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EFFECT OF INTERFACIAL RHEOLOGY ON DROP COALESCENCE IN WATER-OIL EMULSION

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Abstract. *Over the last years several studies have been conducted to understand emulsions formation and its behavior. In some applications, the aim is the phase separation of the emulsions through the coalescence of the drops, as in the oil industry. In this study, the relationship between rheological properties of oil-water interfaces and the drainage time of a thin oil film between two aqueous drops was investigated. We evaluated four different concentrations of a nonionic surfactant (Span 80) dissolved in mineral oil (Primol 352) phase. In order to perform the interfacial rheological measurements it was used the pendant drop method in a Tracker-S tensiometer. The results indicate the relationship between the structure formed on the oil-water interfaces to no coalescence of the drops. When the coalescence process occurs the drainage time seems not to be related with the aging time neither with the surfactant concentrations. The interfacial tension showed similar behaviors for all concentrations, whereas that the elastic and viscous modulii presented significant changes with surfactant concentration and also with interface aging.*

Keywords: *Emulsion Stability, Interfacial Rheology, Coalescence*

1. INTRODUCTION

Emulsion formation and stabilization has been widely studied over the last years. However, in some applications, such as in the transport and separation of the aqueous phase from produced water-in-oil emulsions in the oil industry, the main interest is the destabilization of emulsions through the coalescence of the drops and consequently phase separation.

In oil production, emulsions are formed in the two-phase flow in reservoirs and through tubes, pumps and valves (Fingas *et al.*, 1993). These emulsions may cause a several issues from production to refining, such as scale formation in ducts, storage tanks and pumps, loss of conversion efficiency of catalytic processes and decrease in commercial value of the heavier fractions (Araújo, 2004). In addition, studies show that the viscosity of emulsions is substantially higher than the viscosity of the continuous hydrocarbon phase (Pal and Rhodes, 1985; Johnsen and Rønningsen, 2003). As a consequence, the pressure drop along the production lines increases, which may compromise the efficiency of the process.

Crude oil emulsions are stabilized by the presence of asphaltenes, resins, naphthenic acids and solids clay (Benmekhbi *et al.*, 2014). Some works have shown that the emulsion stabilization by asphatenes could be related to the formation of cross-linked gel phase at the water/oil interfaces (Perles *et al.*, 2018; Rane *et al.*, 2013). Similar behavior can be observed with other types of emulsifiers, such as amphiphilic proteins, small molecule surfactants (e.g., Sorbitan esters) and phospholipids (Benmekhbi *et al.*, 2014). The formed interfacial structures play an important role in formation and stability of emulsions. The interfacial properties, directly related to the characteristics of the adsorbed layers, are recognized as equally important as the behavior of the surface forces operating normally to the liquid film formed between the drops during the coalescence process (Santini *et al.*, 2007; Pandolfini *et al.*, 2017).

The coalescence phenomenon can be studied through two different points of view: one is preparing the emulsions and analyzing the phase separation over a period of time (Santini *et al.*, 2007; Venkataramani *et al.*, 2016), and the other is analyzing a single coalescence event between two dispersed drops. There are different ways to study the latter, using a droplet formed at a needle tip and forced against a planar interface of bulk liquid phase (Aryafar and Kavehpour, 2006; Aryafar *et al.*, 2006; Blanchette *et al.*, 2009; Bochner de Araujo *et al.*, 2017) or forced against another droplet (Wasan, 1992; Wu *et al.*, 2004; Nowak *et al.*, 2016), and using micro devices in which it is possible to place two drops in contact (Feng *et al.*, 2015; Tan *et al.*, 2004, 2007; Bremond *et al.*, 2008). Regardless of the approach adopted, coalescence phenomenon is extremely sensitive to phase composition and therefore it is extremely important to run experiments with well controlled fluid composition and free of impurities (Ban *et al.*, 2000).

In this work, we investigate the relationship between rheological properties of oil-water interfaces and the drainage time of a thin oil film between two aqueous drops. Different concentrations of a nonionic surfactant (Span 80) dissolved in mineral oil (Primol 352) phase were evaluated. The interfacial rheological measurements were performed using the pendant drop method in a Tracker-S tensiometer. It was observed a relationship between the structure formed on the oil-water interfaces and drops coalescence. Strong structures tend to avoid the coalescence.

2. MATERIALS AND METHODS

The water phase used was deionized water produced by the Direct-Q® Water Purification System ($18.2 M\Omega cm$ at 25^oC). The oil phase is composed of a mixture of oil and surfactant. The oil used was Primol 352, that is a medicinal-grade mineral oil (66% paraffinic, 34% naphthenic carbon type) produced from petroleum distillation Benmekhbi *et al.* (2014). The surfactant used was Span-80 (Sorbitan monooleate), molecular weight $= 428.6 g/mol$, HLB 4.3, density $d = 0,994 g/cm^3$ at 20^oC, a non-ionic lipophilic, Fig. 1.

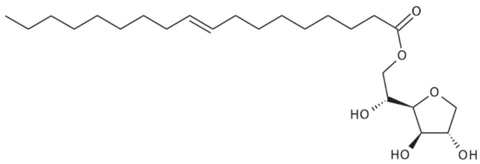

Figure 1. Span 80 (Ushikubo and Cunha, 2014).

The density of each phase, which are used as input parameter in the measurement of the interfacial rheology using the pendent drop method, was measured using the DMA4200M densimeter, from Anton Paar.

The interfacial properties were measured at 23 ± 1^oC with the pendant drop method using a Tracker Teclis tensiometer, equipped with a thermostatic module to control the temperature. A droplet of miliQ water was formed at the tip of a steel needle (2 mm diameter) inside of a glass cuvette ($25 mL$, HELMA 700) containing the oil phase. The droplet area was controlled, via software, by a stepper motor attached to a glass micro syringe ($100 \mu L$) plunger. The effect of surfactant concentration on the interfacial rheological properties were evaluated and the effect of the drop aging time on the interfacial rheological properties was determined for the highest surfactant concentration. The oscillatory tests conditions were: period of $5s$, drop volume of $1.6 \mu l$ and oscillation amplitude of 12.5% of volume. In general, the results showed good repeatability, so all the graphs presented are an average of 2 experiments.

The stability of water/oil interfaces was investigated using a setup composed of: a syringe pump to form the drop attached to the tip of a needle,a pressure transducer to measure the pressure inside the drop and therefore determine the exact time coalescence occured, a high-speed camera to record the events, a light, a computer and a cuvette where the events occur, as represented in the Fig. 2.

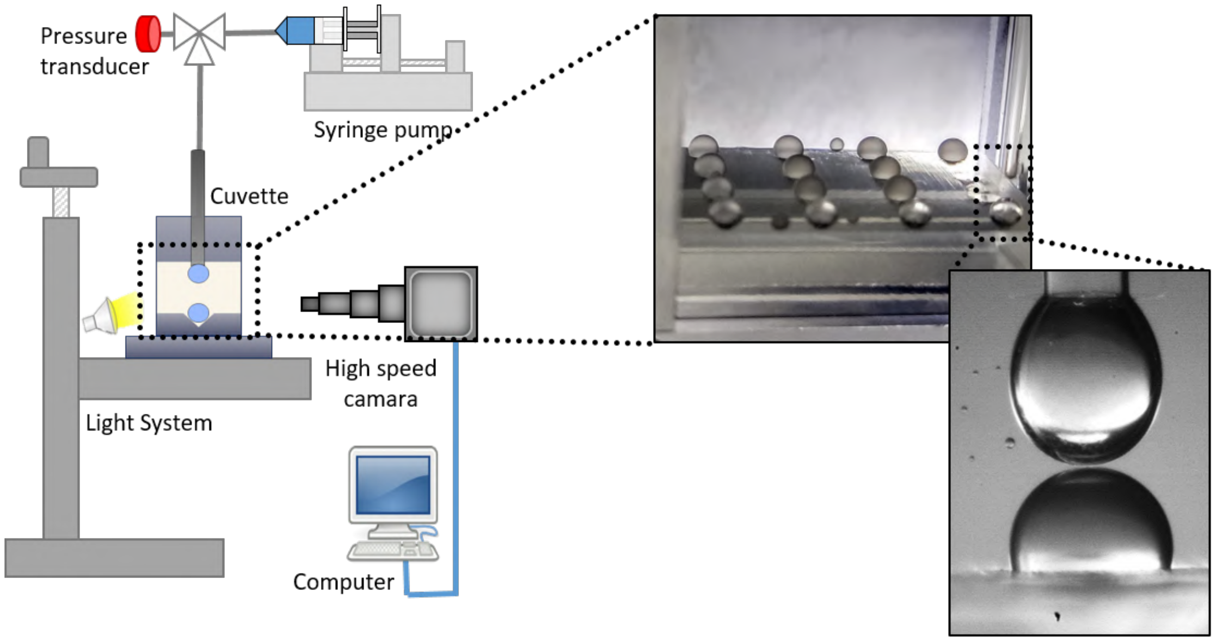

Figure 2. Setup experimental.

After preparing the oil and water phases, and filling the cuvette with the oil phase, each series of coalescence time determination consisted of: forming the first drop at the bottom of the cuvette (Fig.3(a-b)), forming the second drop, wait for the set interface aging time (Fig.3(c)), moving manually the drops against each other (Fig.3(d)) and wait for the coalescence (Fig.3(e-h)). In this figure can be observed that the centering of the drops is more precise using a specific device that also prevents the lateral sliding of the droplet at the bottom of the cuvette.

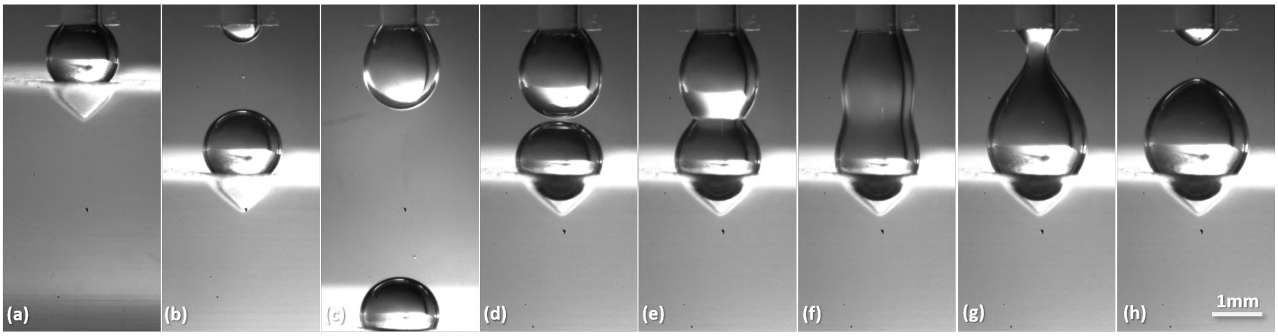

Figure 3. Illustration of formation and coalescence process.

3. RESULTS AND DISCUSSION

3.1 Interfacial Properties

Density values used as imput data for the interfacial rheological experiments are presented in the Table 1. The oscillatory tests to obtain the interfacial elastic and viscous modulii showed a dependence with the surfactant concentration and with the aging time of the drop interface.

Table 1. Density of fluids used in the experiments.

Fluid	**Density** (g/cm^{-3})
Water	0.9982
Primol + 0.5wt.% Span80	0.8621
Primol + 1.0wt.% Span80	0.8627
Primol + 1.5wt.% Span80	0.8632
Primol + 2.0wt.% Span80	0.8637

The interfacial tension measured at the water and pure primol interface was about $14.5mN/m$. When the surfactant was added, it was observed a considerable reduction of this property, as represented in the Fig. 4. For all concentrations analyzed, the initial interfacial tension was around $3-4mN/m$ and decreased with time to values between $1.5-2mN/m$. Comparing all the concentrations, there is not a significant difference in the interfacial tension values that should explain the behaviors observed on the coalescence experiments, as will be shown in the next section. The interfacial elastic and viscous modulii could be responsable for these behaviors.

In general, the viscous modulus started higher than the elastic modulus and after some time they inverted. The moment that this inversion occurred was different for each concentration and should be related to the adsorption time of the surfactant on the interface. The $0.5wt.\%$ Span80 was the concentration that this inversion of modulii values was not too evident. With the surfactant concentration of $1wt.\%$, the inversion point was observed in approximately 30 minutes and, after that, they start to rise in opposite directions. Increasing the surfactant concentration to $1.5wt.\%$ the modulii inversion occurs at around 15 minutes, after that, the elastic modulus rapidly growth whereas the viscous modulus steep decrease with time, reaching zero. For the highest surfactant concentration, the modulii behavior were quite similar for the $1.5wt.\%$ SPAN80, but the modulii inversion occurred few minutes earlier, around 10 minutes.

As the coalescence experiments were performed to evaluate the drainage time of the film by the aging time of the interface, tests were carried out to verify how the interface aging can affect the its properties. Using only the highest surfactant concentration, the time between the drop formation and the beginning of oscillations in the experiments was varied. Figure 5 shows that, the properties behavior do not change with the drop aging before the beginning of experiments. We can see that, if we move the data to begin at the same moment of the experiment without interface aging before the oscillations, the shape of the curves presents similar behavior.

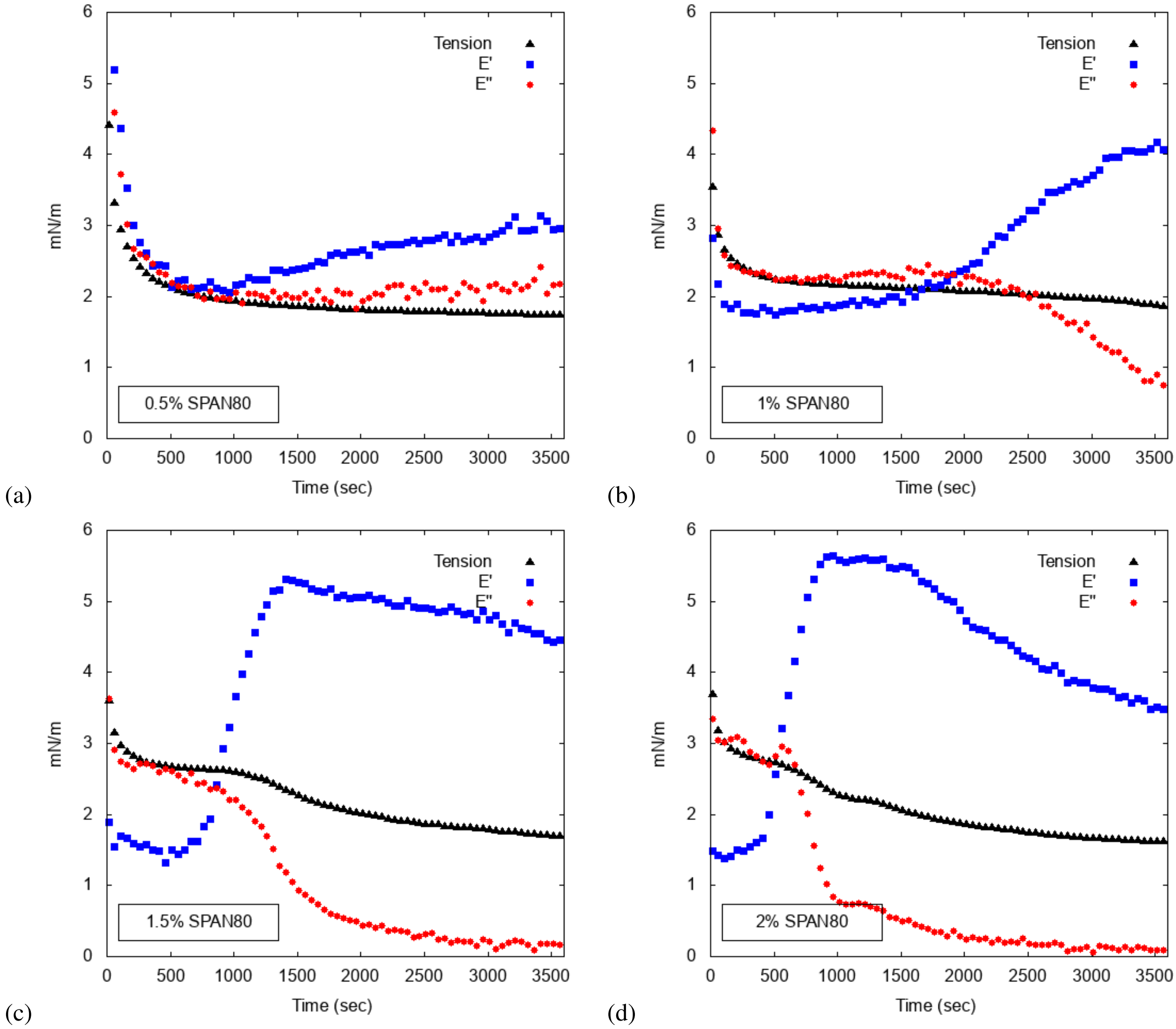

Figure 4. Interfacial properties for all surfactant concentrations.

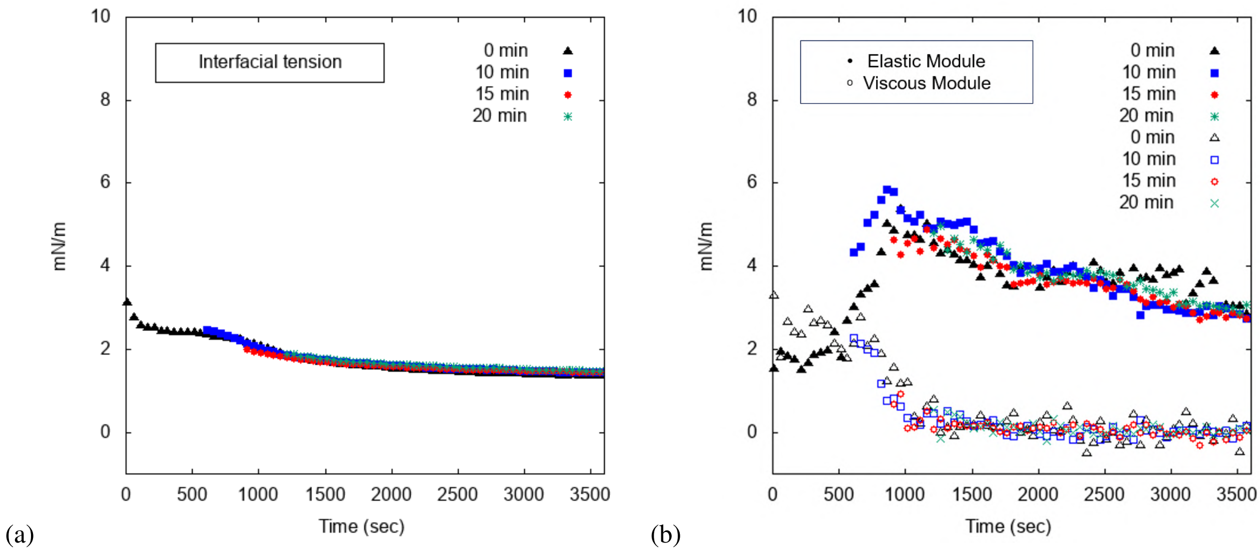

Figure 5. Interfacial properties to $2wt.\%$ of Span80 concentration for analysis with different interfacial aging time.

3.2 Coalescence Experiments

The drop coalescence experiments consisted of measuring the time it took for the drops to coalescence, after the drops are pushed against each other, i.e. the drainage time of the thin film between the two interfaces as a function of surfactant concentration and interface aging time. The relationship between these characteristic times for four surfactant concentrations was investigated and is presented in the Fig. 6. The time referring to the experiment without surfactant is not represented in the graph since the coalescence occurs almost instantly, taking only a few milliseconds, which is much shorter than the others observed. The results are an average of more than six experiments with the respective values of standard deviation.

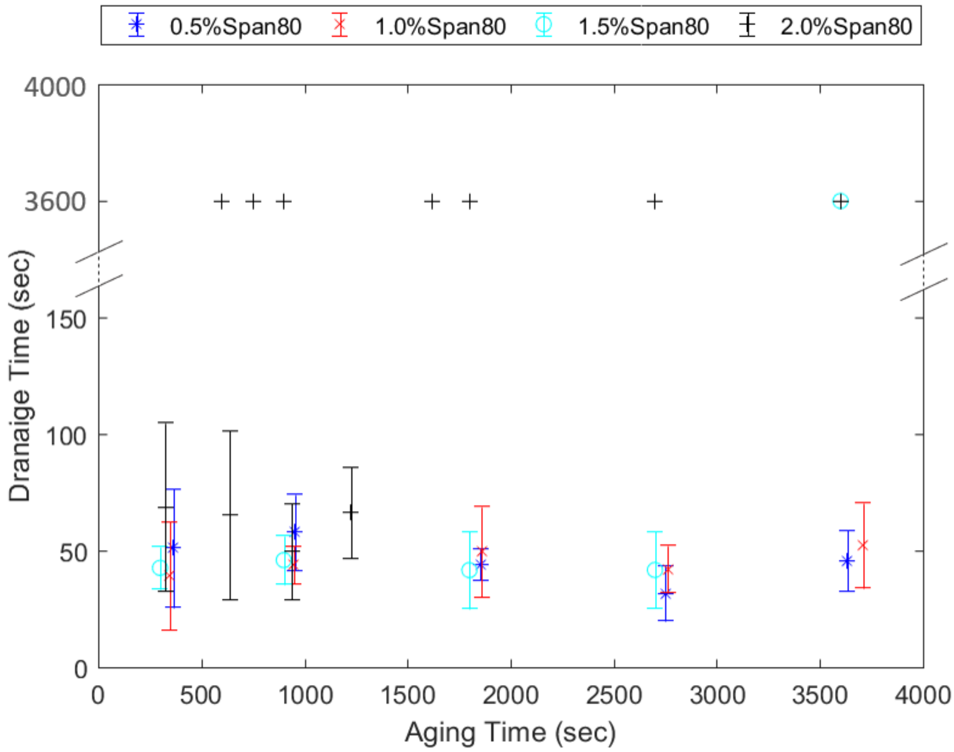

Figure 6. Drainage time for the surfactant concentrations analyzed.

In some cases, the drops did not coalesce, as shown in the Fig. 7. The first frame represents 30 minutes drops aging time (a), followed by the drops approximation after one hour of aging time (b), when the drainage time was started. After at least one hour interval no difference was observed on the system. The sequence of frames (c-f) represents a volume increase showing that there is a solid-like "skin" formed at the oil-water interfaces. Similar behavior was reported on other studies using SPAN80 (Ushikubo and Cunha, 2014; Drelich *et al.*, 2010) and also in some cases using asphaltenes, in which they attributed a thickening of surface layers to the asphaltenes adsorption in the form of aggregates (Jeribi *et al.*, 2002; Poteau *et al.*, 2005; Perles *et al.*, 2018). These results are plotted in the graph with time equal 3600s, only to representation.

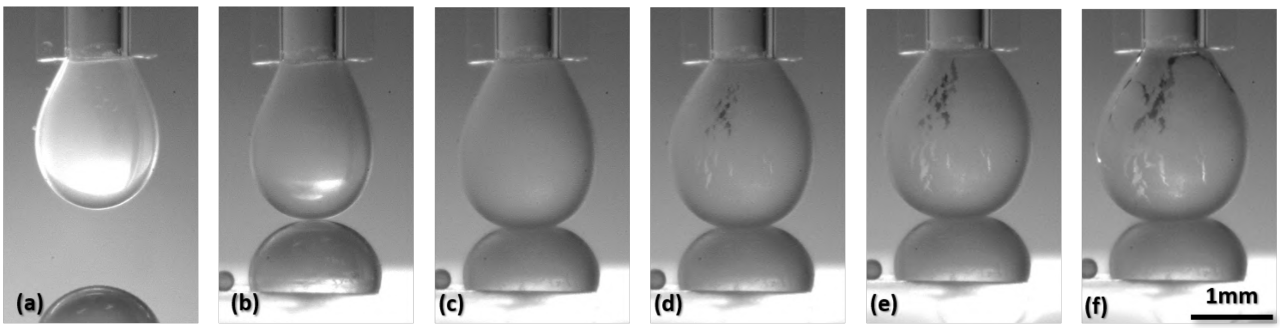

Figure 7. Frame sequence representing: (a) drops aging, (b) no coalescence after contact and (c-f) volume increase evidencing a solid-like "skin" formed at the oil-water interfaces.

For lower concentrations, the coalescence process usually occurs as shown in the Fig. 8. The drainage time seems not to be related with the aging time as well as with these surfactant concentrations, as presented in the Fig. 6. However, as the drop aging time increases it is possible to observe a skin more structure being formed at the drop interface, as we can see in the Fig. 9. In this figure, the first frame shows the beginning of the experiment. It is worth noting a difference in opacity between the two first frames. This is due to the drops interface aging, as a consequence of the surfactant adsorption on the interface over the time. In this example, the surfactant concentration was $1wt.\%$ and the drops aging time was 1 hour. Observe that, the rupture is no longer symmetrical, indicating that there is a higher resistance to coalescence between the drops due to the presence of this "skin", but it is not strong enough to prevent this phenomenon.

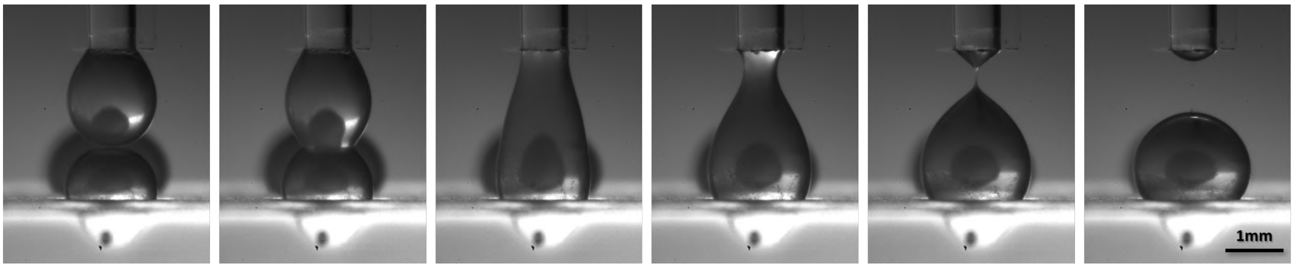

Figure 8. Experiment with surfactant concentration of $1wt.\%$ and 30 minutes of drops aging. This frames sequence represent the coalesncence process.

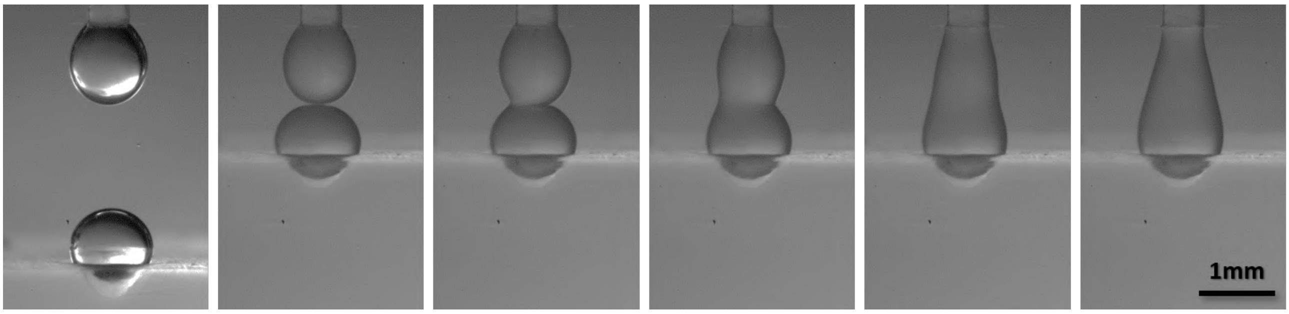

Figure 9. Experiment with surfactant concentration of $1wt.\%$: (a) drops formation, (b) drops approximation after one hour of drops aging and, (c-f) coalesncence phenomenon.

On the other hand, for higher surfactant concentrations, in some aging time, this "skin" had enough time to get stronger and prevent the coalescence process. With concentration of $1.5wt.\%$, this phenomenon was evidenced only after one hour of drops aging whereas, for concentration of $2.0wt.\%$ this behavior begin with 10 minutes. In this concentration, the time interval between 10 and 30 minutes was more investigated, showing results with a random pattern. The same aging time presented both coalescence and no coalescence of the drops.

4. FINAL REMARKS

In this study different Span80 surfactant concentration were evaluated and also the dependence of film drainage time on the aging time of interfaces for each concentration. We observed that the drainage time seems not to be related with the aging time neither with the surfactant concentrations, when the coalescence process occurred. For the cases that coalescence did not happen (concentrations of $1.5wt.\%$ and $2wt.\%$), a formation of a solid like structure was observed on the drops surfaces, representing the strong activity of surfactant migration from the bulk region to the interface and formation of an elastic film at the interface.

The results have not shown any significant difference between the interfacial tension for the surfactant concentrations studied. However, the elastic and viscous modulii presented significant changes with surfactant concentration and interface aging, showing that the surface viscoelasticity plays an important role in coalescence process. The coalescence was prevented when the elastic modulus predominated over the viscous modulus and the latter tends to zero. These behaviors reinforce what some authors highlight, the properties of the adsorbed layers protect the oil-water surfaces, controlling the emulsion behavior and, the knowledge of interface tension alone is not sufficient to understand emulsion properties (Langevin *et al.*, 2004).

Further steps for this research are to investigate how to promote the destabilization of these strong interfaces through weakening the interface elastic modulus chemically or mechanically, for example increasing the drop area.

5. ACKNOWLEDGEMENTS

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