



Influence of the gas-oil ratio on hydrates formation in a crude oil system

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Abstract

Hydrates formation is a main flow assurance issue that can bring economic and environmental problems to the oil and gas companies. The comprehension of this phenomenon can provide means to avoid and mitigate its appearance or improve the hydrate slurry transportability. In the present work, the influence of the gas-oil ratio (GOR) on the hydrates formation is investigated. The study is conducted with water-in-crude oil emulsions in a high-pressure rheometric device. For the system employed, the results show that GOR can play an important role in hydrates formation. The influence of the GOR on hydrates is nonmonotonic and affects the morphology of the deposition obtained, which renders non trivial results.

Keywords

Hydrates; Flow Assurance; Rheology

Introduction

The formation of hydrates is one of the largest issues faced by flow assurance engineers [1]. These inorganic compounds appear when the water hydrogen molecules apprehend hydrocarbon molecules (usually gases) at specific thermodynamic conditions of moderate pressure and low temperatures [2]. The hydrates occurrence is inherent to the offshore process during the oil and gas production, since the hydrates constituents are naturally found at the well or auxiliary lines, and the thermodynamic conditions found in the systems are generally favorable to the stabilization of the hydrates crystals. Therefore, it is not surprising the huge interest in the understanding of these structures. Moreover, hydrates can play an important role in other applications, like the seawater desalination process [3], climate change [4], and gas storage [5].

In the oil or gas industry, hydrates can form during steady-state (continuous production) or transient conditions (production stop or start). This last formation mechanism occurs during a well-restart or shut-in process. Indeed, unblocking the systems – flowlines or equipment, is one of the most problematic scenarios that the field engineers have to deal with. The potential hazard of hydrates formation depends on different variables [6], such as thermodynamic conditions, physical and chemical properties of the fluids, pipes geometry and arrangement, hydrodynamic conditions, water cut, and gas-oil ratio. This last variable has a strong

impact on the practical applications and has been scarce explored in literature. In this sense, the present manuscript intends to help to understand the role of the GOR in hydrate formation, using water in a crude oil emulsion as the liquid phase and ethane gas as the guest molecule.

Methodology

Materials

The components of the emulsions employed were crude oil and deionized water. The crude oil used was provided by Petrobras with API gravity of 20° at 20 °C and with a content of saturates, aromatics, resins, and asphaltenes in wt% of 43.2, 51.6, 4.8, and <1, respectively. The deionized water was obtained from the Gehaka OS 10 LX system and purified through reverse osmosis. To prepare the emulsions, the amount of crude oil and water were weighed and placed in different bottles. Then, to homogenize the oil and remove its shear history, the samples were heated at 80 °C for 1 h and cooled for half-hour at room temperature. The emulsion was obtained by adding water to the oil phase and submitting this sample to agitation at 8000 rpm for 5 min in a Turrax homogenizer (model IKA T25, rotor 18G). The emulsion stability was verified through a periodic macroscopic analysis. The mean droplet diameter measured was 6±2 µm, and the emulsions remained stable for more than 1 week.

Experimental Procedure

A high-pressure system composed of a rheometer, pressure cell, syringe pump, and a thermostatic

bath was used to conduct the experiments. The rheometer employed was a shear stress-controlled Haake Mars III (Thermo Fischer Scientific). The pressure cell (Thermo Fischer Scientific) is placed in the base of the rheometer, and consists of a rotor (vane), stator (cylinder cup), two magnets, and a screw cover. The geometry used is the concentric cylinder/vane, with a 4-blade vane with outer diameter of 35 mm. The emulsion is placed in the cylinder cup. The cell provides three connections in the upper part: a safety valve, a pressure transducer, and a connection for the gas inlet. The cover was used to close the cell (rotor-internal magnet-stator-emulsion) and keep the system sealed. The rotor was conveyed through a magnetic field created between two magnets; one internal that is fixed in the upper part of the rotor, and another external propulsion magnet that was coupled to the rheometer head. As the rotor is supported by two sapphire bearings, it was necessary to calibrate the system, to take off the friction between the geometry and the bearings from the total torque generated by the rheometer. The gap between the vane and the cylinder cup was 2 mm. More information about the cell and its calibrations can be found in Sandoval et al. [7].

A thermostatic bath was used to control the temperature of the system during the experiments. The heat exchange was performed through a metal jacket that coats the rheometric cup. To maintain the pressure constant in the cell and quantify the amount of gas sent to the system, a double syringe pump (Teledyne ISCO) was employed. The gas flux was controlled by a needle valve connected to the cell. The pressure, temperature, and rheometric measurements were acquired for all tests.

To conduct the experiments, the pressure cell was filled with the emulsion and the rotor was sealed and placed in the rheometer. Then, the gas inlet line was connected and the system was pressurized with ethane provided from a gas cylinder. While the system was being pressurized, the rheometer was set at a constant shear rate throughout the test. The experiments were basically conducted in 3 steps: (i) gas dissolution, (ii) cooling until the equilibrium of hydrates, and (iii) waiting time for hydrates formation. During the dissolution step, gas is inserted while the temperature was kept at 25 °C for 4 h. In practical applications, the oil-containing gas dissolved from the well is called “live oil”. After the dissolution, the cooling step was performed, then, the temperature was reduced from 25 to 4 °C at a constant rate. This final temperature was kept constant until the end of the test. The typical subcooling reached in this work were in the range between 6 and 10 °C. Once the system was under the hydrate envelope conditions, a period of up to 24 h was set to detect the formation of hydrates through an increase in viscosity together with a decrease in pressure.

The gas-oil ratio (GOR) was changed by controlling the amount of gas injected through the needle

valve attached to the pressure cell. The needle valve was closed after the dissolution step.

Results and Discussion

Figure 1 shows the results obtained with two different GORs. The tests were carried out with a water-in-oil emulsion with 50% of water cut, a shear rate of 40 s⁻¹, and pressures of 29 and 33 bar, which lead to GROs of 5.7 and 6.6, respectively.

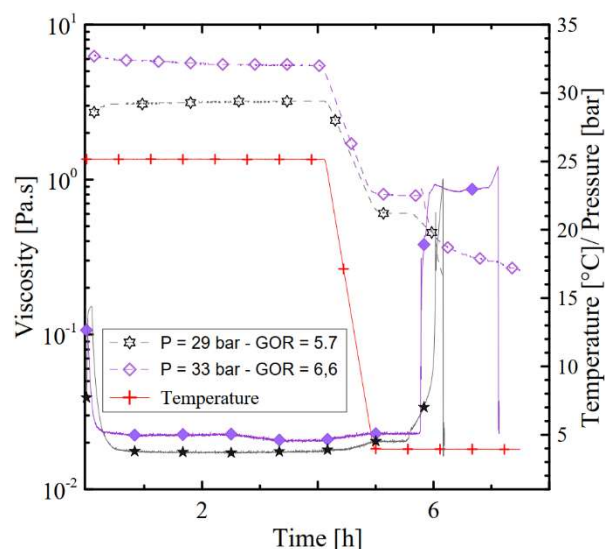


Figure 1. Viscosity and pressure measured with two different GORs. The red line represents the experimental temperature.

As observed in Fig. 1, the viscosity (filled symbols) decreased during the first hour of the test because of the gas dissolution, until achieve a constant value, which indicates saturation of gas in the system. During this first step, the pressure – represented in Fig. 1 by the empty symbols, was kept constant by means of the syringe pump. At this point of the test, the needle valve was closed while the cooling started from 25 to 4 °C, at a rate of 0.4 °C/min. As expected, the pressure decreased due to the temperature decrease, and the viscosity increased slightly. During cooling, the viscosity of the system should increase, however, this increase is counteracted by the dissolution of gas when the temperature decreases. Hydrates formation was identified for both experiments roughly 2 h after the cooling process. As noted in the viscosity curves, a dramatic increase of almost two orders of magnitude was observed. Concomitantly, a pressure decrease was observed. The increment in viscosity is caused by the phase change from the liquid to solid, resulting in a slurry formed by the emulsion, hydrates crystals, and their agglomerates [8,9]. The reduction in pressure is due to gas consumption by the water hydrogen bonds [10].

The spike in viscosity was interrupted when the allowable rheometer torque was achieved, and the experiment stops after that. For these two GORs, hydrates formation became a catastrophic event since the maximum torque was achieved. It is important to indicate that the subcooling difference

was only 0.5 °C between the tests, albeit the GOR difference was almost 1. For these tests, a hydrate plug was noted when the cell was opened after the depressurization.

To obtain an experiment without such a catastrophic formation, another test was performed with the pressure of 27 bar (subcooling of 8 °C and GOR of 4.0), as shown in Figure 2.

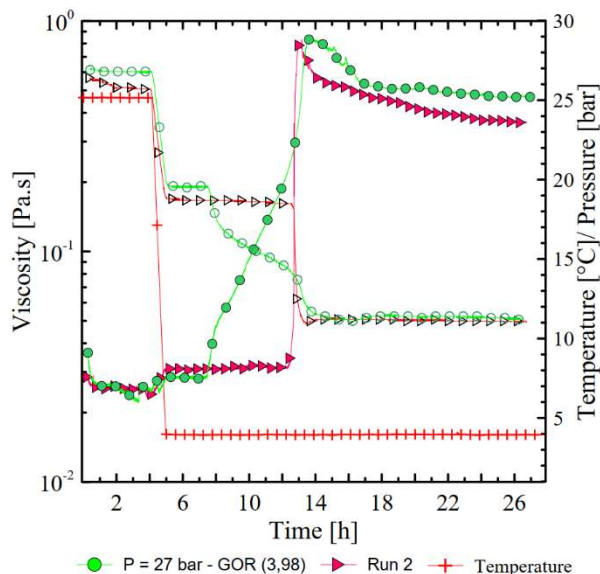


Figure 2. The steady-state regime of hydrates slurry was achieved with a GOR of 4. Run 2 indicates a repeatability test.

Figure 2 illustrates that hydrates formation in these conditions did not block the rheometer and a steady-state regime was obtained, with a constant viscosity value. A second experiment was performed with a different sample and the viscosity curve was close to the first test (see Run 2 in Fig 2). However, it is worth mentioning that the induction and growth period between the curves were different. The results plotted in Fig. 2 were expected since the spike in viscosity was diminished with the reduction of the subcooling [11, 12].

With the purpose of analyzing the influence of the GOR in hydrates formation, three other experiments were performed increasing the GOR, as shown in Fig. 3. The GOR was increased keeping the initial pressure constant until the cooling step, and closing the valve as soon as the temperature of 4 °C was reached in the system.

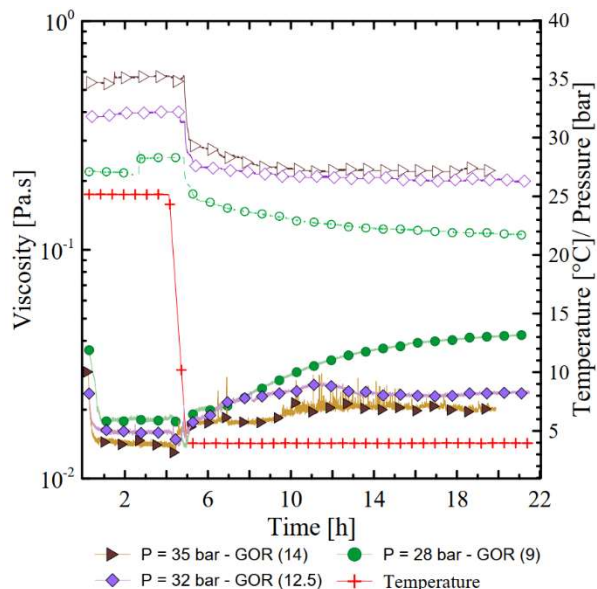


Figure 3. Experiments for larger GORs. The abrupt increase in viscosity and drop in pressure was noted.

The experiments show similar qualitative behaviors of the tests previously presented, during the dissolution and cooling steps. However, it was not noted a strong increment in viscosity during the waiting time, as happened when hydrates formation was detected in the results exhibited in Figs. 1 and 2. The pressure drop obtained after the cooling step (and after closing the needle valve) could be related with two facts. First, the formation or agglomeration of some hydrates particles, which would not be enough to cause a relevant effect on the viscosity of the system, and secondly, because of the thermodynamic equilibrium of the system – pressure was reduced until the system achieves the equilibrium at 4 °C. Interestingly, in this same region (waiting time step), the viscosity increased with the reduction of the GOR. The steady-state viscosity for the experiment with GOR of 9 was almost twice of the one obtained for the test with GOR of 14. It is also important to point out that the difference in subcooling was around 1 bar between the experiments conducted with GORs of 9 and 14. Therefore, such a behavior seems to be due to the effect of GOR.

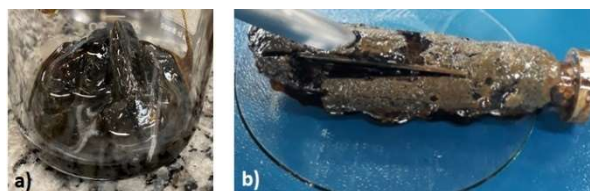


Figure 4. Morphology of hydrates for with (a) a catastrophic event (GOR = 6) and (b) for a GOR of 12.

It seems to be logical that an increase in the GOR leads to a severe hydrate formation, as noted in Figs. 1 and 2. However, this was not observed for the highest GOR tested, as depicted in Fig. 3. Despite the results in Fig. 3 strongly indicate that a

block of hydrates did not form, an unexpected deposition was noted when the sample was removed, as shown in Fig 4b. The sample was adhered to the entire bladed rotor, with a soft and brownish structure, and it was observed that a small amount of gas was coming out of it. A totally different morphology was noted when the catastrophic event was evinced, as shown in Fig 4a. This structure was more rigid, with more gas coming out, and black in color. The analysis of these different hydrate samples are being carried out.

A possible explanation for the deposition found for the highest GORs was given by the topological model on hydrates formation (Bassani et al., 2019). The authors proposed that the water present in the capillary porous structure of hydrates can be sealed by the oil, so the water becomes unavailable to form a capillary bridge, and the particles no longer agglomerate, resulting in what is being called as dry hydrates. It is important to note that the surfactants play an important role in the water seal process since they modify the interfacial properties of the water-oil-hydrates interface, allowing the oil to penetrate the capillaries. In the experiments conducted in this work, the agents responsible to perform this task are the natural surfactants of the oil. Despite the structure formed in this work did not stick to the cell walls and there was no observed free water after the test, more experiments should be conducted with other crude oils, guest molecules, and water cuts to study how the chemical composition of the oil can influence on the results.

Conclusions

In this work, a water-in-oil emulsion was employed to study the effect of gas-oil ratio on hydrate formation. A high-pressure rheological system was used to conduct the experiments, and the GOR was changed increasing the pressure or closing the gas inlet valve connected to the cell at different times during the tests. The results were not monotonic. For the lowest GOR analyzed, equal to 4, a hydrate slurry was formed and the viscosity was measured in a steady state regime. Once the GOR was increased to 5.7 and 6.6, the hydrate formation was catastrophic, with a strong block of hydrate formed. That behavior was expected the increase of the subcooling degree. However, when GOR was further increased for 9 and 14, the increment in viscosity was smoother and a lower steady-state value was obtained, leading to a softer formation/agglomeration of hydrate and a different morphology.

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Responsibility Notice

The authors are the only responsible for the paper content.

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