18th Brazilian Congress of Thermal Sciences and Engineering
November 16-20, 2020 (Online)

ENC-2020-0027
RHEOLOGY OF CYCLOPENTANE HYDRATES FORMED IN WATER-IN-MODEL OIL EMULSIONS

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Abstract. The study of hydrate rheology is becoming increasingly important due to the constant expansion of the oil and natural gas industries in deeper waters. The hydrate formation process in the oil and gas sector is a big concern mainly because, in many cases, it ends up generating the blockage of pipelines, which leads to the production interruption, causing safety problems, and loss of time and money. Hydrates are crystal compounds formed by water and small gas molecules at typical thermodynamic conditions of high pressure and low temperature. In order to study the hydrates phenomenon, chemical compounds that induces their formation at atmospheric pressure are used, such as cyclopentane (CP) and tetrahydrofuran (THF). In this study, an emulsion formed from CP, Primol oil, deionized water, and Span 80 as a stabilizer agent is employed. The results aim to analyze the effect of several parameters on hydrates formation.

Keywords: *Hydrates, Rheology, Emulsions, Cyclopentane*

1. INTRODUCTION

As the technological evolution and the constant energy demand increases, the industry has to focus on finding out new ways of producing energy. Specifically, in the oil and gas industry, mainly at offshore environments, the ultra-deep and icy waters exploration is already a reality. One of the biggest difficulties in this scenario is to ensure the transportation of the oil and gas by the flowlines.

Due to the harsh conditions, large sections of flow pipes are subjected to great thermodynamic variations, which facilitate the formation of paraffins, asphaltenes, and hydrates. This could lead to the partial blockage or, even worse, the full obstruction of the production (Bay, 2010).

Hydrates are crystalline compounds formed basically by water and small gas molecules, such as methane and ethane, which are formed under high pressures (above 5 MPa) and low temperatures (around 4 °C). Under such conditions, the gas molecules are trapped and kept by the water hydrogen bonds (Sloan, 2008).

Some methods are used to mitigate the hydrate formation, but the most used are the chemical inhibitors. Depending on the acting form of these chemical reagents they are divided into thermodynamic inhibitors (TI's) and low dosage hydrate inhibitors (LDHI's). TI's such as methanol, glycol, and saline solutions act changing the hydrate equilibrium curve. That is, the equilibrium temperature for hydrate formation is reduced for a certain pressure, shifting the chemical potential of water. However, a great amount of these inhibitors is necessary to be efficient in the process of hydrate formation. On the other hand, the LDHI's are divided into Kinetic Hydrate Inhibitors (KHI's) and anti-agglomerants (AA) (Fu et al., 2001). The formers act retarding the time for hydrate formation, which makes them time-dependent, while the AAs allow the hydrate crystal to form and maintain the hydrate particles in the oil phase avoiding their aggregation. LDHIs are generally used in amounts of less than 3% of the water produced, resulting in lower costs for the processes (Tohidi et al., 2015).

Although many methods to mitigate hydrate formation had been found, this issue still continues to be a huge problem in the oil and gas industry. An approach that can bring better insight into the phenomenon is through rheology, since hydrates can be analyzed at similar thermodynamic conditions as the ones found in the deep-waters fields or by analogy, through chemical compounds that facilitate the hydrates formation at atmospheric pressure, such as Cyclopentane (CP) and Tetrahydrofuran (THF). These substances permit to understand and to find new cheaper ways of reducing the hydrates impact on the production - see the works reported by De Lima silva et al., (2017 and 2020) and Karanjkar et al., (2016).

The purpose of this work is to study the CP hydrate formation formed from water-in-oil emulsions using a rheological approach. Several parameters that influence the hydrate formation are analyzed.

2. METHODOLOGY

The experiments employed water-in-oil emulsions formed from CP, Primol oil (mineral oil), deionized water and Span 80 as a stabilizer agent. The CP constitutes 22.8% (v/v) of our emulsion and it is always in an excess quantity of the stoichiometric requirement to form hydrate, which is equal to one mole of cyclopentane to 17 moles of water (Lo et al., 2008). The emulsions were prepared using the following methodology: Firstly, the weighted quantities of Span 80 of the continuous phase (Primol oil) where deposited in a bottle, afterwards, the disperse phase (deionized water) was added dropwise, followed by a strong agitation by a Turrax homogenizer, operating at 10000 rpm for 7 min. As CP is very volatile, it was added in a second agitation time using the Turrax homogenizer at 7000 rpm for 5 min. Emulsions were prepared using 30% of water volume fraction and 1.4% of Span 80. The emulsions are found to be stable against coalescence for at least 72h.

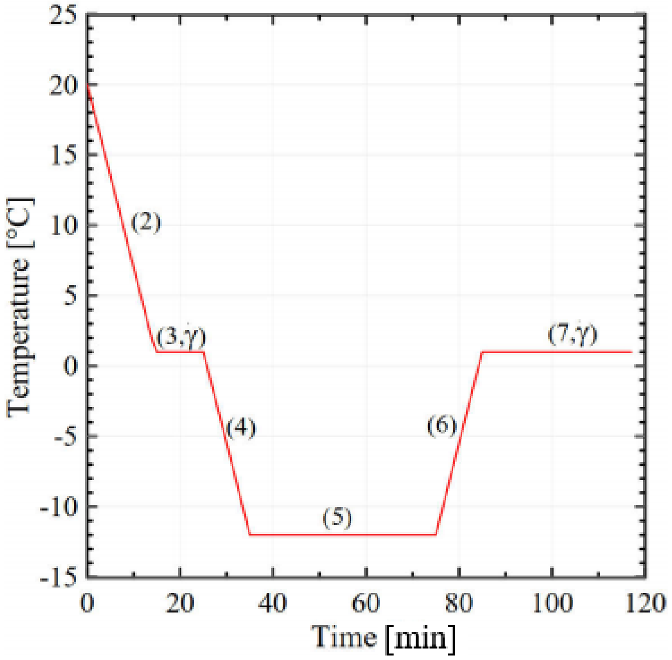

Figure 1: Thermal treatment of the sample for the hydrate's formation tests.

All the tests were performed using the rotational rheometer Physica MCR 301 (Anton Paar). The rheometric geometries employed were the concentric cylinders with rotor and cup radius of 14.460 mm and 13.332 mm, respectively. The bob and cup employed have roughened surfaces to avoid apparent slippage of the bulk fluid, since velocity gradients are produced in the material layers with lower viscosity located next to the wall (Yoshimura and Prud'homme, 1988). Differences in viscosity due to the material layers may arise when the concentration of suspended particles is lower at the wall than in the bulk. Apparent wall slip has been studied in tetrahydrofuran hydrates by De Lima Silva et al., 2019. For that sort of hydrates, the authors reported that for high shear rates ranges (around 500 s^{-1}), no apparent wall slip occurs, even for geometries with smooths surfaces. However, for low shear rates (10 s^{-1}) and transition shear rates (100 s^{-1}) a discrepancy within the viscosity results was noted, indicating an apparent wall slip.

The emulsion was prepared at room temperature, and it was transferred to the rheometer where the temperature was previously set at 20 °C. Fig. 1 shows the temperature profile employed in the rheometer. The first step is the fluid preparation. The steps are denoted in Fig. 1 with numbers in parenthesis. In the second step, a linear temperature ramp from 20 °C to 1 °C is performed. Then, a shear rate is applied for 10 min. After that, another linear ramp from 1 °C to -12 °C is done. The fluid is kept at the temperature of -12 °C for 40 min in order to help the hydrate formation. So, another linear ramp to return to 1°C is finally imposed, when the material is subjected to a constant temperature of 1 °C and hydrate formation is analyzed. This temperature is kept constant until the end of the experiment. For this temperature, our subcooling degree is 5.4 °C taking a hydrate equilibrium temperature of 6.4 °C (Sloan and Koh 2007). After this, the shear rate a priori imposed is initialized and the viscosity behavior and other rheological parameters are monitored over the test time.

3. RESULTS

The preliminary results obtained with this methodology are displayed through viscosity curves versus test time. The results presented in Figs. 2, 3, and 4 show only the hydrate´s formation step, that is to say, only when the temperature reaches 1 °C (step 7 in Figure 1).

3.1 Hydrate formation curve

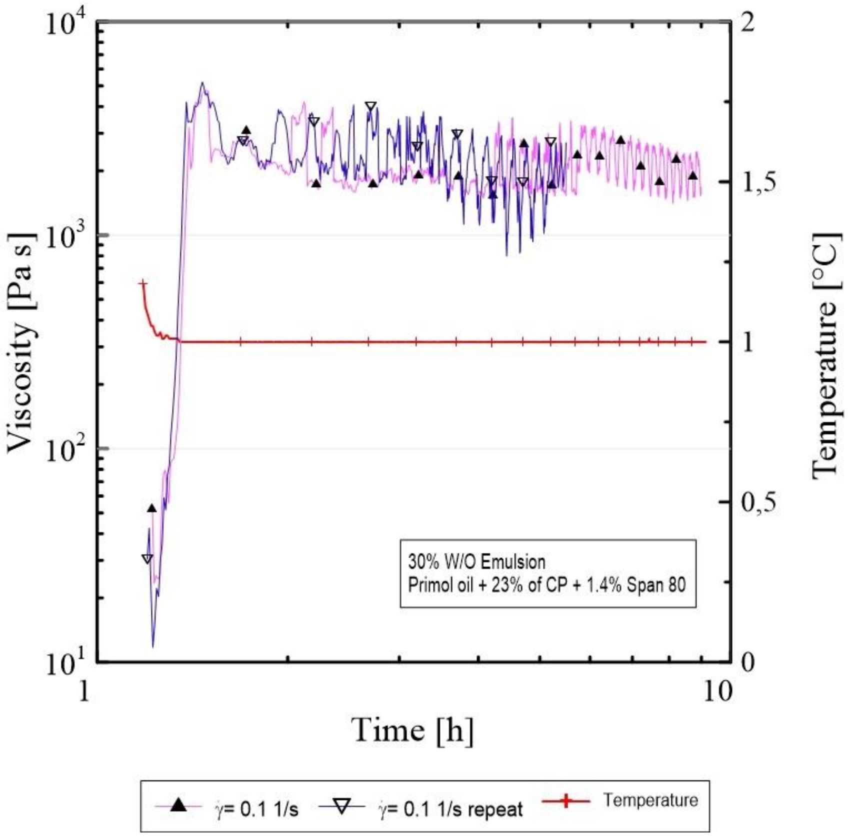

Figure 2 - Viscosity behavior for a 30% water-in-oil emulsion. Repeatability test.

Figure 2 shows the typical behavior of viscosity when hydrate formation occurs. Two different experiments were conducted on different days over the same conditions to achieve higher reliability of the results obtained. The emulsions were prepared with a water volume fraction of 30%, 23% of CP, and 1.4% of Span 80. For this specific case (Fig.2), the tests were conducted at a shear rate of 0.1 s^{-1}. As noted, both curves are qualitative and quantitative similar, as in the induction time when hydrates begin to form after the first hour, as well as when the viscosity attains the maximum value – between the second and third hour of experiment. After a specific experimental time, the viscosities tend to reach the steady state, but both reconstruction and shear forces continues to act through the hydrate crystals, causing a viscosity floating around the final viscosity value. For the particular experiments showed in Fig.2, the difference in the stable viscosity between the two curves after hydrate formation varies around 12%. It is a conservative value for this stochastic phenomenon. The repeatability curve was carried out up to 8 h, since no changes in viscosity were noted from the third hour of the experiment.

3.2 Shear rate effect

Figure 3 shows the hydrate viscosity behavior due to the shear rate variation. All the parameters were kept constant, except the shear rate, which was varied by 4 orders of magnitude, from 0.1 s^{-1} up to 100 s^{-1}. For each test, the same shear rate was applied in both, step 3 and step 7 (shown in Figure 1).

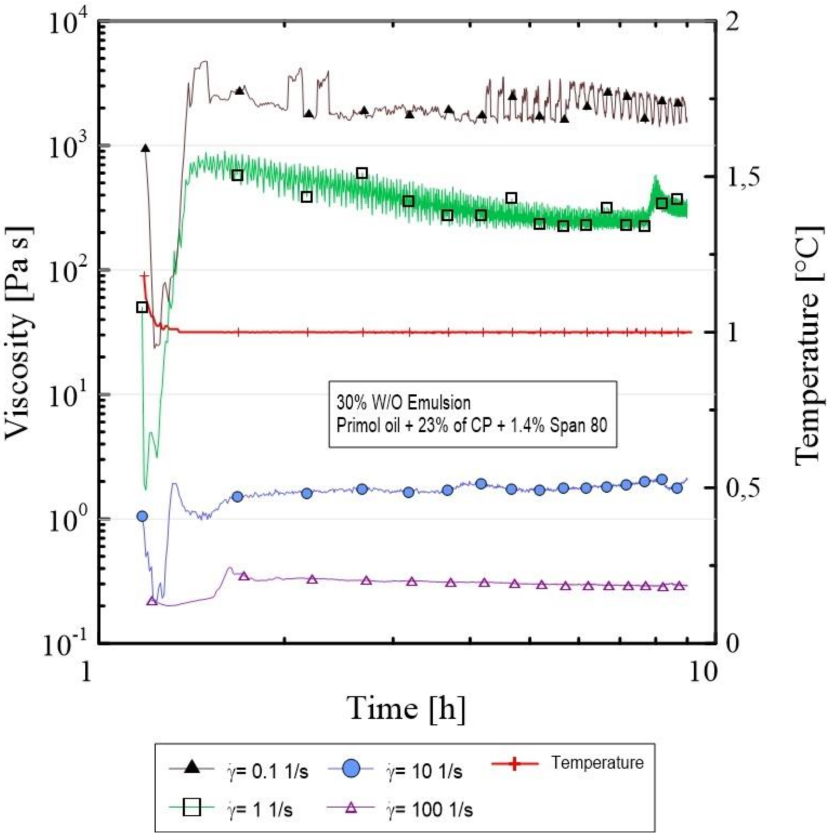

Figure 3 - Viscosity behavior at different shear rates.

As the shear rate increases, the viscosity value obtained at the steady state decreases, indicating that the analyzed material has a shear thinning behavior. At this point, it is worth mentioning that the hydrate slurry formed in each case is not necessarily the same material. Therefore, this shear thinning behavior can be associated not only to the competition between the reconstruction forces of the structure and the shear forces caused by the flow, but it can be also due to a change of the fluid itself because the amount of hydrates formed in each case can be different. In the cases analyzed, for a shear rate of 0.1 s^{-1}, the reconstruction forces are able to achieve and maintain a balance with the breaking shear forces. In contrast, for a shear rate of 1 s^{-1} the shear forces are stronger than the cohesion ones, therefore, the viscosity value gradually decreases as more hydrate aggregates are broken, thus, the time required to reach the steady state is longer. As hydrates do not form homogeneously between the cup and bob geometry, large viscosity fluctuations were observed for the results obtained with both shear rates of 0.1 s^{-1} and 10 s^{-1}. Probably, this behavior is caused by the size of aggregates that could jam and slip between the instrumental gap. No significant viscosity fluctuations were observed for the others shear rates employed, a possible explanation could be related to the fact that the hydrate particles resulted from the formation are broken and flow freely by the gap.

It is worth mentioning that for higher shear rates (such as shown for 100 s^{-1}) an increment in viscosity was not noted, despite hydrate formation was visualized at the upper part of the rotor after the end of the experiments, (see Figure 4). A first explanation could be related to the size of hydrate agglomerates formed. Due to higher levels of shear rate, as soon as hydrates try to agglomerate, they are broken by the shear forces. So, hydrates agglomeration occurs in the upper part of the rotor, due the absent of the shear forces. Moreover, slippage can be occurring next to the wall, which would also lead to the lower viscosity values measured. As observed in Fig. 5, the CP hydrates formed using Span 80 as an emulsion stabilizer could form a specific morphology that could induce jamming (Karanjkar et al., 2016), or in our case, apparent slippage. This specific morphology is characterized by a porous and hairy structure (point out by the red circles in Fig. 5), probably leading to lighter hydrates, which would also help to move the crystals to the top of the geometry**.**

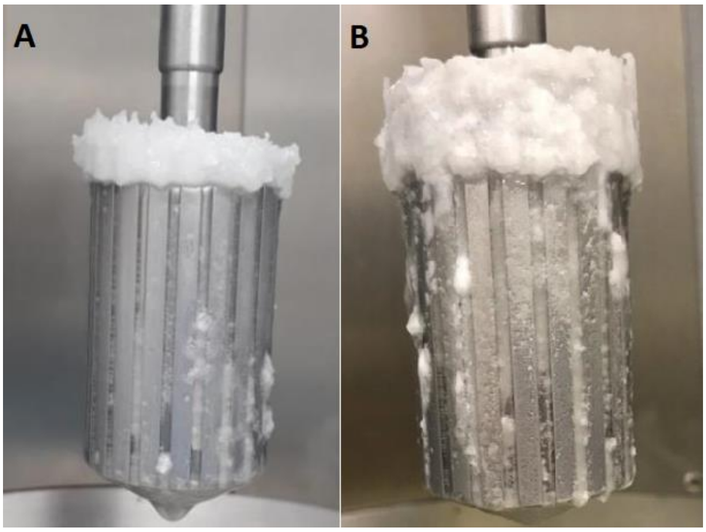

Figure 4 - Hydrate accumulation at the upper part of the rotor for shear rates of 50 s^{-1} (A) and 100 s^{-1} (B). The pictures were taken after the end of each experiment.

Figure 5. CP hydrates with porous and hairy morphology. The red circles denote some visible porous structures.

Finally, it is important to say that CP hydrates also exhibit other sorts of behaviors besides shear-thinning, as yield stress (Ahuja et al., 2015), mild hysteresis (Karanjkar et al., 2016) and probably more rheological characteristics that deserve a deeper investigation.

3.3 Viscosity behavior without CP addition

To avoid combining the effect caused by the pure hydrates and ice, all our experiments were conducted at a temperature higher than 0 °C, at 1 °C, as indicated in step 7 in Figure 1. However, to confirm that the effect observed in viscosity is only caused by the hydrate formation, a test without CP was performed (see Fig. 6). In this case, the emulsion was prepared with 30% water volume fraction and with 1.4% of Span 80 and the shear rate was 1 s^{-1}. The curve of 1 s^{-1} showed in Fig. 3 was plotted again in Fig. 6 for comparison reasons.

As noted in Fig.6, the experiment that was conducted without CP (purple curve) did not form hydrate. When the temperature reached 1 °C, a decrease in viscosity was observed, which confirms that hydrates do not form. This result is expected, since the CP is the substance that promotes hydrate formation, however, the result is valuable to observe that there is no ice in the sample, or that it does not contribute to the increase in viscosity.

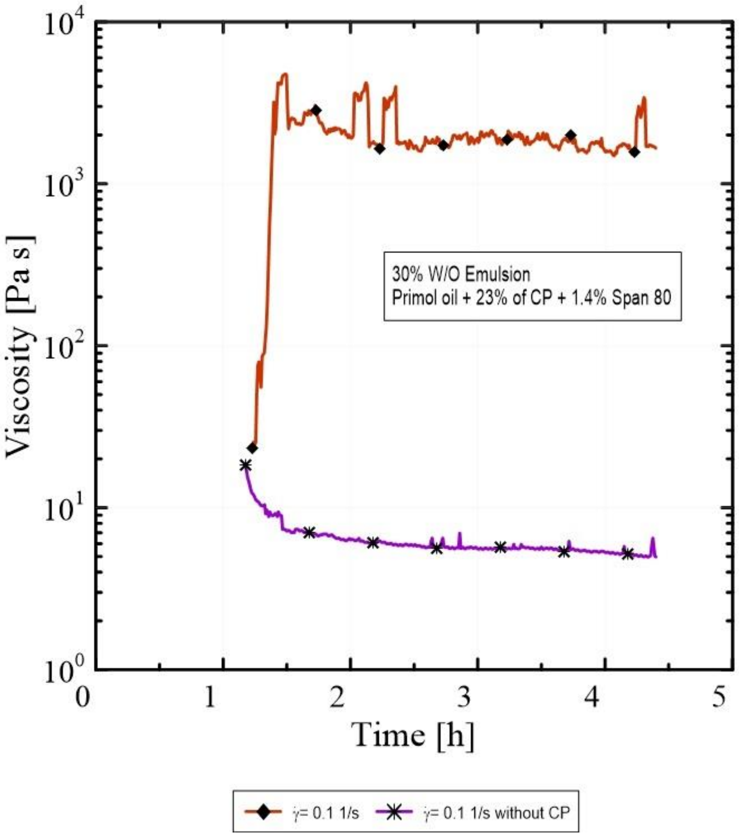

Figure 5. Viscosity behavior with and without CP addition.

4. CONCLUSION

CP Hydrates formation in water-in-oil emulsion has been studied from the rheological point of view. Initially, different components of the emulsion were studied, until a stable one was found, using 30% of deionized water, 23% of CP, 1.4% of Span 80, and Primol Oil. The non-Newtonian behavior of hydrates slurries was analyzed by measuring their viscosity at different shear rates. The lower the shear rate, the higher the viscosity spike and the shorter is the time to reach the steady state. CP hydrates have shear-thinning behavior since its steady state viscosity decreases with increasing the shear rate. At higher shear rates (100 s^{-1}) the viscosity doesn’t show an increase in respect to the value of the pure emulsion; this behavior could be more related to the experimental protocol than for any phenomenological effect. Another sort of experiment was performed without using cyclopentane in order to compare the viscosity behavior when the CP was used. It was noted that the viscosity did not increase because the ice particle did not remain at the working temperature of 1 °C, so the effect observed in the viscosity increment is indeed only due to hydrate formation.

In the following stages of the work, other rheological behaviors will be studied, such as: time dependence, yield stress, and elasticity.

5. REFERENCES

Abay, H. Kinetics of gas hydrate nucleation and growth. 2011. 126p. Pós Doutorado. Faculdade de Ciências e Tecnologia Departamento de Engenharia de Petróleo, University of Stavanger, Noruega.

Ahuja, A., Zylyftari, G., & Morris, J. F. (2015). Yield stress measurements of cyclopentane hydrate slurry. Journal of Non-Newtonian Fluid Mechanics, 220, 116-125.

Bai, Y. and Bai, Q., 2010. “Subsea Engineering Handbook”. Elsevier Science Publichers B.V.

Chhabra, R. P., & Richardson, J. F. (2011). Non-Newtonian flow and applied rheology: engineering applications. Butterworth-Heinemann.

De Lima Silva, Paulo H., Mônica F. Naccache, Paulo R. de Souza Mendes, Adriana Teixeira, and Leandro S. Valim. "Rheology of THF hydrate slurries at high pressure." Oil & Gas Science and Technology–Revue d’IFP Energies nouvelles 75 (2020): 16.

De Lima Silva, P. H., Naccache, M. F., de Souza Mendes, P. R., Campos, F. B., Teixeira, A., & Sum, A. K. (2017). Rheology of tetrahydrofuran hydrate slurries. Energy & Fuels, 31(12), 14385-14392.

E.D. Sloan and C.A. Koh, Clathrate Hydrates of Natural Gases, 3rd ed. (CRC Press, Boca Raton, FL, 2007).

Fu, S. B. et al. A summary of successful field applications of a kinetic hydrate inhibitor. In: SPE international symposium on oilfield chemistry. Society of Petroleum Engineers, 2001.

Karanjkar, P. U., Ahuja, A., Zylyftari, G., Lee, J. W., & Morris, J. F. (2016). Rheology of cyclopentane hydrate slurry in a model oil-continuous emulsion. Rheologica Acta, 55(3), 235-243.

Makogon, Y.F.; Holditch, S.A; Makogon, T.Y. Natural Gas-Hydrates: A Potential Energy Source for the 21st Century. Journal of Petroleum Science and Engineering 56, pp 14-31, Elsevier, 2007.

Sloan Jr, E. D., Koh, C., 2008. “Clathrate hydrates of natural gases”. CRC press.

Tohidi, B., Anderson, R., Mozaffar, H., Tohidi, F., 2015. The return of kinetic hydrate inhibitors. Energy & Fuels 29 (12), 8254-8260.

Webb, E. B., Koh, C. A., & Liberatore, M. W. (2013). “Rheological properties of methane hydrate slurries formed from AOT+ water+ oil micro emulsions”. Langmuir, 29(35), 10997-11004.

Yoshimura, A., & Prud'homme, R. K. (1988). Wall slip corrections for Couette and parallel disk viscometers. Journal of Rheology, 32(1), 53-67.

6. RESPONSIBILITY NOTICE

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