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Interfacial Rheology as a Tool for Understanding Flow Assurance Issues

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Abstract

Interfaces play an important role in flow assurance when multiphase fluid transport systems are present. The intricate dynamics of the interfaces and their properties offer valuable insights into the broader operational challenges. Understanding these complexities becomes essential, as it not only enhances our comprehension of the overall problem but also paves the way for alternative solutions. In this work, we aim to comprehensively analyze the interfaces of water in waxy-oil emulsions and synthetic hydrates (using cyclopentane) by employing various techniques simultaneously. Moreover, we compare the results for different oils and analyze the effect of their chemical characteristics. Our investigation involves obtaining shear and dilatational oscillatory rheology by a rotational rheometer with the double wall ring acessory and by a rising drop tensiometer. In addition, the interfacial pressure of the interface is measured by a unidimensional compressor using a Langmuir trough. We focus on examining several parameters, including how cooling rates impact wax formation, the inhibitory effects of salt on hydrate formation, and the role of wax buildup in both hydrate formation and mitigation.

Keywords

Shear interfacial rheology; interfaces water/crude oil; dilatational rheology; Langmuir trough.

Introduction

In multiphase fluid transport systems, such as those encountered in crude oil transportation, interfaces between different phases play a crucial role in flow behavior and system performance. Understanding the properties and complexities of these interfaces is essential for optimizing flow assurance strategies and ensuring operational efficiency.

The significance of studying interfacial rheology in multiphase flow systems has been well-documented in the literature. Understanding interfacial properties helps improve emulsion stability, prevent the formation of deposits like waxes and hydrates, and enhance transportation efficiency by reducing apparent viscosity and energy consumption. Additionally, it is essential for the effective separation of water, oil, and gas phases during processing and for developing inhibitors and chemical treatments that mitigate operational issues. This also contributes to minimizing environmental impacts by reducing the risk of spills and facilitating the treatment of wastewater.

Several authors delved into shear rheology of interfaces in multiphase systems, elucidating the influence of interfacial shear properties on flow behavior and stability [1]. Similarly, the dilational rheology of interfaces was used to provide insights into their dynamic behavior under varying environmental conditions [2]. Furthermore, the one-dimensional pressure rheology of interfaces was investigated to shed light on the pressure-driven flow phenomena occurring at fluid interfaces [3].

By exploring the properties of interfaces and their physico-chemical interactions within multiphase fluid systems, we can gain insights into flow assurance challenges, and work on developing effective mitigation strategies to ensure operational reliability and efficiency. We aim to understand the intricate interplay between water interfaces in crude oil and synthetic hydrates, with a particular emphasis on the influence of different crude oils and their unique chemical compositions. We present some representative results of the interfacial behavior for each technique, obtaining properties such as shear oscillatory modulus, dilatational oscillatory modulus, surface pressure, and interfacial tension.

Methodology

In this section, we delineate the methodology employed to obtain interfaces that represent real-case scenario, based on the equipment employed.

Shear interfacial rheology

The shear characteristics of crude oil/brine water interface and hydrate films were assessed utilizing a stress-controlled Discovery Hybrid Rheometer (DHR-3) by TA Instruments, with a double wall ring accessory (DWR), and a homemade brass receptacle designed for containing the water and oil subphases. This brass receptacle exhibits high thermal conductivity, facilitating swift transmission of temperature imposed by the Peltier plate throughout the entirety of the system.

First, we poured the heavy phase (water) into the brass cup. We started cooling at 20ºC and kept it at this temperature for 10 minutes. After that, we cooled the system to -10ºC at a rate of 0.7ºC per minute, and the temperature was maintained for 10 minutes to allow the ice to form. This step is crucial because pre-freezing the water helps the ice to form more quickly. Then, we warmed it up to a final temperature of 4ºC, also at a rate of 0.7ºC per minute, and kept the temperature constant for the entire experiment. When the ice melted, leaving a thin layer of liquid water on top, we delicately placed the double-walled ring at the interface. Oscillatory tests were performed with a constant strain amplitude of 0.05% at a fixed frequency of 1 Hz (within the linear viscoelastic region), while the values of the elastic and viscous moduli, G' and G'', respectively, were recorded over time.

Dilatational interfacial rheology

We used the rising drop technique with the tensiometer from Teclis Scientific, France. We measured the interfacial tension and the dilatational modulus (storage modulus - E', and loss modulus - E''), comparing the first fresh droplet with three other droplets aged for different times. These tests were conducted after applying a temperature ramp of 0.7°C, starting from 60°C until reaching the target temperature of 25°C.

Langmuir trough experiments

The isothermal experiment for a specific compound is conducted on a Langmuir Trough, which is connected to a thermostatic bath regulating the analysis temperature. The data obtained comprise interfacial pressure values plotted against the surface area of the interface, measured using a Wilhelmy plate affixed to a balance. Before beginning the test, a meticulous cleaning procedure is undertaken. Deionized water and acetone are used to cleanse the trough and barriers, while flame sterilization is employed for the plate. Following cleaning, 400 mL of the subphase, typically water or brine, is transferred to the trough, followed by the addition of a solution containing 1 mg/mL of crude oil in chloroform (a volatile solvent). The required volume is carefully transferred drop by drop onto the trough surface using a Hamilton syringe. A waiting period of 30 minutes ensues to ensure complete solvent evaporation before commencing the experiment.

Results and Discussion

Shear Interfacial rheology

Figure 1 depicts the shear oscillatory results of the crude oil/brine water interface, focusing on the evaluation of the effect of the temperature ramp (TR) on the values of the storage modulus (G') and loss modulus (G'') over time. We observed a slight difference between the G' modulus in the first seconds of the test, achieving the same value of approximately 80 Pa.m after 3600 s. The results of G'' follow the same trend. Overall, no significant difference was observed, probably because similar crystal sizes of waxes were obtained for these two different temperature ramp.

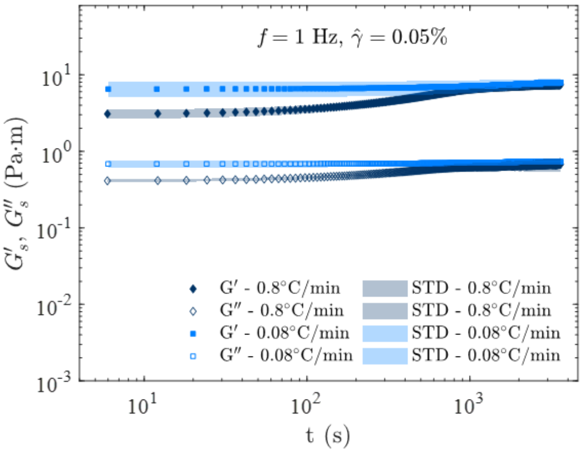

Figure 1. Shear oscillatory result of the crude oil/brine water interface evaluating the effect of the temperature ramp (TR) in the values of Store (G') and loss (G'') modulus with the time.

The graphic depicted in Figure 2 presents a comprehensive analysis of the storage modulus (G') over time for synthetic hydrates under varying ratios of cyclopentene (CP) to crude oil with deionized water. This analysis offers valuable insights into the rheological behavior of hydrate formation as a function of the mixture's composition. The observed trends provide a basis for understanding how changes in the amount of crude oil impact the mechanical properties, kinetic of formation, and stability of the hydrate structures over time.

The analysis of the results has revealed that larger amounts of crude oil lead to faster formation (lower induction times) and larger values of G', indicating a more rigid film at the interface. These findings align with previous studies documented in the literature, which also observed similar effects of crude oil on hydrate formation and stabilization. Crude oil tends to delay the initial induction and formation stages of hydrates, altering their trajectory and consequently affecting both the time and the value of the storage modulus (G') in steady-state conditions. This behavior is likely associated with the precipitation of waxes at the oil-water interface, which accumulates and hinders the contact between water and cyclopentane, thus preventing the formation of hydrate nuclei and their subsequent chain growth [4 - 7].

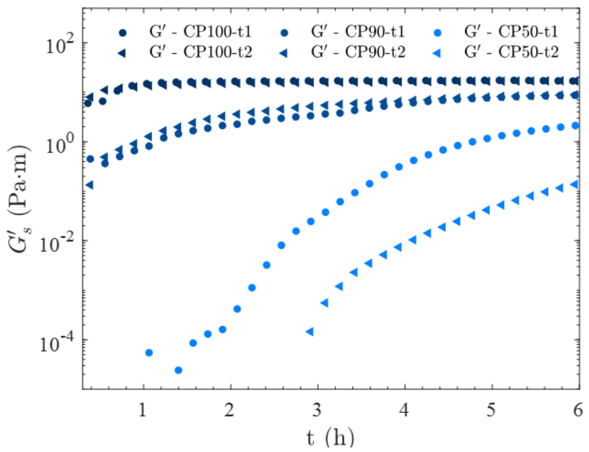

Figure 2. Curves of the storage modulus (G') over time for synthetic hydrates illustrate variations in the ratio between cyclopentene (CP) and crude oil with deionized water, ranging from 100% (CP100) to 50% (CP50) cyclopentene; t1 and t2 denote the test number.

Dilatational Interfacial rheology

Figure 3 illustrates the progressive decrease in the average elastic modulus (E') of the interface over deformation for different aging times. Initially, immediately following the ramp (t = 0s after the ramp), E' is recorded at 10.12 mN/m, representing a 32% reduction compared to the reference (Fig. 4a). Subsequently, approximately 4 hours later, E' declines further to 7.44 mN/m, marking a 50% decrease (Fig. 4b). By around 7 hours, E' diminishes significantly to 1.73 mN/m, indicating an 88% reduction (Fig. 4c). Beyond approximately 7 hours, E' measurements become unreliable due to interface stiffness, resulting in negative (non-real) values, as depicted in Fig. 4d.

In the literature, a limited number of publications have applied this technique involving crude oil and water interfaces [3, 8]. Some articles have utilized synthetic solutions to simulate the complexities of these interfaces, incorporating components such as asphaltenes or naphthenic acids in non-polar solutions [9].

However, understanding the interactions within a more real system remains restricted, and evaluating temperature and pressure effects has been relatively scarce. This underscores the significance of the present research, where we aim to assess the impact of temperature ramps, temperature variations, pressure changes, and the chemical characteristics of crude oil on these interfaces.

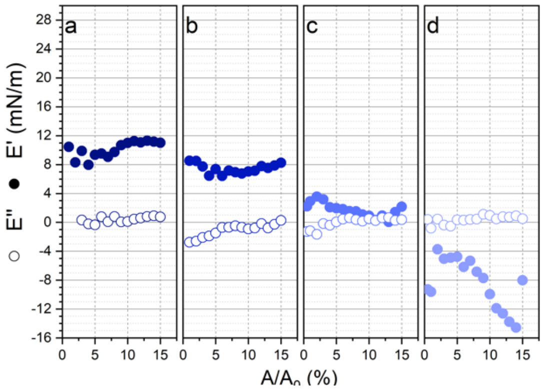

Figure 3. Curves of the storage dilatational modulus (E') and loss dilatational modulus (E'') as a function of deformation for different aging times: a) 0s, b) 4h, c) 7h and d) 15h of aging.

Langmuir trough experiments

Figure 4 depicts the correlation between surface pressure and the area covered by a monolayer of crude oil at various concentrations of molecules. As expected, the increase of volume or molecule quantity per area has a direct impact on surface pressure. Notably, for a maximum area compression, the surface pressure value was 12mN/m at 100μL, surpassing that of volumes 50μL and 25μL.

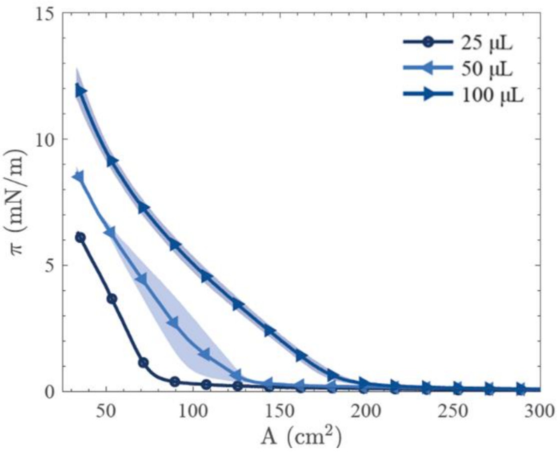

Figure 4. The isotherm curve of surface pressure vs area of a monolayer of crude oil varying the volume of solution (directly associated with the concentration of molecules – approx. 544.4 g/mol).

In Figure 5, the effect of test temperature on surface pressure values can be observed. Lower temperatures resulted in higher surface pressure values. This phenomenon may be associated with the precipitation of paraffins at the interface [7], occupying more space, as they would be present along with the material more chemically active at the interface.

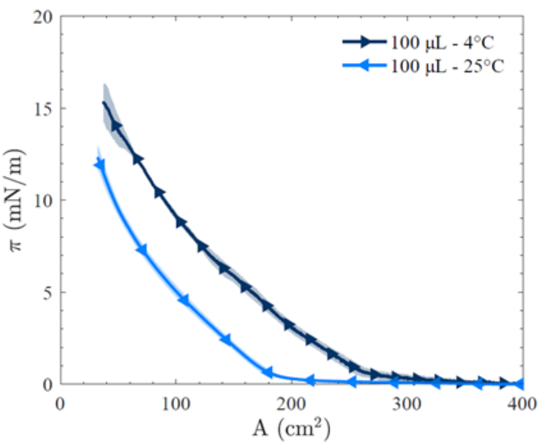

Figure 5. The isotherm curve of surface pressure vs area of a monolayer of crude oil varying the temperature of the test.

Like previously applied techniques, this method has received limited attention in the literature concerning cases that closely resemble real-case scenarios involving crude oil rather than synthesized systems. Few works analyze the effects of low-temperature operation and controlled cooling temperature ramps. Additionally, optical visualization of monolayers through the Brewster angle microscopy (MicroBAM) system [8, 9] is being conducted, enabling visual observation of the monolayer evolution alongside surface pressure changes.

Conclusions

In this work, we have presented results from three different techniques for analyzing rheological properties of interfaces. These techniques include shear, dilatational, and one-dimensional compression of the interface, utilizing a rotational rheometer, the Teclis tensiometer (rising droplet method), and the Langmuir trough, respectively. From these techniques, we have drawn several conclusions. We observed that the cooling rate does not significantly affect the storage and loss moduli at the interface, suggesting that the precipitated crystals may be of similar sizes for both applied cooling rates. Additionally, we noted an increased mitigation effect on the formation of synthetic hydrates for higher concentration of oil in the mixture, leading to larger induction times. Furthermore, our observations of dilatational moduli underscore the importance of careful analysis of the interface aging time, as prolonged molecular contact and organization appear to increase interface rigidity. Another significant finding, derived from Langmuir Trough experiments, is the effect of surface pressure with increased molecular density per unit area and decreased temperature. While these results are preliminary and require further investigation for conclusive insights, they indicate a promising trajectory of learning and understanding the challenges related to flow assurance problems.

Acknowledgments

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Responsibility Notice

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

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