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Measurement of Dissolved Methane in Water in Equilibrium with Its Hydrate

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The amount of methane dissolved in the water phase in the presence of CH_4 gas hydrate has been measured at temperatures between 274 and 285 K and pressures ranging from 35 to 65 bar. It was found that the solubility of methane in the presence of hydrate decreases with decreasing temperature in the hydrate formation region. In the absence of gas hydrate the solubility of methane gas in water increases with decreasing temperature as expected. The results show that the hydrate formation process reverses the gas−liquid solubility trend. This confirms theoretical calculations. It was also observed that pressure was not a strong factor on the solubility in the presence of hydrates.

Introduction

Methane is a suitable guest molecule that can physically combine with water under the proper temperature and pressure conditions to form a structure I gas hydrate. It is also known that gas hydrates, containing mostly methane, have been formed naturally in the earth and exist in vast quantities within and below the permafrost zone and in subsea sediments.[1] The amount of organic carbon entrapped in hydrate exceeds all other reserves (fossil fuels, soil, peat, and living organisms).[2] Naturally occurring methane hydrates are being considered as a future energy source and a potential global climate hazard.[3,4]

Another benefit of CH_4 hydrates is for transportation and storage of natural gas. In the literature Khokhar et al.[5] have demonstrated that economically it is more feasible to transport methane in hydrate form than to cryogenically cool or compress methane. The storage potential of CH_4 in hydrate form is also a very promising alternative.[6]

Knowledge of thermodynamics and kinetics of gas hydrate formation and decomposition is required for successful design of hydrate relevant processes. In particular, solubility measurements in the hydrate formation region may enhance our understanding of hydrate formation kinetics. In Figure 1, a typical methane gas consumption curve during a methane hydrate formation experiment in a semibatch vessel under constant temperature and pressure conditions is shown. The onset of hydrate formation occurs at time t_b, which is known as the turbidity time.[7] The turbidity time denotes the first appearance of stable hydrate crystals and is the beginning of the hydrate growth phase. For modeling purposes, the solubility, or the amount of gas dissolved in the aqueous phase at the turbidity point, n_{eq}, is required. The total number of moles consumed up to the turbidity time is equal to n_{tb}. The difference between n_{tb} and n_{eq} accounts for the amount of gas consumed in the formation of hydrate nuclei, as postulated by Englezos et al.[7]

The objective of the present study was to measure the solubility of methane in the aqueous phase in the presence of methane gas hydrate. The experimental procedure developed for the CO_2 solubility measurements was employed.[8]

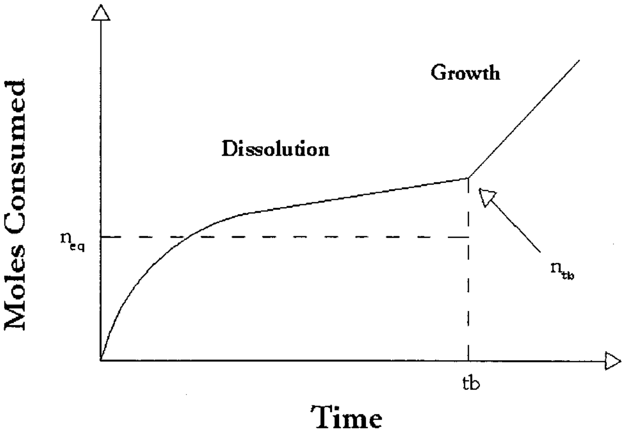

Figure 1. Plot of moles of CH_4 hydrate forming gas consumed versus time in a hydrate formation kinetics experiment.

Experimental Apparatus

The apparatus consists of a high-pressure hydrate crystallizer (cell) immersed in a temperature controlled bath and its associated instruments for mixing and temperature and pressure measurement. The cell has two circular viewing windows on the front and back. A detailed description of the apparatus is available.[8,9] Figure 2 shows a simplified schematic of the main components of the apparatus.

A microfilter is used to obtain a liquid water sample that does not contain any hydrates (Millipore, Bedford, MA). The high-pressure filter assembly is able to withstand a 20 MPa difference across the filter and separate particles of 25 nm in size. A Jefri pump (DBR Engineering, Edmonton, AB) was also required to displace the gas volume in the crystallizer to achieve liquid water−hydrate phase equilibrium. The Jefri pump allows the injection of pure water under high pressure into the crystallizer. A Ruska

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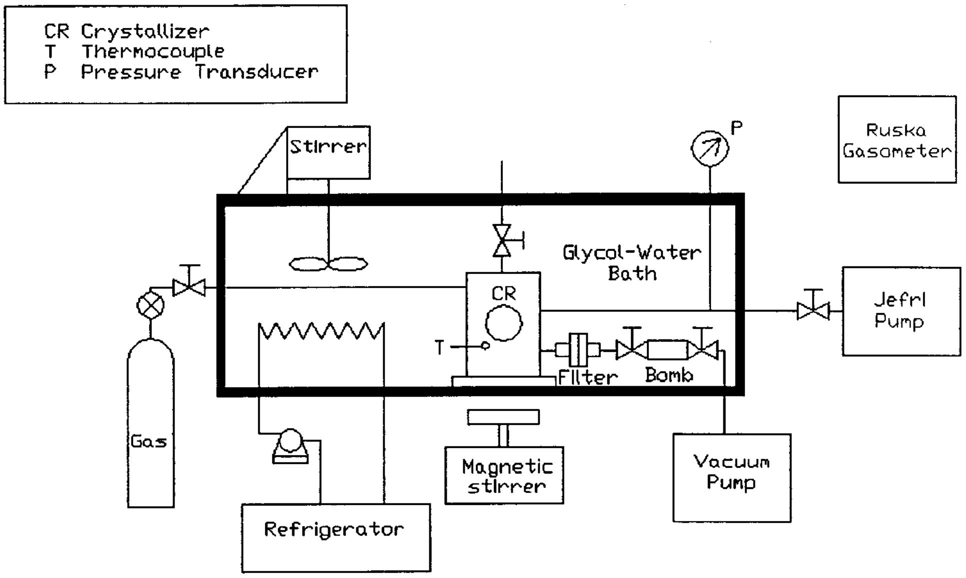

Figure 2. Experimental apparatus.

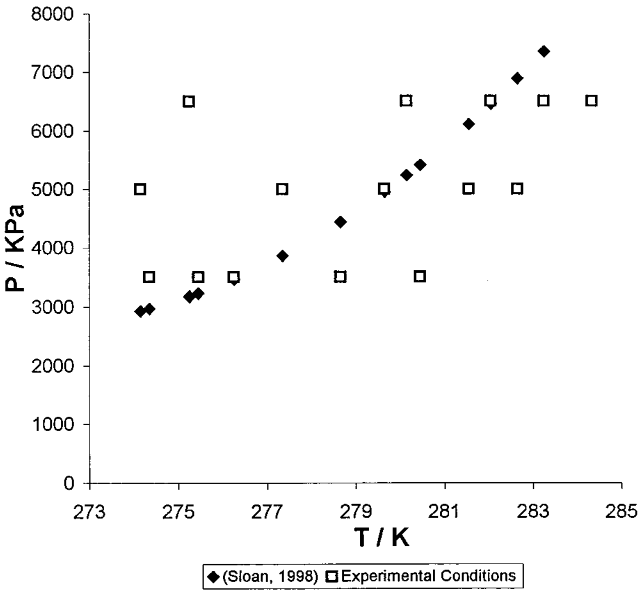

Figure 3. Partial phase diagram of CH_4–water–hydrate. The solid points correspond to the three-phase equilibrium between CH_4, liquid water, and CH_4 hydrate. Below the three-phase conditions only two phases, gaseous CH_4 and liquid water, can exist. Above the three-phase conditions two phases, either gaseous CH_4 and solid hydrate or aqueous liquid and solid hydrate, may be in equilibrium.

Gasometer (Ruska, Houston, TX) with two gas chambers, 1000 cm^3 and 2000 cm^3, is used to measure the volume of expanded gas to ±0.2% of the reading in cubic centimeters.

Procedure. The hydrate crystallizer is filled with 200 cm^3 of distilled and deionized water. UHP grade CH_4 is supplied from the reservoir to the hydrate crystallizer until the desired pressure is obtained, and addition is continued throughout the experiment to ensure constant pressure. Once hydrates have formed, the procedure for measuring the concentration of dissolved CH_4 in the aqueous phase begins. As seen in Figure 3, this procedure is dependent on in which region of the phase diagram the experiment is conducted. If the experiment is to be carried out at the three-phase equilibrium (hydrate, gas, liquid water), a sample of the liquid phase is passed through a filter to ensure that all the hydrate crystals have been separated from the aqueous liquid. The liquid sample is then collected in an evacuated pressure bomb which can be removed from the apparatus after it has been filled and has reached mechanical and thermal equilibrium. If the experiment is to be carried out above the three-phase equilibrium line (hydrate and liquid water present), care must then be taken to displace the gas volume with water while maintaining constant pressure in the presence of hydrates. This is necessary in order to obtain two-phase equilibrium between the liquid and solid hydrate phases. After equilibrium has been obtained between the liquid water and solid hydrate phases, a sample is then taken and passed through the same filter and into an evacuated bomb for analysis.

Subsequently, an analytic flash technique is used to analyze the solubility of CH_4 in liquid water in the high-pressure bomb. This technique involves the use of the Ruska gasometer, which brings the contents of the bomb at room temperature and pressure into two phases, liquid and gas. The gasometer accomplishes this by allowing CH_4 to evolve from solution into a graduated piston where the volume of gas can then be measured. The volume of gas required to come out of solution to bring the system to atmospheric pressure is then recorded. The moles of CH_4 in the vapor phase of the gasometer, $n^{G}_{CH_4}$, is computed by

$$n^{G}_{CH_4} = (P - P^{V}_{H_2O})\frac{V}{ZRT} \qquad (1)$$

where P, V, R, T, and Z are the atmospheric pressure, the volume of the vapor phase in the gasometer, the universal gas constant, room temperature, and the compressibility factor for CH_4, respectively. Values for the compressibility factor of CH_4 were obtained from the Trebble–Bishnoi equation of state.[10] $P^{V}_{H_2O}$ is the vapor pressure of water at room temperature, which is equivalent to the partial pressure of water in the gas phase. This now gives us the number of moles of gas that came out of solution in order to satisfy the equilibrium between CH_4 and water at room temperature and pressure. Since the solubility of CH_4 dissolved in water is known at these conditions[11] as well as the volume of water in the bomb, one can calculate the mole fraction of CH_4, x_{eq}, dissolved in the aqueous phase

Table 1. Mole Fraction of CH_4 in Water at Given Pressures and Temperatures

T/K	P/bar	x_{eq}	phases present[a]
274.35	35	0.001 170	H−Lw
275.45	35	0.001 203	H−Lw
276.25	35	0.001 240	H−Lw−V
278.65	35	0.001 190	Lw−V
280.45	35	0.001 102	Lw−V
274.15	50	0.001 190	H−Lw
277.35	50	0.001 360	H−Lw
279.65	50	0.001 600	H−Lw−V
281.55	50	0.001 524	Lw−V
282.65	50	0.001 357	Lw−V
275.25	65	0.001 201	H−Lw
280.15	65	0.001 567	H−Lw
282.05	65	0.001 850	H−Lw−V
283.25	65	0.001 720	Lw−V
284.35	65	0.001 681	Lw−V

[a] H, Lw, and V are the solid hydrate, liquid water, and vapor, respectively

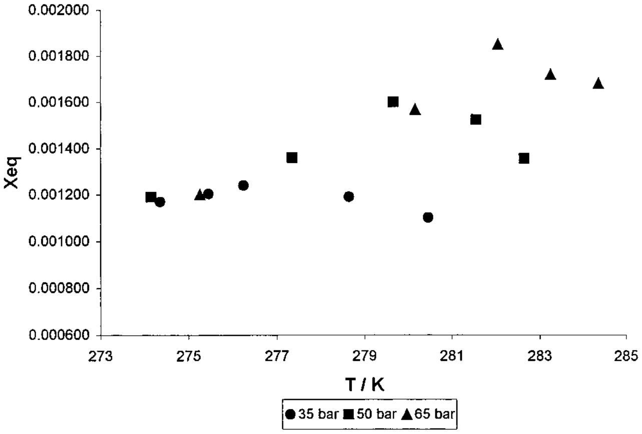

Figure 4. Plot of the equilibrium mole fraction (x_{eq}) of CH_4 in water versus temperature at given pressures.

at the experimental conditions from the following equation.

$$x_{eq} = \frac{\dfrac{x_g^R n_{H_2O}}{1 - x_g^R} + n_{CH_4}^G}{\dfrac{x_g^R n_{H_2O}}{1 - x_g^R} + n_{CH_4}^G + n_{H_2O}} \tag{2}$$

x_g^R is the mole fraction of CH_4 dissolved in water at room temperature and atmospheric pressure, and n_{H_2O} is the moles of water in the high-pressure bomb. Since the volume of the high-pressure bomb is known, the mass and number of moles of pure water can then be computed from steam tables at the experimental temperature and pressure.[12] This method has a relative error in the vicinity of 5−9% of the calculated solubility for the experimental conditions presented in this work.[13]

Results and Discussion

Experiments were conducted at the three-phase equilibrium and in the hydrate formation region. The conditions ranged from 274 to 285 K and 35 to 65 bar. The measurements are given in Table 1 and are also plotted in Figure 4. As seen in Table 1, six measurements of the solubility of CH_4 in water were made below the three-phase equilibrium to illustrate the known trend in the absence of hydrate. In the absence of hydrate, the solubility of CH_4 in water increases with decreasing temperature.

Our results for the solubility of CH_4 in water in the presence of hydrates clearly show that at a given pressure the solubility of gas dissolved in liquid decreases with decreasing temperature in the hydrate formation region. This conclusion is in agreement with the theoretical calculations[14] as well as the conclusions of Ohmura and Mori.[15] It can also be seen that the solubility is not a strong function of pressure over the hydrate formation region.

The results from this work were also used to validate the assumption made by Englezos et al.,[7] where they assumed that x_{eq}, the solubility of methane gas dissolved in liquid in equilibrium with gas hydrates, was given by the following relation

$$x_{eq} = \frac{f(P_{eq}, T_{exp})}{H} \tag{3}$$

in the hydrate formation region. f is the fugacity of the pure gas at the experimental temperature, T_{exp}, and at the three-phase equilibrium pressure, P_{eq}, not the experimental pressure, P_{exp}, and H is Henry's constant. In this work, the fugacity of the gas at the experimental temperature and three-phase pressure was computed using the Trebble−Bishnoi[10] equation of state and Henry's law constants were given by Lekvam and Bishnoi[16] and Carroll and Mather[11] for CH_4. The Poynting correction factor was used for both Lekvam and Bishnoi[16] and Carroll and Mather[11] Henry's constants at elevated pressures. The results were compared with the measurements obtained in this work. Table 2 shows that our experimental results are in very good agreement with the predictions by Englezos et al.[7] The difference between them never exceeds 9.3%.

Conclusions

The solubility of CH_4 in liquid water in the presence of gas hydrate was measured at temperatures varying from 274 K to 285 K. Pressures range from 35 bar to 65 bar. Results show that solubility decreases with decreasing

Table 2. Percentage Difference between This Work's Experimentally Determined Solubility (Mole Fraction of CH_4 in Water) and Those Calculated Using the Assumption of Englezos et al.[7]

T/K	P/bar	x_{eq}	x_{eq}(calc)[a]	x_{eq}(calc)[b]	$100((x_{eq}{}^{a} - x_{eq})/x_{eq}{}^{a})$	$100((x_{eq}{}^{b} - x_{eq})/x_{eq}{}^{b})$
274.35	35	0.001 17	0.001 13	0.001 14	−3.5	−2.7
275.45	35	0.001 20	0.001 17	0.001 18	−2.5	−2.0
276.25	35	0.001 24	0.001 22	0.001 22	−1.8	−1.6
274.15	50	0.001 19	0.001 12	0.001 13	−6.1	−4.9
277.35	50	0.001 36	0.001 29	0.001 29	−5.1	−5.4
279.65	50	0.001 60	0.001 49	0.001 47	−7.4	−8.6
275.25	65	0.001 20	0.001 16	0.001 17	−3.2	−2.6
280.15	65	0.001 57	0.001 54	0.001 52	−1.9	−3.3
282.05	65	0.001 85	0.001 72	0.001 69	−7.4	−9.3

[a] Using Carroll's correlation for Henry's constants. [b] Using Bishnoi's interpolated Henry's constants.

temperature in the hydrate formation region. In addition, the solubility is not a strong function of pressure over the hydrate formation region. Finally, the results are in agreement with the theoretically calculated values using an equation of state and Henry's law.

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