RHEOLOGICAL INVESTIGATION OF HYDRATE SLURRIES

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ABSTRACT
The oil and gas industry is often plagued by the formation of clathrate hydrates in oil pipelines. While the industry originally had a heuristic of avoidance of clathrate hydrates they are moving to a heuristic of risk management. To successfully implement a risk management heuristic, time dependent phenomena of clathrate hydrate formation and flowline plugging must be known. The study of time dependent phenomena of formation and agglomeration are investigated using a TA Instruments AR-G2 rheometer with a pressure cell capable of operating at up to 13.8 MPa. Pressurized rheological experiments examine clathrate hydrates formed in situ. Both shear and oscillatory experiments have been conducted on the samples, giving flow and viscoelastic parameters. Shear experiments show sharp increases in viscosity upon clathrate hydrate formation indicating rapid aggregation. Transient oscillation experiments show a sharp increase in the elastic and loss moduli followed by a decrease in the loss moduli. Thus, both in situ clathrate hydrate formation and annealing are quantified. In addition these oscillatory measurements provided a novel technique for non-destructive investigation of clathrate hydrate aggregation over time.

Keywords: clathrate hydrates, rheology

NOMENCLATURE
G' Elastic modulus [Pa]
G'' Loss modulus [Pa]
\( \dot{\gamma} \) Shear rate [s\(^{-1}\)]
\( \eta \) Plastic viscosity [Pa*s]
\( \tau \) Shear stress [Pa]
\( \tau_y \) Yield stress [Pa]

INTRODUCTION
In 1934 Hammerschmidt discovered that clathrate hydrates block natural gas pipelines [1], since this discovery they have been of particular interest to the oil and gas industry. Initially the oil and gas industries were concerned with understanding the thermodynamics of clathrate hydrates as they implemented a heuristic of clathrate hydrate avoidance. However in recent years, the cost and environmental impact of avoiding hydrate formation in deepwater production and transportation is becoming increasingly impractical. These deepwater conditions have pushed the oil and gas industries towards a heuristic of risk management, that is forming hydrates while trying to avoid blockages. To effectively implement this new heuristic, phenomena like clathrate hydrate rheology must be understood. This paper shows how pressurized rheological measurements can be used to investigate the flow-ability of clathrate hydrate slurries. Rheological properties such as viscosity and yield stress are measured.

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EXPERIMENTAL METHODOLOGY
To investigate clathrate hydrate slurries a commercial TA Instruments AR-G2 rheometer equipped with a pressure cell was utilized (Figure 1). The pressure cell is a constant volume cell with a concentric cylinder geometry (cup radius 14mm and bob radius of 13mm) capable of operating at pressures of up to 13.8 MPa. The pressure cell is also equipped with a Peltier cooler with a temperature range from -10 to 150° C.

The AR-G2 is a controlled stress rheometer capable of conducting dynamic or steady shear tests over time. The dynamic oscillation tests can be performed at a frequency range from $7.5 \times 10^{-7}$ to 628 rad/s. The shear tests can be run with an angular rotation $1.4 \times 10^{-19}$ to 300 rad/s with torque sensitivity from 0.003 µN/m up to 200 mN/m. However, when the pressure cell is attached the sensitivity drops to approximately 100 µN/m.

In this paper shear and oscillatory time sweeps, as well as shear ramp experiments are presented. Shear time sweeps were conducted by running the rheometer at a constant shear rate (or speed). During the entire test torque measurements were recorded (every 10 seconds) and are report as effective viscosities. These measurements were used to detect clathrate hydrate nucleation and changes in the sample over time as it was sheared. Shear ramps are conducted by starting at a low shear rate and increasing the shear rate. Again torque measurements are recorded and reported as effective viscosities. These shear ramps are done on a much shorter time scale than the time sweeps, helping to eliminate convoluting effects. From these measurements information such as shear thinning can measured and yield stresses can be estimated. The last type of measurements was oscillatory time sweeps. Here the rheometer was oscillated at a constant frequency and constant strain. The torque responses were measured over time, reported as the elastic ($G'$) and loss moduli ($G''$). These tests are used to detect clathrate hydrate nucleation and changes in the sample over time, while under relatively quiescent conditions.

For all runs oil from the west African Coast was utilized. The oil was found to have good emulsion stability (on the time scale of months). The oil was originally heated to 60° C to dissolve any solids in the oil and was then homogenized with deionized water resulting in an average droplet size of $\sim 15 \mu m$. The oil was then loaded into the cell and pressurized with methane and allowed to equilibrate for five days, during which time the oil viscosity and system pressure were monitored.

RESULTS
The first experiment shown is clathrate formation during a shear time sweep. The sample was sheared at a constant rate of 100 s$^{-1}$ as it was cooled from 20° to 0° C (at a rate of 0.5° C/minute). After the temperature ramp the viscosity reached a steady value. In Figure 2, at approximately 200 minutes, clathrate hydrate nucleation occurred. Nucleation can be clearly seen by the large viscosity increase from approximately 0.6 to 1.1 Pa·s as the pressure drops from 9.52 to 9.45 MPa.

![Figure 2: Viscosity Increase and Pressure Decrease due to Methane Hydrate Formation During Steady Shear (0° C, 30% water cut, 100 s$^{-1}$)](image-url)
Clearly, clathrate hydrate formation can have a drastic effect on the viscosity of fluid. One can imagine how a similar result in a pipeline could lead to a blockage of the pipeline.

Steady shear is not the only way to detect clathrate hydrate nucleation. Oscillatory time sweep measurements can also show clathrate hydrate nucleation [2]. In Figure 3, clathrate hydrate nucleation can be seen at approximately 110 minutes where an increase in $G'$ and $G''$ is seen. The increase in $G'$ and $G''$ matches results obtained by Chippa et al. [2]. However, an interesting effect not shown by Chippa et al. [2] is that $G''$ peaks then decreases while $G'$ reaches a plateau. This suggests that the sample is annealing over time as it begins to behave almost totally elastically.

Clathrate hydrate nucleation is not the only phase change that can be detected by oscillatory time sweeps. Clathrate hydrate dissociation can also be detected, as shown in Figure 4. After completing a run with one sample, an oscillatory time sweep was run as the sample was heated at a rate of 0.5°C/minute. At the equilibrium temperature for methane hydrate at 10 MPa (~13 °C [1]) there is a notable drop in $G''$. This is a puzzling result as it suggests that the sample is behaving more solidly upon dissociation. Upon further consideration this puzzle can be unraveled, since the sample had been previously sheared several times, causing a breakup of the clathrate hydrate structure (with $G'$ and $G''$ coincident with each other at 0°C). The sample could already flow and was not acting like a solid. When the sample reached the dissociation temperature gas was released into the oil. The gas release could cause the oil to foam, which would cause this type of behavior (a decreased $G''$).

Phase transitions are not the only phenomena that affect $G'$ and $G''$. Shear also affects the moduli, as shown in Figure 5. First the clathrate hydrate nucleation can be seen as $G'$ and $G''$ increase (repeating the results in Figure 3). At approximately 220 minutes a shear ramp was conducted (1 s$^{-1}$ to 300 s$^{-1}$, linear ramp over 3 minutes), after which oscillations were resumed. Here $G'$ decreases and $G''$ increases. Shear clearly changes the macroscopic clathrate hydrate structure.
Shear ramps can be used to help determine the yield stress of a sample (which is important in determining if a sample will flow). The shear ramp that occurred at ~220 minutes in Figure 5 is shown in Figure 6. Here the shear stress is plotted against the shear rate and is fit to a Bingham model (equation 1) [3], which is fit with a yield stress of 66.8 Pa.

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

(1)

Shear Rate (s\(^{-1}\))

0 50 100 150 200 250 300

Shear Stress (Pa)

0 50 100 150 200

Data

Bingham Fit

Yield Stress: 66.8 Pa

Viscosity: 0.425 Pa*s

Figure 6: Bingham Fit to Shear Ramp of Sample that Formed Clathrate Hydrates During Oscillatory Measurements

A shear ramp was also conducted on the system similar to figure 2 (clathrate hydrates were formed while subjected to a constant shear of 100 s\(^{-1}\)). As shown in Figure 7, this fit gives a yield stress of 9.41 Pa. This is nearly seven times lower than the system formed in quiescent conditions, suggesting that forming clathrate hydrates under shear breaks up aggregate structures, and that flowing the system may help to prevent plugging.

Shear Rate (s\(^{-1}\))

0 20 40 60 80 100

Shear Stress (Pa)

0 10 20 30 40 50 60 70

Data

Bingham Fit

Yield Stress: 9.41 Pa

Viscosity: 0.563 Pa*s

Figure 7: Bingham Fit to Shear Ramp of Sample that was Sheared at 100 s\(^{-1}\) During Clathrate Hydrate Formation

CONCLUSIONS

Rheology has been shown to be an effective tool to study clathrate hydrate formation and aggregation. Clathrate hydrate nucleation was observed in both shear and oscillatory time sweep experiments. The oscillatory measurements also provided a novel way to detect clathrate hydrate dissociation, as well as structural evolution over time. In addition, shear reduces the effective Bingham yield stress of the hydrate sample. These results suggests that clathrate hydrate formation may not be overly problematic in a pipeline as long as the clathrate hydrates formed can be sufficiently sheared. Finally a clathrate hydrate sample that is continuously sheared may be breaking up over time, while a sample remaining under quiescent conditions appears to continue to aggregate into larger structures.

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