**SPE Brazil Flow Assurance Technology Congress**
Rio de Janeiro, Brazil, November 06 – 08 2024

# Dilatational rheology of crude oil/water interface

Jairo E. Leiva[1*], Eliana P. Marin[1], Priscilla R. Varges[1], Ludmila Nardaci[1], Osvaldo J. Karnitz[2], Marcia C. Khalil de Oliveira[2], Monica F. Naccache[1], Paulo R. Mendes[1]
[1]Mechanical Engineering, PUC-Rio, Rio de Janeiro, RJ 22793-410, Brazil [*]epmarinc1053@gmail.com
[2]GARESC, CENPES - Petrobras, Rio de Janeiro, RJ 22451000, Brazil

## Abstract
This study investigates the interfacial rheology of crude oil in contact with water, focusing on the impact of temperature variations and aging time. Understanding interfacial properties is crucial for optimizing oil production and transportation processes. The rising drop method with a tensiometer was used to measure interfacial tension and interfacial dilatational modulus. A crude oil droplet was subjected to a temperature ramp (25-60-25°C) with dynamic interfacial measurements of deformation sweep (1-15%), before and after the temperature ramp. The interfacial tension showed minimal change during heating but decreased slightly after cooling. The observed decrease in the interface's elasticity (dilatational modulus) after the temperature ramp and over time suggests rearrangements of crude oil components at the interface. This phenomenon may be related to asphaltene precipitation. Further research using Lissajous figures can provide a deeper understanding of this interfacial behavior.

## Keywords
Dilatation rheology; interfacial properties; crude oil/water interface

## Introduction
Problems related to the yield strength of crude oil in pipelines incur significant costs, both financially and in terms of safety. Factors such hydrate formation, asphaltene precipitation, and the formation of water-in-oil emulsions are the primary contributors to these challenges. Neglecting the interaction between these factors can lead to inaccurate data and erroneous decisions, underscoring the critical importance of comprehensive understanding and management of these complex phenomena.

Analysis of the interfacial rheological properties of droplets formed during the oil extraction process is essential for assessing the risk of pipeline blockage. Given the intricate interactions among components, particularly at interfaces (gas/liquid, gas/liquid/solid, or liquid/liquid), understanding interfacial rheology becomes crucial for a thorough evaluation.

The literature review shows a notable research gap concerning the dilatational interfacial rheology of natural oil samples using the profile drop technique. One of the few studies emphasizes that the presence of salt in the crude oil/water system intensifies interfacial activity induced by crude oil surfactants. Isothermal experiments indicate increased interfacial elasticity and compressibility [1]. Another study [2] suggests that dilatational interfacial rheological properties, such as the modulus of elasticity, in oil systems at constant temperature, are solely dependent on the interfacial coverage.

Due to the limited number of studies addressing the temperature-dependent nature of dilatational interfacial rheological properties, this study aims to fill this gap in research. A comprehensive study of these properties is proposed, with a particular focus on understanding the fundamental role of temperature as a key variable.

The proposed study holds the potential to yield valuable knowledge insights into the interfacial dynamics of crude oil subjected to a temperature ramp. Such findings could enhance the optimization of various industrial processes related to oil handling, such as extraction, transportation, and refining.

## Methodology
For the determination of the interfacial tension ($\gamma_{o/w}$) and the modulus of expansion ($E', E''$) of the crude oil/water interface, the rising drop method was used in an automatic tensiometer for profile analysis (Teclis Scientific, France).

The experiments involve treating the interface of a crude oil droplet in water with a temperature ramp. Strain and frequency sweeps were performed before increasing the temperature to 60°C (1$^{st}$ drop interface), after lowering the temperature to 25°C (2$^{nd}$ drop interface), three hours after remaining at 25°C (3$^{rd}$ drop interface), and a new drop after the temperature ramp (4$^{th}$ drop interface), as shown in

Fig. 1a. The temperature ramp and the points $p_1$, $p_2$, and $p_3$, where dynamic measurements were performed with an amplitude sweep followed by a frequency sweep, are illustrated. The first interface $(0 < t < 900\ s)$ is defined before starting the temperature ramp, the second $(0 < t < \sim 7620\ s)$ is after the temperature ramp, the third $(0 < t < \sim 18420\ s)$ is after three hours of maintaining the temperature at 25°C and the fourth $(7620 < t < \sim 18420\ s)$ is a new drop introduced after the temperature ramp. Fig. 1b shows the tensiometer used for the interfacial tension measurements. Fig. 1c presents a schematic illustration of the experimental setup, and Fig. 1d shows the captured image of the crude oil droplet in water, with a resolution of 744x480 pixels. A digital camera captures the droplet profile, automatically analyzes it, and then uses it in the Laplace equation to obtain the interfacial tension value.

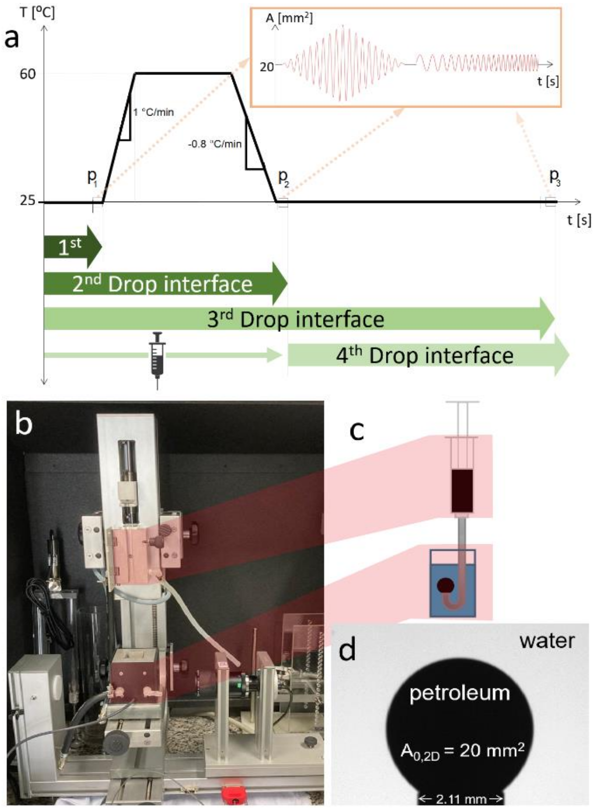


Figure 1. Experimental setup: (a) shows the temperature ramp and the points ($p_1$, $p_2$, and $p_3$) where dynamic measurements are performed, (b) picture of the tensiometer employed, (c) schematic illustration of the experimental setup and (d) the captured image of a droplet (744x480 px).

**Experimental Procedure**

The volume of the crude oil droplet is 10 mm³ subjected to a G14 needle of diameter 2.11 mm (about 0.08 in) in a quartz cuvette (30x30x70 mm) filled with water. Stationary interfacial tension values are averaged from six independent measurements, as shown in Fig. (2). Amplitude sweeps were performed from 1% to 15% at a frequency of 0.1 Hz by automatically controlling the area (2D) enclosed in the droplet profile with an equilibrium value of 20 mm². Frequency sweeps tests from 0.005 to 0.05 Hz, and an amplitude of 1% were performed.

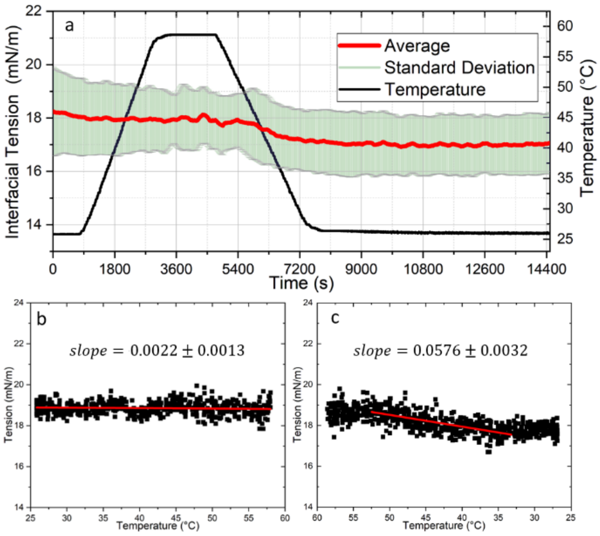


Figure 2. (a) Interfacial tension average values of six independent measurements (red line) performed considering a temperature ramp (black line), (b) the rate of change of the interfacial tension value when the temperature increases from 25 to 60°C and (c) the rate of change of the interfacial tension value when the temperature decreases from 60 to 25°C.

The first drop of crude oil in water is maintained at 25°C for 25 min, followed by an amplitude and frequency sweep. Interfacial tension and dilatational modulus measurements of the first drop serve as a reference. After the sweeps, the droplet is removed from the needle tip, and its volume is increased. The second drop undergoes a temperature ramp to eliminate any "viscoelastic" memory at the crude oil/water interface. It starts at 25°C for 25 minutes and then ramps up to 60°C at a rate of 1°C/min. It remains at 60°C for 30 minutes and then the temperature is reduced to 25°C at a rate of 0.8°C/min. Subsequently, amplitude and frequency sweeps are conducted.

The third drop is formed, allowed to rest for 25 minutes, and promptly subjected to the amplitude and frequency sweep tests. Unlike the second droplet, which experiences the temperature ramp, the third droplet is created with the crude oil sample inside the syringe during the application of the temperature ramp to the second droplet. This distinction underscores that while the bulk sample is subjected to the temperature ramp, its interfacial characteristics may not mirror those of the second drop.

The fourth drop is the one that undergoes the entire temperature ramp and is subjected to the amplitude and frequency sweep after aging for three hours following the ramp's conclusion.

## Results and Discussion

Fig. (2) shows the average interfacial tension values, which starts at 18.4 mN/m when the temperature is 25°C. As the temperature approaches 60°C, the interfacial tension remains relatively constant, showing minimal modification. However, after the temperature drops from 60 to 25°C, the interfacial tension values slightly decrease to 17 mN/m and remain constant for the observed duration of 14400s (approximately 4 hours) from the beginning of the temperature ramp test. The rate of change in interfacial tension values is notably higher when the temperature decreases. At higher temperatures, both liquids molecules possess increased kinetic energy and move faster, resulting in a higher likelihood of crude oil components colliding with water molecules at the interface. It is presumed that decreasing the temperature at a rate of 0.8°C/min facilitates the rearrangement of components at the crude oil/water interface, as evidenced by the disparity between heating (Fig. 2b) and cooling (Fig. 2c).

The storage (E') and loss (E") dilatational moduli vs. deformation ($A/A_0$) for the four interfacial surfaces are shown in Fig 3. The first surface (Fig. 3a) serves as the reference surface with a value close to the average E' =14.86 mN/m. The second interface (Fig. 3b) presents a pronounced non-linear behavior for deformations less than 8%, with average of E' = 10.12 mN/m, which is 32% lower than tehe reference value. Similarly, the third interface (Fig. 3c) displays an average E' of 7.44 mN/m, representing a 50% reduction compared to the reference value. Finally, the fourth interface (Fig. 3d) has an average E' of 13.59 mN/m, which is only 9% lower than the first reference value.

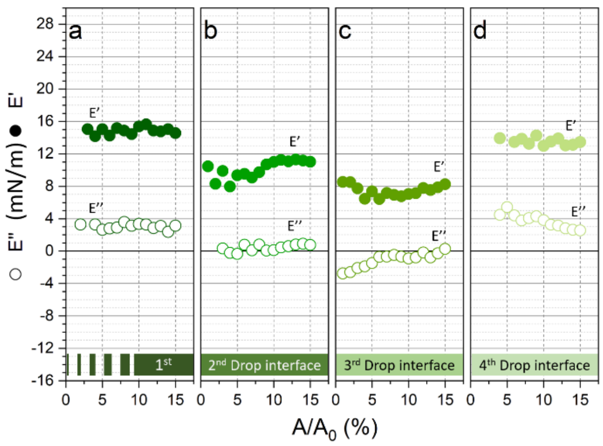


Figure 3. Deformation sweep for the four interfaces with average values of (a) 14.86 mN/m, (b) 10.12 mN/m, (c) 7.44 mN/m and (d) 13.59 mN/m.

The temperature ramp and the duration between points $p_2$ and $p_3$ (Fig. 4) are observed to decrease the average value of the elastic modulus E' of the interface.

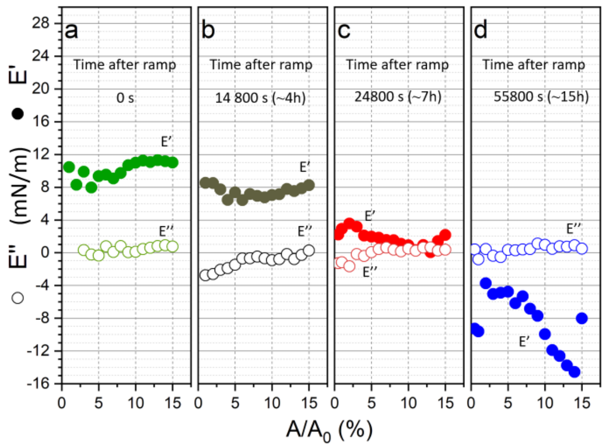


Figure 4. Time-varying deformation sweep after temperature ramp: (a) 0 s after ramp average E' =10.12 mN/m, (b) ~ 4 h after ramp average E' = 7.44 mN/m, (c) ~7h after ramp average E'=1.73 mN/m and (d) ~ 15 hours after showing negative E' values due to interface stiffness.

After the temperature ramp, the average value of the elastic modulus E' decreases over time. Initially, immediately following the ramp (t = 0 s after the ramp), E' is recorded at 10.12 mN/m, marking a 32% decrease compared to the reference (Fig. 4a). Approximately 4 hours later, the E' value declines further to 7.44 mN/m, representing a 50% reduction (Fig. 4b). Subsequently, at around 7 hours after the ramp, E' diminishes significantly to 1.73 mN/m, indicating an 88% decrease (Fig. 4c). It is noteworthy that beyond approximately 7 hours, E' measurements become unreliable due to interface stiffness, resulting in negative values, as depicted in Fig. 4d.

## Conclusions

Interfacial tension plays an essential role in the perception of stiffness. Unlike elastic materials like rubber bands, liquid droplets do not possess inherent elasticity in the traditional sense—they cannot store and release potential energy [3]. However, interfacial tension can create the impression of weak or strong elasticity. When a droplet undergoes slight deformation, interfacial tension acts to restore it to its original spherical shape. In the context of our study, we observe a development of oil and water components at the interface during the temperature ramp and subsequent waiting period. These changes in interface elasticity may be related to phenomena such as asphaltene precipitation and molecular rearrangement at the interface. Consequently, deformation becomes more challenging, as evidenced by the decrease in elastic modulus and the emergence of non-linear effects at small deformations.

For a deeper understanding of the phenomena observed in the storage modulus E', we can leverage Lissajous curves of interfacial pressure versus deformation, which enable us to differentiate between the compression and dilatation behaviors of the droplet interface.

## Acknowledgments

The authors thank Petrobras S. A. (2017/00426-9), CNPq (307976/2018-1), CAPES (PROEX 625/2018), and FAPERJ (E-26/202.834/2017) for the financial support to the Rheology Group at PUC-Rio.

## Responsibility Notice

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