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SURFACTANT EFFECT ON HYDRATE CRYSTALLIZATION MECHANISM

A Thesis

Presented to

The Faculty of the Department of Biomedical, Chemical, & Materials Engineering

San José State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Kevin Dann

May 2017

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The Designated Thesis Committee Approves the Thesis Titled

SURFACTANT EFFECT ON HYDRATE CRYSTALLIZATION MECHANISM

by

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MATERIALS ENGINEERING

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May 2017

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ABSTRACT

SURFACTANT EFFECT ON HYDRATE CRYSTALLIZATION MECHANISM

by Kevin Dann

Gas hydrates pose economic and environmental risks to the oil and gas industry when plug formation occurs in pipelines. A novel approach using interfacial rheology was applied to understand cyclopentane clathrate hydrate formation in the presence of nonionic surfactant to achieve hydrate inhibition at low percent weight compared to thermodynamic inhibitors. The hydrate-inhibiting performance of low ($< \text{CMC}$), medium ($\approx \text{CMC}$), and high ($> \text{CMC}$) concentrations of Span 20, Span 80, Pluronic L31, and Tween 65 at 2 °C on a manually nucleated 2 μL droplet showed a morphological shift in crystallization from planar shell growth to conical growth for growth rates below 0.20 mm^2/min . Monitoring the internal pressure of a droplet undergoing planar hydrate crystallization provided a strong correlation (up to $R = -0.989$) of decreasing interfacial tension to the shrinking area of the water-cyclopentane interface. Results from the high-concentration batch of surfactants indicated that while initial hydrate growth is largely suppressed, the final stage of droplet conversion becomes rapid. This effect was observed following droplet collapse from the combination of large conical growths and low interfacial tensions. The low-concentration batch of surfactants saw rapid growth rates that diminished once hydrate shell coverage was completed. The most effective surfactant was the high-concentration Tween 65 (0.15 g/100mL), which slowed hydrate growth to 0.068 mm^2/min , nearly an order of magnitude slower than that found for pure water at 0.590 mm^2/min . High molecular weight (1845 g/mol) and HLB (10.5) close to 10 contribute to a large energy of desorption at an interface and are believed to be the sources of Tween 65's hydrate-inhibiting properties.

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CHAPTER ONE

INTRODUCTION

Clathrate hydrates are simultaneously nonstoichiometric and crystalline structures composed of guest molecules trapped inside cavities of the surrounding hydrogen-bonded water molecule cages [1]. They are readily found in nature along the sea floor, permafrost, and in glaciers [2]. Hydrates have important applications in many areas, including flow assurance of oil and gas lines, as a potential source of natural gas (primarily methane) from permafrost and deep-sea hydrate deposits, water desalination [3–5], carbon dioxide capture to regulate global warming [6–12], and as a medium for energy storage and transportation [13, 14]. Despite widespread use, there remains a demand to understand the crystallization mechanism of clathrate hydrates as these fields of research continue to explore methods of manipulating hydrate formation and dissociation.

The strongest incentive to understand the mechanisms of hydrate crystallization and inhibition stems from their occurrence in oil pipelines and the resulting difficulties for flow assurance. Understanding hydrate formation plays a primary role in reducing blockages and in subverting future environmental disasters as seen in the 2010 Gulf of Mexico oil spill [15]. With knowledge of the formation mechanism at hand, effective low dose additives can be developed to control pipeline blockages, increase petroleum capture, and improve ecological wellness.

1.1 What is a Clathrate Hydrate?

Clathrate is the term used to categorize a lattice that has trapped guest molecules. *Hydrate* refers to a water containing substance. Thus, clathrate hydrates are compounds of guest molecules that have become trapped inside cages of hydrogen-bonded water molecules. Figure 1 represents a schematic description of the generic clathrate hydrate crystal structure. Molecules as small as nitrogen and

carbon dioxide, all the way through larger guests such as methane, isobutane, propane, and cyclopentane have been confirmed to stabilize various hydrate crystal structures. The structure is able to exist at temperatures above the melting point of ice due to the guest molecules stabilizing the lattice, creating a thermodynamically stable environment among the polar and non-polar molecules [4]. The structures typically form into thin films at the interface of water and the bulk-guest phase, thereby providing a solid barrier to prevent further hydrate solidification once the water and bulk phases are separated [17]. There is evidence to show that bulk agglomeration is accelerated under water and oil emulsions due to the increased

Figure 1. General clathrate hydrate structure with water cages trapping guest molecules (Adapted from Ref [16] by permission of the Royal Society).

interfacial area created between the oil and water phase; the water molecules surround and separate an oil guest molecule, which is then followed by three-dimensional crystal growth [18].

Hydrate structures come in various sizes depending on the optimal arrangement required to house the guest molecule. Table 1 compares selected properties amongst ice I_h and hydrates. Typically, the guest molecule size to cavity diameter ratio is observed near unity, with 0.9 as the minimum [19]. Type 1 structure (sI) and type 2 (sII) encompass the majority of hydrate structures since the larger type H (sH) do not form at normal pressure for simple hydrates [1]. The sI hydrates form a simple cubic structure, sII hydrates form a face-centered cubic crystal structure, and sH hydrate forms a hexagonal crystal structure [20]. Figure 2 depicts the three unit cells and different pathways each structure must follow to form its respective geometry.

There must be a guest molecule of appropriate size in order for a hydrate to form. In the absence of suitable guest molecules water will instead form ice I_h , the hexagonal and most common phase. Following statistical thermodynamic models for

Table 1. Comparison of sI and sII Hydrates to Ice for Select Properties [1, 19, 21].

	Ice (I_h)	sI	sII
Crystal system	Hexagonal	SC	FCC
Formula	—	$5^{12} - 5^{12}6^2$	$5^{12} - 5^{12}6^4$
Cavities/unit cell	—	2 – 6	16 – 8
Ave. cavity radius (Å)	—	3.95 – 4.33	3.91 – 4.73
Waters/unit cell	4	46	136
Ave. lattice parameter (Å)	$a = 4.52, c = 7.36$	12.0	17.3
Young’s at 268 K (GPa)	9.5	8.4	8.2
Poisson’s ratio	0.3301	0.31403	0.31119
CTE (K^{-1})	56×10^{-6}	77×10^{-6}	52×10^{-6}
Heat capacity ($J \cdot kg^{-1}K^{-1}$)	1700 ± 200	2080	2130 ± 40
Refractive index at 632.8 nm	1.308	1.346	1.350
Density ($kg \cdot m^{-3}$)	916	912	940

Figure 2. Hydrate structure types sI, sII, and sH. Notation follows the nomenclature S^F , where F is the number of faces with sides S (Adapted from Ref [22] with permission of The Royal Society of Chemistry).

hydrate equilibria led Sloan *et al.* to present a model for predicting the density (ρ) of any species of hydrate [1], and it may be evaluated by Equation 1.

$$\rho = \frac{N_W MW_{H_2O} + \sum_{J=1}^C \sum_{i=1}^N \theta_{iJ} \nu_i MW_J}{N_A V_{\text{cell}}} \quad \text{Equation 1}$$

where:

- N_W = # of water molecules per unit cell
- N_A = Avogadro's
- MW_J = molecular weight of component J
- θ_{iJ} = fractional occupation of cavity i by component J
- ν_i = # of type i cavities per water molecule in unit cell
- V_{cell} = unit cell volume
- N = # of cavity types in unit cell
- C = # of components in hydrate phase

1.2 Detection

Offshore gas reservoirs exist below the seabed, and an enormous quantity is believed to be trapped both in the hydrate structures themselves as well as in the sediment beneath [23]. Estimates point to quantities far exceeding the known global supply of fossil fuels [24]. Often, a fault or vein will allow subterranean natural gas to contact the open waters and wet sediment of the seabed. Hydrates will accumulate near the site as long as the temperature–pressure conditions are within the range of hydrate stability [25]. An understanding of the necessary stability conditions for a few gas compositions can be gathered from Figure 3. Because ice

Figure 3. Methane and ethane hydrate pressure-temperature stability field (Republished with permission of Springer Science and Business Media, from Ref [26]; permission conveyed through Copyright Clearance Center, Inc.).

(and the related hydrate) has low permeability, gas concentrations below the cap will increase, in turn leading to further probability of hydrate formation [25].

As there are large hydrate concentrations visible on the sea floor near oil reserves, they play a pivotal role in detection of gas and oil reserves visually or acoustically through reflective seismology [24]. Seismic image processing has long been the leading detection method of offshore gas hydrate existence [7]. An increase in seismic velocity is the most readily observable change in sediment properties indicative of hydrate presence [20]. When a pressure wave interacts with an interface, such as between a water column and hydrates, changes in acoustic impedance result in reflected waves capable of characterizing the interface [27]. A material's acoustic impedance (Z_o) is given by Equation 2, where ρ is the density and c is the speed of sound of the material.

$$Z_o = \rho c \quad \text{Equation 2}$$

Gabitto *et al.* [20] consolidated extensive clathrate data regarding hydrate impregnated sediments so that the hydrate signature could be constructed to assist interpretation of geophysical data when processing seismic signals of reflected acoustics. Unconsolidated sediment (50% porosity) with hydrates occupying only 10–20% pore space has a velocity of 1900–2100 m/s, whereas velocity measurements for sediment absent of hydrates range from 1600–1700 m/s. Oil prospectors may implement this technique to enhance hydrate detection by rapidly scanning the seabed for areas of high concentration.

1.3 As a Source of Energy

Gas hydrates not only indicate the location of larger underlying natural gas fields, they also hold a tremendous amount of gas within the clathrate cages.

Sloan *et al.* states that gas hydrates have as much as 90% of their clathrate cages

occupied by guest molecules [1]. Hydrocarbons encapsulated in hydrates have a separation of approximately 0.5 nm, which indicates high energy densities on the same order of compressed gas (equivalence of methane gas at 18 MPa and 273 K) [17]. This concentration of fixed gas, when released from 1 m³ of hydrate, can contain as much as 164 m³ of gas (methane) at standard conditions [23].

Sources agree that the known amount of conventional gas reserve is eclipsed by that of the gas reserves trapped in hydrates [28, 29]. A collection of studies by Sloan *et al.* reveals that estimates of global hydrate reserves are expected to contain between 2×10^{14} – 1.2×10^{17} m³ of methane at STP (which translates to 74,000 Gt of methane, or three orders of magnitude greater than conventional gas reserves) [29]. For comparison, just 1×10^{15} m³ of methane would supply the United States with 1000 years worth of energy [1] at the nation’s peak annular consumption rate, which occurred in 2007 and was reported to be 101.6 quadrillion BTUs (commonly expressed as quads) [30]. The most recent annul energy review by the U.S. Energy Information Administration reports that energy consumption has declined to 95.0 quads. From a review of Figure 4, it is evident that petroleum and natural gas constitute the largest sector of energy sources at 72% when combined [31]. It is therefore highly motivating to pursue additive technologies for hydrate destabilization, both for potential extraction techniques from dissociation, and for continued support in flow assurance of petroleum and natural gas. Current commercial extraction techniques of natural gas from hydrate dissociation is still a developing field, but it is expected to become viable within the next decade [17]. Extraction through decomposition of hydrates and hydrate saturated sediments into water and gas constituents can be accomplished through three primary methods: 1) depressurization, 2) thermal stimulation, and 3) injection of hydrate stability inhibitors (salts and alcohols).

Figure 4. US energy consumption by source and sector in 2012 [31].

One of the world's greatest hydrate concentration is located at the Mallik field in Canada. Moridis *et al.* was first to explore the potential for gas production directly from these hydrate accumulation; however, they merely employed numerical models to affirm the scientific basis for the aforementioned extraction techniques. Moridis *et al.* did not attempt to reconcile the viability of these methods for large-scale production [32]. A comprehensive review by Grace *et al.* determined that there were no futile technological challenges obstructing large-scale harvest of gas from hydrates. They concluded that pressure drawdown within a reservoir would be the most rewarding of all production methods surveyed in their review [7]. If a thermal approach is taken, the energy needed to perform hydrocarbon extraction through thermal dissociation equates to 15% of the equivalent energy gained, representing a loss of efficiency [1]. Thermodynamic and kinetic stability-inhibiting solutions are

vital to future extraction of gas-laden hydrates because they can complement the two previously discussed dissociation methods, and they are easily implemented.

1.4 Hydrates in Petroleum

Gas hydrate formation can severely disrupt production in the context of offshore oil pipelines. The high pressures often used for throughput, combined with the high pressures and low temperatures near the seabed floor, leave many pipelines exposed to conditions favorable to hydrate formation [17]. Even when proper precautions are taken, these conditions continually impair the oil and gas industry's production rate. Hydrate formation is by far the leading cause of technical difficulties for offshore oil pipeline flow assurance [33]. Oil spills caused by the formation of hydrates represent not only a loss of profit to the oil entity, but an ecological catastrophe. The most notorious spillage involving hydrate blockage is the greatly publicized 2010 BP Deepwater Horizon oil spill that took place in the Gulf of Mexico [34]. It was later determined that containment issues were caused when leaking gas contacted the sea water, formed hydrates, and plugged the cofferdam and relief pipe before it could be maneuvered over the leak [15]. In the past century, much of the impetus for hydrate research is due to the oil industry's effort to circumvent hydrate plug agglomeration and the subsequent blockage of flow. In 1934, Hammerschmidt was first to determine that hydrates were responsible for plugged flowlines when above the freezing point of water [35]. Still today, flow assurance propels hydrate research, and the effort to understand the hydrate formation process remains important to oil producers.

It becomes expensive to adequately insulate deep water pipelines in the attempt to prevent hydrate formation, and the additional cost is on the order of \$1 million/km [33]. Other means of prevention, such as injecting thermodynamic inhibitors into wellheads have previously been used. Methanol is an effective

inhibitor; however, large volumetric ratios, as great as 1:1, of water to alcohol are often required [36]. This amount of alcohol usage is not sustainable—not to mention costly. Currently, there is a \$220 million/year global cost attributed to the use of methanol for hydrate prevention [17]. In addition, methanol is environmentally hazardous, rendering it an impractical solution for large-scale transport [17]. There is an alternative method for hydrate prevention: surface modification through the use of surfactants.

Surfactants have demonstrated the ability to suppress hydrate growth through kinetic inhibition and anti-agglomeration at undercoolings of up to 20 °C [1]. The onset of hydrate nucleation can also be delayed by surfactants, which alter surface properties such as surface tension [36]. There are at least two hypotheses that describe a surfactant’s effectiveness: 1) Surfactants are useful because the hydrates are inhibited through the surface modification, and 2) surfactants aid the initial formation of hydrate cells but prevent further agglomeration down the line [37]. Surfactant presence in the bulk phase would drastically reduce, if not eliminate, the large amount of glycols or alcohols needed for hydrate prevention. For example, Karanjkar *et al.* determined that a volumetric concentration of 0.03% Span 80 (a nonionic surfactant) was enough to saturate the water–oil interface [38]. The proposed work that follows aims to explore alternative solutions for hydrate suppression through surfactant utilization.

CHAPTER TWO

LITERATURE REVIEW

2.1 Early Work

The early period of hydrate research is relatively sparse. Sir Humphrey Davy [39] is recognized as the first to document the existence of gas hydrates [1]. While characterizing chlorine gas in 1811, Davy observed that a solution of chlorine and water froze more readily than either separately. This solid was later confirmed by Faraday in 1823 to have the chemical formula of $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, marking the first recognition of hydrates as a crystalline compound [40]. The following century involved little more than classifying which guest molecules were hydrate-forming. However, the progress toward understanding hydrates in the twentieth century is quite interesting. In 1934, Hammerschmidt discovered that hydrates were the cause of natural gas and water vapor freezing at temperatures greater than ordinarily expected in gas lines. The discovery revolutionized modern research of hydrates and immediately demonstrated the importance of moisture regulation in pipelines [1, 35]. What followed was an era of extensive and painstaking studies constructing phase-equilibrium relations to investigate the effects of hydrate inhibitors as preventive solutions in gas lines. At the same time, the crystal structure of sI and sII hydrates were being characterized through von Stackleberg’s X-ray diffraction patterns and Claussen’s structural arrays fitting these patterns [41].

Since Hammerschmidt brought to light the role of hydrate plugs in pipeline blockages, methods for prevention have been sought. The primary methods identified to prevent hydrates included 1) reducing the initial water cut to reduce free water, 2) maintaining temperatures above hydrate stability, 3) maintaining pressures below hydrate stability, and 4) injecting thermodynamic inhibitors of methanol and glycol to alter equilibrium curves [42].

2.2 Formation Mechanisms

Time-independent hydrate properties (e.g. mechanical properties and three-phase equilibria) are well understood and researched. How hydrates form, dissociate, and evolve with time represent the more challenging and interesting areas of research. Although greater difficulty lies with interpreting time-dependent processes (e.g. nucleation and growth), it holds the key to understanding fundamental formation mechanisms which are imperative for kinetic hydrate inhibitor development and testing. The development of time-dependent hydrate formation will be discussed in this section.

2.2.1 Molecular Processes

In 1991, Sloan and Feleyfel proposed a kinetic model of the molecular mechanism with which hydrates form from ice (not liquid water) [42]. Inductive reasoning was used to formulate their hypothesis, and later, experiments with cyclopropane hydrates validated their explanation. The motivation to understand the formation mechanism at the molecular level acknowledged the importance and potential implications of hydrate formation inhibition. The foundation upon which kinetic inhibitor development relied (as an alternative to thermodynamic inhibitors) was carried out by describing the mechanism. Sloan and Feleyfel hypothesized that the necessary steps to formation, illustrated in Figure 5, mandate the following process:

- (1) The energy needed for ice molecule dissociation may be supplied through surface renewal from mechanical agitation and ball-mill like processes or through increases in thermodynamic energy from the environment.

Following the need to form the smallest of clathrate cavities (a dodecahedron of the form 5^{12}), a minimum of twenty ice lattice molecules must participate in mass transfer.

- (2) Clathrate structures take form as the water molecules cluster around the nonpolar guest. The most likely structure is 5^{12} since the ratio of the number of bonds (30) to molecules (20) is maximized. One explanation of the driving force for the clathrate structure assembly around the guest molecule is the minimization of negative entropy associated with the highly ordered cluster system [1, 43]. This process is essentially the second law of thermodynamics in action, where the entropy always increases or stays constant (minimum internal energy at equilibrium). Monte Carlo simulations agree with the 5^{12} organization [44].
- (3) A thin film of liquid water mediating the interface between ice and the guest phase stimulates the transport of fragile individual clathrate cages to form unit cells. At this point, a unit cell by itself is below the critical size for growth, so some percentage of structures will dissociate and return to the previous stage.
- (4) The surviving unit cells that manage to combine with other unit cells and grow beyond the critical size finally form the macroscopic hydrate lattice. This stage concludes primary nucleation. Growth ceases when either ice or the guest phase is depleted.

Figure 5. Kinetic hydrate formation process from ice (Adapted from Ref [42] with permission of John Wiley and Sons).

Sloan’s dated explanation has, so far, stood up to the last few decades of hydrate studies [45]. More recently, nucleation modeling through computational simulations allows processes to be observed on the microsecond scale [46]. These processes show consistency with the above outlined steps.

2.2.2 Shell Model

There is an apparent widespread acceptance in literature for the *shell model* as the primary mechanism of hydrate formation for droplets. As shown in Figure 6, hydrate nucleation is assumed to begin on the exterior of the droplet at the interface between the guest and water phase. This is followed by complete coverage of a thin, porous hydrate shell, and the process concludes with a fully converted solid hydrate once diffusion through the hydrate film stops. In most scenarios, it is unrealistic to assume that the interactions between hydrate forming guest phases and water take place under tranquil conditions. The flowing ocean currents, the churning pipeline oil, and the turbulent drill site all produce shear forces that create a violent environment. This lends credibility to models which explain hydrate formation in terms of a water-in-oil (W/O) emulsion (or an oil-in-water (O/W) emulsion for high water cuts > 70 vol%). Experiments by Açıkgöz *et al.* affirmed that these emulsion-generating flow patterns exist in pipelines [48], and Greaves *et al.* resolved

Figure 6. Shell model of hydrate formation for a water droplet in an oil immersion (Adapted with permission from Ref [47]. Copyright (2009) American Chemical Society).

the typical diameter of water droplets in crude oil to a range between 1–250 μm with a mean of 20–80 μm through focused beam reflectance measurement [49, 50].

In addition, the study of planar interface growth has been conducted, and there is good reason to believe the growth processes are analogous [1]. Simultaneous diffusion is believed to occur across the film, supplying guest molecules from one side to the other while water molecules travel in the opposite gradient. Planar hydrate layers grown in controlled settings exhibit final thickness dependence on the degree of subcooling [1]. Measurements of initial film thickness via interferometry range from 6–12 μm depending on the guest molecule [51].

2.3 Agglomeration

The issue of flow assurance has posed sufficient hazard for the oil and gas industry to employ dedicated flow assurance engineers [1]. Undesirable formations, chiefly asphaltenes (waxes) and hydrates, in flow lines reduce the flow capacity. Pipeline interiors reach conditions within the zone of hydrate stability when phase equilibria parameters (temperature, pressure, and concentration) minimize the free energy. Sometimes shut-in procedures are performed for emergencies or to test leakage rates, and this can have the unintended effect of pushing the system into regions of hydrate stability [52]. Figure 7 illustrates the understood stages of hydrate pipeline blockages. Initially, there must be some nonzero concentration of water present in the pipeline along with the necessary temperature and pressure conditions to place the system in a region of hydrate stability. High flow rates and shear forces promote emulsions, which increase the interfacial surface area used for hydrate formation as previously discussed by the shell model. Once sufficient hydrate crystals have nucleated, agglomeration of hydrates is proposed to occur through capillary action. The onset of hydrate accumulation is called bedding, and bedding results in an associated pressure drop [53]. Finally, if a large enough

Figure 7. Assumed pipeline hydrate plug agglomeration process with capillary action attracting newly formed neighboring hydrate shells (Reproduced from Ref [54] with permission of the PCCP Owner Societies).

hydrate mass beds on interior walls or bottleneck regions such as control valves, a plug has formed.

A macroscopic model of two-phase (oil–water) and three-phase (air–oil–water) systems detailing thermodynamic and hydrodynamic mechanisms for flow in pipelines is described in Zaghloul *et al.* [55]. The probability of forming hydrates can be evaluated from the analytical models they present, and their predicted results are corroborated with field studies concerning the various measurements of oil and water production, pressure drops, interfacial forces, and phase transitions.

A microscopic model of hydrate agglomeration is likewise manageable and is meaningful to investigate kinetic agglomeration mechanisms. An exhaustive discussion on particle–particle forces in a flowing system would include gravity, buoyancy, van der Waals forces, capillary bridge forces, collision forces, and shear forces [56]. The following sections describe the findings from literature relating these forces to agglomeration.

2.3.1 Water Cut

When crude oil is extracted, an unavoidable concentration of water, known as the *water cut*, is introduced into the drilling pipelines. The water cut can be exacerbated by water driven reservoirs which seek enhanced oil recovery by

maintaining pressure on the wellhead as the hydrocarbons are extracted [57, 58]. Post-refinement pipeline quality gas often has less than 1 mol% of a water cut [55]. Higher water cuts require proportionally higher amounts of injected inhibitors for hydrate plug prevention [49]. It is logical to reason that higher water cuts lead to more chances for hydrates to form since additional building blocks are available. Crude oil composition rarely has an effect on the rapid nucleations observed in high water cuts [59]. The effect of high water cuts is not as simple as previously mentioned, and Ning *et al.* [60] and Greaves *et al.* [49] categorized the dependence of hydrate formation and dissociation on various water cuts in oil-based drilling fluid and crude oil with the following behaviors:

- water cut ≤ 10 vol% — shells destroy interfacial films so that intrinsic instability force overcomes the oleophobic force.
- water cut ≈ 30 vol% — mean distance decreases significantly between neighboring droplets, and more droplets are within the critical distance for agglomeration.
- water cut > 50 vol% — more rapid agglomeration facilitated by the excess water (increases in capillary action and high hydrate nuclei concentration), while the severity of hydrate blockage is increased by an order of magnitude at water cuts of 50–70% [61].
- water cut > 70 vol% — agglomeration behavior changes since an emulsion is no longer a W/O system, but an O/W system. Oil is trapped inside hydrate shells, hindering mass transfer of guest molecules, slowing initial hydrate formation rates.

2.3.2 Capillary Action

Hydrate particles in a suspension of oil and water will agglomerate, and according to many sources, the most accurate representations of agglomeration forces are influenced heavily by the capillary bridge force [1, 56, 62–64]. Figure 8 presents the proposed capillary bridge geometry linking two nearby particles of radius R_1 and R_2 separated by a distance S ; the two fluids of densities ρ_1 and ρ_2 form a surface with interfacial energy γ_{LL} ; the bridge forms an internal contact angle θ_p and an embracing angle α with the particle at an immersion depth of d . When a capillary bridge initially forms, the interfacial tension between a curved surface of two different phases (oil and water) can still be minimized, and thus the system is not in a state of lowest energy. A Laplace pressure explains the attraction; when liquid water connects the particles, there will be a pressure differential at the water–oil interface due to minimization of surface tension and energy. Because surface tension tends to shrink interfacial surface area, the bridge is pulled in the direction of the dashed boundary of Figure 8 while the separation is reduced. Based on the capillary bridge parameters, Equation 3 describes the maximum capillary attractive force $F_{\max}$ between two spherical particles [64]. Aman *et al.* provides a

Figure 8. Liquid bridge model and geometry among hydrate particles.

better representation of the capillary bridge force F_{cap} in Equation 4 by adding an additional term to account for the three-phase contact line at the hydrate shell [22].

$$F_{\text{max}} = \frac{4\pi\gamma_{LL} \cos \theta_p}{\frac{1}{R_1} + \frac{1}{R_2}} \quad \text{Equation 3}$$

$$F_{\text{cap}} = \left(\frac{4\pi\gamma_{LL} R_1 R_2}{R_1 + R_2} \right) \left(\sin(\alpha) \sin(\theta_p + \alpha) + \frac{\cos \theta_p}{1 + \frac{S}{2d}} \right) \quad \text{Equation 4}$$

Several independent groups have agreed that capillary action is strongly influenced by temperature; with greater subcooling comes decreased attractive force [1, 64, 65]. Subcooling is an interesting parameter regarding agglomeration because of its coupling to other physical properties of the system. Dieker *et al.* [64] took measurements of interparticle forces between cyclopentane hydrates at various degrees of subcooling in crude oil and observed an increase in hydrate-hydrate cohesive forces as the system approached the melting temperature. They justify their results with the capillary bridge theory while pointing to a quasi-liquid layer on the hydrate surface as evidence of this action. From a thermodynamic point of view, greater subcooling encourages nucleation behaviors. However, from a kinetic point of view, greater subcooling limits interparticle interaction through increased viscosities of the oil phase. And from an interfacial point of view, greater subcooling depletes liquid water which is necessary for the capillary action that dominates.

2.3.3 Other Forces

Aside from capillary action, Wang *et al.* identified several other factors that affect the attractive forces driving hydrate particle agglomeration, though the majority of them are insignificant [56]. Gravity can influence particles of different densities in the vertical displacements. The force is determined by the difference in gravity and buoyancy of agglomerates as seen in Equation 5, where R_a is the radius

of the agglomerate, g is the standard gravity (9.8 m/s²), and ρ_A and ρ_2 is the density of the agglomerate and continuous phase, respectively.

$$F_G = \frac{4}{3}\pi R_a^3(\rho_A - \rho_2)g \quad \text{Equation 5}$$

Van der Waals forces are highly dependent on the distance of separation.

Equation 6 describes the van der Waals force between two agglomerates, where A is the Hamaker constant (5×10^{-21} J), S is the separation, and d_{a1} and d_{a2} are the hydrate agglomerate diameters.

$$F_{vw} = \frac{A}{12 S^2} \frac{d_{a1}d_{a2}}{d_{a1} + d_{a2}} \quad \text{Equation 6}$$

Shear forces are present whenever material is flowing through the pipeline and are modeled according to Equation 7, where μ_o is the viscosity of the dispersed phase, R_a is the agglomeration radius, and γ is the shear rate.

$$F_{\text{shear}} = 6\pi\mu_o R_a^2 \gamma \quad \text{Equation 7}$$

Finally, electrostatic forces arise in flowing systems as hydrate particles produce friction as they collide with pipeline walls and other particles. At the levels of electrostatic charge generated, the system is effectively grounded in the presence of salt water since it can act as an electrical conductor. This contribution is largely ignored.

Recent studies by Wang *et al.* [56, 66] investigated the contributions of shear rate, oil–water interface tension, oil viscosity, and capillary bridge contact angles on agglomeration. They concluded that the primary forces for agglomeration were van der Waals and capillary bridge forces, while the primary forces for separation were shear forces. It was discovered that the largest contributions to agglomeration came from the contact angle, while the smallest contributions came from varying interfacial tension between the water and oil.

Not to be confused with agglomeration rate, Turner *et al.* [67] and Wang *et al.* [66] showed that increased shear rates resulted in increased rates of hydrate formation (measured through gas consumption at constant pressure). It is explained there was enhanced breakup into smaller droplets, resulting in greater surface area capable of forming hydrates at the fresh interface. The diffusive layer thickness was found to decrease, facilitating more rapid mass transport of the guest phase into the water droplet, where hydrate formation can occur. Smaller hydrate particles will decrease the capillary bridge force from the radii contribution; however, two smaller particles also require less energy to attract one another. Clearly, there must exist a pivot in behavior when an ever-increasing shear force producing increased hydrate concentrations eventually becomes violent enough to break down hydrate agglomerations.

2.4 Inhibition of Crystal Growth

While controlling nature’s processes remains an implausible task, what can be done to inhibit hydrate formation? A common practice is to inject a unique solution into the wellhead of a flowline to prevent formations from occurring. These solutions come in several flavors. Thermodynamic hydrate inhibitors (THIs) have been widely utilized for their well known effects on hydrate crystallization, shifting phase boundaries of formation to lower temperatures and higher pressures. Low dosage hydrate inhibitors are effective at much lower concentrations (0.1–1.0 wt%) than seen for THIs. These solutions are sometimes separated into two categories: 1) kinetic hydrate inhibitors (KHIs) that act as kinetic barriers to nucleation and 2) anti agglomerates (AAs) that act to prevent accumulation of hydrates once formed. Special surface coatings on the pipeline interiors have also been pursued as another line of defense to prevent hydrate plugs from nucleating at susceptible pipeline locations.

2.4.1 Thermodynamic Inhibitors

THIs can come in the form of alcohols, glycols, or salts. The previously mentioned modification of thermodynamic equilibrium works by altering the Gibbs free energy. Hydrate formation temperature is lowered with the addition of an inhibitor by increasing the Gibbs free energy. THIs have been found to increase free energy through promotion of nonrandomness in the water phase (non-hydrate structures). At concentrations less than 5%, methanol can actually have the opposite effect and increase the temperature of formation [1], which is a reason much larger concentrations (20–50 wt%) are used [36, 68]. Ammonia is twice as effective as methanol for inhibition, but undesirable side reactions with water and carbon dioxide eventually yield ammonium carbonate, an even harder solid to remove than hydrates. Water cuts above 20% typically call for the addition of a thermodynamic inhibitor, where at least a 30 °C depression in freezing point effect can be seen below 170 bar for a 50 wt% addition of methanol [69]. The Hammerschmidt relation, given in Equation 8, is commonly used to approximate the freezing point depression due to the addition of a THI in water, where W_i is the weight percent of the inhibitor, and M_i is the molar mass of the inhibitor in g/mol [53].

$$\Delta T = \frac{1297 \cdot W_i}{(100 - W_i)M_i} \quad \text{Equation 8}$$

In the context of the oil and gas industry, the previously mentioned use of THIs represent costly efforts to inhibit hydrate nucleation through the expense of the material itself, large additional storage containers, and financial penalties if methanol contamination in refinery feedstock goes above 50 ppm [70]. Nonetheless, its utilization gives engineers another degree of freedom to manipulate when needed. Knowledge of the thermodynamic phase boundaries enables oilfield design and management to be planned with hydrate minimization in mind. One such case

study was conducted for an oilfield off the coast of Nigeria by Useman *et al.*, and through analysis of various pipeline variables such as length, diameter, insulation, heat transfer coefficients, and reservoir temperatures, they determined safe regions of operation and minimum tolerable flow rates before expected hydrate formation [70]. Because steady state operations are designed to operate outside hydrate risk conditions, oil systems rarely rely on a continuous supply of thermodynamic inhibitors. Thermodynamic inhibitor injection is prevalent mainly at start up and shut down [71]. However, gas and multiphase lines benefit the most from thermodynamic inhibitors.

2.4.2 Kinetic Inhibitors

KHIs impede hydrate nucleation and work to slow an already relatively slow crystal growth process. Because hydrate solids form at an interface, an effective barrier naturally separates the necessary components that compose them, slowing down the process of film thickening. KHIs are usually high molar mass water soluble (at least partially) polymers. One of the benefits of using KHIs over THIs is the greatly reduced volume needed for effective hydrate inhibition. In general, sources label these solutions as low dosage hydrate inhibitors (LDHIs) since a comparatively low concentration (< 0.5 vol%) can have great hydrate inhibition performance [72]. Unfortunately, many discoveries of surfactant presence on hydrate interactions and the role they play in hydrate formation are the subject of patented efforts [53]. A comprehensive review by Kelland of over 240 LDHI publishings revealed that about 100 were patent applications [68].

Surfactants are proposed to work on two fronts: 1) inhibit crystal growth mechanically and 2) reduce cohesion through a weakening of the capillary bridge forces [45]. When surfactant molecules migrate to an interface, the surface tension will lower according to the Gibbs adsorption isotherm given in Equation 9, where γ

is the surface tension, C is the surfactant concentration, Γ is the amount of adsorbed surfactant (mol/m^2), R is the gas constant ($8.314 \text{ J}/\text{K}\cdot\text{mol}$), and T is the temperature (K) [73].

$$\frac{d\gamma}{d \ln C} = -\Gamma RT \quad \text{Equation 9}$$

The period of time that KHIs are able to delay hydrate formation is called the induction time, and more effective KHIs have longer associated induction times, which are determined experimentally at the onset of clouding in the liquid. An overview of advances in surfactant hydrate inhibition are listed in Table 2. KHI performance is commonly categorized by the induction time for a specific magnitude of undercooling. High subcoolings result in higher driving forces for hydrate formation, and the efficacy of KHIs subsequently decreases [68]. There eventually exists a point in subcooling where no additional KHI can prevent rapid crystallization, and the best commercially available performing KHIs find this limit

Table 2. Summary of Select Studies on Surfactant Inhibition of Hydrates.

	ΔT ($^{\circ}\text{C}$)	Surfactant
Kuliev <i>et al.</i> [74]		First recorded use of surfactant to deal with hydrate plugging in gas well.
Long <i>et al.</i> [75]	5	PVP (Poly-N-vinylpyrrolidone).
Lederhos <i>et al.</i> [76]	8–9	Proposed that lactam rings of PVCap (poly-N-vinylcaprolactam) adsorbed on hydrate crystal sterically block growth.
Colle <i>et al.</i> [77, 78]	10–11	N-methyl-N-vinylacetamide:vinylcaprolactam.
Edwards [79]		Antifreeze proteins (AFPs) from winter flounder.
Toyama <i>et al.</i> [80]		PolyIPMA (Poly isopropylmethacrylamide).
Daraboina <i>et al.</i> [59]	11	Luvicap-Bio. Best performance in brine.
Wu <i>et al.</i> [81]	12	VC-713, formation observed at 8 days.
Colle <i>et al.</i> [82]	24	Mixed polyIPMA, PVCap, and other polymers.

at 15 °C [83], while other proprietary formulations of KHIs have demonstrated even higher capacities for undercooling [82]. Current work to characterize how altering the rheology of the system inhibits hydrate formation is a chief goal of current research.

2.4.3 Surface Coatings

Along the same lines of anti-agglomerate solutions, reducing heterogeneous nucleation along pipeline structures and preventing the already nucleated hydrates from sticking to pipeline walls via hydrate-phobic coatings has been announced as another line of defense against plug formation. In 2012, Smith *et al.* developed a procedure for testing the adhesion strength of hydrates to surfaces, and they subsequently provided the first report on the viability of various functionalized surface coatings to prevent hydrate adhesion [84]. Due to complete miscibility in water and its ease in forming hydrate structures at ambient pressure below 4.4 °C, Tetrahydrofuran (THF), though slightly polar, is a common guest phase used to study hydrates in the lab setting. Thus, all data collected for the adhesion strength was measured between THF hydrates and the prepared surfaces. Different functionalized coatings are a way to demonstrate the effect that surface chemistry has on hydrate adhesion strength, and all tested coatings were easy to apply through spin coating.

In continuation of the previous group's work, Sojoudi *et al.* utilized a new method, iCVD, to deposit polymers for reduced hydrate adhesion [85]. iCVD stands for initiated chemical vapor deposition, and this method is advantageous in that it is capable of covalently grafting polymers in multiple layers to substrates for superior durability, whether it be the inside of an oil pipeline or any other engineered surface with texture [86]. A schematic of the resulting polymer structure is presented in Figure 9.

Van der Waals, electron acceptor (Lewis acid), and electron donor (Lewis base) interactions are most closely regarded in terms of adhesion mechanism, with the last two increasing in importance in the presence of polar molecules such as water. Efforts to minimize these surface energies had the greatest effect on reducing the observed work of adhesion. Adhesion strength test results from Smith *et al.*, listed in Table 3, show that the best performing surface coating was

Figure 9. p-PFDA hydrophobic polymeric coating deposited through iCVD (Adapted from Ref [86] with permission of John Wiley and Sons).

Table 3. THF Hydrate Adhesion Test Results

Substrate	THF hydrate adhesion strength (kPa)
Bare steel	422 ± 69
Clean glass	283 ± 82
4-Mercapto-1-butanol	185 ± 39
50/50 1-Butanethiol/4-Mercapto-1-butanol	179 ± 45
Methyl 3-mercaptopropionate	160 ± 32
50/50 Butanethiol/Methyl 3-mercaptopropionate	149 ± 20
Trichloro (1H,1H,2H,2H-perfluorooctyl) silane	133 ± 15
1-Butanethiol	121 ± 48
Octadecyltrichlorosilane	114 ± 23
1H,1H,2H,2H-Perfluorodecanethiol	111 ± 24
80/20 PEMA/Fluorodecyl POSS	90 ± 16

Adapted from Smith *et al.* [84].

80/20 PEMA/fluorodecyl POSS, with a reduction in adhesion strength by a factor of four [84], while Sojoudi *et al.* was able to attain a reduction in adhesion by a factor of ten for the bilayer coating of p-PFDA [85] from Figure 9.

2.5 Cyclopentane Based Hydrates

Cyclopentane belongs to a larger class of molecules called cycloalkanes (also naphthenes), which describe hydrocarbon rings containing only sp^3 hybridized bonds. As hydrate cages increase in size, it becomes increasingly important to maximize van der Waals contact between the guest molecule and the cage walls for hydrate stability. Consequently, the size and structure of cyclopentane lends itself to efficient space filling of sII cavities, as shown by Figure 10 [87]. Cyclopentane is at the upper size limit for molecules that promote the formation of sII hydrates, but it can also form sH with helper molecules such as methane to stabilize the structure by filling in small cavities [87–89]. It was not until 2001 that Fan *et al.* first confirmed cyclopentane was capable of forming gas hydrates in the absence of any help-gas [90].

Figure 10. Cyclopentane clathrate hydrate; H_2O molecules in red cage the guest hydrocarbon molecule inside.

The sII hydrates stabilized by cyclopentane represent a realistic model of the hydrates formed in oil transport lines. Table 4 indicates that naphthenes (cycloalkanes) make up, on average, the largest percentage of chemical constituents present in the crude oil that an oil line may contain [91]. And because of cyclopentane's relatively large size and nonpolar nature, it can readily stabilize the sII structure at ambient pressure and temperatures below $7.7\text{ }^\circ\text{C}$, rendering it as a realistic guest phase for the study of hydrates in the laboratory setting (THF is another common guest phase used due to its molecular similarity) [1].

Table 4. Crude Oil Composition by Weight [91].

Hydrocarbon	Average (%)	Range (%)
Naphthenes (cycloalkanes)	49	30–60
Alkanes (paraffins)	30	15–60
Aromatics	15	3–30
Asphaltics	6	remainder

2.6 Summary

Research in hydrate formation and inhibition has made great progress in the last two centuries. The existence of hydrates in oil and gas pipelines initiated efforts to understand hydrate formation mechanisms. The presence of vast quantities of hydrates in ocean floor sediment and permafrost continues to drive research in looking for ways to dissociate the trapped gas molecules as a source of energy. Progress has been made in understanding the macroscopic, time-independent, thermodynamic processes that govern the bulk equilibrium state with the addition of THIs. The potential for hydrate inhibition through the addition of LDHIs has been demonstrated in the lab and in the field; however, due to the impractical nature of observing atomic scale phenomena, questions remain as to the mechanism of action.

After a review of substantial volumes of work linked to hydrate formation and inhibition, one fact is reiterated: the mechanism of action with which surfactants work to inhibit hydrate crystallization requires additional investigation [92]. The complete mechanism of destabilization of hydrates by surfactants is not fully understood. Knowledge of that mechanism may lead to the design of more effective, eco-friendly surfactants, which will have broad applications in offshore natural gas production and seabed oil capture.

CHAPTER THREE

HYPOTHESIS/OBJECTIVE

Due to the absence of a complete model that can explain the effect that surfactants have on hydrate crystallization mechanisms, contributions from researchers have been inconclusive and occasionally contradictory. While it has been demonstrated that surfactants can prolong hydrate induction time at certain subcoolings, others have found exceptions in low surfactant concentrations, where the surfactants actually collapse the droplets and accelerate the process of hydrate formation [93]. It has been proposed that planar hydrate growth is interrupted by the presence of surfactant molecules, and the hollow-conical crystal formation is due to surfactant crowding and increased surface pressure, thus creating a mechanical barrier for growth [38]. The objective of this project is to discover the mechanism through which various nonionic surfactants, of both varying hydrophilic-lipophilic balance (HLB) number and molecular weight, influence the crystallization mechanism of cyclopentane hydrates at the oil–water interface. The application of interfacial and dilatational rheology measurements will be used in combination with visualization techniques in order to track hydrate growth.

Saturation of the water–cyclopentane interfacial area with surfactant requires a unique concentration depending on the type of surfactant molecule present, and thus each surfactant will have its own critical micelle concentration (CMC) in water. Primarily, it is expected that a correlation will be observed between surfactant concentrations, morphology, growth rates, and interfacial tensions. The results of which can validate or reject the hypothesis that if surfactants alter the hydrate crystallization mechanism through crowding at the oil–water interface, then decreased surface tension would be observed with hydrate growth. The proposed mechanism assumes adsorbed surfactant molecules at the guest–water interface of a

droplet will interfere with an advancing hydrate front competing for free sites. At some point in a shrinking guest–water interface, it must become energetically favorable to overcome the energy of desorption for a crowded surfactant before further hydrate growth proceeds. Hydrate growth rate is expected to decrease with surfactants of heavier molecular weights and of HLB numbers close to 10, indicating a strong attraction to the interface. If surfactant concentration at the interface increases as a result of crowding under hydrate growth, then the measured interfacial tension should decrease according to the Gibbs adsorption isotherm.

CHAPTER FOUR

MATERIALS

An attractive guest phase for hydrate study is one stable at ambient pressure and moderate temperatures. This guest phase would offer benefits in visualization, ease of access, cost, and safety. Since tetrahydrofuran and cyclopentane are commonly used hydrate formers which meet the aforementioned criteria [94], cyclopentane was the guest phase of choice for this study. Analysis was conducted with the assorted nonionic surfactants of Table 5, which include various hydrophilic-lipophilic balance (HLB) values, defined in Equation 10, to provide clues concerning its influence on hydrate crystallization and destabilization.

Table 5. Surfactants and Their Properties.

	HLB	Molecular Weight (g/mol)	Formula
Span 20	8.6	346.5	$C_{18}H_{34}O_6$
Span 80	4.6	428.6	$C_{24}H_{44}O_6$
Pluronic L31	3.2	1105	$C_{56}H_{112}O_{20}$
Tween 65	10.5	1845	$C_{100}H_{194}O_{28}$

$$HLB = 20 \cdot \frac{Mass_{hydrophilic}}{Mass_{hydrophilic} + Mass_{hydrophobic}} \quad \text{Equation 10}$$

A purpose-built experimental setup, referred to as the hydrate-visualization cell, was utilized to characterize hydrate formation. This multi-component system is capable of processing dilatational and visual measurements at the interface of a droplet as hydrate formation occurs. Components of the hydrate-visualization cell can be broken up into two categories: 1) the electronics and 2) the plumbing hardware. The major components consist of a power supply, camera, temperature sensor, pressure transducer, tubing, syringe, pump, brass chamber, microcontroller, heatsink, and a Peltier element for temperature control.

4.1 Electronics

Traditional means of temperature control involve electric heaters, which exploit Joule heating if the target temperature is higher than ambient, or refrigeration if the target temperature is lower than ambient. Although heaters can be relatively compact, cooling systems often take up considerable space depending on its complexity to accommodate large heat exchangers, insulated enclosures, compressors, and pumps. An alternative option for temperature control is provided through solid-state thermoelectric controllers (Peltier devices). A Peltier device was chosen due to the advantages offered in settings that require limited space, spot cooling, silence, no moving parts, high reliability, dual heating and cooling directional capabilities, varying cooling loads, or proportional control [95]. This benefits laboratory equipment, portable coolers, and the cooling of electronics. Design and implementation of a programmable temperature regulator via solid-state Peltier components is discussed in this section. The convenience and performance of a thermoelectric device is sufficient to offset the low efficiency (10-15% of Carnot) when compared to Stirling and vapor compression coolers [96].

The hardware assembly shown in Figure 11 represents the basic components of the temperature control loop. The microcontroller is the brain that reads the input from the temperature sensor and responds by sending an output voltage to the transistor gate, which then acts as a relay to allow current from the DC power source through the Peltier element. The heatsink diffuses the excess thermal energy coming from the hot side of the Peltier to the ambient environment as the next reading of the temperature sensor occurs, which starts the process over again. Incorporating digitally programmable microcontrollers was key to implementing this low-cost temperature control system. The Arduino Leonardo open-source

Figure 11. Breadboard schematic of possible component configuration.

microcontroller was chosen as the core component to interface with the peripheral hardware. Arduino's capability to pulse width modulate (PWM) a signal offers capability for tuning the behavior of the system near the set point—although the system was primarily run at either 100% or 0% duty. An output pin (pin 13 was used) is capable of supplying 5 V and around 40 mA of current.

A Peltier element is a heat pump capable of functioning as both a heater and a cooler, depending on the direction of current flow. Direct current (DC) provides the work to diffuse charge carriers across the semiconductor so that one end has more energetic charge carriers. A temperature gradient results across the junction, thus transporting heat in the direction of carrier flow. The powerful TEC1-12710 Peltier plate was used because of its demonstrated high consistency, high current handling (10 A), and rapid heat pumping. The higher current-carrying components have increased thermal flux capabilities, potentially rendering the hot side hotter and the cold side colder. However, efficiency diminishes at high current due to Joule heating, which scales proportionately to the square of current.

The hot side of a Peltier must be mated to a heatsink in order to prevent thermal damage to the device's internal junctions. A Thermaltake NiC C4 120 mm CPU cooler was used to dissipate the thermal energy from the Peltier. Thermal paste was applied between the Peltier and heatsink as it is crucial to obtain maximum heat conduction. The more efficient the heatsink can dissipate heat, the more easily a Peltier cooler can function since there is a limit to the temperature difference achievable across the device.

The waterproof digital temperature sensor used, 1-Wire DS18B20, provided several levels of resolution between 9 to 12-bit. The mode during operation was set to 10-bit, giving resolution equivalent to 0.25 °C. The benefit of using a digital package over an analog sensor comes from the ease of setup and pre-calibration. Integrating the DS18B20 can be seen schematically in Figure 12. Connections for the temperature sensor include a 5 V supply voltage from the Arduino, a 4.7 k Ω pull-up resistor to the data wire, and a neutral.

Figure 12. Wiring schematic with all components of cooling control loop and the pin-outs labeled.

A variable Tooluxe DC power supply was used for its capacity to provide up to 10 A at 30 V, which exceeded the requirements of the system. Under laboratory conditions the Peltier was never operated beyond 7 A at 15 V.

Metal oxide semiconductor field effect transistors (MOSFETs) are ideal for switching high current loads such as a Peltier plate from a microcontroller. Since microcontrollers are highly limited in current output, it is impractical to use bipolar junction transistors for switching large currents because the necessary continuous base current required is unsustainable. In contrast, MOSFETs require minimal current to facilitate turn-on. The circuit design in Figure 12 is capable of controlling over 100 W from 0–100% duty cycle. A low-side design utilizes an N-channel component below the load, while a high-side design would require a P-channel

component above the load. The low-side design was chosen for its efficiency; expense and difficulty in producing low resistance P-channel components renders a high-side switch inferior. For systems with high current at constant duty cycles, it becomes imperative to choose MOSFETs with a low $R_{DS(on)}$ value to minimize thermal buildup. The nMOS, IRFZ44N, was selected precisely for its low on-resistance of $0.017\ \Omega$ and Arduino-compatible threshold voltage level between 2–4 V. Additionally, a 1 in² aluminum heatsink was secured to the nMOS as assurance against excessive heat accumulation over extended durations of use. However, this precaution proved to be unnecessary.

The resistors R_1 and R_2 in Figure 12 were $220\ \Omega$ and $10\ \text{k}\Omega$, respectively. These values were selected to limit current spikes from damaging the output of the microcontroller and to facilitate proper turn-off of the switch. Due to the inherent capacitance of an nMOS gate, the 5 V output of an Arduino has the potential to spike current at initial turn-on higher than the recommended 20 mA or maximum 40 mA. The output of the Arduino is therefore current-limited by the gate resistor R_1 to provide a safe maximum current of 23 mA. ($I = 5\ \text{V}/220\ \Omega$). As a safety precaution to prevent floating, the pull-down resistor R_2 allowed the gate charge to dissipate, thus facilitating turn-off and ensuring that the MOSFET was off during startup. Large pull-down resistors should be avoided in conjunction with MOSFETs of large gate capacitance values since it will increase the decay time and prolong component shut-off, exposing it to unnecessary and potentially hazardous thermal buildup from resistive heating.

4.2 Plumbing and Fixturing

Plumbing was achieved with a combination of flexible Polytetrafluoroethylene (PTFE) tubing and rigid brass tubing of diameter 1/16 in. Scientific Commodities, Inc. 19 gauge PTFE tubing was used from the syringe to the T-fitting, and brass

tubing from K & S Precision Metals connected the transducer and brass hook to the T-fitting as seen in Figure 13. The brass hook was approximately 5 cm in length with a 180° bend at the end. The end of the brass hook was polished with 1500 grit paper to smooth imperfections from the cut surface. This bend ensured that the droplet sat on top of the tube, as opposed to being suspended. This was a necessary configuration to reduce the likelihood of droplet detachment mid-experiment. It also prevented the buoyant hydrates from traveling up into the line, which could cause plug formation and interfere with the pressure transducer supply line. A 1/16 in Swagelok 316 stainless steel T-fitting was used in conjunction with PTFE crush ferrules and PTFE thread tape to seal fittings.

To supply metered water and surfactant solutions, a Chemyx Fusion 100 Infusion Pump was used with a 1 mL Hamilton syringe and a 19 gauge needle (model: 1001 LTSN SYR). The 19 gauge needle was sized to allow a press-fit with the PTFE tubing. Pressure changes in the line were monitored with an OMEGA

Figure 13. Plumbing route with PTFE tubing connecting syringe pump and T-fitting (left). T-fitting with transducer and brass hook connections shown (right).

PX409-10WGUSBH pressure transducer. This transducer is particularly sensitive, with a maximum pressure of 2500 Pa, or the pressure equal to submersion in water at 10 in. The transducer has an accuracy of 0.08% BSL, which denotes the furthest deviation for the measured data from the best straight line fit.

The custom-built brass cell shown in Figure 14 was used to contain the bath of cyclopentane and facilitate the observation of hydrate formation. An acrylic cover (with cutouts for the temperature probe and brass hook) is fixed to the top of the cell in order to limit evaporation of the volatile cyclopentane, therefore stabilizing the submersion depth and preserving the external pressure acting on the outside of the droplet. The viewing windows are double-paned with additional silica desiccant inserted in between the glass slides to combat frosting and fogging which otherwise occurred at the temperature differentials seen in experimentation. Application of Rain-X[®] to the outer window further alleviates fogging.

Figure 14. Brass visualization-cell with cover (left). Visualization-cell window showing silica desiccant (right).

A Basler acA640-750um camera was used to capture monochrome images with VGA resolution (640×480). A Kipon EOS to C-mount adapter coupled with 35 mm of Fotodiox macro extension tubes were used to connect the camera body to a Canon 28–90 mm adjustable lens. This allowed for closeup macro images to be observed at the cost of decreased depth of field. Illumination was provided by an AmScope 150 W fiber optic goose-neck lamp.

All materials related to fixturing were sourced from Thorlabs, Inc. The system was affixed to an 18 in $\times$ 24 in solid aluminum optical breadboard. To dampen vibration and noise, four 1 in thick Sorbothane bumpers served as a buffer between the tabletop and the optical table. The transducer and camera were supported by 1/2 in diameter stainless steel posts and fastened with clamps. The complete schematic is shown in Figure 15.

4.3 Software

The Arduino IDE software v1.6.7 was used to monitor and send commands to the microcontroller for temperature regulation. To interface the pressure transducer the OMEGA PC software, Digital Transducer Application v2.2.1.280, was used. Pylon Viewer v5.0.0.6150 by Basler enabled control of the camera exposure and frequency for image capture. Image scales were determined and labeled in ImageJ v1.50. Hydrate area tracking was performed in the photo editor Paint.net v4.0.3. Images were processed in Mathematica v9.0 to determine hydrate surface area.

Figure 15. Mounting hardware and equipment layout. A) power supply, B) pump, C) syringe, D) heatsink, E) brass visualization cell, F) camera lens, G) transducer, H) Arduino, I) illumination.

CHAPTER FIVE

METHODS

5.1 Surfactant CMC Determination

Measurement of interfacial tension between two immiscible fluids is significantly dependent on the method of measurement [97]. Geometric factors influence the effects of partitioning to alter the distribution of surfactants. For example, a planar oil–water interface has a low interfacial surface area to volume ratio when compared to an emulsion of droplets, which would have a much greater surface area per volume ratio and require additional surfactant to achieve comparable surfactant saturation at the interface. This account of geometry is necessary to effectively compare interfacial tension measurements across different techniques such as the Wilhelmy plate method and droplet methods. Interfacial tension measurements of surfactant solutions were performed by droplet analysis to mimic the geometry seen in oil pipeline emulsions.

The critical micelle concentrations (CMCs) for the selected surfactants were determined as a precursor to find appropriate concentrations for use in the hydrate-visualization cell. The CMCs served as a reference point for the high, medium, and low surfactant concentrations. CMCs were discovered by identifying an inflection point in measured surface tension as a function of concentration. Essentially, it was taken as the concentration at which additional surfactant resulted in diminishing returns. Standard solutions for Tween 65, Pluronic L31, and Span 20 were created by dissolving a measured mass of surfactant into deionized (DI) water; the concentrations ranged from 10^{-4} g/100mL to 10^0 g/100mL. Span 80 was dissolved in cyclopentane due to its high level of hydrophobicity and resulting low solubility in water.

In practice, the syringe pump and syringe were placed vertically as displayed in Figure 16 in order to count falling droplets. The pump was programmed to expel 1 mL of solution at a rate of 0.5 mL/min. Drop volume V was taken as an average by dividing the 1 mL syringe by the number of observed drops. Each standard solution was tested a minimum of three times. All solutions were tested in air due to the undesirable surfactant concentration buildup if performed in cyclopentane.

Interfacial tensions γ of the standard solutions were evaluated using concepts derived from stalagmometry. By balancing the downward gravitational force of a vertically suspended droplet with the upward surface tension holding a droplet to a tube of known diameter, the governing equation can be derived and is given in Equation 11, where g is the acceleration due to gravity, $\Delta\rho$ is the density change at

Figure 16. Drop counting experimental setup for surface tension measurements.

the interface, V is the droplet volume, r is the tube radius, and F is an empirical correction developed by Mori [98] for leftover droplet volume after separation. The correction factor, F , given by the analytical function in Equation 12, is valid when $\frac{r}{V^{1/3}}$ is between 0–0.3, or by tabulated values from Lando *et al.* [99] when $\frac{r}{V^{1/3}}$ is between 0.3–1.2.

$$\gamma = \frac{g\Delta\rho V}{r} F \quad \text{Equation 11}$$

$$F = \frac{1}{2\pi} \left[0.99979 - 1.32045 \left(\frac{r}{V^{1/3}} \right) + \left(\frac{r}{V^{1/3}} \right)^2 \right]^{-1} \quad \text{Equation 12}$$

The drop volume method yielded the surface tension measurements for Tween 65, Pluronic L31, and Span 20, which are displayed in Figure 17. The CMC was only definitively found for Tween 65 at the concentration of 0.026 g/100mL.

Figure 17. Interfacial tensions of stock solutions for CMC determination.

The medium concentrations for Pluronic L31 and Span 20 were estimated to be near 0.1 g/100mL. Interfacial tensions and the CMC for Span 80 were taken from Karanjkar *et al.* [38] as 0.03 g/100mL as determined by the pendant drop method. Table 6 lists the remaining surfactant concentrations of interest that were generated for use in the hydrate-visualization cell.

Table 6. Surfactant Solutions Used with the Hydrate-Visualization Cell.

Surfactant	Solvent	Concentrations (g/100mL)		
		Low	Medium ($\approx$ CMC)	High
Span 20	DI water	0.01	0.1	1.0
Span 80	Cyclopentane	0.003	0.03	0.3
Pluronic L31	DI water	0.01	0.1	1.0
Tween 65	DI water	0.0026	0.026	0.15

5.2 Hydrate-Visualization Cell

The crux of the experimentation is the novel development and utilization of the hydrate-visualization cell. Table 7 indicates the various input values, output measurements, and expected inferences provided by this stage of experimentation with the hydrate-visualization cell. This system, shown schematically in Figure 18, is comprised of several key elements that need to work together to facilitate observation of the time dependent crystallization process. The Peltier must maintain constant cell temperatures in regions of hydrate stability, the camera must have access to a focused view of the droplet, and the pressure transducer must be able to monitor the internal pressure of the droplet. By syncing these systems, the growth rate, surfactant concentration, and interfacial tension could be linked. Operation of the visualization cell is outlined in the following sections and began with the generation of a seed hydrate.

Table 7. Experimental Plan for the Hydrate-Visualization Cell.

Hydrate-Visualization Cell Parameters		
Inputs	Outputs	Goals
-Temperature (2 °C)	-Droplet Pressure (Pa)	-Determine changes in interfacial tension from droplet pressure.
-Concentration (χ g/100mL)	-Growth Rate (mm ² /min)	-Determine if hydrate growth rate is increased or decreased as well as delay in nucleation.
-Drop Volume (2 μ L)		-Categorize morphology.

Figure 18. Camera-eyed view of hydrate-visualization cell schematic of necessary components. The brass cell sits atop the Peltier plate, and the water droplet is delivered by tubing connecting the syringe and pressure transducer.

5.2.1 Seed Hydrate Generation

The existence of a seed hydrate was required for consistent nucleation and tracking of growth rate. Because the presence of melting ice is a necessity for timely initial hydrate conversion, a small volume (50–100 μ L) of pure water was deposited on the floor of the hydrate cell as indicated by the seed hydrate in Figure 18. The brass cell was filled with approximately 30 mL of cyclopentane. The temperature

was lowered to $-5\text{ }^{\circ}\text{C}$ until the small volume of water solidified into ice; nucleation was often expedited by disturbing the supercooled water with a clean, suitable probe.

After ice formation, the temperature was raised to $2\text{ }^{\circ}\text{C}$ and held there for the remainder of the experiment. This temperature ensured the solid ice was converted to hydrate since the system was above the melting point of ice, yet below that of cyclopentane hydrates. At this point the plumbing was primed, and the brass hook was lowered into the cyclopentane to equilibrate for 5 min to reduce expansion and contraction oscillations seen in the droplet volume from the temperature change. While the seed hydrate formed, the next phase prepared for data acquisition.

5.2.2 Data Acquisition

Before droplet production via the syringe pump, the transducer and camera data feed were set to record simultaneously in order to sync the pressure measurements with the visual events across the duration of an experiment. Confirmation of the synchrony in later analysis was observed by noting if the spike in pressure from droplet formation coincided with the visual data at initial droplet expansion. Images of a droplet hemisphere were recorded from the camera at 1 Hz. This frequency provided ample temporal resolution since the relevant timescale concerning observed hydrate growth was on the order of minutes. While high sampling frequency of the camera renders unnecessarily large video files, the transducer does not suffer from this concern as it only records point values; it was sampled at 5 Hz. A three-point moving average was employed to smooth noise from the transducer.

Droplet production followed the 5 min equilibration. The pump was set to expel 2 μL , and the activated syringe plunged the solution of water and surfactant into the cyclopentane bath to form the submerged droplet. Nucleation was facilitated by transferring a minute amount of previously formed seed hydrate onto a suitably

small needle or paper clip tip and manually bringing it into brief contact with the droplet as demonstrated in Figure 19. The seed hydrate is sticky and was easily picked up by an aluminum paper clip when prodded. After the seed hydrate was brought into contact with the droplet, hydrate growth proceeded at the interface.

Figure 19. Heterogeneous nucleation by seed hydrate (left) through contact (right).

5.3 Data Analysis Methods

5.3.1 Image Processing: Surface Area

Tracking the conical and planar hydrate growth was performed with visual analysis methods. ImageJ was used to set the scale for the images based on the known diameter of the 1/16 in (1.588 mm) brass tube at the base of every frame. Seven equally spaced snapshots were selected from each experiment for analysis between the point of nucleation and droplet conversion. As can be seen in Figure 20, the hydrate coverage in each image was painted black, while the droplet edge was outlined in red.

Because the camera only captured the 2D projection of the spherical droplet, a 3D reconstruction was created in Mathematica as a correction to surface area. To achieve this, a Mathematica script was developed which rastered the images from top to bottom, set the outermost black or red pixel as the radius, applied radial

mapping, and applied the correct pixel-to-mm ratio. The surface area was taken as the summation of the arc lengths over all rows. Because only the front hemisphere can be seen, the area was doubled prior to linear fitting to find growth rates.

Figure 20. Example hydrate region for surface area analysis of Span 20_{low}. Observed hydrate regions (left) are painted black (right) to map a 3D surface (bottom).

5.3.2 Droplet Interfacial Tension

Since a dilating or shrinking droplet undergoes a change in surface area, surface tension is dynamic in the moments following initial droplet formation. When a fresh surface is generated at the interface of an expanding droplet, initial surfactant surface coverage is minimal [100]. The relatively large surfactant molecular mass causes a delay in surface adsorption as it takes time to diffuse across the newly created concentration gradient. The interfacial tension could therefore be approximated to be equal to the value of water–cyclopentane ($\gamma = 28 \text{ mN/m}$) in the moment immediately following initial droplet expansion [101]. Based on the relaxation time observed for a pure water droplet in cyclopentane, the initial surface tension for a surfactant solution was set 3 s after droplet formation.

Thereafter, the Young-Laplace relation given by Equation 13 was used to determine changes in interfacial tension, γ , between cyclopentane and the surfactant solution droplet, where R_1 and R_2 are the droplet radii of curvature and ΔP is the change in droplet internal pressure.

$$\Delta P = \frac{\gamma}{\frac{1}{R_1} + \frac{1}{R_2}} \approx \frac{2\gamma}{R} \quad \text{Equation 13}$$

In the initial period following droplet formation, the two radii were approximately equal, and Equation 13 could be approximated further, with the radius of the predetermined 2 μL droplet equal to $R = 782 \mu\text{m}$. After solving for γ , the interfacial tension was linearly approximated from changes in pressure. It should be noted that this method of interfacial tension approximation was only valid while the droplet maintained a spherical shape with some area of liquid interface remaining.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 General Trends

The following three distinct types of hydrate growth were observed: planar, conical, and dendritic. Span 80_{low} saw a mixture of conical and dentritic formations together due to the similar shape—where a dendrite is similar to a flattened cone. The performance of each surfactant is recorded in Table 8. Changes in interfacial tension ranged from the start of hydrate formation to complete shell coverage for droplets with mostly planar growth. The solutions without a value for change in interfacial tension are those that quickly saw non-spherical droplet shape, and thus the Young-Laplace equation failed to meaningfully relate interfacial tensions in these cases. It is interesting to note that the low concentrations had a larger change of interfacial tension when compared to the medium concentrations. An initial

Table 8. Experimental Results Overview. (P=planar, C=conical, D=dendritic).

	Concentration (g/100mL)	Growth Rate (mm ² /min)	Morphology	Tension $\Delta\gamma$ (mN/m)
Span 20 _{low}	0.01	0.370	P	20
Span 20 _{med}	0.1	0.422	P	8
Span 20 _{high}	1.0	0.178	C	-
Span 80 _{low}	0.003	0.282	C, D	28
Span 80 _{med}	0.03	0.242	P	21
Span 80 _{high}	0.30	0.180	C	3
Pluronic L31 _{low}	0.01	0.416	P	26
Pluronic L31 _{med}	0.1	0.384	P	8
Pluronic L31 _{high}	1.0	0.212	P	-
Tween 65 _{low}	0.0026	0.676	P	15
Tween 65 _{med}	0.026	0.498	P	5
Tween 65 _{high}	0.15	0.068	C	-
Water	-	0.590	P	-

explanation may be that there was a more rapid lowering of surface tension for the more concentrated medium solutions in the moments following droplet production. This could have occurred prior to the 3 second mark at which surface tensions were set to the value of water and cyclopentane, thus artificially lowering the starting interfacial tension values of medium concentrations and imparting a systematic error.

5.2 Planar Shell Growth

A common occurrence witnessed with planar hydrate formation was the gradual decrease in interfacial tension. As an example, Figure 21 shows the change in pressure and inferred surface tension during one such planar hydrate growth. There is a clear reduction in internal droplet pressure, and one could argue that this is evidence of increasing surfactant concentration at the interface as predicted by the Gibbs adsorption isotherm, which relates increasing surfactant concentrations to

Figure 21. Span 80_{med} transducer plot indicating a constantly decreasing interfacial tension as planar hydrate growth occurred.

decreasing surface tensions. The interfacial tension is plotted as a function of shrinking liquid area during hydrate growth with Span 80_{med} in Figure 22 to further illustrate this point. The near linear progression of the decreasing surface tension over time is matched by an equally linear decrease in remaining liquid area, and a strong correlation coefficient (least squares fit) of -0.989 was found. The shrinking liquid area was assumed to be equal to the area displaced by growth of the hydrate.

Figure 22. Interfacial tension decreases with shrinking liquid interface as a result of planar hydrate growth with Span 80_{med}. Points correspond to snapshots in Figure 23, starting at 2.1 min.

Comparison of the planar growth of Span 80_{med} in Figure 23 with that of pure water in Figure 24 shows a greater sphericity is maintained for pure water, presumably due to the higher interfacial tension maintained throughout hydrate propagation. The presumed Span 80 concentration buildup and interfacial tension decrease contributed to the deformity and eventual droplet collapse seen from the 8.5 min mark onward. Because a collapsed or deformed droplet greatly increases the surface area to volume ratio, crystallization proceeded rapidly along the newly

Figure 23. Planar hydrate growth for Span 80_{med} at 2 °C in cyclopentane.

Figure 24. Planar hydrate growth for pure water at 2 °C in cyclopentane.

available interface until complete hydrate conversion is achieved. Higher surfactant concentrations are linked to lower tensions, and a droplet is more easily distorted by the advancing hydrate front in these cases.

Describing the observed behavior that relates interfacial tension with planar hydrate growth follows. The undercooling acts as a driving force to propagate the hydrate front at the interface. The outcome is that whether or not there is surfactant at the interface, the hydrate shell increases in size. When planar hydrate

growth advances along a droplet surface, the remaining liquid surface area is decreased. If adsorbed surfactant molecules are to remain within this liquid area, then concentration must increase. Any increase in concentration would effectively lower the interfacial tension unless surfactant molecules desorb from the interface to maintain some maximum concentration. Since a decrease in interfacial tension alone would not prevent an advancing hydrate, it is believed that physical crowding at the liquid interface is the primary cause for inhibiting hydrate growth by competing for the remaining water–hydrocarbon interface. Observing how the interfacial tension decreases with planar hydrate growth, and ultimately results in slower growth as seen in Table 8, the model is assumed to be correct. In summary, a decreasing internal droplet pressure indicated decreasing surface tension from increasing surfactant concentration as hydrate growth displaced and crowded surfactant.

5.3 Conical Morphologies

Conical crystal formations were observed when the surfactant concentration was increased past the CMC. This was true for all surfactants except Pluronic L31. From Table 8 there appears to be a cutoff growth rate which separates planar shell growth from conical growth. Not accounting for differences in surfactant properties, and based solely on the observed morphologies and corresponding growth rates, this cutoff occurred somewhere in the range of 0.212–0.178 mm²/min.

Span 80_{low} saw a few brief conical crystals form; however, the surfactant’s hydrophobicity required dispersal in the much larger bulk volume of the surrounding cyclopentane. The reversal from surfactant-in-drop to surfactant-in-bulk cyclopentane for Span 80 meant there was the potential for more rapid surfactant buildup at the interface. All other surfactants were able to be dispersed in water, which constitutes a small droplet volume (2 µL) and small quantity of surfactant in relation to the cyclopentane bath. It is believed that this

caused conical crystal presence at the Span 80_{low} concentration, while the other low-concentration surfactants saw planar hydrate shell growth.

When a conical crystal becomes large enough, and a portion of the circumference of the cone breaks free from the droplet surface, the remaining solution from inside the droplet redistributes to fill and engulf the cone. Higher surfactant concentrations yielded larger cone growths before separation, sometimes outgrowing the size of the droplet. Figure 25 exhibits such a case for Tween 65_{high}. The slow conical growth proceeds at the circumference of the opening until the physical size of the crystal is too large for the droplet. After the droplet collapsed, rapid hydrate crystallization was observed until complete droplet conversion.

Figure 25. Sequence of conical hydrate growth for Tween 65_{high} at 2 °C in cyclopentane.

5.4 Evaluation of Growth Rates

The most powerful evidence to support surfactant inhibition on hydrate growth came from tracking the time-lapse visual data. The collective growth rates of all tested solutions and water are presented in Figure 26, revealing several interesting

trends. All but one of the surfactant solutions performed better than pure water at retarding hydrate growth. Tween 65_{low} performed worse than pure water for unknown reasons. Conversely, the most effective surfactant studied was Tween 65_{high} with a growth rate ($0.068 \text{ mm}^2/\text{min}$) nearly three times slower than the next best surfactant (Span 20_{high} at $0.178 \text{ mm}^2/\text{min}$). Within each surfactant, Tween 65 showed the largest range in performance, and it was not until the concentration was increased beyond the CMC that growth rate plummeted.

By scanning the surfactant growth rates shown in Figure 26 from low, medium, to high concentrations, it becomes clear there is a downward trend for growth rates with increasing concentration regardless of the specific brand of surfactant. The

Figure 26. Hydrate growth rate across all solutions at 2 °C in cyclopentane.

high-concentration group exhibited the least amount of variance ($0.004 \text{ mm}^2/\text{min}$) across the surfactant types.

Hydrate crystallization proceeded linearly for all droplets in the initial stages after nucleation. The spread of hydrate around a pure water drop is plotted in Figure 27. Here it can be seen that it only took 10 minutes to complete the hydrate shell previously displayed in Figure 24. Hydrate growth proceeded at $0.590 \text{ mm}^2/\text{min}$ when uninhibited for a $2 \text{ }\mu\text{L}$ droplet at $2 \text{ }^\circ\text{C}$. This is a baseline upon which the surfactant performance can be judged.

The low-concentration surfactants performed similar to pure water. Aside from Span 80_{low} as previously discussed, the weak concentrations were not sufficient to alter the growth morphology. The growth behavior of the differing low-concentration surfactants are compared in Figure 28. Tween 65_{low} was the only

Figure 27. Hydrate growth evolution at $2 \text{ }^\circ\text{C}$ for pure water in cyclopentane.

Figure 28. Hydrate growth evolution at 2 °C for low-concentration surfactants in cyclopentane.

solution to display an accelerated growth rate when compared to pure water. Image analysis of Tween 65_{low} indicated that shortly after nucleation there were multiple growth sites which spread from both the top and at the bottom at the droplet-brass tube interface, and growth was therefore propagating on multiple fronts.

The medium concentrations were chosen to be close to the CMC for each respective surfactant. All morphologies at this concentration resulted in a shell of planar growth. Because of the similar growth mechanism between these and the low concentrations, the growth curves follow fairly the same pattern as the low concentration and pure water plots. There was a decreased measured in the growth rates for the medium concentrations compared to the low concentrations. The plot in Figure 29 once again reveals initial linearity ending with a gradual decrease in growth rate as the liquid interface disappears due to hydrate coverage.

Figure 29. Hydrate growth evolution at 2 °C for medium-concentration surfactants in cyclopentane.

From the high concentration plot in Figure 30, it can be seen that all growth rates began slow, and rates ramped up towards the end of droplet conversion. The conical crystals observed with the high-concentration solutions would frequently become so large that the droplet would flatten and rupture, causing many fresh nucleation sites and exponential hydrate conversion. There appears to a clear benefit in using surfactant concentrations past the CMC to inhibit hydrate growth, although there is a downside when high concentrations result in low interfacial tension, and reduced droplet stability causes droplet annihilation. Because unnecessarily high surfactant concentrations would impact the cost for usage on a large scale, it would be most economical to use a minimum concentration greater than the CMC.

Figure 30. Hydrate growth evolution at 2 °C for high-concentration surfactants in cyclopentane.

There are several instances where error may cause misleading results. Based on the drop tension method used to find interfacial tensions of the stock solutions, the CMC concentrations were indeterminate for both Pluronic L31 and Span 20, and estimations were made regarding the medium concentration of interest. If a true CMC were found in these cases, then the growth rate curves may have shifted enough so that its effectiveness among the other surfactants would rank differently. The density of hydrate is roughly 90% that of water; therefore, the more hydrate that has formed on a drop, the more buoyancy the droplet attains. In effect, this buoyant force works to pull the droplet upward away from the plumbing that connects the base of the droplet to the transducer. The possible effects of buoyancy were not taken into consideration when relating the pressure measurements to the surface tensions due to the added difficulty and complexity it would introduce to

model properly. Using small droplet volumes is a viable means to combat the influence hydrate buoyancy may have on the pressure measurements because the internal pressure due to surface tension is much greater than gravitational effects as the droplet radius decreases. Because only the front hemisphere of a droplet was in view of the camera (it was assumed that the back-side growth mirrored the front), subsequent doubling of the observable front hemisphere area for growth rate determination introduced unavoidable error. However, not doubling the growth area would have meant that after complete droplet conversion, the calculated growth rate would represent only half of the true value.

5.5 Other Observations

Figure 31 illustrates three hypothetical directions that a hydrate growth can take, and subsequently, its effect on the droplet morphology. Case 1 shows planar growth remaining relatively close to parallel with the interface, resulting in minimal deviation in droplet size or sphericity. Case 2 is an inward hydrate intrusion such as a dendrite or cone which displaces the spherical volume to larger values. Case 3 is an outward protrusion which lowers the radius of curvature and spherical surface area. For the crystal to form inwards in case 2, it is evident that the impinging

Figure 31. Three cases for hydrate growth morphology: Case 1 is planar. Case 2 is inward. Case 3 is outward. Hydrate shown in magenta.

volume expands the droplet, which increases or maintains the surface area available for the surfactant to preserve the surface concentration. If a crystal were to bulge outwards in case 3 (as one might expect due to the greater internal pressure of the droplet pushing outward), the effective radius and surface area of the sphere would decrease to further concentrate any surfactant present at the interface.

In practice, only cases 1 and 2 were produced while case 3 was never observed. Perhaps this peculiar observation shows the importance of surface area preservation in predicting surfactant behavior at an interface. If surfactant crowds the interface as a mechanism of inhibition, then its affinity for saturating the liquid interfacial area predicts case 2 as a more probable result than case 3. This is because case 3 robs the surfactant of previously held interfacial area during hydrate growth. Essentially, experimental results showed that it is always preferable to expand the droplet instead of removing and desorbing surfactant molecules from the interface. It is surprisingly favorable to form inward growths that overcome the pressure differential across the droplet surface, and work is done by the growing hydrate front to expand the droplet. This also implies that the direction of curvature has more importance than the pressure differential across the interface. This raises the question: Which direction do conical crystals form at a flat interface?

The majority of conical crystals formed angles in the range of 40–50°. No correlation was determined between the angle of the conical crystals to the surfactant concentration or growth rate. Outside the static settings of these experiments, real world applications involving emulsions traveling through a pipeline would have shear forces to break apart hydrate shells, effectively regenerating a surface for new growth to occur. In application, the higher concentration surfactant should stem bulk agglomeration most effectively by severely limiting initial growth.

CHAPTER SIX

CONCLUSION AND FUTURE WORK

Although flow assurance for gas and oil pipelines provided the initial motivation and guidance for this work, understanding hydrate formation under the influence of surfactant was the principal objective. The hydrate-visualization cell and its operating procedures were developed to be a system capable of characterizing the interfacial phenomena of droplet hydrate growth through interfacial rheology and video microscopy. Using an array of four surfactants and three concentrations for each, the behavior of hydrate formation was cataloged and compared.

From the time lapse analysis of 2 μL droplets at 2 $^{\circ}\text{C}$, several conclusions were drawn. The lowest hydrate growth rate observed was 0.068 mm^2/min with Tween 65_{high}, proving it to be the most effective inhibitor tested when used at concentrations above the CMC. The most influential properties associated with Tween 65 are believed to be its comparatively large molecular weight (1845 g/mol) and central HLB (10.5) close to 10, which work to preserve adsorption at the interface. The remainder of the surfactants all had lower weight and were of varying degrees more hydrophobic than Tween 65.

The pressure transducer was effective at monitoring the changing internal droplet pressure as long as the droplet retained a spherical shape. Interfacial tensions from the Young-Laplace equation showed a characteristic decrease with contracting liquid surface area, consistent with predictions from the Gibbs adsorption isotherm. The ability to link visual events to the changing surface tension in real time was necessary for determining the interaction between the competing surfactant and the hydrate at the interface.

With this system, or an improved system in place, further work can be carried out to test the effectiveness of any number of the thousands of available surfactants.

A well planned design of experiments (DOE) could further elucidate to what degree a particular surfactant parameter has on the prevention of hydrates. The HLB number, molecular weight, concentration, anionic/cationic/nonionic classification, and brined solutions could all be potential parameters of interest for a DOE. The specific concentration near which a morphological change occurs perhaps offers the most insight into the inhibiting behavior of surfactants.

Experimentation with different droplet sizes and various temperature ranges may help reveal more on the nature of surfactant behavior. It would be valuable to perform similar experimentation as performed on droplets using a capillary bridge instead, thus monitoring a low-pressure region as opposed to the high-pressure region in a droplet. This may provide further evidence to answer why internal conical crystals of case 2 were only seen and never outward crystals of case 3. It remains unclear whether the direction of surface curvature or the maintenance of water–hydrocarbon surface area plays the dominant role in dictating the direction of conical formations. These considerations can be implemented in future experimentation to acquire additional knowledge of hydrate formation, and help to improve the design of specialized hydrate-inhibiting surfactants.

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