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Evidence for immobile transitional state of water in methane clathrate hydrates grown from surfactant solutions

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HIGHLIGHTS

- Simultaneously monitored methane absorption, visual observation, Raman, and NMR.
- Uptake of CH_4 lags the spectroscopic signatures of the disappearance of liquid H_2O.
- The methane uptake lag depends critically on the concentration of surfactant.
- A temporary immobile solid-like state may play a role in surfactant mediated growth.

ARTICLE INFO

ABSTRACT

We report studies of the kinetics of growth of methane hydrate from liquid water containing small amounts of surfactant (< 500 ppm of sodium dodecyl sulfate, SDS). The kinetics are monitored using simultaneous measurements of the uptake of methane detected by a pressure drop in the gas phase, and either visual observations of the amount of liquid water and solid phase in the reaction vessel, or *in situ* micro-Raman measurements or *in situ* NMR measurements. These diagnostics show that the uptake of methane and the conversion of liquid water to a solid phase do not occur simultaneously; the uptake of gas always lags the visual and spectroscopic signatures of the disappearance of liquid water and the formation of solid. The evidence suggests that the SDS causes water to form an intermediate immobile solid-like state before combining with the methane to form hydrate. This growth mechanism is related to the surfactant and disappears for low SDS concentrations (< 25 ppm).

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1. Introduction

Clathrate hydrates, often referred to as gas hydrates or simply hydrates, are non-stoichiometric ice-like crystalline compounds consisting of host water molecules forming a cage-like structure around guest molecules. Hydrates typically form in low temperature and high pressure environments. A large number of hydrate forming guest species exist and there is a wealth of literature devoted to the equilibrium phase diagrams of hydrates with various guest species (Sloan, 2003). Hydrates of particular current interest include methane, carbon dioxide and hydrogen hydrates. Methane hydrates occur in large abundance in the ocean, typically between depths of 800 and 1000 m on the continental margins, and in permafrost, and may be exploitable as an energy source

(Tanaka et al., 2009; Sum et al., 1997). In petroleum exploration and transportation operations, methane hydrates are a serious safety and economic concern. They can form blockages in pipelines, not only restricting the flow of gas but also causing damage if they become dislodged (Chatti et al., 2005). Methane hydrates are also being investigated as a means to store and transport natural gas (Sloan, 2003). Carbon dioxide hydrates have been proposed as an effective means of gas separation, and as a carbon capture mechanism (Sowjanya and Prasad, 2014; Chun and Lee, 1996; Chatti et al., 2005; Seo et al., 2005), and hydrogen hydrates have been investigated as a means of hydrogen storage (Hu and Ruckenstein, 2006; Strobel et al., 2007).

For applications involving the storage and transport of gas, the efficiency and speed of hydrate growth is a primary concern. Consequently, considerable attention has been devoted to increasing the rate of hydrate formation, and it has been shown that surfactants greatly increase the rate of formation for various hydrates (Zhong and Rogers, 2000; Watanabe et al., 2005; Okutani et al., 2008; Lee et al., 2009; Mitarai et al., 2015). In particular,

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sodium dodecyl sulfate (SDS) at concentrations greater than 200 ppm will increase the growth rate of methane hydrate by one to two orders of magnitude compared to hydrate growth in pure water. Although it is now clear that micelle formation is not required for fast growth (Watanabe et al., 2005), there currently does not seem to be a consensus on how or why surfactants accelerate growth. Other investigators have noted that the morphology of clathrate crystals are more porous when grown from surfactant solutions (Gayet et al., 2005; Okutani et al., 2008; Daniel-David et al., 2015), and that porous films coat the walls of the reaction vessel. It is plausible that the porous clathrate adsorbs a film of water, and that the observed high growth rates are a consequence of the large interfacial area of contact between hydrate, water and gas. Our investigations were focused on testing this hypothesis.

Our initial experiments utilized a reaction vessel with sapphire windows which allowed visual observation of the hydrate growth process. We corroborated previous reports of a porous fractal dendritic morphology, but a careful analysis of time lapse video together with gas uptake measurements showed that the apparent conversion of liquid to solid occurred distinctly before most of the methane was consumed. This transitional solid-like state presumably was not ice because the temperature (3 °C) was too high, and was not conventional hydrate because the methane concentration was too low. The solid subsequently absorbed much more methane to reach a concentration consistent with a conventional hydrate without qualitative changes in its visual appearance. To explore the possible role of adsorbed or imbibed liquid water, we used two spectroscopic techniques, Raman and NMR, which can distinguish between liquid and solid phases at the microscopic level. The NMR signal of liquid water is quite strong, but it relies on motional narrowing, so immobile water in either an ice or hydrate phase is essentially invisible. The combination of the spectroscopic and visual evidence shows that the presence of SDS in water, under conditions that form methane hydrate, causes the water to form an immobile transitional state which only later combines with methane molecules to form hydrate. This state begins to disappear for low SDS concentration (≤ 25 ppm).

2. Experimental apparatus and methods

We designed and built an optical cell capable of withstanding pressures up to 2500 psi. The windows were 2×0.5 in. sapphire which could be switched out for stainless steel blanks if desired. The cell was placed in a custom built cryostat with windows. The temperature inside the cell was monitored and controlled to within 0.06 °C using a Stanford Research Systems CTC100. The pressure was monitored using an Omega-Dyne PX309 pressure transducer. The sodium dodecyl sulfate-DI water solution was made using SDS from Fischer Scientific with concentrations reported on a per unit mass basis. Methane gas was supplied by Airgas (99.5% pure). The volume of the cell was approximately 1.67 l. Samples between 10 and 100 cm^3 of a solution of the desired concentration at room temperature were placed in a glass container and positioned near one of the windows of the pressure cell, which was also initially at room temperature. The cell was then mounted in the cryostat as shown in Fig. 1 and the cell was pumped and flushed with methane three times and then pressurized to approximately 600–700 psi. The valve to the methane supply was then shut and the cell temperature was reduced to approximately 275 K over the course of 1–2 h. These operating conditions were selected because the thermodynamic driving force was low enough that the cell could reach thermal
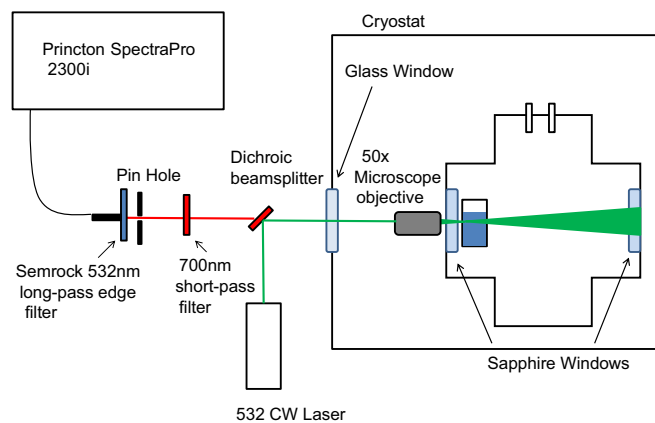

Fig. 1. Schematic diagram of the apparatus, including the pressure cell, the cryostat and the micro-Raman setup. For visual observations, a computer controlled camera was positioned outside the cryostat.

equilibrium before clathration began, which ensured reproducible results.

As the clathrate hydrate forms, the pressure in the chamber drops by an easily measurable few percent (~ 10 psi) because some of the methane gas is incorporated into the hydrate, which occupies less volume than the liquid water and methane gas separately. The number of moles in the gas phase is given by

$$n = \frac{PV}{zRT}$$

where P is the pressure, V the volume, R the gas constant, T the temperature and z the compressibility factor determined from the Peng–Robinson equation of state. Although the maximum methane uptake in the clathrate at our formation conditions is less than the theoretical ideal stoichiometry of 5.75 water molecules per methane (Link et al., 2003; Chen et al., 2009), there is substantial variability in the literature regarding the appropriate value to expect (Handa, 1986) and so we use the ideal stoichiometry as our reference value, and report results on the degree of clathration relative to this value. Because our clathrates were grown with a large excess of methane, all of the liquid water is eventually converted to clathrate. A Nikon D7000 with a Nikkor macro-lens outside the cryostat at room temperature was used to take time lapse photographs of the SDS solution and the growth of solid clathrate.

The micro-Raman spectrometer comprised a Princeton SpectraPro 2300i spectrometer, 532 nm CW laser, and an Olympus long working distance $50 \times$ microscope objective lens, which was mounted inside the cryostat. In addition, a dichroic beamsplitter from Thorlabs, pin hole aperture, Semrock 532 nm long-pass edge filter, and a Thorlabs 700 nm shortpass filter were used as shown in Fig. 1.

For the Raman measurements a solution of SDS in DI water was placed in a glass cuvette which in turn was placed in the optical pressure cell. The cell was evacuated and flushed three times and then pressurized while still at room temperature. The micro-Raman spectrometer was then focused a few mm below the water line and data was continuously taken throughout the remainder of the experiment. The cell was then allowed to cool to 275 K.

Care was taken to minimize the Raman contribution from gaseous or dissolved methane. If the optical path through the high pressure methane gas in the cell was approximately 1 cm, a clear signal peaked at 2917.3 cm^{-1} was observed. By placing the cuvette within 100 µm of the sapphire window of the pressure cell, the gas phase Raman signal was reduced to less than 1% of the hydrate signal. To assess the Raman contribution from dissolved methane