Journal of Natural Gas Science and Engineering xxx (2016) 1–9

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Methane hydrate propagation on surfaces of varying wettability

Shefaza Esmail [1], Juan G. Beltran*

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, ON, Canada

ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form
21 June 2016
Accepted 29 June 2016
Available online xxx

Keywords:
Gas hydrate
Surfaces
Morphology
Methane
Wettability

ABSTRACT

Methane hydrates were crystallized from water droplets on three different surfaces of varying wettability. Contact angles in air were used to classify substrates in decreasing order of wettability as: glass, sapphire, and polyvinyl chloride (PVC). Hydrates grown on glass appeared to have a rougher texture than those grown on sapphire, and those grown on PVC appeared to have the smoothest texture. Hydrate films formed on sapphire and PVC smoothed over time, and depressions on the clathrate films were observed within 3 h of initial crystal growth. Hydrate films formed on glass did not develop depressions over this 3 h period. On glass and sapphire, methane hydrate propagated beyond the original water droplet boundaries. The hydrate propagation velocity on glass was found to be at least 50% higher than that on sapphire. Methane hydrate did not propagate beyond the water droplet boundaries on PVC. Hydrate growth beyond the original water droplet boundary (halo) was found to proceed through water migration by capillary action: first, water migrated onto the bare substrate (glass or sapphire), and second, hydrate grew on the fresh water surface. We posit that static contact angle measurements of water on a solid substrate in air could be used to infer the potential for hydrate propagation onto a solid substrate.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Clathrate hydrates, commonly known as gas hydrates, are crystalline compounds that form from water and volatile compounds, such as methane, carbon dioxide, or natural gas. Gas molecules entrapped within hydrogen-bonded water cages form hydrate structures that are stabilized by weak van der Waals forces at low temperatures and moderate pressures. The arrangement of the hydrate cavities and the size of the guest gas molecules result in different crystalline structures. Methane hydrates, for example, form structure I (sI) hydrates.

Gas hydrates that form in oil and gas pipelines may result in hydrate plugs that block fluid flow within oil and gas transmission pipelines. It has been estimated that the oil and gas industry spends over USD 200 million annually to prevent hydrate formation (Sum et al., 2009). Traditionally, thermodynamic inhibitors, such as methanol or glycol, have been used to shift the conditions of hydrate stability in order to avoid hydrate formation at the operating temperatures and pressures. The gas and oil industry is currently in a transition from hydrate avoidance to risk management using low-dosage hydrate inhibitors (LDHIs) (Zerpa et al., 2011). Kinetic LDHIs slow down the hydrate formation process allowing pipeline fluids to leave hydrate-risk zones before gas hydrates form (Lederhos et al., 1996). Low-dosage antiagglomerants allow hydrates to form but prevent them from agglomerating, keeping them dispersed and flowing within pipeline fluids (Kelland, 2006). Both kinetic inhibitors and antiagglomerants act at the interfaces of hydrate particles, hence the importance of considering surfaces and interfaces in the study of gas hydrates (Zerpa et al., 2011). In the presence of kinetic inhibitors, catastrophic growth and spreading of hydrates in glass columns has been observed (Lee and Englezos, 2006). Water droplets deposited on PTFE, and containing kinetic inhibitors, have been observed to collapse and spread upon hydrate formation. Furthermore, it has been found that the presence of surfactants such as sodium dodecyl sulfate (SDS) can promote extensive hydrate growth on crystallizer walls (Yoslim et al., 2010).

Conceptual pictures of the growth mechanism of hydrates have been put forward at the mesoscopic scale (Mori and Mochizuki, 1997; Davies et al., 2010) and at the pipeline scale (Sum et al., 2012; Sloan and Koh, 2008). Specifically on gas-dominated systems in pipelines, the main hydrate formation mechanism is believed to be deposition on the pipe wall (Sum et al., 2012). Hydrates formed in gas systems with little water may grow directly on

* Corresponding author.
E-mail address: juan.beltran@rmc.ca (J.G. Beltran).
[1] Present address: School of Environment, Resources and Sustainability, University of Waterloo, Waterloo, ON, Canada.

http://dx.doi.org/10.1016/j.jngse.2016.06.068
1875-5100/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: Esmail, S., Beltran, J.G., Methane hydrate propagation on surfaces of varying wettability, Journal of Natural Gas Science and Engineering (2016), http://dx.doi.org/10.1016/j.jngse.2016.06.068

the pipe wall (Austvik et al., 2000) or through deposition of hydrates on an existent hydrate deposit on the solid surface (Sum et al., 2012). Austvik et al. (2000) explained how hydrate films that formed initially in pipe test sections prevented further contact between water and the hydrocarbon.

Hydrate films typically form at gas-water interfaces where the concentrations of guest and host molecules are the highest (Davies et al., 2010); however, the importance of a third surface was early on recognized (Cha et al., 1988). Homogeneous nucleation of hydrates is rare, and heterogeneous nucleation, which occurs in the presence of a surface, occurs much more frequently (Sloan and Koh, 2008). Heterogeneous nucleation is energetically favored over homogeneous nucleation, and smaller wetting angles increase the probability of heterogeneous nucleation (Kashchiev and Firoozabadi, 2002).

In flowlines, the carbon steel surface is hydrophilic and water adsorbs readily on it (Sum et al., 2012). Adhesion forces are higher for water-wet pipeline surfaces, which may be part of the mechanism for hydrate plug formation (Aspenes et al., 2010b). Surface properties for gas hydrate systems such as wettability (Aspenes et al., 2010b), surface tension (Uchida and Kawabata, 1996; Akiba and Ohmura, 2016) and adhesion force (Aspenes et al., 2010a; Aman et al., 2010) have been reported previously. Assessing wettability can be complex as it may vary with the history of contact of the liquid with the surface (Zerpa et al., 2011). Perfeldt et al. (2015) showed that stirred tank reactors with hydrophobic surfaces delayed methane hydrate nucleation times and slowed hydrate growth rates significantly, and Smelik and King (1997) avoided water migration to the coldest regions of their pressure cell by applying a thin layer of light hydrocarbon oil to their water droplet sample. However, hydrate spreading has been shown to occur on teflon (Servio and Englezos, 2003; Lee and Englezos, 2006) and cellophane (Lee et al., 2005).

The effect of various surfaces on growth of carbon dioxide hydrates from liquid CO_2 and water has been studied previously (Tabe et al., 2000). It was found that massive hydrates formed on glass, copper and stainless-steel plates, while very thin films formed on polycarbonate and polytetrafuoroethylene (PTFE). Tabe et al. (2000) hypothesized that for massive hydrate formation to occur, water must wet the hydrate-glass interface so that a thin layer of water can continue to supply hydrate growth adjacent to the glass.

Water movement by capillarity has been theorized as the main mechanism through which water molecules move in the formed hydrate layer (Mori and Mochizuki, 1997). Using high-resolution confocal Raman spectroscopy it has been shown that hydrate growth is controlled by the movement of water within the hydrate film (Davies et al., 2010). In addition, measurements of cohesive, hydrate particle-particle forces support the existence of a water capillary bridge between hydrate particles (Aman et al., 2012).

Servio and Englezos (2010) hypothesized that an undetectable water “bridge” explained almost simultaneous nucleation of multiple water droplets immersed in methane or carbon dioxide atmospheres. Later, Beltran and Servio (2010) filmed methane hydrate propagation beyond the original water boundary on glass substrates. Images showed that this growing front could induce nucleation by creating a bridge between segregated water droplets (Beltran and Servio, 2010). It was hypothesized that once the hydrate film had formed on the droplet surface, liquid water from underneath the hydrate layer was drawn by capillarity toward the water-free glass and the hydrate film formed on the advancing water front (Beltran and Servio, 2010).

1.1. Objectives

The effect of surfaces has been recognized as a key parameter related to gas hydrate nucleation and growth. Previous hydrate research suggests that hydrate propagation can occur on different types of substrates. Also, it has been shown that certain surfaces induce massive hydrate formation, while others result in very thin hydrate films (Tabe et al., 2000). Finally, methane hydrate has been reported to propagate on glass, possibly through capillarity (Beltran and Servio, 2010). Based on the state of the art, we set three objectives for this work:

1. To show the effect that different surfaces have on gas hydrate morphology formed from water droplets.
2. To elucidate the mechanism by which gas hydrates propagate onto surfaces.
3. To show that hydrate propagation on surfaces depends on the surface characteristics as represented by wettability.

2. Experimental

2.1. Materials

Sapphire slides were acquired from Meller Optics (RI, USA). Glass and PVC microscope slides were purchased from Fisher Scientific Canada. The reagents used for this study are summarized in Table 1.

2.2. Apparatus and methods

2.2.1. Gas hydrate growth and propagation

Hydrate crystallization was performed inside a high-pressure, stainless-steel vessel of approximately 80 cm^3 internal volume. Sapphire windows allowed observation through the top and illumination through the bottom of the reactor. Save for minor modifications, the apparatus resembled that of Beltran and Servio (2010). A Schott KL2500 cold light source (Optikon, ON, Canada) provided the necessary lighting, and a refrigerating circulator (Fisher Scientific, Canada) cooled the pressure vessel through a copper coil. Temperature was measured with two, type K, mini-thermocouple probes (Omega Engineering, QC, Canada). Pressure was monitored using a Rosemount 3051S pressure transducer (Laurentide Controls, QC, Canada). Instrumental standard uncertainties were as follows: for temperature $u_T = 1$ K and for pressure $u_p = 0.005$ MPa.

A precleaned glass, sapphire, or PVC slide was set inside the reactor. A water droplet, 20 μL in volume, was transferred onto each slide using a micro pipette. The vessel was then sealed, purged, and pressurized with methane gas (99.99% purity). Pressure was increased slightly above the experimental pressure and the temperature was allowed to stabilize. The pressure was then dropped to achieve the desired experimental conditions. The crystallization process was recorded using a PCO.2000 camera (Optikon Corporation, ON, Canada). A Nikon AF-Micro-Nikkor 60 mm lens (Optikon, ON, Canada) was used for low magnification images, and an Infinity KC microscope with IF-series objectives (Optikon, ON, Canada) was used for high magnification images.

Nucleation times were not tracked. Hydrate formation experiments were allocated a maximum of 24 h. Most crystallization

Table 1
Reagents used in this study.

Chemical name	Source	Purity	Purity units
Distilled water	In-house	18	MΩ•cm
Methane	Air Liquide	99.99%	Mole fraction
Methyl blue	Sigma-Aldrich	Microscopy Grade	–

Please cite this article in press as: Esmail, S., Beltran, J.G., Methane hydrate propagation on surfaces of varying wettability, Journal of Natural Gas Science and Engineering (2016), http://dx.doi.org/10.1016/j.jngse.2016.06.068

Download English Version:

https://daneshyari.com/en/article/5484785

Download Persian Version:

https://daneshyari.com/article/5484785

Daneshyari.com