



## Rheological study of hydrate formation in the presence of paraffin molecules

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### Abstract

Hydrates formation and paraffin deposition integrate a series of flow assurance issues that jeopardize the continuous flow operations desired by the oil and gas companies. Both phenomena can coexist under certain thermodynamic conditions of low temperatures and moderate pressures. In the present work, the interaction between these two structures was analyzed from a rheological point of view. A water-in-oil emulsion with a commercial paraffin was used and it was assessed through a high-pressure rheological approach. The results showed that paraffins act delaying the critical time for hydrate formation, and for a given paraffin content, the formation of hydrates could be avoided. In addition, the amount of hydrates formed decreases as the presence of paraffin increases in the water-in oil emulsions.

### Keywords

Hydrates; Paraffin; Rheology

### Introduction

Hydrates formation and paraffin deposition are the most common and challenging flow assurance issues presented in offshore oil and gas production [1]. Hydrates are formed when the water hydrogen bonds capture and retain molecules (usually gases) at moderate pressures and low temperatures [2]. Hydrates formation is an interface phenomenon that takes place between the aqueous and oil phases [3]. On the other hand, long hydrocarbon chains dissolved in the bulk phase constitute the paraffin component of the oil [4]. If the temperature of the oil falls below the wax appearance temperature (WAT), they precipitate out from the liquid phase, and if exists a negative gradient temperature between the pipe wall and the fluid, the deposition of these paraffins occurs. Since both phenomena happen at low temperatures and high pressures, both species can appear concomitantly, or an appearance preference by either of them can arise. In such a case, it is important to know the interaction between waxes and hydrates to understand how to avoid or remediate its deposition/formation. In literature, there are different opinions regarding the influence of waxy on hydrates formation. Some studies have indicated that the critical time to hydrate formation increase with increasing the wax content [5,6], moreover, the maximum values obtained in the viscosity of hydrates are reduced

when the amount of wax is increased [5], indicating less formation or agglomeration of hydrates crystals. It has been proposed that the paraffins produce an inhibition effect on hydrates formation by considering a limitation in the mass transfer process among the hydrate's constituents [5]. Wang et al. [7] also observed a wax inhibition effect on hydrates kinetic, however, the authors noted that after some waxy content range, hydrates formation was accelerated. On the other hand, Gao. S [8] reported that gas hydrates particles can facilitate wax precipitation and deposition, and wax deposition can potentially increase hydrates agglomeration. The explanation for this fact is that hydrates create a large surface area that serves as nucleation sites for the deposition of waxy crystals. With the purpose of contributing to these meaningful works, this study presents different rheological results obtained in a high-pressure approach for a water-in-oil system with and without the addition of paraffin.

### Methodology

#### Materials

Deionized water, mineral oil, and Span 80 were used to prepare the stable water-in-oil emulsions with and without paraffins. The deionized water was obtained from Êxodo Científica. A mineral oil (Sigma-Aldrich) with a light degree was employed. This oil was colorless, odorless, and with a

kinematic viscosity between 14.2 - 17 cSt at 40 °C. The nonionic surfactant Span 80 was used as an emulsion stabilizer agent in a quantity of 0.5 wt% of the total specimen. The white paraffin, purchased from Sigma-Aldrich was received in the pellets-like form and was composed of normal alkanes with a range of carbon numbers between  $C_{23}$  and  $C_{31}$  classified as long-chain hydrocarbons [9]. The WAT was determined visually by monitoring the morphology change of the paraffin dissolved in the pure oil during a cooling test and measuring the temperature at ambient pressure [10]. The values of WAT obtained were 24.3 and 35.8 °C for the amounts of paraffins (in the total emulsion) of 2 and 6 wt%, respectively. The emulsions were prepared with the following methodology: firstly, the amount of oil, water, paraffin (when required), and Span 80 were weighed. Secondly, the Span 80 and paraffin amount were added to the oil and placed in an oven at 80 °C for 2 h for obtained a melting wax. Then, the mixture was removed from the oven and cooled down until 40 °C. Thirdly, the amount of water was mixed with the specimen obtained in the second step and were agitated by means of an Ultra Turrax homogenizer (model IKA T25, rotor 18G) at a velocity of 12000 rpm for 3 min. The emulsions obtained remained stable for more than 24 h of its preparation and the mean droplet diameter measured for the emulsion with and without paraffin content (until 0.25 wt%) was less than 10  $\mu\text{m}$ .

### Experimental Procedure

The setup employed to conduct the experiments was composed of a Haake Mars II rheometer and a high-pressure cell (both devices from Thermo Fischer Scientific), a thermostatic bath, a gas mass flow meter, and a gas booster. Initially, the methane gas (stored in a gas cylinder outside the laboratory) was conducted to the booster where the gas pressure was increased a little higher than the needed pressure inside the cell. Then, before sending the gas to the cell, it passed through a needle valve where was set the experimental pressure. The high-pressure cell consisted of two main parts, the stator, and the rotor. The stator was the measuring cup, where was placed the sample and the rotor. The rotor was the measuring geometry that was a vane with 4 blades and was supported inside the cell through two opposite sapphire bearings. The rheometric gap formed was 7 mm. To seal the cell, the assembled stator-sample-rotor was closed with a screwed cover. The rotor was driven using a magnetic field created by two magnets. One of them was attached to the rotor, and the other was fixed to the rheometer head. All the calibrations of the cell were performed as indicated in the manufacturer manual, with special attention to the subtraction, of the total torque, the torque created due to the friction between the rotor and the bearings. More information about the cell and its calibrations can

be found in Sandoval et al. [11]. The temperature control was performed through a thermostatic bath connected to a jacket that circulates the fluid that coats the rheometric cup. Finally, a mass flow meter model F-111B from Bronkhorst was used to measure the amount of gas sent to the cell.

To conduct the experiments, the pressure cell previously charged with the emulsion and rotor was sealed and placed in the rheometer, then, the gas inlet line was connected, and the system was pressurized with methane gas. The tests were initialized in the rheometer with a constant shear rate throughout the experiment. The initial set temperature was 40 °C (higher than the WAT for the samples used). The experiments were performed in the following three consecutive steps: gas dissolution, cooling, and waiting time for hydrate formation. The gas dissolution was performed at 40 °C for 4h. In this step, a portion of the gas was dissolved in the oil phase and become in contact with the aqueous phase. After that, the temperature is reduced from 40 °C to 1 °C at a cooling ramp of 0.4 °C/min. At this final temperature, the system is under the hydrate stability region with a subcooling of 12 °C. This final temperature remained constant until the end of the test. Finally, the rheology of the system was monitored to detect or not the hydrates formation. Hydrates formation was noticed to an abrupt increase in viscosity. The experiments were run until the steady-state viscosity was achieved.

### Results and Discussion

Figure 1 shows the rheological results obtained by varying the amounts of waxy crystals. The results are exhibited through viscosity curves as a function of the experimental time. All the tests were performed with a constant pressure of 100 bar, shear rate of 60  $\text{s}^{-1}$ , water volume fraction of 30%, and initial and final temperatures of 40 and 1 °C, respectively. In Fig. 1, the temperature variation is represented by the blue curve.

Initially, one experiment was conducted without paraffin (green curve), subsequently, two different amounts of paraffin were assessed, 2 and 6%. As observed in Fig. 1, during the dissolution, the viscosity is slightly reduced during the first hour of the experiment and then reached a constant value. This behavior is associated with the dissolution of the gas in the emulsion. The saturation of the sample with the gas should occur when the viscosity achieved its minimum value during that 4 h. Once the dissolution step ended, the cooling step was started, and the system reached the equilibrium curve at isobaric conditions ( $P = 100$  bar) at the rough temperature of 13 °C. During the cooling, the viscosity increases due to the reduction in temperature, however, this increment could be counteracted by the continuous dissolution of the gas in the system, due to the temperature drop. During the cooling, the viscosity increased with increasing the paraffin content.

Such a trend was expected since more paraffin was precipitated out from the oil phase.

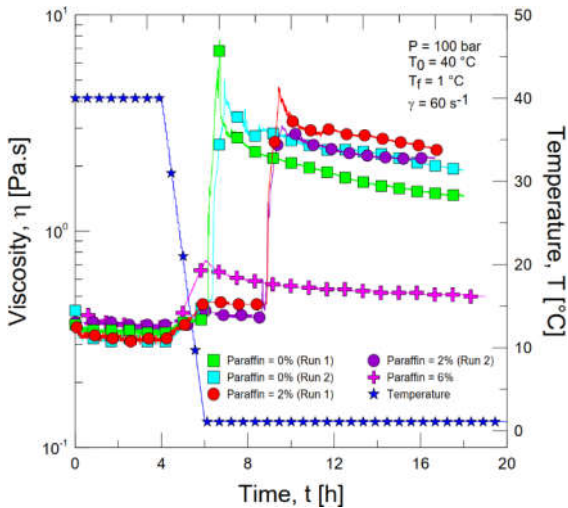


Figure 1. Experiments conducted with different amounts of paraffin.

For the system employed, hydrates and paraffins were inside its equilibrium region at the temperatures of 13 and 10 °C, respectively. It is expected that paraffins precipitate out occurs first than hydrates formation, since the paraffins phenomenon is significantly governed by the temperature reduction. The third experimental step starts when the system passes through the equilibrium conditions favorable to hydrates formation. Figure 1 shows that hydrates without paraffin were formed during the first equilibrium hour. As noticed, the increment in viscosity was almost 20 times. That increment is associated with two main facts, firstly, with a phase change, where the liquid droplets become solid particles, and secondly, with the agglomeration of these particles [12]. Indeed, the hydrate structure formed can trap the free liquid (oil and water) in its porous medium, “sponge-like” hypothesis [13]. This process can generate dry hydrate crystals which can also help to increase the viscosity. The other two experiments were carried out with 2 and 6% of paraffin content in the sample. The induction time of the test with 2% of paraffin content increased in around 4 h regarding the test without paraffin. In fact, the spike in viscosity was lowered, but the steady-state viscosities were similar between these two experiments. For the experiment with 6% of paraffin, hydrates did not occur since the abrupt increase in viscosity was not detected. That means, that hydrates formation was hindered by the increment of paraffins content. The increment in the induction period and the hydrates inhibition effect yielded by the increase in the amount of paraffin have been related to the weakness in the hydrate’s cohesion forces. This fact has been attributed to the hydrophobicity created by the wax molecules in the hydrate surfaces [7]. The paraffins could also interfere in the mass transfer diffusion between the guest and host molecules of hydrates

[6,7]. To obtain more confidence in the results, two more repeatability experiments were performed without the addition of wax and with the addition of 2% of wax, see Run 2 in Figure 1. Despite the stochasticity of the phenomenon, the results attained were similar both in the induction times and in the steady-state viscosity values measured.

Figure 2 represents the amount of methane gas sent inside the pressure cell for each experiment explained before (Fig. 1). Figure 2 displays three main regions where the volume of gas increased throughout the experiments. The first volume increment was due to the pressurization of the cell and the dissolution of the methane gas in the oil phase. As previously indicated, this increment reaches a plateau when the oil phase is saturated by the gas. The volume of gas sent for the experiment with the presence of 6% of paraffin was larger than in the other tests. The same pattern happens in the experiment with 2% of paraffins content in comparison with the test without paraffin. It can be associated with the large paraffins molecules, which can dissolve more gas in their structures, therefore more gas is needed inside the cell to keep the pressure constant.

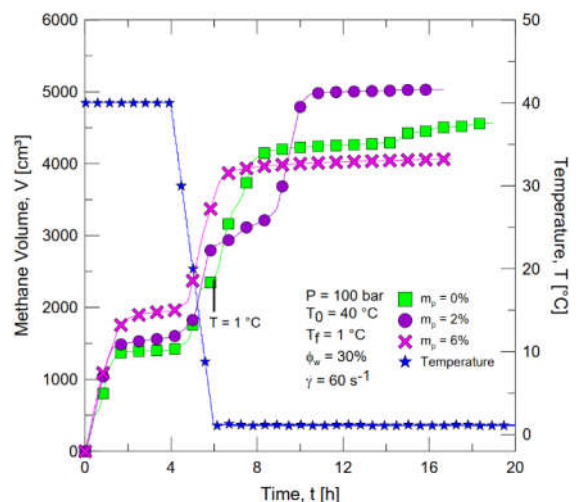


Figure 2. Gas sent to the pressure cell for the experiments shown in Fig. 1.

The second region where the increment in the methane volume was noticed was during the cooling. In this step, more gas was dissolved because of the reduction in temperature. However, more gas seems to be dissolved for the experiments that contain more paraffins. In fact, the volume of gas sent for the experiment with 6% of paraffin was double of the experiment with 2% - and the volume of methane sent for this last one was larger than the test without paraffins. That indicates that again more gas was dissolved in the systems that contain more amount of hydrocarbon molecules. For the experiment with 2% of paraffins content, more volume of gas was sent to the cell after the cooling, until achieving the third main region of gas volume increment, which was the instant of the hydrate formation. When hydrates

form, gas is captured (consumed) by the water hydrogen bonds, therefore, more gas was sent into the cell to keep the pressure constant. For the experiments without and with 2% of paraffins, the volume of gas consumed when the hydrates event occur was 2200 and 1700 cm<sup>3</sup>, respectively. Despite the test without paraffins did not reach a steady-state. Clearly, the experiment conducted without paraffin did not consume gas, since hydrates did not form. Therefore, the results show that the amount of hydrate formed decreases with increasing the paraffins content.

## Conclusions

The formation of hydrates and paraffin precipitation were tackled in this work through a rheological approach. A high-pressure setup coupled with a rheometric cell was employed to assess a colloidal system composed of a water-in-oil emulsion, with and without commercial paraffin. The results obtained showed that the paraffin can act as a hydrates inhibitor. For the system employed, the paraffin precipitation event occurred first in comparison with hydrates formation since the former phenomenon is highly temperature-dependent. Hydrates formation does not necessarily happen by the reduction in temperature. If paraffin is precipitated out from the oil phase, the formation of hydrates can be obstructed by creating a barrier that hinders the diffusion of the hydrate's constituents or due to the hydrophobicity network yields by the long hydrocarbon molecules placed on the hydrates interfaces. This fact can increase the time for hydrate formation as observed for the test conducted with 2% of paraffin, or even, avoid the hydrate formation as observed in the test with the presence of 6% of paraffin. It was also determined that the amount of hydrates formed decreased with the increment in the paraffin content since more gas was consumed during the growth and formation of hydrates for the test without paraffin content. These results help to understand the macroscopic interaction that occurs between hydrates and paraffin in practical applications.

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## Responsibility Notice

The authors are the only responsible for the paper content.

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