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EFFECTS OF SHEAR RATE, SUBCOOLING AND DISSOLUTION TIME ON METHANE HYDRATES FORMATION IN PURE WATER

Guilherme Rainho Melhorim

Will Anderson Grippa

Edson José Soares

Universidade Federal do Espírito Santo, Avenida Fernando Ferrari, 514, Goiabeiras, Espírito Santo 29075-910, Brazil
guilhermemelhorim@gmail.com
will-anderson22@hotmail.com
edson.soares@ufes.br

Renato do Nascimento Siqueira

Instituto Federal do Espírito Santo, campus São Mateus, Rodovia BR-101 Norte, km 58, Litorâneo, São Mateus, Espírito Santo 29932-540, Brazil
renaton@ifes.edu.br

Adriana Teixeira

Leandro Saraiva Valim

CENPES, Petrobras, Avenida Horácio Macedo, 950, CEP: 21941-915, Ilha do Fundão – Rio de Janeiro, Brazil
adriteix@petrobras.com.br
leandro.valim@petrobras.com.br

Abstract: Gas hydrates are solids compounds formed by water and low molecular weight gases in appropriate conditions of temperature and pressure. The hydrates formation can plug the pipeline, causing production losses and restart problems, being an important issue in flow assurance by oil companies. In the present work, we use methane and deionized water to study the effect of shear rates (75, 100 and 125 s⁻¹), subcooling (5 and 8 °C) and dissolution time (0 and 2 h) on hydrates formation, using a high-pressure rheometer system with a pressure cell and a vane rotor. The results indicate strong dependence of induction time on shear rates and subcooling, indicating that an increase in these parameters reduce the hydrates formation time.

Keywords: hydrates, methane, pure water, rheology, flow assurance.

1. INTRODUCTION

Gas hydrates are crystalline solids composed of water that enclosure low molecular weight gases that include methane, ethane, propane and carbon dioxide in certain conditions: low temperatures and high pressures (Sloan et al., 2008). The researchers are concerned in three issues (Hassanpouryouzband et al., 2020): climate changes can make methane escape from natural reservoirs, resulting changes in ocean chemistry; sustainable technologies that use tetrahydrofuran (THF) and cyclopentane (CP) to form hydrates and apply it to gas storage, gas separation, desalinization etc. A recent estimate affirms that if total weight of carbon in hydrates was converted to energy, it would lead to twice the total fossil resources already discovered (Folmann, 2015). This fortify some researches that affirms that hydrates is the energy of the future, justifying the high investments in researches; and flow assurance, theme of this work, crucial for oil industry, because in deep waters, the conditions of hydrates formation exist (low temperature, high pressure, gas and water). These hydrates can plug the pipeline and block the flow.

In flow assurance, the oil industry lost a lot of money and time with hydrates plugs, these values are still high, but they were reduced by the discovery of three classes of inhibitors, described in Hassanpouryouzband et al., (2020), of which: Kinetics Hydrates Inhibitors (KHI) are the polymers, such as polyethylene and PVCap, with low molecular weight that increase the induction and growth times in hydrate formation. The advantage of using KHI is the low dosage, in the order of 3% of produced water (Sandoval, 2019); anti-agglomerants (AA) are surfactants soluble in oil, that allows the hydrate crystal formation and maintain the hydrate particles in the oil phase without aggregation (Sandoval, 2019). An example is Span 80, a surfactant with anti-agglomerants properties; and the Thermodynamic Hydrates Inhibitors (THI) act modifying the equilibrium curve of gas hydrate, that is, higher pressures and/or lower

temperatures are necessary to hydrates formation. Some examples of the most used THI are methanol and ethylene glycol, due to the cost and effectiveness (Sandoval, 2019). Another very common THI is saline solution.

2. STATE OF THE ART

The use of vane rotor in pressure cell is based on the fact that the dissolution of gas in water increase with the increase in the turbulence of the system (Saw et al., 2012). The blades promote more agitation and, consequently, more turbulence than others geometries like concentric cylinders, for example. Besides that, hydrate formation is favored in regions where the fluid velocity is high (Carroll, 2002 apud Saw et al., 2012) and in the interface between water and gas phases (Saw et al., 2012).

Pandey et al. (2017) studied the hydrate formation of the pure methane system at 90 bar, 2 °C and 100 s⁻¹ using two types of geometries and the main difference is that one of them promotes more agitation. The results indicated hydrate formation in this geometry, with an induction time of 1.48 h, while the other geometry did not promote the hydrate formation in 24 hours, concluding that an enhanced mixing of the methane gas phase with the pure water increases a lot the probability of hydrate formation.

Chen et al. (2020) investigated the induction time and memory effect in systems with pure water and methane using a high-pressure flow loop, varying the initial pressure (51.5 and 64.5 bar), the water bath temperatures (-2 and -4 °C) and flow rates. In the case of same bath temperature and flow rate (-2 °C and 1160 kg.h⁻¹, respectively), a sharp increase in the initial pressure of 51.5 bar to 64.5 bar decreased the induction time by half, approximately.

He et al. (2011) analyzed the effect of stirring on induction time in systems with distilled water and carbon dioxide or methane. For both systems, the induction time decreases with increasing stirring speed and, in tests with methane, the stirring speed corresponding to zero of induction time was 1400 rpm, while carbon dioxide systems was 900 rpm.

The work pressure was determined using the phase equilibrium curve of methane, obtained by a software developed at Colorado School of Mines (Fig. 1). Saw et al. (2012) showed that the concentration of salt shifted the phase equilibrium curve to the region of methane hydrate formation, that is, more pressure is necessary to form hydrate in the same temperature, acting as a hydrate inhibitor. On the other hand, there are many researches of hydrate formation using some promoters, as tetrahydrofuran (Inkong et al., 2019; Lee et al., 2012; Mech et al., 2016) and cyclopentane (Ahuja et al., 2015; Chen et al., 2019; Zylyftari et al., 2015). In these cases, the region of hydrate formation becomes larger and those products act as a thermodynamic hydrates promoters.

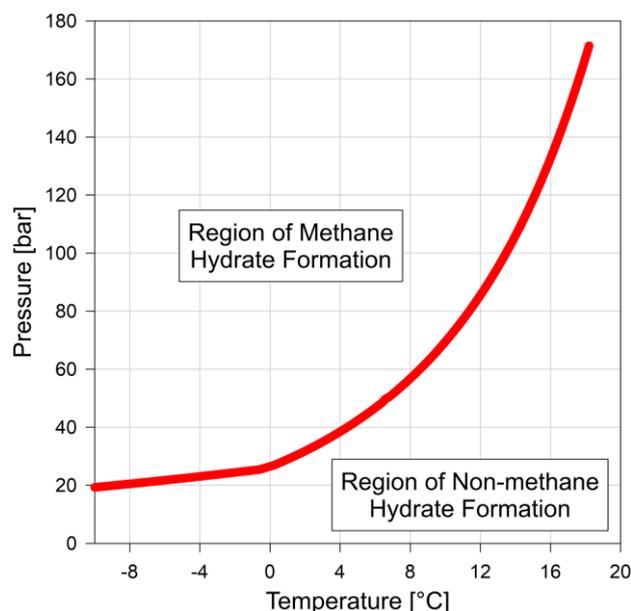


Figure 1: Phase equilibrium curve of methane (Source: CSMGem).

3. EXPERIMENTAL PROCEDURE

The materials used in this work include deionized water (Êxodo Científica) and high-pressure methane (White Martins). The tests were conducted in a shear-stress-controlled rheometer, Haake Mars III (Thermo Fisher Scientific), using a Haake Pressure Cell D400/300 (Thermo Fisher Scientific) and a pressure system to control the test pressure. All tests were performed at constant temperature using a thermostatic bath Haake Phoenix II, model SC-150 (Thermo Fisher Scientific) connected to the rheometer and the geometry used was the vane rotor FL25/93 (Thermo Fisher Scientific) for better mixing. The layout of the system is showed in Fig. 2, which is composed of a gas cylinder with

methane, a gas pressurizing unit to increase the methane pressure beyond of gas cylinder pressure, a serpentine pipe that works as a lung, that is, it works to guarantee a constant gas rate in the pressure cell. The experimental setup is the same used by Sandoval (2019).

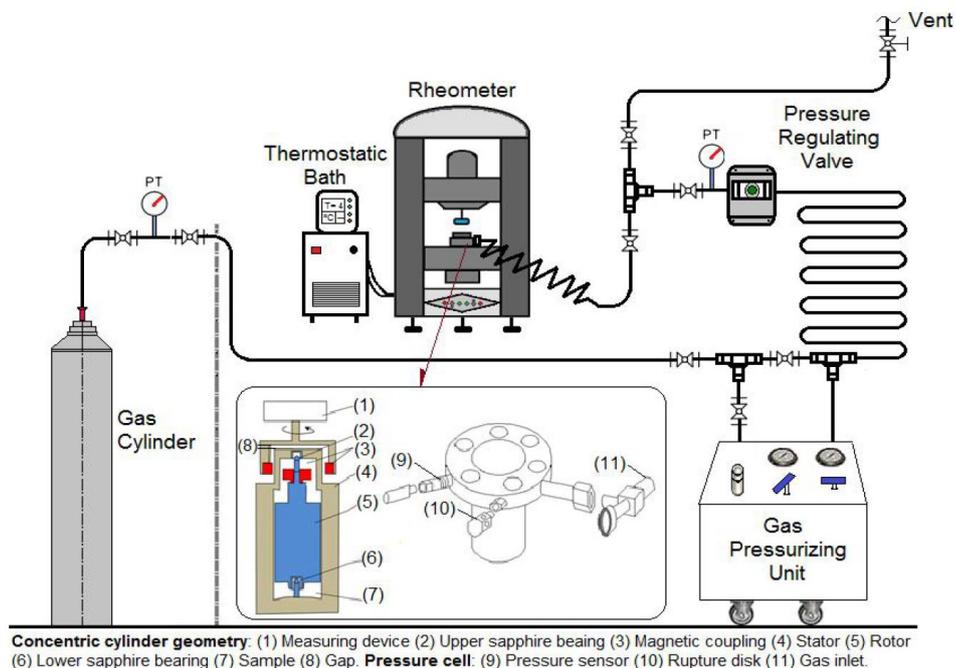


Figure 2: Experimental apparatus for hydrates formation (Sandoval, 2019).

For all experiments, the desired volume of deionized water was placed into the pressure cell and also to lubricate two sapphire bearings located at the bottom and at the top of the stator. We tighten six cylinders head screw with a torque wrench set to 100 Nm. After this step, the pressure cell is put into the cup of the rheometer. The torque applied by the rheometer measuring head is transmitted to the rotor inside the pressure cell by a non-contact (magnetic) coupling then, to obtain the best measures, it is necessary realize the torque correction setting up a RheoWin Job, consisting of a Rotation Time Curve element and a Rotation Step element. After this, we plot three curves in terms of momentum and angular velocity. The best fitting model is the model for which the χ^2 value is the lowest.

The work point of the majority of tests is defined as 70 bar and the initial temperature 25 °C. An important parameter is the subcooling temperature, that is the difference between the test temperature and the equilibrium temperature for hydrate formation. The test temperature varies from 2 to 5 °C, resulting in subcooling of 5 and 8 °C, respectively. In this case, high pressure is necessary to the hydrate formation. The purpose of this work is to analyze the influence of the shear rates, subcooling and dissolution time on induction time and viscosity profile of hydrates formation using pure water system and methane.

4. RESULTS AND DISCUSSION

The first parameter analyzed was the dissolution time because some references showed low solubility of methane in water. Figure 3 shows two tests at a shear rate fixed at 100 s^{-1} , constant pressure of 70 bar and cooling temperature of 2 °C. The analyses were performed visually by the viscosity variation and the results depict small differences in induction time. The test with two hours of dissolution has an approximate induction time of 25 minutes, while for the test without dissolution, the induction is practically instantaneous when the temperature of cooling is reached. These results also indicate that dissolution time in the system with methane and pure water does not improve the induction time. Therefore, as the induction time is smaller without dissolution time, the subsequent tests were conducted in these conditions.

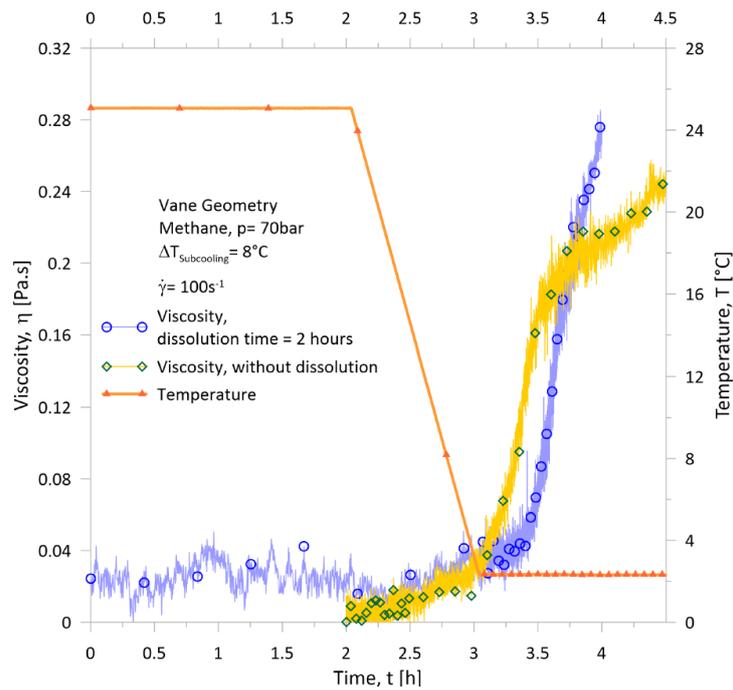


Figure 3: Effect of dissolution time on induction time.

The temperature, as the pressure, is a driving force to hydrate formation and a little increment of temperature leads to large changes in the viscosity profile. Being an important parameter, the subcooling temperature was also investigated. In this case, a decrease in cooling temperature, and consequently increase in subcooling, reduce the induction time, due to the large driving force imposed. It can be seen in Fig. 4 that the test with 5 °C had an induction time of 42 minutes, approximately, while for the test with 2 °C, 22 minutes. That is, a decrease of 3 °C reduce the induction time practically to half. It is possible to conclude that with the increase of the subcooling and, consequently, the driving force, the induction time decreased, as reported by Li et al. (2015) for temperatures between 271.15 K and 277.15 K.

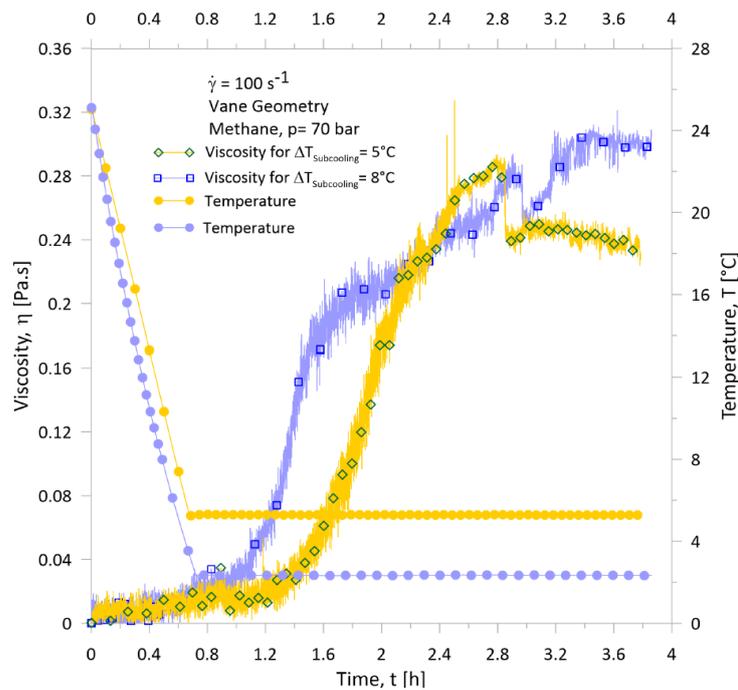


Figure 4: Effect of subcooling on induction time.

The last parameter analyzed was the shear rates, indicating extreme dependence in hydrate formation, which shows that the higher the turbulence in the system the smaller the induction time, as reported by Li et al. (2015) that decreased the induction time while the rotation speed increased until 900 rpm. In Fig. 5, we can note that the test with 125 s^{-1} obtained an induction time of 42 minutes, while the tests with 100 s^{-1} and 75 s^{-1} obtained 50 minutes and 57 minutes, respectively. Besides that, we can note that the growth rate is much larger in test with 125 s^{-1} , which demonstrates that high shear rates promote greater growth of hydrate crystals. In systems with pure water, we can note that higher viscosity measures can be obtained with higher shear rates, opposite to systems with water-in-oil emulsion that demonstrates that higher shear rates can break the agglomerates and reduce the viscosity (Webb et al., 2013).

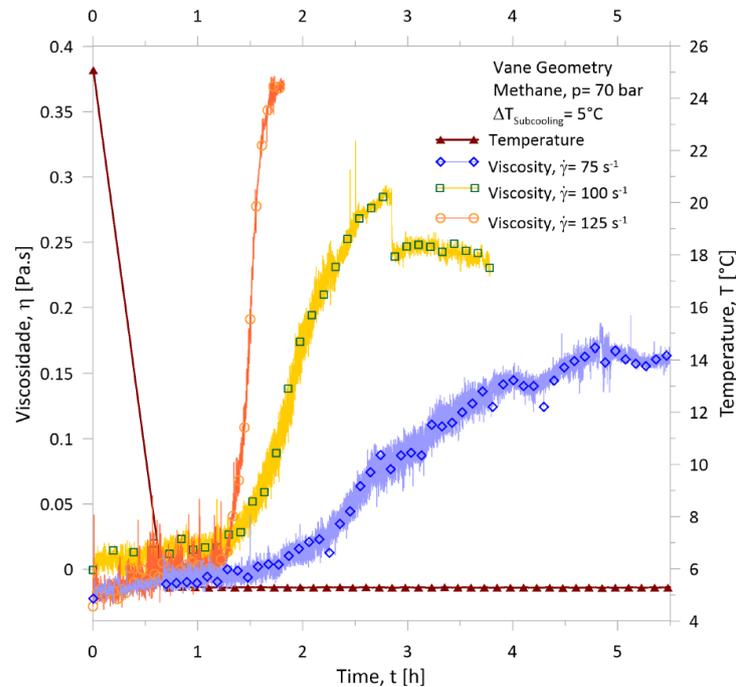


Figure 5: Effect of shear rate on induction time.

At the end of tests, after depressurize the pressure cell and remove the geometry, we can note the formation of a hydrate block. An example is showed in Figure 6 and it is possible to notice the hydrate block is formed around the blades of vane rotor.



Figure 6: hydrate block around the blades of vane rotor.

5. CONCLUSIONS

The hydrates formation is a big issue in the oil and gas industry. They are commonly formed in conditions of high pressure and low temperature and can block the flow inside pipeline. The experiments were performed to study the rheological effects of methane hydrate formation at different subcooling, shear rates and dissolution time, using a high-pressure rheometer system with a pressure cell and a vane rotor. The data showed that higher shear rates tends to increase viscosity and decrease the induction time, while higher dissolution time does not reduce the induction time. It has been also found that higher subcooling affect the induction time, decreasing it. The behavior of induction time in shear rates and subcooling was expected, as reported by some authors, while the dissolution time we believed the longer this parameter, the smaller the induction time, due to the fact, in theory, that the system would have more methane dissolved in water, lacking more investigation about this effect using a flowmeter to fortify the arguments.

6. ACKNOWLEDGMENTS

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