encit 2020

ABCM Associação Brasileira de Engenharia e Ciências Mecânicas

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

ENC-2020-0028
RHEOLOGICAL STUDY OF ETHANE GAS HYDRATES THROUGH A HIGH-PRESSURE CELL

Gustavo A. B. Sandoval
Ana Carolina Guimarães Alves Rebello
Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, RJ, 22451-900, Brazil
gsandoval@puc-rio.br
anarebelloo@aluno.puc-rio.br

Mônica F. Naccache
Paulo R. De Souza Mendes
Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, RJ, 22451-900, Brazil
naccache@puc-rio.br
pmendes@puc-rio.br

Adriana Teixeira
Leandro Valim
Petrobras Research Center (CENPES), Petrobras Av. Horácio Macedo 950, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ 21941-598, Brazil
adriteix@petrobras.com.br
leandro.valim@petrobras.com.br

Abstract. *One of the major problems currently encountered in offshore oil production is the obstruction of the transportation flow lines due to hydrates formation. Hydrates are water-based crystalline solids physically similar to ice, and are formed in the presence of water, gas and oil in conditions of high pressure and low temperatures. Hydrates formation is a critical issue that can lead to production downtime, which can yield economic losses to the companies and jeopardize the safety of production operations. Due to these facts, phenomena related to hydrates, as formation, dissociation, and forms to its mitigation have been studied for years by researchers. Aiming to contribute to these studies, this work presents a rheological analysis of ethane hydrates formed from water-in-oil emulsions. The measurements were performed in a Couette geometry inside a high-pressure cell of a rotational rheometer. The results are shown through viscosity curves as a function of temperature and time. Moreover, the gas consumed during its formation was determined employing the equation of state.*

Keywords: *Ethane Hydrates, Rheology, High-Pressure Cell.*

1. INTRODUCTION

According to Makogon (2010), the discovery of gas hydrates is attributed to the scientific Joseph Priestley in 1778. However, he did not name the phenomenon as "gas hydrate". Almost 30 years later, the British chemist Humphrey Davy observed the phenomenon when working with a solution of oxymuriatic gas in water. The scientist noted that this solution freezed more easily than pure water, a fact that was documented by the author and made him the pioneer concerning the topic. Gas hydrates are also known as clathrates and are crystalline structures composed of water and gas. The clathrate structure depends upon the nature and geometry of the guest molecule (Sloan and Koh, 2008), as well as the pressure and temperature conditions of its formation (Makogon, 2010). These crystalline compounds are similar to ice and form when the water hydrogen-bonds encage and retain one or more molecules under appropriate thermodynamic conditions of high pressure and low temperature (Notz et al., 1996). The molecules that are usually captured are gases of low molecular weight as carbon dioxide, ethane, methane, and natural gas.

The thermodynamic equilibrium conditions of the hydrates govern its formation and dissociation processes, thus, the determination and regulation of hydrate phase equilibrium for a specific guest molecule have always been a significant issue (Demirbas, 2010). According to Kashchiev and Fioozabadi (2003) in the phase diagram of hydrate, the equilibrium curve can be divided into stable and unstable zones. Hydrates can only remain in a thermodynamic equilibrated state when the pressure and temperature are located within the stable zone. In fact, due to the increasing demands of extract oil and gas from places with more severe thermodynamic conditions, flow assurance engineers are

challenged to work within the hydrate stable zone. In this case, the introduction of chemical reagents is required. Depending on how these reagents work, they can be classified as thermodynamic inhibitors (TIs) and Low-Dosage Hydrate Inhibitors (LDHIs). Thermodynamic inhibitors such as alcohols, glycols, and saline solutions work by changing the hydrate equilibrium curve. That is, the equilibrium temperature for hydrate formation is reduced for a given pressure. One of the plausible hypotheses to explain this event indicates that polar substances such as alcohols and glycols form hydrogen bonds with water, which interfere with the arrangement of their molecules. This causes the chemical potential of the water to be altered and therefore decreases the hydrate formation temperature (Sloan Jr & Koh 2008). Low-Dosage Hydrate Inhibitors (LDHIs) are a proven technology to control hydrates in numerous applications and are instrumental in reducing the total cost of operations. As an added benefit, it is possible to co-formulate LDHIs with other production chemicals, such as paraffin and corrosion inhibitors, and thus minimize the number of chemical injection lines (Frostman et al., 2003).These inhibitors are known to be more effective, more environmentally friendly, less corrosive, have lower capital and operational expenses and the dosage requirement of these inhibitors is much lower than that required for TIs (Erfani et al., 2014).

Because of these facts, the study of hydrate rheology has become of great industrial and scientific interest. Although there are a good quantity and quality of works related to the hydrate phenomenon, there are still many questions related to the nucleation, formation, and dissociation of these structures. At the laboratory level, hydrates can be formed at both high and ambient pressure. At ambient pressure, the structure is formed with the assist of chemical agents, such as cyclopentane (CP) and tetrahydrofuran (THF). The study of formation with high pressure allows evaluating the properties of the material under pressure and temperature conditions similar to those found in the field. In addition, the impact that different gases have on formation can be assessed.

The main objective of this work is to study the rheology of the ethane hydrates formed from water-in-oil emulsions through a high-pressure cell in a rotational rheometer. The results are exhibited through viscosity and pressure curves which are associate with the gas consumption during the hydrate formation process.

2. EXPERIMENTAL PROCEDURE

The experiments were conducted in a shear stress-controlled Rheometer Haake Mars III (Thermo Fischer Scientific). The rheometer is connected to a thermostatic bath that allows the temperature control of the sample during the experiments. The pressure cell was designed to be used with the Haake rheometer. The cell consists of a rotor, which is the measuring geometry, and the stator. The stator consists of the cup and a top cover to seal the system. At the top of the cup, there are three connections: for the safety valve, for the pressure transducer and for the gas inlet. The sample and rotor are deposited inside the stator with a magnet. The rotor used (PZ35) is a smooth cylinder concentric with the cup, also smooth, and forms a horizontal gap of 2 mm. The conduction of the rotor is done through a magnetic field created by an external magnet that is connected to the head of the rheometer and the internal magnet that is fixed to the rotor. The rotor is supported by two sapphire bearings, so it was necessary to perform a calibration of the system under analysis to discount the friction caused between the geometry and the bearings from the total torque generated by the rheometer. The calibrations were performed as indicated in the manual provided by the cell supplier. Some of the calibrations are: optimal gap between the external magnet and the top cover, inertia, and friction factor discount. These calibrations are made periodically with the same material used in the hydrate formation tests.

3. METHODOLOGY

The main components of our emulsions are deionized water, mineral oil, and Span 80 as a stabilizer agent. Deionized water was obtained from the Gehaka OS 10 LX system, which purifies water through reverse osmosis. Primol oil, known as “white mineral oil” is highly refined oil, composed of saturated aliphatic hydrocarbons. This oil is stable, colorless and odorless, its density is in the range of 870 kg/m³ at 20 °C and the pour point temperature is -18 °C. Span 80 is a non-ionic oil-soluble surfactant with a hydrophilic-lipophilic balance of 4 $\mp$1. Karanjkar et al., (2016) reported that Span 80 acts as an anti-agglomerant agent for hydrates. The authors observed that the viscosity of the hydrate slurry was reduced as the Span 80 content was increased, improving the fluidity of the material. Thus, it is important to consider this property of Span 80 as a hydrate inhibitor, because although this surfactant is an excellent stabilizer of water-in-oil emulsions, it can also hinder the formation of the hydrate slurry. The water-in-oil emulsions were prepared using the following methodology:

1) Weigh the required masses of Span 80, deionized water and Primol oil;
2) Magnetic homogenization of Span 80 with Primol oil at a speed of 1000 rpm for 5 min;
3) Addition of water in the mixture of Span 80 and Primol oil;
4) Homogenization of the components obtained in step 3 on the Turrax mechanical stirrer (model IKA T25, rotor 18G), at speed of 10000 rpm for 5 min.

The gas selected to conduct the experiments was ethane. Ethane, with chemical formula C_2H_6 is an aliphatic component that is in a gaseous state under normal conditions of pressure and temperature, see the saturation curve inserted in Fig. 1. As shown in Fig. 1, ethane hydrates can form at moderate pressures, for example, at 2 MPa and 4 °C

with a subcooling of 8 °C. This facilitates the formation of the hydrates at the laboratory scale. In this work, the experiments were conducted in a closed system, then, the pressure varies throughout the test as gas is consumed during the process. Henceforth, the conditions of hydrate formation could be different in the experiments.

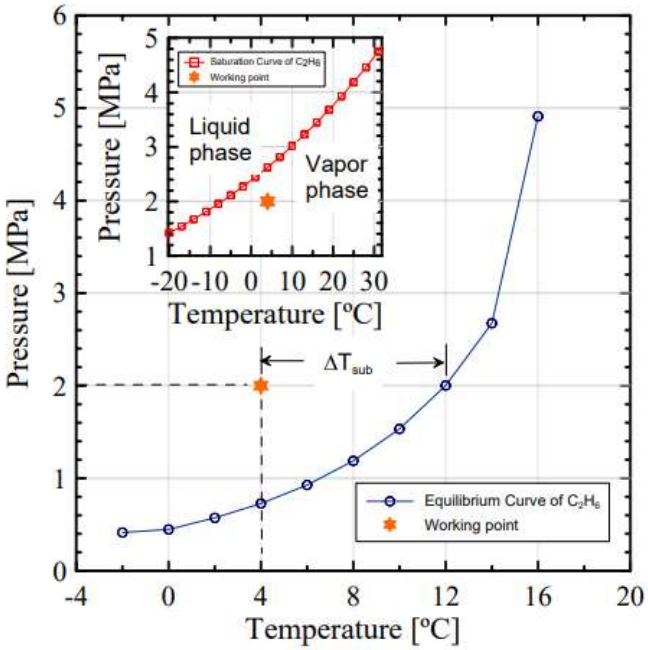

Figure 1 –Ethane equilibrium curve for hydrate formation (blue). Ethane saturation curve (red).

To carry out our experiments, a high-pressure system described next was used: the ethane that is stored in a cylinder is sent to a syringe pump which allows increasing the gas pressure. After this stage, the outlet gas line is conveyed and connected to the pressure cell through a needle valve. The cell is completely sealed and placed in the rheometer, once the measuring cup is filled with the emulsion. Subsequently, the test is started with a constant shear rate throughout the experiment, and the sample temperature is brought to 25 °C, where it is maintained for 4 hours to allowing the emulsion saturation by the gas. Once the experiment is initialized in the rheometer, the cell begins to be pressurized with ethane until it reaches a pressure of 35 bar. Depending on the experiment, the needle valve that is attached to the pressure cell is closed when the working initial pressure is reached, or it remains open for a period of time to allow the inlet of more gas inside the cell. Once the valve is closed, the test is done without adding more gas during the subsequent steps, that is to say, the amount of gas remains constant within the closed system. Following the saturation step, the temperature is linearly reduced from 25 °C until 4 °C at a rate of 0.4 °C/min. This final temperature is maintained until the end of the experiment.

4. DISCUSSION AND RESULTS

During dissolution (in the first 4 h of the experiment) it is observed how the viscosity decreases until it reaches a stable value as shown in Fig. 2. The viscosity decreases due to the gasification of the emulsion, that is, where the material becomes foamier. After the dissolution process, the increment in viscosity is caused by a decrease in temperature to 4 °C. In these thermodynamic conditions of pressure and temperature, the system is within the hydrate formation region.

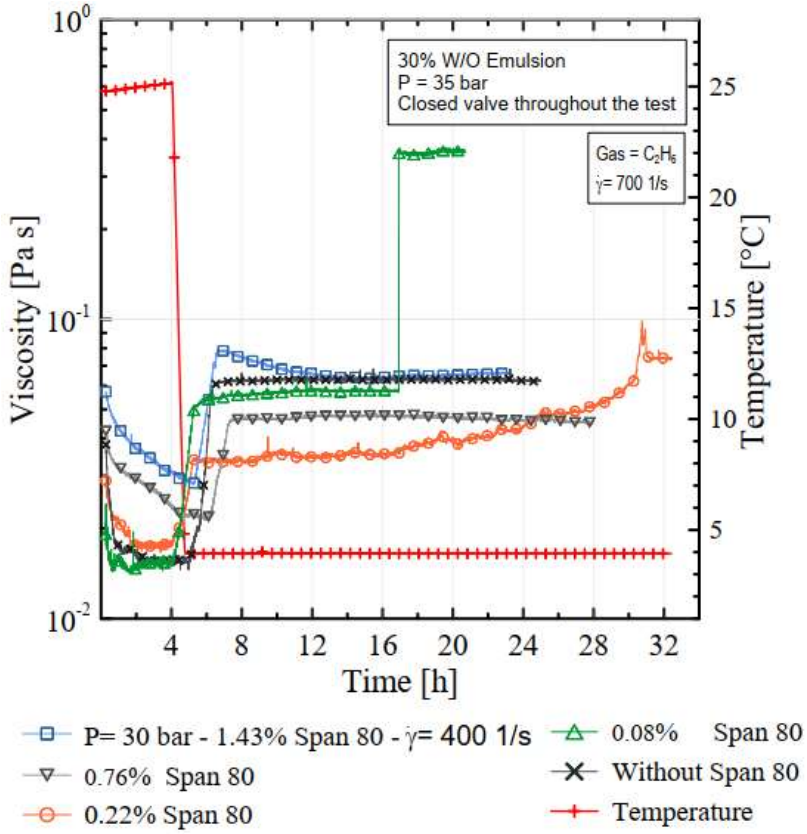

Figure 2– Viscosity behavior versus experimental time for tests under different conditions.

All the tests show in Fig. 2 were conducted with a closed valve (the cell is pressurized until achieve 35 bar and consecutively closed) and at a shear rate of 700 s^{-1}, however, the first of them (blue rectangle), was performed at a shear rate of 400 s^{-1}, pressure of 30 bar, and with 1 g of Span 80 present in the sample, which it is equivalent to 1.43% m/m of surfactant in the emulsion. As noted in Fig 2., for these experimental conditions, there was no hydrate formation, even after 20 h of testing in the formation zone, as a drastic and spontaneous increase in viscosity was not observed, which is the characteristic behavior caused by the agglomeration of hydrate crystals.

To increase the driven forces for hydrate formation, the experimental conditions were changed: firstly, the amount of Span 80 was decreased. Secondly, the shear rate was increased to 700 s^{-1}, as different studies have shown that the hydrate induction time is reduced by the increase in the shear rate, since a greater contact area between hydrate-forming substances is promoted within the cell (Webb et al., 2013; Sandoval et al., 2018). Thirdly, to have more severe formation conditions, the initial system pressure was increased to 35 bar. This pressure was set for all the subsequent experiments presented in this paper. With these conditions, another experiment was conducted with 0.76% of Span 80 in the emulsion, for that case, the viscosity during the dissolution process decreased (indicating more gas dissolved) compare with the former experiment, but did not form hydrate. An experiment with 0.22% of Span 80 (orange circle) was also performed, and as observed, the viscosity decreased in the dissolution step, and when the system reached the temperature of 4 °C, the viscosity increased gradually, and after 20 h in this equilibrium zone, a small peak of hydrate formation was noted. In another attempt, more one test was carried out by reducing the Span 80 to 0.08%, and under this amount of surfactant, the emulsion is stable around 2 h. After approximately 17 h of the experiment, an abrupt increase in viscosity of approximately 7 times in relation to the prior viscosity value was observed, indicating a typical behavior of hydrate formation. Finally, another experiment without a surfactant (non-emulsifying system) was realized, but hydrate formation was not observed. Maybe, the formation of hydrate did not happen for the non-emulsifying system because the geometry of the concentric cylinders does not generate enough mixing for the gas to be in contact with the free water, which probably remains in the bottom of the cell. This topic will be studied in future experiments with another geometry (for more details of non-emulsifying systems see Charin, R & Sum, A. (2017)).

In order to show a new formation, but in shorter induction time, a second test was carried out with 0.08% m/m of surfactant in the emulsion, that is, with 0.057g of Span 80, but the working temperature was reduced to 1°C, as shown in the experiment 2 of Figure 3. The experiment also was performed with closed valve after attained the pressure of 35 bar. After approximately 16 h of experiment, an abrupt increase in viscosity is observed until reaching a value similar to that achieved with the first test performed with the same amount of Span 80, but using a formation temperature of 4 °C. This behavior is indicative of hydrate formation, as well as that observed with the pressure, which decreases during the

growth period, as gas is consumed in the process. The results of pressure and temperature in Figures 3 and 4 were plotted with the shared axis "Y", depicted at the right side of the Figures. As can be noted, the viscosity value and behavior for both experiments were similar, independently of the induction temperature, probably this is due to the closer supercooling degrees between the experiments, which is around 1.5 °C. Initially, both experiments depart from the same pressure (roughly 35 bar), but different rates of gas consumption were noted during the dissolution. For the first experiment (green triangle) the pressure dropped around 10 bar, while for the second one, the pressure dropped 13 bar, this difference of 3 bar noticed at the beginning of the cooling was keeping until the equilibrium temperatures were attained, with values of 17 bar and 14 bar for the first and second experiment, respectively. That means that the pressure values fell the similar quantity for both experiments during the cooling step, around 8 bar. For these thermodynamic conditions (17 bar and 4 °C and 14 bar and 1 °C), the subcooling degree was 7 °C and 8,5 °C for the first and second experiment, respectively. Although during the growth period of the second experiment, the viscosity increased slower than in the first one, perhaps this behavior permitted the capture of the pressure variation by the sensor, which occurs with a delay regarding the initial viscosity increment.

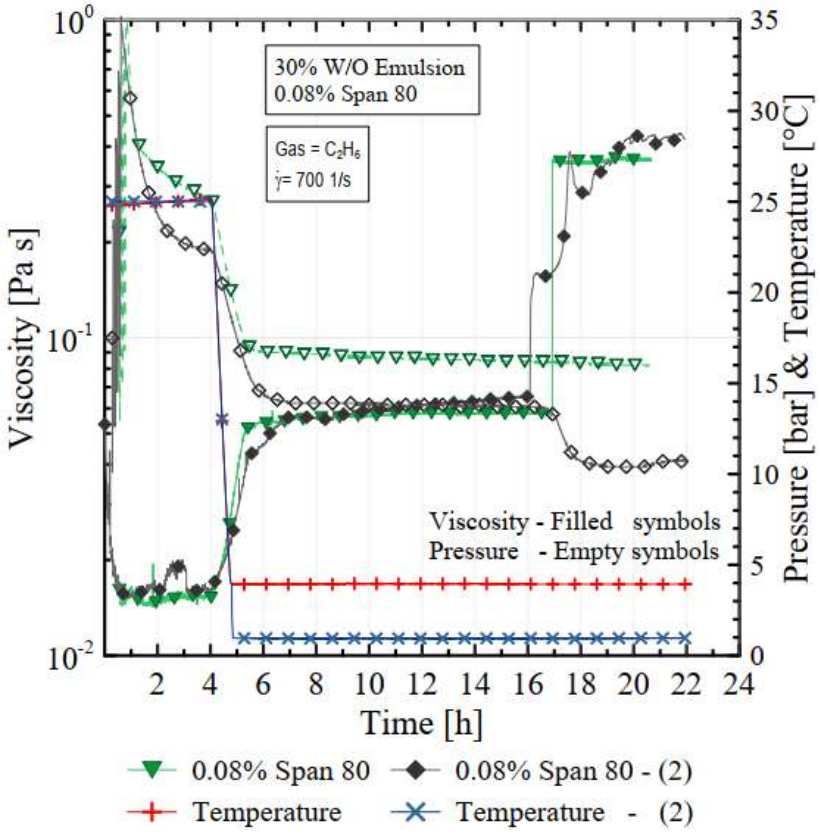

Figure 3–Behavior of viscosity and pressure during ethane hydrate formation.

Once the amount of surfactant to obtain our emulsion was determined, and the experimental conditions to form the hydrate slurry were defined, our next step was to conduct different experiments varying the amount of gas that enter inside the pressure cell. To this end, the needle valve that permits the gas inlet in the cell, remained opened during different periods of the dissolution time. As noted in Fig. 4, two experiments were realized allowing the gas inlet inside the cell, (the experiment (2) presented in Fig. 3 was plotted again for comparison reasons). One of them was conducted letting the valve opened during 2 h (orange curve), the other experiment was performed with opened valve throughout the dissolution time, is to say, for a period of 4 h, as indicated in Fig 4, with the letters VC (valve closed).

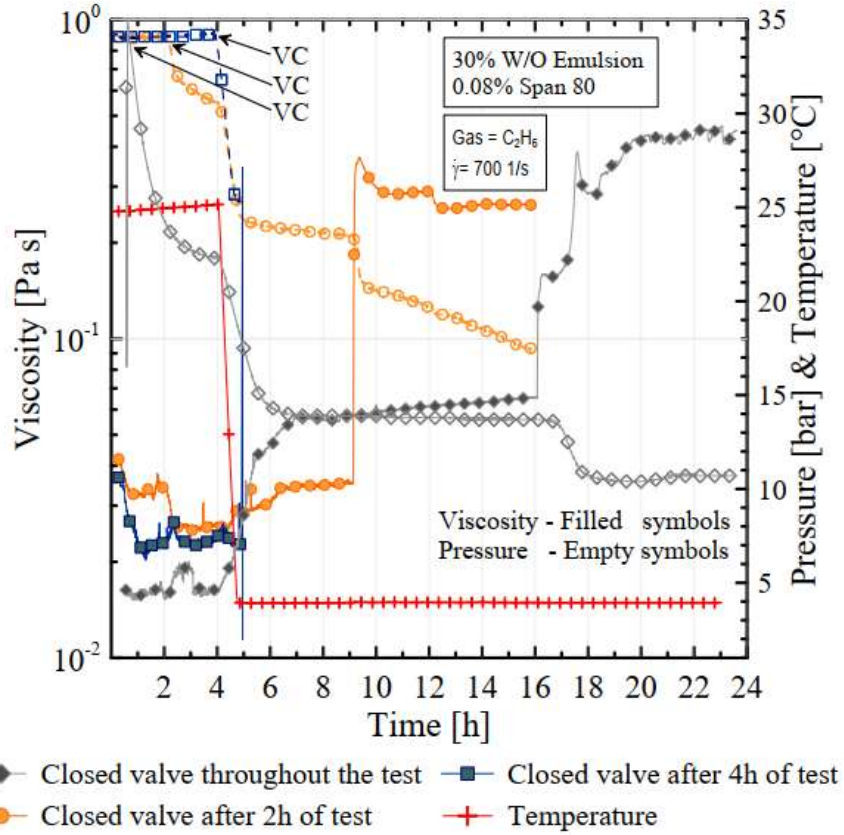

Figure 4–Behavior of viscosity and pressure during hydrate formation with two different amount of ethane gas.

Figure 4 shows the viscosity behavior plotted with the left axes and the pressure and temperature curves plotted with the right axis. These three parameters are depicted as a function of the experimental time. As noted in Fig. 4, for the test conducted with 2 h of opened valve, as prompt as the valve is closed, the pressure begins to decrease, initially at a higher rate than at the end of the dissolution period when a larger amount of ethane has been dissolved into the liquid. From the moment that the valve is closed until the end of the dissolution period, the pressure dropped 3.3 bar at an average rate of 1.76 bar/h. After the dissolution period, the cooling process starts and therefore the temperature is reduced from 25 °C until 4 °C, at this stage the pressure decreases continuously from 30.6 bar until 24.8 bar at a rate of 7.25 bar/h. For the thermodynamic conditions of 24.8 bar and 4 °C, the system is found in the hydrate equilibrium zone with a supercooling degree of approximately 9,3 °C. These thermodynamic conditions remained almost constant until hydrate formation, where the pressure fell 2.5 bar (from 23.5 bar until 21 bar) in a period of 20 min (rate of 7.5 bar/h). On the other hand, the viscosity results obtained for the test conducted with 2 h of open valve showed the typical behavior during the dissolution, cooling and hydrate formation steps. After the hydrate formation, the viscosity remained in a constant value, despite the pressure decreased at a constant rate of 0.55 bar/h. No more hydrate formation was observed after 24 h of experimental time. The experiment realized with opened valve during 4 h (throughout the entire dissolution period), showed a final dissolution viscosity value close to the experiment with 2 h open valve (approximately 30 mPa.s), notwithstanding, the test with 4 h of opened valve did not present a significant viscosity increment during the cooling step, the viscosity value remains almost constant until achieve the equilibrium temperature of 4 °C. However, this issue was not impediment for hydrate formation, since it happens as soon as the 4 °C were reached, and the viscosity spike was as severe that the maximum torque allowable by the rheometer was achieved, and the transmission between the internal and external magnets was lost (for that reason the sudden viscosity decrease in Figure 5). As observed in Fig. 5, the pressure seems to be constant during the hydrate formation time, probably this behavior is more related with an instrumental role, since the formation happens so fast that the pressure sensor does not get to capture the measurement variation, similar behavior as such observed in the experiment (green triangle) displayed in Figure 3.

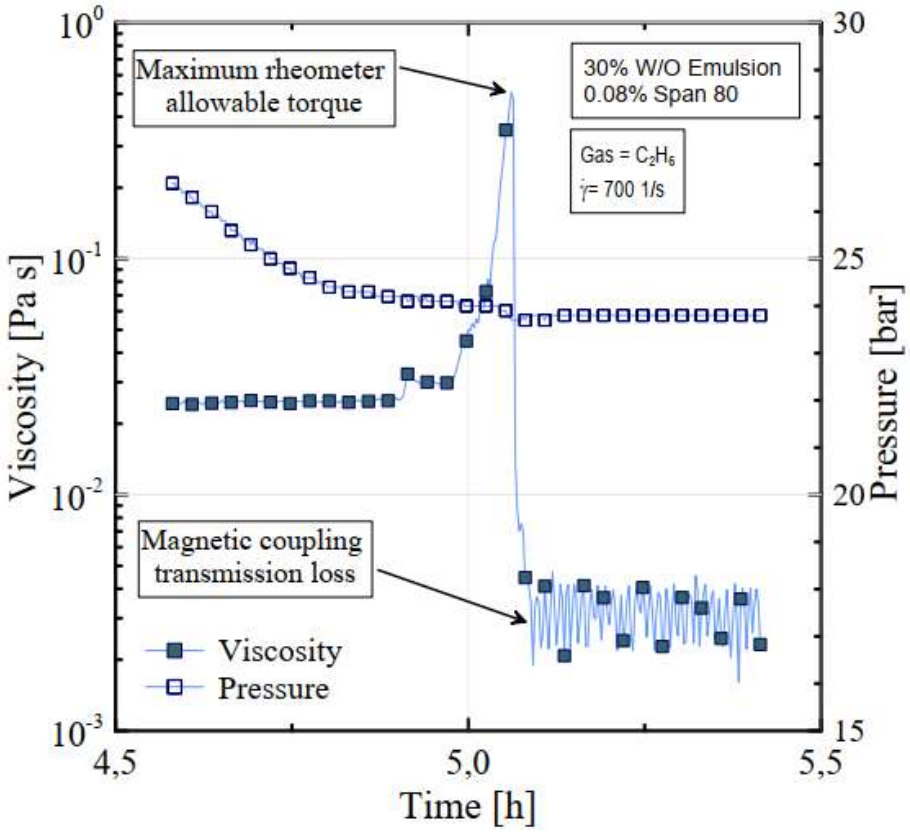

Figure 5–Behavior of viscosity and pressure during ethane hydrate formation step for an experiment with 4 h of opened valve.

As can be seen from Fig. 4, the time taken for the hydrate formation under equilibrium conditions (induction period) is quite affected by the amount of gas present in the system. This can be observed because the formation of the experiment with 4 h of opened valve occurs faster than the test conducted with 2 h, and the latter formed faster than the test made with valve closed during the dissolution period. Regarding the viscosity value reached after hydrate formation, it is noted that the values are similar for the experiment with 2 h of opened valve and the test performed with closed valve. For the experiment with 4 h of opened valve it was not possible to quantify the final viscosity value. To determine the quantity of gas consumed during hydrate formation, the equation of state based on the experimental conditions was used. As the pressure, temperature and system volume are known before and after the hydrate formation, then, the difference of mass consumed can be calculated. For example, from the test of hydrate formation conducted with closed valve (experiment 2 in Fig. 3) the thermodynamic properties before hydrate formation are: pressure 14 bar, temperature 1 °C, and the system volume 97.32 cm^3. With these values and the critical thermodynamic conditions for the ethane, the compressibility factor is determined. With the previous data, the amount of gas at this point (before hydrate formation) is estimated. The same procedure is applied after the hydrate formation, and the mass difference the mass consumed during the formation is determined. The volume is computed with the amount of emulsion deposited inside the pressure cell besides the amount of gas that enters in the cell. The amount of gas is measured through the syringe pump. Employing this methodology to both experiments, with 2 h of opened valve and valve closed throughout the test, the mass amount of gas consumed was equal to 1.7 g and 2.4 g, respectively. Therefore, not necessarily a similar final viscosity level between the experiments indicates the same amount of gas consumed and hydrate formation. Regarding the amount of gas that got into the pressure cell, more gas was consumed during the hydrate formation for the experiment with 2 h of opened valve. That is to say, for the system studied, more gas was consumed by the test with higher subcooling. Future experiments will be done to correlate the effect between the hydrate formation parameters and the amount of gas consuming.

5. CONCLUSION

The rheology of ethane gas hydrates formed from water in mineral oil emulsions was analyzed. The experiments were conducted through a system composed of a rheometer and a high-pressure cell that permits to set up similar thermodynamic conditions of that found in the offshore transmission lines. Hydrates formation was noted by a random

and abrupt increment in the viscosity. Initially, it was shown the properties of the Span 80 to avoid ethane hydrate formation. Subsequently, once the test of hydrate formation was defined, different experiments were conducted to quantify the amount of gas consumed during the formation process. This is feasible using a close system. As reported for the system studied, the induction time is affected by the amount of gas presented in the cell, probably due to the increment in the subcooling degree. Regarding the viscosity values attained after the hydrate formation, not necessarily two similar viscosity values indicate that the same amount of gas is consumed.

6. ACKNOWLEDGEMENTS

These experiments and this research were only possible due to the contribution of Petrobras S.A, FAPERJ, Brazilian Research Foudation (CNPq) and Brazilian Graduate Education Foundation (CAPES).

7. REFERENCES

Camargo, R., Gonçalves, M., Montesanti, J., Cardoso, C. and Minami, 2004. "A perspective view of flow assurance in deepwater fields in brazil". *In Offshore Technology Conference*.

Charin, R. M., & Sum, A. K. (2017). Steady-state and transient studies of gas hydrates formation in non-emulsifying oil systems. *Energy & Fuels,* 31(3), 2548-2556.

Demirbas,A., 2010. "Methane hydrates as potential energy resource: Part 1 – Importance, resource and recovery facilities". *Energy Conversion and Management*, Vol 51, pp. 1547 – 1561.

Erfani, A., Varaminian F., Muhammadi M., 2014. Gas hydrate formation inhibition using low dosage hydrate inhibitions. *National Iranian Conference on Gas Hydrate (NICGH),* At Semnan, Iran.

Frostman, L. M., Thieu, V., Crosby, D. L., & Downs, H. H. (2003, January 1). *Low-Dosage Hydrate Inhibitors (LDHIs): Reducing Costs in Existing Systems and Designing for the Future*. Society of Petroleum Engineers.

Kashchiev, D., Fioozabadi, A.,2003. "Induction time in crystallization of gas hydrates". *Journal of Crystal Growth,*Vol 250, pp. 419 – 515.

Makogon, Y. F., 2010. "Natural gas hydrates - a promising source of energy". *Journal of Natural Gas Science and Engineering* 2 (1), 49-59.

Notz, P. K., Bumgardner, S. B., Schaneman, B. D., Todd, J. L., 1996. "Application of Kinetc Inhibitors to Gas Hydrate Problems". *Offshore Tecnology Conference*, Houston, Texa, EUA.

Sandoval, G. A., Soares, E. J., Thompson, R. L., Siqueira, R. d. N., de Andrade, R. M., Campos, F., Teixeira, A., 2018. "Analysis of CO2 hydrates in crude oils from a rheological point of view". *Energy & Fuels Journal* 32 (3), 2733-2741.

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

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.

8. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.