Dissociation Condition Measurements of Methane Hydrate in Confined Small Pores of Porous Glass

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The dissociation conditions of methane hydrates in confined small pores were measured by the gradual temperature increase method. Significant downward shifts of the dissociation temperature were observed in porous glasses, which had small pores ranging from 100 to 500 Å in diameter, compared with that of the bulk hydrate at a given pressure. Systematic measurements revealed that the temperature offset was in inverse proportion to the pore diameter. The Arrhenius plot of the dissociation conditions suggests that the heat of methane-hydrate dissociation tended to be small compared to that of bulk hydrates in pores smaller than 300 Å in diameter. Applying the Gibbs−Thomson effect to the quantitative analysis of the phenomenon indicated that the dissociation condition of methane hydrates in small pores shifted because of changes in the water activity. The apparent interfacial free energy between methane hydrates and water in the confined condition was estimated to be approximately 3.9×10^{-2} J m^{-2}, which is comparable to that between ice and water in the similar condition.

1. Introduction

Natural gas hydrate is found throughout the world, both on land buried under permafrost and offshore buried under oceanic and deep lake sediments.[1] Gas hydrate is often found dispersed in pores of coarse-grained sediments or fractures in geostrata and is considered to trap the natural gases with cementing the sediments. Gas hydrates are clathrate compounds in which the gas molecules are trapped inside well-defined cages formed by the water molecules. Because natural gas includes various kinds of hydrocarbons, the structures of natural gas hydrates depend on the guest compositions. For example, natural gas which is biogenic in origin has a high concentration of methane and then forms the structure I.[2] The maximum volume ratio of gas to water in structure I is approximately 1.7×10^2 under the standard condition. Gas hydrate fields are therefore expected to be an unconventional resource for natural gas or are considered to be a source of greenhouse effect gas.

The equilibrium conditions of natural gas hydrates are important for estimating the total amount of gas hydrate fields, locating the bottom of the gas hydrate stability zone (BGHS), and establishing the formation/dissociation rates of gas hydrates. Usually these are estimated by using the observation of the bottom simulating reflector (BSR) and the comparison of P−T conditions in sediments with the equilibrium condition of the methane hydrate obtained through laboratory works. The effects of gas composition and solutions on equilibrium conditions have been thoroughly examined in the laboratory by numerous researchers, as summarized by Sloan.[2] Therefore, the equilibrium conditions of methane hydrates can be modified by considering both the gas compositions and solute concentrations to predict the natural condition. Most of the BSR observations in oceanic gas hydrates coincide well with the estimated BGHS.

Precise investigations of the location of BGHS have been carried out by the expedition of the ocean drilling project (ODP) Leg164, which was operated at the Blake Ridge in 1995.[3] The expedition found a large difference between the location of BSR and BGHS. The depth of BGHS was 40 − 100 m shallower than that of BSR.[3] The equilibrium condition of gas hydrates is affected by several conditions as described above. Neither collections of gas composition nor of seawater could provide adequate explanation of this discrepancy.

Handa and Stupin[4] proved that the dissociation pressures of both methane and propane hydrates in small pores were higher than those in bulk phases. This resulted from the effect of the water contained not in the bulk phase but in the small pore space. Discrepancies between BSR and BGHS observed by ODP Leg164 may be affected by the existence of sediments. However, quantitative analysis cannot be performed without knowledge of the effect of sediments.

In terms of the solid−solution model, the stability conditions of clathrate hydrates depend directly on the activity of water.[5] As the activity decreases, hydrates form at increasingly higher pressures at a given temperature or at increasingly lower temperatures at a given pressure. This is observed in systems containing inhibitors that depress the freezing point of water, thereby reducing its activity. It is well-known that the freezing point of pure water is also depressed considerably when confined in small pores.[6] Therefore, the presence of geometrical constraints on the activity of water is equivalent to a change in its activity as determined by the inhibitors.

Most studies on the natural occurrence of hydrates are not based on the recovery of actual samples. Instead, the laboratory results are imposed on the natural system to create scenarios of occurrence, accumulation, and dissociation of gas hydrates. The present study aims to estimate quantitatively the effect of confined small pores on methane−hydrate dissociation. Methane hydrates were formed in confined small pores of porous glass, whose average diameters ranged from 100 to 500 Å. Significant downward shifts of the dissociation temperature were observed

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under these conditions compared with that of the bulk hydrate at a given pressure. The relationship between that shift and pore diameter is discussed while considering the activity change of water. The interfacial free energy between the hydrate and water in the confined pore was estimated from the results by applying the theory of the Gibbs−Thomson effect.

2. Experimental Procedures

Porous silica glass, so-called Vycor glass, forms a network of interconnected, cylindrical pores of a uniform diameter. The porous glasses we used are powders composed of porous particles of three different qualities, which were used for the observation of ice melting.[7] Mean particle diameters were 20 μm, and mean pore diameters were 119, 309, and 495 Å. We denoted these samples as 100, 300, and 500 Å, respectively. The detailed qualities of each porous glass are listed in Table 1 of the literature.[7]

These samples were dried at 392 K for 24 h prior to sample preparation. We prepared the sample to fill the distilled deionized water only in the particle pores. Some amount of dry powder was placed in the container, and an amount of water equal to the total pore volume was added to the powder. After being mixed, the mixture was inserted into a high-pressure vessel. Then it was kept at room temperature for 24 h to ensure that the pores would become completely filled with water. The validity of this method was verified by making comparative measurements of pore-saturated samples that were prepared by long-term storage (more than three months) in a desiccator filled with water.

The equilibrium P−T profiles for methane hydrates with porous glass were determined using a very simple setup. A high-pressure vessel approximately 30 cm³ in volume was connected to a pressure transducer (Kyowa, model PHS-100KA, precision ±0.2% full scale), a vacuum pump, and a gas source through a manifold. A type T thermocouple was used for the temperature measurements and was calibrated by the standard thermocouple in each experiment. The accuracy of the temperature measurement was estimated to be approximately ±0.15 K.

Prior to hydrate formation, air in the high-pressure vessel was evacuated for several minutes. An appropriate amount of methane gas was then introduced such that upon completion of the reaction there was enough gas left over to stabilize the hydrate. We used research-grade methane gas with minimum purities of 99.995 mol %, which was obtained from Daido-Hoxan Co., Ltd.

After the pressure reached the appropriate level, the temperature of the vessel was set to the experimental condition. The program controlling system of the cryostat (Haake model F8−C40) controlled the temperature of the vessel. When the hydrate began to form, the pressure gradually decreased to the equilibrium pressure at the set temperature. The reaction usually finished within 3 to 5 days. After a sufficient amount of hydrate had formed in the porous medium, or the pressure had reduced to the equilibrium level, the temperature of the vessel gradually rose to measure the dissociation pressure at each temperature. The increasing rate of temperature was approximately 0.06 K/h, which is small enough to attain equilibrium within the experimental accuracy range. The validity of the measurement was checked by performing the same measurement on pure bulk water and by making comparative measurements at various increasing rates.

Phase equilibrium measurements of gas hydrates have usually been performed in the presence of excess water. We made measurements in exactly the opposite way, using a very simple
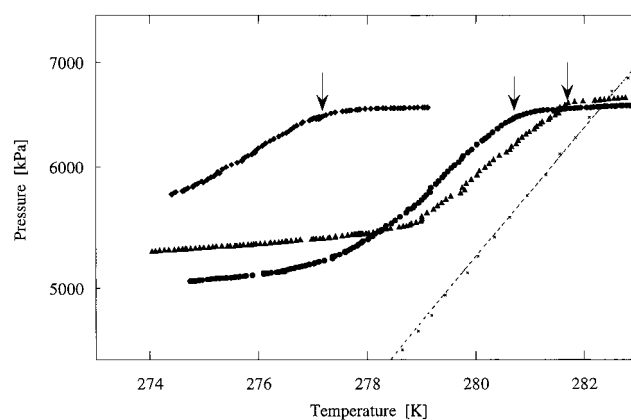
Figure 1. P−T diagram of three experimental runs at approximately 6 MPa (the solid diamond, solid circle, and solid triangle represent the 100, 300, and 500 Å samples, respectively). The broken line shows the equilibrium line for the bulk methane hydrate obtained from the literature.[2] The arrow for each experimental run denotes the final dissociation condition (T_d, P_d). The dissociation curve obtained from the bulk hydrate system is also shown by crosses.

setup that was similar to those of Handa and Stupin.[4] Taking measurements of the sample of bulk methane hydrates also supported the validity of our technique. Repeated measurements verified the reproducibility of the obtained results of the dissociation conditions.

3. Results and Discussions

The phase equilibrium data for hydrates of approximately 6 MPa are plotted in Figure 1. Three different results are shown by different marks: the solid diamond, solid circle, and solid triangle represent the 100, 300, and 500 Å samples, respectively. Because the temperature was raised at a constant rate, the region of rapid increase in pressure denotes the dissociation lines, whereas the nondissociation lines are denoted by a gradual increase. The equilibrium line for bulk methane hydrate obtained from the literature[2] is also shown in this figure by a broken line. To verify the validity of experimental procedures, the dissociation curve obtained from the bulk hydrate system is also shown in Figure 1 by crosses.

From Figure 1, it can be seen that each equilibrium line shifts to lower temperature or higher pressure compared with that of the bulk hydrate. The relative decrease in the dissociation temperature depends on pore diameter. The smaller the pore diameter, the larger the temperature shift of the equilibrium line. This result is consistent with the depressed melting point of ice when confined in small pores.[6]

For bulk hydrate, the phase equilibrium line can be analyzed by the Clausius−Clapeyron equation, which provides the heat for the dissociation of gas hydrates. The inclination of the straight line in Figure 1 is proportional to the heat of dissociation. However, in pore hydrates, there is a gradual change in the slope along the P−T envelope. This is mainly because water melts over a wide temperature range because of the distribution of pore size in porous materials.[6] Therefore, because a different process may be occurring in each pore, the present system cannot be considered univariant, and thus no attempt was made to derive the heat of dissociation for the pore hydrates from the phase equilibrium data.

Not only is it difficult to derive the heat of dissociation, it is also difficult to determine the unique point of each dissociation curve. To clarify the relationship between the shift of dissociation temperature and pore size, we defined the final dissociation temperature (T_d) and pressure (P_d) as the intersection point of

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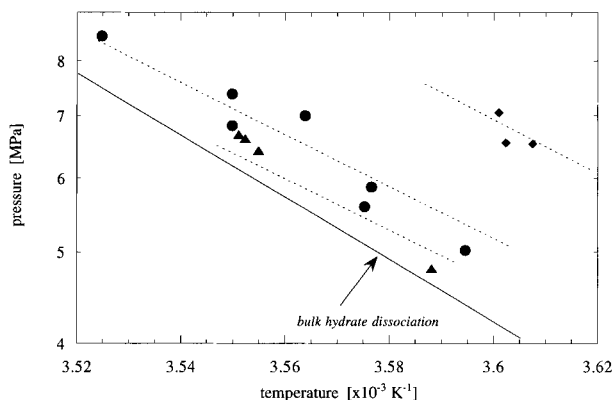
Figure 2. Dissociation conditions (T_d, P_d) of methane hydrates in porous glass (same legend as used in Figure 1). The solid line indicates the equilibrium line for the bulk hydrates and the dotted lines show the estimated equilibrium condition in confined small pores by using the Clausius−Clapeyron equation with considering the smaller heat of diffusion.

TABLE 1: Dissociation Conditions (T_d, P_d) of Methane Hydrates in Porous Glass

| 100 Å		300 Å		500 Å	
T_d (K)	P_d (MPa)	T_d (K)	P_d (MPa)	T_d (K)	P_d (MPa)
277.2	6.5	278.2	5.0	278.5	4.8
277.6	6.6	279.5	5.9	281.3	6.4
277.7	7.1	279.7	5.6	281.5	6.6
		280.6	7.0	281.6	6.7
		281.7	6.8		
		281.7	7.4		
		283.7	8.5		

the extrapolation line of the P−T line after complete dissociation and the tangent of the maximum inclination of the dissociation curve. The arrow in Figure 1 points to the final dissociation point of each curve. Each dissociation condition is shown in Figure 2 using the same legend as in Figure 1. This figure shows that the equilibrium line in each type of porous glass shifts to lower temperature or higher pressure than that of the bulk hydrate. Each value in Figure 2 is listed in Table 1.

Because the final dissociation condition was determined uniquely in each experiment, the relation between ln P_d and T_d^{-1} may be linear. This relation allows us to estimate the heat of dissociation. The dashed lines in Figure 2 indicate the relation derived from the Clausius−Clapeyron equation with employing the value of dissociation heat of the pore hydrate[4] which was obtained to be 45.92 kJ mol^{-1}. This figure indicates that the calculated value coincides well with experimental results in 100 Å porous glass. The relation between ln P_d and T_d^{-1} in 500 Å porous glass, however, relatively fit not to the dashed line but to the solid line and that in 300 Å porous glass is intermediate. This means that the heat of methane−hydrate dissociation in pores smaller than 300 Å differs from that of the bulk hydrate.

To estimate the effect of the pore size on the dissociation condition shift, the temperature offset $\Delta T = T_d - T_e$ was determined where T_e is the dissociation temperature of the bulk methane hydrate at a given pressure. We also consider the data obtained in 140 Å diameter silica gel pores.[4] The analysis indicates that the inverse proportion interprets the relationship between d and ΔT.

Stability conditions of gas hydrates depend on the water activity. The activity ratio between the pore water and the bulk water is related to the difference of the chemical potentials:

$$\mu(r) - \mu(\infty) = kT \ln(a(r)/a(\infty)) \qquad (1)$$
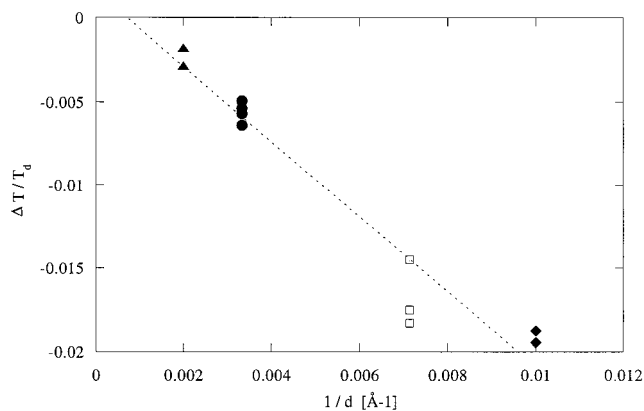
Figure 3. Temperature offset ratio $\Delta T/T_d$ with $1/d$, where $\Delta T = T_d - T_e$: T_e and T_d are the dissociation temperatures of methane hydrates in the bulk phase and in confined small pores, respectively. d is the pore diameter. The tropic line of experimental values is represented by the dotted line.

where $a(r)$ and $a(\infty)$ are the activities of water in the droplet and in the bulk phase. The difference of the chemical potentials can also be explained by the ratio of the equilibrium vapor pressures of both waters and they are correlated with the pore radius by the Gibbs−Thomson effect:

$$\mu(r) - \mu(\infty) = kT \ln(P(r)/P(\infty)) = 2V_L \gamma r^{-1} \qquad (2)$$

where $\mu(r)$ and $\mu(\infty)$ are the chemical potentials of a small water droplet with a radius r and that of bulk water, respectively. $P(r)$ and $P(\infty)$ are the equilibrium vapor pressures of the small droplet and of the bulk water, respectively; k is the Bortzman constant; V_L is the molecular volume, and γ is the surface energy density. On the other hand, the change of the equilibrium vapor pressure is equivalent to the temperature depression ratio:

$$\mu(r) - \mu(\infty) = (T_m - T)LT_m^{-1} \qquad (3)$$

where $T_m - T$ is the depression of the melting point from the bulk phase T_m, and L is the latent heat of ice melting. Substituting eq 3 to eq 2 represents the relation between the temperature offset and the pore radius.

To apply this equation to the system of the present study, which consisted of small cylindrical pores in porous glass, the equation was rewritten as

$$\Delta T/T_d = - 4\gamma_{HW} (\rho_H L_H d)^{-1} \qquad (4)$$

where γ_{HW} represents hydrate-water interfacial free energy, ρ_H is the density of methane hydrates, and L_H is the latent heat of the dissociation of pore hydrates. In Figure 3, the experimental results are plotted by solid marks and the tropic line of these values is shown by the dotted line. The data from Handa and Stupin[4] (140 Å diameter pores in silica gel) are also shown by open squares in Figure 4. This line is evaluated as:

$$\Delta T/T_d = 0.0016 - 2.3/d \text{ [Å]} \qquad (5)$$

The correlation coefficient was 0.97.

The relationship between ΔT and d can be predicted if all parameters in eq 5 are known. We assumed that the pore hydrate has a similar hydration number to the bulk hydrate, CH_4 $6H_2O$. Then the density ρ_H was calculated to be 914 kg m^{-3}. The latent heat of the dissociation of pore hydrates was reported[4] as 45.92 kJ mol^{-1}, which is smaller than that of bulk hydrates. Because no data was available for γ_{HW}, we estimated this value from

the experimental value. From eq 4 and 5, we estimated the apparent value of γ_{HW} to be approximately 3.9×10^{-2} J m^{-2}.

The measurement of developing pressure during the freezing process of ice in the environment of a small temperature gradient with pads of nearly uniform size glass beads[8] estimated the ice–water interfacial energy to be between 3.0 and 3.5 $\times 10^{-2}$ J m^{-2}. This value is larger than that of the bulk ice–water interfacial energy,[9] ranged from 1 to 3 $\times 10^{-2}$ J m^{-2} and is comparable to γ_{HW} estimated in the present study. A study of the interfacial melting of ice in porous glass[10] pointed out that the ice–water interface energy in porous glass was enhanced by the thickness of the unfrozen water film. Therefore, the apparent value of γ_{HW} estimated from the results of the small pore effect may be slightly larger than that of γ_{HW} in the bulk phase. If this assumption is accepted, the interfacial free energy between the hydrate and water is similar to that between ice and water.

Bondarev et al.[11] reported similar results on the dissociation temperature offsets in porous media. They measured the dissociation temperature of THF hydrates formed in sand, loam, and bentonite. It was found that the dissociation temperature in such porous media dropped as compared with that of pure hydrate and the decline of ice melting in the porous media. Although THF hydrate has a different crystalline structure and different solubility compared with methane hydrate, the effect of the porous media on phase equilibrium is similar. The qualitative agreement supports the result that the dissociation condition offsets of clathrate hydrates mainly resulted from the change in the chemical potential of fluid or of water activity.

Melnikov and Nesterov[12] studied the influence of surface and capillary effects on the equilibrium of methane and propane hydrates in porous media. They proposed models to predict differences in the chemical potential of fluid in the pores or in the thin films and bulk water. The resulting shift of equilibrium lines of methane hydrates corresponded qualitatively to the results obtained in the present study. Although they did not show the same results in pores of several hundred angstroms in diameter, their model may support the experimental result.

Miyawaki et al.[13] studied the methane adsorption in nanoschale pores. When water was preadsorbed in the nanoschale pores, the methane molecules reacted with the water to form the layered clathrate structure named nanohydrate. This structure is different from that of bulk cubic hydrate because the pore size is smaller than the lattice constant of the structure I hydrate. This knowledge provides the important information that if the pore size become smaller, the interaction between water, methane, and pore wall will change and then the physical properties of pore hydrate also change. We considered that the physical properties of methane hydrate in confined small pores observed

in the present study, such as the activity of water molecules and the heat of dissociation, may be resulted from these interactions and may change in pores smaller than 100 Å.

The depth discrepancies between BGHS and BSR observed in ODP Leg164 are equivalent to the dissociation temperature offset. The offset is estimated to be less than 3 K. If this offset resulted only from the effect of sediments, the pore diameters of sediments confining gas hydrates are several hundred angstroms. Mineralogical observations showed that the main type of sediment that included gas hydrates was clay. Pore spaces in clay are quite small, so there is a possibility that water activity in the sediment changes. In the present study, we quantitatively revealed the small pore effect on the dissociation conditions of methane hydrates in porous glass while considering changes in water activity. However, detailed observation of hydrate occurrence in sediment has not been reported in the literature. Further detailed observations are required to clarify the effect of sediment on the hydrate occurrence. Furthermore, it is important to note that the results obtained in the present study pertain to solid–liquid–vapor equilibrium, and not solid–liquid equilibrium because the system investigated had no bulk water.

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