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Factors controlling hydrate film growth at water/oil interfaces

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HIGHLIGHTS

- Methane hydrate film growth kinetics on the surface of water droplet suspended in oil was investigated.
- The lateral growth of hydrate film is controlled by mass transfer of methane molecules near film front.
- Hydrate film growth in thickness is controlled by the outward mass transfer of water through hydrate film.
- Hydrate formation behaviors on the surface of water droplets suspended in oil saturated and unsaturated with methane are different.

ARTICLE INFO

Article history:

Received 29 September 2014

Received in revised form

17 January 2015

Accepted 24 January 2015

Available online 3 February 2015

Keywords:

Hydrate

Film

Crystal growth

Mass transfer

Morphology

ABSTRACT

The methane hydrate film growth kinetics on the surface of water droplets suspended in n-octane was investigated. When the water droplet was suspended in n-octane unsaturated with methane, the hydrate formation behavior on its surface showed a hydrate curtain caused by the continuous forming, moving, and dissociating of hydrate crystals. When n-octane was saturated with methane, the lateral growth rates of the hydrate film were measured under different pressures. The mass transfer of methane molecules near the film front was suggested as the control step of lateral growth. For hydrate film growth in thickness, massive apophyses occurred and developed in the outer surface of the hydrate film, indicating an outward water transfer through the film. The sinking of the hydrate film caused by leaking of the inner water was observed. These two phenomena indicated the contribution of the outward growth of water through the hydrate film in thickening growth.

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1. Introduction

Gas hydrates are solid inclusion compounds that are formed when water and gas come into contact at high pressures and low temperatures (Koh et al., 2011). Gas hydrates have received significant attention in recent decades because of their impact on the daily lives of humans. Large deposits of natural gas hydrates below the ocean floor and in permafrost regions are potential new energy resources (Koh and Sloan, 2007; Boswell, 2009). We may also benefit from a series of new technologies based on hydrates (Hu and Ruckenstein, 2006; Sun et al., 2007a; Tsouris et al., 2007; Nagai et al., 2008; Sugahara et al., 2009; Ricaurte et al., 2013; Zhang et al., 2014). On the other hand, gas hydrates may lead to the plugging of equipment in the production and transportation of oil and gas (Koh et al., 2011; Joshi et al., 2013). Understanding the gas hydrate film growth kinetics is

important in controlling hydrate formation in water–oil–gas pipelines and in other gas hydrate applications. Upon nucleation, hydrate films first grow laterally at the interfaces between water-rich and guest-rich phases; a general conclusion is that the film lateral growth rate is controlled by heat transfer (Freer et al., 2001; Mori, 2001; Mochizuki and Mori, 2006; Peng et al., 2007a,b; Sun et al., 2010). Due to difficulty in designing a proper experimental method (Servio and Englezos, 2003; Lee et al., 2005; Tanaka et al., 2009; Zhong et al., 2011; Wu et al., 2013), the lateral growth kinetics of hydrate films at the interface of water and oil with dissolved guest gas have rarely been investigated experimentally (Sun et al., 2010), which is of critical significance for understanding and controlling the plugging of oil and gas pipelines as shown in Fig. 1, based on the idea from the CSM hydrate research group (Davies, 2009; Turner et al., 2009a, b; Joshi et al., 2013). After the lateral growth, the growth vertically in the thickness of the hydrate film is believed to switch to a process limited by mass transfer across the hydrate film (Mori and Mochizuki, 1997, 2000; Taylor et al., 2007). However, an implied question is whether vertical growth of the hydrate film is controlled by the mass transfer of the hydrate formers or the water across the hydrate film. Different methods have been

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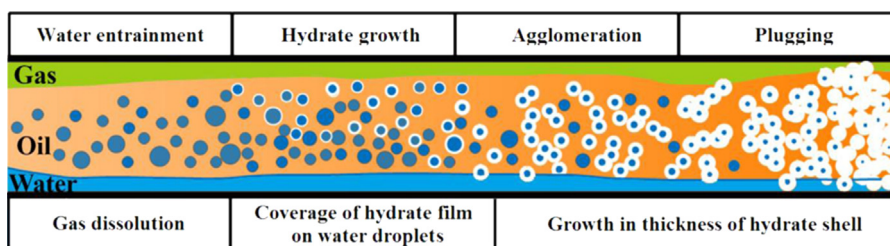


Fig. 1. Schematic diagram of a hydrate formation and plugging mechanism in low water cut systems (water emulsified in oil) (Davies, 2009; Turner et al., 2009a, b; Joshi et al., 2013).

used to study the mass transfer process of hydrate growth in thickness (Taylor et al., 2007; Davies et al., 2010; Liang and Kusalik, 2011). The mobility of water and guest molecules was compared within the hydrate film (Davies et al., 2010) and among the hydrate cages (Liang and Kusalik, 2011). However, there is no direct evidence that the mass transfer of water or guest molecules is responsible for the vertical growth of hydrate films (Sugaya and Mori, 1996; Mori and Mochizuki, 1997, 2000).

Once the interface of the guest/water is covered by a hydrate film, there is a simple rule to determine the mass transfer species by observing the direction of the film growth in thickness, to the water phase or to the guest phase. For instance, if the hydrate film grows to the water phase, the mass transfer species is the guest. However, the hydrate film can also thicken from the diffusion of guest molecules initially dissolved inside the water-rich phase or water molecules initially dissolved in the guest-rich phase (Davies et al., 2010), which makes the previous judgment method insecure. Herein, we design an experimental method to study the thickening direction of hydrate film and the mass transfer species. In this method, a water droplet was suspended in oil saturated with methane. By making a point-contact of the droplet with a pre-existing hydrate layer, the hydrate film on the surface of the water droplet grows from one end to the other, so a regular hydrate film can be formed. Because water does not dissolve in oil, the method was used to exclude the defects caused by the dissolution of water in the guest phase mentioned above. When a microscope is equipped to observe the lateral growth process and the morphological evolution of the outer surface of the film, the measurement of the lateral growth rate, the study of the thickening direction of the film and the mass transfer species can be performed experimentally.

2. Experimental section

2.1. Equipment and materials

The schematic diagram of the experimental device is shown in Fig. 2. The main part of the apparatus is a high pressure cell with an inner space of 36 mm in diameter and 15 mm in axial length. There is a pair of glass windows installed at two opposite sides of the cell, through which the phenomenon in the cell can be observed using a microscope and recorded by a CCD camera. A needle with a diameter of 2.996 mm is extended into the cell from the top, through which water can be injected into the cell to produce a water pendant. The pressure of the cell is controlled by supplying methane from a gas cylinder through a pressure regulating valve with a maximum operating pressure of 20 MPa. The temperature inside the cell is controlled by an air bath, and the temperature can be adjusted in the range of 253.2–293.2 K. The system temperatures are detected by three Eurotherm temperature controllers with an average uncertainty of ± 0.1 K. All of the pressure gauges are calibrated using a standard RUSKA dead-weight pressure gauge with an uncertainty of $\pm 0.25\%$. Analytical

grade CH_4 (99.99%) and n-octane (mass fraction of 0.999) supplied by Beifen Gas Industry Corp. are used in the experiment. The water used in the experiments is distilled twice, and its conductivity is found to be less than 10^{-4} S m^{-1} .

2.2. Experimental procedures

The entire system was purged with methane gas and then evacuated. Subsequently, distilled water was charged into the high-pressure cell until approximately one-third of its volume was filled, and n-octane was then charged into the cell until the thickness of the n-octane layer floating above the water phase was approximately 5 mm, and a needle was emerged in the n-octane. The system temperature was then adjusted to 275.2 K through the air bath. After the system temperature became stable, methane gas was introduced continuously into the cell through an inlet at the bottom until the system pressure was significantly higher than the equilibrium pressure for hydrate formation. Afterwards, distilled water was injected from the needle at the top of the cell to make sure that a water pendant close to the bulk oil/water interface could be formed. The pressure decreased with elapsed time as the methane gas dissolved in the oil and water phase. The establishment of phase equilibrium among the gas, oil, and water phases takes a long time, usually longer than 24 h depending on the value of the initial pressure. The dissolving process was considered to be complete if there were no changes in pressure in the system for 24 h. A methane hydrate layer was induced to form during or after the dissolving process, and then a fresh water droplet was injected to contact the hydrate layer and the hydrate film started to grow on the surface of the water droplet. Fig. 3 shows pictures of the methane hydrate film growth on the surface of a water droplet in n-octane saturated with methane gas, and the corresponding video can be found in the Supporting Materials. As shown in Fig. 3 and Video 1, after the dissolving process of methane gas and the formation of the methane hydrate layer (Fig. 3(a)), a little more water was injected to make the pre-existing water pendant larger and just contact the hydrate layer. The lateral growth of the hydrate film on the water pendant started and eventually terminated when the surface of the water droplet was fully covered with hydrate film (Fig. 3(b)–(d)). Afterwards, the system was left for a long period of time to observe the film growth in thickness. At the end of each experimental run, the pressure was decreased to atmospheric pressure to dissociate the hydrate, and the gas, n-octane, and water were discharged from the cell. Fresh distilled water and n-octane were charged into the cell for another experimental run.

Supplementary material related to this article can be found online at [doi:10.1016/j.ces.2015.01.057](https://doi.org/10.1016/j.ces.2015.01.057).

2.3. Data processing

The whole methane hydrate film growth process was observed using a microscope, recorded by a CCD camera, and stored by a computer. The curving contour line length of the water pendant

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