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HYDRATE RHEOLOGY OF WATER-IN-OIL EMULSIONS WITH CYCLOPENTANE

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Abstract. *Hydrates of natural gases are crystalline solids, composed of water and light hydrocarbon molecules that assemble in special structures under certain conditions of pressure and temperature. For most offshore production facilities, it is a major concern for the oil and gas industry, given that it can lead to a full blockage of subsea and a complete stop of petroleum flow. However, avoidance costs have grown too high, so the industry began shifting towards a risk management methodology. Within this strategy, a promising field is the evaluation of rheological properties of hydrate slurries: its full understanding can help predicting if hydrates formation will lead to a blockage, becoming a valuable tool in risk assessment of many activities. The present work is a part of this effort, employing an emulsion combined with cyclopentane (known hydrate former at atmospheric pressure) to evaluate different methods. In order to fulfill this objective, the rheological behavior of water-in-oil emulsion, with and without cyclopentane, was studied in rotational and oscillatory tests, under hydrate forming conditions. The system response to changes in thermal (minimum temperature and cooling rate) and hydrodynamic (shear) parameters was also briefly investigated.*

Keywords: *Hydrates, Rheology, slurry*

1. INTRODUCTION

Hydrates of natural gases are crystalline compounds, similar to ice, that result from combination of water and light hydrocarbon molecules under specific pressure and temperature conditions. Since its first occurrence, in 1934, it has been a major concern to the oil and gas industry, due to its potential of full pipeline blockage – for this reason, the classical approach has been an "avoid at all cost" strategy, from a project perspective. However, in recent years, the oil and gas industry has been facing a new dilemma: despite the fact that the exploratory frontier is getting more and more challenging, from a hydrate point of view, prevention has become too costly, or even technologically unfeasible. This scenario forced the industry to pursue a risk management solution, searching for methods to evaluate blockage potential and hydrate transportability, both inherently related to the fluid rheological behavior.

Many works, employing different equipments, such as flow loops, rheometers or viscometers, have addressed this problem, but the phenomenon is still poorly understood and prediction tools are unreliable. This scenario encourages the use of low-pressure rheology as a mean to improve its comprehension through easier testing and direct visualization. In fact, Kalbus, *et al.*, 1995, proposed a protocol for hydrate inhibitors identification based on the induction time and the spike in viscosity observed when hydrate forms, using a viscometer at atmospheric pressure. Peixinho, *et al.*, 2010, studied hydrate slurries rheology compared to a simple water-in-oil (w/o) emulsion and concluded that, despite both systems exhibit shear-thinning behavior, each one presents distinct rheological responses, and the hydrate formation process induces a far more aggressive increase in viscosity than ice. More recently, Linares, *et al.*, (2014) made a complete rheological characterization of a w/o emulsion and suggested it would be a good model fluid for hydrate studies – Silva (2014) adapted the proposed fluid which, in turn, is the basis of the present work.

The current study follows this line of work, using cyclopentane (CP) as hydrate former at atmospheric pressure, mixed with a w/o emulsion to make rheology measurements of a hydrate slurry. CP was a suitable choice because its characteristics (forms Structure-II hydrates, insoluble in water, high – and well established (Fan, *et al.*, 2001) - equilibrium temperature with the hydrate phase – 7,8°C, widely available and stable) make it a good analogue to gas hydrates, while not demanding special storage or handling. In order to achieve this goal and slightly inspired by a work by Rensing, *et al.*, 2008, several experiments were conducted to analyze the system response, with and without CP, to shear, stress, sub-cooling and cooling rate. Shear time-sweeps varied the test temperature and, thus, sub-cooling, while oscillatory time sweeps investigated sub-cooling, cooling rate, stress and shear during the cooling ramp.

2. EXPERIMENTAL SECTION

2.1 Materials

The system studied is a w/o emulsion with 37% internal phase (*v*/*v*), based on a model fluid proposed by Silva (2014). The oil phase is Shell Morlina S2 BL 10, a light mineral oil with low viscosity, and the aqueous phase is deionized water. Two surfactants were employed to stabilize the emulsion: sorbitan monooleate, a non-ionic surfactant commercially known as Span80; and dioctyl sodium sulfosuccinate, an anionic surfactant. The CP, added only to the hydrate-forming fluid, is an alicyclic hydrocarbon with very low miscibility in water. Table 1 displays the main properties of each component:

Table 1. Density and Viscosity of fluid components.

Component	Density (kg/m³)	Viscosity (Pa.s) [(1)]
Shell Morlina S2 BL10	881	0,020
Sorbitan Monooleate	986	1,2-2,0
Dioctyl Sodium Sulfosuccinate	1100	-

[(1)] measured at 20°C

2.2 Preparation

The emulsion was prepared in the following steps: first, AOT at 0,5% *w*/*w* was added to the deionized water and solubilized for 15 minutes. Then, Span 80 (4,5% *w*/*w*) was added to the mixture, which was afterwards slowly put together to the mineral oil while being stirred by a high-speed homogenizer at 8000rpm for 8 minutes. The amounts of each surfactant were the same as Silva (2014) and Linares, *et al* (2014). This procedure lead to emulsions stable for almost two months, provided that it was not left idle for over one week, but did not always created w/o emulsions – whenever this was the product, CP was added and homogenized through simple agitation. The resultant water concentration was 28% *v*/*v*, so the hydrate-forming fluid was well above the stoichiometric CP to water molar ratio of 1:17, meaning that CP was in excess for the hydrate formation reaction.

Direct visualization, as displayed at Fig.1, indicated that the water droplet size of the prepared emulsions was very small, which probably explains the strong stability of the emulsion. Additional methods (Mastersizer 2000 and direct image processing through the software FIJI) also confirmed small droplet size distribution, even after several weeks.

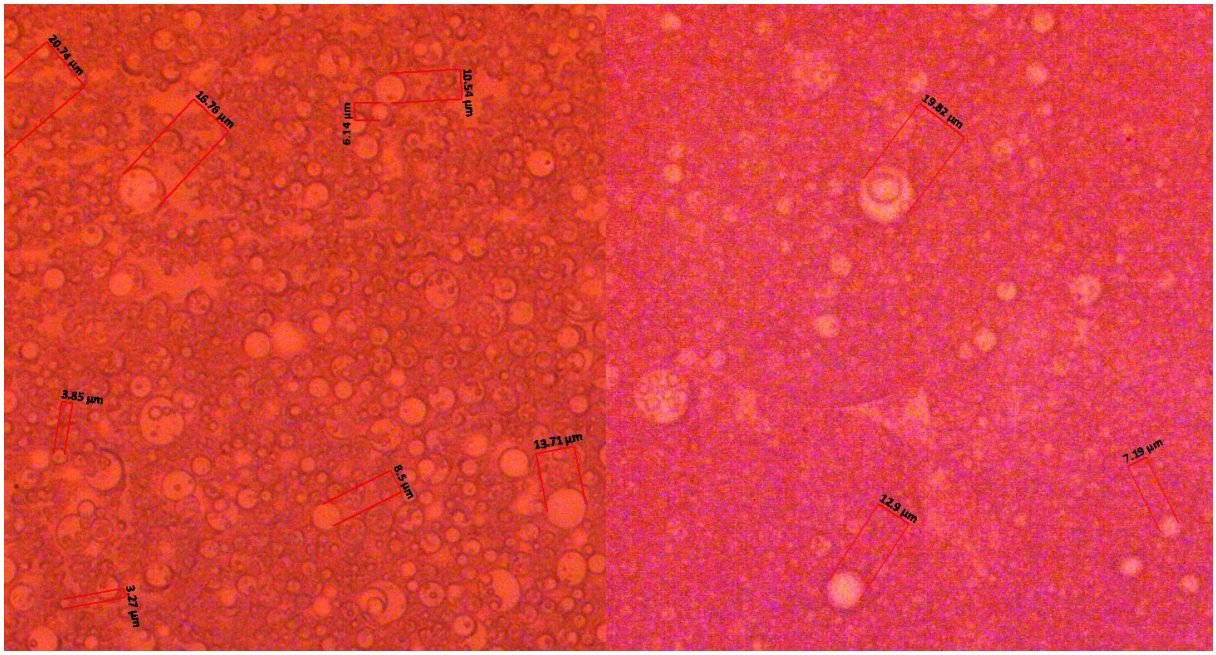


Figure 1. Droplet size measurements for prepared w/o emulsion, without CP.

2.3 Protocol

Once any fluid was prepared, it was left to rest for at least one day before any test – this resting time has proven to be critical to achieve coherent results. After that, a small amount was placed in a Physica MCR301 rheometer equipped with a Couette geometry CC27 12013. The sample was then cooled to the desired test temperature at a defined rate, either -0,1°C/min or -0,3°C/min.

The first set of experiments was shear time sweeps. In these tests, the shear rate was kept constant at $1s^{-1}$ and, after a period of time for thermal stabilization, the sample was cooled down to different minimum temperatures, in order to evaluate the effect of sub-cooling in induction time and the spike in viscosity.

Oscillatory time sweeps were separated into two groups, but every test started at 20°C. The first one did not change shear rate, shear stress nor frequency and investigated thermal variables: cooling rate of -0,1°C/min or -0,3°C/min, and test temperatures of -2°C and 0°C. The second group focused in the effect of shear rate during the cooling stage, imposing shear rates of $0s^{-1}$, $0,1s^{-1}$, $1s^{-1}$ and alternately $0s^{-1}$ and $0,1s^{-1}$. Table 2 and Table 3 summarize the test conditions explored:

Table 2. Summary of test conditions for the first set of oscillatory tests.

	Teste #1	Teste #2	Teste #3	Teste #4, #5 and #6
Final Temperature (°C)	-2	-2	-2	0
Cooling rate (°C/min)	-0,3	-0,3	-0,1	-0,3

Table 3. Summary of test conditions for the second set of oscillatory tests.

	Teste #7	Teste #8	Teste #9	Teste #10 and #11
Final Temperature (°C)	0	0	-2	0
Shear rate (s^{-1})	1	0,1	0	Alternately 0,1 and 0

3. RESULTS AND DISCUSSION

3.1 Shear time sweeps

As expected, the results showed a clear relationship between test temperature, induction time and rheology: the higher the sub-cooling, lower the time required for hydrate formation and higher the spike in viscosity, indicating an increase of hydrates formed. As presented below, Fig. 2 shows a small increase in viscosity at -2°C, opposite to previous thixotropic behavior. Figure 3 displays a significant growth at -5°C, while Fig.4 reveals a huge spike – over 100 times - in viscosity at -10°C. It must be highlighted, however, that many tests failed to show any rise in viscosity during the experiment, reinforcing the stochastic nature of the phenomenon – Figure 5 displays examples of such tests. It must be noted that those were longstanding tests, possibly due to the very small solubility of CP in water (Dirdal, *et al.*, 2012).

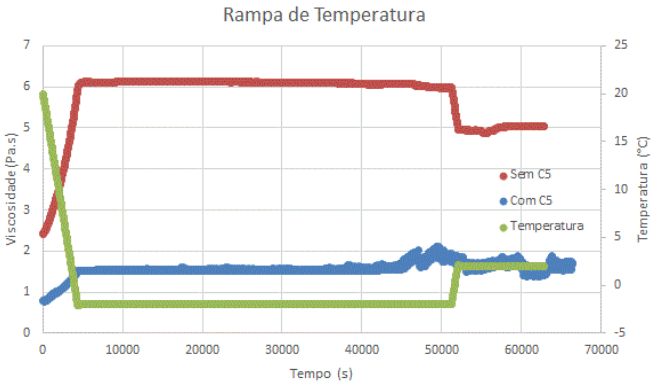


Figure 2. Shear time sweeps at $1s^{-1}$, -2°C.

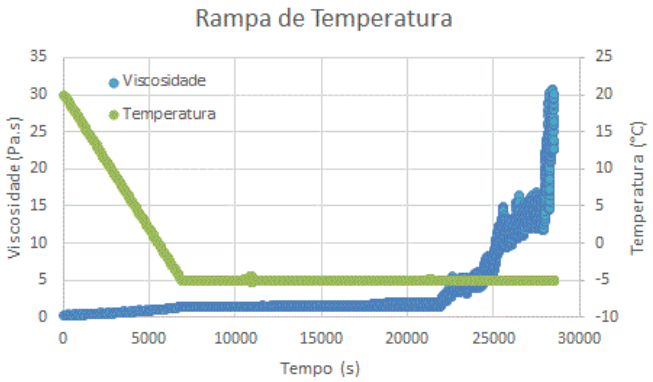


Figure 3. Shear time sweeps at $1s^{-1}$, -5°C.

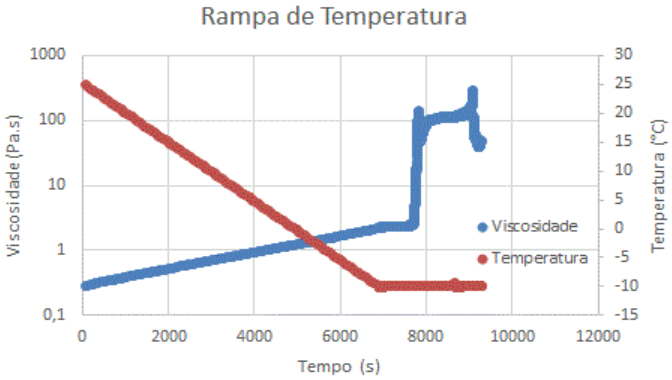


Figure 4. Shear time sweeps at $1s^{-1}$, -10°C.

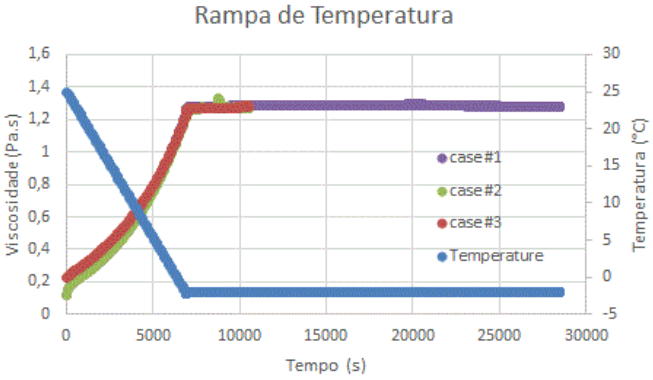
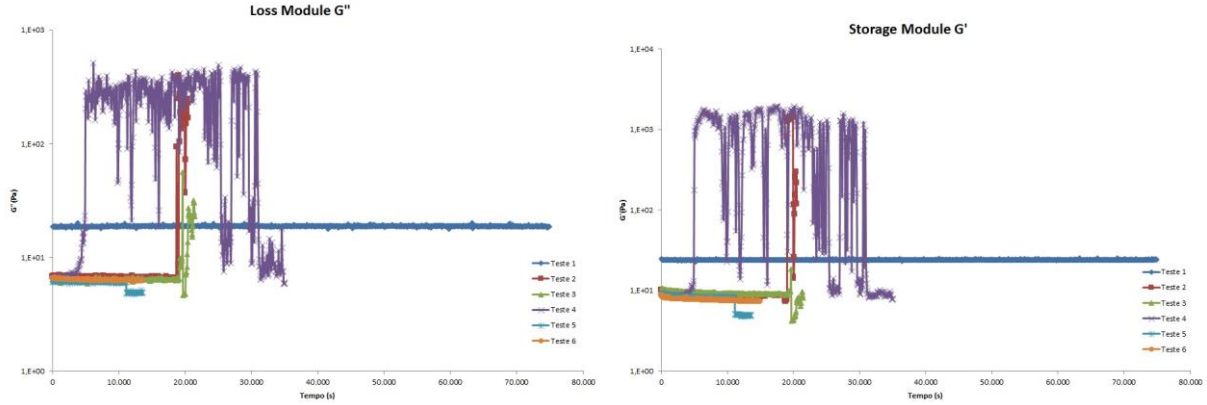


Figure 5. Shear time sweeps at $1s^{-1}$, -2°C.

Every test that displayed signs of hydrate formation showed some fluctuation in viscosity after the spike. This behavior can be understood as a contest between destruction (hydrodynamic) forces, that erode and destroy aggregates, and cohesion forces, that tend to create an agglomeration process. The same dispute happens in real production system and may be the key to predict if a system will flow or form a blockage.

3.2 Oscillatory time sweeps

In order to facilitate data analysis, oscillatory time sweeps results were grouped: for each modulus of each set of tests, one Figure was built to present the results. Figure 6 displays the Loss and Storage Moduli for the first set of experiments, while Fig. 7 shows the same results for the other group.



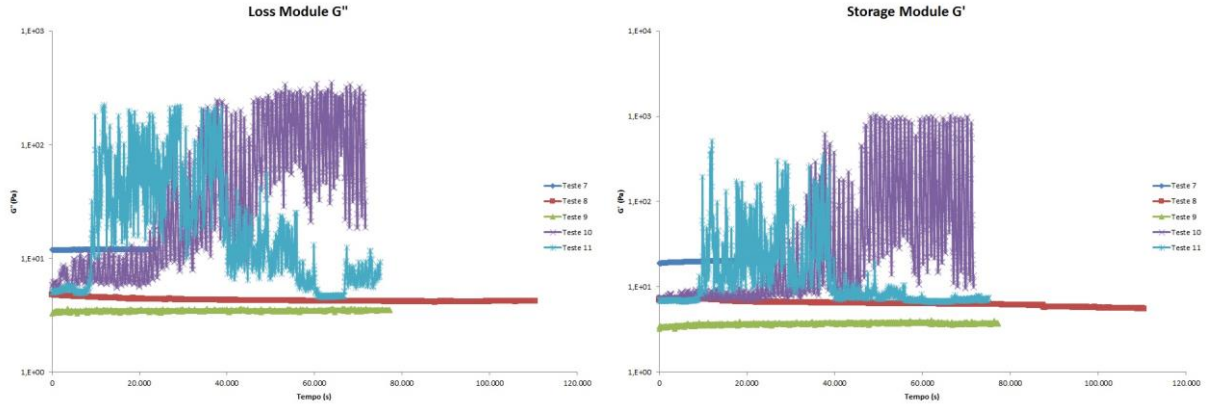
(a) (b)

Figure 6. Oscillatory time sweeps for thermal parameters. (a) Loss Module. (b) Storage Module.

In Fig.6, test#1 represents a fluid without CP – there is no sign of ice formation, and this result is consistent with works from Clausse, *et al.*, 2005, and Heneghan and Haymet (2002), that showed that water droplets of small size can stay liquid well below its freezing point. The Storage Module, which is greater than the Loss Module for all samples, shows a slight decrease over time. The jump in the measurements happens at the same time for both Moduli, manifesting the change in the material's characteristics – since tests #2 and #4 achieve the same magnitude, it is reasonable to allege the same amount of hydrates was formed in both tests, despite the different sub-cooling. Cooling rate did not express significant effect on the experiments, as test#3 was performed at -0,1°C/min and the hydrate formation time was almost the same as other tests.

As in the shear time sweeps experiments, there is fluctuation in the rheological parameters, probably related to the same mechanism of breakage and assembly of agglomerates. The drop in the measures of test#3 and #5 may be associated to lubrication effects resulting from changes in the geometry gap due to particle adhesion to surface.

It's interesting to notice that the smallest induction time was obtained for the minimum sub-cooling – an unexpected result. This behavior was explained by the combined effect of cooling rate and shear rate, as Fig.7 shows.



(a) (b)

Figure 7. Oscillatory time sweeps for shear parameters. (a) Loss Module. (b) Storage Module.

From Fig.7, it's clear that, once again, there is no sign of ice formation (test#7). In addition, test#8 ($0{,}1s^{-1}$) and #9 ($0s^{-1}$) also displayed no footprint of hydrate formation. The remaining experiments, however, present a system response compatible with hydrate formation, even though each sample reacted in a distinct way: while test#10 showed a progressive increase in rheological parameters, test#11 had a jump in both Moduli, followed by a sudden return to original values, possibly reflecting the breakage of a complex structure. Those results indicate that there might be an optimum shear rate during cooling that favors hydrate formation.

4. CONCLUSION

Rheological measurements of a CP-hydrate slurry have been carried out using a Couette geometry and a Physica MCR301 rheometer, from Anton Paar. The experiments were designed to detect hydrate formation and investigate the importance of both thermal (sub-cooling and cooling rate) and hydrodynamic (shear rate) parameters on CP-hydrate slurry rheology.

The results show that, although it may be easy to identify hydrate formation, it can be difficult to promote CP-hydrate (or ice) formation in a system with very small droplet size. Even when such event occurs, it may take a long time – sub-cooling and shear during cooling seem to play a major role in the process. In fact, there seems to be an optimum shearing condition in the cooling stage that favors hydrate formation

From the analysis of the collected data, it is possible to assume that the cooling rate does not affect the test results, at least within the narrow selected range. In addition, oscillatory time sweeps proved themselves more adequate to hydrate slurries studies, since hydrate formation occurred at most tests and within a narrower period, when compared to shear time sweeps.

5. ACKNOWLEDGEMENTS

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