RHEOLOGY OF METHANE HYDRATE SLURRIES FORMED FROM WATER-IN-OIL EMULSIONS

by

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ABSTRACT

Solid structures known as natural gas hydrates can form in subsea pipelines, hindering and sometimes blocking flow completely. A knowledge of the flow properties of hydrate containing slurries could help the oil industry better predict and prevent hydrate formation. In particular, the rheology (e.g., viscosity, yield stress) of hydrate slurries is not well understood. On a more scientific level, the transient rheological properties of an emulsion converting to a suspension has not been studied extensively.

A high pressure rheometer apparatus was developed to study hydrate formation from water-in-oil emulsions. This study conducted investigations on three different emulsions from which hydrates were formed: water-in-West African crude oil (a fluid found in subsea pipelines), water-in-dodecane with AOT surfactant (a model emulsion with low viscosity), and water-in-70T mineral oil with span 80 and AOT surfactants (a model emulsion with high viscosity). Each of these emulsions provides a unique way to observe hydrate rheology. In every emulsion, viscosity increased on the order of minutes upon hydrate formation. Hydrate formation from water-in-oil emulsions increased viscosity, increased shear-thinning behavior, and introduced a yield stress to the original emulsion. The transient viscosity profile as hydrate form and grow were influenced by many factors including conversion of liquid water drops to solid particles, aggregation of hydrate particles, methane depletion and diffusion, and capillary bridging.

In the mineral oil-based system, methane saturated emulsion viscosity was about an order of magnitude larger than methane saturated mineral oil viscosity. The maximum viscosity observed during hydrate formation was on the order of a 10-fold increase in viscosity. So, introduction of water to oil in a pipeline followed by hydrate formation may cause a 100-fold increase in viscosity. Fractional conversion of water to hydrate was calculated from pressure measurements. Hydrate slurry viscosity reached a maximum at less than 100%
conversion of water to hydrate; so, viscosity of this part-suspension-part-emulsion was higher than suspension or emulsion viscosity.

In the dodecane and mineral oil-based emulsions, if significant unconverted water remained after the initial formation event, viscosity increased for a time as additional methane dissolved and converted some remaining water to hydrate. In general, decreased driving force (e.g., temperature) for hydrate formation resulted in increased rheological properties (transient viscosity, yield stress, steady state viscosity).
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<td>112</td>
</tr>
<tr>
<td>6.5</td>
<td>Cross and power law model fit parameters for experiments in this study.</td>
<td>112</td>
</tr>
</tbody>
</table>
Table 7.1  Viscosity of each external phase investigated. Measurements at 100 s^{-1}, 0 °C, and ambient pressure.  

Table 7.2  Change in pressure predicted with no methane diffusion compared to the measured pressure change.  

Table A.1  Time for methane to diffuse into dodecane.  

Table A.2  Sensitivity analysis of four variables on viscosity.
ACKNOWLEDGMENTS

This work was completed through the power of the living God, and all glory goes to Him.
1.1 What Are Hydrates?

Natural gas hydrates, also called clathrate hydrates, or just hydrates, are solid crystal structures formed from water and small guest molecules (Sloan & Koh, 2008). Hydrates typically only form at high pressure and low temperature conditions. The water molecules form cages around each guest molecule. Each cage typically contains one gas molecule. Multiple cages connect together in a regular pattern that repeats and fills space to form a crystal structure. Hydrates can commonly form three different crystal structures. Each structure consists of several different sized cages. Figure 1.1 shows the type and number of cages that go into one unit cell of the three most common hydrate crystal structures.

Structure I hydrates are most commonly formed with pure methane as the guest molecule. These hydrates are abundant in nature, often found on ocean floors. Decaying plant and animal life give off methane, which is then enclathrated by the surrounding water. The ocean depth provides sufficient pressure and temperature conditions for hydrate formation. Structure II hydrates are most commonly formed with a mixture of methane, ethane, and propane. Structure II hydrate is rare in nature; however, it commonly forms in sub-sea oil pipelines, which contain water, hydrocarbons of all sizes, high pressure, and low temperature. Structure H is extremely rare in nature, and is mostly studied as a laboratory curiosity. Unlike structures I and II, structure H requires two different guest molecules. The phase diagrams in Figure 1.2 show the diversity of phases that can be formed from just water and methane (Figure 1.2 a) and the extreme conditions required to form hydrates for light alkane guest molecules (Figure 1.2 b).

Each hydrate structure contains about 85 mole percent water assuming perfect cage filling. If all cages are filled, structure I hydrate has 5.75 water molecules per guest molecule.
Figure 1.1: Common hydrate structures with their cages and unit cells (Sloan & Koh, 2008). The numbers below the cages indicate the number of faces (the superscript number) and the number of sides on each face. The numbers above the arrows show how many cages of each type go into one hydrate crystal unit cell.
while structure II hydrate has 5.67 water molecules per guest molecule. Because of the large water content, hydrates often look like ice and have some similar mechanical properties.

The preferred structure depends on the pressure and temperature conditions as well as the size, shape, and chemical nature of the guest molecule. Typically, hydrates will form in the structure that gives the ratio of guest molecule diameter to cage diameter closest to one. In the presence of multiple guest molecules, each cage type may be occupied by a different guest, e.g., propane in the 5₁₂₆₄ cages and methane in the 5₁₂ cages of structure II hydrate. These are called double hydrates. Chemically, guest molecules fit into four categories: Hydrophobic compounds, water soluble acid gases, water soluble polar compounds, and water-soluble ternary or quaternary ammonium salts. The guest molecule cannot possess one strong hydrogen bond or multiple medium strength hydrogen bonds. Pressure and temperature conditions can also determine structure type. For example, cyclopropane can form structure I or structure II hydrate at different pressure and temperature conditions.
Hydrates possess several other interesting characteristics. First, hydrates sometimes can exist for long periods of time outside the thermodynamically favorable region for hydrate formation. The effect is not well understood and is called the self-preservation effect. Second, hydrate will burn. The burning snowball illustrates this effect (Figure 1.3). Third, hydrates sometimes retain some memory of their structure after melting. The so-called “memory effect” allows hydrates to form more easily from melted hydrate than from a fresh gas and water mixture.

![Figure 1.3: Burning methane hydrate “snowball” (Progress, 2008).](image)

### 1.2 Hydrate Applications

Hydrates are more than just a scientific curiosity. They have at least two major practical applications, one positive and one negative. Hydrates exist in abundance naturally on the oceans floors. These hydrates in nature form mostly structure I hydrate from the methane released by decaying plant and animal life. Figure 1.4 shows a naturally occurring subsea hydrate deposit. Even by conservative estimates, the amount of methane contained in these deposits at least doubles the total amount of energy that could be gained from all the remaining other fossil fuels in the world. Because of this potentially enormous alternative energy source, several labs around the world are performing research to discover safe and economical methods to harvest methane from these hydrates in nature.
The other major application, hydrates in flow assurance, concerns hydrates in subsea pipelines. This time, hydrates are the problem, not the solution. Subsea oil and gas pipelines satisfy all four conditions for hydrate formation, they have water and guest molecules at sufficient temperature and pressure. Hydrates will often form in pipelines and cause blockages in the lines. This most frequently occurs during shut-in or restart operation of the flowline. Figure 1.5 shows a hydrate plug removed from a subsea pipeline.

Figure 1.5: A gas hydrate plug being removed from a pig launcher after pigging. Image courtesy of Petrobras.
Hydrates are the number one flow assurance issue for the oil industry (Sum et al., 2009). The industry annually spends over 200 million USD on hydrate prevention (Sum et al., 2009). Hydrate blockages are safety concerns as well as economic losses. In this work, we are primarily concerned with hydrates in flow assurance. Some results from this work may find application for hydrates in nature, likewise, some work from that field can further our understanding of hydrates in flow assurance.

A long chain of events leads up to hydrate plugging in an oil pipeline. First, hydrates have to nucleate, which is a rare event. Nucleation usually requires emulsified water droplets, since nucleation depends on surface area. Nucleation time decreases with increasing subcooling (the difference between operating temperature and hydrate equilibrium temperature). After nucleation, hydrate crystal growth occurs. Hydrates first form a shell around emulsified water droplets, and then grow inward. If the droplets are small enough, they will fully convert to hydrate. Next, hydrates aggregate with each other, settle, and deposit on walls. When aggregates become large enough, jamming may occur. The mechanisms by which many of these events occur are still largely unknown. Much research goes into qualitatively understanding the mechanisms for each of these events and quantitatively modeling their occurrence. A conceptual picture of the events leading up to jamming in an oil pipeline represents an oil-dominated system with subcomponents water and gas (Figure 1.6). Different events likely occur in gas-dominated and water-dominated systems.

Figure 1.6: Conceptual picture of plug formation in a oil-dominated subsea pipeline.
1.3 What Is Rheology?

Rheology is the study of the deformation and flow of matter (Macosko, 1994; Morrison, 2001). This field can quantitatively explain the differences between fluids such as water, honey, and peanut butter. One difference between fluids, is their viscosity. Viscosity is a mathematical parameter that represents the thickness of a fluid. To help understand viscosity mathematically, imagine a homogeneous fluid placed between two plates with area $A$. The distance between the two plates is $H$. Set the top plate in motion with velocity $v$. Figure 1.7 illustrates the problem. The force required to move the top plate will be directly proportional to the area and the velocity gradient, $v/H$.

![Figure 1.7: Two parallel plates of area A separated by distance H. The top plate moves with velocity v.](image)

\[ F = c \cdot A \cdot \frac{v}{H} \]  \hspace{1cm} (1.1)

$c$ is the proportionality constant. Converting equation 1.1 to differential form:

\[ \frac{F}{A} = c \left( \frac{dv_y}{dy} \right) \]  \hspace{1cm} (1.2)

Equation 1.2 is called Newton’s law. the force divided by area is called the shear stress, and denoted $\tau$. The velocity gradient, $\frac{dv_y}{dy}$, is called the shear rate, and denoted $\dot{\gamma}$. The constant, $c$, is called the viscosity, and denoted $\eta$. Rewriting with the new variables:

\[ \tau = \eta \dot{\gamma} \]  \hspace{1cm} (1.3)
When $\eta$ does not depend on shear rate, the fluid is said to be Newtonian. If $\eta$ varies with shear rate, the fluid is non-Newtonian. When $\eta$ increases with shear rate, the fluid is shear-thickening, or dilatant. Many suspensions of solid particles in a liquid show shear-thickening behavior. Sand in water or a mixture of corn starch and water are examples of shear-thickening fluids (Crawford et al., 2013). When viscosity decreases with shear rate, the fluid is shear-thinning, or pseudoplastic. Many polymer solutions show shear-thinning behavior. As shear rate increases, the long polymer chains transition from a tangled, random orientation to a more streamlined orientation aligning with the flow. This transition reduces the resistance to flow, which is viscosity. Some systems will show shear-thinning behavior in one range of shear rates and shear-thickening behavior in another range (Wagner & Brady, 2009). A plot of shear stress versus shear rate illustrates the different types of non-Newtonian behavior (Figure 1.8). In these plots, viscosity is the slope.

![Figure 1.8: Viscous response of common types of fluids](image)

In all of these fluids, a finite applied stress will produce a finite deformation. Some materials; however, do not deform below a certain critical stress, called the yield stress. Many common household materials possess a yield stress; peanut butter, mayonnaise, and ketchup are just a few.
A rheometer measures parameters such as viscosity and yield stress. Rheometers work in two general ways. First, they could apply a known stress and measure the rate of deformation. These instruments are called controlled stress rheometers. Second, they could deform the material at a known rate and measure the required force. These instruments are called controlled strain rheometers. Many different rheometer designs exist. Morrison (Morrison, 2001) divides rheometer designs into two types: shear flow designs and elongational flow designs. Each class measures different non-zero components of the total stress tensor (Figure 1.9), so the measured viscosity values have different physical significance. Shear flow rheometers measure the off-diagonal components of the total stress tensor, i.e., $\tau_{ij}$, $i \neq j$. Shear flow rheometer designs are much more common, and are typically used when viscosity is the desired material property. Elongational flow rheometers measure the diagonal components of the total stress tensor, i.e., $\tau_{ij}$, $i = j$. Elongational flow rheometers commonly find application with highly viscous liquids, gels, or even solids. Figure 1.10 shows two types elongational flow rheometers; both are uniaxial stretching designs. Biaxial stretching designs are also possible, although they are much more complicated.

Shear flow rheometers can be subdivided into capillary flow and drag flow designs. Figures 1.11 and 1.12 show capillary flow and drag flow designs respectively. Capillary designs can measure very high shear rates and high viscosity fluids; however, the flow is not homogeneous, and several corrections need be applied to interpret the data. Also, the capillary flow designs are single pass instruments. Cone and plate design is typically best because the flow is homogeneous. Parallel plates are best for gel-like samples or suspensions with large particles. Concentric cylinders (couette) are best for low viscosity samples and suspensions.

1.4 What Can Rheology Tell Us About Hydrates?

Flow assurance engineers are faced with several problems when it comes to hydrates. First, they do not know how the amount of hydrates in a pipeline correlates with the flowability of the fluid in that pipeline. In other words, engineers and operators cannot determine the viscosity of the fluid based on the measurements at their disposal, which include pressure,
Figure 1.9: The total stress on a material can be divided into nine components, which are represented by the total stress tensor, $\tau$.

\[
\tau = \begin{bmatrix}
\tau_{11} & \tau_{12} & \tau_{13} \\
\tau_{21} & \tau_{22} & \tau_{23} \\
\tau_{31} & \tau_{32} & \tau_{33}
\end{bmatrix}
\]

Figure 1.10: Extensional rheometer geometries.
Figure 1.11: Capillary rheometer geometries

Figure 1.12: Rotating rheometer geometries
temperature, time, velocity, and composition. Accurate prediction of hydrate viscosity would be helpful during restart of a sub-sea oil pipeline. Flowability will also affect energy costs associated with pumping the slurry. Rheology can help to determine viscosity at various pipeline conditions. Flow assurance engineers also have trouble with plug characterization. If a plug forms, very little can be said about the plug characteristics such as size, strength, and porosity. Again, rheology could help to quantitatively characterize plugs on a laboratory scale.

On a more fundamental level, the rheological properties of sI methane hydrate have not yet been measured in a shear-flow rheometer outside of this research group. So, one principle aim of this work is the quantification of the rheological properties of sI methane hydrate over a broad range of experimental conditions. Rheology tests can also reveal qualitative information about how hydrates form, grow, change under flow, and dissociate.
CHAPTER 2
BACKGROUD

Much of the work described in this document consists of experiments that measure rheological properties of an emulsion as hydrate forms from water droplets in the emulsion. So, in some ways, the emulsion changes to a suspension. In many cases, the transition is incomplete; not all water converts to hydrate. So, the final slurry is often part emulsion and part suspension. Furthermore, the slurry could contain dispersed particles or aggregated particles. The particles could aggregate by fusing together or by capillary bridging using unconverted water.

Hydrate slurries are non-Newtonian fluids. Section 2.1 begins this chapter with a discussion of non-Newtonian fluids and several models to describe them. Much prior research has been performed on the rheological behavior of suspensions and emulsions (Section 2.2); however, studies on rheological properties of emulsions changing to suspensions are rare. This chapter closes with a review of the few existing studies on hydrate rheology in Section 2.3.

2.1 Describing Non-Newtonian Fluids

This section gives an overview of models for predicting viscosity that account for non-Newtonian behavior. Fluids can deviate from Newtonian behavior in several ways. A fluid’s viscosity can be a function of shear rate rather than a constant value, resulting in shear-thinning or shear-thickening behavior. Also, materials can possess a yield stress.

Equations that relate shear stress to shear rate are called constitutive equations. The simplest constitutive equation, Newton’s Law (Bird et al., 2002), has already been discussed in Section 1.3.:

\[ \tau = \eta \dot{\gamma} \]  

(2.1)
Fluids that obey this law are said to be Newtonian. For many fluids, viscosity is not a constant. The models that follow express viscosity as a function of other parameters. These expressions for viscosity can be substituted into Newton’s Law to obtain a new constitutive equation. One of the first and simplest models accounting for non-Newtonian viscosity is the power-law of Ostwald-de-Waele (Baird & Collias, 1998):

$$\eta = m\dot{\gamma}^{n-1}$$ (2.2)

$m$ is called the consistency. $n$ is the degree to which a fluid deviates from Newtonian behavior. The power-law model typically only fits data over a few orders of magnitude in shear rate. The Ellis and Carreau models both give a better fit for many fluids over a wider range in shear rates (Baird & Collias, 1998):

$$\frac{\eta_0}{\eta} = 1 + \left(\frac{\tau_{xy}}{\tau_{1/2}}\right)^{1 - \alpha}$$ (2.3)

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + (\lambda\dot{\gamma})^2\right]^{\frac{n-1}{2}}$$ (2.4)

where $\eta_0$ is the zero shear viscosity (viscosity at zero shear rate), $\eta_{infty}$ is the shear rate as $\dot{\gamma}$ approaches infinity. $\tau_{1/2}$ is the value of $\tau_{xy}$ when $\eta = \frac{\eta_0}{2}$. $\lambda$ represents the point in shear rate where shear-thinning behavior begins. $n$ takes a similar role to that in the power-law model. Each of these models can describe more complex behavior than the power-law model; however, they require extra parameters to do so. The Carreau model fits polymer solution viscosity data particularly well.

The Bingham model introduces yield stress as a parameter (Baird & Collias, 1998):

$$\eta = \begin{cases} \frac{\tau - \tau_0}{\dot{\gamma}} & \text{for } \tau \geq \tau_0 \\ \frac{\tau_0}{\dot{\gamma}} & \text{for } \tau < \tau_0 \end{cases}$$ (2.5)

The parameter $\tau_0$ is the yield stress. The Herschel-Bulkley model contains a non-Newtonian term for viscosity taken from the power-law model and a yield stress term taken from the Bingham model (Baird & Collias, 1998):

$$\eta = \begin{cases} \frac{m\dot{\gamma}^{n-\tau_0}}{\dot{\gamma}} & \text{for } \tau \geq \tau_0 \\ \frac{\tau_0}{\dot{\gamma}} & \text{for } \tau < \tau_0 \end{cases}$$ (2.6)
Two other common models are the Casson model (Equation 2.7) (Macosko, 1994) and the Cross model (Equation 2.8) (Cross, 1965; Macosko, 1994).

\[ \eta^{1/2} = \dot{\gamma}^{1/2} \tau_0^{1/2} + m \dot{\gamma} \]  
\[ \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (m \dot{\gamma})^{1-n}} \]  

The Casson model has found success for many real fluids, including blood (Truskey et al., 2009). The Cross model was applied by Rensing (see Section 2.3.2) to water in crude oil emulsions (Rensing, 2010).

### 2.2 Suspension and Emulsion Rheology

In general, when solid particles are introduced to a liquid continuous phase, the viscosity of the mixture will be larger than the pure liquid (Hiemenz & Rajagopalan, 1997). Add more particles, and the viscosity increases further. In general, viscosity monotonically increases with particle volume fraction; however, the equations describing this relationship are more complicated. No single equation exists to accurately predict the viscosity of all systems as a function of particle volume fraction.

Some industries have settled on a particular equation that generally works well for their systems. For hydrate applications in the gas and oil industry, the closest model to an industry standard was developed by Camargo and Palermo (Camargo & Palermo, 2002). This model uses Mills model (Mills, 1985) for viscosity as a function of particle volume fraction. The Camargo and Palermo model could be improved. First, the model is a function of many parameters, most of which cannot be easily measured in a pipeline. Second, very few models have been tested with hydrate rheological data. We cannot know the best model until the predictions of many models are compared to rheological data. Only two models have been applied to hydrates: Mills’ model, used by Camargo and Palermo, and the Graham, Steele, and Bird model (Graham et al., 1984), applied by Darbouret et. al in 2005 (Darbouret et al., 2005b). Both of these works will be discussed later in Section 2.3.1. Third, the viscosity
predicted by the Camargo and Palermo model does not quantitatively match the viscosity measured in a flow-loop. Perhaps another model could provide a better fit. Furthermore, even if the model fit the experimental data perfectly, the data is all based on a single crude oil. Since crude oils show so much variability, their model may not work as well for other oils.

In the past, researchers have developed many viscosity models for various systems. In 1906, Einstein derived the first suspension viscosity model (Einstein, 1906). His model assumes all particles are non-interacting hard spheres. The equation also assumes each sphere acts independently of the movement of other spheres, so, the model only applies in the limit of infinite dilution. In practice, it should work for any system with less than 1 percent of particle volume fraction. Einstein’s equation predicts viscosity as a function of a single parameter, the particle volume fraction.

\[
\frac{\eta}{\eta_0} = 1 + \frac{5}{2}\phi
\]  

Where \(\eta\) is the suspension (mixture) viscosity, \(\eta_0\) is the continuous phase viscosity, and \(\phi\) is the dispersed phase (particle) volume fraction. The suspension viscosity normalized by the continuous phase viscosity defines the relative viscosity, \(\eta_r\).

A variety of dimensionless viscosity groups are used in other viscosity models. Table 2.1 shows the definitions of many of these groups and a few other variables commonly found in viscosity models (Hiemenz & Rajagopalan, 1997).

At particle volume fractions greater than \(\sim 0.01\), Einsteins equation usually is invalid. Many factors cause a viscosity increase above Einsteins prediction in real systems. At higher particle volume fractions, models must account for hydrodynamic interactions, particle rotation, collisions, mutual exclusion of particles, agglomeration, and mechanical interference (Thomas, 1965). During the 1940s and 50s, researchers retained larger terms in a power series of the same form as Einsteins equation. These equation were of the form:

\[
\frac{\eta}{\eta_0} = 1 + k_1\phi + k_2\phi^2 + k_3\phi^3 + \ldots
\]  

16
Table 2.1: Some common parameters in dispersion rheology (Hiemenz & Rajagopalan, 1997)

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosity</td>
<td>$\eta$</td>
<td></td>
</tr>
<tr>
<td>continuous phase viscosity</td>
<td>$\eta_0$</td>
<td></td>
</tr>
<tr>
<td>dispersed phase viscosity</td>
<td>$\eta_d$</td>
<td>$\eta / \eta_0$</td>
</tr>
<tr>
<td>relative viscosity</td>
<td>$\eta_r$</td>
<td>$\eta_d / \eta_0$</td>
</tr>
<tr>
<td>viscosity ratio</td>
<td>$\lambda$</td>
<td>$\eta_d / \eta_0$</td>
</tr>
<tr>
<td>specific viscosity</td>
<td>$\eta_{sp}$</td>
<td>$\eta_r - 1$</td>
</tr>
<tr>
<td>reduced viscosity</td>
<td>$\eta_{red}$</td>
<td>$\eta_r - 1 / \phi$</td>
</tr>
<tr>
<td>inherent viscosity</td>
<td>$\eta_{inh}$</td>
<td>$\ln(\eta / \eta_0) / \phi$</td>
</tr>
<tr>
<td>intrinsic viscosity</td>
<td>$[\eta]$</td>
<td>$\lim_{\phi \to \phi_{max}} \eta_{red}$</td>
</tr>
<tr>
<td>dispersed phase volume fraction</td>
<td>$\phi$</td>
<td></td>
</tr>
<tr>
<td>effective volume fraction</td>
<td>$\phi_{eff}$</td>
<td></td>
</tr>
<tr>
<td>maximum particle packing fraction</td>
<td>$\phi_{max}$</td>
<td></td>
</tr>
</tbody>
</table>
For the most part, researchers agreed that \( k_1 = 2.5 \), although other values were proposed. Many obtained values of \( k_2 \), with each study using a different set of assumptions. Table 2.2 shows some of the results of these studies with the authors and publication year. Values of \( k_3 \) and higher coefficients became very difficult to calculate theoretically. Some proposed \( k_3 \) values ranged from 16 to 50.

Table 2.2: \( k_2 \) values for equation 2.10. Values compiled by Thomas (Thomas, 1965)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>( k_2 ) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guth and Simha</td>
<td>1936</td>
<td>14.1</td>
</tr>
<tr>
<td>Saito</td>
<td>1950</td>
<td>12.6</td>
</tr>
<tr>
<td>Vand</td>
<td>1948</td>
<td>7.349</td>
</tr>
<tr>
<td>Manley and Mason</td>
<td>1955</td>
<td>10.05</td>
</tr>
<tr>
<td>Batchelor</td>
<td>1977</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Viscosity models should follow following two limiting conditions (Honek *et al.*, 2005). First, the suspension viscosity must approach the continuous phase viscosity as the particle volume fraction approaches zero. Second, the viscosity must go to infinity as the particle volume fraction approaches the maximum particle packing fraction.

\[
\lim_{\phi \to 0} \eta = \eta_0 \tag{2.11}
\]

\[
\lim_{\phi \to \phi_{max}} \eta = \infty \tag{2.12}
\]

All the power series models fail to meet the second limiting condition. An infinite series will meet this condition, but all of the models truncate after a few terms. Also, power series models tend to fit experimental data poorly at higher particle volume fractions \((\phi > 0.40)\). Because of these difficulties, power series models have generally been abandoned in favor of other model forms. Table 2.3 lists a number of common viscosity models. The notes in the table explain key features of some models.
Table 2.3: Models for viscosity as a function of particle volume fraction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equation</th>
<th>Authors and Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$[\eta] = KM^a$</td>
<td>Hiemenz &amp; Lodge (2007); Houwink (1941); Mark (1938)</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{\eta}{\eta_0} = \left[1 + \frac{0.5[\eta]\phi}{1 - \phi_{\max}}\right]^2$</td>
<td>Eilers (1941); Honek et al. (2005)</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{\eta}{\eta_0} = \exp\left[\frac{2.5\phi}{1 - a_2\phi}\right]$</td>
<td>Mooney (1951)</td>
</tr>
<tr>
<td>4</td>
<td>$\frac{\eta}{\eta_0} = \frac{1}{(1 - \phi)[\eta]}$</td>
<td>Brinkman (1952); Roscoe (1952)</td>
</tr>
<tr>
<td>5</td>
<td>$\frac{\eta}{\eta_0} = \frac{1}{(1 - \phi)\eta_{\max}}\eta_{\phi_{\max}}$</td>
<td>Krieger &amp; Dougherty (1959)</td>
</tr>
<tr>
<td>6</td>
<td>$\frac{\eta}{\eta_0} = 1 + 2.5\phi + 10.05\phi^2 + 0.00273 \exp(1.6\phi)$</td>
<td>Thomas (1965)</td>
</tr>
<tr>
<td>7</td>
<td>$\frac{\eta}{\eta_0} = \frac{9}{8} \left[ \frac{\left(\frac{\phi}{\phi_{\max}}\right)^{1/3}}{1 - \left(\frac{\phi}{\phi_{\max}}\right)^{1/3}} \right]$</td>
<td>Frankel &amp; Acrivos (1967)</td>
</tr>
<tr>
<td>8</td>
<td>$\frac{\eta}{\eta_0} = \left[1 + \frac{0.75\left(\frac{\phi}{\phi_{\max}}\right)}{1 - \left(\frac{\phi}{\phi_{\max}}\right)}\right]^2$</td>
<td>Chong et al. (1971)</td>
</tr>
<tr>
<td>9</td>
<td>$\frac{\eta}{\eta_0} = \frac{1}{(1 - \phi_{\text{eff}})^{2.5}}$</td>
<td>Graham et al. (1984)</td>
</tr>
</tbody>
</table>
Table 2.3: Continued.

Table 2.3: Models for viscosity as a function of particle volume fraction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equation</th>
<th>Authors and Reference</th>
</tr>
</thead>
</table>
| 10    | \[
\frac{1}{\phi_{_{\text{max}}}} = \frac{1}{\phi_{_{\text{max},0}}} - \left( \frac{1}{\phi_{_{\text{max},0}}} - \frac{1}{\phi_{_{\text{max},\infty}}} \right) \left( \frac{1}{1 + A\tau^{-m}} \right) \]
\[\text{where } \phi_{_{\text{eff}}} = 1 + 0.35 \left[ 1 - \left( \frac{0.7404 - \phi}{0.7404} \right)^2 \right]^{1/2} \]

Wildemuth & Williams (1984) |
| 11    | \[
\frac{\eta}{\eta_0} = \frac{1 - \phi}{\left( 1 - \frac{\phi}{\phi_{_{\text{max}}}} \right)^2} \]

Mills (1985) |
| 12    | \[
\frac{\eta}{\eta_0} = \left[ 1 + \frac{[\eta]\phi_{_{\text{max}}}}{n(\phi - \phi_{_{\text{max}}})} \right]^n \]

Dabak and Yucel Dabak & Yucel (1986) |
| 13    | \[
\frac{\eta}{\eta_0} = 1 + C \left( \frac{3\pi}{8} \left( \frac{\beta}{\beta + 1} \right) \left[ 3 + 4.5\beta + \beta^2 \right] \frac{1}{\beta + 1} - 3 \left( \frac{\beta + 1}{\beta} \right) \ln(\beta + 1) \right) \]

Probstein et al. (1994) |
|       | \[
\text{where } \beta = \frac{\left( \frac{\phi}{\phi_{_{\text{max}}}} \right)^{1/3}}{1 - \left( \frac{\phi}{\phi_{_{\text{max}}}} \right)^{1/3}} \]

       |
| 14    | \[
\frac{\eta}{\eta_0} = \left[ a(\phi_{_{\text{max}}} - \phi) \right]^{-2} \]

Liu (2000) |
In 1951, Mooney was one of the first to develop a model (number 3 in Table 2.3) that obeys both limiting criteria (Mooney, 1951). His model contains one fitting parameter other than the particle volume fraction. The following year, Roscoe and Brinkman each independently developed model 4 in Table 2.3 (Brinkman, 1952; Roscoe, 1952). Despite the success of the Roscoe and Brinkman model, it fails to meet the second limiting condition (equation 2.12). Other researchers such as Graham, Steele, and Bird (Graham et al., 1984) and Krieger and Dougherty (Krieger & Dougherty, 1959) borrowed from the Roscoe and Brinkman model in developing their own model. The Krieger-Dougherty model (number 5 in Table 2.3) is one of the most commonly used models today. Krieger and Dougherty’s model combines the Mooney equation with the Roscoe and Brinkman equation, and it fits a wide range of data well. The parameters $[\eta]$ and $\phi_{max}$ are tabulated for different systems (Bird et al., 2002).

Mills model (number 11 in Table 2.3) fits both limiting cases and accounts for the maximum particle packing volume fraction (Mills, 1985). This model was chosen as a component of the viscosity model developed by Camargo and Palermo (Camargo & Palermo, 2002).

Data are often plotted as relative viscosity (i.e., suspension viscosity divided by continuous phase viscosity) versus particle volume fraction. A comparison between the models shows that they all show qualitatively similar behavior with the exception of Einstien’s equation (Figure 2.1)

From a rheology perspective, emulsions could be thought of as a special case of suspensions in which the particles may be highly deformable. Often, emulsion and suspension models are used interchangebly. Still, some models have been developed to predict the rheological behavior of emulsions. The brief review presented here is a subset of the work reviewed by Pal Pal (2011).

The viscosity of dilute emulsions is well described by the Taylor equation (Taylor, 1932)

$$\eta = \eta_c \left[ 1 + \frac{2 + 5\lambda}{2(1 + \lambda)} \phi \right]$$

(2.13)
Figure 2.1: Comparison between models of relative viscosity as a function of particle volume fraction. $\phi_{max} = 0.64$, $[\eta] = 2.5$.

where $\eta$ is the emulsion viscosity, $\eta_c$ is the continuous phase viscosity, $\phi$ is the dispersed phase volume fraction, and $\lambda$ is the ratio of the dispersed phase viscosity to the continuous phase viscosity. Droplets in a dilute emulsion are spaced out so far from each other that they behave as if they were alone in a fluid that extends infinitely in all directions. Droplets behave this way at volume fractions less than about 0.02.

Much experimental work has also been performed with emulsions. Crude oil emulsion rheology is most relevant to the present work. de Oliveira and coworkers measured the viscosity of three different waxy crude oils at varying shear rates (20-250 s$^{-1}$), temperatures (5-60 °C), and water volume fractions (0-0.70) (de Oliveira et al., 2010). In all cases, viscosity increased as shear rate decreased, temperature decreased, and water volume fraction increased. Emulsions were found to be shear thinning and were fit to the power law model. All measurements in this study were performed on “dead” crude oils, i.e., crude oil with no dissolved gas.
2.3 Hydrate Rheology

Rheological measurements of gas hydrate slurries are few but growing in number. The paucity of literature may reflect the difficulty of performing rheological tests at high pressure. Much of the past research avoids the high pressure requirement by using guest molecules that form hydrate at atmospheric pressure. Some of the research with ambient pressure hydrate formers is applied towards the refrigeration industry; so, these researchers had no need to form methane hydrate at high pressures. With the exception of work performed at the Colorado School of Mines, all of the remaining hydrate slurry rheology literature does not directly measure shear stress or shear rate. These works typically flow liquid and gas through a pipe, measure flow rate and pressure drop, calculate shear rate and shear stress at the wall, and finally calculate effective viscosity. The hydrate slurry rheology literature is presented in Section 2.3.1.

Traditional rheometers may have been avoided in the literature because they cannot create high interfacial area between water and gas, which is required to form a significant amount of hydrates. Flow in pipes is appealing because they can achieve turbulent flow, which generates high gas-liquid interfacial area. Rheometers can be equipped with geometries that generate mixing (e.g., helical ribbon impeller); however, these require the same kind of correlations to get to viscosity, just like flow in a pipe, so, they are not true rheometers.

Work performed at the Colorado School of Mines used an apparatus which dissolved gas into an emulsion in an external cell, and then pumped that emulsion under pressure into a high pressure rheometer with concentric cylinders geometry (Rensing, 2010; Rensing et al., 2011). This apparatus gives accurate measurements while still reproducing the scenario encountered in oil pipelines. Section 2.3.2 reviews Rensing’s work.

Finally, work on the rheology of solid hydrates (i.e., not suspended in a liquid) is presented in Section 2.3.3.
2.3.1 Rheology of Hydrate Slurries

Research on hydrate rheology was first documented in 2000 with two publications; one from the Institut Français du Pétrole (IFP) (Camargo et al., 2000) and one from the Norwegian University of Science and Technology (NTNU) (Andersson & Gundmundsson, 2000). The NTNU research measured the flow rate and pressure drop as a hydrate slurry flowed through a pipe (Andersson & Gundmundsson, 2000). Shear rate and shear stress at the wall were calculated from the pressure drop, flow rate, and pipe geometry. They could operate at laminar or turbulent conditions and the continuous phase could be oil or water. They had three important conclusions. First, slurry viscosity increased as hydrate concentration increased, and shear-thinning behavior was observed at higher concentrations. Second, sI hydrates showed no difference in viscosity from sII hydrates (Figure 2.2). Third, in the turbulent regime, the frictional pressure drop of hydrate-in-water slurries were the same as that of pure water. So, hydrates did not affect the rheology of the system in the turbulent flow regime. The flow meter readings became unreliable above ~15 vol. % hydrates; so, this work was limited to low hydrate volume fractions.

Figure 2.2: Slurry viscosity as a function of volumetric hydrate concentration. The viscosities are corrected to a temperature of 5.0 °C. Series 1 and 3 are sI hydrate, Series 2 and 4 are sII hydrate (Andersson & Gundmundsson, 2000).
The IFP paper used a stirred PT cell which was converted to a rheometer (Camargo et al., 2000). Since the cell is not a true rheometer, they had to calibrate the cell with Newtonian fluids. Water-in-oil emulsions were prepared at varying water volume fractions, then saturated with gas (90 mol. % methane, 10 mol. % ethane), then cooled to form hydrate. Four main conclusions came out of this work. First, they found that hydrate slurry viscosity increased with increasing emulsion water volume fraction. Second, hydrate slurry viscosity decreased with increasing angular velocity, that is, the slurries were shear-thinning, although only a narrow range of velocities were used (Figure 2.3). Third, they were the first to observe viscosity increase over time as hydrates formed from a water-in-oil emulsion. Fourth, they noted that hydrate suspension viscosity exceeded the original water-in-oil emulsion viscosity at all water contents (Figure 2.4).

Figure 2.3: Slurry viscosity as a function of angular velocity on a water-in-oil emulsion with 0.30 water volume fraction. T = 280.65 K, P = 8 MPa (Camargo et al., 2000).

By number of publications, the IFP group has contributed the most to the small field of hydrate rheology (Camargo & Palermo, 2002; Camargo et al., 2000; Cameirao et al., 2011; Colombel et al., 2009; Gainville et al., 2011; Leba et al., 2010; Palermo et al., 2005; Peysson et al., 2003; Sinquin et al., 2004). In their second hydrate slurry rheology publication, the group develops a model to predict viscosity in a pipeline (Camargo & Palermo, 2002). The
Figure 2.4: Viscosity of water-in-oil emulsions compared to hydrate slurries at varying water volume fraction. \( T = 280.65 \) K, \( P = 8 \) MPa (Camargo et al., 2000).

model is developed using theory and then compared to experimental data from a flow-loop and their modified P-T cell. To start, they chose Mills model for viscosity as a function of particle volume fraction.

\[
\frac{\eta}{\eta_0} = \frac{1 - \phi}{\left(1 - \frac{\phi}{\phi_{\text{max}}}ight)^2}
\]  \hspace{1cm} (2.14)

\( \phi_{\text{max}} \) represents the packing concentration of randomly packed spheres of the same diameter and equals \( 4/7 \). Next, they modified Mills’ (Mills, 1985) model by replacing the volume fraction, \( \phi \), with the effective volume fraction, \( \phi_{\text{eff}} \), where the effective volume fraction is a function of aggregate and particle diameters, fractal dimension, and actual volume fraction. Equations 2.15 and 2.16 shows the modified equations. In real aggregating suspensions, the continuous phase liquid trapped between primary particles in an aggregate acts as part of the aggregate rather than part of the continuous phase (Graham et al., 1984; Hasan & Shaw, 2010; Pal, 2011). Trapped interstitial fluid causes the effective volume of solid particles to
be larger than the sum of the primary particles in the system.

\[ \frac{\eta}{\eta_0} = \frac{1 - \phi_{\text{eff}}}{\left(1 - \frac{\phi_{\text{eff}}}{\phi_{\text{max}}}\right)^2} \]  

(2.15)

where,

\[ \phi_{\text{eff}} = \phi \left(\frac{d_A}{d_p}\right)^{3-f} \]  

(2.16)

Where \(d_A\) is aggregate diameter, \(d_p\) is particle diameter, and \(f\) is fractal dimension.

Next, Camargo and Palermo used a model by Muhle (Mühle, 1993), which gives the maximum aggregate diameter.

\[ d_{A,\text{max}} \approx \left(\frac{F_a(d_p)^{2-f}}{\eta \dot{\gamma}}\right)^{\frac{1}{4-f}} \]  

(2.17)

Where \(F_a\) is the adhesion force between two particles, \(\eta_0\) is the continuous phase viscosity, and \(\dot{\gamma}\) is the shear rate. Muhle’s model only applies in the dilute limit (\(\phi \to 0\)). Potanin proposed replacing the continuous phase viscosity with the apparent viscosity of the suspension would extend the model to systems with a finite volume fraction (Potanin, 1991).

Also, at equilibrium, the maximum aggregate diameter \(d_{A,\text{max}}\) will approximately equal the aggregate diameter \(d_A\). Equation 2.18 shows the modified Muhles model with the above changes.

\[ d_A \approx \left(\frac{F_a(d_p)^{2-f}}{\eta \dot{\gamma}}\right)^{\frac{1}{4-f}} \]  

(2.18)

Substituting Equation 2.15 into equation 2.18 yields the model proposed by Camargo and Palermo:

\[ \left(\frac{d_A}{d_p}\right)^{(4-f)} \cdot \frac{F_a}{d_p^2 \eta \dot{\gamma}} \left[1 - \phi \left(\frac{d_A}{d_p}\right)^{(3-f)}\right]^2 = 0 \]  

(2.19)

When comparing the model to experimental data, the authors fixed all the parameters except the particle-particle adhesion force, which was fit (Figure 2.5). Relative viscosity is obtained by solving equation 2.19 for \(d_A\), and then substituting into equation 2.15 and
solving for relative viscosity. The model seems to show a reasonable fit for the flow loop data, but not a good fit for the P-T cell data. The P-T cell data could be inaccurate because the shear rate is variable in the P-T cell. Unfortunately, it seems the viscosity in the flow loop is also poorly characterized. The authors calculate viscosity of the suspension in the flow loop from the pressure drop, loop geometry (length and diameter), and liquid velocity (Palermo et al., 2005):

$$\eta = \frac{\Delta P D^2}{32 v_l L}$$

(2.20)

Figure 2.5: Viscosity versus shear rate (Camargo & Palermo, 2002). Lines are the Camargo and Palermo model at two different volume fractions. Points are experimental data from a P-T cell (×) and a flow-loop (●).

Where $\Delta P$ is the pressure drop, $D$ the loop diameter, $v_l$ the velocity of the liquid phase, and $L$ the loop length. This method of calculating the viscosity assumes that emulsions and suspensions behave as Newtonian fluids, which is not correct (Andersson & Gundmundsson, 2000; Camargo et al., 2000). So, the experimental flow loop data in figure 2.5 is only as good as the approximation in equation 2.20 (Palermo et al., 2005).

The above questions about the reliability of experimental data used to fit the model parameters are one of the major drawbacks to this model. Another drawback is the large
number of parameters. The model does seem to account for many relevant parameters affecting aggregation; however, a model with so many parameters could be made to fit nearly any set of experimental data. Another concern is that even if the model accurately predicts hydrate viscosity, the parameters involved are difficult to measure in the field.

Later studies by the IFP group explored varying pressure, water amount, and oil type (Sinquin et al., 2004), aggregation mechanisms (Colombel et al., 2009), aggregation from focused beam reflectance measurements (FBRM) (Cameirao et al., 2011; Leba et al., 2010), and flow regime (Gainville et al., 2011).

Another French research group, at Ecole Nationale Supérieure des Mines de Saint-Etienne, has performed several studies on hydrate slurries, often in collaboration with IFP (Cameirao et al., 2011; Colombel et al., 2009; Darbouret et al., 2005b; Fidel-Dufour et al., 2006; Leba et al., 2010). In some of their work, they study the rheological properties of tetra-butylammonium bromide (TBAB) hydrate slurries applied as secondary two-phase refrigerants (Darbouret et al., 2005a,b). In these works, the hydrate slurry is essentially flowed through a pipe at controlled temperature and flow rate while measuring pressure. They indirectly calculate shear rate and shear stress at the wall from pressure drop, flow rate, and geometry. They calculate a yield stress using the Bingham model, but did not observe shear-thinning behavior, rather they observed constant viscosity at all shear rates. Yield stress and relative viscosity increased with increasing hydrate volume fraction and decreasing temperature. The relative viscosity increases with hydrate volume fraction, and is well described by the Graham, Steele, and Bird model (Graham et al., 1984) (Figure 2.6). In the figure, the maximum particle packing fraction was varied to produce the best model fit.

In another work, the St. Etienne group observed the formation and conversion of methane hydrates in a flow loop (Fidel-Dufour et al., 2006). It is unclear how the viscosity is determined. The viscosity is assumed to be determined from the pressure drop, flow rate, and geometry, just as in the previous work (Darbouret et al., 2005b). Viscosity increases as hydrates form (Figure 2.7). Viscosity increases with water cut, as does the slope of the viscosity
versus time during hydrate formation. The second increase in viscosity after formation may be from hydrates accumulating in the riser. The lines in the figure show the predictions of a particle balance model also developed in the paper. Finally, the hydrate conversion with time was calculated.

Another French group from Cemagref-GPAN published several works on hydrate slurry rheology (Clain et al., 2012; Delahaye et al., 2008, 2011). This research is applied towards using hydrates as a phase change material in the refrigeration industry. In these wroks, CO$_2$ hydrates (Delahaye et al., 2008, 2011) or tetra-n-butylphosphonium bromide (TBPB) hydrates (Clain et al., 2012) were flowed through a pipe. Pressure drop and flow rate were measured and then used to calculate shear rate and shear stress at the wall. Shear-thinning and a yield stress was observed in all of the hydrate slurries. Power law parameters were reported in each case.

An American group at the City College of New York (CCNY) has measured the rheological properties of water-in-oil emulsions and hydrate-in-oil slurries with cyclopentane hydrates (Karanjkar et al., 2011; Peixinho et al., 2010; Zylyftari et al., 2013). They use an ARES
Figure 2.7: Relative viscosity (measured viscosity/emulsion viscosity) versus time during methane hydrate formation and growth at varying water volume fractions (Fidel-Dufour et al., 2006). P = 7.5 MPa, T = 4 °C.
strain controlled rheometer with couette geometry. Their oil phase consists of cyclopentane, light mineral oil, and halocarbon oil which is used to density match the oil to water. Density matching is performed to avoid settling or creaming issues. In the first work (Peixinho et al., 2010), the measure flow curves and particle size distributions of emulsions of varying composition at varying temperatures. They used rheology as a tool to measure a critical time probability for hydrate formation. Finally, they observed the dynamic elastic modulus, G’, increase as hydrates formed and decrease as hydrates dissociate. These experiments could be performed at atmospheric pressure because cyclopentane is the hydrate guest molecule. Their second work characterized the surface chemistry, particle size distributions, and heat flow curves from differential scanning calorimetry of hydrate-forming emulsions (Karanjkar et al., 2011). Their newest work reported the viscosity of hydrate slurries over time as they form at varying shear rates, temperatures, and salt concentrations (Zylyftari et al., 2013). Slurries were shear thinning and were fit to the power law model. Slurries also exhibited a yield stress. Viscosity was found to be at a maximum between 60 and 81% of theoretical water conversion to hydrate (not 100%) (Figure 2.8). The authors cite capillary bridging as the cause of this phenomenon. At 100% conversion of water to hydrate, no water is left to form bridges between hydrate particles, so viscosity will decrease.

Several other studies on the rheological properties of low-pressure hydrate formers examined THF or TBAB hydrate in a rheometer (Ding et al., 2008), TBAB hydrate in a single pass pipe reactor (Ma et al., 2010), HCFC-141b or THF hydrate in a flow loop (Wang et al., 2010), TBAB hydrates in a flow loop (Kumano et al., 2011), and TBAB or TBAF (tetra-n-butyl ammonium fluoride) semi-clathrate hydrate in a stress controlled parallel plate rheometer (Hashimoto et al., 2011).

Scientists at Marathon Oil Corporationl constructed a pilot plant that could produce 1 tonne of hydrates per day (Waycuilis et al., 2011). Hydrates could be used to separate undesirable CO₂ from natural gas. This pilot plant forms hydrates from mixtures of CO₂ and methane gas in water in a fluidized-bed heat-exchange reactor. Rheological properties
Figure 2.8: Cyclopentane hydrate (sII) slurry viscosity vs. theoretical water to hydrate conversion (Zylyftari et al., 2013). The points from left to right of each trace correspond to initial salt concentration of 15, 12.5, 10, 7.5, 5, 3.4, and 0 wt.\%
were determined from measurements of pressure loss and flow rate, and the system geometry. Produced hydrate slurries exhibited a yield stress and were shear-thinning. Hydrate volume fraction reached as high as 0.12. Correlating lab scale measurements performed here to larger scale pilot facilities and pipe lines is one of the goals of this thesis.

2.3.2 Patrick Rensing’s Work

Hydrate slurry rheology studies at the Colorado School of Mines were performed by Patrick Rensing for his doctoral studies (Rensing, 2010; Rensing et al., 2011; Webb et al., 2012a). Rensing prepared emulsions by adding water to a “dead” West African Crude oil. Then, emulsions were pressurized with methane gas at 2000 psig and mixed until saturated. Next emulsions were pumped under pressure into a TA instruments AR-G2 rheometer with pressure cell (concentric cylinders geometry), where the following general procedure was followed:

1. Transient hydrate formation: cool down to experimental temperature (usually 0 °C), observe hydrate formation under constant shear of 100 s$^{-1}$ for 12 hours after hydrate formation.

2. Yield stress measurement: let emulsion anneal for a set time, then increase shear stress until emulsion deforms.

3. Shear rate loop: ramp shear rate from 500 to 1 to 500 s$^{-1}$, take steady-state viscosity measurements at each point.

4. Dissociation: heat back up to 25 °C at 100 s$^{-1}$, measure viscosity as hydrate melts.

Rensing studied three different types of slurries: ice, ice + brine, and hydrate. Ice slurry experiments were identical to hydrate experiments except the experimental temperature was -10 °C instead of 0 °C. Ice + brine slurries used -10 °C and 3.5 wt. % aqueous phase.

In all three systems, the viscosity increased as solids formed. When hydrates form, the pressure decreases and the viscosity increases (Figure 2.9). After the viscosity peak, the
pressure remains constant, which indicates hydrates are no longer forming or growing. The viscosity still decreases in this region, despite the constant pressure. Rensing attributes this phenomena to shear alignment. Hydrate formation is a stochastic event, so the time until hydrate formation varies. The rapid viscosity increase usually began within two hours after cooling. In ice slurries (but not ice + brine), the viscosity peaked twice, with a few hours separating the peaks 2.10).

Figure 2.9: Time evolution of viscosity and pressure before, during, and after hydrate formation and growth (Rensing, 2010). $\phi = 0.20$, $\dot{\gamma} = 100$ s$^{-1}$, and $T = 0$ °C.

In all three slurries, the yield stress increased with water cut (Figure 2.11). Each system showed three distinct regimes of yield stress. Below a certain water cut, the yield stress was negligibly small. In ice systems, this low-risk regime occurred below 25% water cut. In ice + brine systems, this occurred below 30% water cut, while hydrate slurries showed low risk values below 50% water cut. At another critical value, the yield stress spiked to a level above the instrument limit, which is 3000 Pa. This jump occurred at 60% water cut for ice slurries, 50% water cut for hydrate slurries, and was not observed in ice + brine slurries up to 60% water cut. Hydrate slurries showed a greater risk of plugging than ice slurries or ice
Figure 2.10: Nucleation of a 0.30 water volume fraction system of water in West African crude oil emulsion at 100 s⁻¹ (Rensing, 2010). (a) Ice formed from fresh water, 10 °C, (b) ice formed from brine of 3.5 wt% NaCl at 10 °C, (c) clathrate hydrates formed from fresh water and methane at 0 °C.
+ brine slurries because they show high-risk yield values at lower water cuts than the other systems. Ice and ice + brine slurries do show larger yield values than hydrate slurries at water cuts below 50%, so they are actually more dangerous at lower water cuts. Finally, note that hydrate slurries do not show middle-risk yield values; they jump straight from low-risk to high-risk.

![Figure 2.11](image)

Figure 2.11: Yield stress as a function of water volume fraction of (a) ice slurry formed from fresh water at 10 °C, 0.30 water volume fraction, (b) ice slurry formed from brine of 3.5 wt% NaCl at 10 °C, 0.30 water volume fraction, (c) clathrate hydrate slurry at 0 °C, 0.40 water volume fraction (Rensing, 2010). 1000 Pa/hr ramp rate.

Hydrate yield stress increased rapidly with annealing time up to 8 hours, and then plateaued (Figure 2.12). This suggests a heuristic for flow assurance engineers: try to remediate a plug within 8 hours. If the problem cannot be fixed within 8 hours, the situation does not get any worse, so there is no need to rush, aside from the money lost due to flow stoppage. In ice slurries, yield stress peaked around 2 hours annealing time, and reached a steady value around 8 hours. In ice + brine slurries, the yield stress decreased with time.
Figure 2.12: Yield stress as a function of time of (a) ice slurry formed from fresh water at 10 °C, 0.30 water volume fraction, b) ice slurry formed from brine of 3.5 wt%NaCl at 10 °C, 0.30 water volume fraction, c) clathrate hydrate slurry at 0 °C, 0.40 water volume fraction (Rensing, 2010). 1000 Pa/hr ramp rate.
Hydrate slurries at all water volume fractions exhibited shear-thinning behavior, i.e., the viscosity decreased as the shear rate increased (Figure 2.13). Rensing observed shear-thinning behavior in all three slurry types at all measured water cuts. As expected, the viscosity increases with water cut. As the water cut increases, the degree of shear-thinning also increases.

Figure 2.13: Viscosity as a function of shear rate at various water cuts for (a) ice slurry formed from fresh water at 10 °C, (b) ice slurry formed from brine of 3.5 wt% NaCl at 10 °C, (c) clathrate hydrate slurry at 0 °C (Rensing, 2010).

2.3.3 Solid Hydrate Rheology

A few studies have been performed on the rheology of solid hydrates. In 2003, Durham et al. deformed samples of pure methane hydrate using conventional triaxial testing (Durham et al., 2003). Samples were synthesized from water and methane. Most crystalline materials follow equation 2.21 given below.

\[
\dot{\varepsilon} = A\sigma^n e^{-\left(\frac{E^* + PV^*}{RT}\right)}
\]  

(2.21)
Where $\dot{\epsilon}$ is the strain rate, $A$ is the preexponential constant, $n$ is the stress exponent, $E^*$ is the activation energy, $V^*$ is the activation volume, $R$ is the gas constant, and $T$ is the temperature. Table 2.4 shows the values of these parameters determined through triaxial testing. They also obtained scanning electron microscope (SEM) images of methane hydrate before and after fracturing. The strength of sI methane hydrate was observed to be about 20 times stronger than ice at temperatures just below the ice point.

Table 2.4: Experimentally determined values of parameters used in Equation 2.21

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$10^{8.55}$</td>
<td>MPa$^{-n}s^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>$E^*$</td>
<td>90000</td>
<td>J/mole</td>
</tr>
<tr>
<td>$V^*$</td>
<td>19</td>
<td>cm$^3$/mole</td>
</tr>
</tbody>
</table>

Two studies on methane hydrate bearing sediments quantified the tensile strength strength (Suzuki & Narita, 2011) and measured strength at varying hydrate amounts and confining pressures (Ghiassian & Grozic, 2011).
A robust, high-pressure rheometer system is presented, which directly measures the viscosity and yield stress of hydrate slurries in situ. A rheometer cell is combined with a mixing cell, which saturates a liquid hydrocarbon phase with gas prior to injection in the rheometer for in situ hydrate formation. A version of this chapter has been published in Review of Scientific Instruments under the title “High pressure rheometer for in situ formation and characterization of methane hydrates.” This chapter is reproduced with permission from Webb et al. (Webb et al., 2012b). Copyright 2012, American Institute of Physics.

3.1 Abstract

We present a novel setup for a high pressure rheometer operating with concentric cylinders geometry for in situ studies of hydrate formation and rheological characterization. The apparatus uses an external high pressure mixing cell to saturate water-in-oil emulsions with methane gas. The capability of mixing combined with a true rheometer design make this apparatus unique in terms of setup and sample formation. We have used the apparatus to form gas hydrates in situ from water-in-oil emulsions and characterize suspension rheological properties such as yield stress and shear-thinning behavior.

3.2 Introduction

In subsea oil and gas pipelines, solid compounds called gas hydrates can form and completely block flow (Sloan & Koh, 2008; Sloan et al., 2011). Hydrates consist of small gas molecules (e.g., methane, ethane, propane, carbon dioxide) encaged by water molecules. Gas hydrates are typically thermodynamically stable at high pressures and low temperatures. In one estimate, the oil and gas industry spends over USD $200 million annually on hydrate
prevention (Sloan Jr., 2003). An understanding of the rheological properties of hydrate slurries in flowlines is essential in the management of hydrates and also a key component in developing strategies to prevent hydrate blockages.

Rheology is concerned with the deformation and flow of materials. Rheological properties of a fluid, such as viscosity and yield stress, can be obtained using a rheometer. For fluids, the viscosity is usually measured in a rheometer with a rotating geometry. Some of the most common rotating geometries are parallel plate, cone and plate, and concentric cylinders. The concentric cylinders geometry is best for studying suspensions and emulsions because it prevents particle ejection, particle exclusion (non-uniform concentration of particles), and uses a larger sample volume. The advantages and disadvantages of common geometries and rheometer types are further discussed in Morrison (Morrison, 2001) and Macosko (Macosko, 1994).

There have been only a selected few studies of hydrate slurry rheology in the applications for air conditioning (Darbouret et al., 2005a), refrigeration (Darbouret et al., 2005b; Delahaye et al., 2008; Ding et al., 2008), and subsea oil and gas pipelines (Camargo & Palermo, 2002; Camargo et al., 2000; Fidel-Dufour et al., 2006; Sinquin et al., 2004). Delahaye et al. formed CO₂ hydrates in a temperature and pressure controlled circulating loop (Delahaye et al., 2008). Several researchers have used tetra-n-butylammonium bromide (TBAB) as a help guest molecule, which enables hydrate formation at atmospheric pressures (Darbouret et al., 2005a,b; Ding et al., 2008). Peixinho et al. studied rheological properties of hydrates formed at atmospheric pressure from water-in-oil emulsions containing cyclopentane as a help guest molecule (Peixinho et al., 2010). Other researchers were able to achieve high pressures and form methane hydrate slurries. These studies used a variety of devices to perform rheology including a modified pressure-temperature cell (Camargo & Palermo, 2002; Camargo et al., 2000), a 2-inch diameter flowloop (Camargo & Palermo, 2002; Camargo et al., 2000; Sinquin et al., 2004), and a 1-cm diameter flowloop with a riser (Fidel-Dufour et al., 2006). High pressure measurements in a rheometer pose a daunting experimental challenge. A more
accurate and flexible method is needed to study the rheological properties of hydrate slurries.

In this paper, we present a robust rheometer system, which directly measures the viscosity and yield stress of hydrate slurries in situ. Here, the rheometer cell is combined with a mixing cell, which saturates the liquid hydrocarbon phase with gas prior to injection in the rheometer for in situ hydrate formation.

3.3 Experimental Apparatus

Most laboratory experiments are completed on so called “dead” oil, which is void of light hydrocarbons. However, oil in pipelines, where hydrates form, contains light hydrocarbons (e.g., methane, ethane, propane) and water. Water can become emulsified in the oil phase during production and sometimes form a free water phase. The volume fraction of water (water cut) emulsified in the crude oil ranges from nearly 0 to above 0.9 depending on the age of the field and other factors (Greaves, 2007). The maximum water cut before the phases invert depends on the composition of the oil. Water droplets in the water-in-oil emulsion are typically polydisperse and less than 100 µm (Greaves, 2007). When oil comes out of the pipeline, the pressure decreases, and the light hydrocarbons gases are flash separated. Crude oil saturated with light hydrocarbons is known as a live crude oil. To accurately recreate hydrate slurry flow in pipelines, one needs to consider a saturated water-in-oil emulsion.

Several rheometers that operate at high pressure have been developed; however, for various reasons, none of them is suitable for our application. There are pressure driven capillary flow rheometers (Binding et al., 1998; Couch & Binding, 2000; Nason, 1945) (difficulties with settling and wall migration), falling body rheometers (Bair, 2001; Brazier & Freeman, 1969; Briscoe et al., 1992; Horne & Johnson, 1966) (cannot observe transient viscosity), sliding plate rheometers (Koran & Dealy, 1999) (limited to high viscosity fluids), and levitating sphere rheometers (Royer et al., 2002) (does not directly measure shear rate).

The instrument for the rheological studies of hydrate slurries must (1) operate at high pressure, (2) perform mixing, and (3) and directly measure shear rate. The high pressure requirement rules out most common existing rheometer geometries. To satisfy the first re-
quirement, our design uses a high pressure cell with a magnetically driven concentric cylinders geometry. The mixing requirement demands using a mixing geometry in the rheometer (e.g., helical ribbon, anchor); however, all the geometries that satisfy the third requirement do not generate mixing. To satisfy requirements two and three, our apparatus uses one vessel for mixing and saturation, and a separate vessel to perform rheology. Both vessels operate at high pressure. A high pressure syringe pump connects the two vessels. A schematic of the complete experimental setup is shown in Figure 3.1. The AR-G2 rheometer and pressure cell with Peltier jacket are commercially available from TA Instruments. Note, since mixing and measurement occur in different vessels, this design is nominally limited to emulsions that are stable for at least one day.

Figure 3.1: Schematic of the high pressure rheometer system.
3.3.1 Mixing Cell

The mixing cell generates a high shear environment that creates sufficient contact between the gas and liquid phases to saturate the emulsion. Two large steel pieces, designed by Autoclave Engineers (Figure 3.2), are sealed together with six 9/16 inch diameter bolts and a teflon seal. The cell operates at pressures up to 4750 psig and a maximum volume of about 300 mL. The mixing cell impeller generates mixing. This type of design would be difficult to use for rheology measurements because the shear rate is not known at any location in the vessel. A motor drives the impeller of the mixing cell at 600 rpm. The saturation of the emulsion can be monitored by closing all valves outside the mixing cell, and measuring the pressure in the cell, which decreases as gas dissolves in the emulsion. When the pressure in the cell stabilizes to a steady value, the emulsion is considered fully saturated (usually on the order of 4 hours). The emulsion can then be moved to the rheometer cell via the syringe pump. The emulsion is piped from the bottom of the vessel out through a port at the top of the mixing cell.

3.3.2 Syringe Pump

The syringe pump is a Teledyne IS 500D model. The pump can hold a maximum pressure of 3750 psig and a maximum volume of 500 mL. The maximum flow rate through the pump is 50 mL/min. A set of valves on the flow lines control the path of the fluid.

3.3.3 Rheometer with Pressure Cell

After saturation, the emulsion is pumped into the pressurized rheometer cell. The pressure cell consists of a steel outer cylinder and a titanium inner cylinder in a concentric cylinders (cup-and-bob) assembly (Figure 3.3). The cup fits into a Peltier jacket and is fixed with two screws (Figure 3.3 c). The Peltier jacket is mounted to the rheometer by a magnet. Three ports access the cup, one for entering liquid, one for entering and exiting gas, and one rupture disk with a 2500 psig limit. The cell is rated for operation up to 2000 psi.
Figure 3.2: Disassembled mixing cell with the various components shown: bottom vessel, top portion with stirrer and magnetic coupled shaft, and bolts to seal cell.
Figure 3.3: Photographs of pressure rheology cell. (a) Disassembled rotor, (b) outer cylinder, (c) assembled pressure cell mounted in a Peltier jacket on the rheometer.
The Peltier heating/cooling jacket has a temperature range from -25 to 150 °C, maximum heating/cooling rate of 2 °C/min, and ±0.1 °C temperature precision. The temperature sensor is imbedded in the jacket. A cooling bath with a water and ethylene glycol mixture supplies the jacket with cooling fluid (i.e., heat sink).

The inner cylinder assembly contains a steel cap, which screws into the outer cylinder, and a rotor assembly, which screws into the steel cap (Figure 3.3 a). A viton O-ring seals the gap between the outer cylinder and the inner cylinder assembly. The rotor consists of several pieces on a carbide shaft, which include the bob, locking nut, sapphire bearing, and 4 pole magnets. The bob attaches to the carbide shaft with two set screws; it can be easily replaced for geometries of different shape or diameter (Nolte & Liberatore, 2011). The outer cylinder has a 14 mm radius, the inner cylinder has a 13 mm radius, thus the geometry has a 1 mm gap. The sample volume used in an experiment is 9.5 mL. The pressure couette cell has been successfully used by this group as a sealed vessel to study sugar glasses (Dave et al., 2007) and biomass pyrolysis oils (Nolte & Liberatore, 2011).

We use a TA instruments AR-G2 rheometer. The rheometer can control either stress or strain. It has a torque resolution of 0.1 nN·m, and a displacement resolution of 25 nrad. The maximum torque is 200 mN·m and the maximum angular velocity is 300 rad/s. We use the TA Rheology Advantage software to calibrate the instrument, setup and run experimental procedures, and analyze data.

3.4 Application to Gas Hydrates

3.4.1 Experimental Procedure

The experimental procedure has five main steps: create an emulsion, saturate the emulsion with methane, calibrate the rheometer, transfer the saturated emulsion to the rheometer pressure cell (under pressure), and perform the rheology procedure. The details of each step are discussed below.

Before performing an experiment, the emulsion must be prepared. First, a large container of crude oil is heated for at least 4 hours at 60 °C. Then, a desired volume of the oil is
removed and cooled to room temperature. Finally, the desired volume of deionized water is added dropwise to the cooled crude oil sample while mixing at 8000 rpm for 3 minutes in a VirTis Cyclone I.Q.² homogenizer. The crude oil used in this work is a West African crude oil (WAC) provided by ExxonMobil. The composition, SARA analysis, and other characterization of this oil can be found elsewhere (Rensing, 2010). We use 30% water cut (water volume fraction) in all of the emulsions to demonstrate the utility of this experiment.

The water-in-oil emulsion is initially a dead crude oil as the continuous phase. To make a live crude oil, the emulsion is placed in the external pressurized mixing cell for 24 hours. The mixing cell is pressurized to 1500 psig of methane gas directly without a purge cycle. The consumption of methane into the emulsion primarily occurs in the first 4 hours of mixing (Figure 3.4).

![Figure 3.4: Pressure in the mixing cell as a function of time. The pressure remains constant after 4 hours, which indicates saturation of the emulsion. Liquid phase is 0.30 water volume fraction water-in-crude oil emulsion. Gas phase is methane.](image)

Before every experiment, we must calibrate the bearing friction and perform rotational mapping. These calibrations are standard for this instrument and must be performed independent of geometry. The bearing friction is calibrated until an acceptable value is obtained
(<10 \mu N\cdot m/(rad\cdot s)). This calibration removes inaccuracies due to residual friction. Then, rotational mapping for two iterations at precision settings ensures accurate torque control over the 360 degree range of rotation. Once the rheometer calibrations are complete, the saturated emulsion is pumped through the lines, via the syringe pump, and into the cell. The desired sample volume of the emulsion in the pressure rheometer cell is 9.5 mL.

The standard measurements involve a number of steps, as outlined below:

1. Cooling to set the system in hydrate forming conditions: 25 to 0 °C at 0.5 °C/min, 100 s\(^{-1}\) shear rate.

2. Hydrate formation under shear: Hold at 100 s\(^{-1}\), 0 °C. After a 40% increase in viscosity, continue to hold at 100 s\(^{-1}\), 0 °C for an additional 12 hours. The additional time allows the hydrate slurry to approach a steady state before additional measurements are performed.

3. Annealing of hydrate slurry: oscillatory measurement. 2% strain, 1 Hz frequency for 8 hours, 0 °C. This is a non-disruptive step that allows the hydrate to harden.

4. Yield stress measurement: ramp shear stress from 0.1 to 3000 Pa at 1000 Pa/hr on a linear scale, 0 °C. Terminate at 3000 Pa or 100 s\(^{-1}\), whichever occurs first.

5. Steady-state flow curve: hold shear rate at 500 s\(^{-1}\) for 1 hour. Then, incrementally step down to 1 s\(^{-1}\) taking 10 points per decade on a log scale. Step back up to 500 s\(^{-1}\) in the same manner. During the shear ramps, each point is taken at steady-state, defined as three viscosity readings within 3% of each other.

6. Heating to dissociate hydrates: 0 to 25 °C at 0.5 °C/min, 100 s\(^{-1}\) shear rate.

The viscosity is recorded every 10 seconds during all transient steps. All steps are performed with the system pressurized, typically at 1500 psig before hydrate formation. Hydrate slurry phenomena are explored by varying one of the parts in this procedure while keeping
all the others constant; another publication will detail our studies of hydrate slurries using this system.

3.4.2 In Situ Hydrate Formation and Characterization

Hydrates are formed during the first two steps of the procedure (Figure 3.5). The initial pressure decrease and the viscosity increase are caused by the temperature ramp. This behavior is well known and expected for liquids. The viscosity spike around two hours, in this case, is suggested to indicate hydrate formation. The pressure decreases around the same time, which also suggests hydrate formation. The temperature is expected to rise upon hydrate formation because the process is exothermic (Sloan & Koh, 2008); however, our temperature data do not show an increase because the temperature is measured in the Peltier jacket rather than in the fluid. Alternatively, the Peltier jacket may be removing heat fast enough to maintain the setpoint temperature.

A combination of three factors may account for the spike in viscosity upon hydrate formation. First, the viscosity is expected to increase upon hydrate formation because solids are created from the emulsified water droplets. Second, we expect a viscosity increase from the depletion of methane in the liquid oil phase to form the hydrates (the concentration of methane in the hydrate is about 1:6 methane:water). This depletion of methane may partially accounts for the increase in slurry viscosity. From our measurements, the viscosity of the saturated and unsaturated emulsion with methane is 0.35 and 1.33 Pa.s, respectively, at 0 °C. Third, hydrate particles may aggregate during the viscosity spike, as particle aggregation is expected to increase the viscosity of the slurry (Hasan & Shaw, 2010).

Four hours after hydrate formation, the viscosity decreases. The decrease in the slurry viscosity is presumed to not be related to further hydrate formation or growth, as the pressure in the cell remains relatively constant. We suggest that the decrease in slurry viscosity results from the break-up of hydrate aggregates, which is consistent with the observations by Hasan and Shaw (Hasan & Shaw, 2010), Pal (Pal, 2011), and Graham et al. (Graham et al., 1984). In particular, Pal explains how aggregates effectively contain a larger volume than
Figure 3.5: Viscosity profile of a West African crude oil emulsion as hydrates form, aggregate, and break-up. Emulsion contains 30% water by volume. Measurement performed at 0 °C and 1500 psig.
the sum of their primary particles because some of the interstitial liquid is immobilized. When aggregates break-up, the interstitial liquid is released, which decreases the effective volume fraction of particles and thus decreases the viscosity.

Hydrates often are of great concern during the shut-in and restart of oil pipelines as they may tend to agglomerate and plug when allowed to anneal over time; hydrate plugs rarely occur under steady-state operation (Sloan et al., 2011). As such, the yield stress of the hydrate slurry is an important quantity to measure. We perform a non-disruptive oscillatory time sweep in which the hydrate anneals over the duration of the step. The storage and loss moduli slowly increase over the length of this step (Figure 3.6). Then, we measure the yield stress of the formed hydrate slurry after an 8 hour simulated shut-in. The measured pressure does not change during either of these steps; so, there is no further hydrate formation. The yield stress may serve as a good indicator of the slurry flowability in the restart of a pipeline.

Several well known methods exist to determine yield stress (Dzuy & Boger, 1983). Yield stress is taken here as the point where the shear rate becomes non-negligible as the shear stress increases. Figure 3.7 shows an example of shear rate versus shear stress data used to obtain the yield stress of the hydrate slurry.

After the stress ramp, we hold the shear rate at 500 s\(^{-1}\) for 1 hour in order to break up large aggregates that may have formed during the annealing step. This step causes a \(~15\%\) decrease in hydrate slurry viscosity at all shear rates. Additional stress ramps after this step always showed that the hydrate slurry no longer had a yield stress. Then, the subsequent shear rate ramps show that hydrate slurries are shear thinning (Figure 3.8), i.e., the viscosity decreases as the shear rate increases. The values below about 10 s\(^{-1}\) generally show much more scatter since they are obtained at or below the low torque limit of the cell. This sample shows no hysteresis since the flow curves in each direction are nearly identical.

Another valuable result can be obtained by measuring the hydrate slurry viscosity as the temperature of the cell is increased to dissociate the hydrate. As shown in Figure 3.9, the viscosity decreases as the hydrate slurry dissociates, although a spike in the viscosity
Figure 3.6: The storage ($G'$) and loss ($G''$) moduli over an 8 hour non-disruptive oscillatory time sweep. The emulsion is West African crude oil with 30% water by volume at 0 °C and 1500 psig.

Figure 3.7: Stress ramp performed on the hydrate slurry to determine yield stress. In this experiment, the yield stress is about 20 Pa. The emulsion is West African crude oil with 30% water by volume at 0 °C and 1500 psig.
Figure 3.8: Shear rate ramped from 500 to 1 s$^{-1}$ and then from 500 s$^{-1}$. The starting emulsion is a West African crude oil with 30% water by volume at 0 °C and 1500 psig.

is observed around 13 °C, which is near the hydrate dissociation temperature for methane hydrates at 1500 psi (as predicted by CSMGem (Ballard & Sloan, 2002a,b, 2004a,b; Jager et al., 2003)). The spike in viscosity likely occurs because the hydrate particles form sticky water shells as they dissociate. Other studies on hydrates (Dieker, 2009) shows an increase in the cohesion forces between particles as the temperature approaches the dissociation point. Eventually, all the hydrates particles dissociate, and both the viscosity and pressure returns to near that of the original emulsion at the start of the experiment.

3.5 Conclusion

We have developed an apparatus which performs high pressure rheology experiments with a concentric cylinders geometry targeted at the \textit{in situ} formation of gas hydrates in water-in-oil emulsions. While other high pressure rheometers exist, this setup combines both measurements of a true shear rate and pre-mixing for gas saturation of the emulsion. Initial results using this setup to study the rheology of hydrate slurries show clear changes in the viscosity associated with hydrate formation and growth, hydrate agglomerate break-up, and
hydrate dissociation. A variety of other tests can be performed such as a stress ramp to determine yield stress or flow steps to obtain flow curves. We have developed this apparatus to study hydrate slurry rheology, but it is possible to use the identical setup to study the rheology of other suspensions under high pressure.
CHAPTER 4
HYDRATE RHEOLOGY FROM WATER-IN-WEST AFRICAN CRUDE OIL EMULSIONS

Work with the high pressure rheometer apparatus studied water-in-crude oil emulsions (West African crude oil). A version of this chapter has been published in Energy and Fuels under the title “High-pressure rheology of hydrate slurries formed from water-in-oil emulsions.” This chapter is reproduced with permission (Webb et al., 2012b). Copyright 2012, American Chemical Society. A portion of the data from this chapter was collected by Patrick Rensing (Rensing, 2010).

4.1 Abstract

A unique high pressure rheology apparatus is used to study the in situ formation and flow properties of gas hydrates from a water-in-crude oil emulsion. Viscosity and pressure of the hydrate slurry are measured during hydrate formation, growth, aggregation, and dissociation. The rheology of the hydrate slurries varies with time, shear rate (1-500 s$^{-1}$), water content (0-50%), and temperature (0-6 °C). Hydrate slurry viscosity increases rapidly with time when hydrates form, and then decays after going through a maximum as hydrate aggregates breakup or rearrange. Yield stress increases with annealing time up to 8 hours and then remains constant. Hydrate slurry viscosity decreases with increasing shear rate (i.e., they are shear thinning). Viscosity and yield stress both increase with increasing water content. During dissociation, the viscosity increases just before the hydrate equilibrium temperature. Finally, transient viscosity measurements at varying temperatures suggest that mechanisms such as cohesion forces and shear forces competitively affect hydrate slurry viscosity.
4.2 Introduction

In subsea oil and gas pipelines, solid compounds called gas hydrates can form and completely block flow (Sloan & Koh, 2008; Sloan et al., 2011). Hydrates consist of small gas molecules (e.g., methane, ethane, propane, carbon dioxide) encaged by water molecules. Gas hydrates are typically thermodynamically stable at high pressures and low temperatures (e.g., at 4 °C, CSMGem (Ballard & Sloan, 2002a,b, 2004a,b; Jager et al., 2003) predicts methane hydrate forms at 3.9 MPa). In one estimate, the oil and gas industry spends over USD $200 million annually on hydrate prevention (Sloan Jr., 2003) or 5% to 8% of the total product plant cost (Chandragupthan, 2011) An understanding of the rheological properties of hydrate slurries in flowlines is essential in the management of hydrates and also a key component in developing strategies to prevent hydrate blockages.

Flow of oil and gas in a pipeline often contains multiple phases, including water, oil, gas, hydrates, precipitated solids, and sand. This work will focus on multiphase flow with a continuous liquid oil phase, an emulsified water phase, and a gas phase. If the pressure and temperature are within the hydrate formation region, then hydrates will first form on the surface of the water droplets, at the interface between the oil and water, and then grow radially inward (Sloan & Koh, 2008). If the droplets are small enough (< 20 – 40µm), they will fully convert to hydrate, while larger droplets may only form a hydrate shell (Sloan & Koh, 2008). After hydrates form, the hydrate particles can aggregate by either (1) sticking to other hydrate particles, or (2) colliding with a water droplet, and inducing hydrate formation in that droplet. Aggregation of hydrate particles may lead to hydrate plug formation.

The above phenomena may be quantified and explained using rheology. Measuring rheological properties, such as viscosity and yield stress of hydrate slurries is complicated by several factors. First, rheology experiments must be performed in a high pressure environment when dealing with gas hydrates. Second, water in crude oil emulsions must be recombined with light hydrocarbons (e.g., methane) in order to recreate a live crude oil, and provide a hydrate forming guest molecule. Gas recombination is necessary because the light
components contained in crude oil during production are flashed as soon as the crude oil is removed from the flowline under low pressure.

In the literature, studies on hydrate slurry rheology have been applied to air conditioning (Darbouret et al., 2005a), refrigeration (Darbouret et al., 2005b; Delahaye et al., 2008; Ding et al., 2008), and subsea oil and gas pipelines (Camargo & Palermo, 2002; Camargo et al., 2000; Fidel-Dufour et al., 2006; Sinquin et al., 2004). Delahaye et al. formed CO₂ hydrates in a temperature and pressure controlled circulating loop (Delahaye et al., 2008). Several researchers have used chemicals such as tetra-n-butylammonium bromide (TBAB) (Darbouret et al., 2005a,b; Ding et al., 2008) or cyclopentane (Peixinho et al., 2010), which enable hydrate formation at atmospheric pressures. Other researchers were able to achieve high pressures and form methane hydrate slurries. These studies used a variety of devices to perform rheological measurements including a modified pressure-temperature cell (Camargo & Palermo, 2002; Camargo et al., 2000), a 2-inch diameter flowloop (Camargo & Palermo, 2002; Camargo et al., 2000; Sinquin et al., 2004), and a 1-cm diameter flowloop with a riser (Fidel-Dufour et al., 2006).

To the best of our knowledge, the following is the first study which directly measures the viscosity and yield stress of gas hydrate slurries formed in situ from water-in-crude oil emulsions. Experimental results at varying time, shear rate, water content, salt content, and temperature will improve our understanding of hydrate slurry flow in oil and gas pipelines, and lead to new heuristics for hydrate plug remediation.

4.3 Experimental Method and Setup

Before performing an experiment, the water-in-crude oil emulsion must be prepared. First, a large container of crude oil is heated for at least 4 hours at 60 °C. Then, a desired volume of the oil is removed and cooled to room temperature. Finally, the desired volume of deionized water is added dropwise to the cooled crude oil sample while mixing at 8000 rpm for 3 minutes in a VirTis Cyclone I.Q.² homogenizer. The crude oil used in this work is a West African crude (WAC) oil provided by ExxonMobil. The composition, SARA analysis (a
method which separates crude oils into four solubility classes: saturates, aromatics, resins, and asphaltenes), and other characterization of this oil can be elsewhere (Rensing et al., 2011). At 0.3 water volume fraction, water droplets in the emulsion were measured at 1.5 ± 0.3 µm (quantified using optical microscopy).

The water-in-oil emulsion initially contained a dead (no light hydrocarbons) crude oil as the continuous phase. To make a live crude oil, the emulsion was pressurized with methane from a high pressure cylinder until the oil phase was fully saturated with methane. The saturation process had to be performed in a separate cell from the high pressure rheometer because the concentric cylinder geometry used in the rheometer cannot generate enough mixing to dissolve methane on a reasonable timescale. Other geometries, such as a helical ribbon or an anchor can generate sufficient mixing; however, these cannot analytically determine the shear rate in the cell. In order to have both an analytically determined shear rate and a saturated oil phase, we use two separate vessels, a mixing cell and a rheometer pressure cell (Figure 4.1). With the external mixing cell, dissolution of methane into the emulsion occurs in the first two hours of mixing (Webb et al., 2012b).

The mixing cell (Autoclave Engineers) consists of two large steel pieces sealed together with six 9/16 inch diameter bolts and a teflon seal. The cell operates at pressures up to 4750 psig and a maximum volume of about 300 mL. A belt connected to an air-powered motor drives the impeller of the mixing cell at 600 rpm. The syringe pump is a Teledyne ISCO 500D model. The pump can hold a maximum pressure of 3750 psig and a maximum volume of 500 mL. The rheometer is a TA Instruments AR-G2 rheometer.

The rheometer pressure cell fits in a Peltier heating/cooling jacket (both from TA Instruments), which mounts on the rheometer. The Peltier jacket has a temperature range from -25 to 150 °C, maximum heating/cooling rate of 2 °C/min, and ± 0.1 °C temperature precision. A cooling bath with a water and ethylene glycol mixture supplies the jacket with cooling fluid. The pressure cell consists of a steel outer cylinder and a titanium inner cylinder in a concentric cylinders (cup-and-bob) arrangement. The cell is rated for operation up
to 2000 psi. The inner cylinder assembly contains a steel cap, which screws into the outer cylinder, and a rotor assembly, which screws into the steel cap. The 4-pole magnet couples with an outer magnet, which is attached to the rheometer spindle. The sample volume used in an experiment is 9.5 mL. A full description of this apparatus is shown elsewhere (Webb et al., 2012b).

![Figure 4.1: Schematic of high pressure rheometer apparatus.](image)

The standard measurements involve a number of steps, which are outlined below:

1. Cooling to hydrate forming conditions: 25 to 0 °C at 0.5 °C/min, 100 s⁻¹ shear rate.

2. Hydrate formation under shear: 100 s⁻¹, 0 °C. After a 40% increase in viscosity, continue measurement for 12 hours.

3. Annealing of hydrate slurry: oscillatory measurement. 2% strain, 1 Hz frequency for 8 hours, 0 °C. A non-disruptive step that allows the hydrate to anneal.

4. Yield stress measurement: ramp shear stress from 0.1 to 3000 Pa at 1000 Pa/hr on a linear scale, 0 °C. Terminate at 3000 Pa or 100 s⁻¹, whichever occurs first.

5. Steady-state flow curve: hold shear rate at 500 s⁻¹ for 1 hour. Then ramp down to 1 s⁻¹ taking 10 points per decade on a log scale. Ramp back to 500 s⁻¹ in the same
manner. During the shear ramps, each point is taken at steady-state, defined as three points within 3% of each other.

6. Heating to dissociate hydrates: 0 to 25 °C at 0.5 °C/min, 100 s⁻¹ shear rate.

All transient steps record the viscosity every 10 seconds. All steps were performed with the system pressurized, initially typically at either 1500 or 2000 psig before hydrate formation. Hydrate slurry phenomena are explored by varying one of the parts in this procedure while keeping all the others constant. In some early experiments, an additional flow curve after step 3 and additional stress ramps after step 2, after the 500 s⁻¹ shear rate hold in step 5, and after step 5 were performed. The additional flow curve gave viscosity values about 15% higher than those obtained in step 5 of the standard procedure. In the additional stress ramps, a yield stress was never observed, so, the additional ramps were removed in later experiments.

Most experiments were performed three times, and found to be qualitatively reproducible. We report one representative data set for each experiment, except for yield stress values, which we report as the average value from all replicate runs.

4.4 Results and Discussion

Hydrates are typically formed during the first two steps of the experimental procedure (Figure 4.2). The initial pressure decrease and the viscosity increase are caused by the temperature ramp from 25 °C to the set temperature. The viscosity spike around two hours, in this case, is suggested to indicate hydrate formation. The pressure in the cell decreases around the same time, which also suggests hydrate formation. Hydrate formation can also be monitored from a temperature rise (exothermic process) (Sloan & Koh, 2008); however, our temperature data do not show an increase because the temperature is measured in the Peltier jacket rather than in the fluid. In addition, the Peltier jacket may be removing heat fast enough to maintain the setpoint temperature.
A combination of three factors may account for the spike in viscosity upon hydrate formation. First, the viscosity is expected to increase upon hydrate formation because solids are created from the emulsified liquid water droplets. Second, once hydrate particles convert to hydrate, they are free to move around and collide with other hydrate particles or water droplets, which may lead to aggregation. Aggregation will increase suspension viscosity (Pal, 2011). Third, we expect a viscosity increase due to the depletion of methane from the oil phase to the hydrate phase (the concentration of methane in the hydrate is about 1:6 methane:water). This depletion of low molecular weight methane increases the continuous phase viscosity and may partially account for the increase in slurry viscosity. From our baseline measurements, the water-in-West African crude oil emulsion viscosity at 0 °C and 0.3 water volume fraction is 0.35 Pa.s when saturated with methane and 1.33 Pa.s when unsaturated.

After the slurry viscosity reaches a maximum value, we observe a monotonic decrease in the viscosity. The decrease in slurry viscosity is presumed to not be related to further
hydrate formation or growth, since the pressure in the cell remains relatively constant. We suggest that the decrease in slurry viscosity results from the break-up and rearrangement of hydrate aggregates, which is consistent with the observations of Hasan and Shaw (Hasan & Shaw, 2010), Pal (Pal, 2011), and Graham et al. (Graham et al., 1984). In particular, Pal explains how aggregates effectively contain a larger volume than the sum of their primary particles because some of the interstitial liquid is immobilized. When aggregates break-up, the interstitial liquid is released, which decreases the effective volume fraction of particles and thus decreases the viscosity.

Next, the hydrate slurry viscosity increases as the water volume fraction increases (Figure 4.3). Each viscosity peak occurs at a different time because hydrate formation is a random event. We also see that the transient viscosity profiles show greater fluctuations as the viscosity peaks with increasing water volume fraction. To explain the erratic viscosity fluctuations at higher water volume fractions, we believe that aggregates have grown so large that their size approaches the width of the gap between the concentric cylinders. If this happens, the aggregates could jam, and slip causing the observed erratic behavior.

Figure 4.3: *In situ* formation of methane hydrates formed from a water-in-oil emulsion. West African crude oil emulsion at 0 °C, 2000 psig initially, and 100 s⁻¹ shear rate.
Hydrate blockages rarely occur under steady-state operation (Sloan et al., 2011). Hydrates often cause the most severe problems in pipelines in shut-in and restart situations, as the down time allows hydrates to anneal when present. As such, the yield stress of the hydrate slurry is an important quantity to measure. We measure the yield stress of the formed hydrate slurry after an 8 hour simulated shut-in. The yield stress may serve as a good indicator of the slurry flowability in the restart of a flowline. Several well known methods exist to determine yield stress (Dzuy & Boger, 1983). Here, yield stress is taken as the point where the shear rate becomes non-negligible as the shear stress increases. Before this point, the shear rate will be near zero, independent of shear stress. After this point, the shear rate will increase monotonically with shear stress (Webb et al., 2012b). As shown in Figure 4.4 for the hydrate slurry formed with 0.4 water volume fraction, the yield stress of the hydrate slurry increases as the annealing time increases for the first 8 hours, and then levels to an asymptotic value. These results have significant practical implication when dealing with hydrates formed from water-in-oil emulsions in flowlines: it is best to treat the flowline as soon as possible so that the hydrate slurry will have a small yield stress and be more easily moveable.

Three concentration regimes in the magnitude of yield stress at varying water volume fraction were measured (Figure 4.5). Below 0.3 water volume fraction, there was no measurable yield stress. From 0.3 to 0.5, the hydrate slurry exhibited a small yield stress (<25 Pa) that increased with water volume fraction. Above 0.5, the yield stress of the hydrate slurry was so large that it could not be measured with our rheometer (>3000 Pa). These results are also of significant practical importance for hydrates in flowlines: a critical water volume fraction exists above which hydrates may likely jam flowlines and below this critical water volume fraction, hydrates may not significantly affect flow in restart scenarios. From measurements at different temperatures, we see a weak dependence of the hydrate slurry average yield stress on temperature, which varied from 18 to 21 to 4 Pa for 0, 2, and 4 °C, respectively (for comparison, the yield stress of ketchup is about 15 Pa).
Figure 4.4: Time dependence of methane hydrate slurry yield stress for a West African crude oil at 0 °C, 0.4 water volume fraction, and 2000 psig initially methane.

Figure 4.5: Methane hydrate slurry yield stress shows three regimes with water volume fraction: no yield stress from 0 to 0.3, small yield stress from 0.3 to 0.5, and large yield stress above 0.5. West African crude oil at 0 °C, 2000 psig initially, and 2 hours annealing time. Error bars are ± 1 standard deviation from a sample of three or four replicate experiments.
All hydrate slurries exhibit shear-thinning (Figure 4.6), with more pronounced thinning as the water volume fraction increased. All samples showed statistically identical shear curves for the ramp down (500 to 1 s\(^{-1}\)) and the ramp up (1 to 500 s\(^{-1}\)). The values shown in the figure are the average of both shear ramps.

![Figure 4.6](image)

Figure 4.6: Shear-thinning behavior of methane hydrate slurries at different water volume fractions. Lines show that the power law model (Bird et al., 2002) fits to the data well. Measurements performed at 0 °C and 2000 psig initially.

Many models exist to fit viscosity as a function of shear rate. One simple model is the two parameter power law model (Bird et al., 2002):

\[
\eta = m\dot{\gamma}^{n-1} \tag{4.1}
\]

where, \(\eta\) is viscosity, \(\dot{\gamma}\) is shear rate, \(m\) is the consistency, and \(n\) is the flow behavior index. \(m\) and \(n\) are fitting parameters. Table 4.1 shows the power law model parameters for four different water volume fractions. The consistency parameter, \(m\), increases with particle volume fraction, as would be expected for a suspension with increasing particle concentration (Macosko, 1994). The values of the flow behavior index, \(n\), are all between 0.83 and 0.89, which indicates a weakly thinning suspension.
Table 4.1: Power law parameters for hydrate slurry flow curves at varying water volume fraction formed from water in West African crude oil emulsions. See 4.6 for a comparison of the model to the measured data.

<table>
<thead>
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<th>φ</th>
<th>m(Pa⋅s^n)</th>
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<td>0.20</td>
<td>0.73</td>
<td>0.89</td>
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<tr>
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<td>1.0</td>
<td>0.89</td>
</tr>
<tr>
<td>0.40</td>
<td>1.9</td>
<td>0.84</td>
</tr>
<tr>
<td>0.45</td>
<td>3.1</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The viscosity of the hydrate slurry viscosity was also measured during the dissociation process. Slurry viscosity decreases as the temperature of the cell is increased to dissociate the hydrate (Figure 4.7). An increase in the viscosity is observed around 15 °C. At the conditions of this experiment, the hydrate dissociation temperature for methane hydrate at 2000 psi is 15.6 °C, as predicted by CSMGem (Ballard & Sloan, 2002a,b, 2004a,b; Jager et al., 2003). This increase in viscosity likely occurs because the hydrate particles start to pre-melt, forming a thin water shell around the particle. Other studies on hydrates (Dieker, 2009) have shown that the water shell on particles causes an increase in the cohesion forces between hydrate particles as the temperature approaches the dissociation point. So, the increased “stickiness” of the particles may cause more aggregation, which will increase viscosity. At the higher water cuts, these water shells are significant enough to cause a viscosity increase. At the lower water cuts, the water shells cause a shoulder in the curves. All these effects occur before the hydrate dissociation temperature, above which, viscosity drops rapidly as hydrates fully melt. Eventually, all the hydrate particles dissociate, and the viscosity returns to a value close to the original emulsion.

Rheological measurements were performed for hydrate slurries at three different temperatures: 0, 2, and 4 °C (Figure 4.8). The procedure was identical to the one described earlier except that the setpoint temperature was changed. We note that in Figure 4.8, the y-axis shows the relative viscosity, defined as the suspension viscosity divided by the emulsion viscosity before hydrate formation. We also normalize the x-axis so that time zero corresponds
Figure 4.7: Viscosity of hydrate slurry during warming of cell to dissociate hydrates. All systems were initially charged to 2000 psig and measurements performed at 0 °C. Heating rate of 0.5 °C/min used during the dissociation.

to the start of hydrate formation at each temperature. As the experiment temperature is increased, the viscosity decreases for all points in time. Also, the initial slope and peak viscosity decrease as the temperature increases. A steep slope indicates rapid hydrate formation, because the driving force for hydrate formation increases as temperature decreases.

These measurements suggest that fewer hydrates were formed at the higher temperatures. Surprisingly, the viscosity shows a different trend after the peak viscosity for all three temperatures. At 0 °C, the slurry viscosity decreases after the spike, which as discussed earlier was suggested to be related to aggregate breakup. At 4 °C, there is a small and gradual increase in the slurry viscosity after the viscosity peaks initially. At 2 °C, the slurry viscosity seems to remain relatively constant after the initial viscosity peak, which suggests constant aggregate size. As discussed earlier, the slurry viscosity response after the peak is most likely related to re-structuring of the hydrate suspension formed, as the pressure in the cell remains constant, indicating hydrates are no longer forming. One possible explanation of the different slurry viscosity dependence at the different temperatures can be related to
the multiple forces competitively affecting the aggregation of the hydrate particles, possibly including shear forces and cohesion forces. Shear forces break up aggregates while cohesion forces cause re-aggregation. The shear forces should be nearly constant at all temperatures; however, cohesion forces will decrease with decreasing subcooling (Aman et al., 2011; Dieker, 2009).

Figure 4.8: Viscosity profile of hydrate slurries at different temperature. The relative viscosity is defined as the measured viscosity divided by emulsion viscosity just before hydrate formation. All systems contained 0.3 water volume fraction in West African crude oil emulsion, initially charged to 1500 psig with methane gas. Measurements performed with a shear rate of 100 s$^{-1}$.

We also performed a few experiments using 3.5 weight percent NaCl water instead of deionized water to make our emulsions. In these experiments, we did not observe significant differences in the salt system, except for the yield stress measurement (step 4). We performed three repeat experiments at 0.3 and 0.5 water volume fractions. Table 4.2 shows that the brine slurry has a much lower yield stress at 0.5 water volume fraction. This suggests that salt shifts the critical volume fraction for jamming the rheometer to a higher value.

The complexity of these systems make the data interpretation quite difficult, as the crude oil used for the oil continuous phase is a complex mixture. Since we are unable to see
Table 4.2: Yield stresses of hydrate slurries formed in deionized water compared to 3.5 weight percent salt water.

<table>
<thead>
<tr>
<th>Emulsion Type</th>
<th>Water Volume Fraction</th>
<th>(\tau_0) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt water</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>DI water</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>Salt water</td>
<td>0.5</td>
<td>37</td>
</tr>
<tr>
<td>DI water</td>
<td>0.5</td>
<td>&gt;3000</td>
</tr>
</tbody>
</table>

inside the high pressure cell, we are limited in conceptualizing the actual phenomena taking place during and after hydrate formation. Nonetheless, these results are the first step in demonstrating the potential of using a high pressure rheometer to quantify hydrate slurry properties, which are critical in the management of gas hydrates in flowlines.

4.5 Conclusions

Methane hydrates were formed \textit{in situ} from water-in-crude oil emulsions in a high pressure rheology apparatus. The viscosity, temperature, and pressure profiles of the slurry over time can identify hydrate formation, restructuring, and dissociation. The hydrate slurry viscosity increases to the peak value in about 20 minutes when hydrates form, and then decays after going through a peak value as the hydrate suspension is continuously sheared. During hydrate formation, steady state shear ramp, and dissociation, the hydrate slurry viscosity increased at all points as the water volume fraction increases. Yield stress of the hydrate slurry increases with annealing time up to 8 hours and then remains relatively unchanged. The yield stress gradually increases with particle volume fraction until it dramatically increases at and above 0.5 water volume fraction. Also, all of the hydrate slurries shear thin. During dissociation, the slurry viscosity increases just before the hydrate equilibrium temperature. In summary, this study provides a collection of data to the growing field of hydrate slurry rheology. While many open questions remain to fully understand how hydrates are actually impacting the rheological behavior of the slurry, there is significant new insight from these systematic experiments and their results.
A version of this chapter has been published in Langmuir under the title “Rheological properties of methane hydrate slurries formed from AOT + water + oil emulsions.” This chapter is reproduced with permission from Webb et al. (Webb et al., 2013). Copyright 2013, American Chemical Society. The supporting information from this paper can be found in Appendix A.

5.1 Abstract

The in situ formation and flow properties of methane hydrates formed from water-in-oil microemulsions composed of water, dodecane, and aerosol OT surfactant (AOT) were studied using a unique high pressure rheometer. AOT microemulsions have high stability (order of months), well characterized composition, and yield reproducible results compared to hydrate studies in water-in-crude oil emulsions. Viscosity increases on the order of minutes upon hydrate formation, and then decreases on the order of hours. If significant unconverted water remained after the initial formation event, then viscosity increases for a time as methane slowly dissolves and converts additional water to hydrate. In addition to transient formation measurements, yield stresses and flow curves are measured for a set of experimental conditions. Hydrate slurry viscosity and yield stress increase with increasing water volume fraction, increasing initial pressure, decreasing temperature, and decreasing formation shear rate.

5.2 Introduction

Natural gas hydrates are solid crystal structures composed of water and gas that exist at high pressures and low temperatures. Water molecules form cages around small gas molecules such as methane, hydrogen, and carbon dioxide. Each cage typically contains one
gas molecule. Multiple cages connect together in a regular pattern that repeats and fills space. Common patterns are Structure I (e.g., for methane and hydrogen) and Structure II (e.g., for mixed gas systems) (Sloan & Koh, 2008).

The unique properties of hydrates lead to many applications. Because hydrates store gas at a very high density, hydrates draw interest as a material for energy storage (e.g., of hydrogen) (Grim et al., 2012; Strobel et al., 2009). Transportation of natural gas in solid hydrate pellets (Stern et al., 2001; Takeya et al., 2011) may be economically feasible because of the hydrate self-preservation effect (Sloan & Koh, 2008). Other researchers seek to improve fundamental scientific understanding of hydrates, such as the nucleation mechanism (Walsh et al., 2009). Hydrates can limit and sometimes fully block flow in subsea oil and gas pipelines, where water, gas, high pressure, and low temperature are all present (Sloan et al., 2011). This aspect of hydrate science, often called hydrates in flow assurance, is the motivation for this work.

An improved understanding of how hydrates nucleate, grow, and aggregate at different pressures, temperatures, flow conditions, and compositions could lead to better prediction, prevention, and management of hydrates in flow assurance. Rheology, the study of how matter flows and deforms, directly measures mechanical properties of hydrate suspensions. From rheological measurements of hydrate slurries, we can develop heuristics for operation of subsea oil and gas pipelines and develop predictive models of rheological properties as a function of pipeline conditions such as pressure, temperature, shear rate, and water volume fraction.

Past work on rheology of hydrate suspensions typically falls into two categories. Some work focused on measurements in flowloops or high pressure mixing cells, where viscosity is calculated rather than directly measured (Camargo & Palermo, 2002; Camargo et al., 2000; Delahaye et al., 2008, 2011; Fidel-Dufour et al., 2006; Sinquin et al., 2004). Other work may have measured viscosity of hydrate suspensions in a rheometer; however, the hydrate was formed at atmospheric pressure by using guest molecules like cyclopentane or
tetra butylammonium bromide, which may not form hydrate slurries that are representative of those found in subsea pipelines (Darbouret et al., 2005b; Ding et al., 2008; Peixinho et al., 2010). Hydrate slurry rheology measurements are challenging because they require an emulsion with dissolved gas; so, the rheometer must provide mixing to dissolve the gas and operate at high pressure.

Alternatively, a novel apparatus that saturates emulsions with methane in an external mixing cell, and then pumps the emulsion under pressure to a high pressure rheometer cell with concentric cylinders geometry provides a method to study hydrate rheology in detail (Webb et al., 2012a,b). Initial work with this apparatus studied hydrate slurries and ice slurries formed from water-in-crude oil emulsions (Rensing et al., 2011; Webb et al., 2012a). Although water-in-crude oil emulsions are found in subsea pipelines, crude oil suffers from two significant problems when studied experimentally. First, crude oil is very complex chemically. Crude oil refers to a wide variety of liquids that each behave uniquely. Each oil contains thousands of components, and technology is not yet able to give a complete composition of crude oil (Freitas et al., 2009). Because crude oil is difficult to characterize chemically, crude oil is often characterized by physical properties like density, viscosity, or SARA analysis, which separates the oil into four solubility classes. Second, experiments with crude oil are difficult to reproduce. Large molecular weight components such as waxes and asphaltenes may precipitate out of solution or settle during storage, requiring vigorous heating and mixing each time a sample is drawn. Also, the composition of produced oil changes with time; so, each batch of oil received from a pipeline will be different.

Due to the difficulties with crude oil, model emulsions are studied instead. Ideally, a model emulsion will (1) be stable for at least one week, (2) remain stable over a range of temperatures and pressures, (3) reproducibly form hydrates under flow, (4) have a known chemical composition, and (5) behave physically like a water-in-crude oil emulsion (density, viscosity, droplet size, etc.). In this work, microemulsions of water-in-dodecane stabilized with AOT surfactant are studied as a model for water-in-crude oil emulsions found in subsea
pipelines. Water/dodecane/AOT emulsions were selected because they fit all five criteria better than any other emulsions that were examined.

5.3 Experimental Section

5.3.1 Materials and Emulsions

Emulsions were made from deionized water, dodecane (Sigma-Aldrich, ≥99% purity), and aerosol OT (dioctyl sodium sulfosuccinate) surfactant (Fisher, solid (anhydrous)). Aerosol OT is a two-tailed anionic surfactant (Figure 5.1). Emulsions are made by measuring the desired amount of dodecane by mass, measuring the desired amount of AOT by mass, and then adding the AOT to the dodecane. The solution is shaken by hand until all of the AOT visibly dissolves. Finally, water is added dropwise and the solution is shaken by hand. All microemulsions used a ratio of 20 moles of water to 1 mole of AOT (i.e., $w_o = 20$). Microemulsions are optically transparent and show no visual phase separation at room temperature after two months (and longer).

![Figure 5.1: AOT molecular structure.](image)

Dynamic light scattering was used to measure the size of water droplets (Table 5.1). Measurements were performed on a ZetaPALS instrument from Brookhaven at 25 °C. Emulsions showed a bimodal distribution, which has been observed elsewhere (Law & Britton, 2012). The measured droplet sizes compare favorably to literature values (Ganguly & Choudhury, 2012; Gochman-Hecht & Bianco-Peled, 2005; Law & Britton, 2012). Because of their small
droplet size and long term stability, these systems are classed as microemulsions (Cassin et al., 1995; Eastoe et al., 1992; Ganguly & Choudhury, 2012; Gochman-Hecht & Bianco-Peled, 2005; Law & Britton, 2012; Tsukahara et al., 2011).

Table 5.1: Median droplet size and number average droplet size for H$_2$O/C$_{12}$/AOT microemulsions.

<table>
<thead>
<tr>
<th>$\phi_w$</th>
<th>$d_{\text{median}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>48</td>
</tr>
<tr>
<td>0.10</td>
<td>47</td>
</tr>
<tr>
<td>0.20</td>
<td>38</td>
</tr>
<tr>
<td>0.25</td>
<td>29</td>
</tr>
<tr>
<td>0.30</td>
<td>22</td>
</tr>
</tbody>
</table>

5.3.2 Apparatus

We have developed a novel high pressure apparatus consisting of a high pressure rheometer, an external mixing cell, and a high pressure syringe pump between the two cells (Figure 5.2). The mixing cell (Autoclave Engineers) operates at pressures up to 4750 psig and a maximum volume of 302 mL. A belt connected to an air-powered motor drives the impeller of the mixing cell at 600 rpm. The syringe pump is a Teledyne ISCO 500D model. The pump can hold a maximum pressure of 3750 psig and a maximum volume of 500 mL. The rheometer is a TA Instruments AR-G2 rheometer.

The rheometer pressure cell fits in a Peltier heating/cooling jacket (both from TA Instruments), which mounts on the rheometer. The Peltier jacket has a temperature range from -25 to 150 °C, maximum heating/cooling rate of 2 °C/min, and ± 0.1 °C temperature precision. A cooling bath (Neslab RTE 100) with a water and ethylene glycol mixture supplies the jacket with cooling fluid. A cooled circulating fluid allows for the low temperature (~0 °C) operation of the rheometer cell for the multi-day duration of the hydrate experiments. The pressure cell consists of a steel outer cylinder and a titanium inner cylinder in a concentric cylinders (cup-and-bob) arrangement. The outer cylinder internal radius is 14.00 mm,
while the inner cylinder radius is 13.00 mm, giving the cell a 1.00 mm gap size. The cell is rated for operation up to 2000 psi. The inner cylinder assembly contains a steel cap, which screws into the outer cylinder, and a rotor assembly, which screws into the steel cap. The 4-pole magnet couples with an outer magnet, which is attached to the rheometer spindle. The sample volume used in an experiment is 10 mL. A full description of this apparatus is published elsewhere (Webb et al., 2012b).

5.3.3 Procedure

Prior to starting an experiment in the rheometer, we first make a emulsion, and then saturate the emulsion with methane gas (Matheson Trigas, 99.99% purity) in the external mixing cell for at least four hours. Then, 10 mL of the emulsion are pumped under pressure into the rheometer pressure cell. Next, we set up a procedure using the rheometer’s software. The typical experimental procedure with control values for pressure, temperature, shear rate, and transient step time are shown in Table 5.2. The initial pressure, experimental temperature, initial shear rate, emulsion water volume fraction, and the length of the transient hydrate formation step were changed from experiment to experiment.
Table 5.2: Detailed rheology procedure. Microemulsion is saturated externally and the rheometer cell is pressurized with CH$_4$ before the first step.

<table>
<thead>
<tr>
<th>Step</th>
<th>Duration</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibration</td>
<td>30 minutes</td>
<td>25 °C</td>
</tr>
<tr>
<td>Cooling</td>
<td>50 minutes</td>
<td>Ramp temperature from 25 to 0 °C at 0.5 °C/minute, 100 s$^{-1}$</td>
</tr>
<tr>
<td>Hydrate Formation</td>
<td>24 hours</td>
<td>0 °C, 100 s$^{-1}$</td>
</tr>
<tr>
<td>Annealing</td>
<td>8 hours</td>
<td>0 °C, 2% oscillatory strain, 1 Hz frequency</td>
</tr>
<tr>
<td>Yield Stress Measurement</td>
<td>~10 minutes</td>
<td>0 °C, ramp shear stress from 0 to 3000 Pa at 1000 Pa/hr</td>
</tr>
<tr>
<td>Conditioning</td>
<td>1 hour</td>
<td>0 °C, 500 s$^{-1}$</td>
</tr>
<tr>
<td>Flow Curve</td>
<td>~30 minutes</td>
<td>0 °C, ramp shear rate from 500 to 1 to 500 s$^{-1}$, steady state measurements: 3 s sample period, 3% tolerance, 3 consecutive within tolerance, 2 minute maximum point time</td>
</tr>
<tr>
<td>Dissociation</td>
<td>50 minutes</td>
<td>Ramp temperature from 0 to 25 °C at 0.5 °C/minute, 100 s$^{-1}$</td>
</tr>
</tbody>
</table>

5.4 Results

5.4.1 Transient Hydrate Formation

Hydrate formation under flow from a water/C$_{12}$/AOT microemulsion is characterized by a significant spike in the viscosity of the fluid (Figure 5.3). First, the temperature ramps down from 25 to 0 °C over 50 minutes. Cooling causes a pressure loss of ~130 psi (this is independent of the liquid phase composition). After cooling, hydrate formation becomes thermodynamically favorable; however, since hydrate formation is a random event, much like ice nucleation, we do not observe hydrate formation for some time (10 minutes to 10 hours) after cooling. About 4.5 hours into one experiment (Figure 5.3), the viscosity increases rapidly, indicating hydrate formation. A viscosity increase upon hydrate formation has been observed in other hydrate forming systems (Delahaye et al., 2008; Fidel-Dufour et al., 2006). After the initial peak, the viscosity continues to increase for the next ~15 hours and the pressure continues to decrease (Figure 5.3). Starting at ~20 hours, the viscosity
decreases (Figure 5.3). The viscosity values after hydrate formation for water/C\textsubscript{12}/AOT microemulsions are similar to those of water-in-crude oil emulsions studied previously, even though water/C\textsubscript{12}/AOT microemulsions have a much lower viscosity before hydrate formation (Webb et al., 2012a).

![Figure 5.3: Typical data of transient hydrate formation from a water/AOT/C\textsubscript{12} microemulsion.](image)

Experiments at varying water volume fraction show transient slurry viscosity increases with increasing water volume fraction (Figure 5.4). The viscosity profile after the initial viscosity spike strongly depends on water volume fraction. At high water volume fractions ($\phi_w = 0.25, 0.30$), the viscosity increases for a time, and then decreases. At lower water volume fractions ($\phi_w = 0.05, 0.10, 0.20$), the viscosity decreases monotonically after the initial viscosity peak. This behavior was reproducible at all water volume fractions.
Figure 5.4: Hydrate slurry viscosity versus time after nucleation at varying water volume fractions.

Most experiments were run for 24 hours, which was sometimes not long enough to observe viscosity decreasing, especially at higher water cuts. One experiment at 0.3 water volume fraction lasted 72 hours (Figure 5.5) and showed both pressure and viscosity approach steady values.

The rheological behavior of hydrate slurries also depends on the experimental conditions; namely, initial pressure, temperature, and formation shear rate (i.e., the shear rate set during the transient hydrate formation step). Hydrate slurry viscosity increased with increasing initial pressure (Figure 5.6), decreasing temperature (Figure 5.7), and decreasing formation shear rate (Figure 5.8). The driving force for hydrate formation increases with increasing pressure and decreasing temperature. Figures 5.6 and 5.7 also show the combined effect of changing water volume fraction and pressure or temperature. Similar to the studies at constant temperature and pressure (Figure 5.4), the viscosity increases with water volume fraction even as temperature and pressure are varied. High shear rates could break up aggregates and also force particles to align more under flow, thus decreasing viscosity as formation shear rate increases (Figure 5.8) (Graham et al., 1984; Hasan & Shaw, 2010; Pal, 2011). As
Figure 5.5: Transient hydrate formation run until viscosity and pressure remained constant. 0.30 water volume fraction microemulsion.
formation shear rate increased, the system approached steady values for viscosity and pressure more rapidly. Therefore, higher shear rates may promote faster hydrate formation by increasing the probability that droplets and hydrates and gas interact.

![Image](image_url)

Figure 5.6: Hydrate slurry viscosity versus time after nucleation at two pressures.

### 5.4.2 Yield Stress Measurements

After hydrate formation, steady shear is stopped and the sample is allowed to anneal for eight hours. Then, the shear stress is ramped from 0 to 3000 Pa. We define the yield stress as the shear stress at which the shear rate increases rapidly (Dzuy & Boger, 1983; Webb et al., 2012b). In our measurements, yield stress generally increased with increasing water volume fraction, increasing pressure, decreasing temperature, and decreasing shear rate (Figure 5.9). Thus, yield stress followed the same trends as transient viscosity. Several experiments were performed at atmospheric pressure and -10 °C, where ice particles form instead of hydrate. No trend was found between yield stress and water volume fraction with ice experiments. Furthermore, ice slurry yield stress was generally smaller than hydrate slurry yield stress at the same water volume fraction. Finally, yield stresses measured for hydrate slurries formed
Figure 5.7: Hydrate slurry viscosity versus time after nucleation at two temperatures.

Figure 5.8: Hydrate slurry viscosity versus time after nucleation at varying shear rate.
from H₂O/C₁₂/AOT microemulsions were comparable to those measured in water-in-crude oil emulsions (Webb et al., 2012a).

![Figure 5.9](image)

Figure 5.9: Slurry yield stress versus water volume fraction at varying pressures, temperatures, and shear rates.

### 5.4.3 Viscosity of Hydrate Slurries

After the yield stress measurement, the slurries flow at 500 s⁻¹ for one hour to homogenize the system. Then we ramp the shear rate from 500 to 1 s⁻¹ and then back to 500 s⁻¹ to check for hysteresis. Only the decreasing shear rate step is presented because no hysteresis was found. H₂O/C₁₂/AOT microemulsion viscosity is always lower than hydrate suspension viscosity at the same water volume fraction (Figure 5.10); so, hydrates increase the viscosity of the fluid. Dodecane viscosity is lower than all of the microemulsion viscosities. Dodecane and H₂O/C₁₂/AOT microemulsions are Newtonian over the range of shear rates studied. Hydrate suspensions formed from H₂O/C₁₂/AOT microemulsions show shear-thinning behavior (i.e., viscosity decreases as shear rate increases) at 0.2 water volume fraction and above. The data for the 0.05 water volume fraction microemulsion are not shown because the measurements were below the resolution of the instrument.
Figure 5.10: Viscosity measured from a shear rate ramp from 500 to 1 s$^{-1}$ at 0 °C. Dodecane and H$_2$O/C$_{12}$/AOT microemulsions (open symbols), hydrate suspensions formed from H$_2$O/C$_{12}$/AOT microemulsions (closed symbols).

Trends from the steady state flow curves are consistent with the transient experiments. Hydrate and ice slurry viscosities increased with increasing water volume fraction (Figure 5.11a and 5.11b). Typically, the ice slurry viscosity is greater than the hydrate slurry viscosity at the same water volume fraction, which may be related to hydrate conversion. Slurry viscosity increase with particle volume fraction is analogous to colloidal suspension (e.g., Krieger-Dougherty model (Krieger & Dougherty, 1959)) Hydrate slurry viscosity increased slightly as pressure increased from 1000 to 1500 psig methane (Figure 5.11c). As pressure increases, the driving force for hydrate formation increases, which could increase the amount of hydrate formed and thus viscosity. Hydrate slurry viscosity decreased some as temperature increased from 0 to 2 °C (Figure 5.11c). Two mechanisms cause viscosity to decrease as temperature increases. First, the liquid components (i.e., dodecane and water) thin with temperature, which is typical of liquids. Second, the driving force for hydrate formation decreases as temperature increases, so, less solid hydrate may form. The initial shear rate used during the transient steps weakly affects the hydrate slurry viscosity measured in the
flow curve step (Figure 5.11d). The experiment at 500 s\(^{-1}\) shows lower viscosity across the entire range of shear rates than hydrates formed at lower shear rates.

The shear-thinning behavior was fit to the four parameter Cross model (Cross, 1965) for viscosity as function of shear rate:

\[ \eta = \frac{\eta_0 - \eta_\infty}{1 + (C\dot{\gamma})^m} + \eta_\infty \]  

(5.1)

Where \(\eta_0\) is the viscosity at zero shear rate, \(\eta_\infty\) is the viscosity at infinite shear rate, \(1/C\) is the lower bound shear rate of the shear-thinning regime, and \(m\) is the slope of the shear-thinning regime. Table 5.3 summarizes the Cross fit parameters for 15 experiments. The parameters for the ice and hydrate experiments at 0.10 water volume fraction were fit to the power law model (Equation 5.2) rather than the Cross model as no zero-shear rate plateau was observed.

\[ \eta = m\dot{\gamma}^{n-1} \]  

(5.2)

where, \(\eta\) is viscosity, \(\dot{\gamma}\) is shear rate, \(m\) is the consistency, and \(n\) is the flow behavior index.

5.4.4 Dissociation

In the final step of each experiment, the microemulsion is heated back to 25 °C at a rate of 0.5 °C/minute and 100 s\(^{-1}\) shear rate. In each experiment, the viscosity monotonically decreased as temperature increased, eventually returning to the initial viscosity observed before hydrate formation. The current results are different from the increase in viscosity near the hydrate equilibrium temperature during dissociation observed with past work on water-in-crude oil emulsions (Webb et al., 2012a,b).

5.5 Discussion

In the initial increase in viscosity from hydrate formation (at \(~4.5\) hours in Figure 5.3), several physical changes contribute to the change in viscosity. First, hydrate formation consumes methane, which is the least viscous component in the liquid (Webb et al., 2012a). Second, the conversion of deformable liquid droplets to more rigid solid particles is known
Figure 5.11: Unless otherwise noted, $\phi_w = 0.3$, $P = 1500$ psig, $T = 0$ °C, and $\dot{\gamma} = 100$ s$^{-1}$. Points are measured data, solid green on the $\phi_w = 0.25$ data set in (a) is an example fit to the Cross model. Slurry viscosity versus shear rate for (a) hydrate slurries at varying water volume fraction, (b) ice slurries at varying water volume fraction, (c) hydrate slurries at varying initial pressure and temperature, and (d) hydrate slurries at varying formation shear rate. Error bars are 95% confidence intervals, $n = 4$. 
Table 5.3: Cross fit parameters for experiments in this study.

<table>
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<th>experimental conditions</th>
<th>Cross model parameters (Cross, 1965)</th>
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<td>P (psig)</td>
</tr>
<tr>
<td>0.2</td>
<td>1500</td>
</tr>
<tr>
<td>0.25</td>
<td>1500</td>
</tr>
<tr>
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<td>0</td>
</tr>
<tr>
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<td>0</td>
</tr>
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<table>
<thead>
<tr>
<th>experimental conditions</th>
<th>power law model parameters</th>
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<td>$\phi_w$</td>
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<td>1500</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
</tr>
</tbody>
</table>
to increase viscosity (Bird et al., 2002). Third and finally, particle aggregation may occur during hydrate formation. If particles aggregate, viscosity will increase, partly due to an increase in the effective volume fraction (Graham et al., 1984; Hasan & Shaw, 2010; Pal, 2011). Hydrate formation is confirmed by the pressure trace, which decreases about 20 psi at the same time as the viscosity increase (at about 4.5 hours in Figure 5.3). When hydrates form, the methane dissolved in the liquid phase is likely consumed due to its proximity to the water droplets. Methane consumption decreases the volume of the liquid phase, and thus decreases the pressure of the gas phase. Temperature should also increase upon hydrate formation since the process is exothermic (Sloan & Koh, 2008); however, the Peltier system removes the heat quickly and no temperature change is measured. Hydrate formation would produce at most $\sim 3$ W of power while the chiller has a cooling capacity of 350 W.

Two mechanisms can explain the observed decrease in pressure after the initial viscosity increase. First, any methane remaining in the liquid phase after the initial hydrate formation event may interact with unconverted water, and form hydrate. Hydrate formation decreases the volume of the liquid phase, and thus lowers the measured pressure. Second, methane from the gas phase can dissolve into the liquid. For a 0.30 water volume fraction emulsion, calculations using the first mechanism predict a pressure loss of 13 psi (see supporting information for details). The experiment at 0.30 water volume fraction (Figure 5.5) shows a pressure loss of 148 psi. So, the first mechanism, i.e., liquid volume contraction, is not sufficient to account for the experimentally observed pressure loss. Calculations using the first and second mechanisms predict a 172 psi pressure loss. This calculated pressure change assumes that all water converts to methane, and that the liquid phase becomes completely resaturated with methane. Since this calculation assumes the most extreme case, we expect it to slightly overestimate the 72 hour experiment. Overall, the experimental observations support the need for both mechanisms of methane transport.

A comparison to past work also supports this hypothesis. In past work on water-in-crude oil emulsions, the pressure did not change after the initial viscosity peak, but the
viscosity decreased monotonically (Webb et al., 2012a). Since the pressure was constant, neither significant additional hydrate formation, nor gas dissolution occurred. The difference between the pressure behaviors of crude oil based emulsions and the current dodecane based microemulsions could be explained by the difference in viscosity between crude oil and dodecane. At 100 s$^{-1}$ and 0 °C, West African crude oil viscosity is about 1 Pa·s (Rensing et al., 2011), while dodecane viscosity is about 0.002 Pa·s. Will methane diffuse on the timescale of the experiment, which is about 24 hours? The diffusivity of methane into dodecane could be estimated as $7.6 \times 10^{-9}$ m$^2$/s based on the work of Jamialahmadi and coworkers (Jamialahmadi et al., 2006). The distance from the gas-liquid interface in the rheometer to the bottom of the cell is about 50 mm. To estimate diffusion time (see Supporting Information for details), assuming one dimensional diffusion, it would take about 180 hours for the concentration to reach 99% of the saturation concentration at the bottom of the rheometer. After about 22 hours, the ratio of concentration to saturation concentration in the middle of the rheometer (i.e., 25 mm below the gas-liquid interface) is 0.5. There is no data for methane diffusivity in West African crude oil, but diffusivity is inversely related to viscosity (Wilke & Chang, 1955). Since West African crude oil has a viscosity 500 times greater than dodecane, we would expect methane to take about 11,000 hours to achieve 50% saturation 25 mm below the gas-liquid interface. Experiments last about 24 hours after initial hydrate formation, so, we expect to see a significant amount of methane diffuse into dodecane on the timescale of these experiments, but not in more viscous crude oils. When flow is introduced to the system, methane diffusion from the continuous phase liquid to a water droplet should increase. Methane diffusion from continuous phase liquid to a water droplet should be much faster in dodecane than in crude oil, by the same above arguments for methane diffusion from gas phase to bulk liquid.

Several forces could be competitively affecting viscosity. As mentioned earlier, methane depletion, conversion of emulsions to suspensions, and aggregation all work to increase viscosity. Viscosity could decrease due to aggregate break-up under flow, particle and aggregate
alignment under flow (shear alignment), and thinning of the continuous phase from methane dissolution. Also, capillary bridging could have a complicated effect on viscosity (Koos & Willenbacher, 2011; Zylyftari et al., 2013). As some water converts to hydrate, capillary bridging will occur, where water forms a capillary bridge between two hydrate particles. Capillary bridging will increase aggregation and the effective volume fraction, thus, viscosity will increase. However, as water continues to convert, the system will eventually run out of water for capillary bridging, and viscosity will decrease (i.e., the capillary bridges themselves are consumed to form hydrate) (Koos & Willenbacher, 2011; Zylyftari et al., 2013). Zylyftari et al. observed peak viscosity occurred between 61-85% water conversion to hydrate in cyclopentane hydrate slurries (Zylyftari et al., 2013).

In the initial viscosity peak, most of the limiting species in the liquid phase, either water or methane, are consumed to form hydrates. This initial consumption occurs in about 10 minutes (Figure 5.4). The experiments at 0.05 and 0.1 water volume fraction do not form enough hydrate to significantly affect the viscosity. The experiments at 0.2, 0.25, and 0.3 water volume fraction all have an initial viscosity peak around the same magnitude of 1.6 ± 0.2 Pa·s. After the initial viscosity peak, if unconverted water remains in the liquid phase, then water will continue to convert to hydrate as methane from the gas phase slowly dissolves into the liquid phase. Continued hydrate conversion can cause viscosity to increase for a time, but eventually, viscosity will decrease because the forces that work to decrease viscosity will dominate (i.e., weak capillary bridging, aggregate breakup, methane dissolving, and shear alignment).

Material balance calculations of the hydrate amount help elucidate the observed phenomena throughout each experiment (Figure 5.12). Based on the amount of methane measured in the mixing cell, either methane or water is the limiting species. Then, the assumption that the limiting species is fully consumed is applied. To determine the limiting species, we have to measure the amount of methane in the liquid phase at the start of each experiment. We measure the methane concentration in the liquid by placing some of the liquid in the mixing
cell, pressurizing with methane, and then measuring the change in pressure as methane dissolves under mixing (Table 5.4 and Supplementary Figure 1). If water is the limiting species for hydrate formation, then no additional hydrate forms after the initial viscosity spike ($\phi_w = 0.05$ and 0.10). If methane is the limiting species, then water will continue to convert to hydrate as methane dissolves from the gas phase into the liquid/slurry.

Figure 5.12: (a) amount of hydrate formed after initial formation event, (b) percent of water converted to hydrate after initial hydrate formation event.

Figure 5.12: (a) amount of hydrate formed after initial formation event, (b) percent of water converted to hydrate after initial hydrate formation event.
As water volume fraction increases, the amount of methane dissolved in the liquid phase decreases (Table 5.4); so, water is the limiting species at low water volume fractions, and methane is the limiting species at high water volume fractions. The transition from water limited to methane limited occurs between 0.10 and 0.20 water volume fraction (Table 5.4). The amount of hydrate that could form, if all of the limiting species was consumed, is very similar for 0.2, 0.25, and 0.3 water volume fractions (Figure 5.4). This similarity could explain why the initial peak viscosity for the three hydrate forming experiments at 0.2, 0.25, and 0.3 water volume fractions are so close (Figure 5.4). The behavior following the initial viscosity peak for these three experiments can be explained by the amount of unconverted water remaining (Table 5.4). At 0.2 water volume fraction (0.017 moles water remaining after initial peak), viscosity decreases immediately after the initial viscosity peak. At 0.25 water volume fraction (0.055 moles water remaining), viscosity decreases after about 5 hours. At 0.3 water volume fraction (0.083 moles water remaining), viscosity decreases after about 10 hours. The length of time after the initial spike until the viscosity decreases depends on the amount of unconverted water remaining.

Table 5.4: Fraction of water converted to hydrate based on measured initial mole fractions of methane and water in liquid phase. At full occupancy, sI hydrate contains 5.75 water molecules per 1 methane molecule.

<table>
<thead>
<tr>
<th>fluid</th>
<th>$x_{CH_4}$</th>
<th>$x_{H_2O}$</th>
<th>limiting species</th>
<th>% water converted</th>
</tr>
</thead>
<tbody>
<tr>
<td>dodecane</td>
<td>0.28</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$\phi_w = 0.05$</td>
<td>0.21</td>
<td>0.30</td>
<td>water</td>
<td>100</td>
</tr>
<tr>
<td>$\phi_w = 0.10$</td>
<td>0.16</td>
<td>0.49</td>
<td>water</td>
<td>100</td>
</tr>
<tr>
<td>$\phi_w = 0.20$</td>
<td>0.095</td>
<td>0.71</td>
<td>methane</td>
<td>83</td>
</tr>
<tr>
<td>$\phi_w = 0.25$</td>
<td>0.072</td>
<td>0.78</td>
<td>methane</td>
<td>56</td>
</tr>
<tr>
<td>$\phi_w = 0.30$</td>
<td>0.067</td>
<td>0.83</td>
<td>methane</td>
<td>49</td>
</tr>
<tr>
<td>$\phi_w = 0.30$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.6 Conclusions

A unique high pressure rheology apparatus is used to study the in situ formation and flow properties of gas hydrates formed from water-in-dodecane + AOT microemulsions.
AOT microemulsions solve many of the problems that plague experiments using crude oil. AOT microemulsions have high stability (order of months), well characterized composition, and very good reproducibility. High pressure rheology experiments on AOT microemulsions measured yield stress, flow curves, and transient viscosity as hydrates form, grow, aggregate, and dissociate. Viscosity increases rapidly upon hydrate formation, and then decreases. Viscosity continues to increase for a few hours if a large amount of unconverted water remains in the liquid phase after the initial hydrate formation event (e.g., 0.25 and 0.30 water volume fraction). Peak viscosity upon hydrate formation, zero shear rate viscosity, and yield stress all increase with increasing water volume fraction, increasing initial pressure, decreasing temperature, and decreasing shear rate. Overall, this study begins to elucidate the role of unconverted water on the rheology of hydrate slurries, which will likely be expanded upon in future studies.
CHAPTER 6
HYDRATE RHEOLOGY FROM WATER/70T MINERAL OIL/SPAN 80/AOT EMULSIONS

A version of this chapter has been prepared for publication under the title “High Pressure Rheology of Hydrate Slurries Formed From Water-in-Mineral Oil Emulsions.” The supporting information from this paper can be found in Appendix B.

6.1 Abstract

Structure I methane hydrates are formed in situ from water-in-mineral oil emulsions in a high pressure rheometer cell. Viscosity is measured as hydrates form, grow, change under flow, and dissolve. Experiments are performed at varying water volume fraction in the original emulsion (0-0.40), temperature (0-6 °C), and initial pressure of methane (750-1500 psig). Hydrate slurries exhibit a sharp increase in viscosity upon hydrate formation, followed by complex behavior following the initial increase dictated by a combination of factors including continued hydrate formation, shear alignment, methane depletion/dissolution, aggregate formation, and capillary bridging. Hydrate slurries possess a yield stress and are shear-thinning fluids, which are described by the Cross model. Hydrate slurry viscosity and yield stress increased with increasing water volume fraction. As driving force for hydrate formation decreases (increasing temperature, decreasing pressure), hydrate slurry viscosity increases, suggesting that slower hydrate formation leads to larger and more porous aggregates. In total, addition of water to a methane saturated oil can cause more than a fifty-fold increase in viscosity if hydrates form.

6.2 Introduction

In subsea oil and gas production, a variety of events can occur which hinder or fully stop flow in the pipeline (Sloan et al., 2011). Some of the problems that can occur in a
subsea pipeline include wax precipitation, scale formation, asphaltene precipitation, sand deposition, and hydrate formation. The study of these phenomena is called flow assurance. Of all these phenomena, hydrate formation occurs much more rapidly than the others (Sloan et al., 2011). Natural gas hydrates are solid crystal structures composed of water cages that form around small gas molecules (e.g., methane) (Sloan & Koh, 2008). The most common crystal structures formed are structure I (e.g., from methane, ethane, and carbon dioxide guests) and and structure II (e.g., from propane, hydrogen, and mixed gas guests). Structure I methane hydrate only forms at high pressures and low temperatures. For example, hydrate thermodynamic phase equilibria software CSMGem (Ballard & Sloan, 2002a,b, 2004a,b; Jager et al., 2003) predicts methane hydrate requires a pressure of 3.9 MPa at 4 °C.

In an oil pipeline, hydrate slurries often form from a water-in-oil emulsion under flow with a gas headspace. Oil pipeline operators need to know if hydrate formation will occur and to what extent flow in the pipeline will be impeded. The rheological properties (e.g., viscosity, yield stress) of hydrate slurries are important factors in determining the flowability of hydrate slurries. Due to the complexity of hydrate slurries in pipelines (e.g., emulsions which partially convert to aggregated suspensions), their rheological properties are not yet well understood.

Prior work on the rheological properties of hydrate slurries could be divided into two groups. First, several studies were performed using flowloops, pipes, or mixing cells (Andersson & Gundmundsson, 2000; Camargo et al., 2000; Clain et al., 2012; Darbouret et al., 2005b; Delahaye et al., 2008; Fidel-Dufour et al., 2006; Gainville et al., 2011; Jerbi et al., 2013; Ma et al., 2010; Peng et al., 2012; Sinquin et al., 2004). These studies have the advantage of nearly replicating hydrate slurry flow in subsea pipelines; however, as these devices are not true rheometers, they can only determine viscosity through correlations, such as calculating shear stress and shear rate at the wall from pressure drop and flow rate. These correlations reduce the accuracy of the measurement, and sometimes require significant assumptions. Other studies used rheometers; however, hydrates were formed from guest molecules that do
not exist in oil pipelines, such as cyclopentane or tetra butylammonium bromide (a semi-clathrate former), and thus the measured rheological properties may not be representative of those found in oil pipelines (Clain et al., 2012; Darbouret et al., 2005b; Delahaye et al., 2008; Ding et al., 2008; Hashimoto et al., 2011; Jerbi et al., 2013; Ma et al., 2010; Zylyftari et al., 2013). Most rheometers cannot operate at high pressure, and even when they do, rheometers are unable to generate enough mixing to dissolve gas, which may be necessary for significant hydrate formation.

This work uses an apparatus that saturates emulsions with methane in an external mixing cell, and then pumps the emulsion under pressure to a high pressure rheometer cell with concentric cylinders geometry provides a method to study hydrate rheology in detail (Webb et al., 2012a,b, 2013). Earlier work using this apparatus studied hydrate slurries and ice slurries formed from water-in-crude oil emulsions (Rensing et al., 2011; Webb et al., 2012a). Crude oil is difficult to study experimentally because it is extremely complex and difficult to use repeatably. Crude oil is not a single chemical, but rather a class of chemicals, each of which contains thousands of components. The components are so numerous that they cannot all be determined (Freitas et al., 2009). Also, the composition of oil changes over time as it is produced from a well; so, each batch of crude oil received from a well will be different. These concerns and others led us to study model emulsions rather than pipeline fluids.

6.3 Experimental Method and Setup
6.3.1 Emulsion Synthesis and Characterization

Emulsions are composed of deionized water, Crystal Plus tech grade 70T mineral oil (STE Oil Company), span 80 surfactant (Sigma-Aldrich), and dioctyl sodium sulfosuccinate (AOT) surfactant (Fisher scientific). Emulsion compositions and physical properties of the components are shown in Table 6.1. Emulsions are prepared by dissolving surfactants (span 80 and AOT) in mineral oil at 35 °C on a magnetically stirred hotplate at 350 rpm. Then, water is added dropwise and mixed at 8000 rpm in a Virtis Cyclone I.Q.² homogenizer for
three minutes. The volume fraction of water in each emulsion is denoted $\phi_w$. The average droplet size is 2-3 $\mu$m. No coalescence was visually observed in a bottle test after one week Delgado-Linares et al. (2013), and all experiments in this work are completed within one week of preparing each emulsion. Further details on the emulsions are discussed in the recent work by Delgado et al (Delgado-Linares et al., 2013).

Table 6.1: Emulsion composition and component physical properties

<table>
<thead>
<tr>
<th>Component</th>
<th>$\rho$ (g/mL)</th>
<th>MW (g/mol)</th>
<th>$\phi_w = 0.1$</th>
<th>$\phi_w = 0.2$</th>
<th>$\phi_w = 0.3$</th>
<th>$\phi_w = 0.4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1</td>
<td>18.0</td>
<td>10.0</td>
<td>20.0</td>
<td>30.0</td>
<td>40.0</td>
</tr>
<tr>
<td>mineral oil</td>
<td>0.856</td>
<td>313</td>
<td>73.3</td>
<td>64.7</td>
<td>56.0</td>
<td>47.4</td>
</tr>
<tr>
<td>span 80</td>
<td>0.986</td>
<td>429</td>
<td>3.94</td>
<td>4.01</td>
<td>4.08</td>
<td>4.14</td>
</tr>
<tr>
<td>AOT</td>
<td>1.1</td>
<td>445</td>
<td>0.44</td>
<td>0.45</td>
<td>0.45</td>
<td>0.46</td>
</tr>
</tbody>
</table>

6.3.2 High Pressure Rheometer Apparatus

In order to form hydrates in an emulsion, methane gas must be dissolved in the emulsion. Dissolving gas in the emulsion requires either high mixing or long time (tens of hours). The rheometer is unable to generate high mixing, and full saturation through diffusion takes too long; so, we dissolve gas in an external mixing cell, then pump the saturated emulsion through a syringe pump into the rheometer cell under pressure. Based on previous work in our laboratory (Webb et al., 2012a,b, 2013), Figure 6.1 shows a schematic of the apparatus. The mixing cell (Autoclave Engineers) has a volume of 302 mL and operates at pressures up to 4750 psig. A belt connected to an electric motor drives the impeller of the mixing cell at 170 rpm. The mixing cell is placed in an ethylene glycol-water cooling bath set to 10 °C (temperatures lower than 10 °C could result in hydrate formation during saturation). The mixing cell is connected to a Teledyne ISCO 500D model syringe pump. The pump can hold a maximum pressure of 3750 psig and a maximum volume of 500 mL.

During emulsion saturation, the mixing cell is connected to the syringe pump, but isolated from the rheometer pressure cell. To begin saturation, a synthesized emulsion is placed in the
mixing cell and then pressurized to the desired pressure with methane gas. Then, the syringe pump is set to hold at a constant set pressure by moving the piston (changing total system volume). After five minutes, the system is assumed to have reached thermal equilibrium, and the mixing cell motor is started. The system volume decreases until gas is fully dissolved into the liquid. The volume trace is used to calculate the amount of methane dissolved in the emulsion.

Following saturation, 10 mL of emulsion are pumped from the mixing cell to the rheometer pressure cell. The rheometer is a TA Instruments DHR-2 rheometer. A pressure cell in a Peltier heating/cooling jacket (both from TA Instruments) is mounted on the rheometer. The Peltier jacket has a temperature range from -25 to 150 °C, maximum heating/cooling rate of 2 °C/min, and ± 0.1 °C temperature precision. A refrigerated/heated circulating bath (VWR) with a water and ethylene glycol mixture supplies the jacket with cooling fluid. A cooled circulating fluid allows for the low temperature (-5 °C) operation of the rheometer cell for the multi-day duration of the hydrate experiments. The pressure cell consists of a steel outer cylinder and a titanium inner cylinder in a concentric cylinders (cup-and-bob) arrangement. The outer cylinder internal radius is 14.00 mm, while the inner cylinder radius
is 13.00 mm, giving the cell a 1.00 mm gap size. The cell is rated for operation up to 2000 psi. The inner cylinder assembly contains a steel cap, which screws into the outer cylinder, and a rotor assembly, which screws into the steel cap. Rotation is achieved through a 4-pole magnet attached to the rheometer spindle which couples with another magnet on the inner rotor assembly. Further information for this apparatus is published elsewhere (Webb et al., 2012b).

### 6.3.3 Experimental Procedure

Once an emulsion is pumped into the rheometer pressure cell, a series of rheological tests are performed. Whenever hydrates are formed, the same experimental procedure is used except at varying temperature, pressure, and emulsion water volume fraction (Table 6.2). Every experiment is performed at constant volume, i.e., nothing is added or subtracted from the system.

<table>
<thead>
<tr>
<th>Step</th>
<th>Duration</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>4-10 hours</td>
<td>Emulsion saturated with CH$_4$ at 1500 psig, 10 °C, and 170 rpm</td>
</tr>
<tr>
<td>Equilibration</td>
<td>10 minutes</td>
<td>25 °C</td>
</tr>
<tr>
<td>Cooling</td>
<td>50 minutes</td>
<td>Ramp temperature from 25 to 0 °C at 0.5 °C/minute, 100 s$^{-1}$</td>
</tr>
<tr>
<td>Hydrate Formation</td>
<td>24 hours</td>
<td>0 °C, 100 s$^{-1}$</td>
</tr>
<tr>
<td>Hardening</td>
<td>8 hours</td>
<td>0 °C, 2% oscillatory strain, 1 Hz frequency</td>
</tr>
<tr>
<td>Stress Ramp</td>
<td>0-3 hours</td>
<td>0 °C, ramp shear stress from 0 to 3000 Pa at 1000 Pa/hr</td>
</tr>
<tr>
<td>Conditioning</td>
<td>30 minutes</td>
<td>0 °C, 500 s$^{-1}$</td>
</tr>
<tr>
<td>Flow Curve</td>
<td>~1 hour</td>
<td>0 °C, ramp shear rate from 500 to 1 to 500 s$^{-1}$, steady state measurements: 3 s sample period, 3% tolerance, 3 consecutive within tolerance, 2 minute maximum point time</td>
</tr>
<tr>
<td>Dissociation</td>
<td>50 minutes</td>
<td>Ramp temperature from 0 to 25 °C at 0.5 °C/minute, 100 s$^{-1}$</td>
</tr>
</tbody>
</table>
6.4 Results and Discussion

This study seeks to understand the rheological properties of a hydrate slurry formed from a gas saturated emulsion. A hydrate slurry could contain water, continuous phase oil, surfactants, dissolved gas, and hydrate particles. In order to make informed observations on complex hydrate slurries, we first characterized simpler systems composed of one or more constituents of hydrate slurries. To begin, the viscosity of pure mineral oil was measured at varying shear rates and temperatures (Figure 6.2). Mineral oil viscosity increased with decreasing temperature and was Newtonian (i.e., did not depend on shear rate) in the range of shear rates measured. Mineral oil viscosity follow the well known Arrhenius relationship:

$$\eta = Ae^{Ea/RT}$$  \hspace{1cm} (6.1)

Where \( \eta \) is viscosity, R is the gas constant, T is absolute temperature, and A and \( E_a \) are fitted parameters.

Next, one degree of complexity was added by introducing methane gas to mineral oil. Mineral oil was saturated with methane gas in the pressure cell, and then pumped into the rheometer cell where viscosity was measured in a flow sweep from 500 to 1 s\(^{-1}\) (Figure 6.3). Viscosity decreased drastically as saturation pressure (and thus methane amount) increased.

![Figure 6.2: Arrhenius fits to emulsion viscosity at varying water volume fraction and temperature. Each data point is taken at 100 \( -1 \) from the flow curve for each fluid.](image-url)
Viscosity at 1500 psig methane is almost an order of magnitude lower than methane free mineral oil. Large sections of each flow curve gave torque values below the instrument limit; therefore, only the data point at the highest shear rate (500 s\(^{-1}\)) is shown.

Figure 6.3: Viscosity of 70T mineral oil with varying amount of dissolved methane gas. Measurements performed in rheometer pressure cell.

Next, emulsions (without dissolved gas) were characterized over a range of shear rates (0.1-1000 s\(^{-1}\)), water volume fractions (0-0.50), and temperatures (0-25 °C). Emulsion viscosity increased with temperature and showed shear thinning behavior (Figure 6.4). Emulsions showed shear thinning behavior at 0.20 water volume fraction and above (Figure 6.5). The degree of shear thinning increased with water volume fraction. All flow curves show an anomalous raised viscosity from about 30-300 s\(^{-1}\) at 25 °C only. The bump is observed when surfactants are present without water, so the surfactants must be forming some temperature activated structure between 20 and 25 °C. Omitting the 25 °C flow curves, the emulsions follow an Arrhenius temperature relationship (Figure 6.2, parameters in Table 6.3). The full set of flow curves are shown in the Supporting Information.

The last two systems to examine are saturated emulsions and hydrate suspensions. Since hydrate suspensions are formed from methane saturated emulsions, both of these systems were studied simultaneously. Experiments on these systems follow the procedure given in
Figure 6.4: Steady state viscosity of a 0.30 water volume fraction emulsion at varying shear rate and temperature.

Figure 6.5: Steady state emulsion viscosity at 0 °C and varying shear rate and water volume fraction.
Table 6.3: Fitted Arrhenius parameters for each fluid used in this study

<table>
<thead>
<tr>
<th>fluid</th>
<th>$E_a$ (J/mol)</th>
<th>$A$ (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70T mineral oil</td>
<td>$3.6 \times 10^4$</td>
<td>$1.15 \times 10^{-8}$</td>
</tr>
<tr>
<td>70T mineral oil + AOT + span 80</td>
<td>$3.2 \times 10^4$</td>
<td>$4.89 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\phi_w = 0.05$ emulsion</td>
<td>$3.2 \times 10^4$</td>
<td>$6.14 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\phi_w = 0.10$ emulsion</td>
<td>$3.2 \times 10^4$</td>
<td>$7.29 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\phi_w = 0.20$ emulsion</td>
<td>$3.3 \times 10^4$</td>
<td>$7.79 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\phi_w = 0.30$ emulsion</td>
<td>$3.1 \times 10^4$</td>
<td>$2.39 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\phi_w = 0.40$ emulsion</td>
<td>$2.9 \times 10^4$</td>
<td>$6.87 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\phi_w = 0.50$ emulsion</td>
<td>$2.7 \times 10^4$</td>
<td>$2.65 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Table 6.2. Experiments were performed at varying water volume fraction (0, 0.05, 0.10, 0.20, 0.30, 0.40, and 0.50), temperature (0, 2, 4, and 6 °C), and pressure (750, 1000, 1250, and 1500 initial pressure methane). Many of the same qualitative features are observed in all or most of these experiments; so, the results of one experiment are presented first as an example. The conditions of this experiment are 0.30 water volume fraction, 0 °C, and 1500 initial pressure methane.

During the cooling step, the pressure decreases and the viscosity increases in response to the temperature change (Figure 6.6). The pressure and viscosity shifts are only a reflection of the temperature change, not an indication of hydrate formation. After the cooling step, the system conditions are such that hydrate formation is thermodynamically favorable; however, hydrate formation does not occur for some time because nucleation of hydrate crystals in the emulsion is a random event. Hydrate formation is detected by a large increase in the viscosity coupled with a sharp decrease in pressure measured in the gas headspace (Figure 6.6).

At least three factors contribute to the initial viscosity increase during hydrate formation. First, liquid water drops are converted to solid hydrate particles. Viscosity of rigid particles is expected to be higher than deformable liquid droplets (Bird et al., 2002; Camargo et al., 2000). Second, methane is removed from the external oil phase. Since methane is the lightest component in the oil phase, methane depletion will cause an increase in the continuous
phase viscosity (Webb et al., 2012b). Third, prior to hydrate formation, liquid droplets are stabilized by surfactant molecules. When water converts to hydrate, the surface chemistry of the suspended particle changes, allowing particles to collide with one another, creating aggregates. Aggregated systems exhibit higher viscosity than non-aggregated systems (Graham et al., 1984; Hasan & Shaw, 2010; Pal, 2011). Changes in pressure can be explained by two possible phenomena. First, since the system is at a constant volume, any change to the liquid volume will also change the gas phase volume, and thus the pressure. Second, methane molecules can diffuse from the gas phase to the liquid, decreasing the moles of methane in the gas phase, and thus decreasing the pressure. During hydrate formation, the liquid volume decreases, and thus pressure decreases. The initial hydrate formation event occurs over about 10 minutes. This timescale is too short to expect significant pressure change from the second mechanism, methane diffusion from gas to liquid.

The initial viscosity spike ends when either all methane or all water is converted to hydrate in the liquid phase; whichever is limiting. In the example experiment, methane is the limiting reactant. So, at the end of the initial viscosity increase, the liquid phase contains continuous phase oil, hydrate, and unconverted water, but no methane.

After the initial increase in viscosity, each experiment shows different behavior depending on the temperature, pressure, and water volume fraction of the emulsion. Many experiments show a rapid decrease in viscosity immediately following the initial increase in viscosity (Figure 6.6). This could be explained by the alignment of newly formed aggregates under flow (Quemada, 1978). After this decrease, some experiments continue to show decreasing viscosity, while others show increasing viscosity. In the example experiment (Figure 6.6), methane from the gas phase slowly diffuses back into the liquid (at a rate of about 5 psi/hour), causing pressure and viscosity to slowly decrease. However, once dissolved, methane is enclathrated with the remaining water to form hydrate, which increases viscosity. Once all water has been converted to hydrate, viscosity will no longer increase. Rather, viscosity and pressure will decrease because gas continues to dissolve back into the liquid (Figure
Figure 6.6: pressure, temperature, and viscosity evolution of a methane saturated water-in-mineral oil emulsion with 0.30 water volume fraction over time at $\dot{\gamma} = 100 \text{ s}^{-1}$. 
6.6 from 7-25 hours). Finally, one further phenomenon confuses the analysis even more. When both water and hydrate are present, water can form capillary bridges between hydrate particles. These capillary bridges hold aggregates together, which increases viscosity (Koos & Willenbacher, 2011). So, when all of the water is eventually converted to hydrate, no more water exists for capillary bridging, and viscosity is actually expected to decrease. Recent work by Zylyftari et al. (Zylyftari et al., 2013) indicates maximum viscosity is expected to occur when between 60-80% of water is converted to hydrate.

After transient hydrate formation (constant shear rate and temperature), the hydrate slurry is held under no shear conditions for eight hours at the experimental temperature (usually 0 °C). During this step, hydrate particles may harden. Previous work with water-in-crude oil emulsions showed no change in measured yield stress for slurries hardened for eight hours compared to longer than eight hours (Webb et al., 2012a). Following the hardening step, hydrate slurry yield stress is measured by ramping shear stress from 0 to 3000 Pa on a log scale over three hours. The yield stress is measured at the point the shear rate begins to increase. The yield stress for the example experiment is 19 Pa (Figure 6.7).

Figure 6.7: Stress ramp used to determine hydrate slurry yield stress. 0.30 water volume fraction water-in-mineral oil emulsion at 0 °C after 8 hour hardening step.
Next, the hydrate slurry is sheared at 500 s$^{-1}$ for 30 minutes to homogenize structures formed from the hardening step (Figure 6.8). Then, the shear rate is ramped from 500 to 1 to 500 s$^{-1}$. In every experiment, hydrate slurries were found to be shear-thinning, including the experiment shown in Figure 6.8. Most experiments show an s-shaped curve with a zero shear plateau (the viscosity approaches a constant value, $\eta_0$ as shear rate approaches zero), a shear-thinning regime, and a high shear plateau (the viscosity approaches a constant value, $\eta_\infty$ as the shear rate approaches infinity). S-shaped curves are fit the four-parameter Cross model (Cross, 1965):

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (C\dot{\gamma})^m} + \eta_\infty$$  \hspace{1cm} (6.2)

Where $\eta_0$ is the viscosity at zero shear rate, $\eta_\infty$ is the viscosity at infinite shear rate, $1/C$ is the lower bound shear rate of the shear-thinning regime, and $m$ is the slope of the shear-thinning regime. In all cases, the data is expected to follow an s-shaped pattern; however, some experiments could only obtain steady-state values in the shear-thinning regime. These data sets are fit to the two parameter power law model:

$$\eta = m\dot{\gamma}^{n-1}$$  \hspace{1cm} (6.3)

Where, $\eta$ is viscosity, $\dot{\gamma}$ is shear rate, $m$ is the consistency, and $n$ is the flow behavior index.

Finally, the hydrate slurry is heated back to 25 °C at 0.5 °C/minute and 100 s$^{-1}$ shear rate (Figure 6.9). As the slurry warms, the viscosity decreases; however, there is a viscosity increase near 12 °C. The measured pressure at 12 °C was 1274 psig. The methane hydrate equilibrium temperature at 1274 psig is predicted to be 11.9 °C by CSMGem (Colorado School of Mines Gibbs Energy Minimization) (Ballard & Sloan, 2002a,b, 2004a,b; Jager et al., 2003). Previous research shows that as temperature increases, a water layer on the surface of hydrate particles grows thicker, allowing stronger adhesion forces between hydrate particles, thus increasing viscosity (Dieker et al., 2009). Past the hydrate equilibrium temperature, the hydrate particles fully melt, and the viscosity returns to a lower value (Figure 6.9). In the remaining experiments, viscosity shows similar qualitative behavior, with viscosity shifting
to higher values as increasing water volume fraction, and the anomalous viscosity increase occurring at lower temperatures as driving force decreases.

Experiments were performed at five different water-in-mineral oil emulsion compositions: 0.1, 0.2, 0.3, 0.4, and 0.5 water volume fraction. The experiment at 0.5 water volume fraction could not be performed because the emulsion could not be pumped from the mixing cell to the pressure cell. The viscosity increased as water volume fraction increased in every stage of the experiment (Figures 6.10 and 6.11). The fraction of water converted to hydrate is denoted $\chi$, and was calculated during transient hydrate formation (Figure 6.10). The calculations are based only on the pressure trace, not viscosity. The calculation scheme for $\chi$ is further explained in the supporting information. At both 0.10 and 0.20 water volume fraction, there is sufficient methane dissolved in the liquid at the beginning of the experiment to convert all water to hydrate. So, all water is converted during the initial increase in viscosity, or shortly thereafter (Figure 6.10). Note the smooth decrease in pressure observed at 0.10 and 0.20 water volume fraction compared to the pressure decreases for 0.30 and 0.40. At 0.30 and 0.40,
there seems to be two distinct regions of pressure change; an initial region of fast pressure loss (~20 psi/hour) followed by a slower region (~2 psi/hour), similar to those observed at 0.10 and 0.20 water volume fraction. At 0.30 and 0.40 water volume fraction, the amount of methane initially dissolved in the liquid phase is not sufficient to convert all water to hydrate. So, partial conversion of water to hydrate occurs during the initial viscosity increase ($\chi = 0.68$ for 0.30 water volume fraction and $\chi = 0.42$ for 0.40 water volume fraction). After the initial viscosity increase, methane begins to dissolve back into the liquid from the gas phase, where it becomes enclathrated with the remaining unconverted water. So, the 0.30 and 0.40 water volume fraction experiments show a second increase in viscosity as water continues to convert. Note that the maximum in viscosity value for each experiment occurred at less than $\chi = 1$; that is, less than 100% conversion of water to hydrate (Figure 6.10). Capillary bridges formed by water between hydrate particles may help increase viscosity; so, at high $\chi$, capillary bridges are depleted, causing viscosity to decrease.
Figure 6.10: Pressure, fraction of water converted to hydrate ($\chi$), and viscosity over time as hydrates form in water-in-mineral oil emulsions at $0 \degree C$, 1500 psig initial pressure of methane, and $100 \text{ s}^{-1}$. 
Yield stress increased as water volume fraction increased (Table 6.4). As a general rule, the trend in yield stress for as set of experiments was the same as the trend in viscosity.

Table 6.4: Hydrate slurry yield stress

<table>
<thead>
<tr>
<th>$\phi_w$</th>
<th>T (°C)</th>
<th>$P_o$ (psig)</th>
<th>$\tau_o$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0</td>
<td>1500</td>
<td>3</td>
</tr>
<tr>
<td>0.2</td>
<td>0</td>
<td>1500</td>
<td>11</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
<td>1500</td>
<td>18</td>
</tr>
<tr>
<td>0.4</td>
<td>0</td>
<td>1500</td>
<td>21</td>
</tr>
<tr>
<td>0.3</td>
<td>2</td>
<td>1500</td>
<td>43</td>
</tr>
<tr>
<td>0.3</td>
<td>4</td>
<td>1500</td>
<td>110</td>
</tr>
<tr>
<td>0.3</td>
<td>6</td>
<td>1500</td>
<td>30</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
<td>750</td>
<td>380</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
<td>1000</td>
<td>75</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
<td>1250</td>
<td>65</td>
</tr>
</tbody>
</table>

Hydrate slurries were shear-thinning at each water volume fraction (Figure 6.11. Steady state hydrate slurry viscosity increased with increasing water volume fraction, the same trend as the transient viscosity. The steady state viscosity typically follows the same trend as the transient viscosity for varying water volume fraction, temperature, or pressure. The Cross model and power law parameters for each experiment are shown in Table 6.5.

Table 6.5: Cross and power law model fit parameters for experiments in this study.

<table>
<thead>
<tr>
<th>experimental conditions</th>
<th>Cross model parameters</th>
<th>Cross (1965)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_w$</td>
<td>P</td>
<td>T</td>
</tr>
<tr>
<td>psig</td>
<td>°C</td>
<td>Pa-s</td>
</tr>
<tr>
<td>0.10</td>
<td>1500</td>
<td>0</td>
</tr>
<tr>
<td>0.20</td>
<td>1500</td>
<td>0</td>
</tr>
<tr>
<td>0.30</td>
<td>1500</td>
<td>0</td>
</tr>
<tr>
<td>0.40</td>
<td>1500</td>
<td>0</td>
</tr>
<tr>
<td>0.30</td>
<td>1500</td>
<td>2</td>
</tr>
<tr>
<td>0.30</td>
<td>1500</td>
<td>4</td>
</tr>
<tr>
<td>0.30</td>
<td>1500</td>
<td>6</td>
</tr>
<tr>
<td>0.30</td>
<td>750</td>
<td>0</td>
</tr>
<tr>
<td>0.30</td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>0.30</td>
<td>1250</td>
<td>0</td>
</tr>
</tbody>
</table>
Four experiments were performed on 0.30 water volume fraction emulsions at 1500 initial pressure of methane and 0, 2, 4, and 6 °C. At higher temperatures, the driving force for hydrate formation is lower. We expected higher temperatures would cause lower viscosity because the driving force for hydrate formation is lower; however, the results did not follow our intuition. Viscosity was observed to increase as temperature increased (Figures 6.12 and 6.13), i.e., as driving force decreased. Work on crystallization of supercooled liquids indicates crystal growth rate is inversely related to liquid viscosity (Ediger et al., 2008). Also, much hydrate research shows that growth rate increases as driving force increases (Englezos et al., 1987; Freer et al., 2001; Peng et al., 2007; Vysniauskas & Bishnoi, 1983). It follows that we should expect viscosity to increase as driving force for hydrate formation decreases. This result has strong implications for the oil industry, as it suggests that the worst case scenario for hydrate formation in pipelines may occur under mild conditions.

Shortly after hydrate formation, at three hours after initial hydrate formation, viscosity shows an inverse trend with temperature; the 0 °C experiment shows the highest viscosity,
followed by the 2, 4, and 6 °C experiments (Figure 6.12). Increasing temperature decreases hydrate formation rate; so, at short times after initial formation, experiments at low temperature may have more hydrate formed (and thus higher viscosity) than experiments at higher temperatures. Later, after all water has converted to hydrate, each experiment should have the same amount of hydrate; but, the morphology of the hydrate aggregates may differ significantly because they were formed at different rates. At 15 hours after initial hydrate formation, the viscosity trend is opposite of that observed at three hours (Figure 6.12). The highest viscosity occurs at 6 °C and the lowest viscosity at 0 °C.

At 17 hours after formation, the experiment at 6 °C undergoes a strong decrease in pressure and viscosity (Figure 6.12). It is possible that hydrate may have initially only formed at the gas-liquid interface. The hydrate film that forms at the interface could block gas from diffusing to the liquid, hence the small pressure decrease before 17 hours compared to the other three experiments. At 17 hours, the film may have broken, causing a rapid decrease in viscosity and allowing gas to dissolve into the liquid.

The flow curves show increasing viscosity with decreasing driving force; the same trend observed in the transient step after full conversion of water to hydrate (Figure 6.13). The 6 °C experiment is an exception to the trend. The data at 6 °C could be skewed because of the event that occurred at 17 hours during the transient step.

Four experiments were performed on 0.30 water volume fraction emulsions at 0 °C and 750, 1000, 1250, and 1500 psig initial pressure methane gas. Each emulsion was saturated at the same experimental pressure in the mixing cell prior to the start of each experiment. Much like the experiments at varying temperature, viscosity was typically found to increase with decreasing pressure, i.e., decreasing driving force (Figure 6.14). Again, decreasing driving force causes decreasing hydrate formation rate (Englezos et al., 1987; Freer et al., 2001; Peng et al., 2007; Vysniauskas & Bishnoi, 1983), which causes higher viscosity (Ediger et al., 2008). Shortly following initial hydrate formation, around three hours, the measured viscosity decreased in the order 1500 > 1250 > 1000 > 750 psig for the four varying pressure
Figure 6.12: Pressure, fraction of water converted to hydrate ($\chi$), and viscosity over time as hydrates form in 0.30 water volume fraction water-in-mineral oil emulsions at 500 psig initial pressure of methane and 100 s$^{-1}$. 

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Figure 6.13: Steady state viscosity of hydrate slurries formed from 0.30 water volume fraction water-in-mineral oil emulsions at 1500 psig initial pressure of methane. Symbols represent data from 500 to 1 s\(^{-1}\), lines are model fits to the data.

experiments. At 15 hours after initial hydrate formation, the viscosity decreased in the order 750 > 1000 > 1250 > 1500 psig; opposite the trend at three hours. At short times (before 100% conversion of water to hydrate), the driving force is directly proportional to viscosity because the higher driving force experiments contain more hydrate. At long times (after 100% conversion of water to hydrate), the viscosity is inversely related to driving force because each experiment contains the same amount of hydrate, but the lower driving force experiments have larger aggregates.

The flow curves (Figure 6.15) show the same trend as the transient data at long times: viscosity increases with decreasing pressure (decreasing driving force).

In this study, six systems types of systems were characterized: (1) pure 70T mineral oil, (2) mineral oil with AOT and span 80 surfactants, (3) mineral oil saturated with methane gas, (4) emulsions (water + mineral oil + surfactants) at varying water volume fraction, (5) emulsions saturated with methane gas, and (6) hydrate slurries (water, mineral oil, surfactants, methane, sI hydrate) (Figure 6.16). All six systems are shown in the leftmost part of
Figure 6.14: Pressure, fraction of water converted to hydrate ($\chi$), and viscosity over time as hydrates form in 0.30 water volume fraction water-in-mineral oil emulsions at 0 °C and 100 s$^{-1}$. 
Figure 6.15: Steady state viscosity of hydrate slurries formed from 0.30 water volume fraction water-in-mineral oil emulsions at 0 °C. Symbols are data from 500 to 1 s\(^{-1}\), lines are model fits to the data.

the figure for comparison. The difference in mineral oil viscosity with an without surfactants is very small compared to any of the other systems. Addition of methane to pure mineral oil can decrease the viscosity by more than an order of magnitude. Emulsion viscosity is always larger than pure mineral oil viscosity, and saturated emulsion viscosity is larger than saturated mineral oil; so, the addition of an internal phase to a pure liquid increases the viscosity. Hydrate viscosity is always larger than the one point for saturated emulsions, so hydrate aggregates always have larger viscosity than water droplets. Hydrate slurries sometimes but not always have higher viscosity than emulsions. The methane in hydrate slurries decreases viscosity below the emulsion value, but the hydrate particles increase viscosity above the emulsion value. Hydrate slurries are more strongly shear-thinning than emulsions, so usually hydrate slurries have a higher viscosity at low shear rates while emulsions have a higher viscosity at high shear rates.

In an oil pipeline, flow begins with a saturated oil phase, analogous to system 3. During oil production, water is inevitably produced with oil with the amount of water increasing
Figure 6.16: Steady state viscosity at varying shear rate across six different systems and varying water volume fractions. All experiments at 0 °C and 1500 psig methane initially. Circles - methane saturated emulsion, diamonds - emulsion (no methane), upward pointing triangles - hydrate slurries.

over the lifetime of the field, which leads to a saturated oil-in-water emulsion, system 5. Finally, hydrates may form (system 6). Viscosity of these systems increases in the order saturated mineral oil < saturated emulsion < hydrate slurry (Figure 6.16). At 0.40 water volume fraction, at 100 s⁻¹, saturated mineral viscosity is 0.008 Pa·s, saturated emulsion viscosity is 0.091 Pa·s, and hydrate slurry viscosity is 0.479 Pa·s. So, introduction of water to saturated oil can increase viscosity by over an order of magnitude. Hydrate formation from a saturated emulsion causes another about five-fold increase in viscosity.

6.5 Conclusions

Structure I methane hydrate was formed from methane saturated water-in-mineral oil emulsions with AOT and span 80 surfactants. At full conversion of water to hydrate, hydrate slurry viscosity and yield stress increased with increasing water volume fraction, increasing temperature, and decreasing pressure. A scheme was devised to calculate the fraction of water converted to hydrate (χ) based primarily on the pressure evolution with time during hydrate formation. The evolution of viscosity was neither monotonically increasing nor decreasing with χ; indicating a complex interplay of factors affecting viscosity, including
hydrate formation, aggregation, methane depletion and dissolution, and capillary bridging. Steady state viscosity was found to increase with decreasing driving force because hydrates aggregates at lower driving forces likely are larger even though the amount of hydrate is comparable to higher driving forces. Hydrate slurry viscosity was about one order of magnitude larger than saturated emulsion viscosity, which was about five times larger than saturated oil viscosity. So, the introduction of water to a pipeline can cause a fifty-fold increase in viscosity.
CHAPTER 7
COMPARISON OF HYDRATE SLURRIES ACROSS THREE DIFFERENT SYSTEMS

Hydrate slurries formed from three separate types of water-in-oil emulsions have been investigated in the present work: water/West African crude oil (w/WAC), water/dodecane/AOT (w/C12), and water/70T mineral oil/span 80/AOT (w/70T). These investigations were performed with essentially the same apparatus and experimental procedure; so, a comparison of similar experiments across different types of water-in-oil emulsions should reveal effects of initial emulsion composition. In the first part of this chapter, the experimental results of the three investigations reported in this thesis are compared. In the second part, several mechanisms that potentially contribute to changes in pressure and viscosity are identified and discussed. Some other work comparing hydrate rheology across different systems is included in Appendix E. Appendix E includes a comparison of hydrate rheology measurements in literature and our attempts to model hydrate slurry viscosity.

7.1 A Comparison of Three Investigations Performed at CSM

Over time, both the apparatus and procedure for hydrate forming experiments was modified. The modifications allowed better measurements; however, it is important to understand a few differences in the measurements performed in each investigation. The important differences are as follows:

1. Some of the experiments on water/West African crude oil emulsions (the four experiments at varying water volume fraction) were performed at 2000 psig methane. All other experiments shown here were performed at 1500 psig methane.

2. The same four water/West African crude oil experiments had an annealing time of 2 hours, rather than 8 hours used elsewhere.
3. Water/West African crude oil emulsions were saturated by connecting the mixing cell to an open methane gas cylinder regulated to 1500 psig. So, saturation was performed at constant pressure; however, the amount of gas dissolved was not measured. One experiment was performed at constant volume, and the pressure change was measured. The amount of gas dissolved in this experiment is used for all calculations of any experiment with water/West African crude oil emulsions.

4. Water/dodecane/AOT emulsions were saturated at constant volume (closed system, measure pressure change). Water/70T mineral oil/span 80/AOT emulsions were saturated at constant pressure (Isco pump adjusts volume to maintain set pressure). Also water/70T mineral oil/span 80/AOT emulsions were saturated in a temperature controlled mixing cell, set to 10 °C; prior experiments had no temperature control.

The relationship between viscosity and hydrate amount in a pipeline could be valuable for flow assurance engineers. Viscosity is directly measured through the process of hydrate formation and growth; however, hydrate amount is not directly measured. Instead, the pressure over time in the gas phase headspace is used to calculate hydrate amount. Coupled with a knowledge of the initial gas and liquid compositions, volumes, and temperature, the hydrate amount can be determined. In what follows, we report the fraction of water (by volume) which has been converted to hydrate, denoted $\chi$. Appendix B contains a full explanation of how $\chi$ is determined.

Before examining hydrate rheology measurements, note the differences in continuous phase viscosity between the three emulsions (Table 7.1). The most viscous fluid, West African crude oil, is about 200 times more viscous than the thinnest fluid, dodecane. Despite the large range of continuous phase viscosities, the measured hydrate slurry viscosities are all of the same order of magnitude across the three different emulsions (Figure 7.1). In fact, the hydrate viscosity from the dodecane-based emulsion is the highest at 0.30 water volume fraction even though dodecane is the least viscous continuous phase. The continuous phase
viscosity does not have a simple, monotonic affect on hydrate slurry viscosity in these three investigations.

Table 7.1: Viscosity of each external phase investigated. Measurements at 100 s\(^{-1}\), 0 °C, and ambient pressure.

<table>
<thead>
<tr>
<th>fluid</th>
<th>viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>West African crude oil</td>
<td>0.51</td>
</tr>
<tr>
<td>dodecane</td>
<td>0.0026</td>
</tr>
<tr>
<td>70T mineral oil</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Hydrate slurry viscosity increases with increasing water volume fraction in all three systems (Figure 7.1). In Figure 7.1, we show one representative set of measurements at each set of conditions (\(\phi_w\), T, P, \(\dot{\gamma}\)). Also, hydrate formation begins with sharp rise in viscosity that occurs over a short time. In w/WAC experiments, the time of the initial viscosity spike was on the order of tens of minutes. In w/C12 and w/70T experiments, the initial viscosity increase was on the order of minutes. Water droplets which convert to hydrate may be more mobile in the lower viscosity emulsions (w/C12 and w/70T), which would lead to more rapid consumption of water and dissolved methane compared to the thicker w/WAC emulsions.

A sharp decrease in pressure coincides with each sharp increase in viscosity. Pressure decrease could come from either diffusion of methane gas from the gas phase to the liquid phase (i.e., loss of moles), or a decrease in the liquid volume from hydrate formation, causing an expansion of volume in the gas phase. Diffusion is a slow process that could not account for more than a 1 psi pressure change in 10 minutes. So, the change in pressure during the initial viscosity increase can be almost entirely attributed to changing volume in the liquid phase due to hydrate formation.

We hypothesize that hydrate formation proceeds very rapidly (<1 hour) until either all methane or all water is consumed. If all methane is consumed, then additional methane can diffuse from the gas phase to the liquid phase, where it can be consumed to form hydrate.
Figure 7.1: Pressure change, fraction of water volume converted to hydrate, and viscosity evolution beginning at the initial hydrate formation event at varying water volume fraction. Hydrate formation from w/WAC, w/C12, w/70T emulsions. 0 °C, 100 s⁻¹, and 1500 psig initial pressure methane except w/WAC emulsions at 2000 psig methane.
After the initial viscosity increase, the behavior of viscosity and pressure vary depending on the emulsion and water volume fraction. w/WAC emulsions have the highest viscosity continuous phase, and methane diffusion is inversely related to liquid viscosity, so we expect the slowest methane diffusion in the w/WAC system. We observe very little pressure change after the initial viscosity increase and no further viscosity increase. The \( \chi \) parameters also suggest that very little hydrate formation proceeds following the initial viscosity increase. w/C12 and w/70T emulsions show a second viscosity increase at higher water volume fractions (above 0.20). The lower water volume fractions (0.20 and lower) show monotonically decreasing viscosity after the initial viscosity increase.

Hydrate formation consumes about six moles of water for every one mole of methane (Sloan & Koh, 2008). As water volume fraction increases, the amount of water available for hydrate formation increases; however, the amount of dissolved methane decreases because the continuous phase volume decreases. Methane has very low solubility in water, so dissolved methane mainly exists in the oil continuous phase (A PT flash calculation using Multiflash 4.1 at 0 °C and 1500 psig for 0.30 water volume fraction water/dodecane/AOT emulsion determined that 99.99994% of dissolved methane by mole was in the oil phase). At lower water volume fractions (0.20 or less), water is limiting (i.e., water moles/dissolved methane moles < 6); so, hydrate formation stops after the initial viscosity increase. At higher water volume fractions (above 0.20), methane is limiting, so hydrate formation can continue, limited by the rate of methane diffusion from the gas phase.

The peak viscosity in each experiment occurs at less than 100% conversion of water to hydrate (Figure 7.2). The \( \chi \) values at each viscosity are determined from the measurements reported in Figure 7.1. Capillary bridging may have the strongest effect at less than \( \chi = 1 \). Peak viscosity occurred between \( \chi = 0.40 \) and 0.70. The location of peak viscosity does not seem to depend on water volume fraction.

Steady-state viscosity measurements show that hydrate slurries from all emulsions at all water volume fractions are shear-thinning (Figure 7.3). Also, viscosity increases as water
Figure 7.2: Hydrate viscosity from w/70T emulsions versus fraction of water volume converted to hydrate at varying water volume fraction.
volume fraction increases. w/WAC and w/70T hydrate slurries showed less dependence on water volume fraction compared to w/C12 hydrate slurries. Many experiments exhibit low shear and high shear plateaus, which is common among shear-thinning fluids.

![Viscosity vs. Shear Rate](image)

Figure 7.3: Steady state hydrate slurry viscosity versus shear rate at varying water volume fraction in (a) w/WAC, (b) w/C12, and (c) w/70T emulsions at 0 °C. The numbers in parentheses in the legend indicate the number of repeated measurements. When the number of repeats is more than two, error bars were determined as 95% confidence intervals.

During hydrate dissociation, most experiments showed a viscosity increase or shoulder near the hydrate equilibrium temperature (Figure 7.4). Generally, higher water cut experiments showed stronger viscosity increases near the equilibrium temperature.
Figure 7.4: Hydrate slurry viscosity as temperature increases during hydrate dissociation in (a) w/WAC, (b) w/C12, and (c) w/70T emulsions at varying water volume fraction. Hydrate slurries formed at 0 °C, 100 s⁻¹, and 1500 psig initial pressure methane except w/WAC emulsions at 2000 psig methane.
In all three investigations, at least two experiments were performed at different temperatures (Figure 7.5). In w/WAC and w/70T experiments, viscosity increased with increasing temperature. As temperature increases, hydrate crystal growth rate decreases (Englezos et al., 1987; Freer et al., 2001; Peng et al., 2007; Vysniauskas & Bishnoi, 1983), which could cause formation of larger aggregates and thus higher viscosity (Ediger et al., 2008). In contrast, viscosity increases as temperature increases in the w/C12 experiments. Several phenomena may explain the disagreement in the direction of the viscosity trend with temperature. First, at the end of the w/C12 transient measurements, the 0 °C viscosity is decreasing while the 2 °C viscosity is increasing. It appears the 2 °C experiment would have a higher viscosity than the 0 °C experiment if the tests were performed for a long enough time. Second, water/dodecane/AOT emulsions are thermodynamically stable microemulsions with very small droplets (~50 nm). The morphology of the surfactant shell is such that it is very difficult to induce coalescence or alter the shape and size of the droplet. These less deformable droplets likely form aggregates of a different morphology than w/WAC and w/70T, which have larger, less stable droplets.

The flow curves at varying temperature show the same trends observed in the transients step (Figure 7.6). w/WAC and w/70T viscosity increases with increasing temperature while w/C12 viscosity increases with decreasing temperature.

The dissociation measurements at varying temperature generally have an increase or shoulder near the hydrate equilibrium temperature (Figure 7.7). Past the equilibrium temperature, all curves collapse together for each emulsion.

7.2 Identifying Mechanisms Affecting Hydrate Slurry Rheology

Comparing experimental measurements across the three systems studied here combined with other studies in literature suggest at least six possible mechanisms by which viscosity and/or pressure changes are observed (Figure 7.8). The simplified picture depicts a cross-section of the rheometer cell and a zoomed in section near the gas-liquid interface. The gas phase contains nearly pure methane (green dots), while the liquid phase contains the
Figure 7.5: Pressure change, fraction of water volume converted to hydrate, and viscosity evolution beginning at the initial hydrate formation event at varying temperature. Hydrate formation from w/WAC, w/C12, w/70T emulsions. 0.30 water volume fraction, 100 s\(^{-1}\), and 1500 psig initial pressure methane except w/WAC emulsions at 2000 psig methane.
Figure 7.6: Steady state hydrate slurry viscosity versus shear rate at varying temperature in (a) w/WAC, (b) w/C12, and (c) w/70T emulsions at 0.30 water volume fraction.
Figure 7.7: Hydrate slurry viscosity as temperature increases during hydrate dissociation in (a) w/WAC, (b) w/C12, and (c) w/70T emulsions at temperature (i.e., the temperature at which the slurry was formed). Hydrate slurries formed at 0.30 water volume fraction, 100 s\(^{-1}\), and 1500 psig initial pressure methane except w/WAC emulsions at 2000 psig methane.
continuous phase liquid (light blue), water (dark blue) either emulsified in droplets or as a capillary bridge, dissolved methane (small green circles), and hydrate particles (dark gray large circles). The right half of the picture shows the physical consequences of six possible mechanisms which effect either viscosity, pressure, or both. The evidence from both measurements and literature for each of the six mechanisms is presented below.

Figure 7.8: Physical events which affect viscosity and pressure during transient viscosity measurement of hydrate slurries.
7.2.1 Gas Dissolution

Methane gas diffuses from the gas phase to the liquid phase, causing a pressure decrease and a viscosity decrease. Gas diffusion is observed experimentally because the measured change in pressure during hydrate formation is larger than the predicted maximum pressure change without gas diffusion. Hydrate formation causes a small decrease in total liquid volume. Because experiments are performed at constant volume, a decrease in liquid volume is matched by an expansion of the gas volume thus decreasing pressure. The predicted pressure change from gas expansion alone is much smaller than the observed total gas phase pressure change (Table 7.2). Gas diffusion could explain the change in pressure above that expected from gas expansion alone. The measured pressure change is much larger in w/C12 and w/70T emulsions than w/WAC emulsions. w/WAC emulsions have the highest viscosity continuous phase; so, methane is expected to diffuse more slowly through West African crude oil than dodecane and 70T mineral oil.

The presence of methane was observed to decrease viscosity in each of the three systems studied. In the w/WAC system, saturated West African crude oil at 0 °C and 1500 psig had a viscosity of 0.35 Pa·s compared to a 1.33 Pa·s viscosity for pure West African crude oil at 0 °C (Webb et al., 2012b). In the w/C12 system, a saturated emulsion with 0.30 water volume fraction at 0 °C, 1500 psig saturation pressure, and 100 s⁻¹ had a viscosity of 0.0327 Pa·s. The same emulsion without methane had a viscosity of 0.175 Pa·s at the same conditions (Webb et al., 2013). In the w/70T system, saturated mineral oil viscosity (1500 psig, 0 0 °C) was 0.0080 Pa·s compared to 0.075 Pa·s for pure mineral oil.

The literature shows that methane diffusivity is inversely related to viscosity (Hayduk & Buckley, 1972; Wilke & Chang, 1955). Diffusivity of methane in dodecane was measured twice as $3.15 \times 10^{-9} \text{ m}^2/\text{s}$ (Hayduk & Buckley, 1972) and $7.6 \times 10^{-9} \text{ m}^2/\text{s}$ (Jamialahmadi et al., 2006). Diffusivity of methane in mineral oil or crude oil has not been measured for the particular fluids studied in this work.
Table 7.2: Change in pressure predicted with no methane diffusion compared to the measured pressure change.

<table>
<thead>
<tr>
<th>experiment</th>
<th>$n_{CH_4}/n_{H_2O}$</th>
<th>limiting species</th>
<th>$\Delta P_{predicted}$</th>
<th>$\Delta P_{measured}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/WAC, $\phi_w = 0.20$</td>
<td>9.7</td>
<td>CH$_4$</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>w/WAC, $\phi_w = 0.30$</td>
<td>17</td>
<td>CH$_4$</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>w/WAC, $\phi_w = 0.40$</td>
<td>26</td>
<td>CH$_4$</td>
<td>10</td>
<td>71</td>
</tr>
<tr>
<td>w/WAC, $\phi_w = 0.45$</td>
<td>32</td>
<td>CH$_4$</td>
<td>8</td>
<td>46</td>
</tr>
<tr>
<td>w/C12, $\phi_w = 0.10$</td>
<td>2.7</td>
<td>H$_2$O</td>
<td>22</td>
<td>49</td>
</tr>
<tr>
<td>w/C12, $\phi_w = 0.20$</td>
<td>7.3</td>
<td>H$_2$O</td>
<td>41</td>
<td>84</td>
</tr>
<tr>
<td>w/C12, $\phi_w = 0.25$</td>
<td>11</td>
<td>CH$_4$</td>
<td>25</td>
<td>121</td>
</tr>
<tr>
<td>w/C12, $\phi_w = 0.30$</td>
<td>16</td>
<td>CH$_4$</td>
<td>18</td>
<td>148</td>
</tr>
<tr>
<td>w/70T, $\phi_w = 0.10$</td>
<td>2.4</td>
<td>H$_2$O</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>w/70T, $\phi_w = 0.20$</td>
<td>5.7</td>
<td>H$_2$O</td>
<td>50</td>
<td>109</td>
</tr>
<tr>
<td>w/70T, $\phi_w = 0.30$</td>
<td>8.8</td>
<td>CH$_4$</td>
<td>51</td>
<td>132</td>
</tr>
<tr>
<td>w/70T, $\phi_w = 0.40$</td>
<td>14.3</td>
<td>CH$_4$</td>
<td>43</td>
<td>200</td>
</tr>
</tbody>
</table>

Both experimental measurements and literature strongly suggest that methane diffusion is a mechanism that plays a significant role in hydrate rheology measurements.

### 7.2.2 Hydrate Formation

Conversion of deformable liquid drops to solid hydrate particles causes viscosity to increase. Hydrate formation also causes pressure to decrease, but this section focuses only the affect of changing a deformable liquid droplet to a more rigid solid particle. Liquid contraction from hydrate formation is discussed later. Measurements in this work all show an increase in viscosity associated with hydrate formation; however, other mechanisms, namely methane depletion and aggregation could explain the viscosity increase instead of a change from liquid droplets to solid particles. Another hydrate rheology study found emulsion viscosity was less than suspension viscosity (Camargo et al., 2000). Taylor explains that internal currents of liquid within droplets cause emulsions to have lower viscosity than hard particle suspensions (Taylor, 1932).
7.2.3 Aggregation

Aggregation causes viscosity to increase, but has no effect on pressure. Aggregation can be thought to occur through two possible mechanisms. One type, capillary bridging could occur when two hydrate particles collide, and the water layers on the surface of the particles form a capillary bridge which joins the two hydrate particles. Alternatively, a hydrate particle could collide with an unconverted water droplet and cause the water droplet to convert to hydrate. This second mechanism is called sintering. Measurements of cohesion forces of between cyclopentane hydrate particles have demonstrated that both types of aggregation are possible (Aman et al., 2011). The measurements in this work are not able to distinguish between the types of aggregation; we merely want to acknowledge that aggregation could proceed in at least two ways.

Aggregation is thought to increase viscosity because it effectively increases the volume fraction of the system (Graham et al., 1984; Hasan & Shaw, 2010; Pal, 2011). Continuous phase liquid becomes trapped in aggregates and effectively acts as part of the aggregate rather than the continuous phase.

Experimental evidence for aggregation can be seen in Figure E.2 later in Appendix E. The figure shows that hydrate viscosity measurements across multiple labs generally yields higher values than predicted by hard sphere rheology models. Also, in experiments presented in this work, viscosity increases sharply at one point after an induction period. If particles never aggregate; then one must assume that many droplets nucleated independently without contacting each other at the exact same induction time; an impossibly unlikely event.

One study of concentrated suspensions yielding under oscillatory flow measured the displacement of droplets and found that droplets are irreversibly displaced from their flow lines under shear (Hebraud et al., 1997). Emulsions in this study were hexadecane in water stabilized by sodium dodecyl sulfate giving 0.9 micron diameter droplets. Another study by some of the same researchers showed suspended particles are irreversibly displaced above a critical strain amplitude, which is easily exceeded in shear flow experiments (Pine et al., 2005).
7.2.4 Liquid Contraction

Hydrate formation causes a net decrease in total liquid volume, which causes an increase in total gas volume, which decreases measured pressure in the gas phase. Liquid contraction has no effect on viscosity. Liquid contraction is evident from the sharp pressure decrease associated with hydrate formation. This decrease occurs on the order of minutes or tens of minutes; much too short of a time for significant diffusion to occur in any of the three systems. Since the pressure decrease cannot be explained by gas diffusion, the only other possibility is expansion of the gas phase.

Consider a 1 mL change in water volume from hydrate formation. Water density and molecular weight are known; so, the change in moles is determined. The change in methane moles will then equal about six times the change in water moles (Sloan & Koh, 2008). Change in methane mass is determined via methane molecular weight. Methane density in an emulsion at a known temperature and pressure is calculated using Multiflash 4.1. Change in methane volume is determined using methane density. Now, since mass is conserved, the mass of hydrate formed equals the sum of the change in methane and water masses. Hydrate density is determined at a known pressure and temperature using CSMGem (Ballard & Sloan, 2002a,b, 2004a,b; Jager et al., 2003). Finally, change in hydrate volume is determined via hydrate density and mass. In conclusion, the unit change in methane, water, and hydrate can be determined. The sum of the changes in volume is negative, meaning hydrate formation causes a decrease in total liquid volume.

The liquid level in the rheometer cell should have little influence on the torque (which is used to determine viscosity) as long as the liquid level is above the top of the inner cylinder (bob). Torque is directly proportional to the radius squared (Macosko, 1994), and the radius of the bob is much greater than the radius of the shaft above the bob; so, overfilling the cell does not significantly increase viscosity. Our calculations indicate the liquid volume never decreases enough to go below the top of the bob.
7.2.5 Flow Alignment

“Flow alignment” is used here as a catch all to describe all of the hydrodynamic affects on hydrate slurry viscosity. Hydrate particles decrease their resistance to flow by aligning or breaking up aggregates. Flow alignment decreases viscosity and has no effect on pressure. The hydrodynamic effects of flow are evident in any of the flow curves which show shear-thinning behavior. Shear-thinning behavior is attributed to an overall breakdown of fluid structure (Cheng et al., 2011; Quemada, 1978; Wagner & Brady, 2009). Ordering of colloidal particles into layers occurs during shear, decreasing colloidal suspension viscosity (Loose & Hess, 1989).
CHAPTER 8
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

8.1 Conclusions

Hydrate formation from water-in-oil emulsions is indicated by increasing viscosity, increasing shear-thinning behavior, and the appearance of a yield stress. In this document, a high pressure rheometer apparatus was developed to study hydrate formation from water-in-oil emulsions (Chapter 3). The apparatus was used to study hydrate formation from three different starting emulsions: water-in-West African crude oil (Chapter 4), water-in-dodecane with AOT surfactant (Chapter 5), and water-in-70T mineral oil with span 80 and AOT surfactants (Chapter 6). Each of these emulsions provided a unique way to observe hydrate rheology. The water-in West African crude oil system is an example of a fluid that may be found in an oil pipeline; however, the complicated oil chemistry and inherent irreproducibility of crude oil were serious drawbacks. The other two systems are model emulsions with better characterized fluids and improved reproducibility over crude oil-based emulsions. Water-in-dodecane with AOT emulsions are very well understood, have low viscosity, and are optically clear with droplet size on the order of 50 nm. Water-in-70T mineral oil with span 80 and AOT has a higher viscosity and droplet size on the order of 1 micron, similar to West African crude oil emulsions; however, mineral oil chemistry is very diverse. Some of the most significant results from each investigation are summarized here.

8.1.1 Water-in-West African Crude Oil Emulsions

1. Hydrate slurry viscosity increases to the peak value in about 20 minutes when hydrates form, and then decays after going through a peak value as the hydrate suspension is continuously sheared.

2. Hydrate slurry yield stress increases as annealing time increases up to 8 hours, and then remains about constant.
3. Hydrate slurry yield stress slowly increases with particle volume fraction until it dramatically increases at and above 0.5 water volume fraction.

4. During dissociation of hydrate slurries, viscosity increases around the hydrate equilibrium temperature, and then decreases.

8.1.2 Water-in-Dodecane with AOT Emulsions

1. Hydrate slurry viscosity and yield stress increased as water volume fraction increased, temperature decreased, initial pressure increased, and shear rate decreased.

2. Hydrate slurries were shear-thinning and well described by the Cross model.

3. During the initial increase in hydrate slurry viscosity upon hydrate formation, the limiting reactant for hydrate formation in the liquid phase is rapidly (about 10 minutes) and completely consumed.

4. If all water was consumed during the initial viscosity increase, then viscosity will decrease to a steady value. If a large amount of water remains after the initial viscosity increase, then viscosity will increase again for a time, and then decrease.

5. Viscosity was sensitive to system parameters in the following order from most sensitive to least sensitive: water volume fraction > temperature > pressure > shear rate.

8.1.3 Water-in-70T mineral oil with Span 80 and AOT Emulsions

1. The fractional conversion of water to hydrate was determined and found to have a strong effect on hydrate slurry viscosity.

2. At full conversion of water to hydrate, viscosity and yield stress increased with increasing water volume fraction, increasing temperature, and decreasing pressure. Hydrate formation proceeds more slowly as driving force decreases, which causes higher viscosity.
3. The viscosity evolution over time after hydrates form is determined by a combination of factors including conversion of liquid water to solid hydrate, methane depletion and diffusion from gas phase to liquid phase, hydrate particle aggregation, and capillary bridging.

4. Emulsification of a saturated oil increased steady-state viscosity about 10-fold. Hydrate formation from a saturated emulsion caused about a five-fold viscosity increase. So, hydrate formation can increase viscosity over 50 times above a saturated oil.

Generally viscosity measured in both the transient step and steady state flow curve was sensitive to water volume fraction, temperature, pressure, and shear rate.

8.2 Recommendations for Future Work

Over eight years, the high pressure rheology apparatus has been steadily improved, while experiments have revealed more and more information about hydrate slurry rheology. Still, further work can be performed. Although several researchers around the world have released hydrate rheology studies since this work began, the work in this group is still the only investigation using both high pressure and a rheometer. Some possible ideas for future work in hydrate slurry rheology are listed below.

One of the main differences between flow of hydrate slurries in a subsea pipeline and flow in a rheometer is mixing. Subsea pipelines often operate in turbulent or transition flow, whereas the rheometer uses laminar flow. The rheometer can be equipped with geometries which generate high mixing, such as the double helical ribbon geometry or the anchor impeller. A mixing geometry eliminates the need for an external mixing cell, and reproduces the turbulent flow often observed in subsea pipelines. However, mixing geometries cannot directly measure shear rate; rather, calibrations are performed for every fluid studied to correlate torque and angular velocity to shear stress and shear rate. These correlations introduce much error in the measurement. Also, a sophisticated knowledge of the flow patterns in the cell is required to properly interpret the results; so, CFD modeling is probably required.
In rheology, oscillatory shear flow is common. The geometry oscillates at a set frequency, and the elastic and viscous moduli, G’ and G”, are determined. Hydrate formation might be observable in oscillatory flow. This may help decouple the effect of shear because oscillatory flow is essentially zero shear. Hydrate formation in oscillatory flow may be analogous to hydrate formation during shut-in in a subsea pipeline.

In this work, flow curves (viscosity vs. shear rate) were only obtained late in the experiment, after hydrates formed to their fullest extent. It would be profitable to obtain flow curves at varying times after hydrate formation.

In this work, viscosity depended on the driving force for hydrate formation. Contradictory results were obtained in the water-in-dodecane emulsions versus the water-in-70T mineral oil emulsions. The differences between these two investigations are difficult to explain with our current understanding. A study of hydrate slurry viscosity as a function of thermodynamic driving force should be further investigated. The presence of salt is another parameter that could be introduced in this investigation. A quantitative description of the effect of salt, pressure, and temperature on hydrate slurry viscosity would be very useful.

Some improvements could be made to the model emulsions studied. The water-in-dodecane system is well characterized, but droplet size is very small. The water-in-70T mineral oil emulsion has a larger droplet size, but 70T mineral oil is chemically diverse and may vary batch to batch. Mineral oil is nominally characterized only by density and viscosity; therefore, chemical composition could change from batch to batch. Is it possible to develop a model emulsion with a well characterized continuous phase and micron sized droplets?

Hydrates and waxes have both been studied extensively; however, the interaction of hydrates and waxes together has not been studied much. A rheological characterization of waxes and hydrates would be interesting. This study may not be possible in a concentric cylinders geometry because wax will deposit on the walls; and the data become difficult to interpret after deposition occurs. Perhaps this system would be best studied in a parallel
plate apparatus with hydrate deposition on the bottom plate, and a rotating top plate. Hydrates would have to be formed from an ambient former like cyclopentane since parallel plates cannot operate under pressure.

Most work on hydrate rheology has used methane gas to form sI hydrate. sII hydrate is the most common type found in subsea oil pipelines. The current apparatus could easily swap out the cylinder of methane for a cylinder of a gas mixture such as methane-ethane or methane-ethane-propane which would form sII hydrate.


A.1 Pressure Loss Calculations

Calculations were performed to predict the pressure loss after hydrate formation. Two different assumptions were made. First, assume methane does not dissolve into the liquid during the experiment. In this case, the only methane available for hydrate formation is that already dissolved in the liquid. All pressure changes come from a contraction of the liquid phase after hydrate formation. Second, assume all methane consumed during hydrate formation is completely replaced by methane dissolving from the gas phase. For each assumption, we started by calculating the composition of the emulsion, then calculating the new composition after saturation with methane in the mixing cell. This was done using a PT flash at 1500 psig and 25 °C using the RKS advanced equation of state with the program Multiflash 4.2 by Infochem Software. Then the emulsion compositions were normalized to 10 mL total volume, which is the amount pumped into the rheometer cell in experiments. Finally, the composition was calculated assuming all of the limiting species in the liquid phase (either water or methane) was consumed to form hydrate. A ratio of 6 moles of water consumed for every 1 mole of methane consumed for each 1 mole of hydrate produced was used. Pressure loss was determined by performing a TV flash at 0 °C and the determined density. Density was obtained from the pressure cell headspace volume of 11.2 mL plus any added volume from liquid contraction and from the constant moles of methane gas (with the first assumption, this does not change throughout the experiment). For the second assumption, the calculations follow the same procedure, except (1) water is assumed to be fully consumed and converted to hydrate in all cases, and (2) methane is taken from the gas phase to resaturate the liquid phase at the end of the experiment.
A.2 Saturation Experiments

Several experiments were performed to measure the amount of methane dissolved in pure dodecane and H$_2$O/C$_{12}$/AOT emulsions. Saturation experiments were performed in both the mixing cell and the pressure cell. The procedures for each experiment are as follows:

Mixing cell:

1. Place 100 mL of emulsion in the mixing cell (cell total volume is 302 mL)
2. Seal the cell
3. Open the valve to the CH$_4$ cylinder; pressurize to about 1500 psig
4. Close the valve to the CH$_4$ cylinder
5. Turn on the air motor to begin mixing
6. Observe pressure over time until pressure reaches a constant value

Methane dissolution is measured in six liquid phases: pure dodecane and H$_2$O/C$_{12}$/AOT emulsions with water volume fractions of 0.05, 0.10, 0.20, 0.25, and 0.30. Pressure and temperature are measured over time until the pressure remains constant (Figure A.1). The mixing cell operates at room temperature (22 ± 3 °C).

The amount of methane dissolved in the liquid phase after saturation is calculated using Equation A.1:

\[
\begin{align*}
    n_2 - n_1 &= \frac{P_2(V_{\text{cell}} - V_{\text{liquid},2})}{Z_2RT_2} - \frac{P_1(V_{\text{cell}} - V_{\text{liquid},1})}{Z_2RT_1} \\
\end{align*}
\]  

(A.1)

Where subscript 1 refers to the initial state immediately following pressurization, subscript 2 refers to the final state when pressure reaches a constant value, $n$ is moles of methane, $P$ is measured pressure, $T$ is measured temperature, $Z$ is the compressibility factor calculated as a function of $P$ and $T$ using the Soave-Redlich-Kwong (SRK) equation of state, and $R$ is the gas constant. $V_{\text{cell}}$ is the measured cell volume, 302 mL. $V_{\text{liquid}}$ is the volume of liquid in the cell, 100 mL. $V_{\text{liquid},1}$ is 0.9 times $V_{\text{liquid},2}$ because of liquid swelling.
Supplementary Figure A.1: Pressure evolution with time as methane dissolves in pure dodecane and water/C\textsubscript{12}/AOT emulsions in the external mixing cell.

When methane dissolves into liquid, the liquid volume increases. To determine the extent of swelling, we saturated 100 mL of dodecane with methane in the mixing cell. Then, we pumped the saturated liquid into the rheometer pressure cell in 20 mL increments. After depressurization, the liquid volume was measured three times to be 18.0, 18.2, and 17.8 mL, yielding an average liquid volume decrease of 10%. We use this value for all calculations.

The methane concentrations measured in the saturation experiments are used to predict the amount of hydrate formed in the rheometer pressure cell during the initial viscosity peak. These calculations require several assumptions:

1. Hydrates form by consuming species in the liquid phase only

2. 6 moles of water combine with 1 mole of methane to form 1 mole of hydrate

3. A significant amount of methane does not dissolve during the initial formation peak (~10 minutes)
4. All of the limiting species for hydrate formation is consumed during the initial formation peak

5. The concentration of methane in the liquid just before hydrate formation is the same as the concentration measured in the saturation experiments

Several saturation experiments were performed in the rheometer pressure cell as well. These experiments were performed at the same conditions as the control experiment for hydrate formation (0 °C, 1500 psig, 100 s\(^{-1}\) shear rate). Hydrates will form in these experiments after some time, so, we prepared emulsions without adding water (only dodecane and AOT). The saturation experiment for methane dissolving in an H\(_2\)O/C\(_{12}\)/AOT emulsion shows that methane dissolves significantly over 11 hours (Figure A.2). The transient hydrate formation experiments usually set 24 hours for hydrate formation, so, we can reasonably expect methane to dissolve at a significant rate after methane is depleted from the liquid phase in hydrate forming experiments.

Supplementary Figure A.2: methane dissolving in a mixture of dodecane and AOT at 0 °C and 100 s\(^{-1}\). The amount of each species used is the same as that used in an H\(_2\)O/C\(_{12}\)/AOT emulsion with 0.05 water volume fraction.
A.3 Estimating Time to Diffuse

We want to describe how methane concentration in a liquid changes with time and position. Assume methane only diffuses in one dimension. The continuity equation reduces to:

$$\frac{\partial C_A}{\partial t} + \frac{\partial (C_A v_z)}{\partial z} = 0 \quad (A.2)$$

Where $C_A$ is the concentration of methane in a liquid, $t$ is time, and $v_z$ is velocity in the $z$-direction. Now, apply Fick’s first law:

$$\frac{\partial C_A}{\partial t} - \frac{\partial}{\partial z} \left[ D_{AB} \frac{\partial C_A}{\partial z} \right] = 0 \quad (A.3)$$

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial x^2} \quad (A.4)$$

Where $D_{AB}$ is the diffusivity of methane in a liquid. The latter equation is Fick’s second law. As a first approximation, assume no convection and no reaction. In reality, the laminar flow in the theta-direction should decrease diffusion time and reaction with water to form hydrate will decrease diffusion time. So, these calculations will result in an overestimate of diffusion time.

The boundary conditions and initial condition for Equation A.4 are:

at $z = 0$, \quad $C_A(t, 0) = C_{A,sat}$ \quad (A.5)

at $z = L$, \quad $\frac{\partial C_A(t, L)}{\partial z} = 0$ \quad (A.6)

at $t = 0$, \quad $C_A(0, z) = 0$ \quad (A.7)

Switch to dimensionless variables:

$$\zeta = \frac{z}{L} \quad (A.8)$$

$$\tau = \frac{t D_{AB}}{L^2} \quad (A.9)$$

$$\phi(\tau, \zeta) = \frac{C_{A,sat} - C_A}{C_{A,sat} - C_{A,o}} \quad (A.10)$$
Rewrite Equation A.4 and the Boundary and Initial conditions with the new dimensionless variables:

\[
\frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial \zeta^2} \quad \text{(A.11)}
\]

\[
\phi(\tau, 0) = 0 \quad \text{(A.12)}
\]

\[
\frac{\partial \phi}{\partial \zeta} \bigg|_{\zeta=1} = 0 \quad \text{(A.13)}
\]

\[
\phi(0, \zeta) = 1 \quad \text{(A.14)}
\]

Solve Equation A.11 using separation of variables:

\[
\phi(\tau, \zeta) = T(\tau)X(\zeta) \quad \text{(A.15)}
\]

\[
\frac{1}{T} \frac{dT}{d\tau} = \frac{1}{X} \frac{d^2X}{d\zeta^2} = -\lambda^2 \quad \text{(A.16)}
\]

We have two separate ordinary differential equations:

\[
\frac{dT}{d\tau} + \lambda^2 T = 0 \quad \text{(A.17)}
\]

\[
\frac{d^2X}{d\zeta^2} + \lambda^2 X = 0 \quad \text{(A.18)}
\]

Solve Equation A.17 by direct separation and integration:

\[
T = I_1 e^{-\lambda^2 \tau} \quad \text{(A.19)}
\]

Solve Equation A.18 by assuming a solution of the form \( X = K e^{\lambda \zeta} \):

\[
X = K_1 \cos(\lambda \zeta) + K_2 \sin(\lambda \zeta) \quad \text{(A.20)}
\]

Apply the first boundary condition (Equation A.12):

\[
K_1 = 0 \quad \text{(A.21)}
\]

Apply the second boundary condition (Equation A.13):

\[
0 = K_2 \lambda \cos(\lambda) \quad \text{(A.22)}
\]
Writing the solution so far:

\[ \phi(\tau, \zeta) = \sum_{n=0}^{\infty} A_n \exp \left[ -\left( \frac{2n+1}{2} \right)^2 \pi^2 \tau \right] \sin \left[ \left( \frac{2n+1}{2} \right) \pi \zeta \right] \]  

(A.24)

Apply initial condition:

\[ \phi(0, \zeta) = 1 \]  

(A.25)

\[ 1 = \sum_{n=0}^{\infty} A_n \sin \left[ \left( \frac{2n+1}{2} \right) \pi \zeta \right] \]  

(A.26)

Multiply both sides by \( \sin \left[ \left( \frac{2m+1}{2} \right) \pi \zeta \right] \) and take \( \int_0^1 d\zeta \).

\[ \int_0^1 \sin (\lambda_m \zeta) d\zeta = \sum_{n=0}^{\infty} A_n \int_0^1 \sin (\lambda_n \zeta) \sin (\lambda_m \zeta) d\zeta \]  

(A.27)

Because the differential equation for \( X(\zeta) \) (Equation A.18) is of Sturm-Liouville type, the integral on the right hand side of the above equation \( = 0 \) when \( m \neq n \).

\[ A_n = \frac{\int_0^1 \sin (\lambda_n \zeta) d\zeta}{\int_0^1 \sin^2 (\lambda_n \zeta) d\zeta} = \frac{2}{\lambda_n} \]  

(A.28)

Write the solution:

\[ \phi(\tau, \zeta) = \sum_{n=0}^{\infty} 2 \frac{2}{\lambda_n} \exp (-\lambda_n^2 \tau) \sin (\lambda_n \zeta) \]  

(A.29)

Where

\[ \lambda_n = \left( \frac{2n+1}{2} \right) \pi \quad n = 0, 1, 2, ... \]  

(A.30)

It is more intuitive to substitute in the definition of \( \phi \):

\[ \frac{C_A}{C_{A,\text{sat}}} = 1 - \sum_{n=0}^{\infty} 2 \frac{2}{\lambda_n} \exp (-\lambda_n^2 \tau) \sin (\lambda_n \zeta) \]  

(A.31)

Mathematica 8.0’s NSolve function is used to determine dimensionless time at several relevant values of dimensionless position and fractional concentration (Table A.1). To convert dimensionless time bact to time, use \( D = 7.6 \cdot 10^{-9} \text{ m}^2/\text{s} \) and \( L = 0.05 \text{ m} \).
Table A.1: Time for methane to diffuse into dodecane.

<table>
<thead>
<tr>
<th>$\frac{C_A}{C_{A,\text{sat}}}$</th>
<th>$\zeta$</th>
<th>$\tau$</th>
<th>time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99</td>
<td>1</td>
<td>2.0</td>
<td>180</td>
</tr>
<tr>
<td>0.90</td>
<td>1</td>
<td>1.0</td>
<td>94</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.24</td>
<td>22</td>
</tr>
</tbody>
</table>

A.4 Sensitivity Analysis

We performed sensitivity analysis to determine the relative effect on hydrate slurry viscosity from the four main variables studied in this work: water volume fraction, initial pressure, temperature, and formation shear rate. We define sensitivity as the percent change in viscosity divided by the percent change in a variable:

$$sensitivity = \frac{(\eta_{\text{experiment}} - \eta_{\text{reference}})}{(\eta_{\text{reference}})} \frac{(x_{\text{experiment}} - x_{\text{reference}})}{(x_{\text{reference}})}$$ \hspace{1cm} (A.32)

We compare the percent change in viscosity to a percent change in one of the four parameters (i.e., water volume fraction, temperature, initial pressure, and formation shear rate) to determine the sensitivity of hydrate slurry viscosity. A large sensitivity indicates that hydrate slurry viscosity strongly depends on the parameter, while a small sensitivity indicates weak dependence. Viscosity values from five different points in the experiment were analyzed (numbers correlate to entry in Table A.2): (1) at the initial peak value following hydrate formation in the transient step, (2) at 10 hours after the initial peak value, (3) at the maximum viscosity value in the transient step (often the same as the initial peak value), (4) the zero shear rate viscosity ($\eta_0$) fit from the Cross model, and (5) at 100 s$^{-1}$ during the shear rate ramp. The sensitivity of the yield stress to the four experimental parameters was also computed. The reference experiment parameters are 0.3 water volume fraction microemulsion, 1500 psig initial pressure of methane, 0 °C temperature, and 100 s$^{-1}$ shear rate. Experiments used to calculate sensitivity changed one of these four parameters. The deviations were to 0.2 water volume fraction, 1000 psig initial pressure methane, 2 °C temperature, and 500 s$^{-1}$ shear rate.
Table A.2: Sensitivity analysis of four variables on viscosity.

<table>
<thead>
<tr>
<th>measurement</th>
<th>sensitivity to each parameter</th>
<th>ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) initial peak</td>
<td>T  86 0.27 P 1.4 (\dot{\gamma}_{\text{form}}) 0.087</td>
<td>(T &gt; P &gt; \phi_w &gt; \dot{\gamma}_{\text{form}})</td>
</tr>
<tr>
<td>(2) 10 hours after formation</td>
<td>T 100 2.5 P 1.3 (\dot{\gamma}_{\text{form}}) 0.15</td>
<td>(T &gt; \phi_w &gt; P &gt; \dot{\gamma}_{\text{form}})</td>
</tr>
<tr>
<td>(3) maximum in transient</td>
<td>T 72 0.87 P 0.93 (\dot{\gamma}_{\text{form}}) 0.13</td>
<td>(T &gt; P &gt; \phi_w &gt; \dot{\gamma}_{\text{form}})</td>
</tr>
<tr>
<td>(4) Cross parameter (\eta_0)</td>
<td>T 49 2.7 P 0.27 (\dot{\gamma}_{\text{form}}) 0.098</td>
<td>(T &gt; \phi_w &gt; P &gt; \dot{\gamma}_{\text{form}})</td>
</tr>
<tr>
<td>(5) at 100 s(^{-1}) on flow curve</td>
<td>T 38 2.4 P 0.20 (\dot{\gamma}_{\text{form}}) 0.080</td>
<td>(T &gt; \phi_w &gt; P &gt; \dot{\gamma}_{\text{form}})</td>
</tr>
<tr>
<td>yield stress</td>
<td>T 120 3 P 3 (\dot{\gamma}_{\text{form}}) 0.2</td>
<td>(T &gt; \phi_w = P &gt; \dot{\gamma}_{\text{form}})</td>
</tr>
</tbody>
</table>

Viscosity and yield stress were most sensitive to temperature, then water volume fraction, then initial pressure, and finally formation shear rate (Table A.2). Independent of parameter sensitivity, all five viscosity measurements and the yield stress measurement followed the same trends with changing experimental parameters; viscosity and yield stress increased with increasing water volume fraction, increasing pressure, decreasing temperature, and decreasing shear rate.
B.1 Emulsion Flow Curves

This section reports the flow curves obtained for 70T mineral oil, 70T mineral oil with surfactants, and water/70T/surfactant emulsions at varying water volume fractions. The procedure consists of shear rate ramp from 1000 to 0.1 s\(^{-1}\) taking 10 points per decade. A point is recorded once 3 consecutive measurements occur within 3% of each other where measurements are acquired every 10s. If steady state is not achieved in two minutes, no point is reported. Measurements were recorded with a TA Instruments DHR-2 rheometer fitted with cone-and-plate geometry (60 mm diameter, 2\(^\circ\) angle) at atmospheric pressure. Temperature is set through a Peltier heating/cooling plate.

![Figure B.1: Steady state viscosity of 70T mineral oil at varying shear rate and temperature.](image-url)
Figure B.2: Steady state viscosity of 70T mineral oil with 5 wt.% AOT + span 80 at varying shear rate and temperature.

Figure B.3: Steady state viscosity of 0.05 water volume fraction water/70T/surfactant emulsion at varying shear rate and temperature.
Figure B.4: Steady state viscosity of 0.10 water volume fraction water/70T/surfactant emulsion at varying shear rate and temperature.

Figure B.5: Steady state viscosity of 0.20 water volume fraction water/70T/surfactant emulsion at varying shear rate and temperature.
Figure B.6: Steady state viscosity of 0.30 water volume fraction water/70T/surfactant emulsion at varying shear rate and temperature.

Figure B.7: Steady state viscosity of 0.40 water volume fraction water/70T/surfactant emulsion at varying shear rate and temperature.
Figure B.8: Steady state viscosity of 0.50 water volume fraction water/70T/surfactant emulsion at varying shear rate and temperature.

B.2 $\chi$ Calculation

This section details the scheme used to calculate the fraction of water converted to hydrate, $\chi$. To begin, we need to determine the initial compositions and amounts of all materials in the gas and liquid phases. The emulsion composition is based on 100 mL total liquid, with a given water volume fraction, 5 wt.% total surfactant, of which 90 wt.% is span 80 and 10 wt.% is AOT, and the balance 70T mineral oil. Since molecular weight and density of all four components are known, the weight, volume, and mole fractions and amounts can be determined for all four components through algebra. The 100 mL emulsion is saturated with methane, at constant pressure. Initial moles of methane gas in the mixing cell are determined by:

$$n_1 = \frac{P_1 V_i}{Z_1 RT_1} \quad (B.1)$$

Where $n$ is the moles of methane, $P$ is the pressure of methane in the mixing cell measured by a pressure transducer, $V$ is the volume of the isco pump plus the volume of the methane gas head space, which is 202 mL, $Z$ is the compressibility factor determined by the Soave-Redlich-Kwong equation of state, $R$ is the gas constant, and $T$ is the temperature measured
by the thermocouple in the gas headspace of the mixing cell. Subscript 1 indicates the initial state, and subscript 2 indicates the end of saturation, when the volume stops decreasing. As methane dissolves, the isco pump piston compresses the gas phase, decreasing the gas phase volume. The change in moles from state 1 to 2 is the amount of methane dissolved in the liquid phase:

$$n_1 - n_2 = \frac{P_1 V_1}{Z_1 RT_1} - \frac{P_2 V_2}{Z_2 RT_2}$$  \hspace{1cm} (B.2)$$

Here, \( V_2 \) is the isco pump volume plus the mixing cell volume, where the mixing cell volume is \( 202 - (100(10/9) - 100) \) mL (this assumes the liquid volume increased by 10% from saturation).

Now, the density of methane in the liquid is determined by two calculations using the commercial software Multiflash 4.1. A PT flash is performed inputing the initial emulsion composition and a second PT flash is performed with the initial emulsion composition plus excess methane. The difference of the total liquid phase volumes from the two calculations divided by the moles of methane (from equation B.2) multiplied by the molecular weight of methane. To finally determine the initial composition of the liquid phase, scale the total mass, volume, and moles of each component to 10 mL of total volume, since 10 mL are pumped from the mixing cell to the rheometer cell. The headspace in the rheometer is 11.2 mL, and assumed to be completely methane at the experimental pressure.

The next calculations are broken up into two steps. First, pressure will change rapidly until either all methane or all water is consumed. During this stage, the moles of methane in the gas phase are assumed constant, because the step is too short to expect significant dissolution of methane into the liquid phase. Therefore, changes in pressure are fully accounted for by changes in liquid phase volume:

$$\Delta V_{liq} = -\Delta V_{gas} = V_{gas}(t) - V_{gas}(0) = \frac{Z(t)nRT}{P(t)} - \frac{Z(0)nRT}{P(0)}$$ \hspace{1cm} (B.3)$$

Where 0 indicates the initial state and t indicates a value a time t. If water is the limiting reactant, then the calculation ends when all water is consumed. If methane is the
limiting reactant, then we move on to the second step of the calculations when all methane is consumed.

\[ \chi = \frac{V_{H_2O}(0) - V_{H_2O}(t)}{V_{H_2O}(0)} = \frac{-\Delta V_{H_2O}}{V_{H_2O}} \]  

(B.4)

Where \( V_{H_2O}(0) \) is the initial volume of water, \( V_{H_2O}(t) \) is the water volume at time t, and \( \Delta V_{H_2O} \) is the change in water volume.

The molecular weight of methane and water is known, the density of methane, water, and sI hydrate is known, and six moles of water are assumed to be consumed for every one mole of methane (Sloan & Koh, 2008). If we consider an arbitrary change in water volume, we have enough information to calculate the resulting change in total liquid volume and gas phase moles of methane. In other words, the ratios of change in water volume to change in total volume and change in total volume to change in gas phase moles are constants:

\[ A = \frac{\Delta V_{H_2O}}{\Delta V_{total}} \]  

(B.5)

\[ B = \frac{\Delta n_{CH_4}}{\Delta V_{total}} \]  

(B.6)

Where A and B are constants, \( \Delta V_{H_2O} \) is an arbitrary change in water volume from hydrate formation, \( \Delta V_{total} \) is the change in total liquid volume resulting from a change in water volume, and \( \Delta n_{CH_4} \) is the change in methane moles in the gas phase.

So, water volume change can be linked to total volume change, which is equal to the opposite of total gas phase volume change since the system is at a constant volume. Now:

\[ \chi = -\frac{\Delta V_{H_2O}}{V_{H_2O}} = \frac{-\Delta V_{total} \times A}{V_{H_2O}} = \frac{\Delta V_{gas} \times A}{V_{H_2O}} = A \times \frac{V_{gas}(t) - V_{gas}(0)}{V_{H_2O}} \]  

(B.7)

Solving Equation B.6 for V(t):

\[ V_{gas}(t) = \frac{n(0) - BV(0)}{\frac{P(t)}{Z(t)RT} - B} \]  

(B.8)

All of these parameters are known, so \( \chi \) can be determined.
The following contains detailed information on the high pressure rheometer apparatus as it is currently constructed. Figure C.1 shows a cartoon schematic of the apparatus as currently constructed. The current apparatus has several new features different from that reported in previous publications (Rensing, 2010; Webb et al., 2012b). The apparatus was moved from Alderson Hall room 494 to room 391. In the new laboratory, the apparatus shares a methane cylinder with several other devices (Figure C.1). A cooling bath was added to the mixing cell. The bath enables temperature control and saturation at lower temperatures. A liquid knockout unit was added to each vent line to prevent liquids from entering the vent lines during depressurization. The TA Instruments AR-G2 rheometer has been replaced with a TA Instruments DHR-2 rheometer. The DHR-2 can perform all of the same functions as the AR-G2, but it has an improved torque resolution of 0.05 nN·m (twice as good as the AR-G2) and uses upgraded software. Polycarbonate shielding was added around the mixing cell because it is a large piece of rotary equipment.

The old chiller was replaced with a VWR advanced digital controller refrigerated/heated circulating bath model number 89202-978. The VWR chiller has a 7 L capacity, -40 to 200 °C temperature range, 5.3 gpm maximum pressure flow rate, and 1100 watts heater wattage.

The mixing cell was stirred via a belt attached to an air driven motor. The motor was replaced with an Dayton 4Z248D electric motor. The speed of the motor was calibrated to the position of the control dial using a Neiko DT2234A digital tachometer (Figure C.2). Motor speed was measured three times for each data point, and the averages are reported. At the lower positions of the motor speed control (below 15), the motor rotated very slowly, and below 10 it did not rotate at all. All experiments were performed with the motor speed control set to 20, which corresponds to a measured speed of 167 RPM.
Figure C.1: Cartoon diagram of high pressure rheology apparatus as currently constructed.
Figure C.2: Calibration curve for motor speed versus motor speed control position. Points are the average of three measurements from a digital tachometer. Standard deviation error bars are shown, but are all smaller than the size of each point.

An emergency shutdown procedure is posted on the apparatus and is reproduced here for future use (Figure C.3).

A standard procedure was developed for starting and finishing an experiment with the high pressure rheometer (Figure C.4). The procedure includes blanks for the operator to enter various experiment parameters.
Emergency Shutdown Procedure

Vent mixing cell:
(1) Turn this 3-way valve so the pointed end is downward.
(2) Open this valve (slowly if possible).

Vent pressure cell:
(1) Turn this 3-way valve so the pointed end is downward.
(2) Open this valve (slowly if possible).

Figure C.3: Emergency shutdown procedure for high pressure rheometer.
High Pressure Rheometer Standard Procedure

Setup:
1. Sample:   
2. Remove air bearing clamp, turn on rheometer, turn on chiller   
3. Open rheometer software   
4. Create new folder:   
5. Set procedure and fill out notes in software   
6. Set T = 25 °C

Flush and fill lines:
7. Open valves to CH₄ cylinder, pressurize pressure cell   
8. Fill Isco pump to ~30 mL:  V_isco =   
9. Pump ~10 mL solution into pressure cell.  V_isco =   

Calibrations:
11. Calibrate instrument inertia:  
   Trial | Inertia (µNms²) 
   1     |               
   2     |               
12. Attach rotor, attach large magnet, lower head, zero gap, and raise to backoff distance (3500 µm)   
13. Calibrate bearing friction:  
   Trial | Bearing friction (µNm/(rad/s)) 
   1     |                    
   2     |                    
14. Perform rotational mapping (precision, 2 iterations)

Charge cell:
15. Pressurize pressure cell   
16. Pump 10 mL solution into pressure cell.  V_isco =   
17. Run experiment, record pressure in Labview.  Start time:   
18. Close valves to CH₄ cylinder

Cleanup:
19. Depressurize pressure cell   
20. Raise head, remove large magnet, remove rotor   
21. Measure liquid volume in cup:  V_final =   
22. Clean rotor and cup with acetone   
23. Turn off rheometer, turn off chiller, attach air bearing clamp

Figure C.4: Standard procedure to set up and clean up an experiment using the high pressure rheometer apparatus.
This thesis aims to understand the rheological behavior of hydrates suspended in water-in-crude oil emulsions. Several significant obstacles confound the study of crude oil. First, every crude oil is different. A research project could study one or two crude oils extensively, but the outcomes of the research may only apply to those crude oils. Even then, results may not apply since the composition of a single crude oil changes over its production lifetime. Second, crude oil contains so many components that they cannot all be identified (Freitas et al., 2009). It is difficult to make any scientific conclusions on a fluid of unknown composition. Since crude oil is such broad classification of poorly defined and poorly understood fluids, the decision was made to study model system. The goal is to use a model system that behaves physically like a water-in-crude oil emulsion, but is chemically much simpler.

As a first approximation, we selected glass beads suspended in mineral oil with a small amount of water. In this model system, the glass beads are analogous to hydrate particles, and the mineral oil is the suspending medium. Addition of a small amount of water dramatically increases the viscosity of the system by forming capillary bridges between the glass beads, created an aggregated structure (Koos & Willenbacher, 2011; McCulfor et al., 2011). This system was chosen because it is simple, it can model hydrate without requiring high pressure, and it has been studied before (McCulfor et al., 2011).

We use solid glass beads in three sizes: 30-50, 63-75, and 90-106 µm. The 30-50 µm beads come from Polysciences with density 2.50-2.55 g/mL. The other two sizes come from Whitehouse Scientific, with a density of 2.43-2.49 g/mL. Mineral oil from Acros Organics (ρ = 0.877 g/mL, η = 0.154 Pa·s) functioned as the dispersing medium. To make a suspension of beads, the materials were added to a plastic tube in this order: Beads, deionized water, mineral oil. The tube was then mixed with a vortex mixer on the highest setting for three minutes.
In all experiments, we use a TA Instruments AR-G2 rheometer. Before using the rheometer, we calibrate the instrument for inertia, bearing friction, and rotational mapping. These calibrations help ensure the instrument accurately measures torque changes as low as 0.1 nN.m and displacement down to 25 nrad. We used the parallel plate geometry with a 60 mm diameter stainless steel plate attached to the rheometer spindle and an immobile Peltier plate on the bottom with a 500 µm gap between the plates. In each experiment, the rheometer performs a 2 minute pre-shear step at 942 s$^{-1}$ ($= 15.71$ rad/s = 150 RPM) to destroy any preformed structures in the suspension. Then, shear rate ramps from 0.1 to 1000 s$^{-1}$ as viscosity is recorded.

Capillary bridges on aggregated glass beads are visually observed in micrographs with 20% beads and 1% water by volume (Figure D.1).

![Figure D.1: Micrographs of solid glass beads. d = 30-50 µm, $\phi_{\text{beads}} = 0.20$, $\phi_{\text{water}} = 0.01$.](image)

Water addition changes the suspension from a Newtonian fluid to a shear-thinning fluid (Figure D.2). The glass bead suspension viscosity compares favorably to previous work (McCulfor et al., 2011).

Glass bead suspension viscosity increased with increasing concentration of glass beads (Figure D.3). Below about 10 s$^{-1}$, no difference was observed between the different suspensions. Data generally agreed with previously reported work, with deviations appearing at
Figure D.2: Solid glass bead suspension viscosity versus shear rate with 1% water by volume (solid symbols) and without any water (open symbols) obtained at CSM (red circles) and at Rose-Hulman Institute of Technology (blue diamonds) (McCulfor et al., 2011). Error bars are ±1 standard deviation for 5 repeat measurements on each of four repeat suspensions (20 total measurements). Pure mineral oil viscosity shown as a dotted line for comparison.
higher bead volume fractions and lower shear rates.

Figure D.3: Solid glass bead suspension viscosity versus shear rate at varying glass bead volume fraction. Water volume is always 10% of glass bead volume. Solid symbols obtained at CSM; open symbols obtained at Rose-Hulman Institute of Technology (McCulfor et al., 2011).

As glass bead particle size increased, suspension viscosity decreased (Figure D.4). Again, data compared favorably to previously reported work (McCulfor et al., 2011).

In a hysteresis loop, the high viscosity values at low shear rates could not be recovered (Figure D.5 a). The flow curves with and without the preshear step cannot be distinguished (Figure D.5 a). Hysteresis at low shear rates was reproducible (Figure D.5 b). If the hysteresis loop starts at 1000 s$^{-1}$ instead of 0.1 s$^{-1}$, the high viscosity values never appear at low shear rates (Figure D.5 c). When several hysteresis loops were performed consecutively, no hysteresis was observed after the first (Figure D.5 d).
Figure D.4: Solid glass bead suspension viscosity versus shear rate at varying glass bead particle diameter. 20% glass beads and 1% water by volume. Solid symbols obtained at CSM; open symbols obtained at Rose-Hulman Institute of Technology (McCullof et al., 2011). Points are the average values from three repeat experiments.
Figure D.5: Solid glass bead suspension viscosity versus shear rate with hysteresis loops. In all plots, 30-50 µm beads were used, $\phi_{\text{beads}} = 0.20$, $\phi_{\text{water}} = 0.01$. Solid symbols are ramps from 0.1 to 1000 s$^{-1}$, open symbols are ramps from 1000 to 0.1 s$^{-1}$. (a) hysteresis loop with and without 2 minute preshear step at 942 s$^{-1}$. (b) three repeated hysteresis loops. A fresh sample is charged for each run. (c) a hysteresis loop from 1000 to 0.1 to 1000 s$^{-1}$. (d) 5 consecutive hysteresis loops performed on a single sample. total time for these five loops was 146 minutes.
A glass bead suspension held at a constant shear rate appeared to become less viscous over time (Figure D.6). The data suggests glass beads may be settling rapidly during the experiment. As beads settle, the fluid nearest the parallel plate becomes depleted of particles, so the measured viscosity will be lower than the actual viscosity. Stokes law indicates a direct relationship between settling velocity and the density difference between particles and the continuous phase:

\[ \nu_s = \frac{2R_s^2(\rho_s - \rho_f)g}{9\eta} \]  

(D.1)

Where \( \nu_s \) is particle settling velocity, \( R_s \) is particle radius (= \( \sim 20 \) \( \mu \)m), \( \rho_s \) is particle density (= \( \sim 2.5 \) g/mL), \( \rho_f \) is mineral oil density (= 0.877 g/mL), \( g \) is gravitational acceleration, and \( \eta \) is mineral oil viscosity (= 0.154 Pa.s). Stoke’s law yields a settling velocity of 9.2
$\mu m/s$. In the 500 $\mu m$ parallel plate gap, a particle would take 54 s to travel from the upper plate to the lower plate. We do not observe settling this rapid, but Stoke’s law does suggest that settling is a problem.

Photographs confirm settling of glass beads in mineral oil (Figure D.7). Here, full settling occurs over a $\sim$1 inch depth in one hour. Settling also occurs when water is present, however, settling proceeds much more slowly (Figure D.8). Here, some phase separation is apparent almost immediately (within 15 minutes); however, not much further separation occurs over the next 151 hours. When water is present, only a small layer of clear mineral oil is visible above the settled beads. In the absence of water, the beads settle to a more compact structure (Figure D.7).

![Photograph of glass beads settling in mineral oil](image)

Figure D.7: Solid glass beads settling in mineral oil (no water). 30-50 $\mu m$ beads, $\phi_{beads} = 0.20$, $\phi_{water} = 0$.

In an effort to eliminate settling, we performed experiments with hollow glass beads, which have a much lower density (1.1 g/mL) than solid glass beads (2.5 g/mL). The density difference between mineral oil and hollow glass beads is 0.24 g/mL, compared to 1.65 g/mL for solid glass beads. Hollow glass beads were purchased from AGSCO corporation. The average diameter is 8-11 $\mu m$, with 80% of the beads between 5 and 17 $\mu m$ (Figure D.9a). Visual observation showed large aggregates upon addition of water (Figure D.9b).
Figure D.8: Water coated solid glass beads settling in mineral oil. Varying bead diameter, $\phi_{beads} = 0.20$, $\phi_{water} = 0.01$.

Figure D.9: Micrographs of hollow glass beads suspended in mineral oil (a) without water and (b) with water ($\phi_{water} = 0.01$). $\phi_{beads} = 0.20$. 
Viscosity of hollow glass bead suspensions was measured using concentric cylinders geometry rather than parallel plates. Concentric cylinders eliminates the possibility of particle ejection. The radius of the inner cylinder is 14 mm, while the radius of the outer cylinder is 15.00 mm, giving a gap of 1.00 mm. The height of immersed cylinder is 42.00 mm. Suspensions were sheared at 1000 s$^{-1}$ for 2 minutes and then subjected to a shear loop from 1000 to 0.1 to 1000 s$^{-1}$. 10 values of shear rate were measured per decade. measurements were only accepted if 3 points were obtained within 3% of each other in a 1 minute window. Experiments were performed at varying glass bead volume fraction ($\phi_{\text{beads}} = 0.05$ or 0.10), water volume fraction ($\phi_{\text{water}} = 0, 0.05, 0.1$, and $0.2\phi_{\text{beads}}$), temperature ($0$ or $25$ °C), and mixing method (with or without sonication after vortex mixing). Viscosity increased as bead volume fraction increased (Figures D.10 and D.11). Viscosity increased with the addition of water; however, the concentration of the water had little effect (Figures D.10 and D.11). Viscosity decreased significantly at 0 °C compared to $25$ ° (Figures D.10 and D.11). Finally, the mixing method had no effect on glass bead suspension viscosity (Figures D.10 and D.11).

Although hollow glass beads have much lower density than solid glass beads; settling was still observed in the rheometer (Figure D.12). The viscosity of suspensions of hollow glass beads was measured at a constant shear rate over time. All suspensions had at least a 20% viscosity after 10 hours. The two suspensions that contain water had at least a 37% decrease in viscosity within one hour (Figure D.12).

Visual observation of hollow glass bead suspensions also confirmed that settling occurs (Figure D.13). Hollow glass beads actually rose to the surface of the mineral oil rather than settling.

We originally planned to form hydrates with the glass bead suspensions by converting the water bridges to hydrate. Hydrate formation typically takes hours; however, significant settling occurs in less than one hour. So, we could not perform hydrate forming experiment with glass bead suspensions. After studying glass bead suspensions, we began a search for potential model emulsions which act physically like water in crude oil but with simpler
Figure D.10: Viscosity of hollow glass beads suspensions in mineral oil and water at varying shear rate. Suspensions mixed in vortex mixer. Flow loop from 1000 to 0.1 s$^{-1}$ (closed symbols) and then 0.1 to 1000 s$^{-1}$ (open symbols). (a) $\phi_{\text{beads}} = 0.05$, $T = 0^\circ C$, (b) $\phi_{\text{beads}} = 0.10$, $T = 0^\circ C$, (c) $\phi_{\text{beads}} = 0.05$, $T = 25^\circ C$, (d) $\phi_{\text{beads}} = 0.10$, $T = 25^\circ C$. 
Figure D.11: Viscosity of hollow glass beads suspensions in mineral oil and water at varying shear rate. Suspensions mixed in vortex mixer and then sonicated in an ultrasonic bath. Flow loop from 1000 to 0.1 s$^{-1}$ (closed symbols) and then 0.1 to 1000 s$^{-1}$ (open symbols). (a) $\phi_{\text{beads}} = 0.05$, $T = 0$ °C, (b) $\phi_{\text{beads}} = 0.10$, $T = 0$ °C, (c) $\phi_{\text{beads}} = 0.05$, $T = 25$ °C, (d) $\phi_{\text{beads}} = 0.10$, $T = 25$ °C.
Figure D.12: Hollow glass bead suspension viscosity versus time at 100 s$^{-1}$ shear rate and 25 °C

Figure D.13: Hollow glass bead suspensions settling over time. Varying water volume fraction, $\phi_{beads} = 0.10$ and 25 °C
chemistry.
E.1 A Comparison of Hydrate Rheology Measurements in Literature

Comparing hydrate rheology measurements from literature can help explain the effect of measuring apparatus and also show the scope of work performed. Each study was performed in a different way. In some ways, this is beneficial because the diversity of measurements will help scientists have a good estimate of hydrate viscosity in many different scenarios. Unfortunately, since no two studies were measuring hydrates in exactly the same fashion, it is difficult to compare results.

Sometimes not enough information was provided to compare results of one study to others. Here, measurements from 18 studies are compared, including the three studies discussed in this document. Data was extracted from tables and graphs in published journal articles. Data from graphs was extracted using the software DataThief version 1.6 (downloaded from http://www.datathief.org), a shareware program. Performing data extraction on the curves in Figure 7.3b gave 2.1% error on the shear rate (x-axis) and 3.7% error on the viscosity (y-axis).

A compilation of literature data for relative viscosity at varying shear rate shows that relative viscosity values have been measured over a span of five orders of magnitude (Figure E.1). Relative viscosity is here defined as the measured viscosity divided by the unsaturated continuous phase viscosity. Sometimes, this definition leads to relative viscosities less than one. Many measurements contain dissolved methane (which lowers viscosity) and hydrate particles (which raises viscosity). At low volume fractions, the contribution of methane to viscosity can be more significant than the contribution of hydrates. In Figure E.1, each curve was obtained under unique conditions, namely, pressure, temperature, fluid composition, flow regime, and apparatus. This comparison is only intended to qualitatively show some
of the features of hydrate rheology. One commonality is shear-thinning behavior, observed in almost every data set. Also, viscosity always increased with water volume fraction (there are too many curves to label each water volume fraction in the figure).

Figure E.1: Relative viscosity versus shear rate for various studies in the literature.

Hydrate relative viscosity at varying particle volume fractions was extracted and compared (Figure E.2). The Krieger-Dougherty and Mills models were also plotted at two different maximum particle packing fractions for comparison. The models underestimate the measured values in most cases. The data by Zylyftari et al. (Zylyftari et al., 2013) reported viscosity at varying conversion of water to hydrate (green triangles in Figure E.2). This set of measurements indicates that temperature, shear rate, and water volume fraction are not sufficient to predict hydrate slurry viscosity. The fraction of water converted to hydrate is a key parameter that has a strong effect on viscosity.
Figure E.2: Relative viscosity versus water volume fraction for various studies in the literature.
E.2 Hydrate Rheology Modeling

Results across the three systems and other studies in literature indicate key variables in determining hydrate slurry viscosity. Key parameters include continuous phase viscosity ($\eta_{ext}$), initial water volume fraction ($\phi_w$), shear rate ($\dot{\gamma}$), and fraction of water converted to hydrate ($\chi$). The driving force for hydrate formation, which depends on temperature, pressure, salt concentration, and others is very important; however, it’s effect is lumped into the $\chi$ parameter, i.e., $\chi$ is a function of the driving force for hydrate formation. Temperature also appears in the $\eta_{ext}$ term.

The dependence of viscosity on each parameter in isolation has been studied. The dependence of viscosity on water volume fraction could be described by the Krieger-Dougherty model:

$$\frac{\eta}{\eta_{ext}} = \frac{1}{\left(1 - \frac{\phi}{\phi_{max}}\right)^{2.5\phi_{max}}}$$ \hspace{1cm} (E.1)

Where $\eta$ is viscosity, $\eta_{ext}$ is the viscosity of the continuous phase, $\phi$ is particle volume fraction, and $\phi_{max}$ is the maximum particle packing fraction. $\phi_{max}$ is taken to be 0.63 for random packing of hard spheres (Song et al., 2008). Note the notation for the continuous phase viscosity. $\eta_0$ is typically used; however, $\eta_{ext}$ is used for this section to distinguish from the Cross model parameter zero shear viscosity, $\eta_0$. Figure E.3a shows the curve for relative viscosity as a function of particle volume fraction.

The dependence of viscosity on shear rate is described by the Cross model:

$$\eta_r = \frac{\eta}{\eta_{ext}} = \frac{\eta_0 - \eta_\infty}{1 + (C\dot{\gamma})^m} + \frac{\eta_\infty}{\eta_{ext}}$$ \hspace{1cm} (E.2)

Where $\eta_0$ is the viscosity as the shear rate approaches zero (the zero-shear viscosity), $\eta_\infty$ is the viscosity as shear rate approaches infinity (the infinite-shear viscosity), $C$ is the inverse of the shear rate at which the viscosity begins bending towards the zero shear plateau, and $m$ is logarithmic slope of the shear-thinning regime. Figure E.3b shows the shape of a typical curve for relative viscosity as a function of shear rate.
Figure E.3: Typical shape of relative viscosity as a function of (a) particle volume fraction, (b) shear rate, (c) fraction of water converted to hydrate, and (d) inverse temperature (for continuous phase viscosity).
The dependence of viscosity on $\chi$ does not seem to follow any consistent trend (Figure 7.2). Especially notable is the lack of dependence on water volume fraction. Two further observations are notable. First, viscosity is maximum at some point near $\chi = 0.5$, although there is much variation from experiment to experiment. Second, from looking at the transient hydrate viscosity measurements (Figure 7.1), the maximum viscosity is about twice the viscosity measured at the end of the step. From these observations, the dependence of viscosity on $\chi$ could be described as a first approximation by:

$$\eta_r = \frac{\eta}{\eta_{ext}} = 2 - 4(\chi - 0.5)^2$$

(E.3)

Figure E.3c shows the curve for relative viscosity as a function of fraction of water converted to hydrate.

Finally, the continuous phase viscosity could be described by an Arrhenius type equation:

$$\eta_{ext} = A \exp\left(\frac{E_a}{RT}\right)$$

(E.4)

Where $A$ and $E_a$ are fitted parameters. Figure E.3d shows the shape of a typical curve for the natural logarithm of continuous phase viscosity versus inverse temperature.

As a first approximation, hydrate slurry viscosity as a function of all four parameters could be the product of each equation for viscosity as a function of only one parameter:

$$\eta_r = (\eta_{r,\phi_w})(\eta_{r,\dot{\gamma}})(\eta_{r,\chi})$$

(E.5)

Where $\eta_{r,\phi_w}$ is defined by equation E.1, $\eta_{r,\dot{\gamma}}$ is defined by equation E.2, and $\eta_{r,\chi}$ is defined by equation E.3. The fourth parameter, temperature, is accounted for in the continuous phase viscosity. Writing the model this way assumes that the dependence of viscosity on one parameter is independent of the other parameters. This assumption is not correct. The hydrate slurry viscosity for each emulsion clearly depends on both shear rate and water volume fraction (Figure 7.3).

A second version of the model can be formulated by writing the Cross model parameters as functions of water volume fraction and the continuous phase viscosity. Cross model parameters were determined from experimental data for hydrate slurry viscosity at varying
continuous phase viscosities, water volume fractions, and shear rates. Empirical equations were found for each of the four Cross model parameters as a function of continuous phase viscosity and water volume fraction:

\[ \eta_0 = \eta_{ext} \exp\left( (-25\eta_{ext} + 20)\phi \right) \]  \hspace{1cm} (E.6)

\[ \eta_\infty = 0.1\eta_0 \]  \hspace{1cm} (E.7)

\[ m = 1.8 \exp (-2.6\eta_{ext}) \]  \hspace{1cm} (E.8)

\[ C = 0.1 \]  \hspace{1cm} (E.9)

The complete model is written:

\[ \eta_r = \left( \frac{\frac{\eta_0-\eta_\infty}{1+(C\dot{\gamma})^m} + \eta_\infty}{\eta_{ext}} \right) (2 - 4(\chi - 0.5)^2) \]  \hspace{1cm} (E.10)

Where the Cross model parameters are defined by equations E.6 through E.9. This model requires a knowledge of shear rate, particle volume fraction, fraction of water converted to hydrate, temperature, and the Arrhenius constants for the oil phase.