



Flow assurance combined effects

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Abstract

Halting production lines due to the formation of hydrates, emulsions, waxes, and asphaltenes presents significant challenges for the crude oil industry. While existing studies often address these issues individually, they frequently co-occur in operational scenarios, necessitating a comprehensive approach to understand the combined effects. This study aims to analyze the simultaneous occurrence of these phenomena using different rheological techniques. Our primary focus is on characterizing the bulk rheology of crude oil, emulsion, and hydrates under extreme temperature and pressure conditions to mimic operational environments. Additionally, we conducted interfacial rheology analysis to complement the bulk results, recognizing the critical role of water/crude oil and gas/water/crude oil interfaces in defining fluid behavior within these systems. Furthermore, we integrated microstructural characterization of the systems and interfaces using scanning electron microscopy with a cryosystem (Cryo-SEM) and optical microscopy techniques, enhancing our understanding of the rheological properties. This comprehensive set of tests comprises an experimental methodology proposed as a potential standard procedure for validating the occurrence of flow assurance issues and improving the effectiveness of solutions.

Keywords

Hydrate; emulsion; crude oil; bulk rheology; high pressure; interfacial rheology; waxes.

Introduction

Transporting multiphase fluids—comprising gas, solid, and liquid phases—under extreme conditions, such as high pressure and low temperature, presents a significant challenge in the crude oil industry. These conditions give rise to numerous issues that can lead to production halts. Flow assurance covers all the development, processes, and engineering activities in the oil and gas industry, need to ensure an uninterrupted flow of hydrocarbons from the reservoir to the platform. These include the buildup of solid deposits like hydrates, asphaltene, wax, and naphthenates. Various studies in literature focus on analyzing each problem individually. However, comprehending these phenomena as a collective global challenge, wherein these issues can occur simultaneously, poses a significant obstacle. Addressing these deposition issues separately may be inefficient and risky due to their potential coexistence and interaction [1].

There are few comprehensive studies in the literature that have address together more than one flow assurance occurrence. Most studies have utilized synthetic systems to simulate various fluid compositions with two or more simultaneous occurrences. These studies typically conclude by emphasizing the inhibitory effects of certain

occurrences, such as hydrate formation [2-4]. The precipitation of waxes and asphaltenes can disrupt mass transfer, leading to the blockage of gas transportation at water/oil interfaces [3]. Fewer articles have investigated the problem using real crude oil samples [1, 5-7]. These studies have observed a reduction in hydrate formation with increasing hydrocarbon content and varying chemical compositions of crude oil [4]. Additionally, they have identified the coexistence of combined mechanisms of inhibition and promotion, which influence thermodynamic, kinetic, and consequently rheological properties [1,8]. However, some of these conclusions have been deemed premature by other authors, who suggest conducting further studies [5].

This study aims to systematically investigate the relationship between gas, salt, water, and crude oil concerning flow assurance and their impact on fluid performance. Experiments were conducted under high pressure and low temperature, considering atmospheric pressure experiments as a baseline. A comprehensive characterization of hydrocarbons, emulsions, and hydrates was undertaken using various experimental methods to ensure a thorough analysis. Bulk rheology measurements such as yield stress and viscosity, as well as interfacial rheology properties including

dilatational and shear oscillatory modulus, pressure, and interfacial tension, were obtained. Microstructural analysis was conducted using optical and electron microscopy techniques. Ultimately, an experimental methodology was established to analyze these occurrences, providing insights into potential issues and strategies for addressing them effectively. Due to constraints within this extended abstract, detailed microscopy analysis of emulsions and hydrates, as well as interfacial rheology data, will not be presented.

Methodology

In this study, we have outlined methodologies of bulk rheology for a specific crude oil, emulsion, and hydrate at atmospheric and high pressure, and the interfacial rheology.

Materials

The crude oils were given by CENPES/Petrobras, with water content of 0.5%. The composition of the synthetic sea water was 2,0g/L CaCl₂ and 55 g/L NaCl. The protocols of preconditioning the crude oil and emulsion preparation followed a protocol given by CENPES.

Experimental Procedure

• Preconditioning of crude oil

Initially, the crude oil is heated to 80°C. This temperature was chosen because it's higher than the WAT (Wax Appearance Temperature). The WAT of crude oil is approximately 30 °C. A mechanical stirrer placed atop the oven stirs the oil at 300 rpm for 3 hours, ensuring the sample is well mixed and any crystals are completely dissolved. Afterwards, 800 ml of crude oil is poured into 1-liter Schott glass bottles. Each bottle is then stored at 80°C in an oven for 2 hours before being divided into samples of 25 ml. This smaller volume is about right for testing in the rheometer. Before testing, each small bottle is kept at 80°C for an additional hour, with the lid partly closed to prevent volatile loss while allowing pressure to be released.

• Emulsion preparation

All experiments were carried out using a 50/50 volumetric ratio between water and oil. The crude oil from the previous step is heated in an 80°C oven for 1 hour. Afterwards, it is transferred to a 500 mL bottle, and water is added under manual agitation. Following this, the emulsion is stirred using a Turrax (manufactured by IKA) for 3 minutes at 8000 rpm. Considering prior stability analysis of the emulsion using the TURBISCAN technique, the maximum storage time to guarantee emulsion stability was one day at 25 °C.

• Bulk rheology at atmospheric pressure

All bulk rheology tests under atmospheric pressure were performed using the TA Instruments DHR-3 hybrid rheometer. The samples were inserted into

the rheometer geometry, which had been preheated to 60°C. The sample was then subjected to shearing for 15 minutes at 10 s⁻¹ at this temperature. Subsequently, the sample underwent a controlled cooling process at a rate of 0.8°C/min until reaching 4°C. Upon reaching 4°C (the temperature of interest for all tests), the sample was conditioned for one hour.

We employed both the stress ramp and creep tests to ascertain the yield stress of both crude oil and emulsion at two different cooling rates (0,8 °c/min and 0,08°C/min).

We incremented stress levels from 1 to 1000 over 30 minutes, using this ramp to estimate the initial stress for subsequent creep tests. Figure 1 (a) shows stress ramp curves for crude oil and emulsion, where the shear rate initially increases slowly, then abruptly at the static yield stress, indicating fluid flow. Creep curve were then generated, plotted in the Figure 1 (b). These the yield stress values of both crude oil and emulsions for all cooling rate are summarized and compared in Figure 2.

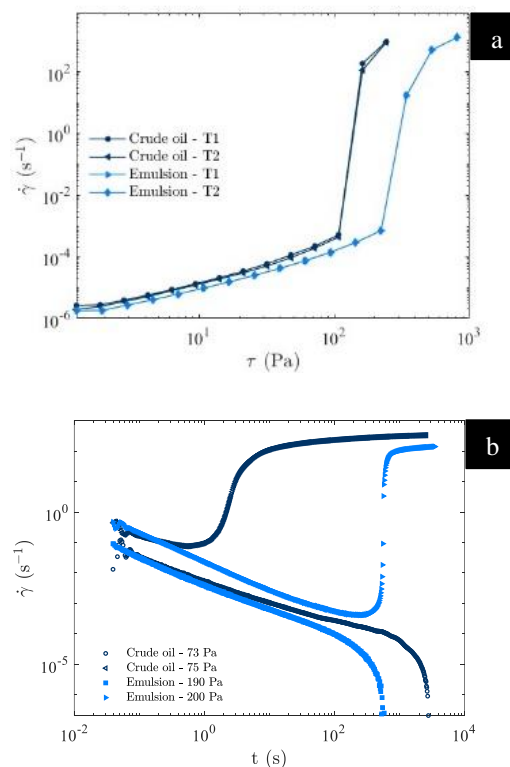


Figure 1. (a) Stress ramp of crude oil and emulsion at atmosphere pressure, and (b) creep test of crude oil and emulsion at atmosphere pressure.

• Bulk rheology at high pressure

We used the Haake Mars III rheometer featuring Vane geometry and pressure cell for high-pressure rheometric testing. The emulsion sample of 25 ml was carefully placed within the pressure cell, marking the onset of the experiment at 60°C and a pressure of 150 bar, with a shear rate of 50 s⁻¹. Throughout the test, the pressure within the cell remained constant. Following an hour of gas

incorporation at 60°C, the temperature was gradually decreased to 4°C at a cooling rate of 0.8°C per minute. Viscosity measurements were taken over time to monitor hydrate formation at this target temperature. Subsequently, the yield stress was determined through a stress ramp test.

- **Interfacial rheology**

An oscillatory test was conducted to analyze the rheological behavior of the interface between water and a synthetic system composed of cyclopentene and crude oil, simulating hydrate formation under atmospheric conditions. The optimal parameters for the sweep time test were a frequency of 1 Hz and an amplitude of 0.05%, at 4°C.

Results and Discussion

Combine effects of wax and emulsion

Figure 2 shows the static yield stress values for crude oils and their emulsions. We observed increased yield stress from crude oils to emulsions, which aligns with expectations.

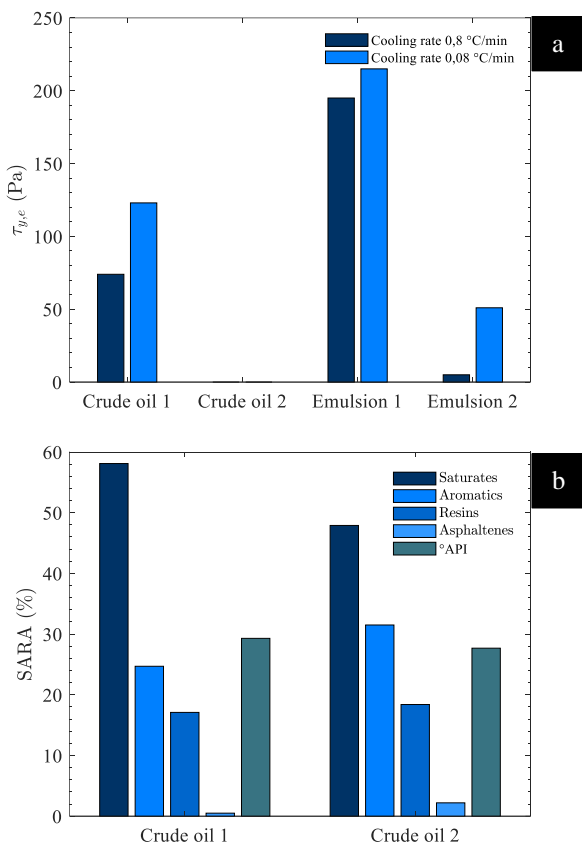


Figure 2. (a) Bar graph of static yield stress values from creep tests of two crude oils and their respective emulsions, comparing two different cooling rates, and (b) SARA analysis of these two crude oils

The presence of dispersed droplets significantly increases the viscosity of crude oil, especially when the concentration exceeds 5% v/v, surpassing the linear behavior predicted by the

Einstein equation. Given that a 50% v/v emulsion is considered concentrated, the viscosity of these emulsions is expected to be much higher than that of crude oil [10].

We also noted the influence of the cooling rate, where higher yield stress values were associated with slower cooling rates, likely due to the formation of larger wax crystals in both fluids. These larger crystals caused greater blockage to fluid flow. Interestingly, the second crude oil did not exhibit a yield stress value, whereas its emulsion did. This difference in behavior may be attributed to the SARA chemical characteristics (see Figure 2 (b)), as crude oil 2 has a lower wax content and a higher asphaltene content compared to crude oil 1.

Combine effects of hydrate and emulsion

Figure 3 illustrates the variations in viscosity, pressure, and temperature over time. By examining the viscosity pattern, we can infer whether hydrate formation occurs and when it begins, i.e., the induction time. In Figure 3, during the cooling phase highlighted in blue, the viscosity of the emulsion starts to rise due to wax appearance. As it reaches 4°C, we observe a rapid increase in viscosity, likely attributed to hydrate formation (yellow color highlight). After 3 hours of testing, the viscosity stabilizes, indicating the cessation of the hydration process. This stable viscosity value is crucial for determining the yield stress value of the hydrate slurry.

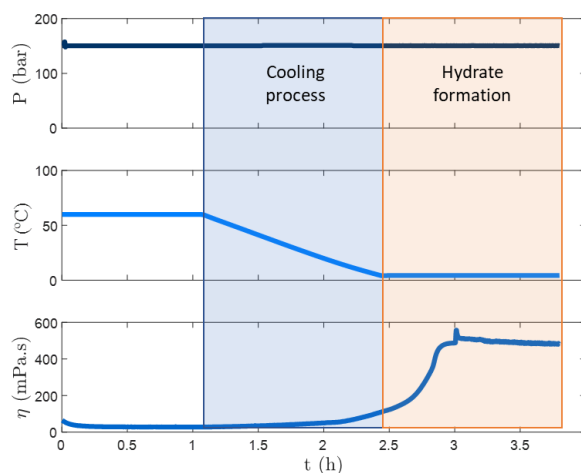


Figure 3. Pressure, temperature and viscosity vs time curve of hydrate at 100 bar with natural gas.

The stress ramp of the hydrate slurry is depicted in Figure 4. This initial approximation allows us to measure the yield stress of this complex fluid. It's a challenging task due to the involvement of three phases simultaneously. The yield stress value falls between 30 and 40 Pa. Given the complexity of the task, further analysis and experimentation are required to ensure a reliable and accurate result. Figure 4 displays a micrograph capturing hydrate, along with a schematic model illustrating the water

molecule cage (Fig. 4. b) containing natural gas molecules

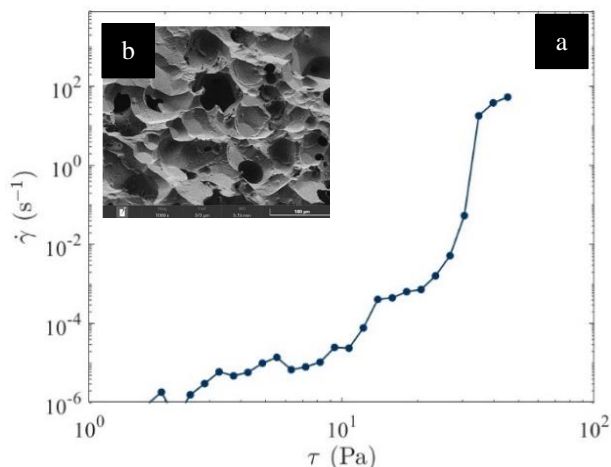


Figure 4. (a) Stress ramp curve of hydrate formed at 100 bars with natural gas, and (b) cryo-SEM micrograph of hydrate formed at 100 bars with natural gas.

Additionally, micrograph took of the hydrate formed after opening the pressure cell. The distinct sizes of hydrate cages are observable in the image. Similar cage structures have been reported by other authors [9].

Combine effects of hydrate and wax

Figure 5 shows the interfacial rheology of synthetic hydrate formed from cyclopentane (CP100) and in mixture with two relation of crude oil, CP90 and CP50.

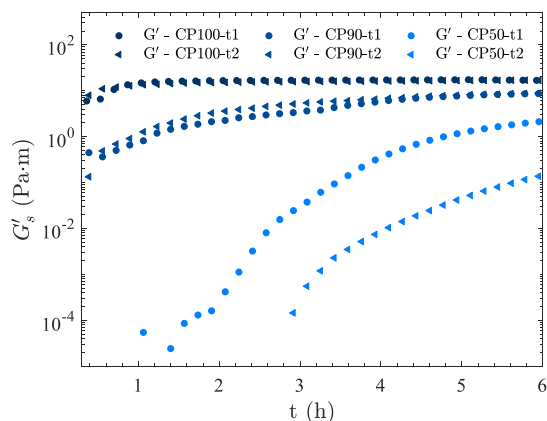


Figure 5. Oscillatory sweep test of interface between brine water/(cyclopentene + crude oil) for different relation of CP and crude oil.

In this figure we can see the important role of crude oil in the nucleation and growth of gas hydrates. Our findings indicate that waxes significantly inhibit hydrate nucleation and retard the overall formation process [2]. Additionally, the presence of crude oil alters the kinetics of hydrate formation, with a noticeable reduction in hydrate growth rates as the oil content increases. These results provide

valuable insights for developing strategies to mitigate hydrate-related flow assurance issues.

Conclusions

The results obtained are promising from a broad perspective. We successfully measured the yield stress of crude oil and emulsions with good repeatability across various temperature ramps. Furthermore, we established a procedure for forming hydrates that do not obstruct rheometer measurements, allowing for effective yield stress measurement. Additionally, we developed a methodology to assess the interfacial rheology characteristics of these complex interfaces. These procedures, along with similar outcomes, will be replicated across multiple crude oils to establish a baseline and compare their behavior with their respective chemical characteristics.

By comparing the results across different flow assurance challenges, we observed the influence of wax content on both bulk and interfacial rheology. The presence of wax inhibited hydrate formation and increased yield stress with slower cooling rates. These findings represent a small part of a larger project. We are in the early stages of rheological characterization and plan to conduct more tests, gather additional experimental data, and make further comparisons to better understand the interaction between these flow assurance issues. We anticipate having more conclusive results by the time of the conference.

Acknowledgments

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Responsibility Notice

The authors are the only ones responsible for the paper content.

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