NaCl + water mixtures in 15.0 nm silica gel pores were measured at the NaCl concentration ranges of 3-10 wt% and presented along with model calculations in Figures 1 and 2. As expected, the presence of either geometrical constraints or electrolytes caused the H-L_w-V curves to be shifted more to inhibition

region represented by the lower temperature and higher pressure condition when compared with the ones in the either bulk or pure state. However, in the present work the combined effects of porous media and electrolytes that closely simulate real marine sediments were examined through checking the shift of the experimentally measured H-L_w-V curve. Three-phase H-L_w-V equilibria for the ternary CH₄ + CO₂ + water mixtures of various CO₂ vapor compositions (20, 40, 60 and 80 mol %) in 15.0 nm silica gel pores were also measured and presented along with model calculations in Figure 3. As generally expected, the H-L_w-V lines of the ternary CH₄ + CO₂ + water mixtures existing between those of the binary CH₄ + water and CO₂ + water mixtures showed the pore inhibition. In particular, three-phase H-L_w-V equilibria for the ternary CH₄ + CO₂ + water mixtures of 40 mol % CO₂ in silica gel pores of nominal diameters 6.0, 15.0 and 30.0 nm were represented along with model calculations in Figure 4. The decrease of pore diameter made the H-L_w-V equilibrium line more shifted toward higher pressure region at a specified temperature.

Even though the operative interface of hydrate and liquid water phases plays a key role in understanding the pore effect on hydrate formation, no reliable data of the interfacial tension between hydrate and liquid water phases (σ_{HW}) have been reported in the literature. Recently, Uchida et al. [3] presented the values of σ_{HW} from fitting their experimental values by the Gibbs-Thomson equation; 0.017 J/m² for CH₄ hydrate and 0.014 J/m² for CO₂ hydrate. By using the values suggested by Uchida et al. [3], it was found that the predicted H-L_w-V values of pure CH₄ and CO₂ hydrates in silica gel pores were in much better agreement with our experimental ones. To establish the proper interpretation of mixed hydrates in porous media the values of interfacial tension between hydrate and liquid water phase (σ_{HW}) for CH₄ + CO₂ mixed hydrates must be obtained from either theoretical or possibly experimental methods, but unfortunately, up to now, have not yet been reported. Accordingly, in this work, the mole additivity of CH₄ and CO₂ compositions was adopted to determine the following values of interfacial tension; 0.0164 J/m² for 20 mol %, 0.0158 J/m² for 40 mol %, 0.0152 J/m² for 60 mol %, and 0.0146 J/m² for 80 mol % (CO₂ basis). For the prediction of the H-I-V equilibrium lines the interfacial tension between ice and hydrate phases (σ_{IH}) was assumed to be zero for all the mixtures. For model calculations it was assumed that the electrolytes do not enter the hydrate lattice and their presence in the vapor phase can be also neglected. The calculated results agreed well with the experimental data, but a little higher deviations were observed at higher concentration of NaCl, higher composition of CO₂ and smaller pore size due to the intrinsic limitation of the used model and particularly a large solubility of carbon dioxide in aqueous solutions. More importantly, the accurate values of σ_{HW} must be anyhow provided for better improvement.

A cage dependent ¹³C NMR chemical shift of the enclathrated CH₄ molecules can be used to determine structure types of the formed hydrates. From the preliminary experiments, the structure and hydration number of CH₄ hydrates in silica gel pores (6.0, 15.0 and 30.0 nm) were found to be identical with those of bulk CH₄ hydrate. For the CH₄ + NaCl + water and CH₄ + CO₂ + water mixtures in 15.0 nm silica gel pores the positions of two peaks from CH₄ molecules trapped in large and small cages of hydrate lattice were also confirmed to be identical with those of bulk CH₄ hydrates and consistent through different NaCl concentrations and CO₂ compositions.

Conclusion

Three-phase H-L_w-V equilibria for the ternary CH₄ + NaCl + water and CO₂ + NaCl + water mixtures in 15.0 nm silica gel pores and for the ternary CH₄ + CO₂ + water mixtures of various CO₂ compositions in silica gel pores with nominal diameters of 6.0, 15.0 and 30.0 nm were newly measured and compared with model calculations. The presence of geometrical constraints and electrolytes made H-L_w-V equilibrium lines shifted to higher pressure region at a specified temperature. A Pitzer model for electrolytes solutions and a correction term for capillary effect were adopted to estimate the activity of water in the aqueous electrolyte solutions within silica gel pores. The hydrate structures of the CH₄ + NaCl + water and CH₄ + CO₂ + water mixtures in 15.0 nm silica

gel pores were confirmed to be identical with that of CH_4 + water mixture in bulk state through ^{13}C NMR spectroscopy.

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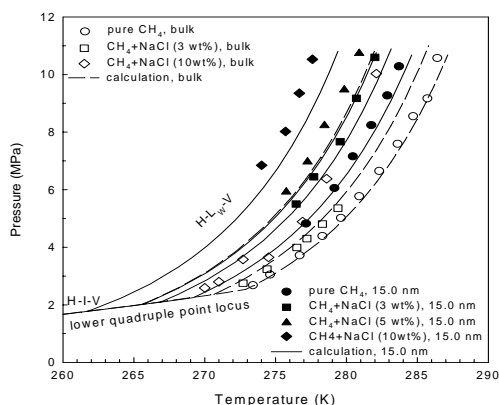


Figure 1. Hydrate phase equilibria of the ternary CH_4 + NaCl + water mixtures in 15.0 nm silica gel pores.

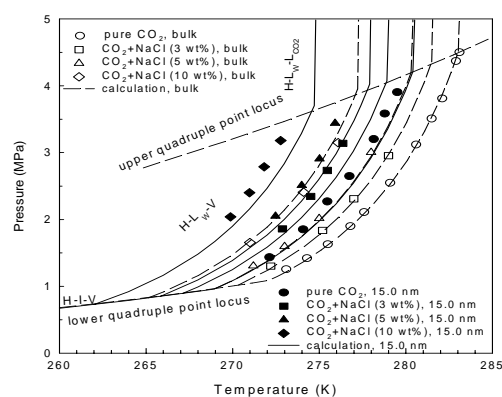


Figure 2. Hydrate phase equilibria of the ternary CO_2 + NaCl + water mixtures in 15.0 nm silica gel pores.

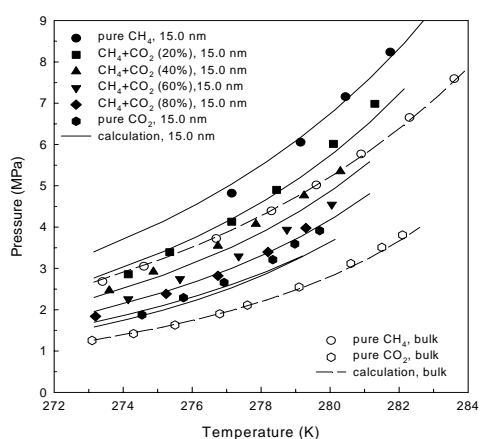


Figure 3. Hydrate phase equilibria of the ternary CH_4 + CO_2 + water mixtures of various CO_2 compositions (20, 40, 60, 80 mol%) in 15.0 nm silica gel pores.

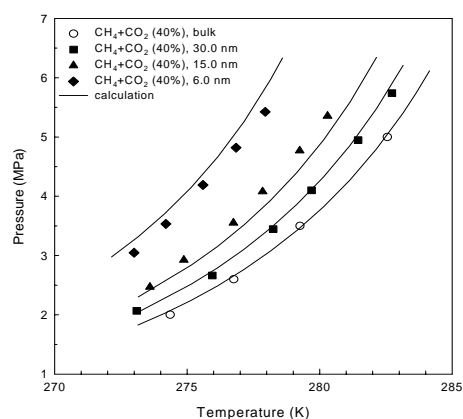


Figure 4. Hydrate phase equilibria of the ternary CH_4 + CO_2 + water mixtures of 40 mol% CO_2 in silica gel pores (6.0, 15.0 and 30.0 nm).