STUDYING THE INFLUENCE OF ANTIFOAMING ADDITIVES ON CRUDE OIL/AIR INTERFACE: PROPOSAL OF A NEW METHODOLOGY

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ABSTRACT

Foams generated during oil production are complex systems. The complexity of their continuous phase makes it difficult to understand what occurs in the foam layers. Some studies have shown that the main species that stabilize foams are asphaltenes, because they reduce the surface tension of the bubbles with their interfacial activity, causing this surface to become viscoelastic. To understand surface viscoelasticity, it is necessary to investigate the rheology of the crude oil/air interface. Since the great majority of works published have used a Du Noüy ring or BiCone accessory to evaluate the surface only of model asphaltene systems, the aim of this work is to study the crude oil/air interface of different crude oil samples and different antifoaming products using the BiCone accessory.

KEYWORDS

foams; interfacial rheology; crude oil; BiCone accessory

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1. INTRODUCTION

Each crude oil reservoir has unique conditions of temperature and pressure, where the crude oil has different amounts of dissolved gas in its constitution. During production, as the fluid rises in the pipes, pressure and temperature decrease, causing the previously dissolved gas to be liberated. This activity, along with the agitation that occurs during the extraction process, leads to the formation of foams (Wylde, 2016).

Since non-aqueous foams are less common than aqueous ones, literature review about the former type are scarce, a situation that is aggravated by the complexity of the continuous phase, i.e., the oil, in relation to non-aqueous foams (Blázquez et al., 2016).

With respect to the composition of crude oil, some studies have shown that asphaltenes are adsorbed at the oil-water interface, stabilizing water-in-oil emulsions (Mohammed et al., 1993; Førdedal et al., 1996), and others have indicated that asphaltenes are responsible for stabilizing foam in crude oil (Zaki et al., 2002; Adil & Maini, 2007; Poindexter et al., 2002). Asphaltenes are defined as the oil fraction that is insoluble in n-alkanes and soluble in aromatic solvents (Lobato et al., 2014). Besides this, asphaltenes are the components of oil with the greatest polarity and molar mass (Honse et al., 2012; Khoshandam & Alamdari, 2010). Due to their interfacial activity, they can organize at the interface, reducing the interfacial tension in the medium where they are introduced (Lobato et al., 2009; Fan et al., 2010; Álvarez et al., 2010).

Viscosity also plays an important role in foam formation (aqueous or non-aqueous) because it is related directly to the drainage of the interstitial fluid in foam (Sheng et al., 1999; Sheng et al., 1997; Wang et al., 2009; George et al., 2005). Besides reducing the drainage rate, systems with high viscosity can also diminish the rate of gas diffusion between the bubbles, a phenomenon known as Ostwald ripening, which is the reduction of the polydispersion of gas bubbles, promoting the stability of foam (Koehler, 2012). Poindexter and collaborators (Poindexter et al., 2002) indicated that crude oils with viscosities below 150 cP (37.8 °C) produce little to no foam. On the other hand, Fraga and collaborators (Fraga et al., 2011)

evaluated high-viscosity oil samples and reported that they do not generate foam, even when containing high levels of stabilization species.

Depending on the stress applied and the timing of application, foams can behave as solids or liquids. By increasing the gas-liquid interfacial area and energy per unit of volume, the foam will become elastic due to the stress applied. When the stress applied is greater than what the liquid film can withstand, the bubbles will become rearranged and the foam will flow like a non-Newtonian viscous fluid (Höhler & Cohen-addad, 2005).

Liquid foams are systems that resemble emulsions, since surfactants are present to stabilize the liquid-gas interface. Like an emulsion, the interfacial layer of the foam becomes viscoelastic due to the presence of amphiphilic species, which have superficial action and can be adsorbed through the dispersed or continuous phase. Therefore, rheological analysis of this interface is necessary to understand its characteristics and stability, since the lifetime of this foam is closely associated with these conditions (Langevin, 2000).

Interfacial rheology permits studying the interface flow properties of systems controlled by the presence of surfactants adsorbed at the interface (Krägel & Derkatch, 2010). Rheological investigations are very important to supply information about the behavior of emulsions, such as the kinetics of film formation, adsorption of surfactants, and rupture of the interfacial film (Tadros, 2004; Spiecker & Kilpatrick, 2004; Ekott & Akpabio, 2010; Phukan et al., 2010).

Interfacial rheology also provides information on the functional interplay of the deformation of an interface, the forces acting on it, and the resulting flows in the adjacent phases of the fluid. This can be accomplished by applying dilatation and shear methods (Krägel & Derkatch, 2010).

Presently, basically two methods are used to measure the rheology of interfacial films using the shear method: one with the Du Noüy ring and the other with the BiCone accessory. The BiCone accessory is more robust than the ring, facilitating its positioning on the surface of the liquid with much greater precision. This makes the analyses more reproducible than when using the Du Noüy ring (Heyer & Läger, 2008).

Some studies have evaluated the asphaltene/air and asphaltene/water interfaces of solutions using the Du Noüy ring (Oliveira et al., 2017), while others have used the BiCone accessory (Fan et al., 2010; Spiecker & Kilpatrick, 2004; Kilpatrick & Spiecker, 2001). However, to the best of our knowledge, no studies have been published involving rheological analysis applied at the crude oil/air interface to investigate the formation of foams.

Therefore, the aim of this study is to develop a method involving interfacial rheology applied to the crude oil/air interface focusing on the formation of foams with or without the presence of antifoaming additives.

2. EXPERIMENTAL PART

2.1 Materials

Foam formation tests in crude oil and the rheology of the crude oil/air interface were performed with and without the presence of antifoaming additives. Two commercial silicone-based antifoaming agents were used, here called AF1 (with high silicone content) and AF2 (with low silicone content), both donated by the Petrobras Research Center (CENPES, Rio de Janeiro, Brazil).

Tests were also conducted with a formulation composed of a nonionic surfactant based on poly(ethylene oxide)-poly(propylene oxide) block copolymer (Pluronic 31R1), supplied by Sigma Aldrich (São Paulo, Brazil). This formulation was prepared using solvents Solbrax 175-235 (S), donated by CENPES, and butanol (B), purchased from Vetec (Rio de Janeiro, Brazil). The surfactant Pluronic 31R1 was dissolved in this solvent mixture in the S:B ratio of 50:50 v/v, and the product:mixture ratio was 50:50 v/v. This formulation is identified as FP31R1.

Foam formation tests in oil and of crude oil/air interfacial rheology were conducted using two samples of crude oil from Brazilian wells, donated by CENPES. These were characterized regarding °API density and viscosity, and were identified as crude oils P1 and P2.

The solvents used were n-heptane and toluene, purchased from Vetec (Rio de Janeiro, Brazil).

2.2 Methods

2.2.1 Characterization of the crude oil samples

Crude oil samples were characterized for obtaining their densities and viscosities.

The density of crude oil is expressed, based on specific conditions, as the API gravity, which is a dimensionless metric (Szklo, 2005). It was created by the American Crude Oil Institute, and can be obtained by Equation (1):

$$^{\circ}API = \frac{141.5}{\rho_{16.5\text{ }^{\circ}C}} - 131.5 \quad (1)$$

where $\rho_{16.5\text{ }^{\circ}C}$ is the density of the oil at temperature of 16.5 °C.

The densities of the crude oil samples were measured with an Anton Paar DMA 4500 M digital density meter.

The absolute viscosity values of the crude oil samples were determined in the shear rate ($\dot{\gamma}$) interval from 0 to 400 s⁻¹ with a Haake Mars 60 rotational rheometer, with C60 geometry and angle of 1° (cone-plate).

Viscosities of the samples P1 and P2 were determined at temperatures of 60 and 30 °C, respectively. Besides these analyses, the viscosities were measured of the samples diluted in mixtures of n-heptane:toluene (Heptol), with P1 containing 33% Heptol (7:3) or 24% Heptol (3:7), and P2 containing 5% Heptol (7:3) or 5% Heptol (3:7) were measured. These analyses were performed at 25 °C.

2.2.2 Foam formation test

The tests of the foam formation in the two crude oil samples were carried out according to the method described by Fraga (Fraga et al., 2011) and Rezende (Rezende et al., 2011). The tests were performed using a Fann High Temperature Aging Cell®, containing 150 mL of the pure samples or mixtures with additives. After inserting each sample, the cell was closed and connected to a compressed air line at pressure of 200 psi for 3 minutes. Then, the cell was placed in a Fann 704Es roller oven at rotation of 50 rpm, preheated to 60 °C for crude oil P1 and to 30 °C for P2, for a period of 1 hour.

Following, the compression cell was placed in vertical position and its outlet was connected to a 150 mL graduated cylinder. Then, the cell's valve was slowly opened to allow the foam to escape, until reaching an initial height of 80 mL. The height of the foam was read at intervals of 15 seconds until reaching a constant height to obtain consecutive values indicating the total breakdown of the foam. The percentage of foam was calculated by Equation (2):

$$Foam (\% v/v) = \frac{H - H_F}{H_F} \times 100 \quad (2)$$

where H is the initial height reached by the foam and H_F is the final height of the liquid after total breakdown of the foam.

All the tests were performed in duplicate and the means of the data were used to plot the graphs.

The tests, in the presence of the antifoaming additives, were carried out at concentrations of 20 ppm of antifoaming agent AF1, 20 ppm of AF2, and 100 ppm of the formulation FP31R1.

2.2.3 Evaluation of the precipitation of asphaltenes

Asphaltene precipitation tests were performed to evaluate the percentage of n-heptane necessary to start the precipitation of asphaltenes in the crude oil samples P1 and P2.

The precipitation onset point refers to the volume of the flocculant (n-heptane) necessary to start the precipitation of the asphaltenes present in 1 mL of a model solution or crude oil sample. The asphaltene precipitation onset was measured with a near-infrared (NIR) spectrophotometer, at a wavelength of 1600 nm, utilizing an external probe with 5 mm optical path inserted in a flask containing the crude oil. The flocculant (n-heptane) was added with the help of a chromatographic pump with flow of 2 mL/min (Kallevik et al., 2000). In this test, 10 grams of crude oil was used, so the volume of flocculant (n-heptane) relative to the lowest absorbance value was divided by 10 to express the asphaltene precipitation onset point in terms of mL of flocculant/g of sample.

2.2.4 Evaluation of the rheological properties of the crude oil/air interfacial films

The rheological properties of the interfacial films of the crude oil/air systems were determined with a Haake Mars 60 rotational rheometer using the BiCone accessory. This device works by imposing torque on the measurement instrument (BiCone), which responds by applying oscillatory shear forces at the interface of the system being analyzed and collecting data to calculate the properties of the fluid in question.

The measurement cell comes with a glass cuvette insert with a recess mark in the middle for correct filling. The interface layer of the test sample can be observed through openings in the external measuring cup, which is closed with a two-piece lid with a hole in the center for the measuring shaft of the BiCone rotor. For temperature control, the measuring cup can be positioned at the base of the rheometer (Peutier).

The main objective of this study was to observe the influence of the antifoaming formulations on the values G' and G'' (elastic modulus and viscous modulus, respectively) of the interfacial films. These properties are very important to understand the antifoaming action mechanism at the crude oil/air interfacial layer. In all tests, crude oil samples, with or without antifoaming formulations, were left in the accessory for 17 hours (aging time), to assure adsorption of the asphaltenic fractions at the crude oil/air interface.

Initially, oscillatory shear tests were performed with variation of deformation in an interval between 1 and 5000%, at a constant frequency of 1 Hz, with the pure crude oil samples (P1 and P2), to determine the linear viscoelasticity region. Then, tests were performed at constant frequency and deformation, selected in the linear viscoelastic region of the graphs plotted previously, for a period of 1 hour. These tests were run with crude oil P1, with or without the antifoaming agents, adjusted so that the oil temperature value during the analysis was 60 °C, and with sample P1 diluted to different concentrations of Heptol, at 25 °C. Tests were also performed with pure crude oil P2, adjusted so that the oil temperature value during the analysis was 30 °C. Before all tests, crude oil samples containing the formulations were homogenized for 3 hours.

Figure 1. Efficiency of the antifoaming additives in the crude oil samples: a) P1 (at 60°C) and b) P2 (at 30°C): (■) pure crude oil; (♦) with FP31R1; (▲) with AF2; (●) with AF1.

3. RESULTS AND DISCUSSION

3.1 Characterization of crude oil samples

Crude oil P1 had a density of 19° API, classified as heavy crude oil, while P2 had a 26° API value, being classified as light crude.

Viscosity analyses showed that crude oil P1 had viscosity of 213 cP and P2 had viscosity of 78 cP, both at temperature of 25 °C. In turn, P1 presented viscosity of 40 cP at 60 °C and P2 had viscosity of 70 cP at 30 °C.

3.2 Tests of the antifoaming efficiency of the additives

Tests were performed with pure crude oil samples P1 and P2 and with the presence of the antifoaming formulations investigated in this work: AF1 or AF2, both at concentration of 20 ppm, or FP31R1, at concentration of 100 ppm. The tests with P1 (Figure 1a) were carried out at a temperature of 60 °C and those with P2 (Figure 1b) were performed at 30 °C.

The products typically used to minimize the

Figure 2. Absorption in the near-infrared range in function of n-heptane concentration, of: (■) P1; (◆) P2.

problem of foaming in separator vessels of production wells contain silicone in their composition, more precisely polydimethylsiloxane (PDMS). These products have the greatest efficiency as antifoaming agents (Fraga et al., 2011; Blázquez et al., 2014; Blázquez et al., 2017; Rocker et al., 2011). Results found in this study corroborate those findings, as can be seen in Figure 1. The efficiency of AF1 is slightly better than the efficiency of AF2, and both have better efficiency than FP31R1.

3.3 Evaluation of asphaltene precipitation

The tests to determine asphaltene precipitation onset in crude oils P1 and P2 (Figure 2) were performed by near-infrared (NIR) spectrometry. These tests sought to identify the volume of n-heptane for dilution of these samples to be used in interfacial rheology analyses. This volume should be below the asphaltene precipitation point, since, from that point onwards, the asphaltene molecules start to precipitate, impairing the use of that dilution. Here, the n-heptane was used in solution with toluene (Heptol) in the study of the influence of dilution of the crude oil samples on interfacial rheology.

The curves in Figure 2 show the NIR absorbance as a function of volume of n-heptane added to the pure crude oil. The lowest point on the curve of P1 is at n-heptane volume of 27 mL, while the minimum point on the curve of P2 is 15 mL. These

points indicate asphaltene precipitation onset, i.e., the quantity of flocculant necessary to promote the appearance of the first asphaltene aggregates. These values correspond to onsets of 2.7 and 1.5 mL of n-heptane/g of oil (after dividing by 10, since the tests were conducted with 10 g of crude oil), respectively.

A simple rule-of-three calculation gives the corresponding volume of n-heptane at the onset represented on the graph, that is, about 64%v/v for P1 and 50%v/v for P2. Therefore, all concentrations of n-heptane, in Heptol, utilized in the tests of viscosity and interfacial rheology were lower than these values.

3.4 Evaluation of pure and diluted crude oil samples viscosities

To evaluate the effect of diluting the oil samples on the formation of crude oil/air interfacial film, the n-heptane/toluene (Heptol) mixture was added in proportions of 7:3 and 3:7 for P1 (Figure 3) and P2 (Figure 4), respectively. The purpose was to reduce the viscosity of the samples to reduce the viscous modulus, without causing a significant influence on the aggregation state of the asphaltenes.

Initially, continuous shear tests were performed to obtain flow curves (viscosity as a function of shear rate).

Figure 3. Influence of shear rate on viscosity for: (♦) P1 at temperature of 60 °C and (▲) P1; (o) P1 with 33% Heptol (7:3) and (□) P1 with 24% Heptol (3:7), at temperature of 25 °C.

Figure 4. Influence of shear rate on viscosity for: (♦) P2 at temperature of 30 °C and (▲) P2; (o) P2 with 5% Heptol (7:3); (□) P2 with 5% Heptol (3:7), at temperature of 25 °C.

These rheological tests were performed to determine the mixture of Heptol. These tests also determined the concentration in the crude oil samples with the same viscosity as the pure samples, when these were analyzed at the temperatures at which the foam efficiency formation tests were carried out. Results indicated the best systems for the interfacial rheology tests at temperature of 25 °C, by reproducing the behavior of the pure crude oil samples at the test temperature of 60 °C.

Results shown in Figures 3 and 4 demonstrate

that the variation of shear rate did not cause a significant change in the viscosity of crude oil samples. They also show that the variation of temperature from 25 °C to 60 °C caused a significant change in the viscosity of crude oil P1 (at 25 °C, the viscosity was around 213 cP while at 60 °C it was nearly 40 cP). In turn, at 30 °C temperature, sample P2 had approximate viscosity of 70 cP.

Under these conditions, it was possible to observe that the systems (at temperature of 25 °C) that presented viscosities similar to those of P1 (at

temperature of 60 °C) were composed of crude oil diluted with 33% (v/v) Heptol 7:3 and 24% (v/v) Heptol 3:7. With these mixtures, the final concentrations of heptane in the crude oil were about 23% and 7%, respectively.

In turn, for crude oil P2, even for the lowest concentration of 5% (v/v) for both Heptol mixtures (7:3 and 3:7), the sample at this dilution had lower viscosity than the pure crude oil. Since Heptol concentrations lower than 5% (v/v) would not have produced a diluted system, no interfacial rheology tests were conducted with diluted crude oil.

The selected crude oil/Heptol systems were, then, submitted to oscillatory tests using the BiCone accessory to evaluate the crude oil/air interface in the presence of the antifoaming products AF1, AF2, and FP31R1, which were also used in the foam formation tests.

3.5 Evaluation of the rheological properties of the crude oil/air interfacial films

The stability of foam results from the formation of an elastic interfacial film. Aggregates of the oil phase are adsorbed at the crude oil/air interface, mainly composed of asphaltenes, forming a physical barrier that impedes the collapse of the bubbles forming the foam (Poindexter et al., 2002). Therefore, it is necessary to study the interfacial properties involving the foam

breakdown process. Interfacial phenomena such as variation of the viscous modulus (G') and elastic modulus (G'') determine the stability and other properties of the foam.

The rheological properties of the interfacial films obtained with samples P1 and P2 were evaluated with a Haake Mars 60 rotational rheometer employing the BiCone accessory. Since we did not find any studies of crude oil/air interfacial rheology, it was necessary to develop a testing method.

-Results obtained with crude oil P1 in the presence of the Heptol mixture

Initially, rheological tests were performed with crude oil P1 (19° API) containing 33% Heptol (7:3) and also containing 24% Heptol (3:7). The tests were conducted with deformation variation of 1 to 5000% and fixed frequency of 1 Hz to observe the maximum deformation until rupture of the interfacial film (Figures 5 and 6).

The elastic modulus was greater than the viscous one, indicating the formation of an elastic film, which ruptured with deformation of around 900% in the test conducted with 33% Heptol 7:3 (Figure 5), and about 268% in the test with 24% Heptol 3:7 (Figure 6). These results indicate greater resistance of the interfacial film formed in the presence of a larger quantity of asphaltene flocculant (n-heptane, Figure 5).

Figure 5. Measures of G' (○) and G'' (●) in function of variation of deformation of the interfacial film formed by crude oil P1 (19° API) + 33% Heptol (7:3), aged for 17 hours, at frequency of 1 Hz and temperature of 25 °C.

Figure 6. Measures of G' (○) and G'' (●) in function of variation of deformation of the interfacial film formed by crude oil P1 (19 °API) + 24% Heptol (3:7), aged for 17 hours, at frequency of 1 Hz and temperature of 25 °C.

The behavior observed in Figure 5 might be associated with the dilution of the crude oil, favoring the formation of larger quantities (or sizes) of asphaltene agglomerates, due to the greater quantity of flocculant (n-heptane). In this case, it appears that the excess of flocculant favors the formation of a more resistant interfacial film. Nevertheless, a larger quantity of toluene (asphaltene dispersant) apparently diminishes the size of the aggregates and, thus, lowers the resistance of the crude oil/air interfacial film (Figure 6). It is also possible to observe an increase in the viscous modulus in the presence of more toluene, indicating better dispersion of the asphaltenes in the crude oil.

Following, we performed an oscillatory shear test with a variation of time, at a constant shear rate of 10% and constant frequency of 1 Hz. These conditions were determined based on the inspection of the linear viscoelastic region of the graphs shown in Figures 5 and 6 (where the interfacial film was still intact). In these tests, the behavior was monitored for the elastic modulus (G') and viscous modulus (G'') as a function of variation of time in the interfacial films formed in:

- Crude oil 1 (19 °API) + 33% (v/v) Heptol 7:3, at temperature of 25 °C (Figure 7);
- Crude oil 1 (19 °API) + 24% (v/v) Heptol 3:7, at temperature of 25 °C (Figure 8).

These systems were also evaluated in the presence of antifoaming agents AF1 and AF2, both

at a concentration of 20 ppm, and also in the presence of the formulation FP31R1 at a concentration of 100 ppm.

All the graphs present the elastic modulus/viscous modulus as a function of time of analysis, to evaluate the film formed at the crude oil/air interface (Figures 7 and 8).

Figure 7 compares the curves of the elastic modulus/viscous modulus in function of time for the systems formed with crude oil 1 (19° API) containing 33% (v/v) Heptol (7:3). As a result, no significant variation occurred between the interfacial film formed at the crude oil/air interface with or without the presence of the additives. But these results were inconclusive because the dilution carried out with the higher amount of the asphaltene flocculant might have favored an increase in resistance of the interfacial film due to the increased size or quantity of asphaltene aggregates.

Figure 8 shows the variation of the elastic modulus/viscous modulus ratio as a function of time for the systems formed by crude oil 1 (19 °API) containing 24% Heptol (3:7), with or without the presence of the additives. In these systems, the presence of the antifoaming additives AF1 and AF2 did not cause a significant variation in the interfacial film, but in the presence of FP31R1 (with lower efficiency in breaking down foam), there was a significant increase in the elasticity of the interfacial film.

Figure 7. Elastic modulus in function of viscous modulus: (■) crude oil P1 diluted with 33% (v/v) Heptol (7:3); and this solution containing: (♦) FP31R1; (▲) AF2; and (●) AF1, at shear rate of 10%, frequency of 1 Hz and temperature of 25 °C.

Figure 8. Elastic modulus in function of viscous modulus: (■) crude oil P1 diluted with 24% (v/v) Heptol (3:7); and this solution containing: (♦) FP31R1; (▲) AF2; and (●) AF1 at shear rate de 10%, frequency of 1 Hz and temperature of 25 °C.

In this case, in the presence of the mixture containing the larger quantity of toluene (Heptol 3:7), asphaltene aggregates were more solvated and more dispersed in the crude oil, able to alter both the values of G' and G'' . This can hamper the formation of a film composed by the asphaltenes at the crude oil/air interface. This behavior is indicated by the reduced strength of the interfacial film formed in the system consisting of crude oil 1 (19° API) containing this mixture of solvents compared to the system diluted with 33% Heptol (7:3).

In the presence of the antifoam additives AF1 and AF2, the strength of the interfacial film was similar to that in the system without addition of the products (crude oil containing Heptol 3:7), showing that these additives did not influence the strength of the superficial film.

Diversely, in the crude oil containing the formulation FP31R1, there was a significant increase in the elasticity of the interfacial film, showing that this additive migrated better to the crude oil/air interface if compared to the other systems tested. Furthermore, the presence of this

Figure 9. Values of G' (○) and G'' (●) in function of the variation of deformation for crude oil P1 (19 °API), aged for 17 hours at frequency of 1 Hz and temperature of 60 °C.

Figure 10. Values of G' (○) and G'' (●) in function of the variation of deformation for crude oil P2 (26 °API), aged for 17 hours at frequency of 1 Hz and temperature of 30 °C.

additive increased the elasticity of the interfacial film, possibly because Pluronic 31R1 is a nonionic surfactant.

-Results obtained with the samples of pure crude oil P1 and P2

During preliminary tests, to adjust the interfacial rheology technique, we observed the occurrence of a temperature gradient from the base of the glass cuvette to the surface of the liquid, where the BiCone accessory was positioned. Because of this, it was necessary to perform tests at a higher temperature, so that the interface being analyzed would reach the desired temperature (60

°C for crude oil P1 and 30 °C for the tests conducted with sample P2).

Oscillatory tests also were performed with a deformation variation of 1 to 5000%, and fixed frequency of 1 Hz, with the objective of observing the maximum deformation applied until rupture of the interfacial film (Figures 9 and 10, respectively, for P1 and P2). In both cases, the elastic modulus was greater than the viscous modulus, although with low significance, at low deformation levels, indicating the formation of an elastic film, and its rupture occurred at a deformation of around 20% for P1 (Figure 9) and 200% for P2 (Figure 10).

Figure 11. Elastic modulus in function of viscous modulus: (■) pure crude oil P1; and containing: (♦) FP31R1; (▲) AF2; (●) AF1 at shear rate of 10%, frequency of 1 Hz and temperature of 60 °C.

Figure 12. Elastic modulus in function of viscous modulus: (■) pure crude oil P2; and containing: (♦) FP31R1; (▲) AF2; (●) AF1 at shear rate of 10%, frequency of 1 Hz and temperature of 30 °C.

These results showed that the interfacial film formed with crude oil P2 was more resistant than that of P1, even though elastic and viscous modulus values were very similar for these samples. This behavior might have been caused by the higher viscosity of P2 at the testing temperature (70 cP, at 30 °C) than P1 (40 cP, at 60 °C).

Finally, we performed oscillatory shear tests with variation of time but constant shear rate of 10% and frequency of 1 Hz. In these tests, we monitored the behavior of the elastic modulus (G') and viscous modulus (G'') in function of the variation of time in interfacial films formed in crude

oil P1 (19 °API) at a temperature of 60 °C (Figure 11) and crude oil P2 (26 °API) at temperature of 30 °C (Figure 12).

As before, these tests were carried out in the presence of the commercial antifoaming agents AF1 and AF2, both at concentration of 20 ppm, and formulation FP31R1 at concentration of 100 ppm. The graphs also show the ratio of elastic modulus to viscous modulus in function of testing time to evaluate the film formed at the crude oil/air interface.

The results shown in Figure 11 indicate there was a reduction of the G'/G'' ratio of the interfacial

film formed by sample P1 with addition of 20 ppm of the two commercial antifoaming agents in relation to the pure crude oil. A suggested explanation for this behavior is the greater impediment imposed by the commercial additives regarding migration and aggregation of asphaltenes at this interface, causing a reduction in the elasticity of the interfacial film in comparison with the pure crude oil with 19 °API. This interfacial rheology result corroborates the results of the foam formation efficiency tests (Figure 1a), where it was possible to observe that the height of the foam formed by that crude oil sample with the addition of AF1 and AF2 was considerably lower than that of the pure crude oil.

However, for crude oil P1 containing FP31R1, the interfacial film was similar to that of the pure crude oil, showing that this formulation did not contribute to destabilize this film; a result also in line with the data obtained for foaming test (Figure 1b), where the crude oil mixed with that formulation produced foam with similar height as the pure crude oil.

In Figure 12 one can observe that G'/G'' ratios for the pure crude oil P2 and its mixture with additives were very close to each other. This behavior might be due to the greater resistance of the interfacial film formed with this oil sample.

In the case of the interfacial film observed in crude oil P2 in the presence of the formulation FP31R1, results indicate that the foam is more stable than that observed in the presence of the two commercial antifoaming agents. Results of the antifoaming efficiency test show that the interfacial film is more fragile, generating an unstable foam, as also observed in the foam formation test (Figure 1b).

The results obtained with sample P2 supported the results obtained previously with crude oil P1 (Figure 11).

4. CONCLUSIONS

The present study shows that rheology measurements of the crude oil/air interface utilizing the BiCone accessory can be correlated with foam formation tests of crude oil samples.

When diluting crude oil, the presence of a larger quantity of flocculant solvent, heptane, promoted greater resistance of the interfacial film. This behavior can be attributed to the larger quantities or levels of asphaltene aggregates present at the crude oil/air interface. Nevertheless, the dilution with a larger quantity of solvent toluene promoted dispersion of the asphaltenes in the crude oil, hindering the formation of aggregates.

The evaluation of the antifoaming agents used in this work by means of rheology tests of the crude oil/air interface without the dilution of the oil sample presented good results. These test results corroborated those obtained from the tests of foam formation, and the additives that were more efficient in reducing foaming were those containing higher concentrations of silicone.

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