AN INVESTIGATION ON THE VISCOSITY AND TRANSPORTABILITY OF METHANE HYDRATE SLURRIES USING A HIGH PRESSURE RHEOMETER AND FLOWLOOP

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemical Engineering).

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ABSTRACT

In this doctoral work, the viscosity and transportability of gas hydrate slurries were investigated using a high pressure rheometer and an industrial-scale high pressure flowloop. A model water-in-oil emulsion was developed specifically for this study and consists of mineral oil (350T and 70T), a surfactant mixture (sorbitane monooleate, Span 80 and Aerosol OT, AOT) and de-ionized water. The water volume fraction (water cut) that will form a stable water-in-oil emulsion depends on the type of mineral oil used. Mineral oil 70T can form a stable emulsion for water cuts in the range of 10 – 70 vol.% water, while mineral oil 350T can form a stable emulsion for water cuts in the range of 10 – 40 vol.% water. Characterization tests were conducted on these model emulsions, and the results show that the emulsions are relatively stable (no phase separation, sedimentation and coalescence) for a period of one week. In addition, the average water droplet size was determined to be in the range of 2 – 5 μm. Finally, high pressure autoclave tests were conducted using the model emulsions, and showed that the emulsions have similar properties (i.e. relation of motor current versus hydrate volume fraction) to that of water-in-crude oil emulsions.

In order to understand the effect of hydrate particles on the viscosity of the system, viscosity measurements of the emulsions (prior gas hydrate formation) were conducted at various temperatures, pressures and water cuts. A generalized equation that is a function of temperature, water volume fraction and saturation of the oil phase was developed. This generalized equation is able to predict the viscosity of the emulsion fairly accurately (within ± 13%) at low temperature (≤ 10 °C).

In-situ gas hydrate formation and hydrate slurries viscosity measurements were also performed in this work. Measurements were made using a high pressure rheometer connected to a high pressure ISCO pump. A four-blades vane impeller was used to mix the slurries. Experiments were conducted using the two model emulsions that were developed in this work. Viscosity measurements were conducted at a constant temperature of 1 °C, constant pressure of 1500 psig and constant mixing speed of 477 RPM. The water cut was set to be between 5 – 30 vol.% water. In addition, for mineral oil 70T emulsions, experiments were also performed near the emulsion inversion point. The results of this work shows that the relative viscosity of gas hydrate slurries can be modeled as a function of the hydrate volume fraction of the systems. In
addition, emulsion breaking after hydrate formation was observed for hydrate slurries tests near the emulsion inversion points.

Next, gas hydrate transportability was also investigated in an industrial-scale flowloop. Investigations were made at two different flow conditions (fully dispersed and partially dispersed systems). The different flow conditions were achieved by changing the water cut, as well as the flowloop pump speed (fluid mixture velocity). Results of the tests shows that the relative pressure drop, $\Delta P_{rel}$ decreases with increasing pump speed. In addition, there is a higher tendency for hydrate plugging to occur at low fluid mixture velocity. Similar to gas hydrate studies in the high pressure rheometer, emulsion breaking was also observed in the high pressure flowloop for tests near the emulsion inversion point. In addition, initial investigations comparing the results obtained in the high pressure rheometer with results obtained in the industrial-scale rheometer were also conducted. Results of the comparison shows that even though the systems studied were different (different oil and different flow system), there are relatively similar increases in the relative calculations (relative $\Delta P$ and relative viscosity) when hydrates have formed in the system.

Lastly in this doctoral work, the droplet size distribution in water-in-oil emulsions was determined using Diffusion-Transverse Relaxation ($T_2$) using low field Nuclear Magnetic Resonance (NMR). The proposed method provides several advantages over the traditional optical microscopy image analysis, such as giving a better representation of the droplet size in flowlines, since the measurement uses the entire sample to determine the droplet size. In addition, the method is relatively fast and has a low cost compared to high field NMR tests. In the low field NMR method, knowledge of the composition of the oil is not needed, which is not the case for the corresponding high field NMR method. Results from low field NMR tests were compared with the results obtained from optical microscopy image analysis. Both methods show that the average size of water droplets is relatively similar across all water volume fractions investigated, but a minimum in size was observed by both methods at 50 vol.% water, which is close to the emulsion inversion point.

The research conducted in this doctoral thesis has made several contributions towards both advancements in academic research, as well as industrial flow assurance research. In the area of academic research, the model emulsion that was developed in this doctoral work (discussed in Chapter 2) has been applied in a wide range of research including wax deposition studies by
several other researchers. In addition, the research conducted in this doctoral thesis has been acknowledged by the hydrate flow assurance community as a breakthrough in the hydrate slurry rheological characterization. The work performed here was the first work that decoupled the effect of emulsion/gas saturation/oil swelling on the viscosity of hydrate slurries. In summary, the new findings and model/method developments presented in this thesis collectively are critical to advancing the understanding of gas hydrate slurry properties and transportability. The latter is required in the development of new hydrate management strategies during oil/gas production.
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Adhesion force between two particles .................................................................................................. $F_A$
Aggregates diameter .......................................................................................................................... $d_A$
Calculated data .................................................................................................................................. $X_{model,i}$
Density difference between particles and suspending fluids ............................................................. $\Delta \rho$
Diffusion time ..................................................................................................................................... $\Lambda$
Einstein Coefficient ........................................................................................................................... $B$
Experimental data ............................................................................................................................. $X_{data,i}$
Fractal dimension ............................................................................................................................... $f$
Function on the effect of composition on viscosity ........................................................................... $A_2(\phi)$
Function on the effect of temperature on viscosity ............................................................................. $A_1(T)$
Gradient pulse duration ...................................................................................................................... $\delta$
Gravitational acceleration .................................................................................................................... $g$
Hydrate volume fraction ..................................................................................................................... $\varphi_{hyd}$
Interaction parameter between gas and oil ......................................................................................... $B_1, B_2$
Maximum packing of particle ............................................................................................................. $\phi_{max}$
Mole fraction ....................................................................................................................................... $x$
Mole of methane consumed for hydrate ............................................................................................. $n_{hyd}$
Mole of methane per volume of hydrate ............................................................................................. $\beta$
Moles of methane dissolves in oil phase ............................................................................................. $n(T, P)$
Number of data point ......................................................................................................................... $n$
Particle diameter .............................................................................................................................. $d_p$
Particle interaction parameter ............................................................................................................ $\sigma$
Particle radius ................................................................................................................................. $R$
Pre-exponential term of viscosity model ............................................................................................ $A_0$
Pressure ............................................................................................................................................. $P$
Pressure drop ........................................................................................................................................... $\Delta P$
Relative pressure drop ........................................................................................................................... $\Delta P_{\text{rel}}$
Relative viscosity ....................................................................................................................................... $\eta_r$
Shear rate ............................................................................................................................................... $\frac{dv_x}{dy} \gamma$
Shear stress ............................................................................................................................................ $\frac{F}{A} \tau$
Terminal velocity ...................................................................................................................................... $V_T$
Viscosity ................................................................................................................................................ $\eta, \mu$
Viscosity of a mixture .............................................................................................................................. $\eta_{\text{mix}}$
Viscosity of continuous phase .................................................................................................................. $\eta_0$
Volume of flowloop ............................................................................................................................... $V_{\text{loop}}$
Volume of hydrate particle ..................................................................................................................... $V_{\text{hydrate}}$
Volume of oil .......................................................................................................................................... $V_{\text{oil}}$
Volume of water ...................................................................................................................................... $V_{\text{water}}$
Water volume fraction .............................................................................................................................. $\phi$

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<td>AA</td>
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<td>Bulk Relaxation</td>
<td>Bulk relaxation</td>
<td>$T_{2B}$</td>
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<td>Carr-Purcell-Meiboom-Gill</td>
<td>Carr-Purcell-Meiboom-Gill</td>
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<td>Computational Fluid Dynamics</td>
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<td>Critical Concentration of Aggregation</td>
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<td>Loss modulus</td>
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<td>Low dosage hydrate inhibitor</td>
<td>LDHI</td>
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<td>Low Field</td>
<td>Low field</td>
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<td>Material safety data sheet</td>
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<tr>
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<td>Monoethylene glycol</td>
<td>MEG</td>
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<td>Nuclear magnetic resonance</td>
<td>NMR</td>
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<td>Particle video microscope</td>
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<tr>
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<td>Pulsed field gradient</td>
<td>PFG</td>
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<tr>
<td>Pulsed Field Gradient- Carr-Purcell-Meiboom-Gill</td>
<td>Pulsed field gradient Carr-Purcell-Meiboom-Gill</td>
<td>PFG-CPMG</td>
</tr>
<tr>
<td>Signal to Noise Ratio</td>
<td>Signal to noise ratio</td>
<td>SNR</td>
</tr>
<tr>
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<td>Sodium-di-Ethylhexylsulfosuccinate</td>
<td>AOT</td>
</tr>
<tr>
<td>Sorbitane Monooleate</td>
<td>Sorbitane monooleate</td>
<td>Span 80</td>
</tr>
<tr>
<td>Storage Modulus</td>
<td>Storage modulus</td>
<td>$G'$</td>
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<td>Structure I hydrate</td>
<td>sI</td>
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<tr>
<td>Structure II Hydrate</td>
<td>Structure II hydrate</td>
<td>sII</td>
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</table>
Structure H Hydrate ............................................................... sH
Surface Relaxation .................................................................................... T_{2S}
Thermodynamic Hydrates Inhibitors ....................................................... THI
Water Cut / Water Volume Fraction ..................................................... WC
Water-in-Oil ...................................................................................... w/o
West African Crude ........................................................................ WAC
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CHAPTER 1
INTRODUCTION

This chapter provides an introduction to gas hydrates including common gas hydrate structures, as well as common gas hydrate formers. Problems of gas hydrate formation in flowlines was discussed. Finally, the definition of viscosity and how it may help in flow assurance was discussed.

1.1. Introduction to Gas Hydrates

Gas hydrates, (also known as clathrate hydrates, or simply hydrates) are crystalline structures that contains small gas molecules (methane, ethane, propane,) that are enclathrated by hydrogen-bonded water cages (Sloan and Koh 2007). In forming gas hydrates, the water molecules will form a hydrogen-bonded network of water cages around the gas molecules. These gas molecules are called guests, which must be small enough to be trapped by the water cages. Gas hydrates typically form at low temperature and high pressure (10 MPa, 277 K for methane hydrates). Due to these formation conditions, hydrates can be found naturally in sediments under the ocean sea floor, as well as under the permafrost in arctic regions (Sloan and Koh 2007). In addition, gas hydrates can form in subsea oil/gas pipelines where they can cause problems such as pipeline plug formation that can lead to safety and economical concerns.

Figure 1.1 shows the three commonly found structures of gas hydrates; structure I (sI), structure II (sII) and structure H (sH). In general, the van der Waals radii of the guest molecules determine the type of hydrate structure that can be formed (Sloan and Koh 2007). As shown in Figure 1.1, for sI hydrate, there are two types of cages; a small \(5^{12}\) cage and a large \(5^{12}6^2\) cage. Specifically, sI has two small \(5^{12}\) cages and six large \(5^{12}6^2\) cages, resulting in a total of 46 water molecules for each unit cell. The common gas molecules that will form sI hydrates include methane, ethane and xenon (Sloan and Koh 2007). Since there is an abundance of methane gas in nature (derived by biogenic processes), sI hydrate is the most common structure of hydrates in nature.

The next common hydrate structure is sII hydrates. Similar to sI hydrate, sII hydrate contains two types of cages; sixteen of the small \(5^{12}\) cages and eight of the large \(5^{12}6^4\) cages. Therefore, sII hydrate contains 136 water molecules per unit cell. Examples of gas molecules
that will form sII hydrate include cyclopentane and natural gas mixtures, such as methane+ethane+propane (Sloan and Koh 2007). Unlike sI hydrate, sII hydrate is less common in nature, but is typically formed in subsea oil/gas flowlines.

![Common structures of hydrates with the corresponding unit cells (Sloan 2000).](image)

**Figure 1.1:** Common structures of hydrates with the corresponding unit cells (Sloan 2000).

The last common form of hydrate structures is sH. sH is rare when compared to sI and sII hydrates. sH requires two different guest molecules (a small and a large gas molecule) to stabilize its structure (Sloan and Koh 2007). sH consists of three types of cages; three small (5^{12}) cages, two medium (4^{56}6^3) cages and one large (5^{12}6^8) cage.

### 1.2. Hydrates in Flow Assurance

The turbulent flow coupled with the high pressure and low temperature in subsea oil/gas flowlines provide favorable conditions for the formation of gas hydrates. The formation of gas hydrates in flowlines can lead to problems such as flowline blockage (as shown in Figure 1.2) and are considered to be a nuisance. Hydrate blockage can cause severe safety, economic and environmental concerns. Hydrate formation in subsea oil/gas flowlines is often considered the number one flow assurance problem for the industry (Sloan and Koh 2007).
Traditionally, the main method to deal with hydrates in flowlines is the use of a “Hydrate Avoidance” method. In this method, the formation of gas hydrates is completely prevented (or avoided) by injecting Thermodynamic Hydrates Inhibitors (THIs) such as methanol and monoethylene glycol (MEG) in the flowlines. THIs operate by shifting the hydrate phase equilibrium curve as shown in Figure 1.3. As shown here, when a certain amount of THI is added (e.g. methanol in Figure 1.3), higher pressures and lower temperatures are required for hydrates to form in the flowlines. In this method, a large quantity of THI (e.g. ~40 vol.%) is needed for complete avoidance of gas hydrate formation (Sloan and Koh 2007). In addition, it has been shown that as an oil field matures, the amount of water produced during the drilling process increases significantly (Gluyas and Hichens 2003). These two factors (large quantities of THI needed and the increased amount of water produced as the field matures) result in higher operating costs and thus this method of “Hydrate Avoidance” becomes uneconomical. Specifically, it has been reported (Creek, 2012) that operators incur an additional cost of $84 per barrel of water produced (at a methanol cost of $2 per gallon). At this cost, operators might not be able to pay the cost of hydrate avoidance even when the oil sale price is listed at $100 per barrel (Creek 2012).
Another method that is currently being used by the oil/gas industry to prevent hydrate formation in flowlines is called a “Physical Method”. In this method, the pressure and temperature of the flowlines are kept outside the hydrate stable region (Figure 1.3) by using certain equipment, such as insulation and direct electrical heating (Moradpour 2011; Sloan and Koh 2007). The research that has been done in this area has shown that “Physical Method” can be economically attractive, but it may not be able to prevent hydrates from forming during immediate shut-in due to emergency situations (Moradpour 2011).

As the method for complete prevention (and avoidance) becomes more uneconomical, a relatively new method in dealing with hydrates is being proposed. The method is called “Hydrate Management”, where hydrates are allowed to form in the flowlines but are managed/controlled (relative to the hydrate formation rate and properties). This can be done by injecting Low Dosage Hydrate Inhibitors (LDHIs) into flowlines. LDHIs work by either delaying the formation of hydrates, or by preventing individual hydrate particles from agglomerating. Currently, there are two types of LDHIs; Kinetic Hydrate Inhibitors (KHI) and Anti-Agglomerants (AAs). KHI works by delaying the formation of gas hydrates at the hydrate prone sections of the flowlines (Lachance 2008). AAs, on the other hand, work by preventing hydrate particle agglomeration and thus create a transportable gas hydrate slurry. A major advantage of using LDHIs (both KHI and AAs) is that only a small amount is needed (~1 – 2 wt.%). The low quantity of LDHIs required has led to the oil/gas industry being interested in this method, as it can be more economical compared to a “Hydrate Avoidance” method. However, the use of LDHIs is limited,
as certain LDHIs have been shown to be ineffective at higher subcooling, i.e. around 10 °C (Sloan 2000). Regardless of this concern, the “Hydrate Management” method has gained a lot of interest in the oil/gas industry, and thus there is a need for better understanding of the rheology of gas hydrate slurries.

1.3. Viscosity of Fluids

Fluids are defined as substances that flow when an external force is exerted upon it, while viscosity is defined as the resistance property of the fluids when the force is exerted (Wilkes 2008). Fluids that are high in viscosity require a high magnitude of force to flow and vice versa.

![Figure 1.4: Conceptual picture for the definition of viscosity, in which a fluid is being sheared between two parallel plates.](image)

The term viscosity can be depicted by the conceptual picture in Figure 1.4, in which a fluid is being sheared between two parallel plates. From this figure, assume that the area of the two parallel plates are both \( A \) and the gap between the plates is \( h \). At a certain point of time, the top plate is being moved at a constant velocity of \( v_x \) and the bottom plate is stationary. As a result of the top plate being moved, the fluid will move as well and it has been determined that the force per unit area to move the top plate is directly proportional to the velocity gradient, as described in (1-1) (Wilkes 2008).

\[
\frac{F}{A} = \eta \frac{dv_x}{dy}
\]  

(1-1)
Equation (1-1) is a well-known equation in the field of rheology and fluid transport phenomena and is called the Newtonian law (Wilkes 2008). In general, the term $\frac{F}{A}$ of Equation (1-1) is called the shear stress, $\tau$, while the velocity gradient, $\frac{dv}{dy}$, is known as shear rate, $\gamma$. Additionally, the term $\eta$, which is the proportionality constant in the equation, is called viscosity. Thus, using the latter definition, Equation (1-1) can be simplified into Equation (1-2). This equation describes how the viscosity of the fluid changes with the external force exerted upon it.

$$\tau = \eta \gamma$$  \hspace{1cm} (1-2)

From Equation (1-2), it can be determined that the unit for viscosity is mass per unit length per unit time. Thus, the basis for viscosity is kg.m$^{-1}$.s$^{-1}$. However, the common unit for viscosity is known as Poise (P) (or g.cm$^{-1}$.s$^{-1}$) (Wilkes 2008).

1.4. Types of Fluids

In general, all fluids are characterized on how they respond when an external force is applied. A fluid can be either: (1) Newtonian, or (2) Non-Newtonian fluid. Figure 1.5 shows the response of both type of fluids (Newtonian and Non-Newtonian) when an external force is exerted.

![Figure 1.5: Relationship between shear stress and strain rate for two different fluid types (adapted from (Wilkes 2008)).](image)
1.4.1 Newtonian Fluids

Newtonian fluids are defined as fluids with viscosity that does not depend on the shear rate, \( \gamma \), applied. Thus, for Newtonian fluids, the shear stress is linearly proportional to the shear rate. Graphically, a graph of shear stress, \( \tau \), against shear rate, \( \gamma \), for Newtonian fluids is a linear line that intercepts at the origin (as shown in Figure 1.5). Mathematically, since the viscosity of Newtonian fluids does not depend on shear rate, \( \gamma \), Equation (1-2) can be simplified to Equation (1-3). It should be noted that shear stress, \( \tau \), and shear rate, \( \gamma \), are both scalar and depend on the temperature and pressure of the system (Wilkes 2008).

\[
\tau = \eta = \mu
\]  

(1-3)

1.4.2 Non-Newtonian Fluid

The next category is Non-Newtonian fluid. Simply put, fluids that do not obey Equation (1-3) are considered to be Non-Newtonian fluids. Non-Newtonian fluids can be further categorized into several types depending the response of the fluid when the shear is applied (Wilkes 2008). Three most common types of Non-Newtonian fluids are shear thinning, shear thickening, and Bingham plastic fluids.

Shear Thinning Fluids (Pseudoplastic)

Shear thinning fluids are also called pseudoplastic. Fluids that behave as shear thinning fluids show viscosity decreases with increasing strain rate (Figure 1.5). In other words, for shear thinning fluids, the fluids become easier to flow at higher flow rates. Most polymer solutions behave as shear thinning fluids (Wilkes 2008).

Shear Thickening Fluids (Dilatant)

Shear thickening fluids (also known as dilatants) show viscosity increases with increasing strain rate (Figure 1.5). Thus, for a shear thickening fluid, it will be more difficult to flow at higher flow rates. It has been reported that shear thickening fluids are not as common as shear thinning fluids (Wilkes 2008). However, an interesting and common example of a shear thickening fluid is a suspension of sand and water.
Bingham Plastic  

Bingham plastic is a unique set of fluids that requires a certain amount of stress before it can flow. Once the fluid flows, the viscosity of the fluid can be constant (as shown in Figure 1.5), increasing or decreasing (Wilkes 2008). An example of a Bingham plastic is toothpaste.

1.5. Application of Hydrate Rheology Understanding for Flow Assurance  

Several studies have shown that the addition of solids, including solid hydrate particles, in a fluid can change the behavior of the suspending fluids (Mueller, Llewellyn, and Mader 2009). In fact, it has been shown that the formation of hydrate particles from an emulsion will increase the viscosity of the system (Webb, Koh, and Liberatore 2014; Webb et al. 2012; Peixinho et al. 2010). It is thus important for the flow assurance engineer to understand the effect of hydrate particles on the viscosity of the system.

In this thesis work, it was proposed that the viscosity of a hydrate slurry is affected by several variables, such as the amount of hydrate formed, temperature, pressure and particle size distribution. Thus, if the effects of each variable on the viscosity of the system can be quantified, this can lead to more accurate prediction of the susceptibility of flowlines to hydrate blockage/plugging. This information can ultimately lead to improved hydrate management strategies for flow assurance in oil/gas flowlines.

1.6. Thesis Outline  

This doctoral thesis summarizes the work performed to provide new understanding on the rheological properties of gas hydrate slurries to advance the development of improved “hydrate management” methods in oil/gas subsea flowlines. The thesis comprises seven chapters, all of which describe the development and application of rheological and related properties for advanced hydrate plugging prevention.

In Chapter 1, presents an introduction of gas hydrates and their role in flow assurance; as well as an introduction to rheological and related properties, and their significance in flow assurance. Chapter 2 describes the development of a model water-in-oil (w/o) emulsion for hydrate rheology studies. A stable (model) w/o emulsion system is required to perform fundamental and repeatable rheological measurements (under limited shear conditions). Chapter 3 focuses on the development of a viscosity model for emulsion systems developed in this work. In Chapter 4, viscosity models for gas hydrate slurries are described. The developed model is for both model
emulsion systems (mineral oil 350T and 70T), and is a function of composition (hydrate volume fraction). Chapter 5 describes the use of an industrial-scale high pressure flowloop to study the flow properties and transportability of gas hydrate at two flow conditions (fully and partially dispersed systems). Next, Chapter 6 describes the development of a low field Nuclear Magnetic Resonance (NMR) method to determine the droplet size distribution of w/o emulsions. The results obtained from these NMR studies were compared with results obtained from optical microscopy. Finally, Chapter 7 describes the conclusions and recommendation for future work for the study of rheological properties of gas hydrate slurries.
CHAPTER 2
DEVELOPMENT OF MODEL WATER-IN-OIL EMULSION SYSTEMS
modified from a paper published in *Energy and Fuels*\(^1\)
José G Delgado-Linares\(^a\), Ahmad A A Majid\(^b\), E Dendy Sloan\(^c\), Carolyn A Koh\(^d\), Amadeu K Sum\(^e\)

Stable water-in-oil (w/o) emulsions for the use of gas hydrate investigations have been developed. The emulsion consists of either mineral oil 70T or 350T as the continuous phase. A mixture of a non-ionic-anionic surfactant mixture was used as the emulsifier agent. The surfactant mixture consists of sorbitane monooleate (Span 80) and sodium-di-ethylhexylsulfosuccinate (AOT). Stable emulsions can be formed up to 70 vol.% water cut for mineral oil 70T, and up to 40 vol.% water cut for mineral oil 350T. Microscopy tests conducted on these emulsions show that the average droplet size is in the range of 2 – 3 µm for mineral oil 70T emulsions, and 3 – 5 µm in size for mineral oil 350T emulsions. Characterization experiments show that the emulsions are highly stable (up to one week) and have similar characteristics to crude oil emulsions. The tests conducted confirmed that the model emulsions are suitable to be used for hydrate studies.

2.1. **Background and Motivation for Model Emulsion System**

Figure 2.1 depicts an oil-dominated system that can be found in oil/gas flowlines. In this condition, the flowline begins by having three different components; oil, water and gas. Due to the high fluid velocity of the system, the system will be in turbulent flow condition. This turbulent flow causes water to be emulsified into the oil phase, creating a w/o emulsion (Sloan and Koh 2007).\(^1\)

The water droplets formed in the oil phase will be converted to individual hydrate particles. Depending on the size of the water droplets, the hydrate particles can be detrimental to the

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\(^c\) Professor and co-author

\(^d\) Professor, co-author and thesis advisor

\(^e\) Professor and corresponding author
system. If the water droplets are large enough and the system is not being chemically treated with chemicals such as anti-agglomerants, there can be an interaction between hydrate particles. This interaction will lead to the formation of large hydrate aggregates than can plug the flowlines (Sloan and Koh 2007).

![Figure 2.1: Conceptual picture of hydrate plug formation in an oil-dominated system (edited from Sloan and Koh 2007).](image)

As shown in Figure 2.1, hydrate formation occurs at the water droplet interface. Thus the studies of hydrates slurry rheology require the use of w/o emulsions. It would be of interest to use water-in-crude oil emulsions in this work. However, the use of crude oil emulsions causes several issues among which, is the reproducibility of crude oil chemistry. It is known that the chemistry of crude oil is different from one type to the other (Sjöblom et al. 2010; Webb et al. 2012). Additionally, it has been observed that the chemistry of crude oil may change from batch to batch, and the precipitation of the wax during storage may also change the chemistry of crude oil (Sjöblom et al. 2010; Webb et al. 2012). As a result of this change of chemistry, the results of a hydrate slurry rheology study using crude oil might not be reproducible, and thus a challenge to interpret the results. Therefore, in this work, the use of a well-defined model w/o emulsion was considered necessary, as it could provide reproducible results (Delgado-Linares et al. 2013).

### 2.2. Requirements for Model Emulsion System

The results and findings from this thesis work need to be able to be applied to actual oil and gas flowline systems. Consequently, the model w/o emulsion developed needs to behave similarly to emulsions found in flowlines. Several requirements of the model w/o emulsion were
outlined in order to achieve the aforementioned goal. The requirements of the model emulsions are as follows:

1. Oil continuous system
   
   *The scope of this work is an oil-dominated system. Thus, the model emulsion needs to be oil continuous*

2. Has a density and viscosity similar to that of typical crude oils
   
   *Physical properties of the model emulsion need to be similar to an emulsion in a crude oil system in flowlines*

3. Oil has a well-defined surface active chemical
   
   *This allows the separation of the effect of hydrate formation from other crude oil components (e.g. waxes and asphaltenes). This also ensure the reproducibility of results*

4. Water droplets in the range of ~1-100 μm
   
   *This is the typical size of water droplets in oil and gas flowlines.*

5. Stable for ~one week period
   
   *Hydrate rheology studies may require several hours to days to be completed. The model emulsion needs to remain homogenous throughout the entire experiment*

2.3. Model Emulsion Systems

Model w/o emulsions that meet the requirements mentioned in Section 2.2 have been developed. The model emulsions consist of mineral oil, a mixture of surfactant, and deionized water. Two types of mineral oils were used in this work; mineral oil 70T and mineral oil 350T. Both mineral oils were purchased from STE Oil Company, Inc. The physical properties of the two mineral oils are listed in Table 2-1. Viscosity measurements show that both mineral oils behave as Newtonian fluids.

Two different surfactants were used as emulsifier agents. The first surfactant is a nonionic surfactant, Span 80 purchased from Sigma Aldrich. The molecular structure of Span 80 is shown in Figure 2.2(a). According to the material safety data sheet (MSDS) provided by the supplier, Span 80 has a molecular weight of 428.61 g/mol. In addition, Span 80 has a reported Hydrophilic Lipophilic Balance (HLB) value of 4.3 (Peixinho et al. 2010). The HLB value is a concept developed to determine the degree of hydrophilicity or lipophilicity of nonionic surfactants. By its definition, the value of HLB is defined as 1/5 of the weight percent of ethylene oxide in a surfactant’s molecular structure (Griffin 1949; Griffin 1954). Surfactants with a high value of
HLB are highly hydrophilic and vice versa. The second surfactant used in the model emulsion is an ionic surfactant known as AOT. The molecular structure of AOT is shown in Figure 2.2(b). Similarly, from the MSDS obtained from the supplier, AOT has a molecular weight of 444.56 g/mol. As AOT is an ionic surfactant, the HLB concept does not apply to it.

**Table 2-1**: Physical properties of the two mineral oils used in this work.

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>70T</th>
<th>350T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (20°C) [g/cm³]</td>
<td>0.853 ± 0.003</td>
<td>0.870 ± 0.017</td>
</tr>
<tr>
<td>Viscosity (25°C) [cP]</td>
<td>21 ± 0.18</td>
<td>65 ± 1.1</td>
</tr>
<tr>
<td>Interfacial Tension [mN/m]</td>
<td>58.3 ± 1.71</td>
<td>53.6 ± 0.16</td>
</tr>
</tbody>
</table>

![Molecular structures of the surfactants used in this work. (a) Span 80 and (b) AOT.](image)

**Figure 2.2**: Molecular structures of the surfactants used in this work. (a) Span 80 and (b) AOT.

The concentration of the surfactant depends on the continuous phase/mineral oil used. 5 wt.% of surfactant was used for mineral oil 350T, while 1 wt.% surfactant was used for mineral oil 70T. Both concentrations of surfactant were measured with respect to the total mass of the emulsion. In addition to the different concentration of surfactant, the mass ratio of Span 80 to AOT is also different for each mineral oil. The ratio of Span 80 to AOT for the mineral oil 70T
emulsion system is 90 to 10 by mass, while the mass ratio for the mineral oil 350T emulsion system is 75 to 25 by mass.

The water content or water fraction (water cut) for the model emulsion depends on the mineral oil used to prepare the emulsion. A stable emulsion w/o emulsion could be formed from 10 – 70 vol.% water by using mineral oil 70T. On the other hand, a stable emulsion could only be formed up to 40 vol.% water for mineral oil 350T.

2.3.1 Emulsification Process for Model Emulsion Systems

As mentioned in Section 2.3 on Model Emulsion Systems, two different surfactants were used as the emulsifier agent. One of the surfactant used in this work, AOT, is solid at room temperature. Thus, the emulsification process for this model emulsion began by dissolving the pre-measured amount of surfactant in the mineral oil. To ensure that the surfactants were completely dissolved in the mineral oil, low heat and medium stirring were applied using a hot plate and magnetic stirrer to the mixture of mineral oil and surfactants. Once the surfactants had completely dissolved in mineral oil, the sample was left to cool to room temperature before proceeding to any further emulsification step.

Once the temperature of the sample reached room temperature, it was then stirred using a high-speed homogenizer (IQ Cyclone) at a mixing speed of 8000 RPM. During this mixing process, the water was added dropwise using a syringe (Sjöblom et al. 2010). The total stirring time depends on the both the type of mineral oil as well as the water cut of the emulsion to be prepared. For the mineral oil 70T emulsion system, the total stirring time for water cuts of 50 vol.% and below (≤50 vol.%) was 3 minutes, where water was added during the first minute. For 60 and 70 vol.% water cuts, the total stirring time was 6 minutes, and water was added during the first 4 minutes. As shown in Table 2-1, mineral oil 350T has a higher viscosity compared to mineral oil 70T. Due to this higher viscosity, the emulsification process requires a longer stirring time. Thus, for the mineral oil 350T emulsion system, the sample was stirred for 5 minutes, where water was added during the first 2 minutes.

2.4. Characterization of Model Emulsion Systems

In order to confirm that the model emulsion systems were suitable to be used for hydrate studies, several characterization tests were conducted on the emulsion systems. These
characterization tests to be performed on the emulsion were determined based on the requirement stated in Section 2.2 on Requirements for Model Emulsion System.

In this work, five characterization tests were conducted on the emulsions. The tests performed include:

1. Classical Bottle Test
   *The test was conducted to determine the stability of emulsion*

2. Microscopy Image Test
   *The test was conducted to determine the water droplet size*

3. Interfacial Tension (IFT) Measurement
   *The test was conducted to determine the Critical Concentration of Aggregation (CCA) of the emulsion*

4. Viscosity Measurement
   *The test was conducted to determine the flow properties and behavior of the emulsion*

5. Differential Scanning Calorimetry (DSC)
   *The test was conducted to determine the stability of the emulsion upon hydrate/ice formation/dissociation.*

### 2.4.1 Classical Bottle Test

In the classical bottle test, the stability of the emulsion was determined by visually observing any sign or evidence of emulsion instability. This classical bottle test was conducted throughout a certain period of time and at a certain frequency. In this work, classical bottle tests were conducted at two different temperatures; room temperature (~22 °C) and at 2 °C. The emulsions were observed daily for a period of one week.

Generally, there are three outcomes for the classical bottle test study on emulsions: (1) stable homogeneous emulsions, (2) stable with sedimentation emulsions, and (3) unstable emulsions (or phase separation). The outcomes of classical bottle test are portrayed in the conceptual picture shown in Figure 2.3. As stated, the first outcome is stable homogeneous emulsions, where the water droplets remain separated and well dispersed. Additionally, there is no coalescence of water droplets and thus the size of water droplets remain unchanged with time. Stable homogeneous emulsions are the outcome that is intended from the model emulsions to be used in this work.
The second outcome of classical bottle test is stable with sedimentation. For this outcome, the emulsion is still considered as stable since the droplets remain dispersed in the oil phase. However, due to the density difference between the dispersed and continuous phase as well as gravitational force, the water droplets settle at the bottom (Lachance 2008). Thus, there is a heterogeneous distribution of water droplets in the emulsions; there is a higher amount of water droplets at the bottom of system compared to at the top.

![Figure 2.3: Three outcomes of the classical bottle test on emulsions.](image)

The third outcome of classical bottle test is unstable or phase separation. In this case, the emulsion is unstable such that the water droplets that form during agitation quickly coalesce and/or phase separate when the agitation is stopped, or it may take a few minutes to days for the two phases to separate.

Figure 2.4 shows the sample of emulsions prepared using mineral oil 70T at two different times after preparation. As can be seen from this figure, there is no evidence of phase separation and sedimentation. Therefore, from the results of the classical bottle tests, it can be concluded that the model emulsion sample prepared using mineral oil 70T produces stable and homogenous emulsions. However, it should be stated that small sedimentation of water droplets was observed.
in the classical bottle test performed at a low temperature of 2 °C. This sedimentation was only observed for emulsions at 10 and 20 vol.% water cut.

Classical bottle tests were also conducted for model emulsions prepared using mineral oil 350T; the test results are shown in Figure 2.5. Similarly, results of the tests show that there is no evidence of sedimentation and phase separation. Thus, it can be concluded the model emulsion prepared using mineral oil 350T for water cut ranges from 10 – 40 vol.% is highly stable.

Figure 2.4: Samples of water-in-mineral oil emulsions prepared using mineral oil 70T for water cut ranging from 10 – 70 vol.% at (a) 24 hours and (b) one week after preparation.

The high stability of the model emulsion can be attributed to two mechanisms of stabilization, as stated in literature (Salager 2000; Walstra 1996). These two mechanisms of stabilization are: steric and electrical repulsion, both represented in Figure 2.6. Typically, a surfactant molecule consists of a hydrophilic and lipophilic region. The lipophilic region consists of long hydrocarbon tail. Thus, in steric repulsion, the long hydrocarbon tail of both Span 80 and AOT prevents the water droplets from coalescing, which results in well-dispersed water droplets. Moreover, the negative charge that is present at the head group of the AOT molecule (Figure
2.2(b)), provides an additional mechanism of stabilization. The negative charge provides electrical repulsion between water droplets and thus it prevents water droplets from coalescing.

![Figure 2.5: Samples of water-in-mineral oil emulsions prepared using mineral oil 350T for water cut ranges from 10 – 40 vol.% at (a) 24 hours and (b) one week after preparation.](image)

![Figure 2.6: Two mechanisms of emulsion stabilization: steric and electrical repulsion.](image)

**Figure 2.5:** Samples of water-in-mineral oil emulsions prepared using mineral oil 350T for water cut ranges from 10 – 40 vol.% at (a) 24 hours and (b) one week after preparation.

**Figure 2.6:** Two mechanisms of emulsion stabilization: steric and electrical repulsion.
2.4.2 Microscopy Images

Microscopy images of the model emulsion samples were collected using an optical microscope (Olympus IX71). This microscope is connected to a digital camera (Olympus XM10) that captured and recorded the images. Microscopy images were collected for both model emulsion systems at all water cuts. Once microscopy images have been collected, the images were analyzed using ImageJ software to determine the average size of the water droplets. In this work, a minimum of 250 water droplets were measured at each water cut for each mineral oil system to determine the average droplet size. The droplet size reported in this work is the numerical average of the droplet size.

Microscopy images of the model emulsions for mineral oil 70T and mineral oil 350T are shown in Figure 2.7 and Figure 2.8 respectively. Droplet size analysis of the microscopy images shows that the average water droplet size for mineral oil 70T model emulsion is in the range of 2 – 3 μm across all water cuts. A subsequent independent study performed by Zheng et al. also confirmed that the water droplets is in the aforementioned size range across all water cuts (Zheng and Fogler 2015). Additionally, the average water droplet size for model emulsions formed with mineral oil 350T is in the range of 3 – 5 μm. The size of water droplets for these model emulsions is consistent with the size of water droplets for a typical water-in-crude oil system reported by other researchers (Noïk, Trapy, and Mouret 2002).

Figure 2.7: Microscopy images of water droplets in the model emulsion prepared using mineral oil 70T for (a) 10 vol.% and (b) 50 vol.% water cuts.
Figure 2.8: Microscopy images of water droplets in the model emulsion prepared using mineral oil 350T for (a) 10 vol.% and (b) 30 vol.% water cuts.

2.4.3 Interfacial Tension Measurements (IFT)

In this work, IFT measurements were conducted at ambient pressure and temperature using a pendant drop method. Measurements were conducted using a pendant drop tensiometer manufactured by KSV Instrument Ltd. The main objective for performing IFT measurements was to determine the critical concentration of aggregation (CCA). A similar and more commonly used term is critical micelle concentration (CMC). CMC refers to the concentration above this value micelles will form in the emulsion. CCA on the other hand is defined as the concentration above this value inverse micelles form. Thus, from the definition, CMC is to be used for water continuous emulsions, while CCA is for oil continuous emulsions. As in this work the model emulsion is oil continuous, the proper terminology to be used is CCA.

The CCA of an emulsion can be determined by the change in the IFT values of the system. The IFT value decreases with an increase in concentration of surfactant up to a certain concentration. At this concentration, the interface between oil and water is fully covered with the surfactant molecules. When any additional surfactant is added into the system, there is no available interface where the molecules can go, and micelles or inverse micelles will begin to form. Therefore, the addition of further surfactant will not decrease the IFT value.

In order to determine the CCA for the model emulsions, the IFT value needs to be measured over a wide range of surfactant concentrations. In this work, the IFT values were measured at concentrations of surfactant from 0 to 5 wt.%. Figure 2.9 shows a plot of the IFT value at
different concentrations of surfactant for both mineral oils. As mentioned earlier, that addition of surfactant above the critical concentration will not decrease the IFT value. Thus, the CCA for the model emulsions were determined by the change in the slope of the IFT – concentration curve in Figure 2.9 (cf. Salager, 2000). The results of IFT measurements show that the CCA value is approximately 0.1 wt.% of surfactant for both mineral oils.

![Figure 2.9: IFT value as a function of surfactant concentration for (a) mineral oil 70T and (b) mineral oil 350T + surfactant systems.](image)

2.4.4 Viscosity Profile

Another characterization test performed on the model emulsions is the viscosity profile at various shear rates. This test was performed to determine the characteristic of the fluid (Newtonian, shear thinning or shear thickening). The viscosity of the model emulsions was also measured at ambient pressures and two different temperatures: room temperature and 1°C. All measurements were performed using a TA Instruments Discovery Hybrid Rheometer 3 (DHR-3). A cone and plate geometry was used in the measurements. The cone has a diameter of 40 mm and an angle of 1.995°. The gap between the Peltier and the cone was set to 52 μm. The viscosity of the emulsions was measured at shear rates between 0.1 to 1000 s⁻¹. In this work, viscosity values were only measured at steady state, which was defined as three consecutive points within 3% variation.

Viscosity profiles of the model emulsions are shown in Figure 2.10 and Figure 2.11. It can be seen from these viscosity measurement results that the viscosity of the emulsion increases with increasing water cut of the system for both mineral oils and at both temperatures. This is as expected as several studies on emulsions and dispersions have shown that the viscosity of emulsions is proportional to the amount of the dispersed phase (Salager 2000; Mueller,
Additionally, it has been reported by other researchers that the viscosity of the emulsion increases due to the increase in the packing of water droplets and thus the interaction among them (Tadros 2005).

In analyzing the results further, it can be seen that both model emulsions behave as shear thinning fluids, even though both mineral oils behave as Newtonian fluids. For mineral oil 70T, the shear thinning behavior is more significant above 30 vol.% water cut at room temperature and above 20 vol.% water cut at 1°C. For the mineral oil 350T emulsion system, the shear behavior is more significant at lower water cuts, specifically above 20 vol.% water cut for room temperature and above 10 vol.% water cut at 1°C. Reviewing the viscosity profiles of emulsions, shear thinning behavior is found to be typical for emulsions. The shear thinning behavior is believed to be due to breakup of water droplets aggregates and/or re-alignment of water droplets under shear (Quintero 2008). As a result of this re-alignment and aggregates breakup, shear thinning behavior is more prominent at high water cut, since the system becomes more tightly packed and there is more interaction among the water droplets.

Figure 2.10: Viscosity profiles of model emulsions prepared using mineral oil 70T at various water cuts measured at (a) room temperature and (b) 1°C.

An interesting behavior can be seen at high water cut (70 vol.% water cut for mineral oil 70T emulsion and 40 vol.% water cut for mineral oil 350T emulsion). As can be seen in Figure 2.10(b) and Figure 2.11(b), there is an abrupt drop in the viscosity of the emulsion at high shear rates (~800 s⁻¹ for mineral oil 70T emulsion and ~900 s⁻¹ for mineral oil 350T emulsion). In this work, it is hypothesized that the abrupt drop in the viscosity of the emulsion is due to phase
inversion. This hypothesis was confirmed by performing a simple dispersion test. In this test, the emulsion was sheared using the rheometer at 1000 s\(^{-1}\) for 2 minutes. Next, a small sample of the sheared emulsion was taken and dropped into DI water. In dispersion test, if water is the continuous phase, the emulsion will completely disperse in DI water. The results of this dispersion test shows that the sheared emulsion dispersed in DI water, thus confirming that water is the continuous phase (Ese and Kilpatrick 2004). Due to the phase inversion that occurs at low temperatures and high shear rates, measurements for the viscosity of the hydrate slurry were set to be performed at shear rates below the shear rate that can cause emulsion phase inversion.

![Figure 2.11: Viscosity profiles of model emulsions prepared using mineral oil 350T at various water cuts measured at (a) room temperature and (b) 1°C.](image)

2.4.5 Differential Scanning Calorimetry (DSC)

In this work, DSC tests were conducted using a micro-differential scanning calorimeter VIIa (\(\mu\)-DSC VIIa, Setaram Inc.). The main objective of the test is to determine the stability of the model emulsions with ice and hydrate formation/dissociation. The stability of an emulsion with ice and hydrate formation/dissociation can be determined by evaluating the intensity of the endothermic peaks across several consecutive cooling and heating cycles. In ice and hydrate formation/dissociation, there are two possible outcomes, as shown in Figure 2.12 (Lachance 2008). (1) The first outcome is ice or hydrate formation without aggregation. In this outcome, ice or hydrate forms during the cooling period. Since, particle aggregation is prevented, the particles remain separated. During the heating period, ice or hydrates dissociate and since the particles
remain separated, the size of the water droplets is similar to the original size. Therefore, in the next cooling and heating cycle, similar amounts of ice or hydrates form, and thus the intensity of endothermic peak remains unchanged (Lachance 2008).

(2) The second outcome is that there is particle aggregation with ice or hydrate formation. Similarly, in this outcome, ice or hydrate will form during the cooling period. However, particle aggregation occurs in the system and thus the particles adhere together. During the heating period, ice or hydrates dissociate and since the particles are adhered together, they dissociate into larger water droplets. As the water droplets become larger, there is less total surface area of water droplets for ice or hydrate to form. Consequently, in the next cooling and heating cycle, the intensity of the endothermic peak decreases since there is less ice or hydrate formed (Lachance 2008).

In this work, DSC tests were performed at two different conditions: ambient pressure and high pressure. Ambient pressure DSC tests were conducted to determine the stability of the emulsion upon ice formation/dissociation, while high pressure DSC tests were conducted to determine the stability of the emulsion upon hydrate formation/dissociation.

Figure 2.12: Two possible outcomes for hydrate formation and dissociation. (a) No hydrate aggregation and (b) with hydrate aggregation (edited from Lachance 2008).
2.4.5.1 Ambient Pressure DSC Tests

As mentioned earlier, ambient pressure DSC tests were conducted to determine the stability of the emulsion upon ice formation and dissociation. An ambient pressure DSC test began by adding ~15 mg of an emulsion sample into the sample cell. The cell was then inserted into the DSC equipment. Next, the sample was cooled from 30 °C to -45 °C at a rate of 0.3 °C/min. The sample was then heated back to 30 °C at similar rate of 0.3 °C/min. The cooling and heating cycle was repeated for another two cycles (Lachance, Sloan, and Koh 2008).

A thermogram of the ambient pressure DSC test for a model emulsion prepared using mineral oil 70T at 10 vol.% is shown in Figure 2.13(a). There are two exothermic peaks during the cooling process for each cycle. The first exothermic peak is at -18 °C (cycles 1 and 2) and at -19 °C (cycle 3). The second exothermic peak is at -42 °C for all the three cycles. As homogeneous nucleation of ice from water droplets typically occurs at around -45 °C, the peak at -42 °C confirms that the model emulsion formed is indeed a w/o emulsion with relatively small water droplets (Lachance 2008; Lachance, Sloan, and Koh 2008; Dalmazzone, Noïk, and Clausse 2009; Santini et al. 2007). Furthermore, it can be observed from Figure 2.13(a) that the second exothermic peak is nearly symmetrical and thus it can be concluded that the water droplets are well dispersed. The exothermic peaks at -18 °C and -19 °C are believed to be due to formation of ice from bulk water or from aggregates of water droplets. These peaks are relatively small in intensity, and thus indicate there is only a small amount of bulk water or water droplet aggregates. In analyzing the endothermic peaks, it can be seen that the intensity of the peaks are relatively similar in all cycles, indicating that similar amounts of ice formed in each cycles. Thus, it can be concluded that the emulsion remains stable upon ice formation and dissociation.

Figure 2.13(b) shows the thermogram of the ambient pressure DSC test for the mineral oil 70T model emulsion at 50 vol.% water cut. Similar to the 10 vol.% water cut results, there are two exothermic peaks during the cooling process: at -20 °C and at -40 °C. Similarly, the exothermic peaks at -40 °C confirm that the emulsion is indeed a w/o emulsion, with relatively small and well dispersed water droplets (Lachance 2008; Lachance, Sloan, and Koh 2008; Dalmazzone, Noïk, and Clausse 2009; Santini et al. 2007). Comparing the thermogram for 10 vol.% water cut with the thermogram for 50 vol.% water cut, it can be seen here that the exothermic peak for 50 vol.% water cut is at a higher temperature (-40 °C compared to -42 °C). Since the exothermic peak occurs at higher temperature, it can be concluded that the size of the
water droplets is slightly larger at higher water cuts (Dalmazzone, Noïk, and Clausse 2009). The exothermic peak at -20 °C is believed to be due to ice formation from bulk water or water droplet aggregates. The intensity of these peaks is slightly higher compared to the 10 vol.% results, indicating that there is more bulk water or water droplet aggregates as the water cut of the system increases. Similarly, in analyzing the endothermic peak, it can be seen that the intensity of the peak is unchanged from one cycle to the next, indicating that the emulsion remain stable upon ice formation and dissociation.

Figure 2.13: Ambient pressure DSC thermograms for emulsions prepared using mineral oil 70T for (a) 10 vol.% and (b) 50 vol.% water cuts, and emulsion prepared using mineral oil 350T for (c) 10 vol.% and (d) 30 vol.% water cuts. Three cycles performed: cycle 1 (red), cycle 2 (blue) and cycle 3 (green).

Ambient pressure DSC tests were also conducted on model emulsions prepared using mineral oil 350T. The result of the ambient pressure DSC test for mineral oil 350T emulsion at 10 vol.% water cut is shown in Figure 2.13(c). The thermogram of the system shows that there are two
exothermic peaks during the cooling process concentrated at two different regions. The first exothermic peaks are concentrated at between -15 °C and -25 °C, while the second exothermic peaks are concentrated at -40 °C. Similar to the previous analysis of the thermograms, the peaks at -40 °C confirm that the emulsion is w/o emulsion (Lachance 2008; Lachance, Sloan, and Koh 2008; Dalmazzzone, Noïk, and Clausse 2009; Santini et al. 2007). The exothermic peaks concentrated between -15 °C and -25 °C are believed to be due to ice formation from bulk water, or from large water droplet aggregates (Santini et al. 2007). In the heating section of the thermogram, there is only one endothermic peak at 0 °C with similar intensity across all the three cycles performed for ice melting.

Lastly, the thermogram for the ambient pressure DSC test for model emulsion prepared using mineral oil 350T at 30 vol.% water cut is shown in Figure 2.13(d). There are exothermic peaks at -18 °C during the cooling process. It is believed that the peaks are likely due to ice formation from large water droplets. However, ice formation from bulk water is also a possibility and cannot be neglected (Santini et al. 2007). In the heating section of the thermogram, it can be seen that there is only one endothermic peak at 0 °C for ice melting.

2.4.5.2 High Pressure DSC Tests

Analogous to ambient pressure DSC tests, high pressure DSC tests were conducted to determine the stability of the emulsion upon hydrate formation and dissociation. The high pressure DSC test began by inserting ~15 mg of the emulsion sample into the sample cell. Next, the cell was placed into the DSC furnace and was gently tighten to ensure that there was no leakage. The system was then pressurized with methane gas (99.99% ultra high purity, General Air) to 1813 psig. The sample was left at 30 °C and 1813 psig for 3 hours to allow the oil to be saturated with gas. After the saturation process, the sample was cooled from 30 °C to -25 °C at a rate of 0.3 °C/min. Next, the system was heated to 30 °C at similar rate of 0.3 °C/min. Likewise, the cooling and heating process was repeated for another two cycles for the stability test (Lachance 2008).

It should be stated that hydrate formation is a stochastic process. Hydrate formation occurs randomly when the condition is suitable for its formation. Due to the stochastic nature of hydrate formation, in DSC tests, the exothermic peaks for hydrate formation can occur at any temperature. Thus, in analyzing the DSC thermogram for high pressure DSC tests, the endothermic part of the thermogram is more important.
The high pressure DSC test thermogram for mineral oil 70T emulsion at 10 vol.% water cut is shown in Figure 2.14(a). There are several exothermic peaks during the cooling process. These peaks are located at temperatures between -15 °C to -20 °C in all the three cycles performed. At the aforementioned temperature range, the exothermic peaks may be due to either ice or hydrate formation. However, as there is no endothermic peak at 0 °C during heating, there is no ice formation during the cooling process. Thus all of the exothermic peaks are due to hydrate formation. In addition, Figure 2.14(a) shows endothermic peaks at approximately 15 °C for all the three cycles. This endothermic peak is due to hydrate dissociation, and is in good agreement with the methane hydrate equilibrium temperature at 1813 psig, which is reported to be 14.82 °C (Sloan and Koh 2007). It can be also observed that the intensity of endothermic peak for hydrate dissociation remains unchanged in all the cycles performed. Thus, similar amounts of hydrates formed in each cycle, and from discussion earlier, it can be concluded that the emulsion remains stable with hydrate formation and dissociation (Lachance 2008).

Figure 2.14(b) shows the thermogram from the high pressure DSC test for mineral oil 70T emulsion at 50 vol.% water cut. Similarly, there are several exothermic peaks during the cooling process, which correspond to both ice and hydrate formation. The results for this test show that during the first heating cycle there is only one endothermic peak at ~15 °C. corresponding to hydrate dissociation (Sloan and Koh 2007). However, in the second and third heating cycles, Figure 2.14(b) shows that there are two endothermic peaks; one at ~0 °C and the other at ~15 °C. The first endothermic peak (at ~0 °C) is for ice melting, while the second endothermic peak (at ~15°C) corresponds to hydrate dissociation (Sloan and Koh 2007). In analyzing the endothermic peaks, it can be observed that the intensity of the peak decreases from one cycle to the next. Thus, from the discussion earlier, the amount of hydrate formed decreases with the additional cycle performed. Therefore, it can be said that hydrate aggregation occurs upon hydrate formation and dissociation (Lachance 2008; Lachance, Sloan, and Koh 2008).

The thermogram for high pressure DSC studies for mineral oil 350T emulsion at 10 vol.% water cut is shown in Figure 2.14(c). The figure shows that there are several exothermic peaks during the cooling process due to ice and hydrate formation. The heating portion of the thermogram in Figure 2.14(c) shows that there are two endothermic peaks. The first endothermic peak at ~0 °C is due to ice melting, while the second endothermic peak that at ~15 °C is due to methane hydrate dissociation (Sloan and Koh 2007). It can be observed from this figure that the
endothermic peak for ice melting increases from one cycle to the next, while the endothermic peak for hydrate dissociation decreases from one cycle to the next. Thus, the amount of ice formed in the system increases, while the amount of hydrate formed decreases. Due to the decrease in the amount of hydrate formed from one cycle to the next consecutive cycle, it is to be concluded that hydrate particle aggregation occurs in the system upon hydrate formation and dissociation (Lachance 2008; Lachance, Sloan, and Koh 2008).

Figure 2.14: High pressure DSC thermograms for emulsions prepared using mineral oil 70T for (a) 10 vol.% and (b) 50 vol.% water cuts, and emulsions prepared using mineral oil 350T for (c) 10 vol.% and (d) 30 vol.% water cuts. Three cycles performed: cycle 1 (red), cycle 2 (blue) and cycle 3 (green).

High pressure DSC tests were also conducted on model emulsion with mineral oil 350T at 30 vol.% water cut and the results are shown in Figure 2.14(d). Again, it can be seen that there are several exothermic peaks upon cooling, which correspond to both ice and hydrate formation. As
for the heating portion of the thermogram, there are two endothermic peaks; one at ~0 °C for ice melting, while the other at ~15 °C for hydrate dissociation (Sloan and Koh 2007). Similar to the test at 10 vol.% water cut, the intensity of the ice melting peak increases slightly from one cycle to the next, while the intensity of the hydrate dissociation peak decreases slightly from one cycle to the next. Thus, a similar conclusion can be made for this system, where there are hydrate aggregates with hydrate dissociation (Lachance 2008; Lachance, Sloan, and Koh 2008).

2.5. Tests of Model Emulsions for Hydrate Studies

In this work, tests were conducted using the model emulsions systems with in-situ hydrate formation to determine its behavior when gas hydrates are present. The results of the tests were compared with results obtained from studies using crude oil emulsion.

2.5.1 High Pressure Autoclave Study

A high pressure autoclave study was conducted on the model emulsions to compare their behavior from the behavior of an actual crude oil emulsion system. The tests were conducted using a 2-L stainless steel cell that is 9 inches in height and 4 inches in inner diameter. The cell was designed with a false bottom to change the total volume of the system. When the removable false bottom is in place, the total volume of the cell is 1.89 L. The cell has been pressure tested and results shows that it can withstand up to 1494 psig. Agitation of the system was done using a four blades vane impeller. Each blade is 5.5 inches in height and 0.9 inches in diameter. The blades are at a 90° angle from each other. In addition, the high-pressure autoclave setup is equipped with Particle Video Microscope (PVM, Mettler-Toledo®, model 800) and Focus Beam Reflectance Measurement (FBRM, Mettler-Toledo®, model D600X) probes to measure the size of particles. In any autoclave experiment, the cell is placed in an ethylene glycol bath to control the temperature of the system. A schematic of the high pressure autoclave equipment is shown in Figure 2.15. In this work, all high pressure autoclave experiments were performed at constant pressure. The pressure of the system was maintained using an air pressure valve and a reservoir tank. If the pressure in the cell is below the desired set point pressure, the air pressure valve will open and gas from the reservoir tank will be injected into the cell.

The high pressure autoclave experiment begins by first adding 1 L of the emulsion sample into the cell. Next the cell was tightly sealed ensuring there will be no gas leakage. The cell was then placed in the ethylene glycol bath that has been set to a temperature of 20 °C. The motor of
the stirrer was then switched on and the stirring speed was set to 300 RPM. Next, the cell was pressurized to 950 psig. The cell was left at this condition (20 °C, 950 psig and 300 RPM stirring speed) for saturation purposes. The oil is fully saturated with methane when the pressure of the reservoir tank remains constant. This may take up to ~12 hours. Once the oil is fully saturated, the temperature of the cooling bath was changed to 1 °C for the hydrate formation condition, while still maintaining the pressure of the cell at 950 psig and stirring speed of 300 RPM. When hydrates formed in the system, methane molecules in the cell were consumed. Thus, there was a decrease in the pressure of the system. Therefore, there will be rapid injection of methane gas into the cell when hydrate starts to form in the system. The point at which there was rapid injection of methane gas from the reservoir tank was taken to be the first hydrate formation.

Figure 2.15: Schematic of high pressure autoclave equipment (Greaves et al. 2008).

In all experiments, the stirring speed was maintained at 300 RPM. In order to maintain this stirring speed, a different magnitude of current is being supplied to the motor depending on the viscosity of the system; the higher viscosity, the higher magnitude of current needed to be supplied. Thus, for this scope of work, the motor current needed to maintain the stirring speed at 300 RPM was observed throughout the experiment and was used as an indication of the relative viscosity of the fluid/slurry in the cell. In addition to observing the motor current of the system, the amount of methane gas consumed throughout the experiment was used to determine the amount of hydrate formed in the system.

In this work, four different emulsion systems were tested and the results were compared. All of the emulsions are at 30 vol.% water cut. The first emulsion system is mineral oil 70T with 5
wt.% surfactant (Span 80 and AOT). The second system is mineral oil 70T without surfactant, while the third system is mineral oil 350T with 5 wt.% surfactant (Span 80 and AOT). The fourth system is water-in-crude oil emulsion. The crude oil used in this work is West African Crude (WAC).

Results of the high pressure autoclave test are shown in Figure 2.16. In comparing the results in terms of concentration of surfactant, it can be seen that the motor current for mineral oil 70T without surfactant is higher when compared to the motor current for the mineral oil 70T emulsion system (with surfactant). This indicates that without the surfactant, the viscosity of the slurry is much higher, which may be due to the different morphology of the hydrate formed in each system. In order to determine the morphology of the hydrate slurry formed in the cell, the system was quickly vented and the cell was opened. It should be noted that the system needs to be vented quickly so that the morphology of hydrate slurry can be observed before the hydrate dissociates. For mineral oil 70T without the addition of surfactant, large hydrate chunks were seen when the cell was opened, Figure 2.17(a). The hydrate chunks were hard and difficult to be broken up. In contrast, the hydrate slurry observed at the end of the test for the mineral oil 70T emulsion system is shown in Figure 2.17(b). This hydrate slurry is soft and can be easily broken up by hand. The large and hard hydrate chunks for the mineral oil 70T system (without surfactant) is the reason it has a higher relative slurry viscosity.

From the results presented in Figure 2.16(a), the effect of the continuous phase on the hydrate slurry viscosity could be also evaluated. As can be seen, the motor current for the hydrate slurry formed from the mineral oil 70T emulsion is much lower compared to the motor current for the hydrate slurry formed from the mineral oil 350T emulsion, indicating that the latter has much higher relative slurry viscosity. When observing the morphology of hydrate in the different systems, both systems formed a soft hydrate slurry, Figure 2.17(b) and (d). Unlike the effect of surfactant concentration discussed earlier, the difference in relative slurry viscosity of the two systems is due to the viscosity of the continuous phase. From the plot on Figure 2.10(a) and Figure 2.11(a), the viscosity of mineral oil 70T is 20 cP at 25 °C, while the viscosity of mineral oil 350T at similar temperature is 65 cP.

The results of the high pressure autoclave tests for both mineral oil emulsion systems (mineral oil 70T and mineral oil 350T) are being compared with the results obtained from the WAC emulsion test. It can be seen in Figure 2.16(a), for all emulsion tests, the motor current has a
relatively similar general trend. In fact, the value of the motor current for the mineral oil 350T emulsion system is similar to that of the value of motor current for the WAC emulsion system initially and at the end of the experiment. These systems have similar motor current values since the two oils have relatively similar viscosity values. The viscosity of WAC is 60 cP at 25 °C (Rensing 2010). In addition, it was observed that WAC emulsion also formed a soft hydrate slurry (Figure 2.17(c)), similar to that observed for the mineral oil 70T emulsion and mineral oil 350T emulsion. From these results and observations, it can be concluded that the model emulsions developed in this work behave similar to a crude oil emulsion system.

![Figure 2.16](image)

**Figure 2.16:** (a) Absolute motor current required to maintain the stirring speed at 300 RPM and (b) hydrate volume fraction formed in the cell as a function of time for four different systems; mineral oil 70T emulsion (red), mineral oil 70T without surfactant (blue), mineral oil 350T emulsion (green) and WAC emulsion (brown).

As stated earlier, the amount of hydrates formed in the system was also determined and the results are presented in Figure 2.16(b). The results of this analysis show that, all of the emulsion systems formed similar amounts of hydrates, but the formation rate is different for each system. When comparing the formation rate for the mineral oil 70T emulsion with the formation rate for mineral oil 70T without surfactant, it can be seen that hydrate formation is faster in the emulsion system. The different formation rates are due to the size of water droplets. As stated in Section 2.4.2 Microscopy Images, the size of water droplets for mineral oil 70T emulsion is 2 – 3 μm,
while the mineral oil 70T without surfactant is unstable and thus it only creates large water entrainments. The small water droplets in mineral oil 70T emulsion provide large total surface area for hydrate formation, and thus a faster hydrate formation rate. This hypothesis also supports our observation that the initial hydrate formation rate for mineral oil 70T emulsion is faster since the size of water droplets is the smallest compared to other systems.

Figure 2.17: Morphology of hydrate slurries observed at the end of the experiment for (a) mineral oil 70T without surfactant, (b) mineral oil 70T emulsion, (c) WAC emulsion, and (d) mineral oil 350T emulsion.

In comparing the hydrate formation rates for mineral oil 350T emulsion with WAC emulsion, it can be seen that the formation rate for mineral oil 350T emulsion is faster. Both emulsion systems have an average water droplet size in the range of 3 – 5 μm. Thus, the difference in
formation rate may be due to the methane diffusion rate in each oil. The faster the methane diffusion rate, the faster the hydrate formation in the system.

2.6. Chapter Concluding Remarks

Stable emulsions without phase separation and sedimentation have been developed for gas hydrate studies. The emulsions use either mineral oil 70T or mineral oil 350T as the continuous phase. A mixture of Span 80 and AOT at a mass ratio of 90:10 for mineral oil 70T and 75:25 for mineral oil 350T were used as the surfactant agents. For mineral oil 70T, stable emulsions could be formed up to 70 vol.% water cut; while for mineral oil 350T, stable emulsions could only be formed up to 40 vol.% water cut.

Characterization tests have been performed on these w/o emulsions. Classical bottle tests show that the emulsions are highly stable against water droplet coalescence, up to one week after the emulsification process. Next, optical microscopy image analysis conducted on these emulsions show that the average size of water droplets is in the range of 2 – 3 μm and 3 – 5 μm for mineral oil 70T and mineral oil 350T emulsions, respectively. Rheological measurements show that there is a strong dependency of the viscosity on the water volume fraction (water cut); increases in water cut increase the viscosity of emulsion. In addition, the emulsion shows shear thinning behavior above certain water cuts (≥30 vol.% water (25 °C) and ≥20 vol.% water (1 °C) for mineral oil 70T; ≥20 vol.% water (25 °C) and ≥10 vol.% water (1 °C) for mineral oil 350T). The DSC tests performed also show that the emulsions are highly stable upon ice and hydrate formation/dissociation. Finally, tests performed using this model emulsions using a high pressure autoclave show that the emulsions have similar behavior as water-in-crude oil emulsions.
Viscosity measurements of both model emulsion systems (water in 70T and 350T mineral oil) were made at various temperatures, pressures and water cuts. Measurements were made over a small temperature and pressure range. The experimental conditions were based on the experimental conditions that would be used for rheology investigations of gas hydrate slurries. Based on the work performed by Grunberg et al. (1949) and Sudduth (1993), generalized equations for both model emulsions were developed. The generalized equations are functions of the aforementioned variables (P,T, water vol.%). Comparisons between the experimental data and the generalized equations show that the generalized equations were able to predict the viscosity of the emulsion fairly accurately at low temperatures (≤ 10 °C) that are in the hydrate stability region.

3.1. Background and Motivation of Work

As stated in Chapter 1, a new method for controlling hydrate formation in subsea oil/gas flowlines is “hydrate management”. One hydrate management method is the application of a low dosage hydrate inhibitor – anti-agglomerant (LDHI-AA). In this case, hydrate particles are allowed to form in the pipelines, but their properties are controlled by injecting a small amount of LDHI (~ 1-2 wt. % of LDHIs compared to ~ 40 vol.% THIs) to prevent flowlines blockage. Due to the low concentration of LDHIs needed to prevent blockage, LDHIs can be more economical than THIs, and thus “hydrate management” has gained a lot of interest in the oil/gas industry. However, it is noted that for “hydrate management” to be implemented safely, there is a need for better prediction of the viscosity of hydrate slurries. This will allow flow assurance engineers to prevent flowline plugging. Thus, this doctoral thesis focused on understanding and quantifying the effect of gas hydrate particles on the viscosity of fluids in flowlines. In order to understand the viscosity of hydrate slurries, the viscosity of the emulsion (prior to hydrate formation) needs to be investigated and understood first. From this understanding, the effect of hydrate particles on the viscosity of the system can be quantified.
3.2. Complexity of Hydrate Slurries Rheological Measurements

The study of hydrate slurry rheological properties is a complex process as there are several variables that can affect the viscosity of the slurry. Figure 3.1 is a conceptual picture that describes this complexity. As can be seen from this figure, there are at least five different variables that can affect the viscosity of the system; the type of oil used, amount of water, temperature, composition of dissolved gas (pressure), as well as the amount and distribution of hydrate particles in the system.

![Diagram of hydrate slurries rheological measurements.](image)

**Figure 3.1:** Complexity of hydrate slurries rheological measurements. The variables that can affect the viscosity of the slurries.

The first variable that can affect the viscosity of the system is the type of oil used. In general the viscosity of the oil depends on the composition of the oil. As the amount of longer carbon chains in the system increases, the viscosity of the system increases (Bird, Stewart, and Lightfoot 2007). Therefore, the results of absolute viscosity of a hydrate slurry experiment will depend on the type of oil used in the study. In addition, the composition of the oil also affects the amount of gas dissolved, and thus affects the viscosity of the system.

The second variable that can affect the viscosity of a hydrate slurry is the amount of water in the system. In this work, water is added in the system creating an emulsion. The interaction between water droplets increases the viscosity of the system (Minana-Perez et al. 1986). Thus, as the amount of water increases (water cut), there will be more water droplets present and thus
more interactions in the system. These interactions increase the viscosity of the system (Pérez et al. 2002).

The third variable, that adds complexity in the study of rheological measurements of gas hydrate slurries, is the composition of dissolved gas. In this scope of work, hydrates are formed at high pressure conditions. At high pressure, some of the gas molecules dissolve in the oil phase. As gas molecules dissolve in the oil, the viscosity of the oil is reduced. As stated earlier, the amount of gas dissolved in the oil depends on the composition of the oil. The more gas dissolved in the oil, the larger the viscosity decrease observed in the system (Bird, Stewart, and Lightfoot 2007). In order to quantify the effect of hydrates on the viscosity of the system, the composition of gas dissolved in the oil phase, as a function of temperature and pressure needs to be determined. Furthermore, the viscosity of the system as a function of amount of dissolved gas needs to be determined.

In this work, the temperature of the system is the fourth variable that can affect the viscosity of hydrate slurry. In this work, the temperature of the system has two competing effects. Firstly, it is widely known that when the system temperature decreases, the viscosity of the system increases (Wilkes 2008; Deen 1998; Bird, Stewart, and Lightfoot 2007). Simultaneously, as the temperature of the system decreases, the amount of gas dissolved in the oil phase increases. This will then decrease the viscosity of the system. This competing effect adds complexity to hydrate slurry investigations.

Finally, the last variable that affects the viscosity of the system is the amount and distribution of hydrate particles. Since hydrate particles are solid, the viscosity of the system increases dramatically when hydrates start to form in the system (Rutgers 1962b). The more solid particles present (i.e. more hydrate particles formed) in the system, the larger the increase in the viscosity of the system (Rutgers 1962b; Sudduth 1993). Furthermore, the distribution of solid particles can also affect the viscosity of the system. For instance, when the system has a narrow particle size distribution, the viscosity of the system is higher compared to when the system has a large particle size distribution (Rámirez et al. 2002; Pérez et al. 2002).

In summary, there are several variables that affect the viscosity of a hydrate slurry. The effects of each variable on the viscosity of the system need to be investigated and quantified independently, in order to predict the net effect of all variables on the viscosity of the system.
From this understanding, it is suggested that the viscosity of a hydrate slurry at any given conditions (oil, temperature and pressure) can be predicted.

### 3.3. Baseline Viscosity Measurements

As stated in Section 3.2 Complexity of Hydrate Slurries Rheological Measurements, there are five different variables that can change/affect the viscosity of the system. Thus, in this work baseline measurements were conducted to determine and quantify the effect of each variable on the viscosity of the system. Each of the aforementioned variables was investigated independently ensuring that hydrate particles did not form during the experimental process.

Several tests were conducted in this work over a specific pressure and temperature range. These tests were chosen based on the temperature and pressure range that a hydrate slurry experiment would be performed. Table 3-1 summarizes the variables that were investigated as baseline measurements in this work.

**Table 3-1:** Experimental matrix of the baseline measurements.

<table>
<thead>
<tr>
<th>Type of Oil</th>
<th>Water Cut [%]</th>
<th>Temperature [°C]</th>
<th>Pressure [psig]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Oil 350T (350T)</td>
<td>0-30</td>
<td>5,10,20</td>
<td>0,800-1500</td>
</tr>
<tr>
<td>Mineral Oil 70T (70T)</td>
<td>0-30</td>
<td>5,10,20</td>
<td>0,800-1500</td>
</tr>
</tbody>
</table>

**3.3.1 Experimental Procedures for Baseline Measurements**

The experimental procedures for baseline measurements consist of two parts. The first part is sample/emulsion preparation, while the second part is viscosity/torque measurements.

**3.3.1.1 Sample/Emulsion Preparation**

In this work, the sample/emulsion was prepared using the experimental procedures described in Section 2.3.1 Emulsification Process for Model Emulsion Systems.

**3.3.1.2 Viscosity/Torque Measurements**

The viscosity/torque measurements were conducted using the procedures described below.
1. Rheometer calibration: Two different calibrations of the rheometer were performed: friction calibration and inertia calibration.

2. Sample addition to the rheometer cell: The sample/emulsion was added into the rheometer cell. The amount of sample needed is ~27 ml. This is enough to cover the vane impeller at full saturation of the oil.

3. Temperature set point: the temperature of the system was set to the desired temperature condition.

4. Pressure set point: the pressure of the system was set to the desired pressure condition. The pressure of the system was kept constant by the use of an ISCO pump.

5. Flow curve: The sample was stirred at 477 rpm for approximately 2 hours, or until the system reaches steady state. In this work, the steady state condition is defined as the minimal change in both viscosity/torque values obtained from the rheometer and the volume of the ISCO pump. This indicates there is no further saturation of the gas molecules into the oil phase.

6. Steps 4 and 5 were repeated at other conditions, as described in Table 3-1.

3.3.2 Experimental Results for Baseline Measurements

The experimental results of the baseline measurements performed on mineral oil 350T and mineral oil 70T at various water cuts and temperatures are shown in Figure 3.2 and Figure 3.3, respectively. Regardless of the water cut, the viscosity of the emulsion decreases exponentially with increasing pressure. This observation is in qualitative agreement with viscosity measurements of saturated oil at various pressures and temperatures reported by others (Simon and Graue 1965; Bird, Stewart, and Lightfoot 2007). Based on the literature review performed, most researchers modeled the viscosity data based on Equation (3-1) shown below.

\[
\eta = A_0 e^{b_0 P}
\]  

(3-1)

In Equation (3-1), \(\eta\) is viscosity of the emulsion, \(P\) is the pressure of the system, \(A_0\) is a pre-exponential term and is defined as the viscosity of the emulsion at atmospheric pressure. It should be noted that from the results were obtained in this work, it was observed that the term \(A_0\) depends on other variables including temperature and water cut. The final term in Equation
(3-1), $B_0$ is related to the properties of the oil. In other words, the term $B_0$ represents the interaction between the components in the mineral oil and the gas molecules.

**Figure 3.2:** Experimental results for mineral oil 350T baseline measurements for two different temperatures (a) 10°C and (b) 5°C, at three different water cuts (10 vol.% in red, 20 vol.% in blue, and 30 vol.% in green).

**Figure 3.3:** Experimental results for mineral oil 70T baseline measurements for two different temperatures (a) 10°C and (b) 5°C, at three different water cuts (10 vol.% in red, 20 vol.% in blue, and 30 vol.% in green).

From Figure 3.2 and Figure 3.3, the viscosity of the model emulsion is observed to depend on three different variables; temperature, composition (water cut of the emulsion), as well as the
saturation of the oil (depends on both temperature and pressure). Thus, the general equation that needs to be developed must contain all of the aforementioned variables.

### 3.3.3 Development of Generalized Equation for Emulsion Systems

As mentioned earlier, the term $B_0$ in Equation (3-1) is related to the properties of the oil and the amount of gas dissolved in the oil phase. Since the saturation of oil depends on both the temperature and pressure conditions, Equation (3-1) was updated with the term $n(T, P)$, the moles of methane dissolved in the oil phase as shown in Equation (3-2). Further analysis of the data confirmed that the data fit was improved by using the saturation term, rather than the pressure variable in the exponential.

$$
\eta = A_0 e^{-B_0 n(T, P)} \tag{3-2}
$$

Next, Equation (3-2) was updated to take into account a higher order interaction between the oil and gas molecules. Based on the literature review performed, the viscosity of ideal mixtures can be expressed by Equation (3-3) shown below, where $\eta_{mix}$ is the viscosity of the mixture, $\eta_1$ and $\eta_2$ are the viscosities of individual components, and $x_1$ and $x_2$ are the mole fractions of each component (Zhmud 2014; Grunberg and Nissan 1949).

$$
\ln(\eta_{mix}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) \tag{3-3}
$$

As Equation (3-3) was designed for ideal mixtures, Grunberg and Nissan improved the equation to take into account the non-ideality of the mixtures. The updated equation is shown in Equation (3-4), whereby the term $g$ in the equation is the interaction between component 1 and 2.

$$
\ln(\eta_{mix}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + x_1 x_2 g \tag{3-4}
$$
For a binary system, the mole fraction can be simplified by noting that $x_2 = 1 - x_1$. Thus by simplification, Equation (3-4) can be expressed by Equation (3-5).

\[
\eta_{mix} = \eta_2 \left( \frac{\eta_1}{\eta_2} \right)^{x_1} e^{a(x_1, x_2)} \tag{3-5}
\]

Equation (3-2) was used as the basis for developing a generalized equation for the emulsion system used in this work, and was compared with the equation for mixtures, shown in Equation (3-5). It can be seen that Equation (3-5) contains a quadratic equation in the exponential term. This quadratic term takes into account higher order interactions between the two components. Similarly, in the generalized equation higher order interactions between the gas and oil molecules needs to be taken into account. Therefore, an updated equation of the generalized equation is shown in Equation (3-6).

\[
\eta = A_0 e^{(B_0 \eta(T,P) + B_1 \eta^2(T,P))} \tag{3-6}
\]

As stated earlier, that the viscosity of the system depends on three different variables; composition, temperature and saturation. Equation (3-6) above takes into account the effect of saturation. In order to take into account the effect of composition and temperature, an assumption was made to further improve Equation (3-6). In this work, it was assumed that the effect of composition and temperature are independent of each other. Therefore, the term $A_0$ in Equation (3-6) can be expressed in terms of two different functions, as shown in Equation (3-7).

\[
\eta = A_1(T) A_2(\phi) e^{(B_0 \eta(T,P) + B_1 \eta^2(T,P))} \tag{3-7}
\]

In this equation, $A_1(T)$ describes the effect of temperature on the viscosity of the continuous phase (oil). $A_2(\phi)$ on the other hand describes the effect of composition (water cut) on the
viscosity of the system. It should be noted that $A_2(\phi)$ is expressed as relative viscosity, that is, the viscosity of the emulsion relative to the viscosity of the continuous phase.

Further discussions in this chapter (Section 3.3.3.1 to 3.3.3.2) explain how each of the functions and terms in Equation (3-7) were obtained.

3.3.3.1 Obtaining the $A_1(T)$ Function

In order to obtain the function of $A_1(T)$ in Equation (3-7), several simplifications had to be made. The first simplification that was made is on the composition term $A_2(\phi)$ of the equation. As stated in Section 3.3.3 Development of Generalized Equation for Emulsion Systems, the function $A_2(\phi)$ is expressed relative to the viscosity of the continuous phase. Thus, data on the viscosity of the continuous phase (i.e. 0 vol.% water cut) were analyzed. By this simplification, the function $A_2(\phi)$ can be expressed as Equation (3-8), and therefore Equation (3-7) is simplified to Equation (3-9).

$$ A_2(\phi) = 1 \quad (3-8) $$

$$ \eta = A_1(T)e^{b_P(T,P)\beta_2n^2(T,P)} \quad (3-9) $$

The next simplification that was made on Equation (3-9) was for the saturation term in the equation. Similarly, the viscosity data at 0 psig were analyzed. By this simplification, there is no methane gas dissolved in the oil phase. Mathematically, this simplification can be expressed as Equation (3-10). Thus, Equation (3-9) is simplified to Equation (3-12).

$$ n(T, 0) = 0 \quad (3-10) $$

$$ \therefore \ e^{B_P(T,P)\beta_2n^2(T,P)} = e^0 = 1 \quad (3-11) $$

$$ \eta = A_1(T) \quad (3-12) $$
From Equation (3-12), it can be seen that the function \( A_i(T) \) describes the effect of temperature on the viscosity of the continuous phase. It is known that the viscosity of fluid is inversely proportional to the absolute temperature of the fluid (Bird, Stewart, and Lightfoot 2007; Deen 1998). Figure 3.4 below shows the relationship between temperature of the fluids and the corresponding viscosity for both mineral oils that were used in this work.

![Figure 3.4](image)

**Figure 3.4:** Relationship between temperature and viscosity for the two mineral oils: (a) mineral oil 350T and (b) mineral oil 70T.

As can be seen in both plots in Figure 3.4, the viscosity of the two mineral oils is linearly proportional to the inverse temperature of the fluids, in the temperature range that was investigated in this work, which is consistent with literature (Deen 1998; Bird, Stewart, and Lightfoot 2007). The relationship between temperature of the oils and viscosity is shown in Equation (3-13) and Equation (3-14) for mineral oil 350T and mineral oil 70T, respectively. It should be noted that in this correlation, the coefficient of determination, \( R^2 \) for both equations are 0.97 for mineral oil 350T and 0.94 for mineral oil 70T.

\[
A_{i,(350T)}(T) = 6.81 \times 10^5 \left( \frac{1}{T} \right)^{-2.27 \times 10^3} 
\]

\[
A_{i,(70T)} = 2.08 \times 10^5 \left( \frac{1}{T} \right)^{-695} 
\]
where

\[ T = \text{Temperature [K]} \]

### 3.3.3.2 Obtaining the \( A_2(\phi) \) Function

The function \( A_2(\phi) \) in Equation (3-7) describes the composition effect on the viscosity of an emulsion. There are several models in the literature that describe the relative viscosity of suspensions as a function of concentration (Rutgers 1962a; Rutgers 1962b; Mueller, Llewellin, and Mader 2009; Sudduth 1993). In rheology of suspensions studies, the relative viscosity of a suspension can be divided into dilute and concentrated regimes (Mueller, Llewellin, and Mader 2009).

For a dilute regime, the particle volume fraction \( \phi \), should be less than 0.01 (\( \phi \leq 0.01 \)) (Rutgers 1962a). For this regime, the most common relative viscosity model is the Einstein equation, as shown in Equation (3-15). In this equation, the term \( \eta_r \) is the relative viscosity of the system and the term \( B \) is the “Einstein Coefficient”. According to the work performed by Mueller et al., the value of \( B \) is usually taken to be 2.5, but has been reported to be in the range of \( 1.5 \leq B \leq 5 \) (Mueller, Llewellin, and Mader 2009).

\[
\eta_r = 1 + B\phi \tag{3-15}
\]

For the concentrated regime, Krieger and Dougherty developed an expression for relative viscosity \( \eta_r \) taking into account the interaction between particles (Rutgers 1962a; Rutgers 1962b). The equation developed by Krieger and Dougherty is shown in Equation (3-16). In this equation, the variable \( B \) is the “Einstein Coefficient”, while \( \phi_{\text{max}} \) is the maximum packing of the particle and are taken to be either 0.74 or 0.64 (Rutgers 1962a; Rutgers 1962b; Mueller, Llewellin, and Mader 2009).

\[
\eta_r = \left(1 - \frac{\phi}{\phi_{\text{max}}} \right)^{-B\phi_{\text{max}}} \tag{3-16}
\]
However, in analyzing the data obtained in this work, both Einstein and Krieger Dougherty equations fail. Thus, improvements on these models were made based on the work performed by Richard D. Sudduth (Sudduth 1993). In summary, Sudduth stated that the models of relative viscosity available in the literature differ only in the interaction parameter (fitting parameter). Therefore, according to the Sudduth, the model of relative viscosity can be expressed by the differential equation shown in Equation (3-17), where $\sigma$ is the interaction/fitting parameter that is not necessarily a whole number.

\[
\frac{d\eta}{\eta} = B \left(1 - \frac{\phi}{\phi_{\text{max}}}\right)^\sigma d\phi
\]  

(3-17)

Based on Equation (3-17), if $\sigma$ has a value of 0, the differential equation integrated to the Einstein equation; while if $\sigma$ has a value of 1, the differential equation integrated to the Krieger Dougherty equation. In this work, the value of $\sigma$ was determined by the method of minimization of error using viscosity data of the emulsion at only 0 psig at various water cuts. The value of $\sigma$ for the two emulsion systems used in this work is shown in Table 3-2 below. Figure 3.5 shows the comparison between the data and the model developed using Equation (3-17) and the parameters stated in Table 3-2 for both emulsion systems: mineral oil 350T and mineral oil 70T.

![Figure 3.5: Comparison between the data and model developed in this work for (a) mineral oil 350T and (b) mineral oil 70T.](image-url)
Table 3-2: Value of $\sigma$ parameters used in Equation (3-17) for emulsion system.

<table>
<thead>
<tr>
<th>Type of Mineral Oil</th>
<th>350T</th>
<th>70T</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>1.78</td>
<td>1.58</td>
</tr>
</tbody>
</table>

3.3.3.3 Obtaining Methane Saturation in Oil, $n(T, P)$

In this work, the moles of methane gas dissolved in the oil phase at various temperatures and pressures were determined experimentally. In addition, based on the composition analysis of the two mineral oils that were used in this work, a simulation study was conducted using Multiflash® to determined the moles of methane dissolved in the oil phase. In both calculations, the amount of methane dissolved in the oil, $n(T, P)$ is reported in the units of moles of methane dissolves per volume of oil [mol/cm$^3$]. The compositions of the two mineral oils are provided in the APPENDIX A. Comparison results of methane gas saturation determined from Multiflash® simulations and from the experimental results for mineral oil 350T and mineral oil 70T are shown in Figure 3.6.

![Figure 3.6](image)

**Figure 3.6:** Comparison between the saturation of methane gas obtained from Multiflash® and experimental results for mineral oil 350T and mineral oil 70T.

From Figure 3.6, it can be seen that the result obtained from Multiflash® simulations is relatively close with the result obtained from experiment. Analysis of these results shows that the
error between the Multiflash® simulation and experimental data is within 5% and 8% for mineral oil 350T and mineral oil 70T respectively.

### 3.3.3.4 Obtaining the $B_1$ and $B_2$ constants

In Equation (3-7), there are two constants that describes the interaction between the gas molecules and the oil composition; $B_1$ and $B_2$. In this work, the values of these constants were determined using minimization of error between the data and the equation. It should be noted that only the viscosity data of the emulsion at 10 vol.% water cut were used to determine the values of the two constants. The values of these two constants are reported in Table 3-3.

**Table 3-3:** Values of the two constants $B_1$ and $B_2$.

<table>
<thead>
<tr>
<th>Type of Mineral Oil</th>
<th>350T</th>
<th>70T</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$ [cm³/mol]</td>
<td>-95</td>
<td>-68</td>
</tr>
<tr>
<td>$B_2$ [cm⁶/mol²]</td>
<td>990</td>
<td>666</td>
</tr>
</tbody>
</table>

### 3.3.4 Comparison Between Emulsion Viscosity Data with Generalized Model

Figure 3.7 and Figure 3.8 show the comparison between the viscosity data and model at two different temperatures for mineral oil 350T and mineral oil 70T, respectively. It should be noted that in developing the generalized model equation for the emulsion, only a small range of selected data mentioned earlier were used to develop each function in (3-7). A small temperature range was chosen, since this is the range that the rheology investigations would be performed for gas hydrate slurries. Furthermore, this is also the temperature range that is typically found in subsea oil/gas flowlines. From Figure 3.7 and Figure 3.8, it can be concluded that regardless of the type of mineral oils and water cut of the emulsion, the model was able to predict the viscosity of the emulsion fairly accurately (i.e. within ±13 %).
3.4. Chapter Concluding Remarks

In summary, the viscosity of the model emulsions was measured over a range of temperature (5 – 20 °C) and pressure (0 – 1500 psig) conditions. This range is within the typical subsea oil and gas flowline condition. Based on the work of Grunberg et al. (1949) and Sudduth (1993), as well as by making certain simplifications, generalized equations were developed for both the...
model emulsions. The generalized equations are a function of temperature, pressure and water cut. Tests on the generalized equations show that the equations are able to predict the viscosity of emulsions fairly accurately (within ± 13%) in the hydrate stable region. Thus, the equations can be used to quantify the effect of hydrate particles on the viscosity of the system.
CHAPTER 4
VISCOSITY MEASUREMENTS AND ANALYSIS OF GAS HYDRATE SLURRIES FORMED FROM MODEL WATER-IN-OIL EMULSIONS

In-situ viscosity measurements of gas hydrate slurries formed from model w/o emulsions were conducted using a high pressure rheometer equipped with a four-blades straight vane impeller. Similar to viscosity measurements of emulsions (discussed in Chapter 3), two model emulsion systems were used for hydrate slurries studies: mineral oil 350T emulsion and mineral oil 70T emulsion. In this work, viscosity measurements were made at a constant pressure of 1500 psig, a constant temperature of 1 °C and a constant mixing speed of 477 RPM. The water cut of the system was varied from 5 – 30 vol.% for mineral oil 350T emulsion and from 5 – 50 vol.% water cut for mineral oil 70T emulsion.

Results of the viscosity measurements are presented in terms of relative viscosity, where the viscosity of the continuous phase was chosen as the baseline for the analyses. A new relative viscosity model for hydrate slurries at steady state flow has been developed as a function of hydrate volume fraction. Relative viscosity was also analyzed at the extreme peaks of the hydrate slurries viscosity profile. For the first time, the relative viscosity at extreme peaks was analyzed using a proper baseline to determine the possibility of using it as an early warning sign for potential plugging. However, results of the analysis the values of relative viscosity alone could not be used as an early warning sign.

Finally, hydrate formation and viscosity of gas hydrate slurries were also investigated near the inversion point of the emulsion in a rheometer. The test results show that emulsion breaking occurs after a certain amount of methane hydrate had formed in the system. Emulsion breaking is defined as a phenomenon where the two immiscible liquids (oil and water) phase separated. This emulsion breaking was confirmed by dispersion tests conducted at the end of rheology measurements.

4.1. Background and Motivation of Work

It is known that the formation of gas hydrates in oil/gas pipelines will increase the viscosity of the fluid/slurry (Webb, Koh, and Liberatore 2013; Webb 2013; Rensing 2010; Zylyftari, Lee, and Morris 2013; Peixinho et al. 2010; Camargo and Palermo 2002). Since the “hydrate management” method has gained a lot of interest by the industry and hydrate field, there is a
growing need to understand the effect of gas hydrates on the viscosity of w/o emulsions. In fact, it is believed that by having a reliable and accurate viscosity model for gas hydrate slurries, there will be better prediction and prevention of gas hydrate plugging in pipelines.

Several attempts have been made to develop a model for gas hydrate slurries. One such attempt was made by Camargo et al., where a flowloop was used to predict the viscosity of the gas hydrate slurry (Camargo and Palermo 2002; Camargo et al. 2000). The use of a flowloop provides a major advantage, as the system is closer to actual conditions in oil/gas pipelines. However, in this method, the viscosity was calculated rather than directly measured. This may lead to low accuracy in the viscosity values obtained.

In order to improve the accuracy of viscosity values obtained, some researchers have used a rheometer to directly measure the viscosity of gas hydrate slurries. Peixinho et al. performed measurements on cyclopentane hydrate slurries (Peixinho et al. 2010). As cyclopentane hydrates form at atmospheric pressure, this system might not be a good representation of oil/gas pipelines. In 2010, P J Rensing used a high-pressure rheometer to investigate the viscosity of methane hydrate as well as ice slurries using a crude oil emulsion (Rensing et al. 2011; Rensing 2010). However, there was an issue of reproducibility of the results due to the variability of crude oil samples/compositions. Hence, in 2013, E B Webb used a model w/o emulsion to perform viscosity measurements of methane hydrate slurries (Webb, Koh, and Liberatore 2013; Webb 2013). However, the model emulsion used in the mentioned work was comprised of small water droplets that are not representative of that found in oil/gas pipelines.

Therefore in this doctoral thesis work, the viscosity of gas hydrate slurries was investigated using model w/o emulsions, that have been shown to have similar behavior of crude oils. These systematic and repeatable measurements were used to develop a new viscosity model for hydrate slurries.

4.2. Experimental Methodology

This section describes the high pressure rheometer setup that was developed for the hydrate slurry rheology experiments. This setup consists of high pressure rheometer and high pressure ISCO pump. In addition, this section also describes the experimental procedures used in this doctoral work to measure the viscosity of gas hydrate slurry formed from model water-in-oil (w/o) emulsion.
4.2.1 Rheometer Equipment Setup

Figure 4.1 shows a schematic diagram of the high pressure rheometer system, which consists of two major components. The first major component is the Discovery Hybrid Rheometer-2 (DHR-2) purchased from TA-Instruments. The rheometer contains a pressure cell that can withstand a maximum pressure of 2000 psia. The operating temperature for this rheometer is between -40 to 150 °C. The dimensions of the pressure cell are 28 mm in diameter and 50 mm in height. In this work, viscosity measurements were conducted using a straight four blades vane impeller such as shown in Figure 4.1. Each blade is 13 mm in width and 48.1 mm in height and at 90° to each other. The impeller is connected to a rotor that has a magnet. Another high power magnet is connected to the rheometer spindle. The use of these magnets allows viscosity measurements to be performed at high pressure.

![Image of high pressure rheometer system]

Figure 4.1: Schematic of high pressure rheometer system.

The second component of the rheometer system is the high pressure ISCO pump. This high pressure ISCO pump is directly connected to the rheometer pressure cell to maintain the pressure in the rheometer cell. In this work, an ISCO 500D syringe pump by Teledyne Isco was used. ISCO 500D has a capacity of 507 ml and a maximum operating pressure of 3750 psi. The system can be operated in constant pressure mode or constant flow mode, with a flow range between 0.001 to 204 ml/min.
4.2.2 Experimental Procedures for Viscosity Measurements of Gas Hydrate Slurries

The viscosity measurements of gas hydrate slurries using the high pressure rheometer consist of three main steps, as listed below:
1. Emulsification process
2. Saturation of emulsion with methane gas
3. Gas hydrate viscosity measurements

4.2.2.1 Emulsification Process

The emulsion used in this work was prepared using the procedures described in Section 2.3.1 Emulsification Process for Model Emulsion Systems.

4.2.2.2 Saturation of Emulsion with Methane Gas

After the emulsification process, ~27 mL of the emulsion was injected into the rheometer pressure cell. The temperature of the system was then set to 20°C. The rheometer cell was then purged with methane gas to remove air the rheometer cell. Next, the cell was slowly pressurized to 1500 psig. Subsequently, an ISCO pump was then set to operate in a constant pressure mode (constant P = 1500 psig). Following this step, the rheometer was set up to stir the sample at 477 rpm for 4 hours. This provides enough time for the emulsion to reach full saturation. Full saturation of the emulsion was confirmed when the volume of the ISCO pump remain unchanged.

4.2.2.3 Gas Hydrate Slurry Viscosity Measurements

After the emulsion is fully saturated with methane gas, viscosity measurements of the gas hydrate slurry can be performed. The viscosity measurements consist of the steps listed below:

1. Cooling of sample:
The sample was cooled from 20 °C to 1 °C at a rate of 0.5°C/min, while maintaining the pressure of the system at 1500 psig and stirring speed of 477 RPM.
2. Hydrate formation under flow and viscosity measurements:
The system was stirred at 477 RPM, 1 °C, and 1500 psig until gas hydrates formed in the system. The formation of gas hydrate was confirmed by a sudden and rapid increase in the viscosity of the system. In addition, the formation was also confirmed by the decrease in the volume of the ISCO pump. Since the ISCO pump was set to operate at a constant
pressure mode, the decrease in the ISCO pump indicates that methane is being consumed for hydrate formation. The system was continued to be stirred at 477 RPM, 1 °C, and 1500 psig until the system reaches steady state. Steady state is defined as minimal change in both the viscosity values and volume of the ISCO pump.

3. *Heating of the sample (dissociation):*

After the system has reached steady state, the system was heated back to 20 °C at a rate of 0.5 °C/min, while maintaining the pressure at 1500 psig and stirring speed at 477 RPM.

4.3. **Experimental Results and Analysis**

This section of the thesis describes the experimental results and analysis of the experiments. The results of the tests include the different regions of viscosity profiles and the mass balance calculated for hydrate volume fraction determination. In addition, results of the viscosity profiles were also analyzed in terms of relative viscosity for model development.

4.3.1 **Hydrate Slurries Viscosity Profiles**

The results of the in-situ hydrate formation and viscosity measurements for both model emulsion systems are shown in Figure 4.2. In both model emulsion systems, hydrate slurry experiments were conducted for water cut range of 5 to 30 vol.% water cut. In general, regardless of the water volume fraction, the viscosity profile of a gas hydrate slurry can be divided into four different regions: (1) initial viscosity increase region, (2) constant viscosity region, (3) sudden and rapid viscosity increase region, and lastly (4) gradual viscosity decrease region.

In the first region, which is the initial viscosity increase region, the emulsion is slowly being cooled from 20 °C to 1 °C. Due to this cooling process, the viscosity of the emulsion gradually increases as the temperature of the system decreases (*cf.* Bird, Stewart, and Lightfoot 2007; Deen 1998). Following this initial increase region (1), there is a constant viscosity region (2), during which there is relatively no change in the viscosity of the system. The reason for this is that gas hydrates have not formed in the system since hydrate formation is stochastic. Therefore, in this region, the reported viscosity values are the viscosity of the saturated emulsion at the experimental conditions (1 °C and 1500 psig of methane).
When gas hydrates start to form in the system, the viscosity profile enters the next region (3), in which there is a sudden and rapid increase in the viscosity. In previous studies of hydrate rheology, this sudden increase was attributed to the formation of gas hydrates in the system (Webb 2013; Webb, Koh, and Liberatore 2014; Peixinho et al.). In this work, it is believed that there are two reasons for this rapid increase in the viscosity of the system. Firstly, the viscosity increases because hydrate formation changes the system from being an emulsion to a solid suspension. The viscosity of a solid suspension has been shown to be higher than the viscosity of emulsions (Rutgers 1962a). Secondly, the rapid increase in the viscosity is believed to be due to the depletion of methane gas in the oil phase of the slurry. For an oil-dominated system, hydrate formation consumes gas that is present in the oil phase (Sloan and Koh 2007). Therefore, when hydrates start to form, this depletes the methane composition in the oil phase (Webb 2013). As discussed in Chapter 3, this gas depletion increases the viscosity of the continuous phase and at same time increases the viscosity of the slurry.

![Figure 4.2: In-situ methane hydrate formation and viscosity measurements at various water cuts formed from (a) mineral oil 350T and (b) mineral oil 70T model emulsion. The conversion of water to hydrates for mineral oil 350T is above 68% while for mineral oil 70T is above 49 vol.%](image)

The last region (4) in hydrate slurry profile shows a gradual decrease in viscosity. Currently there are two hypotheses for this observation. The first hypothesis considers the re-saturation of the oil with methane gas. Since gas hydrate formation depletes the methane gas in the oil phase, there is a strong driving force for the methane in the gas phase to re-dissolve in the oil phase. In
this work, the phenomenon is called the re-saturation of the oil. As more methane gas dissolves in the oil phase (after hydrates have formed), the viscosity of the oil starts to decrease (as shown in Chapter 3). Consequently the viscosity of the slurry decreases. The second proposed hypothesis is that the decrease in viscosity may be due to particle break-up and rearrangement. When the large particles break up, the effective volume fraction decreases and this decreases the viscosity of the slurry (Hasan and Shaw 2010; Pal 2011).

Several observations can be seen in Figure 4.2. Firstly, in both emulsion systems, the viscosity of the gas hydrate slurry generally increases with increasing water cut. The increase in the viscosity is due to the increased amount of solid hydrate volume fraction (cf. Mueller, Llewellyn, and Mader 2009; Jeffrey and Acrivos 1976; Rutgers 1962a). Noted that the increase in solid hydrate volume fraction as the water volume fraction increases was also confirmed by mass balance calculations performed (Table 4-1 and Table 4-2).

As described in Section 4.2.1 Rheometer Equipment Setup, the system used for hydrate slurry experiments is a closed system. Therefore, by calculating the difference between the moles of methane at the beginning and at the end of test, methane consumption for both oil saturation and hydrate formation can be determined. The results of the mass balance studies are shown in Table 4-1 and Table 4-2.

In this work, consumption of methane is only due to the following two reasons: (1) saturation of the oil and (2) formation of gas hydrates. As discussed in Chapter 3, the moles of methane required for full saturation of the oil phase has been determined from baseline measurements, as well as Multiflash® simulations. The moles of methane needed for full conversion can be determined using CSMGem (Sloan and Koh 2007). Therefore, the values reported in the second column of Table 4-1 and Table 4-2, theoretical methane consumption, was the total methane needed for full saturation of the oil and the full conversion of water to hydrate (determined both from Multiflash and CSMGem). On the other hand, the actual methane consumption reported in the third column, was determined using the temperature, pressure and volume conditions and an equation of state at the beginning and end of the experiment. The fourth column in Table 4-1 and Table 4-2, the percentage difference, is the difference between the theoretical and actual values. Finally, in the last column, is the volume fraction of gas hydrates, determined based on the consumption of methane.
As can be seen in these tables, the actual consumption of methane increases with increasing amounts of water (from 5 to 25 vol.% water). Thus, the results show that as the water volume fraction increases, more hydrates are formed. Further analysis of the mass balance performed shows that there is high conversion of water to hydrates with higher conversion observed for mineral oil 350T system as compared to mineral oil 70T system. The lowest conversion observed for the mineral oil 350T system was observed for the 15 vol.% water fraction experiment, in which only 68 vol.% of water was converted to hydrates. On the other hand, the lowest conversion observed for the mineral oil 70T system was seen for the 30 vol.% water cut experiment, in which only 49 vol.% of water was converted to hydrates.

Furthermore, the results for the mineral oil 70T system at 30 vol.% water cut experiment, show a low conversion of water to gas hydrates. The low conversion of water to gas hydrates may be due to high extent of hydrate agglomeration. When hydrate particle agglomerate, some of the liquid water is trapped between the particles (Webb 2013; Vijayamoham et al. 2014). It then becomes difficult for methane gas to diffuse through the hydrate shell to form a fully converted hydrate particle. As a result, there is lower water conversion to hydrates, and therefore less methane consumption.

**Table 4-1**: Mass balance performed on hydrate slurries experiments using mineral oil 350T emulsion.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.051</td>
<td>0.053</td>
<td>-3.9</td>
<td>5.9</td>
</tr>
<tr>
<td>7</td>
<td>0.055</td>
<td>0.064</td>
<td>-16.4</td>
<td>8.15</td>
</tr>
<tr>
<td>10</td>
<td>0.061</td>
<td>0.055</td>
<td>9.8</td>
<td>8.79</td>
</tr>
<tr>
<td>15</td>
<td>0.072</td>
<td>0.060</td>
<td>16.7</td>
<td>12.02</td>
</tr>
<tr>
<td>20</td>
<td>0.082</td>
<td>0.085</td>
<td>-3.7</td>
<td>20.21</td>
</tr>
<tr>
<td>25</td>
<td>0.092</td>
<td>0.097</td>
<td>-5.4</td>
<td>24.05</td>
</tr>
<tr>
<td>30</td>
<td>0.102</td>
<td>0.088</td>
<td>13.7</td>
<td>24.33</td>
</tr>
</tbody>
</table>
Table 4-2: Mass balance performed on hydrate slurries experiment formed from mineral oil 70T emulsion.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.062</td>
<td>0.070</td>
<td>-12.9</td>
<td>5.9</td>
</tr>
<tr>
<td>10</td>
<td>0.0712</td>
<td>0.0714</td>
<td>-0.3</td>
<td>11.18</td>
</tr>
<tr>
<td>15</td>
<td>0.081</td>
<td>0.070</td>
<td>13.6</td>
<td>12.13</td>
</tr>
<tr>
<td>20</td>
<td>0.091</td>
<td>0.089</td>
<td>2.2</td>
<td>19.71</td>
</tr>
<tr>
<td>25</td>
<td>0.100</td>
<td>0.094</td>
<td>6.0</td>
<td>22.48</td>
</tr>
<tr>
<td>30</td>
<td>0.110</td>
<td>0.073</td>
<td>33.6</td>
<td>18.21</td>
</tr>
</tbody>
</table>

Comparing the hydrate slurries viscosity results for both mineral oil systems, Figure 4.2 shows that the viscosity profile of gas hydrate slurries formed from mineral oil 70T has much larger and more frequent fluctuations compared to the viscosity profile of the gas hydrate slurries formed from mineral oil 350T. Currently, there are two hypotheses that may explain these larger more frequent fluctuations in viscosity profile for mineral oil 70T. The first hypothesis with regards to the transportability of gas hydrates particles. In most recent work performed by Vijamohan et al, it was observed that the transportability of gas hydrate depends on the viscosity of the oil (Vijayamoham et al. 2014). From the work, it was observed that there is lower transportability of gas hydrates when the viscosity of the oil low. This low in transportability of gas hydrates leads to settling of gas hydrates particles and thus fluctuations in the viscosity readings. To confirm the lower transportability of gas hydrate in the mineral oil 70T emulsion system compared to the mineral oil 350T emulsion system, terminal velocity of the gas hydrates was calculated based on Stokes’ law. The equation for Stokes’ law is shown in Equation (4-1) (Deen 1998; Bird, Stewart, and Lightfoot 2007).

\[ v_t = \frac{2R^2g\Delta
}{9\mu} \]  

(4-1)
In Equation (4-1), \( v \) is the terminal velocity, \( R \) is the radius of suspended particles, \( g \) is the gravitational acceleration, \( \Delta \rho \) is the density difference between the particles and fluid, and \( \mu \) is the viscosity of the fluid. In order to use Equation (4-1), hydrate particles were assumed to be spherical in shape and in addition, the radius of hydrate particles was assumed to be similar to the radius of the water droplets. Thus, with the information stated in Table 2-1, the terminal velocity for hydrate particles suspended in mineral oil 70T was calculated to be \( 1.33 \times 10^{-2} \mu m/s \), while the terminal velocity for hydrate particles suspended in mineral oil 350T was calculated to be \( 8.38 \times 10^{-3} \mu m/s \). From these values, the terminal velocity for mineral oil 70T is 1.59 greater than that of mineral oil 350T. Therefore, this suggests that mineral oil 70T has a lower transportability of gas hydrate particles.

It should be noted that the calculated terminal velocities of hydrate particles suspended in both mineral oils are small in magnitude. As a result, it is believed there are other phenomena that are more dominant than the settling of hydrate particles. Therefore, in this work, the second hypothesis for these fluctuations is likely due to the aggregation phenomenon. As discussed in Section 2.3.1 Emulsification Process for Model Emulsion Systems, the concentration of surfactant for mineral oil 70T emulsion is lower compared to mineral oil 350T (1 wt.% compared to 5 wt.%). Therefore, it is believed that there is a higher degree of aggregation in the mineral oil 70T system that was confirmed by the lower conversion of water to hydrate (at higher water cut) for mineral oil 70T emulsion. These hydrate aggregates are larger in size and thus the settling rate for this system is faster and leads to more fluctuations in the viscosity profiles.

### 4.3.2 Hydrate Slurries Relative Viscosity

In order to compare the results of hydrate slurries investigation across different water cut, the relative viscosity of the system was calculated from experiment. Relative calculations were also used for the analysis in order to normalize the results and compare between different continuous phases. In addition, the results of relative viscosity calculated from rheometer results may be used to compare with the results obtained in the recent flowloop experiments, as discussed in Chapter 5. The equation used to calculate the relative viscosity is shown in Equation (4-2).

\[
\eta_r = \frac{\eta(T, P, \phi_{\text{hydr}})}{\eta(T, P, \phi_{\text{wc-o}})} \quad (4-2)
\]
In Equation (4-2), the numerator is the viscosity of the gas hydrate slurries at a certain temperature, pressure and water volume fraction, while the denominator is the viscosity of the continuous phase which is the viscosity of the saturated oil at similar temperature and pressure.

It should be stated that initial analysis of these hydrate slurries investigations focused on the relative viscosity of the system at steady state. Steady state was defined as where there is minimal change in the viscosity of the slurries and minimal change in the volume of the ISCO pump for a period of one hour. The average values during the one-hour steady state period were then used to calculate the relative viscosity of the systems. It should be stated that the objective of this thesis was to develop a model for gas hydrate slurries. Therefore, steady state values were chosen, as there is minimal change in the system. Thus, it is easier to model since there are fewer assumptions that need to be made.

The results of relative viscosity calculations for both emulsion systems as a function of hydrate volume fraction are shown in Figure 4.3. The relative viscosity of the slurries increases with increasing hydrate volume fraction in the system. When there are more solid hydrate particles in the system, the viscosity of the system increases, and thus the relative viscosity also increases (Rutgers 1962a; Rutgers 1962b; Jeffrey and Acrivos 1976; Camargo et al. 2000).

![Figure 4.3: Relative viscosity at steady state for hydrate slurries formed from (a) mineral oil 350T and mineral oil 350T emulsions.](image-url)
Comparing the relative viscosity of the mineral oil 350T system with the relative viscosity of the mineral oil 70T system; it can be seen that at low hydrate volume fraction (≤ 10 vol.% hydrate), both systems have similar relative viscosity. However, at higher hydrate fraction (>10 vol.% hydrate), the relative viscosity of mineral oil 70T is much higher than that of mineral oil 350T at similar water volume fraction. The higher relative viscosity for the mineral oil 70T system may be due to aggregation in the system since the concentration of surfactant was lowered for this emulsion.

In order to confirm the aggregation phenomenon at higher water cut, the size of water droplets before and after hydrate formation was measured using an optical microscopy method. As discussed in Section 2.4.5 Differential Scanning Calorimetry (DSC), if aggregation occurs in the system, the average size of water droplets after dissociation is larger when compared to the average size of water droplets before hydrate formation. Calculation of the weighted average of the droplet size before and after hydrate formation for the mineral oil 70T emulsion system is 2.5 ± 0.7 μm and 3.2 ± 1.5 μm, respectively. It should be stated here that the errors reported in this work, are the standard deviation in the measurements of the droplets size. Based on the standard deviation reported, the size of water droplet before hydrate formation is concentrated at 28% around the average reported value. On the other hand, the size of water droplet after hydrate formation is concentrated at a higher value that is 47% of the reported weighted average value. The results indicate that there are more large water droplets in the emulsion after hydrate formation. In contrast, analysis of the droplet size for the mineral oil 350T emulsion system shows the numerical average size of the water droplets before hydrate formation is 2.7 ± 1.9 μm; while the size of water droplets after hydrate formation is 2.8 ± 1.0 μm.

Figure 4.4 and Figure 4.5 show the microscopic images that were obtained before and after hydrate formation for the mineral oil 350T and mineral oil 70T emulsion system respectively. From Figure 4.4, it can be seen that the size of water droplet does not change upon hydrate formation for mineral oil 350T. However, in Figure 4.5, there are a couple of large water droplets in the microscopic images of the emulsion after hydrate formation indicating that hydrate aggregation might have occurred in the system upon hydrate formation.

It should be noted that in this work, microscopy images were taken immediately after hydrate dissociation, by heating the system to 20 °C and the system has been slowly depressurized to atmospheric pressure (~1.5 hours after hydrate dissociation). Microscopy images were taken
immediately in order to get a better representation of the water droplet size distribution. If images were taken at a later time, coalescence of water droplets might occur in the system, and thus not a good representation of the system with regards to hydrate agglomeration. As such, there is still gas saturated in the system and as a result, gas pockets between the glass slides could not be prevented since the emulsion was releasing gas when images were taken. Therefore, in the images (Figure 4.4 and Figure 4.5), there are large irregular circles with a clear inside (marked by red in Figure 4.4 and Figure 4.5) that are actually gas bubbles rather than water droplets. These gas bubbles are not taken into account when calculating the average droplet size after hydrate formation. The small circles with white/grey inside are the water droplets. In the Figure 4.4 and Figure 4.5, the water droplets are marked as yellow circles.

Figure 4.4: Microscopic images of mineral oil 350T emulsion (a) before and (b) after hydrates formation.

Figure 4.5: Microscopic images of mineral oil 70T emulsion (a) before and (b) after hydrates formation.
4.3.2.1 Development of Relative Viscosity Model for Gas Hydrate Slurries at Steady State

In this work, attempts were made to model the relative viscosity as a function of hydrate volume fraction of the system. The well-known model to predict the viscosity of gas hydrate slurries was proposed by Camargo and Palermo in 2002 (Camargo and Palermo 2002). The proposed model is shown in Equation (4-3) below.

\[
\left( \frac{d_A}{d_p} \right)^{1+f} \left( 1 - \frac{\phi}{\phi_{\text{max}}} \left( \frac{d_A}{d_p} \right)^{3-f} \right)^{\chi_A} - \frac{F_A}{d_p \eta_0 \gamma \left[ 1 - \frac{\phi}{\phi_{\text{max}}} \left( \frac{d_A}{d_p} \right)^{3-f} \right]} = 0
\]

In this equation, \(d_A\) is the aggregates diameter, \(d_p\) is particle diameter, \(f\) is fractal dimension, \(\phi\) is particle volume fraction, \(\phi_{\text{max}}\) is the maximum packing for randomly packed spheres of the same diameter, \(F_A\) is the adhesion force between two particles, \(\eta_0\) is the continuous phase viscosity and \(\gamma\) is the shear rate. As can be seen here, there are many parameters involved in the equation. Some of the parameters, especially the aggregates diameter could not be determined in this work. Therefore, the model proposed Camargo Palermo could not be applied and tested in this work.

As discussed in Section 3.3.3.2 Obtaining the \(A_2(\phi)\) Function, a common viscosity model for solid suspensions is the Krieger Dougherty equation. The expression for the Krieger Dougherty equation is shown below in Equation (3-16). As can be seen here, unlike the model proposed by Camargo and Palermo, the Krieger Dougherty equation is just a function of the volume fraction of the particle. However, in this equation, there is a limited freedom in the equation in which only the Einstein Coefficient, \(B\) may be changed. Hence, there is poor accuracy of the model, as shown in Figure 4.6. As can be seen in this figure, the Krieger Dougherty equation was only able to predict the relative viscosity of the hydrate slurries at low particle volume fraction (< 10 vol.% hydrate). Above this particle volume fraction, the model was not able to predict the relative viscosity of the system.
Another commonly used relative viscosity model for solid suspensions is an equation proposed by M Mooney in 1950. Similar to that of the Krieger Dougherty equation, this equation is a function of particle volume fraction, as shown in Equation (4-4). Similarly, the equation has limited freedom in changing the parameters in which only the Einstein Coefficient can be changed. As a result, similar to the Krieger Dougherty equation, this model was only able to predict the relative viscosity of both mineral oil systems at low volume fraction of particles for the hydrate slurries investigated.

\[
\eta_r = \left(1 - \frac{\phi}{\phi_{\text{max}}} \right)^{n_{\eta_{\text{max}}}}
\]

(3-16)

Due to the poor accuracy and prediction of relative viscosity for gas hydrate slurries at high particle volume fraction, a relative viscosity model for gas hydrate slurries was developed based on the work proposed by Sudduth; whereby the relative viscosity can be expressed in terms of the differential equation shown in Equation (3-17) in Chapter 3, and also reproduced below (Sudduth 1993).

\[
\frac{\partial \eta}{\eta} = B \left(1 - \frac{\phi}{\phi_{\text{max}}} \right)^{\sigma} \, d\phi
\]

(3-17)

In this doctoral work, the values of the Einstein Coefficient, \( B \) as well as the interaction parameter \( \sigma \) need to be determined. Therefore, the values for hydrate slurries systems (mineral oil 350T and mineral oil 70T) were determined by the method of minimization of error. The values of \( B \) and \( \sigma \) are shown in Table 4-3. Comparison between the experimental data and
relative viscosity model for hydrate slurries shows that the model is able to predict the relative viscosity for both mineral oil systems reasonably well (Figure 4.6).

However, it should be mentioned that the new model was not able to predict the relative viscosity of gas hydrate slurries formed from mineral oil 70T at 30 vol.% water cut accurately. It is believed that the model fails to predict the relative viscosity at this condition due to high extent of hydrate aggregation, as discussed earlier. Due to the hydrate aggregation, the actual effective volume fraction of hydrate particles may be larger than predicted since the particles can occlude some unconverted water (Vijayamoham et al. 2014). Since the hydrate volume fraction calculated in this work is based on the consumption of methane, the calculation might under-predict the actual volume fraction of the system.

![Figure 4.6: Comparison of relative viscosity at steady state between experimental data and three different models (Sudduth, Mooney and Krieger Dougherty) for hydrate slurries formed from (a) mineral oil 350T and (b) mineral oil 70T.](image)

**Table 4-3:** Values of \( \sigma \) and \( B \) parameters used in Equation (3-17) for hydrate slurries systems.

<table>
<thead>
<tr>
<th>Type of Mineral Oil</th>
<th>350T</th>
<th>70T</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma )</td>
<td>1.98</td>
<td>2.30</td>
</tr>
<tr>
<td>( B )</td>
<td>5.33</td>
<td>6.91</td>
</tr>
</tbody>
</table>

The quality of the new model developed in this doctoral work was tested by comparing the predicted value calculated from the new model with the predicted value calculated using the
Camargo and Palermo model (Equation (4-3)). In this analysis, actual measured values for shear rate, viscosity of oil and particle diameter were used in the calculations. For all other parameters needed in the equation, the values reported by Camargo and Palermo were used (Camargo and Palermo 2002). The results of the comparison are shown in Figure E-1 in Appendix E.

4.3.3 Analysis of Hydrate Extreme Peaks

As discussed in the earlier section, Section 4.3.1 Hydrate Slurries Viscosity Profiles, typical hydrate slurries profiles consist of four regions. The third region is the sudden and rapid viscosity increase. As shown in Figure 4.2, in this region, there are maximum peaks, which usually occur within a few minutes after hydrate onset. In this work, these peaks are referred as the extreme peaks.

In evaluating the extreme peaks, it can be observed that the magnitude of the extreme peaks depends on the water volume fraction of the system. It was proposed to determine the whether the relative viscosity at extreme peaks can be used to as an early warning sign for potential plugging. In order to evaluate this possibility, the relative viscosity of the hydrate slurries at the extreme peaks needs to be evaluated.

In order to calculate the relative viscosity of the system at the extreme peaks; it is necessary to know the condition of the system, especially the condition of the continuous phase. In calculating the relative viscosity of the hydrate slurries at steady state (Section 4.3.2 Hydrate Slurries Relative Viscosity), the viscosity of the oil phase at full saturation was used. However, at extreme peaks, the oil viscosity at full saturation is not suitable to be used as the baseline for relative viscosity calculations, since the oil is not fully saturated (due to methane consumption for hydrate formation). As such, a more accurate viscosity value needs to be determined.

In this work, two assumptions were made to determine the viscosity of the continuous phase at the extreme peak. The first assumption is that the methane gas for hydrate formation comes from the oil phase; the methane that dissolves in the oil. The second assumption that was used is that the conversion at extreme peaks is similar to that observed at steady state condition.

The procedure to calculate the viscosity of the continuous phase at the extreme point is as follows.

1. The amount of methane needed to form hydrate, at a similar conversion as steady state, was determined using CSMGem (Sloan and Koh 2007).
2. The amount of methane dissolved in the oil at full saturation was determined using Multiflash®

3. The difference between the values obtained in Steps 1 and 2 is the methane that is left in the oil phase.

4. Using the number of moles obtained in Step 3, as well as the equation (3.17) developed in Chapter 3, the viscosity of the continuous phase at the saturation of oil determined from step 3.

Based on the procedures described above, the viscosity of the oil continuous phase at the extreme peak condition was determined, and used to calculate the relative viscosity of hydrate slurry at extreme peaks. Note that since the conversion of water to hydrate is different at each water cut, the saturation and thus the viscosity of the oil is different at each water cut. The results of the relative viscosity calculations are shown in Figure 4.7.

From Figure 4.7, it can be seen that for both hydrate slurry systems (mineral oil 350T and mineral oil 70T), the magnitude of increase for extreme peaks and steady state peaks with increasing water cut (vol.%) are on the same order of magnitude. In fact, in some cases, the relative viscosity at steady state matches with the relative viscosity value at extreme peaks. This observation holds true for both slurry systems.

Three conclusions can be made from these results. The first conclusion is that proper viscosity baselines are needed to obtain relative viscosity of the system. A proper viscosity for the baseline is a viscosity that represents the actual condition of the system. For instance, if the viscosity of fully saturated oil were to be used in calculating the relative viscosity of hydrate slurries at extreme peaks, the values obtained will be large in magnitude since the calculated values capture both the effect of saturation as well as the distribution of solid hydrate particles. The second conclusion for this observation is that the gradual decay in the viscosity of the slurries after the extreme peak is mainly due to the re-saturation of the oil. This conclusion is consistent with the fact that the relative viscosity of the hydrate slurry at extreme peaks is fairly similar to the relative viscosity of the hydrate slurry at steady state by using a proper viscosity value as the baseline of analysis. The third and final conclusion of these results is that relative viscosity at the extreme peak alone cannot be used as an early sign for potential hydrate plugging. Thus, other variables such as hydrate particle size distribution, conversion, as well as rate of re-saturation needs to be taken into account.
4.3.4 Hydrate Slurry Investigation Near the Emulsion Inversion Point

In this work, the hydrate slurry investigation was also conducted near the emulsion inversion point. However, in this doctoral work, investigation near the emulsion inversion point was only conducted for the mineral oil 70T emulsion system. Investigation was not conducted using the mineral oil 350T system, since inversion occurred even during the saturation process. The inversion was confirmed by the viscosity of the emulsion at full saturation.

In a typical viscosity plot for a w/o emulsion system as a function of water cut, there is an increase the viscosity of the emulsion with an increase in the water cut. However, near the inversion point of the emulsion, the viscosity of the emulsion starts to decrease to the viscosity of water (Minana-Perez et al. 1986). These changes in the trend for viscosity are due to phase inversion. Since the viscosity of emulsions is proportional to the viscosity of the continuous phase, there will be a decrease in viscosity value after phase inversion occurs (Minana-Perez et al. 1986). Figure 4.8 shows initially there is an increase in the viscosity of the emulsion as the water volume fraction increases. However, there is a decrease in the viscosity of the emulsion when the water volume fraction of the system increases from 30 vol.% to 40 vol.% of water. Based on the discussion above, this decrease is attributed to the phase inversion. Since phase
inversion occurred during the saturation process, hydrate slurry investigations near the emulsion inversion were not conducted for the mineral oil 350T emulsion system.

![Viscosity at saturation for mineral oil 350T emulsion as a function of water volume fraction.](image)

**Figure 4.8:** Viscosity at saturation for mineral oil 350T emulsion as a function of water volume fraction.

As stated previously, the hydrate slurry experiment near emulsion inversion was only conducted for the mineral oil 70T system, specifically mineral oil 70T with 1 wt.% surfactant mixture of Span 80 and AOT and water cut of 50 vol.%. It should be noted that the experimental procedure for this experiment is similar to the procedure described in Section 4.2.2.3 Gas Hydrate Slurry Viscosity Measurements.

The viscosity profile for this experiment is shown in Figure 4.9. Seen here, at the initial time (0 to 0.7 hr), there is an increase in the viscosity profile of the system as time progresses. This increase is due to the decrease in temperature of the system from 20 °C to 1 °C. After the cooling period, there is a relatively short time where there is no hydrate in the system. Thus, the viscosity of the system is constant. Following this region, there is a rapid and sudden increase in the viscosity indicating that hydrate particles have started to form in the system. The viscosity continues to rise until a certain point, where it drops rapidly (at ~0.8 hr. in this experiment). The viscosity of the system decreases for ~ 10 minutes before it increases back and continues to increase for ~ 3 hours. After this point, the viscosity of the system starts to gradually decrease, similar to that observed for the hydrate experiment with 30 vol.% water cut and below (≤ 30 vol.% water content).
Figure 4.9: In-situ methane hydrate formation and viscosity measurements at 50 vol.% water fraction formed mineral oil 70T model emulsion.

In this experiment, the first decrease in the viscosity of the system that occurred at ~0.8 hours (Figure 4.9) is hypothesized to be due to emulsion breaking. Emulsion breaking is a phenomenon where the two immiscible liquids of the emulsion phase separated. It is believed that when hydrate starts to form, the interface changes from water-oil to hydrate-oil. The change in the interface resulted in less ability for the surfactant mixture to stabilize the system and thus the emulsion phase separated (Salager and Forgiarini 2012).

Emulsion breaking was confirmed by a dispersion test that was conducted. The dispersion test was conducted at the end of the test where the hydrate has been dissociated. In the dispersion test performed, a small sample of the emulsion was taken and dropped into DI water. If the sample completely dispersed in the DI water, it indicates that the system is water continuous (Ese and Kilpatrick 2004). The result of the dispersion test shows that at the end of the experiment, the emulsion is water continuous. This proves that emulsion breaking occurred since the emulsion is oil continuous at the beginning of the test (before hydrate formation).

Emulsion breaking can result in a decrease in the viscosity of the slurry. The viscosity of the slurry decreases since water is the continuous phase and water has a lower viscosity, compared to mineral oil 70T (Table 2-1). Figure 4.9 shows that after the decrease that starts at ~0.8 hr, there is an increase in the viscosity. This increase is because more hydrate particles are forming in the
system. It is known that the viscosity of the system increases with an increasing amount solid fraction (Rutgers 1962a; Rutgers 1962b).

The increase in viscosity from 1 – 4 hr is then followed by a gradual decrease in the viscosity. Similar to the oil-continuous hydrate slurry investigation, this decrease is due to re-saturation of the oil, as well as the hydrate particle break-up and rearrangement (Hasan and Shaw 2010; Pal 2011; Rensing 2010; Webb 2013).

4.4. Chapter Concluding Remarks

In this work, the viscosity of gas hydrate slurries were measured using a commercially available high pressure rheometer (TA Instruments). Gas hydrates was formed from model w/o emulsions that were specially developed for gas hydrate studies (Chapter 2). In these viscosity measurements, a four-blade straight vane impeller was used as a stirrer of the system in order to improve the saturation of the gas. All experiments were conducted at constant pressure of 1500 psig of methane, constant temperature of 1 °C and constant mixing speed of 477 RPM. The variables that were varied are the type of continuous phase, as well as water volume fraction. Two different mineral oils were used as the continuous phase: mineral oil 350T and mineral oil 70T. As for the water cut, tests were conducted with water fractions ranging from 5 to 30 vol.% water cut. In addition, for mineral oil 70T, an additional experiment at 50 vol.% water cut was conducted. This experiment was conducted, since it is near the inversion point of the emulsion.

Results of these tests were analyzed and presented in terms of relative viscosity. To describe the viscosity of hydrate slurries at steady state, the viscosity of the continuous phase (saturated oil) was used as the baseline of analysis. For these results, a relative viscosity model as a function of hydrate fraction was developed. Comparison between experimental data and the new model shows that the model was able to predict the relative viscosity value with reasonable accurately (±17% error). On the other hand, for the viscosity of hydrate slurries at extreme peaks, the viscosity of oil at extreme peaks condition (partially saturated oil) was used as the baseline for relative viscosity calculations and analysis. Results shows that relative viscosity at the extreme peak alone could not be used as an early warning sign for potential hydrate blockage.

Finally, a hydrate slurry experiment was also conducted for the model emulsion system near its inversion point. In this test, emulsion breaking where the two immiscible liquids (oil and water) phase separated was observed when a certain amount of hydrates had formed in the system.
Gas hydrate formation and slurry properties at different flow conditions were investigated using an industrial-scale high pressure flowloop. Two flow conditions were investigated: fully and partially dispersed systems. The work presented in this doctoral thesis is the first research to study the slurry properties of gas hydrate slurries in partially dispersed systems using crude oil. Prior to this, studies on partially dispersed systems used a model oil. The flow conditions were modified by changing both the water cut and the fluid mixture velocity (pump speed). Tests were conducted at three different water cuts: 30, 50 and 90 vol.% water cut (WC) and at three different pump speeds: 350, 750 and 1200 RPM. Results of the study show that as the pump speed increases, the relative pressure drop, $\Delta P_{\text{rel}}$ decreases. In addition, hydrate plugged the flowloop at 50 vol.% water cut and at pump speeds of $\leq 750$ RPM, as well as 90 vol.% water cut and pump speeds of $\leq 350$ RPM. Finally, emulsion breaking, where the two immiscible liquid phases separated, was observed in all the 90 vol.% water cut experiments performed.

5.1. Background and Motivation of Work

As mentioned in earlier chapters, there are currently two methods for controlling gas hydrate formation in subsea oil/gas flowlines; hydrate avoidance and hydrate management. The increasing interest in the “hydrate management” method drives the gas hydrate research community to perform research on understanding the mechanism of gas hydrate formation at various flow conditions. In addition, certain research groups have also focused on understanding hydrate slurry properties and hydrate accumulation phenomena (bedding, jamming and deposition) under flow conditions.

Figure 5.1 shows conceptual pictures of the two flow conditions typically formed in oil/gas flowlines. These flow conditions are fully dispersed and partially dispersed systems. In the fully dispersed system (Figure 5.1(a)), water in the system is completely emulsified in the oil phase. In other words, water is only present as water droplets and oil is the continuous phase. This flow condition usually forms at low water content (water cut) and/or at high fluid mixture velocity. For some oils, it is possible for the system to be oil continuous even at high water content. The second flow condition is the partially dispersed system. In contrast to the fully dispersed system, the partially dispersed system typically forms at high water cut and/or at low fluid mixture velocity.
velocity. As shown in Figure 5.1(b), in this flow condition, only a certain amount of water is emulsified in the oil phase, while the remaining water is present as a free water layer at the bottom of the flowline. The amount of water emulsified on the oil phase depends on the fluid mixture velocity, as well as the properties of the oil (specifically, the concentration of surface active components in the oil).

Figure 5.1: Types of flow conditions typically found in oil/gas pipelines: (a) fully dispersed (Davies 2009) and (b) partially dispersed (Vijayamoham et al. 2014) systems.

Several experiments were previously performed to study hydrate formation in these two flow conditions. One such attempt was made by Davies et al. in 2009 (Davies et al. 2010; Davies et al. 2009; Boxall et al. 2009). In this work, Davies et al. studied gas hydrate formation and attempted to model the kinetics of gas hydrate formation in an oil dominated/fully dispersed system. In this work, the gas hydrate formation was investigated using industrial-scale high pressure flowloops (at ExxonMobil and the University of Tulsa flowloop). In 2014, Grasso et al. also performed a similar investigation for oil-dominated systems. Similar to the current work, Conroe crude oil was used in the experiment. However, these previous investigations of hydrate formation and slurry properties were not performed on partially dispersed systems. In Grasso et al.’s work, the fluid mixture velocities chosen were high enough or the water cut is low enough
that the water is completely emulsified in the oil phase. Recently in 2014, Vijayamohan et al. performed a similar study to understand the gas hydrate formation mechanism for partially dispersed systems (Vijayamohan et al. 2014). Similarly, in this thesis work, an industrial-scale high pressure flowloop was used in the investigation (University of Tulsa flowloop). In addition to these experiments, in 2013 Joshi et al. performed flowloop experiments for high water cut systems, specifically the water/gas system as depicted in Figure 5.2 (Joshi 2012b; Joshi et al. 2013). Since the experiments did not contain oil, hydrate formation and slurries properties for this system are completely different from those observed for fully and partially dispersed system measured in this current doctoral work.

![Water Dominated System](image)

**Figure 5.2**: Conceptual picture of water dominated system as studied by Joshi et al. (edited from (Joshi 2012b)).

Since all of the previous studies were conducted separately, there are several challenges in comparing the results of the two studies. One such challenge is that the two studies used different oils in the studies. 2010 Conroe crude oil was used in Davies et al. and Grasso et al’s study (Davies et al. 2010; Davies 2009); while mineral oil 350T, mineral oil 70FG and kerosene were used in the work performed by Vijayamohan et al. (Vijayamohan et al. 2014). The second challenge is with regard to the geometry of the flowloop. As stated, Vijayamohan et al. only performed tests using the University of Tulsa flowloop. Thus, the differences in the results might be due to geometry effects, rather than different hydrate formation mechanisms.

Therefore, in this work, hydrate formation and slurry properties were investigated at the two flow conditions mentioned earlier using the same oil and flowloop. This eliminates the effect of oil properties and flowloop geometry on gas hydrate slurries transportability conditions. As a result, better comparison of hydrate slurries properties conditions between the two different flow conditions (fully dispersed and partially dispersed) could be performed.
5.2. Experimental Methodology

This section describes the high pressure industrial-scale flowloop setup for hydrate formation and transportability studies. This setup consists of high pressure gas accumulator to maintain the pressure of the system and particle video microscope. In addition, this section also describes the experimental conditions and procedures followed in this doctoral work.

5.2.1 Flowloop Setup

![Flowloop Setup Diagram]

**Figure 5.3:** Schematic diagram of the ExxonMobil flowloop that is located in Friendswood, TX (Davies et al. 2010).

Experiments in this thesis study were conducted using an industrial-scale high pressure flowloop. The flowloop setup is owned and operated by ExxonMobil Upstream Research Company that is located at Friendswood, TX, USA. A schematic diagram of the flowloop is shown in Figure 5.3. The flowloop has a total length of 314 ft. and is 4 inch in nominal diameter. The flowloop was specifically designed with a dipped section to mimic the low spot of flowlines. At this dipped section, a particle video microscope (PVM) was installed. The PVM can take images of the particles in the flowloop during an experiment. Images can be taken manually or can be programmed to take images at a pre-determined time interval. The entire flowloop with an exception of the piston driven, high pressure gas accumulator is located in a temperature controlled test chamber. The gas accumulator is used to maintain the pressure of the flowloop. By controlling the temperature in the test chamber, the loop can be operated in a temperature...
range of 20°F to 120°F. Furthermore, the flowloop has been tested to withstand pressures of up to 1800 psig (Davies et al. 2010).

5.2.2 Fluids Characteristics and Experimental Conditions

2014 Conroe crude oil (2014 Conroe) was chosen as the oil phase, while the aqueous phase was set to 5 wt.% of synthetic salt. Measurements were made to determine the properties of 2014 Conroe. In this work, it was determined that 2014 Conroe oil has an API gravity of 33.2°API. The viscosity was measured at ambient conditions (ambient pressure and 20°C), and 2014 Conroe oil has a viscosity of 4.2 cP. It should be stated that even at this low viscosity, 2014 Conroe is a highly emulsifying oil, with emulsion phase inversion determined to be at 95 vol.% water cut, based on bottle tests. In addition, the 2014 Conroe oil has a measured Interfacial Tension (IFT) value of 24.5 mN/m at ambient conditions. Table 5-1 summarizes the properties of the 2014 Conroe crude oil used in this work.

Table 5-1: Summary of 2014 Conroe crude oil properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity °API</td>
<td>33.2 ± 0.01</td>
</tr>
<tr>
<td>Viscosity (20°C, 0 psig) cP</td>
<td>4.2 ± 1.4</td>
</tr>
<tr>
<td>Interfacial Tension mN/m</td>
<td>24.5 ± 0.5</td>
</tr>
</tbody>
</table>

In this work, three experimental variables were set constant. The first variable is the experimental pressure. All experiments were conducted at constant pressure mode and the pressure was set to 1000 psig, which provided a sufficient driving force for hydrate formation to occur readily. The second experimental variable that was set constant is gas composition. In this work, it was decided to use pure methane. Thus, structure I (sI) hydrate will form in the flowloop. Lastly, the liquid loading (LL) of the system was also set constant. The LL for this study was chosen to be 60 vol.%. 

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5.2.3 Experimental Variables

In this phase of the project, two experimental variables were chosen, based on the need to investigate both flow conditions: fully dispersed and partially dispersed systems. Therefore, the variables in this work are the amount of water (water cut) and fluid mixture velocity (pump speed).

For the water cut variable, three different water cuts were investigated. The water cuts that were chosen in this work are 30, 50 and 90 vol.%. As for the second variable, pump speed, three different pump speeds were chosen 350, 750 and 1200 RPM. The fluid mixture velocity of the aforementioned pump speed was determined to be 3.0, 6.2 and 9.8 ft/s respectively. Table 5-2 is the experimental matrix of the tests performed in this work.

<table>
<thead>
<tr>
<th>Water Cut [%]</th>
<th>Pump Speed [RPM]</th>
<th>Fluid Mixture Velocity [ft/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>750</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>9.8</td>
</tr>
<tr>
<td>50</td>
<td>350</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>9.8</td>
</tr>
<tr>
<td>90</td>
<td>350</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>9.8</td>
</tr>
</tbody>
</table>

5.2.4 Experimental Procedures

Gas hydrate formation experiments in the flowloop began by charging the flowloop with the two fluids (2014 Conroe oil and 5 wt.% aqueous salt solution) at the desired WC and a LL of 60 vol.%. Next, the entire system including the gas accumulator was pressurized with methane gas to the desired pressure of 1000 psig. Next, the pump was switched on and was set to the desired pump speed. Following this step, the temperature of the test chamber was lowered down to 38°F; as a result, the temperature of the fluid inside the flowloop also decreased. When the temperature
of system reaches the desired temperature of 38°F, the fluid was maintained at this condition (constant pressure and pump speed) for a 24 hours period for hydrate formation, and also to investigate the slurry properties. It was assumed that 24 hours is enough for the system to reach steady state (no further hydrate formation). After the 24 hours formation and slurry flow study period, the temperature of the test chamber was raised back to room temperature. The temperature of the fluid then slowly increased and the hydrate started to dissociate at its equilibrium temperature.

However, it should be noted that in certain experiments, the temperature of the test chamber was raised back to room temperature even before the 24 hour period was over. This occurred when a hydrate plugged was observed and the system had consumed all of the gas in the gas accumulator, indicated by position of the piston in the gas accumulator. If the system has consumed all of the methane gas, the piston will be at the bottom of the gas accumulator. In this work, a hydrate plug is defined as limited flow of hydrate particles, with most of the particles settled at the bottom of the loop. Thus, if a hydrate plug was observed and all methane gas had been consumed, the temperature of the test chamber was raised to room temperature.

5.3. Results of Hydrate Formation in the Flowloop

This section of the thesis describes the experimental results and analysis flowloop experiments. The results of the tests include determination of fluid mixture velocity that will provide a partially and fully dispersed system. In this work, results of the tests were presented in terms of relative pressure drops. The effect of water cut and fluid mixture velocity were investigated in this work.

5.3.1 Tests of Flow Conditions

In all of the experiments, the flow conditions of the system were determined prior to hydrate formation to assess whether the system was fully or partially dispersed. Therefore, in this work, tests of the flow conditions were conducted at all water cuts and two temperatures (room temperature and 50°F).

During these tests, the flow condition was determined by visual observation through the visual port. The test began by starting the pump at 350 RPM. Once the flow was stabilized at the pump speed, the flow condition observed from the visual port was recorded. Next, the pump speed was increased to 400 RPM and the flow condition observed was recorded after the flow has
stabilized. This process was repeated with ~50 RPM pump speed increments, until there is no longer a water layer observed in the flowloop.

The results of these tests showed that a fully dispersed system was only observed when the pump speed was greater than 750 RPM. This observation holds true at both temperatures (room temperature and 50 °F) and at all water cuts performed. Therefore, in thesis work, the tests at pump speeds of 750 and 350 RPM were considered to be partially dispersed systems, while the test at 1200 RPM was considered to be a fully dispersed system.

5.3.2 Data Analysis

In flowloop experiments, gas hydrate formation and flow conditions are evaluated from the pressure drop (ΔP) of the system. These ΔP readings can be monitored across the entire loop or at a certain section of the flowloop. In this work, the ΔP across the entire loop was monitored and analyzed. By evaluating ΔP of the system, one can obtain significant information, such as the viscosity and flow condition of the system. For instance, as the water cut of the system increases, the viscosity of the emulsion also increases (cf. Delgado-Linares et al. 2013; Minana-Perez et al. 1986; Graham, Steele, and Bird 1984). The increase in the viscosity of the emulsion will increase the ΔP of the system (Davies et al. 2010). In addition, if flowloop plugging occurred in the system, there would be large fluctuations in the ΔP of the system.

Since the ΔP of the system increases with increasing amounts of water in the system (due to an increase in viscosity), it provides a challenge in terms of comparing the results across all water cuts investigated. In addition, the ΔP of one system will be different at a different pump speed, even at the same water cut. In order to compare the effect of hydrate formation and slurry properties on ΔP, the absolute value of ΔP needs to be normalized. Therefore, comparisons across all water cuts and pump speeds were made by comparing the relative pressure drop (ΔP_rel) of the system, rather than absolute ΔP. ΔP_rel calculations and analyses were made using Equation (5-1) shown below.

\[
\text{Relative } \Delta P \ (\Delta P_{\text{rel}}) = \frac{\Delta P\left(T, P, \phi_{\text{hydrate}}\right)}{\Delta P\left(T, P, \phi_{\text{WC,emulsion}}\right)}
\]  

(5-1)

\(\Delta P_{\text{rel}}\) is defined as the absolute ΔP of the hydrate slurry at a certain temperature, pressure and
amount of hydrates divided by the absolute $\Delta P$ of the emulsion at similar temperature, pressure and the initial water cut of the system. Since in Equation (5-1), the two absolute values of $\Delta P$ are at similar temperature and pressure, the relative (or normalized) value provides the effect of changing water droplets to hydrate particles on the $\Delta P$ of the system. Hence, comparisons of results at different water cuts or different pump speeds could be made.

Furthermore, the amount of hydrates formed in the system was also determined. The amount of hydrates formed in the system was determined based on the methane consumption obtained from the change in the volume of the gas accumulator, temperature and pressure (Davies 2009; Davies et al. 2010). The amount of hydrates formed in the flowloop is presented as hydrate volume fraction, $\varphi_{\text{hyd}}$ as shown in Equation (5-2) shown below.

$$
\varphi_{\text{hyd}} = \frac{V_{\text{hydrate}}}{V_{\text{loop}}}
$$

In Equation (5-2), $V_{\text{hydrate}}$ is the total volume of gas hydrate particles that have formed in the flowloop, while $V_{\text{loop}}$ is the total volume of the flowloop, which is taken to be a constant value of 734.4 L.

### 5.3.3 Effect of Water Cuts

As stated, in Section 5.2.3 Experimental Variables, three different water cuts were investigated. Plots showing comparisons between different water cuts at a constant pump speed of 750 RPM are shown in Figure 5.4. It should be stated that time 0 s in this work is taken to be the hydrate onset time (first hydrate crystal formation). In all ExxonMobil flowloop experiments, hydrate onset was confirmed by a slight increase in temperature of the fluid (since hydrate formation is exothermic). In addition, the hydrate onset was also confirmed by the decrease in the volume of the gas accumulator. When hydrate forms, it consumes methane gas and decreases the pressure of the system. In order to maintain the pressure, the volume of gas accumulator needs to decrease.

From Figure 5.4(a), it can be seen that the $\Delta P_{\text{rel}}$ for 30 and 50 vol.% water cuts continue to increase as time progresses. This is as expected, because as time progresses there will be more hydrate particles formed in the system; the viscosity of the system will then increase and
therefore the $\Delta P_{\text{rel}}$ increases (cf. Mueller, Llewellin, and Mader 2009; Sinquin, Palermo, and Peysson 2004; Camargo et al. 2000; Camargo and Palermo 2002).

Figure 5.4: Relative pressure drop ($\Delta P$) traces: (a) as time progresses and (b) as a function ofhydrate volume fraction for 750 RPM tests at three water cuts: 30 vol.% (red), 50 vol.% (blue) and 90 vol.% (green) water cuts.

However, the opposite trend was seen in the case of the 90 vol.% water cut experiment. A decrease in $\Delta P_{\text{rel}}$ upon hydrate onset was seen instead. This decrease was hypothesized to be due to emulsion breaking (Salager and Forgiarini 2012). In the surface chemistry area, emulsion breaking is defined as a phenomenon where two immiscible liquid phases (oil and water) phase separate (Salager and Forgiarini 2012). At very high water cut and near the inversion point of the emulsion, the water droplets are tightly packed and are only separated by a thin layer of oil. When hydrate starts to form in the system, the interface changes from oil-water to oil-hydrates. Thus, the interactions at the interface changes and the surface components in the oil lose theirs ability to keep the hydrate particles suspended in oil. As a result, the two immiscible liquids phase separated. Since the system is at a very high water content (90 vol.% water cut; emulsion inversion point for 2014 Conroe oil is ~ 95 vol.% at atm. P, confirmed by classical bottle test), hydrate particles remain suspended in the water phase. A conceptual picture that describes emulsion breaking is shown in Figure 5.5. This emulsion breaking was confirmed by the Particle Video Microscope (PVM) images that were collected during the experiment.
Figure 5.5: Conceptual picture of emulsion breaking that occurred upon hydrate formation in the 90 vol.% water cut experiment.

The PVM image for the 90 vol.% water cut experiment at 750 RPM obtained after emulsion breaking is shown in Figure 5.6. Firstly from this figure, it can be seen that there are large hydrate particle aggregates suspended in the system. This large hydrate particles were determined to be ~500 μm. In comparing the PVM images obtained from this work, it was observed that this image is similar to the typical PVM images for hydrate slurry experiments for 100 vol.% water cut (Greaves 2007; Greaves et al. 2008; Joshi 2012b; Joshi et al. 2013). Thus, Figure 5.6 confirms the hypothesis that the decrease in ΔP_{rel} of the system for 90 vol.% water cut experiment is due to emulsion breaking and the system changes from being oil continuous to water continuous.

Figure 5.6: PVM image for the 90 vol.% water cut experiment at 750 RPM collected after emulsion breaking.

The results of ΔP_{rel} as a function of hydrate volume fraction for three different water cuts and constant pump speed of 750 RPM is shown in Figure 5.4(b). Similarly, the ΔP_{rel} for 30 and 50
vol.% water cuts gradually increases with increasing amounts of hydrate formed in the system. In fact, the $\Delta P_{rel}$ traces for 30 and 50 vol.% water cuts overlay each other up to 20 vol.% hydrates. This indicates that similar flow conditions are occurring in the systems. Above 20 vol.% hydrates, there is no further hydrate formation in the 30 vol.% water cut experiment; while for the 50 vol.% water cut experiment, hydrate continues to form, the $\Delta P_{rel}$ gradually increases, and eventually the flowloop plugged. A plug is defined as limited flow of gas hydrate particles, with most of the hydrates remaining settled at the bottom of the loop. In this 50 vol.% water cut experiment, the plug was confirmed by the large fluctuation in the $\Delta P_{rel}$ data, as can be seen at ~4 hours in Figure 5.4(a), or at ~23 vol.% of hydrates in Figure 5.4(b).

For the 90 vol.% water cut experiment, the green trace in Figure 5.4(b) shows the $\Delta P_{rel}$ of the system decreases at the initial stage of hydrate formation (up to 2.5 vol.% hydrate fraction). Above this hydrate volume fraction, the $\Delta P_{rel}$ starts to increase. As stated earlier, the initial decrease in the $\Delta P_{rel}$ is due to emulsion breaking, where the continuous phase changes from oil to water. Since the viscosity of water is lower than the viscosity of oil, the $\Delta P_{rel}$ of the system decreases. As more hydrates form, the viscosity starts to increase and this increases the $\Delta P_{rel}$.

Figure 5.7 shows the comparison between three water cuts at a constant pump speed of 1200 RPM. Similar to the 90 vol.% water cut and 750 RPM experimental results, the 90 vol.% water cut and 1200 RPM experiments (green traces in Figure 5.7(a) and Figure 5.7(b)) show a decrease in the $\Delta P_{rel}$ of the system upon hydrate onset. However, after ~2.5 vol.% of hydrate particle, the $\Delta P_{rel}$ of the system starts to increase to a value of ~1. Similar to previous case, the decrease in $\Delta P_{rel}$ is due to emulsion breaking when hydrates start to form in the system. However, as more hydrate forms, the viscosity starts to increase and this increases the $\Delta P_{rel}$ of the system. The emulsion breaking that occurred was confirmed by the PVM images that were collected after emulsion breaking had occurred.

In contrast to the 750 RPM experimental results, it can be seen in Figure 5.7 that for 1200 RPM tests $\Delta P_{rel}$ for all water cuts investigated stabilizes at ~1 after a certain time and amount of hydrates has formed. Since $\Delta P_{rel}$ (determined from Equation (5-1)) represents the effect of hydrate particle formation on the $\Delta P$ of the system, $\Delta P_{rel}$ ~1 indicates the absolute value of $\Delta P$ remains unchanged, or there is only a small increase in $\Delta P$ when the system changes from emulsion to hydrate slurries. One explanation that the $\Delta P_{rel}$ stabilizes at ~1 is that the hydrate particles in the flowloop remain suspended with little to no hydrate particle settling or bedding.
Thus, at 1200 RPM (mixture velocity of 9.0 ft/s), the internal kinetic energy of the fluid is large enough for hydrate particles to remain suspended in the continuous phase.

**Figure 5.7:** Relative pressure drop (ΔP) traces: (a) as time progresses and (b) as a function of hydrate volume fraction for 1200 RPM test at three water cuts: 30 vol.% (red), 50 vol.% (blue) and 90 vol.% (green) water cuts.

Tests were also conducted to compare hydrate formation with different water cuts at a low pump speed of 350 RPM. Results of this test are shown in Figure 5.8. It should be stated that at this low pump speed, tests were only conducted for 50 and 90 vol.% water cut experiments due
to the limitation of time. As mentioned earlier, at this low pump speed, a partially dispersed system is formed, where a free water phase at the bottom of the loop was observed (Vijayamoham et al. 2014). Similar to flowloop tests at other pump speeds, emulsion breaking that resulted in a decrease in the $\Delta P_{rel}$ was observed for the 90 vol.% water cut experiment (green trace in Figure 5.8). Furthermore, tests for 50 and 90 vol.% water cut performed at this pump speed resulted in a plugged flowloop, where it was observed that hydrate particles form a bed at the bottom of the flowloop and there is limited flow of the liquid phase. For the 50 vol.% water cut test, plugging was confirmed by observations at the flowloop visual port, PVM images collected after plugging (Figure 5.11(a)), and $\Delta P$ readings. There are large fluctuations in $\Delta P_{rel}$ readings for 50 vol.% water cut after 2 hours (see Figure 5.8(a)) or at 13 vol.% hydrate particles (see Figure 5.8(b)). These large fluctuations are an indication that the momentum from the liquid phase is trying to lift the particles that have bedded at the bottom of the flowloop. Hence, these fluctuations are signals that the system has plugged (cf. Joshi 2012; Vijayamoham et al. 2014).

However, for the 350 RPM, 90 vol.% water cut test, flowloop plugging was only confirmed by observations at the visual port and the PVM images (Figure 5.12(a)). The absence of large fluctuation can be explained by the densities of each component. Methane hydrate has a reported density of 0.91 g/cm$^3$ (Sloan and Koh 2007), Table 5-1 shows that the density of 2014 Conroe oil is 0.85 g/cm$^3$ and the density of the 5 wt.% aqueous salt solution is 1.0 g/cm$^3$. Thus, by comparing the density of each component, it can be said that in the 50 vol.% water cut test, the hydrate particles tend to bed at the bottom of the flowloop, as hydrate particles are more dense compared to the continuous phase (2014 Conroe). As stated earlier, the large fluctuations are an indication that the internal momentum of the fluid is trying to lift the particles at the bottom of the flowloop. In contrast, for the 90 vol.% water cut tests where the aqueous phase is the continuous phase, hydrate particles are less dense than salt solution. Therefore, there is natural buoyancy that helps lift the particles. This is the reason there is an absence of large fluctuations in the 90 vol.% water cut test results.

### 5.3.4 Effect of Fluid Mixture Velocity (Pump Speed)

Figure 5.9 shows comparisons of different fluid mixture velocities at a constant water cut. From Figure 5.9(a) and (b) (30 vol.% and 50 vol.% water cut experiments), a clear trend between the $\Delta P_{rel}$ and the fluid mixture velocity can be observed. Specifically, as the fluid mixture velocity increases, the $\Delta P_{rel}$ of the system at similar hydrate volume fraction decreases. In fact,
for 1200 RPM and at 30 and 50 vol.% water cuts, the $\Delta P_{\text{rel}}$ stabilizes at ~1, indicating that there is a relatively small increase in $\Delta P$ when the system changes from an emulsion to a hydrate slurry. As discussed previously (Section 5.3.3 Effect of Water Cuts), a pump speed of 1200 RPM provided enough kinetic energy for the liquid phase to lift hydrate particles and prevent the hydrate bedding phenomenon. As such, hydrate particles in the flowloop are suspended in the oil phase.

![Graphs showing comparisons of $\Delta P_{\text{rel}}$ profiles as a function of hydrate volume fraction for different water cuts and fluid mixture velocities.](image)

**Figure 5.9:** Comparisons of $\Delta P_{\text{rel}}$ profiles as a function of hydrate volume fraction for: (a) 30 vol.%, (b) 50 vol.%, and (c) 90 vol.% water cuts at different fluid mixture velocity: 350 RPM (red), 750 RPM (blue) and 1200 RPM (green).
As shown in Figure 5.9(c), in all the 90 vol.% water cut experiments conducted in this work, there is an initial decrease in $\Delta P_{\text{rel}}$ and based on the discussion earlier, this decrease in $\Delta P_{\text{rel}}$ is due to emulsion breaking. Similar to the 30 and 50 vol.% water cut experiments, the 90 vol.% water cut system shows $\Delta P_{\text{rel}}$ decreases when the fluid mixture velocity increases from 350 RPM to 750 RPM. However, a decrease in $\Delta P_{\text{rel}}$ was not observed when the pump speed was increased to 1200 RPM for the 90 vol.% water cut system. In fact, the $\Delta P_{\text{rel}}$ traces for 750 RPM and 1200 RPM at 90 vol.% water cut are relatively similar. This indicates that the latter systems have relatively similar flow conditions, and the size of hydrate particles is relatively similar. This statement is confirmed by the PVM images that show for both cases (750 and 1200 RPM), water is the continuous phase for 90 vol.% water cut, and the size of hydrate aggregates is in the range of ~500 μm (Figure 5.12). In summary, $\Delta P_{\text{rel}}$ is shown to decrease when the fluid mixture velocity increases.

Two hypotheses have been proposed for the decrease in $\Delta P_{\text{rel}}$ as the fluid mixture velocity (pump speed) increases. The first proposed hypothesis is related to the hydrate particle aggregation phenomenon (Greaves 2007; Boxall 2009). It was observed that at high fluid mixture velocity, hydrate particles that are carried by the liquid. At high velocity, when two hydrate aggregates collide, they will collide at a high magnitude of momentum. This high momentum provides a large enough force for the large hydrate aggregates to break into small hydrate particles. In other words, a higher mixture velocity can prevent the agglomeration of hydrate particles. Smaller hydrate particles in the system lead to a smaller $\Delta P$ (cf. Greaves et al. 2008; Greaves 2007).

The first hypothesis with regard to the size of hydrate aggregates and agglomeration is confirmed by the PVM images. Figure 5.10 shows the PVM images for 30 vol.% water cut experiments at 750 and 1200 RPM. Analysis of the PVM images shows that the size of hydrate aggregates at 750 RPM is ~180 μm and at 1200 RPM is 150 μm. These results confirm our hypothesis that the reduction in $\Delta P_{\text{rel}}$ is due to the smaller size of hydrate aggregates at high fluid mixture velocity. In Figure 5.10, hydrate aggregates are marked with yellow circles.

Similar observations were made for the 50 vol.% water cut experiments. The PVM images of the tests are shown in Figure 5.11. For the 350 RPM test shown in Figure 5.11(a), individual hydrate particles could not be seen. In fact, a large and connected hydrate network was seen instead. This figure confirms that the flowloop was plugged at this condition, as discussed earlier.
(Section 5.3.3 Effect of Water Cuts). Further, analysis using ImageJ of the PVM images shows that for the 750 RPM test, the hydrate aggregates are around 280 μm in size; while for the 1200 RPM test, hydrate aggregates are smaller, with the size averaged at 180 μm. From Figure 5.11, it can be seen that at constant water cut, when the pump speed changes from 350 to 1200 RPM, the system changes from a large and connected hydrate network to individual hydrate particles of around 180 μm diameter. Similarly, the PVM images confirm the hypothesis that at higher mixture velocity, there are lower readings of ΔP_{rel} that are due to the smaller size of hydrate aggregates.

Figure 5.10: PVM images of 30 vol.% water cut gas hydrate slurries in the flowloop at (a) 750 RPM and (b) 1200 RPM. Hydrates particles are marked by blue lines in the images.

The PVM images for the 90 vol.% water cut experiments at three different fluid mixture velocities are shown in Figure 5.12. Similar to the 50 vol.% water cut test, a plug was observed for the 90 vol.% water cut experiment at 350 RPM. Therefore, the PVM image at this condition (Figure 5.12(a)) shows a large and connected hydrate network, that confirms the flowloop plugged even with the absence of large fluctuations in ΔP_{rel}. The PVM images collected in this study were also analyzed using ImageJ software, and the results show that for both 750 and 1200 RPM tests at 90 vol.% water cut, the systems have changed from being oil-continuous to water continuous, with hydrate aggregates of ~500 μm size. Hence, the images support the hypothesis that ΔP_{rel} of the system decreases as the fluid mixture velocity increases due to the smaller size of hydrate aggregates present.
Figure 5.11: PVM images of 50 vol.% water cut gas hydrate slurries in the flowloop at (a) 350 RPM, (b) 750 RPM, and (c) 1200 RPM.
Figure 5.12: PVM images of 90 vol.% water cut gas hydrate slurries in the flowloop at (a) 350 RPM, (b) 750 RPM, and (c) 1200 RPM.
The second hypothesis used to explain the decrease of $\Delta P_{rel}$ as the fluid mixture velocity increases is with regard to the hydrate/particle transportability. As the mixture velocity increases, the internal kinetic energy of the fluid also increases. As a result, when the mixture velocity increases, there is more momentum present in the system to prevent hydrate particle bedding in the flowloop. Therefore, the probability of hydrate bedding decreases with increasing fluid mixture velocity. This hypothesis is consistent with Vijayamohan et al. finding that the fluid has more capable to transport gas hydrate particles when it has higher mixture fluid velocity (Vijayamohan et al. 2014).

5.4. Chapter Concluding Remarks

In this doctoral work, hydrate formation and slurry properties were studied for the first time at two flow conditions (fully dispersed and partially dispersed systems) using an industrial-scale high pressure flowloop. In addition, the work is also the first studies on partially dispersed systems using crude oil. The results show that $\Delta P_{rel}$ decreases with increasing fluid mixture velocity at all water cuts investigated in this work. This is attributed to the high fluid mixture velocity providing the fluid with high internal kinetic energy that it is able to break large hydrates aggregates into smaller particles. In addition, this high kinetic energy also helps in preventing the hydrate particles from bedding in the flowloop.

A plug is defined by limited oil flow and where most hydrate particles settle at the bottom of the flowloop; as observed for 90 vol.% water cut and pump speed of 350 RPM. A plug was also observed for 50 vol.% water cut tests at pump speeds of 350 and 750 RPM.

Finally, emulsion breaking upon hydrate onset was observed in all of the 90 vol.% water cut experiments conducted in this study. This emulsion breaking resulted in a decrease in the $\Delta P_{rel}$ after hydrate formation. The decrease in $\Delta P_{rel}$ results from the system changing from oil continuous to water continuous. Since 2014 Conroe oil is slightly more viscous than the aqueous salt solution, and the viscosity of a solid suspension depends on the viscosity of the continuous phase, there is a decrease in the $\Delta P_{rel}$ when the emulsion’s continuous phase is changed.
An important variable that can affect the viscosity of a solid suspension is the particle size and distribution. Hydrate particles are formed via shell formation on water droplets emulsified in the oil phase. It is thus necessary to determine the size and distribution of water droplets in emulsions. This doctoral thesis proposed a new method using Nuclear Magnetic Resonance (NMR) to determine the water droplet size distribution. There are several advantages of the new proposed method. Firstly, the new proposed method used low field NMR rather than high field NMR. Consequently, the process is fast and has low experimental cost. Traditionally, the conversion of relaxation time ($T_2$) to droplet size requires some knowledge of the composition and properties of the oil. However, in this work, the proposed method does not require knowledge of composition or properties of the oil. This is one of the major advances made by this doctoral thesis. Finally, the new method is believed to be able to be applied for gas hydrate slurries systems. In this work, size distributions of water droplets of a model water-in-oil (w/o) emulsion prepared using mineral oil 70T with water cuts ranging from 10 – 70 vol.% were determined. The size was determined using two different methods: Diffusion-Transverse Relaxation ($T_2$) using low field (2MHz) Nuclear Magnetic Resonance (NMR) spectroscopy and microscopy image analysis. From this work, the size of water droplets measured using microscopy image analysis was calculated to be 2 to 3 $\mu$m, while the size of water droplets determined using the NMR method was calculated to be 3.5 to 4.5 $\mu$m. Regardless of the method used, both results show relatively similar water droplet size distributions across all water cuts investigated, with a minimum size observed at 50 vol.% water cut. The work performed here

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shows that the size of water droplets in w/o emulsions can be determined using low field NMR spectroscopy.

6.1. Background and Motivation of Work

As stated, the size distribution of water droplets in w/o emulsions is a major variable that can affect the viscosity of the suspension. A suspension that has a narrow particle size distribution will have higher viscosity, when compared to a suspension that has a large particle size distribution (Minana-Perez et al. 1986). Further, the size of water droplets in an emulsion can provide significant information regarding the tendency of pipeline plugging. For instance, when the size of water droplets in emulsions is small enough, there will be less of a gas diffusion barrier to form hydrates. Therefore, the water droplets will be fully converted to gas hydrates, and hence this reduces the probability of hydrate agglomeration and eventually pipeline plugging (Sloan and Koh 2007).

Currently, there are several techniques to determine the size of water droplets. The most common techniques are microscopy image analysis and Nuclear Magnetic Resonance (NMR) (Delgado-Linares et al. 2013; Aichele et al. 2007; Fridjonsson, Flux, and Johns 2012; Opedal, Sørland, and Sjöblom 2009). Both of these methods have their own advantages over the other. Most researchers prefer the optical microscopy image analysis method, as it is the simplest method currently available. In this method, a small amount of the emulsion is squeezed between two glass slides and microscopy images are taken using any type of optical microscope. The images are then analyzed using image analysis software. As can be seen here, the method is relatively fast. However, the downside of using this method is that only a small sample of the emulsion (a few drops) is used to measure the droplet size. Consequently, the result obtained in this method may not reflect the actual droplet size distribution in the emulsion. In contrast, in the NMR method, the entire sample is used to determine the size of water droplets. This gives a better description of the droplet size in the emulsion. Furthermore, analysis can be performed on dark oils that cannot be visualized with optical microscopy, and also since NMR uses the entire sample, the method is non-destructive. However, obtaining the droplet size using the NMR method may require a long time, mainly in terms of data processing. This technique is therefore suitable for research purposes, but might not be desirable for oil and gas operators since they might need the information rather quickly.
In this work, droplet size distribution was determined using two methods and the comparison of the two methods is shown here. The proposed NMR method is relatively simple and can be applied to w/o emulsion system without prior knowledge of the composition of the oil. Previous work on droplet size determination using NMR required some knowledge on the composition of the oil. The proposed work is highly beneficial as it provides an alternative to determine the water droplet size distribution of w/o emulsion using low field NMR that is fast and low cost. The work presented in this thesis also is believed can be applied to determine gas hydrate particle size and has not been applied by any other researchers.

6.2. Experimental Methodology

This section describes the procedures used to prepared the model emulsion systems. In addition, this section also describes the procedures and parameters used for the pulse sequence experiments conducted on the emulsion to determined the water droplet size distribution for both microscopy image analysis and low field NMR.

6.2.1 Emulsion Sample and Preparation

The model w/o emulsion that was used in this study is mineral oil 70T emulsion at 5 wt.% of surfactants: Span 80 and AOT. The mass ratio of Span 80 to AOT is 90 to 10. The properties of mineral oil 70T are listed in Table 2-1 on Section 2.3 Model Emulsion Systems. In addition, the molecular structure and properties of the two surfactants used in this work are also described in Section 2.3 Model Emulsion Systems.

Prior to any measurement using NMR and microscopy image analysis, model w/o emulsions needs to be prepared. The preparation steps for this emulsion are described in Section 2.3.1 Emulsification Process for Model Emulsion Systems.

6.2.2 Microscopy Droplet Size Measurement

Microscopy images of the model w/o emulsion were taken using an optical microscope (Olympus IX71) connected to a digital camera (Olympus XM10). These microscopy images were then analyzed using ImageJ software to determine the size of water droplets. Discussion on the procedures in analyzing the microscopy images have been discussed in Section 2.4.2 Microscopy Images of this thesis.
6.2.3 NMR Droplet Size Measurement

Droplet size measurements using NMR were conducted at ambient conditions (room temperature and pressure) using a 2 MHz Magritek Rock Core Analyzer. Two pulse sequences were used in this measurement: Carr-Purcell-Meiboom-Gill (CPMG) and Pulsed Field Gradient-CPMG Pulse Sequence.

6.2.3.1 Carr-Purcell-Meiboom-Gill (CPMG) Pulse Sequence

In the CPMG pulse sequence method, the $T_2$ relaxation mechanism consists of three relaxation components: bulk relaxation ($T_{2B}$), surface relaxation ($T_{2S}$) and diffusion induced relaxation ($T_{2D}$). This mechanism can be represented by Equation (6-1) (Dunn, Bergman, and Latorraca 2002).

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}$$  \hspace{1cm} (6-1)

![Figure 6.1: Schematic of CPMG pulse sequence (edited from (Aichele et al. 2007)). In this figure, FID is referred as free induction decay. $\pi$ and $\pi/2$ are the 180° and 90° pulses respectively. TE is called echo spacing, where it is the time between two consecutive 180° pulses (Majid et al. 2015).](image)

Using the optimum value of echo spacing (shown as TE in Figure 6.1), a simplification can be made on Equation (6-1). By this optimization, the diffusion induced relaxation ($T_{2D}$) mechanism of $T_2$ relaxation becomes negligible (Coates, Xiao, and Prammer 1999). The surface relaxation mechanism is a function of surface relaxivity, $\rho$, and the ratio of surface area, $S$, to volume, $V$, of the water droplets. Therefore, by assuming that the water droplets are spherical in shape, Equation (6-1) can be written (via Equations (6-2, 6-3)) as Equation (6-4).
By simple algebra, Equation (6-4) can be written as Equation (6-5). From this equation, it can be seen that the size of water droplet (radius of the water droplet) can be determined by measuring the bulk and T$_2$ distribution of the w/o emulsions, as well as the surface relaxivity of the oil.

$$r = 3\rho \left( \frac{1}{T_2} - \frac{1}{T_{2B}} \right)^{-1}$$  (6-5)

In this work the T$_2$ distributions were determined using low field (2MHz) NMR using the following parameters: 400 $\mu$s of echo spacing, 50,000 is the number of echoes, constant pulse length of 20 $\mu$s for 90° and 180°, and the signal to noise ratio (SNR) was chosen to be 250.

### 6.2.3.2 Pulsed Field Gradient-CPMG Pulse Sequence

Pulsed Field Gradient-CPMG (PFG-CPMG) pulse sequence consists of two sequences that include Pulse Field Gradient (PFG) and CPMG pulse sequences. In general, the pulse sequence captures two phenomena, which are the diffusion of water molecules restricted by droplet walls and the chemical properties of water and oil. The results of a pulse sequence experiment can be then converted to produce 2D D-T2 maps using inverse Laplace transform, such as shown in Figure 6.3 (Lawson and Hanson 1974; Hürlimann et al. 2002; Song 2010; Venkataramanan, Song, and Hürlimann 2002; Dunn and LaTorraca 1994).

Figure 6.3 shows the 2D D-T2 maps of a model w/o emulsion system at 20 vol.% water cut. In generating the 2D D-T2 maps, the parameters that were used are: a long diffusion time of 30 ms, 5 ms gradient pulse duration, 0.5 T/m maximum gradient and 40 gradient steps. From Figure
6.3(a) and using the correlation proposed by Lo et al. the diffusion responses for both water and oil could be separated (Lo et al. 2002).

In the w/o emulsion system, the diffusion of water molecules is restricted by the droplet walls. Hence, the diffusion value is lower compared to the diffusion in bulk water, as can be seen in Figure 6.3(a). This decrease in the diffusion value depends on the size of water droplets, as well as the parameters used in the PFG measurements. The diffusion values obtained from the 2D D-T2 map can be then converted to the size (radius) of water droplets. In this work, the values of diffusion coefficient were converted to the size (radius) of water droplets using a model developed by Murday and Cotts (Murday and Cotts 1968).

**Figure 6.2:** Schematic of PFG-CPMG pulse sequence (edited from (Aichele et al. 2007)). In this figure \( \delta \) is gradient pulse duration while \( \Delta \) is called the diffusion time where it is defined as the time between two gradient pulses. (Majid et al. 2015)

**Figure 6.3:** (a) A 2D D-T2 map of model w/o emulsion at 20 vol.% water cut. The dash blue line represent the diffusion coefficient of water measured in bulk water and the red oil line is calculated based on the correlation in (Lo et al. 2002) (b) Corresponding normalized diffusion coefficient, D and T2 distribution obtained from 2D D-T2 map.
6.3. Experimental Results

This section describes the results and comparison of the droplet size distribution determined from the two methods (microscopy image analysis and low field NMR). In addition, this section also discussed possible reasons of the difference results obtained by both methods.

6.3.1 Microscopy Droplet Size Measurements

Microscopy images of the model w/o emulsion prepared using mineral oil 70T are shown in Chapter 2, Figure 2.7. As reported in Chapter 2, the average droplet size for this emulsion was determined by microscopy image analysis to be $2 \sim 3 \mu m$. Figure 6.4 shows the average water droplet size across all vol.% water cuts investigated in this work. The error bars in the plot represent the standard deviation of the measurements.

![Figure 6.4: Average droplet size at various vol.% water cuts for model w/o mineral oil 70T emulsion determined from microscopy images analysis.](image)

From Figure 6.4, it can be seen that the average droplet size remains similar across all water cuts investigated. However, it appears that there is a minimum in the size of water droplets observed at 50 vol.% water cut. The size of water droplets is not expected to change across all water cuts, due to the high concentration of surfactant added in the system (Lingwood et al. 2012). Discussed in Section 2.4.3 Interfacial Tension Measurements (IFT), the CCA value for this emulsion system was determined to be 0.1 wt.%. 
6.3.2 NMR Droplet Size Measurements

Figure 6.5 shows the T2 distribution of both bulk systems (water and oil) and emulsion systems measured using the CPMG pulse sequence. From the measurements conducted on the bulk systems, it can be seen that there is a clear distinction between the oil and water T2 distributions (Figure 6.5(a)). However, this is not always the case for the emulsion system, Figure 6.5(b). A clear separation between oil and water T2 distributions could only be seen when the water cut is 50 vol.% and higher (≥50 vol.% water cut). In addition, when comparing the T2 distribution of the oil obtained from the bulk and from the emulsion, it can be seen that the T2 relaxation time does not change for the oil phase, since oil is the continuous phase. In contrast, as water is emulsified in the oil phase, the water T2 relaxation times are affected; there is a lower T2 relaxation time in the emulsion as compared to the bulk condition. In calculating the water droplet size distribution, the T2 relaxation time for water is needed. As stated, a clear separation between oil and water T2 distributions was only seen above 50 vol.% water cut. Thus, deconvolution of the peaks was conducted to separate the two peaks. The T2 distribution for water was then used for water droplet size distribution determinations.

![Figure 6.5: T2 distribution for (a) bulk water and oil and (b) emulsions at all vol.% water cuts studied.](image-url)
The size of water droplets was then calculated using the water T2 distribution measured in the emulsion system, and results are presented in Figure 6.6. It can be seen that the size of water droplets averaged at 4 μm. It should be stated that in this plot the error bars represent the smallest and largest water droplets detected in these measurements. Similar to results obtained using microscopy image analysis method, the results obtained from the NMR method show that there is minimal change across all vol.% water cuts investigated. As discussed, this minimal change is due the high concentration of surfactant in the system (Lingwood et al. 2012). However, as also seen in the microscopy method, a minimum size of water droplets was also observed at ~50 vol.% water cut using the NMR method. This minimum in the average water droplet size was observed near the inversion point of the emulsion, as discussed in Chapters 2 and 5. In this work, phase inversion occurred near 50 vol.% water fraction, and the emulsions at 60 and 70 vol.% water cut were all water continuous. Water continuous emulsions could be formed at these higher water cuts using different methods (slower water addition rate and longer stirring time), as discussed in Section 2.3.1 Emulsification Process for Model Emulsion Systems.

**Figure 6.6:** Average droplet size at various vol.% water cuts for model w/o mineral oil 70T emulsion determined from the NMR method.

### 6.3.3 Comparison Between NMR and Microscopy Results

A plot of the comparison between the two proposed methods is shown in Figure 6.7. In terms of similarity between the two results, both systems reported the average droplet sizes to be similar in order of magnitude. Furthermore, the results obtained from both measurement methods
show a similar trend, whereby there is an apparent minimum droplet size observed at 50 vol.% water cut.

![Comparison of water droplet size at all vol.% water cuts determined by NMR and microscopy image analysis methods.](image)

**Figure 6.7:** Comparison of water droplet size at all vol.% water cuts determined by NMR and microscopy image analysis methods.

Even though the size reported in both methods is similar in magnitude, the NMR method reported that the average droplet size is 1 μm larger compared to the microscopy image analysis method. In addition, the results show that there is larger deviation in the microscopy image analysis technique. The smaller droplet size distribution and larger deviation in microscopy image analysis results are likely to be due to the inherent error in the optical microscopy analysis method. In microscopy image analysis, images are taken only on the x-y plane. Therefore, the vertical position (z-axis) of the water droplet is unknown. As a result of this, water droplets that are far from the lens appear smaller in the image. In this microscopy image analysis method, regardless of the vertical position, all water droplets in the images were used to determine the average droplet size. As a result of this inherent error, a smaller average and larger deviation is obtained.

### 6.4. Chapter Concluding Remarks

The work performed in this thesis study shows that Diffusion-Transverse Relaxation using low field (2MHz) NMR spectroscopy could be used to determine the droplet size of w/o emulsions. The main advantage of using this method is that no prior knowledge on the composition of the oil is needed. In addition, the NMR method proposed in this thesis work is relatively simple, fast and has low experimental cost. The work presented in this thesis chapter
could also be extended to provide a new and efficient low field NMR method to determine gas hydrate particle size in slurry systems. In this work, the size of water droplets obtained by this method was compared with the traditional optical microscopy image analysis. The results from both studies show a similar trend of water droplet size across all water cuts investigated. There is minimal change in the size of water droplet across of the water cuts studied, although there is a minimum of water droplet size at 50 vol.% water cut. This minimum occurs near the inversion point of the emulsion. In this work, oil continuous emulsions could be formed at 60 and 70 vol.% water cut using slower water addition rates and longer stirring times. However, results show that the average droplet size determined by the NMR method is on average 1 μm larger than the size obtained by microscopy image analysis. In any case, the LF NMR method proposed has been shown to be useful to determine the size distribution of water droplets in a w/o emulsion.
CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

As discussed in Chapter 1 of this doctoral thesis, the oil/gas industry is moving towards “hydrate management” methods in dealing with gas hydrates in flowlines. In this method, hydrates are being allowed to form in the flowlines, but are managed and controlled to avoid flowline plugging. Successful “hydrate management” requires advanced understanding on the transportability of gas hydrates slurries. In this doctoral thesis, two different methods were used to investigate the transportability of gas hydrate slurries; (1) a high pressure rheometer and (2) an industrial-scale high pressure flowloop. Since the transportability of gas hydrates in flowlines also depends on the particle size distribution, studies on the measurements of droplet size distribution using NMR were also conducted in this work. The summary and conclusions of the work performed in this thesis are summarized below.

(1) Chapter 1:
The two methods that can be used to deal with gas hydrates slurries in flowlines were described (hydrate avoidance and hydrate management). Introductions on the application of rheological properties of gas hydrate slurries for better hydrate management were also discussed.

(2) Chapter 2:
Model emulsion systems consisting of mineral oil (350T or 70T and surfactant mixture, Span 80 and AOT) were developed for gas hydrate studies. Characterizations tests were conducted on the emulsions and showed that the emulsions have an average water droplet size in the range of 2 – 5 μm, and are highly stable. In addition, tests conducted using these emulsions show that these model emulsions behave similarly to water-in-crude oil emulsions

(3) Chapter 3:
Viscosity measurements prior to hydrate formation were conducted on the model emulsions at various temperature and pressure conditions. The measurements were used as the baselines
for the analysis of viscosity of gas hydrate slurries. A generalized equation was developed, that is a function of temperature, water volume fraction and saturation of oil phase.

(4) Chapter 4:
Viscosity measurements were conducted on gas hydrate slurries. Measurements were made at constant pressure of 1500 psig of methane, constant temperature of 1 °C and constant mixing speed of 477 RPM. The concentration of gas hydrate particles was varied by changing the water volume fraction of the emulsion from 5 – 30 vol.% . A model for relative viscosity of gas hydrate slurries that is a function of hydrate fraction was also developed. In addition, emulsion breaking upon hydrate formation was observed in the hydrate slurry experiments near the inversion point of the emulsion.

(5) Chapter 5:
The transportability of gas hydrates was also investigated in an industrial-scale high pressure flowloop. Investigations were made at two different flow conditions: fully dispersed and partially dispersed systems. Results shows that the transportability of gas hydrate slurries increases with an increase in fluid mixture velocity. There is also a lower tendency for hydrate particles to form a bed at the bottom of the flowloop when there is higher mixture velocity. Emulsion breaking upon hydrate formation was also observed near the inversion point of the emulsion.

(6) Chapter 6:
Droplet size distributions of w/o emulsions were determined using low field NMR. The new method developed in this work provides several advantages over other NMR methods. Firstly, it is relatively fast and has low cost. In addition, unlike other methods, knowledge of the composition of the oil is not needed. It is also proposed that the method can be applied to gas hydrate systems. Results of the low field NMR tests were compared with results obtained from optical microscopy image analysis. The comparisons shows that the droplet size reported in both methods are relatively similar (within ± 1.5 μm difference)

As can be seen, the work performed in this thesis consists of three main areas of research: (1)
rheological measurements of water-in-oil emulsions and hydrate slurries using high pressure rheometer (High Pressure Rheometer), (2) hydrate slurry conditions in a high pressure flowloop (Flowloop) and (3) droplet size distribution using low field Nuclear Magnetic Resonance (NMR) spectroscopy. As such, the recommendations for future work will be based on these three areas of research.

7.1. High Pressure Rheometer

Listed are the recommendations for the high pressure rheometer study:

1. Study the effect of shear rates

   As presented in this work (Chapters 3 and 4), the rheology of water-in-oil (w/o) emulsions and hydrate slurries were investigated at a high mixing speed of 477 RPM. This high mixing speed was chosen as it was observed in previous studies that the saturation of oil from dead to live oil, as well as the re-saturation of the oil with methane gas after the formation of hydrate, could significantly affect the viscosity of the hydrate slurries (Webb 2013; Rensing 2010). Therefore, a high mixing speed was chosen to improve the saturation rate.

   However, as only one mixing speed was used in this study, the behavior of gas hydrate slurry whether it behaves as shear thinning could not be determined. Therefore, it is recommended to perform hydrate slurries experiments at different shear rates to observe and validate this non-Newtonian behavior.

   The test can be performed by forming the gas hydrates at a high shear rate, and once the system reaches steady state, the shear rate can be reduced to lower rates. The shear rate of the system can be ramped back up to observe any evidence of hysteresis.

2. The use of different geometry

   The density difference between hydrate particles and the continuous phase might result in the hydrate particles settling at the bottom of the rheometer pressure cell. This heterogeneous distribution of hydrate particles leads to misleading information on the viscosity of hydrate slurries. As such, a mixing geometry that can ensure the hydrate particles remain homogeneous is needed.

   In this work, it was proposed to use a four blades vane impeller, which was a significant improvement in the couette geometry previously used. However, it was observed that hydrate particles can be trapped between the blades. Thus, to improve the gas saturation rate and
ensure the hydrate particles remain dispersed, it is recommended to use a double-sided helical impeller as shown in Figure 7.1 (Sjöblom et al. 2010). This type of impeller is believed to be able to improve the saturation rate as well as help prevent the settling of hydrate particles.

**Figure 7.1:** (a) Design for double-sided helical impeller proposed for future work and (b) double-sided helical impeller built and designed for the autoclave system.

Initial Computational Fluid Dynamics (CFD) simulations for the helical impellers were performed using COMSOL®, to determine the flow velocity path of the system. Results of the simulations at 300 RPM mixing speed are shown in Figure 7.2.

**Figure 7.2:** Result of CFD modeling using COMSOL® for helical impeller stirred at 300 RPM.
In Figure 7.2, the black lines are the velocity flow paths (streamlines). Based on the streamlines, it can be seen that both vertical and horizontal flows are present in the system. Therefore, with vertical flow, it is believed that settling of hydrate particles can be prevented or reduced. This helps the hydrate particles to remain homogeneous and thus enables better accuracy in the viscosity measurements.

3. Shut-in condition and yield stress

An important aspect of rheological properties of gas hydrate slurries in flowlines are the shut-in and subsequent restart conditions, e.g. when the flowlined have to be shut-in due to unplanned maintenance, or severe weather conditions, such as a hurricane, and then restarted after these shut-in events. When the flow of oil in flowlines has to be stopped, the morphology of hydrates in the system may change: large hydrate aggregates could form. This will certainly affect the rheological properties. Therefore, it is recommended to perform viscosity measurements after the system has been put in shut-in mode for several hours, and also after restart.

In addition, it is also important to determine if gas hydrate slurries exhibit any yield stress. Yield stress is the minimum force that is required for the fluid to flow. In this measurement, the system has to be put into a shut-in condition. This allows the hydrate particles to anneal over the shut-in duration. During this shut-in process, storage ($G'$) and loss ($G''$) moduli measurements can be performed. After the shut-in condition, the yield stress can be then measured (cf. Webb 2013; Rensing 2010).

4. The effect of salt

In an actual subsea oil/gas flowline, the aqueous phase typically contains a certain amount of salt (typically 3.5 wt.% salinity). The presence of salt has two effects on hydrate properties. Firstly, salt is known to be a thermodynamic hydrate inhibitor. As a result, the subcooling of the experiment will be different to the case without salt. In a study conducted by Aman, hydrate aggregation phenomena are affected by the subcooling of the system (Aman 2012). Since the size of aggregates can then influence the viscosity of the slurry, it is thus recommended to perform hydrate slurry viscosity measurements with the presence of salt.
Furthermore, studies on emulsions have shown that the properties of the emulsion (stability and droplet size) can be affected by the concentration of salt (Ese and Kilpatrick 2004; Zhang et al. 2012; Gao et al. 2010). As discussed, if the water droplets are small enough, the droplet will be fully converted to hydrates, and thus agglomeration can be prevented. In separate studies, the effectiveness of an Anti-Agglomerant (AA) can be improved by the addition of salt. This prevents the formation of large hydrate aggregates (Majid et al. 2014). It is necessary to perform hydrate slurries viscosity measurements in the presence of salt.

5. Rheology of hydrate slurries formed from water-in-crude oil

In this work, a model w/o emulsion was used rather than water-in-crude oil. As discussed, model emulsions that have similar behavior as water-in-crude oil emulsions were used in order to obtain reproducible results. In addition, by eliminating certain components of the crude oil, such as asphaltenes, fundamental interactions of gas hydrates can be investigated.

However, it is also important to perform rheological studies of gas hydrates slurries using a crude oil system. By doing this study, a comparison between results obtained in the rheometer can be compared with results obtained in the flowloop (using the same crude oil system). The comparison between rheometer and flowloop data would add tremendous value to the data obtained in a high pressure rheometer.

Initial work has been conducted to compare the results obtain in the rheometer and the high pressure flowloop data. Result of this comparison is shown in Figure 7.3. As discussed in Chapters 4 and 5, model water-in-oil emulsions were used in the rheometer studies, while crude oil emulsions (2014 Conroe) were used in the flowloop. The experiments were also performed at different conditions: 1500 psig of methane in the rheometer and 1000 psig of methane in the flowloop. Further, the flow conditions in the system might also be different. Regardless of these differences, relative calculations (relative ΔP and relative viscosity) were performed; Figure 7.3, shows the results obtained in both systems are relatively similar.

Since the two systems in this study are different, a definitive conclusion could not be made with from results. However, the results indicate that it may be possible to develop a correlation between rheometer and flowloop data. Hence, it is strongly recommended to
perform rheometer tests using a crude oil emulsion, specifically using 2014 Conroe so that comparisons between the two apparatuses can be done.

![Graph showing comparison of relative ΔP and relative viscosity between high pressure flowloop and high pressure rheometer.](image)

**Figure 7.3:** Comparison of the relative ΔP and relative viscosity between the high pressure flowloop and high pressure rheometer, respectively.

### 7.2. High Pressure Flowloop

Listed below are the recommendations for high pressure flowloop studies.

1. **Study the effect of AA**

   The use of AAs has gained a lot of interest by the oil/gas industry. AAs have been proven to be capable of avoiding pipeline plugging (Majid et al. 2014). An AA can reduce the cohesion force between hydrate particles (Aman et al. 2011; Aman 2012). The change in interaction parameters can affect the viscosity of the hydrate slurries. Thus, it will be interesting to observe the effect of an AA on the viscosity of gas hydrate slurries.

2. **Study the flow regime in the loop**

   In work performed by Hegde et al., the formation of gas hydrates can affect the flow regime (Hegde et al. 2014). Thus, it is important to determine the flow regime of each of the experiments performed in the flowloop. The flow regime of the system is important information when comparing the results obtain in the flowloop with the results from the rheometer.
7.3. **Nuclear Magnetic Resonance**

Listed are the recommendations for NMR studies:

1. **Experiments at low temperature**

   In a work performed by Boyd et al., the authors showed the coalescence rate of water droplet decreases with temperature (Boyd and Road 1972). From their study, it can be inferred that the water droplet size of a w/o emulsion depends on the temperature at which it is being measured. Since hydrates form at low temperature, it would be beneficial to determine the droplet size at the experimental temperature of the rheological measurements. By performing the experiments at low temperature, this would give a better representation of the size distribution of hydrate particles.

2. **Effect of saturation**

   It is believed that water droplet size depends on the saturation of gas in the oil phase. However, it is difficult to study the effect of saturation on the water droplet size mainly due to the limitation of equipment. For instance, microscopy image analysis using simple microscope could not be used to study this effect. Thus NMR is a better option to study the effect of saturation on the water droplet size of emulsion.

3. **Nano size water droplets**

   As discussed in Chapter 6, the use of NMR to determine the water droplet size distribution has been applied in several fields. In these fields, most of the water droplets are in the range of micrometers. As a result, there are limited studies on the limitations and capability of NMR methods to determine smaller water droplets size (in the range of nanometers) (Opedal, Sørland, and Sjöblom 2009; Packer and Rees 1972; Fridjonsson, Flux, and Johns 2012). In addition, some researchers believe that there are small water droplets in the size of nanometer that could not be detected by microscopy images. Therefore it is a great interest and importance to apply the method proposed in this thesis to other systems to determine its capability to measure the smaller droplets size.
4. Experiments at low temperature and high pressure (hydrate particle size)

It has been shown in Chapter 6 that the proposed NMR method was able to be applied to determine the size of water droplet in a w/o emulsion. From this work, it is believed that the method can be performed at high pressure conditions. However, some upgrade of the equipment is needed to be performed and is currently still in the design stage.

If tests could be performed at high pressure and low temperature, the hydrate particle size distribution could be determined in-situ. The latter particle size may also be affected by the extent of gas saturation, which could also be investigated. The results from such studies would provide valuable information, such as hydrate conversion and hydrate particle size distribution. This will then improve the relative viscosity model proposed for gas hydrate slurries.
REFERENCES CITED


A.1 Composition of Mineral Oil 70T

Table A-1: Composition of mineral oil 70T.

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### A.2 Composition of Mineral Oil 350T

**Table A-2:** Composition of mineral oil 350T.

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APPENDIX B
CALIBRATION BETWEEN TORQUE AND VISCOSITY

B.1 Calibration Plot for Torque and Viscosity

Figure B-1: Relationship between viscosity and torque.

Figure B-2: Relationship between log of viscosity and log of torque.
C.1 Equation for Minimization of Errors

\[
\min \left( \sum_{i}^{n} \sqrt{(X_{\text{data},i} - X_{\text{model},i})^2} \right)
\]  \hspace{1cm} (C-1)

where:

\(X_{\text{data},i}\) = the \(i^{th}\) experimental data

\(X_{\text{model},i}\) = the \(i^{th}\) data calculated from model

\(n\) = number of data points
APPENDIX D
HYDRATE VOLUME FRACTION CALCULATIONS

D.1 Hydrate Volume Calculations

\[ V_{\text{hydr}} = \frac{n_{\text{hydr}}}{\beta} \]

where

\[ V_{\text{hydr}} = \text{Volume of hydrates (cm}^3\text{)} \]

\[ n_{\text{hydr}} = \text{Mole of methane consumed for hydrates (mol)} \]

\[ \beta = \text{Mole of methane per volume of hydrates (mol/cm}^3\text{)} \]

(CSMGem)

D.2 Hydrate Volume Fraction Calculations

\[ \varphi_{\text{hydr}} = \frac{V_{\text{hydr}}}{V_{\text{total}}} \]  \hspace{2cm} (D-1)

\[ \varphi_{\text{hydr}} = \frac{V_{\text{hydr}}}{V_{\text{oil}} + V_{\text{water}} + V_{\text{hydr}}} \]  \hspace{2cm} (D-2)

where

\[ V_{\text{hydr}} = \text{Volume of hydrates (cm}^3\text{)} \]

\[ V_{\text{total}} = \text{Total volume of system (cm}^3\text{)} \]

\[ V_{\text{oil}} = \text{Volume of oil (cm}^3\text{)} \]

\[ V_{\text{water}} = \text{Volume of unconverted water (cm}^3\text{)} \]
APPENDIX E
COMPARISON WITH CAMARGO AND PALERMO MODEL

E.1 Comparison with Camargo and Palermo Model

Figure E-1: Comparison between the new model developed in this work with the well-known Camargo Palermo model for (a) mineral oil 350T and (b) mineral oil 70T hydrate slurries.
Appendix F

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8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court. If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.