Laboratory Study of Natural Gas Clathrate Hydrates

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ABSTRACT

Natural gas clathrate hydrate formation has been well studied, both in laboratory settings in situ. This study expanded on previous work by taking a novel approach to studying deep-sea hydrate formation by utilizing the principals of mass spectrometry and a high pressure/low temperature chamber to simulate and monitor extreme conditions that exist in the hydrate stability zone. Knowledge of exactly how a particular mixture of hydrocarbons tend to form hydrates in a given environment could have far-reaching applications in real-world situations, for example in oil spill responses, where these compounds have recently caused havoc during the Deepwater Horizon oil spill in the Gulf of Mexico. The concentration of light hydrocarbons in a sample of water was monitored by utilizing a gas permeable membrane inlet connected to a residual gas analyzer (RGA). It was hypothesized that a drop in instrument response would signify hydrate formation since hydrated compounds are too bulky to pass through the membrane. A significant drop in signal was indeed observed close to the hydrate stability curve during the initial experiment. Subsequent experiments performed at higher temperatures where hydrates cannot form, however, also exhibited the same drop in concentration, which clearly demonstrated that the drop in signal response was not associated with hydrate formation. This result will be beneficial for future hydrate studies with this chamber because it suggests that there was some instrumental or design error involved that will need to be addressed.
1. Motivation for study

In light of the recent developments in the Gulf, it is an exciting and relevant time to study gas hydrate formation as a function of temperatures and pressures akin to those found in the vicinity of the Deepwater Horizon incident in the Gulf of Mexico. These findings will then be compared to actual observations made during the clean-up effort. One of the first efforts that BP (British Petroleum) made to contain the ongoing spill caused by the April 20, 2010 drilling rig explosion in the Gulf of Mexico was to lower a containment dome the size of a small house on top of the gusher. This was intended to divert the flow of crude oil to a waiting tanker on the surface. In theory, the dome was intended to operate essentially as an oversized funnel covering the riser and directing the crude oil into a pipeline. Unfortunately, the wellhead is located at a depth of 1.5 km, in a region of extreme pressures and temperatures. The hydrate stability zone at these depths extends to almost a kilometer above the wellhead so to no surprise of the hydrate community, ice-like natural gas hydrates formed inside the containment dome, rendering the mission a failure. Hydrate formation also complicated subsequent cleanup efforts by depositing on AUV’s (Autonomous Underwater Vehicles) and ROV’s (Robotic Underwater Vehicles). Footage from cameras aboard these vehicles shows an eerie “snowstorm” of hydrates, which hindered the ability of the vehicles to perform their intended tasks.

There is currently a gap in research investigating hydrate formation in the aftermath of an oil spill. The goal of this study is to investigate the composition of mixed-gas hydrates as a function of temperature and depth in the water column which will build a solid foundation for improved understanding of hydrate formation in deep water environments. We hypothesize that the favored “guest molecules” will change given different pressure and temperature conditions.
Knowledge of exactly how a particular mixture of hydrocarbons tends to form hydrates in a given environment could have far-reaching implications in oil spill responses and how taxpayer money is spent on containment and cleanup efforts.

2. Background

Clathrate hydrates, commonly known as gas hydrates, are inclusion compounds that are formed with small hydrocarbon fragments as hosts in water (Buffett 2000). They occur worldwide (fig. 1) but in natural settings are usually restricted to polar continental environments and in deep-water sediments of the shallow geosphere (<2000 m below the solid surface). As seen during the Deepwater Horizon relief effort, they can also form spontaneously in the water column under favorable pressure and temperature conditions.

Fig. 1 (Worldwide Gas Hydrate Sites)

Discovery of the clathrate hydrate (1811) is generally attributed to Sir Humphry Davy, a chemist from Cornwall, England, when he, along with his lab assistant (Michael Faraday) accidentally (and rather explosively) discovered the chlorine hydrate. The existence of these hydrates remained mostly an academic curiosity until the 1930’s when hydrate formation was
discovered to be the culprit behind blockages in natural gas transmission lines (Hammerschmidt 1934). At this point, it was in the interest of the oil companies to invest in researching these compounds in an effort to minimize losses stemming from gas line blockages. Since these early discoveries, research has focused on investigating clathrate hydrate crystal structure, defining some of the basic physical chemistry and investigating their role in energy storage and separation. It has also been stated that hydrates offer a largely unexploited means of energy recovery and transportation, and additionally, could play a significant role in past and future climate change (Sloan Jr 2003). One of the more recent finds has confirmed suspicions that degradation products of chemical weapons such as 1-4 Thioxane, (a breakdown product of mustard gas) can also form hydrates in the presence of a stabilizing molecule (such as methane) greatly increasing the lifetime of these hazardous materials on the seafloor (Xhan, et al. 2009).

There are three known crystal units that make up gas hydrate structures for low weight hydrocarbons and various other small molecules, I (sI), II (sII) and H (sH). Cubic structure I predominates the Earth’s environments, and contains small (0.4-0.55 nm) guest molecules; cubic structure II generally occurs with larger (0.6-0.7 nm) guests and structure H occurs only with mixtures of both small and large (0.8-0.9 nm) molecules (Sloan Jr 2003). Graphic renderings of these elementary crystal units are provided in figure 2 below. Figures three, four, and five represent a complete unit cell of structures sI, sII and H, respectively.
**Fig. 2 (Elementary Crystal Units)**

Falenty, 2009

**Fig. 3 (Type I Structure)**

Falenty, 2009

**Fig. 4 (Type II Structure)**

Falenty, 2009
3. Instrumentation

a. Pressure Chamber
In order to simulate the pressures and temperatures found at depth in the ocean, a high pressure/low temperature chamber (fig. 6) was developed.
The chamber was cooled by pumping a cold antifreeze solution (from an external bath) thorough a cooling loop attached to the lid of the chamber (fig. 7a.).

Fig. 7 (Pressure Chamber Lid)

The chamber contained a gas permeable membrane assembly, which allowed the continuous monitoring of the concentration of gases present in the water column. This assembly can be seen in fig. 7b. The sample in the chamber was continuously flowed over the membrane with a high-pressure pump (fig. 7c). The pressure of the entire system was manipulated by pumping liquid sample into the chamber with an HPLC (High Performance Liquid Chromatography) pump.

b. Residual Gas Analyzer

A residual gas analyzer (RGA) (fig. 8) was used to monitor the concentration of hydrocarbons in the water column as a function of time, temperature, and pressure.
This instrument was connected to the pressure chamber and analyzed the gas that diffused through the membrane inlet. The molecules were first impacted by an electron beam and thereby ionized. The ions were then separated according to their mass/charge ratio by a quadruple mass analyzer. After the mass analyzer, the particles were detected and categorized by a detector.

4. Experimental Procedure

a. Experiment 1

1. Any atmospheric gases were evacuated from the chamber with a vacuum pump.
2. A sample of methane-saturated water was introduced to the chamber.
3. Internal temperature was dropped to ~7.1 °C.
4. Pressure was increased to 1200 psi.
5. Changes in methane instrument response were monitored with the RGA.
b. Experiment 2

1. The chamber was allowed to come to equilibrium after experiment one.
2. Temperature was decreased to 11.5 °C.
3. Pressure was varied between ~0 and 1600 psi.
4. Changes in methane instrument response were monitored with the RGA.

5. Results and Discussion

a. Experiment 1

The first experiment was to decrease the temperature of the chamber to ~7 °C and isothermally pressurize it and monitor the drop in methane response as a result of exclusion from the liquid phase by the hydrate formation process. As can be seen figure 9 at point a, the point of hydrate formation at this temperature should be in the vicinity of 880 psi.

Fig. 9 (Methane Hydrate Stability Curve)

Modified from Kvenvolden, 2003
The first observed CH$_4$ response was a significant drop in the range of 300-350 psi, which does not agree with the value predicted by the stability curve.

**Fig. 10 (Exp. 1 Pressure and Instrument Response versus Time)**

![Pressure and CH$_4$ Response vs. Time (7.1-8.2 °C)](image)

It was hypothesized that this drop was not due to hydrate formation since it was observed at such a low pressure, where hydrate formation should not occur.

**b. Experiment 2**

To bolster the argument that the observed drop in methane response could not have been due to hydrate formation, the next experiment was performed at a higher temperature, where no signal drop due to hydrate formation should be observed until the pressure approached values in the vicinity of 1500 psi. The results of this experiment can be seen in figure 11.
It appears that the first drop in methane response again appears around 300-350 psi. This behavior was repeated when the pressure in the chamber was released and cycled two more times. This virtually rules out all possibility that the drop was caused by hydrate formation since it should not be observed until pressure reaches the vicinity of 1500 psi, as predicted by the stability curve (fig. 9). What exactly caused the methane signal from the RGA to drop at around 300-350 psi is still unknown. This will be investigated and presented at a later date, along with results from experiments investigating the properties of hydrate formation in mixed gas systems.
Works Cited


