

NOTE

Pressure and temperature conditions for methane hydrate dissociation in sodium chloride solutions

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(Received April 3, 1995; Accepted August 4, 1995)

The pressure and temperature conditions were experimentally determined for methane hydrate dissociation in sodium chloride solutions, and an empirical equation of the conditions was obtained in the pressure range up to 18 MPa. The present results indicate that the maximum depth of oceanic sediments where methane hydrate is stable increases as water depth to seafloor increases, and that the maximum depth in saline water is smaller than that in pure water. The difference in the depth between saline and pure waters increases with decreasing the water depth, indicating that salinity of pore water affects significantly the amount of methane hydrate in oceanic sediments, in particular, beneath seafloor at relatively shallow depths.

INTRODUCTION

Methane hydrate is ice-like solid which is composed of methane and water, and a kind of clathrates in which methane molecules are trapped in a cage-like crystal lattice of water molecules. Methane hydrate contains a large amount of methane gas; 1 m³ of methane hydrate can contain up to 164 m³ of methane gas at standard temperature and pressure (Kvenvolden, 1993). Methane hydrates are stable in conditions where high pressure, low temperature and abundant supply of methane are present, and naturally occur in stable form in the permafrost and sediments beneath seafloor. The total amount of methane trapped in methane hydrates in the world is estimated to be 2×10^{16} m³ (1×10^{19} g of methane carbon). Since the amount of carbon in methane hydrates is twice as large as the amount of organic carbon in fossil fuel deposits known until now, methane hydrate could be a major reservoir of carbon in the crust (Kvenvolden, 1988). Because methane hydrates are

globally widespread and contain a large amount of methane in the crystalline structure, methane hydrates are expected to be a potential energy resource in the near future.

Most of methane hydrates are suggested to occur in oceanic sediments in outer continental margins. The methane hydrates form from the mixture of naturally occurring methane and pore water whose salinity is similar to seawater; about 3.5%. It has been known that the stability of methane hydrate in saline water decreases as the salinity of water increases. It is therefore important to investigate the stability of methane hydrate in saline water for estimating the amount of methane hydrate in oceanic sediments.

The conditions for methane hydrate dissociation in saline water up to 13 MPa has been determined by several studies (Kobayashi *et al.*, 1951; de Roo *et al.*, 1983). However, natural methane hydrates often occur at depths deeper than 1300 m, equivalent to hydrostatic pressure of 13 MPa. Therefore, it is necessary to know the stability

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conditions of methane hydrates in a higher pressure range. In this study, we have determined the stability of methane hydrate at pressures up to 18 MPa in sodium chloride solutions with different concentrations; 0 wt% (pure water), 3.5 wt% (similar to seawater), 10 wt% and 20 wt%.

EXPERIMENTS

Apparatus

The apparatus used in this study consists of a high-pressure hydrate cell of stainless steel where methane hydrate is synthesized (Fig. 1). The hydrate cell with a volume of about 100 ml is immersed in a water bath in which temperature is controlled by a heater and a refrigerator. The temperature of the solution in the cell is measured with a K-type thermocouple. The solution is agitated by a magnetic stirrer. The pressure of methane gas is measured with a pressure gauge using semi-conductor transducer. The cell has two glass windows in the walls facing each other for visual observation and optical detection of methane hydrate formation and dissociation.

The detector of formation and dissociation of methane hydrate consists of a halogen lamp, an optical sensor and an optical power meter. The

light beam from the lamp is introduced into the solution through the window from one side of the hydrate cell. Optical sensor on the other side measures the intensity of the light penetrating through the solution. When methane hydrates form on the free surface of solution exposed to the methane gas, the light is scattered by the methane hydrate crystals, and the light intensity detected by the optical sensor sharply changes. On the other hand, when the methane hydrate crystals dissociate, light intensity also sharply changes for the same reason. Therefore, the formation and dissociation of methane hydrate can be detected by measuring the change of light intensity.

Procedures

In this experiment, methane hydrates form from the pressured methane gas and the sodium chloride solution in the hydrate cell. In the first place, the sodium chloride solution was added to the hydrate cell until the surface of the solution was observed through the window. Then, methane gas was pressed into the cell up to the starting pressure by a compressor.

The formation and dissociation of methane hydrate was regulated by changing the temperature of the solution after a constant volume of methane

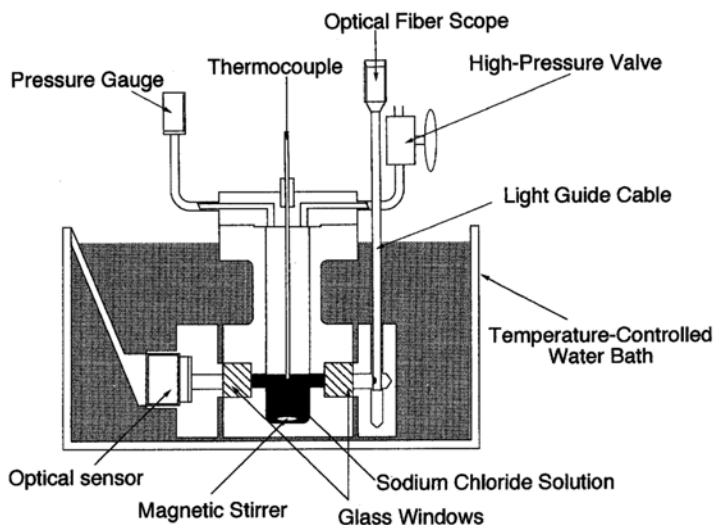


Fig. 1. Schematic diagram of the experimental apparatus for hydrate studies.

gas was sealed in the hydrate cell. The temperature in the hydrate cell was lowered to form methane hydrate, with a slight pressure decrease by cooling. When the methane hydrate formed, the light intensity detected by the optical sensor sharply changed. The formation of methane hydrate was also confirmed by visual observation using an optical fiber scope. The temperature was raised after the formation of methane hydrate. During the heating, the light intensity changed again and recovered to the original light intensity when methane hydrate dissociated. The condition for methane hydrate dissociation was determined by measuring the pressure and temperature at which the change of light intensity occurred during heating.

RESULTS AND DISCUSSION

Conditions for methane hydrate dissociation in sodium chloride solution

The conditions for methane hydrate dissociation

were obtained for sodium chloride solutions with four different concentrations; 0 wt%, 3.5 wt%, 10 wt% and 20 wt%. The results are shown in Fig. 2 together with previous results compiled by Sloan (1990). The conditions for methane hydrate dissociation in pure water determined by this study agree well with the results from other studies. Our results show that the dissociation pressure of methane hydrate increases and the dissociation temperature decreases as increasing the concentrations of sodium chloride in the solutions (Kobayashi *et al.*, 1951; de Roo *et al.*, 1983). The data of this study agree well with those of Kobayashi *et al.* (1951), although their data is slightly scattered due to the systematical overestimation of the stability of methane hydrate in sodium chloride solutions (Diamond, 1994).

De Roo *et al.* (1983) have made similar experiments in a pressure range up to 11 MPa and obtained an empirical equation to explain their results of methane hydrate dissociation in sodium chloride solutions. Since their experiments were

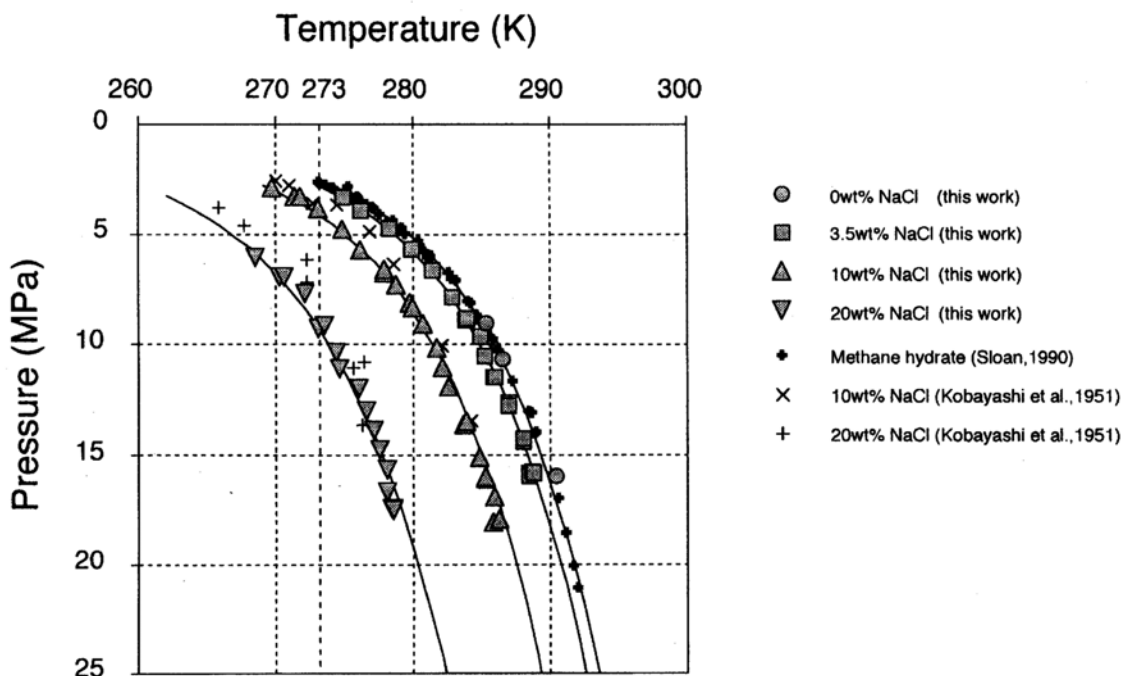


Fig. 2. Pressure and temperature conditions for methane hydrate dissociation in sodium chloride solutions. Solid curves are fitted to Eq. (1) of methane hydrate dissociation conditions for respective concentrations of sodium chloride.

performed using sodium chloride solutions with concentrations different from our experiments (11.7 wt%, 20.5 wt%, 21.6 wt% and 24.2 wt%), their individual data are not compared in Fig. 2. Our data agree well with the values calculated by their empirical equation in the pressure range up to 11 MPa. However, their empirical equation cannot be applied above 11 MPa.

We obtained a new empirical equation by the least-squares method using our data together with the data for the methane-pure water system compiled by Sloan (1990). The experimental data can be described very well in the pressure range up to 18 MPa by the following empirical equation:

$$\ln(p/p^0) = -926.815 + 31979.3/T + 144.909 \ln T + 5847.92x + 3220.26x^2 + 5840.50 \ln(1-x), \quad (1)$$

where p is the pressure [MPa] of methane hydrate

dissociation, p^0 is the atmospheric pressure [MPa], T is the temperature [K] of methane hydrate dissociation, and x is the mole fraction of sodium chloride in the liquid phase.

Using the empirical equation, we can calculate the difference in the dissociation temperature of methane hydrate between sodium chloride solution and pure water at any given pressure. The dissociation temperature in 3.5 wt% sodium chloride solution is 1.1°C lower than that in pure water up to 18 MPa. The result is similar to that of Dholabhai *et al.* (1991) which was obtained by using synthetic seawater (salinity = 3.5%), and that of Dickens and Quinby-Hunt (1994) using actual seawater (salinity = 3.35%).

Estimation of the depth of the base of methane hydrate stability beneath seafloor

It is important to estimate the maximum depth of methane hydrate stability beneath seafloor to

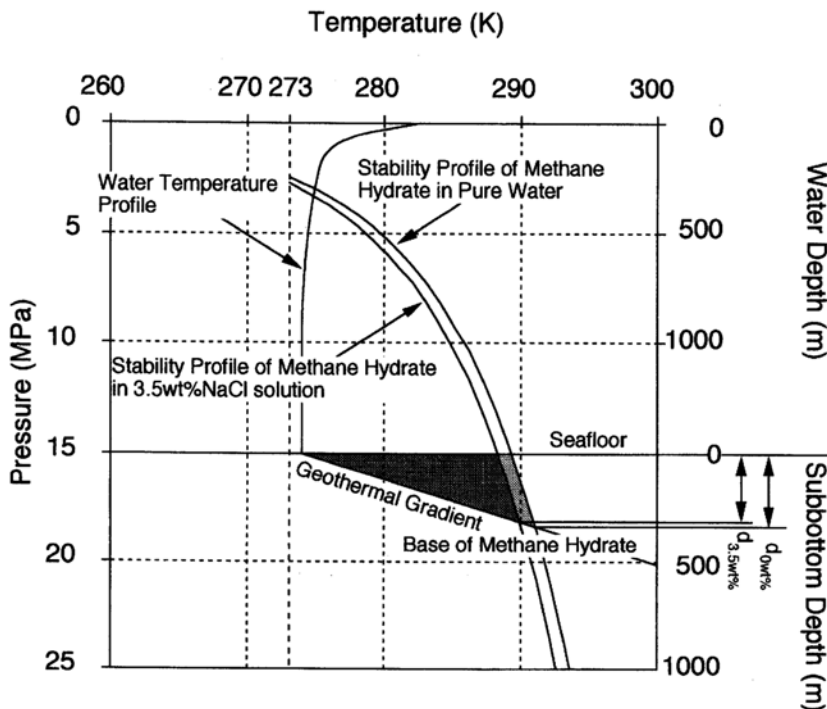


Fig. 3. Estimation of the base of methane hydrate stability. Methane hydrate stability zone is shown as the shaded area enclosed by the seafloor, geothermal gradient and the stability curve of methane hydrate. The diagram of Fig. 1 by Kvenvolden (1988) was modified on the basis of our data.

evaluate the amount of natural methane hydrate in oceanic sediments. The maximum depth is estimated on the basis of the stability conditions of methane hydrate, the temperature of seawater at seafloor, and geothermal gradients in oceanic sediments (Field and Kvenvolden, 1985). Figure 3 shows the pressure (depth)-temperature zone in which methane hydrates are stable (methane hydrate stability zone). The pressure and temperature at the base of methane hydrate (the bottom of methane hydrate stability zone) are equal to those for methane hydrate dissociation. In sediments deeper than the base of methane hydrate, methane hydrate is not stable and dissociated into water and methane gas.

In Fig. 3, the depth of the base of methane hydrate in oceanic sediments is estimated for saline water (3.5 wt% NaCl solution) and pure water. The depth of the base of methane hydrate in saline water ($d_{3.5 \text{ wt\%}}$) is smaller than that in pure water ($d_0 \text{ wt\%}$). The difference ($\Delta d = d_0 \text{ wt\%} - d_{3.5 \text{ wt\%}}$) increases as the water depth decreases; for example, Δd is 20 m at 2000 m water depth, while Δd is 31 m at 500 m, assuming that water temperature at seafloor is 1°C and geothermal gradient is 50°C/km. This indicates that the salinity of water strongly affects the depth of the base of methane hydrate that occurs at relatively shallow water depths.

CONCLUSIONS

We determined the conditions for methane hydrate dissociation in saline water with different concentrations of sodium chloride at pressures up to 18 MPa. The results show that the dissociation pressure of methane hydrate increases and the dissociation temperature decreases as the concentrations of sodium chloride increase. Our data agree with the empirical equation obtained by de Roo *et al.* (1983) in a limited pressure range below 11 MPa. We obtained a new equation by the least-squares method applicable to a higher pres-

sure range up to 18 MPa.

Using the new empirical equation for methane hydrate dissociation in saline water, we found that the salinity of pore water affects significantly the depth of the base of methane hydrate beneath seafloor at relatively shallow depths. Therefore, the salinity of pore water is important to the estimation of the amount of natural methane hydrate, especially, in oceanic sediments beneath seafloor at relatively shallow depths.

Acknowledgments—We are grateful to Dr. Y. Okuda of Geological Survey of Japan for his advice and critical comments on this study.

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