EFFECT OF HYDRATE GUEST ON CLATHRATE MORPHOLOGY

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ABSTRACT
It is generally accepted that clathrate macroscopic morphology is independent of the hydrate guest [1]. However, our latest results suggest that morphology is dependent on the type of guest molecule. Carbon dioxide clathrate formation on water films without previous hydrate formation history was studied. It was found that carbon dioxide clathrate grew concentrically from several nucleation points within the water film. Eventually, the water film surface was completely covered with clathrates of a unique morphology. Carbon dioxide results are in direct contrast with previous studies where it has been shown, that in systems without previous formation history, methane hydrates form in two layers, each with a clearly distinct morphology [2]. To the best of our knowledge, this is the first time it is shown that the type of hydrate guest has a clear effect on the morphology of structure I clathrates.

Keywords: gas hydrates, morphology, carbon dioxide

INTRODUCTION
Clathrate hydrates (or simply hydrates), are nonstoichiometric crystalline compounds whose hydrogen-bonded water molecules have formed cages that enclose one or more guest species. Hydrates are nonstoichiometric because the presence of a molecule in each cavity depends on the species of the molecule, the temperature, and the pressure at which the hydrate is formed [3]. The introduction of a generally non-polar guest molecule to liquid water is necessary to form hydrates [1]. Otherwise, the clathrate structure would be thermodynamically unstable [4]. These solid compounds can form in nature and, more problematically, in oil and gas pipelines. Yearly, millions of dollars are spent worldwide in order to prevent clathrate formation in pipelines and wells [5].

Understanding the nature of hydrate formation is necessary in order to devise physically sound models that describe the growth and propagation of these crystals [6]. Observational studies such as the one presented here provide a unique insight into clathrate growth mechanics under quiescent conditions. There are many different kinds of guests known to form hydrates; two were chosen in this study for examination and comparison: carbon dioxide and methane. Carbon dioxide hydrates are known to form cubic structure, Stackelberg's structure I (sI) [7]. Similarly,
methane forms structure I in the presence of liquid water [8]. This study observed the formation of carbon dioxide hydrate from water droplets with no previous hydrate formation. Results were compared with similar studies performed on methane [2].

Carbon dioxide hydrate formation morphology has been found to depend on the driving force when formed in liquid water with no previous formation history [9]. Servio and Englezos [9] have found that carbon dioxide hydrates formed as either polyhedra or dendrites, at low and high driving forces, respectively. Similarly, Ohmura et al. [10] have observed that the morphology of methane hydrates formed in liquid water with no formation history could differ, depending on the driving forces applied to the system. As with carbon dioxide, Ohmura and coworkers have observed that methane formed polyhedra at low driving forces and dendrites as high driving forces [10].

As it has been well established that morphology patterns are strongly dependent on the deviation from equilibrium conditions or driving forces [9,10], this study focused on differences in morphology dependent on guest molecule. It is generally accepted that clathrate macroscopic morphology is independent of the hydrate guest [1]. In particular, no noticeable effect on crystal morphology has been observed between methane and carbon dioxide hydrate [9].

It is known that hydrate crystals tend to agglomerate near the gas-liquid interface [11], and that lateral, crystal-growth rates are faster than the thickness growth rate of the hydrate layer [12]. Moreover, it has been observed that hydrate film formation begins at the gas/water interface and subsequently grows into the water phase [10,13-15]. For this reason an experimental setup that allows for clear observation of lateral growth rates is desirable.

Here, with the aid of a custom-designed pressure vessel coupled to a high resolution video microscope, we present preliminary experimental data that offer a unique view of carbon dioxide hydrate formation morphology.

**EXPERIMENTAL APPARATUS**

The experimental apparatus was designed to enable the observation, through a microscope, of water droplets resting on a glass slide, while immersed in a gaseous atmosphere under controlled temperature and pressure. The core of the apparatus was a 316 stainless steel pressure cell with two sapphire windows (Meller Optics, RI, USA) (Figure 1). The cell had several ports in order to enable gas input, gas purge, thermocouple insertion, and to communicate pressure to a pressure transducer. Temperature and pressure inside the vessel were measured using a type K mini thermocouple probe (±1K) (Omega Engineering, QC, Canada) and a Rosemount 3051 pressure transducer (Rosemount, MN, USA) with an accuracy of ±0.025% of the span. A Neslab RTE740 refrigerated bath (Thermo Scientific, Canada) provided the necessary cooling to the reactor, by re-circulating a mixture of ethylene glycol and water (50/50, V/V) inside copper tubing wound tightly around the exterior of the cell. Images were acquired using a PCO.2000 high resolution video camera (Optikon Corp, ON, Canada) fitted with an InFocus KC/S Infinity lens (Optikon Corp, ON, Canada). Lighting to the interior of the pressure vessel was provided through a light pipe, fitted to a Schott KL 2500 (Optikon Corp, ON, Canada) light source. The video camera, the pressure transducer, and the thermocouples were connected to a personal computer in order to monitor, record, and analyze data. The pressure cell, the video camera, and the light source were mounted on a granite table (McMaster-Carr, NJ, USA) in order to minimize the effect of environmental vibration.

**EXPERIMENTAL PROCEDURE**

At the beginning of every experiment, a pre-cleaned glass microscope slide was placed inside the high pressure cell (Figure 1). Using a micropipette, a drop of distilled, de-ionized water was placed in the center of the slide. Gaseous carbon dioxide was then let into the cell, and used to purge the reactor several times in order to flush ambient air out of the system. After purging, the pressure in the reactor was increased well above the hydrate-liquid-vapour equilibrium line for carbon dioxide until hydrate formation was observed. A hydrate formation experiment was terminated when it became apparent that no liquid water remained in the system.
RESULTS AND DISCUSSION
The experimental conditions for carbon dioxide hydrate formation are summarized in Table 1. Figures 2 and 3 present still frames of hydrate formation and growth on a water droplet with no previous hydrate formation history.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>T/K</th>
<th>p/MPa</th>
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<tbody>
<tr>
<td>1</td>
<td>276</td>
<td>1.8</td>
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<tr>
<td>2</td>
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<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>276</td>
<td>1.9</td>
</tr>
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Table 1. Experimental Conditions for CO₂ Hydrate Formation on Water Droplets without Previous Hydrate Formation History

Figure 2 presents frames from experiment 1 (T = 276 K, p = 1.8 MPa). Figure 2a shows the water droplet prior to visible hydrate growth. Nucleation became apparent throughout the droplet, both on the interior of the surface as well as the periphery (Figure 2b, t = 0 s). Only one type of morphology appeared to develop concentrically from multiple single points throughout the water droplet. This is in direct contrast to the macroscopic formation pattern reported for methane previously, where two growth habits occurred simultaneously within a water droplet [2]. In addition, these preliminary results suggest a change in the traditionally accepted paradigm that the hydrate guest does not affect hydrate morphology within the same structure family [1]. Figure 2c (t = 2 s) shows the hydrate completely covering the water surface and how hydrate growth patterns remained consistently concentric. Finally, Figure 2d (t = 65 s) shows the point when hydrate propagation is complete inside the original water droplet boundary and no more hydrate growth internal to the boundary was visually detected.

As previously reported for methane [2], hydrate growth was observed on the glass slide and outside of the original water surface. Servio and Englezos hypothesized in the past that this clathrate growth could be caused by microscopic water droplets present on the surface outside of the visible water boundary [8]. Like Beltran and Servio [2], we did not find evidence of micro droplets in our experiments.

Figure 3 shows sequential still frames of a replicate experiment for carbon dioxide hydrate formation (T = 278 K, p = 2.2 MPa). Figure 3a presents the original water droplet before nucleation is observed. As in experiment 1, at t = 0 s (Figure 3b), the location of nucleation points appears to be random, with concentric hydrate growth patterns throughout the water droplet. Figure 3c (t = 0.5 s) presents the hydrate completely covering the water droplet and Figure 3d (t = 1.1 s) presents the moment at which no further hydrate growth is perceived within the original water droplet boundary.
These preliminary results suggest that carbon dioxide hydrates propagate with a concentric growth pattern from various nucleation points within the water droplet on which hydrates are formed. Furthermore, nucleation site locations appear to be aleatory within the water droplet. It is plausible that the dissimilarity in morphological behavior of methane and carbon dioxide is due to the difference in solubility of both gases in water. Further experimentation is required in order to establish a dimensionless figure of merit that allows direct comparison between methane hydrate and carbon dioxide macro morphology. This should facilitate a discussion based on a numerical value for driving forces.

CONCLUSION
Morphology studies on the formation of carbon dioxide hydrates on water droplets without previous formation history were presented. In comparison to methane hydrate morphology reported in the literature, and in contrast to previous studies on carbon dioxide hydrate morphology, it was found that carbon dioxide hydrates grew in a habit different than that of methane. Furthermore, hydrate growth beyond the original water surface was observed for carbon dioxide hydrate. A manuscript that incorporates different driving forces and discusses a dimensionless figure of merit that allows comparison between carbon dioxide and methane is under preparation.

REFERENCES
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