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# DESTABILIZATION OF WATER-OIL EMULSION BY DROP INTERFACE DEFORMATION

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***Abstract.*** *Emulsion formation and stabilization have been widely studied over the last years. The ability to stabilize emulsion is important in many applications, such as food, pharmaceutical, and cosmetics industries among others. However, sometimes due to a natural stabilizing component, undesired stabilization is obtained, as occurs in the oil industry, for example. In this case, the main interest is the destabilization of emulsions through the coalescence of drops and consequently phase separation, which is the purpose of this study. Hence, better understanding of the role of droplet deformation regarding the stability of water-in-oil (w/o) emulsions can allow the development of more efficient separation strategies. For this, stable w/o emulsions were prepared with Milli-Q water and a nonionic surfactant (Span 80) dissolved in mineral oil (Primol 352), varying the surfactant concentration, all above the critical micelle concentration (CMC). It was observed that the coalescence process is directly influenced by the structure formed at the drop interface due to the adsorption of the surfactant. This structure has been studied microscopically (using the optical microscope) and it was observed the appearance of small water droplets formed at the interface by spontaneous emulsification. We found that the emergence rate of these microdroplets is directly related to the surfactant concentration. As the surfactant concentration increases, faster the spontaneous emulsification process occurs, which confirms the results obtained with the interfacial rheology. Finally, a new method to promote emulsion destabilization by imposing a perturbation of the interfacial film by flowing the drops through constricted capillaries was proposed and tested. In this method, the flow through a constricted microchannel was used to deform the drop, increasing its interfacial area, and creating a strong shear stress to disturb the drop interface. The results showed that depending on the surfactant concentration the cleaning of the microdroplets interface formed along the drops is efficient allowing a rapid phase separation after production.*

***Keywords:*** *Coalescence, Spontaneous Emulsification, Emulsion Destabilization*

## 1. Introduction

The complex molecules present in crude oil can migrate towards the water/oil interfaces and form interfacial structures that play an important role in the formation and stability of emulsions. The presence of a structure at the droplet interface that influences coalescence has been demonstrated previously by Botti *et al.* (2022).

Typically, a high energy input is used to induce emulsion formation. However, there is a special case in which they form spontaneously. This work-free emulsification process is called spontaneous emulsification (SE). Also known as self-emulsification, this easy and reproducible way to generate submicrometer droplets without energy input (López-Montilla *et al.*, 2002) has been widely investigated due to its intrinsic basic interest and extensive use in numerous applications, such as improved detergents, pesticides, food production, drug delivery systems, nanoparticles, and lubricant oils (Li *et al.*, 2020). Nevertheless, the spontaneous creation of oil and water droplets is detrimental to oil/water separation processes in the oil industry (Bochner de Araujo *et al.*, 2019).

Spontaneous emulsions represent thermodynamically stable configurations in which the total system free energy is at a minimum (López-Montilla *et al.*, 2002; Solans *et al.*, 2016). There are two main mechanisms that can explain what happens at liquid/liquid interfaces when SE takes place: mechanical breakup and chemical instability. Interfacial turbulence or interfacial bending can cause the mechanical breakup of the interface (López-Montilla *et al.*, 2002). Whereas, diffusion and stranding result from the chemical instability of the interface (Ruschak and Miller, 1972). Low surfactant concentrations are sufficient to cause SE when mechanical breakup is the driving phenomenon. Differently, when the predominant phenomenon is chemical instability, high surfactant concentrations are required. Actually, the swelling of inverted micelles due to osmotic pressure drives the SE in the last case (Greiner and Evans, 1990).

Interfacial turbulence is generated by a mechanical instability of the interface induced by unsteady motions, developed when two liquid phases are put in contact. A nonuniform distribution of surfactant at the liquid-liquid interface can generate localized interfacial tension gradients that induce strong Marangoni stresses and lead to violent interfacial motions (López-Montilla *et al.*, 2002). Another mechanical mechanism that induces SE is the interfacial bending. In this mechanism, the interfacial free energy coming from bending stresses (associated with changes in the mean curvature) balances the energy cost from increasing the interfacial area (Rodríguez-Hakim *et al.*, 2020). Spontaneous emulsification can also occur when the diffusion of the solvent into an immiscible phase generates regions of local supersaturation, which can nucleate and develop into droplets (Miller, 1988). This mechanism is a chemical phenomenon and is, therefore, independent of the magnitude of the interfacial tension (López-Montilla *et al.*, 2002); however, it requires the presence of a solute in one of the phases, which can be surface active or not (Rodríguez-Hakim *et al.*, 2020).Thus, the SE process can be influenced by different variables, such as surfactant structure, concentration and initial location, oil phase composition, addition of co-surfactant and non-aqueous solvent, as well as salinity and temperature (Li *et al.*, 2020).

González-Ochoa and Arauz-Lara (2007) investigated two-dimensional spherical crystalline colloidal structures formed at the oil-water interface as a result of spontaneous emulsification and colloidal self-assembly. They showed that smaller water droplets of uniform size are spontaneously produced at the spherical interface of a water droplet introduced in oil containing Span 80. In the beginning of the process, the small droplets are of submicrometer size, forming ordered structures, then they grow uniformly with time until reaching a size of a few micrometers, maintaining the crystalline structure. Santana-Solano *et al.* (2012), on the other hand, evaluated SE through a planar interface in order to minimize the effects of the interface's curvature on the rate of surface enlargement, using the same system of fluids studied by González-Ochoa and Arauz-Lara (2007), water/dodecane-Span 80. They established an equation that allows for the calculation of the rate of interfacial area production by means of droplets growth for the fluid system.

Recently, Schmitt *et al.* (2017) conducted an experimental investigation of the kinetics of SE with a water pendant drop in a paraffin oil solution loaded with Span 80. They showed a darkening of the drops due to interface modification under different surfactant concentrations and that SE for low concentrations is slow, producing micrometer-sized droplets, whereas for large concentrations is fast and forms bush-like microstructures at the interface.

To better understand the phenomenon of non-coalescence, we study the structure of the interfacial film microscopically and observe the appearance of small water droplets formed at the interface by spontaneous emulsification. We found that the emergence rate of these microdroplets is directly related to the surfactant concentration. As the surfactant concentration increases, the spontaneous emulsification process occurs faster. Finally, a new method to promote emulsion destabilization by imposing a perturbation of the interfacial film by flowing the drops through constricted capillaries is proposed and tested.

## 2. Experimental Section

### 2.1 Materials

Milli-Q water was produced by the Direct-Q Water Purification System (18.2 $M\Omega.cm$ at 25 $^oC$) and the oil phase was a mineral oil (Primol 352) containing varying concentrations of a nonionic surfactant (Span 80). Primol 352 (Exxon Mobil) is a medicinal-grade mineral oil (66 % paraffinic, 34 % naphthenic carbon type) produced from petroleum distillation (Benmekhbi *et al.*, 2014). Span 80, sorbitan monooleate, (Sigma Aldrich) is a nonionic oil soluble surfactant frequently used to make W/O emulsions, with an HLB of 4.3. The concentrations used were 0.25; 0.50; 2.00 $\%wt.$ and according previous study Botti *et al.* (2022), all these concentrations are above the critical micelle concentration (CMC) (0.05 $\%wt.$).

### 2.2 Spontaneous Emulsification

To evaluate the spontaneous emulsification single water drops were produced using a coaxial flow (co-flow) microfluidic device. As an adaptation of the used by Michelon *et al.* (2020), this device is composed of a cylindrical glass-capillar (World Precision Instruments Inc., USA) inserted into a square capillary (Atlantic International Technology Inc., USA). The square capillary has an inner dimension of 1.05 mm and the cylindrical glass-capillar has inner and outer diameters of 0.58 mm and 1 mm, respectively. However, the glass-capillar was tapered with a micropipette puller (model P-1000, Sutter Instrument Co., USA) to obtain a final inner diameter of 50 $\mu m$. This system is fixed in a glass microscope slide. To ensure that the two capillaries have a coaxial alignment, capillaries should be chosen such that the outer diameter of the circular capillary is the same as the inner dimensions of the square capillary (Shah *et al.*, 2008). The dispersed phase (water) flows through the injection capillary (cylindrical glass-capillar) while the continuous phase (oil) flows in the inner square tube. Both fluids flow in the same direction.

It was evaluated droplets with three different diameters, around 200, 400, and 600 $\mu m$. The size was controlled by changing the flow rate of the phases, where $Q_o$ is for oil rate and $Q_w$ is for water rate, as represented in Table 1. And all analysis were performed at the temperature of $23^oC$.

Drop formation was monitored with a Carl Zeiss inverted optical microscope, model Axiovert 40MAT. Then, the drops were collected in a microscope slide with a single concave depression cavity and its interface structure behavior was evaluated in a Nikon polarized microscope, model Eclipse LV100N pol. Images of the drop were taken at different time intervals. Due to the spherical shape of the drop, images in different focal planes were taken and subsequently joined

| | 0.25%wt. | | 0.50%wt. | | 2.0%wt. | |
|---|---|---|---|---|---|---|
| D ($\mu m$) | $Q_o$ | $Q_w$ | $Q_o$ | $Q_w$ | $Q_o$ | $Q_w$ |
| 200 | 10 | 0.8 | 10 | 0.6 | 5.0 | 0.5 |
| 400 | 5.0 | 2.5 | 5.0 | 1.0 | 1.0 | 1.0 |
| 600 | 0.8 | 1.0 | 0.5 | 3.0 | 0.1 | 2.0 |

Table 1. Formation flow rates for each drop size desired and surfactant concentration, $Q_o$ (ml/h) and $Q_w$ ($\mu l/min$).

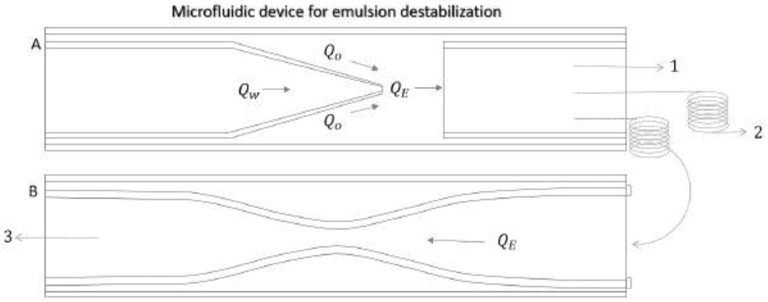

Figure 1. Scheme of the coaxial flow microfluidic device connected to the capillary with constriction. In this scheme is represented the cases enumerated in the text: case 1 - collection right after the production; case 2 - collection after the emulsions passing through a long line to allow the aging of the droplets; and case 3 - collection after the drops of the second case passing through the capillary with constriction.

to reconstruct a three-dimensional image.

### 2.3 Emulsion destabilization

The production of the emulsions was performed using a coaxial flow microfluidic device similar to the described before (Fig. 1). Part A of this device is composed of capillaries arranged to form a flow focusing geometry for the production of the drops. Its output was connected to lines of different lengths according to the desired interfacial aging time. Part B is composed of a constricted glass capillary with a ratio of channel diameter to constriction diameter of $D_0/D_c = 580/180 \approx 3.2$. The constriction was made using the micropipette puller. This ratio was chosen such that the drop extension was not large enough to cause a drop breakup but able to increase the interfacial area and create a shear stress near the interface.

Three different scenarios were explored, as sketched in Fig. 1:

1. Case 1: production and collection of the drops with small aging time.
2. Case 2: drops were produced and collect with time interval of at least one hour, allowing the formation of the interfacial solid-like structure.
3. Case 3: following Case 2, before collection, the drops flow through a constricted capillary, in order to perturb the interfacial structure.

The experimental apparatus used consisted of syringe pumps (model Pump 11 Elite from Harvard Apparatus) to inject the phases at constant flow rate; a Carl Zeiss inverted optical microscope equipped with a high speed camera (model Fastec Imaging IL5H) to record real time images of drops passing through the constriction; a microfluidic device described in Fig. 1; a long line (Scientific Commodities, Inc.) through which drops flow during the aging of the interfaces when necessary; and a small vial to collect the emulsions. The line is a polyethylene micro tubing with inner diameter of 863.6 $\mu m$ connected to the capillaries. The emulsion destabilization was evaluated by observing if there was a free water phase at the bottom of the vial. The water phase was dyed with blue color using a water-based dye (0.6 %vol.) to improve visualization of the phases during the visualization experiments.

Different combinations of oil and water flow rates have been used for the preparation of emulsions. Table 2 presents these combinations and the size of the drops obtained for each condition. According these flow rates there is a specific residence time (Table 3) for each one of the cases presented in Fig. 1. For Case A, the drops remain a short time in the line before being collected, which corresponds to the case without interface aging of the drops. For Case B, the residence time was increased by using a long line (9 meters) to allow the interface aging. Case C corresponds to the continuation of case B now with a constriction where the drops pass before to be collected and brought into contact. However, for the highest surfactant concentration (2.0 %wt.), case B was not tested, as shown in the results. For this concentration, the drops from case A pass through the constriction. Thus, the residence time of the drops before constriction is short.

| $\Phi$(%wt.) | $Q_o(ml/h)$ | $Q_w(ml/h)$ | $D_{mean}(\mu m)$ |
|---|---|---|---|
| 0.25 | 3.3 | 0.2 | 450 |
| 0.50 | 5 | 0.5 | 450 |
| 2.0 | 2.5 | 1.0 | 350 |

Table 2. Formation flow rates for each surfactant concentration of emulsions analyzed and mean diameter obtained for each condition.

|  | Residence time (min) |  |  |
|---|---|---|---|
| $\Phi$(%wt.) | Case 1 | Case 2 | Case 3 |
| 0.25 | 0.8 | 90 | 90/0.8 |
| 0.50 | 0.8 | 60 | 60/0.8 |
| 2.0 | 1.3 | - | 1.3/1.3 |

Table 3. Residence time for each case analyzed.

## 3. Results

### 3.1 Spontaneous Emulsification

The evidence of SE is assessed by means of optical microscopy as described above. Figure 2 shows the time evolution of self emulsification for water drops immersed in an oil solution with different surfactant concentrations, 0.25, 0.50, and 2.0 %wt. (5, 10 and 40 times CMC) respectively. The first image that represents the water drop at the beginning of the experiment always shows a clean interface of the drop. With time, smaller spherical drops appear, covering the entire spherical surface of the large water drop. However, the covering rate will depend on the surfactant concentration.

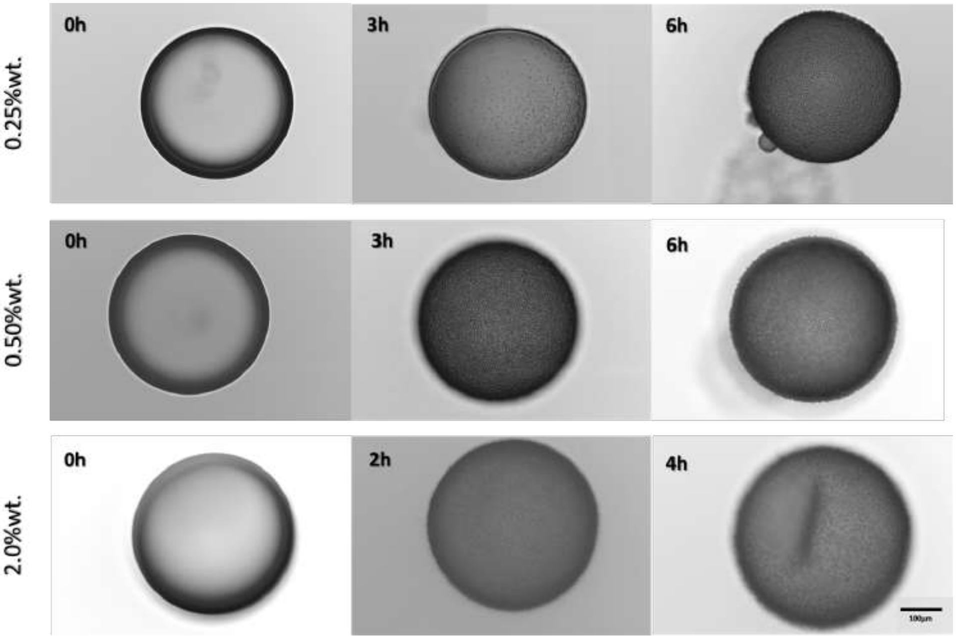

Figure 2. Time evolution of the SE presented at the interface of the water droplet immersed in a oil solution with 0.50%wt. of Span 80.

The rate of self emulsification increases with surfactant concentration. This behavior reinforces the theory that the amount of surfactant determines the kinetics of the process and other specific features (González-Ochoa and Arauz-Lara, 2007). The size of the droplets emerging at the interface of the main drop increases with time. After the interface becomes saturated with the small droplets, it can be noted a shadow region around the original drop that represents the migration of a large number of emerging droplets to the bulk of the oil phase. For the highest concentration (2 %wt.) the drop interface buckles losing their spherical shape after some time. At high surfactant concentration, the rate of self emulsification is high such that the interface becomes saturated by the small drops relatively quickly, forming a solid-like structure at the interfaces. As new small droplets are formed beyond this point and the volume of the large drop falls, a compressive stress acts along the interface, leading to the observed buckling.

The analysis presented up to now was focused on the interface aging of single drops. However, by analyzing a group of drops, we can note the same phenomena. Figure 3(a) shows an emulsion of polydisperse water drops in an oil phase with a surfactant concentration equal to $0.5\%wt$ without interface aging. Initially, we observe that the interface of drops is clean and, as time evolves (Fig. 3(b)), the self emulsification leads to the formation of an interface structure of drops.

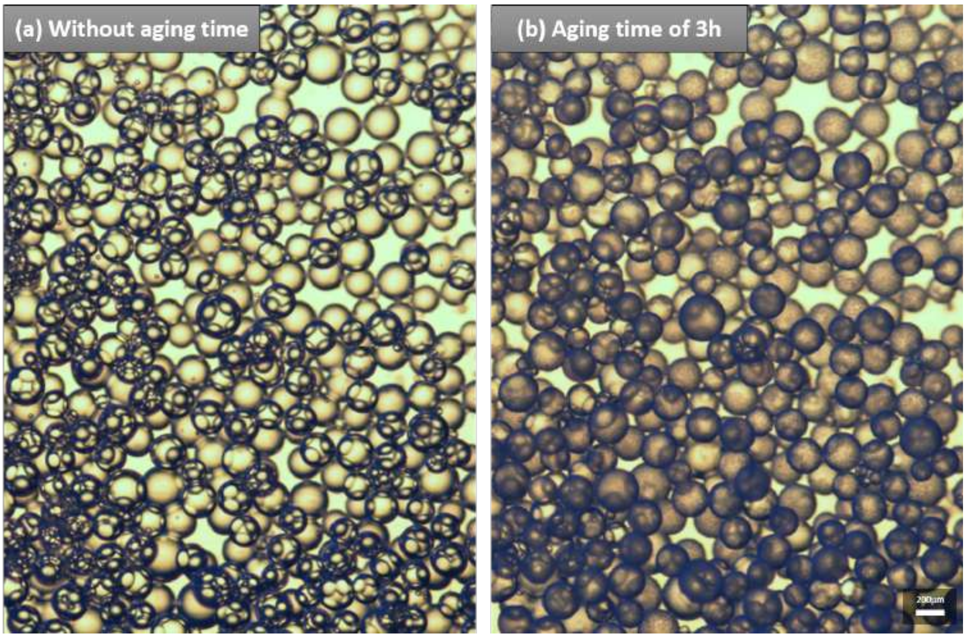

Figure 3. Drops from a polydispersed emulsion immersed in an oil phase of surfactant concentration equal 0.5 $\%wt$.

González-Ochoa and Arauz-Lara (2007) observed similar behavior in their studies. They used pure deionized water and dodecane containing Span 80. They assumed that the formation of water droplets at the oil-water interface is a result of a sequence of physical processes starting with the self-assembly of surfactant molecules in a thick (multilayer) film around the initial water drop. Driven by chemical potential gradients, the film swells at the layer of lower interfacial tension. Liquid bridges are formed by the water accumulated in the surfactant layers, supported by a balance between wetting and surface tension and continued to form until they undergo an instability transition, driven by capillary forces, similar to the Plateau-Rayleigh instability, breaking off in small droplets to reduce internal energy. Regarding the growth of the small water droplets at the interface, they affirmed that it is not due to either coalescence or Oswald-Ripening, but it should occur at the expense of the large drop, once they observed a decrease of its diameter. The film of surfactants provides the required connection between the large water drop and the small water droplets at the interface, which acts as a permeable membrane.

### 3.2 Destabilization of water-oil emulsion breaking the interfacial structure

Once understanding what are happening with the drop interface by the spontaneous emulsification, a way to destabilize the emulsions formed with the fluid system studied was proposed, based on the removal of the interface structure formed by small droplets achieved during the flow of the drops through a constricted capillary.

#### 3.2.1 Behavior of a single drop passing through a constriction

First of all, it was evaluated the behavior of a single drop when passing through the constriction. Figure 4 shows snapshots of the flow of a drop suspended in an oil phase with surfactant concentration of 0.50 $\%wt.$ with and without aging time. Experiments were repeated at least 3 times for each one of them. Comparing the first frame of the different aging, we observe the effect of interface aging. For the case without interface aging, the drop is clean and clear, while for the case with aging time the interface is opaque. Moreover, the drop with 1 hour of interface aging has a cracked look in the interface. This is due to the high concentration of microdroplets accumulated at the interface during the spontaneous emulsification process.

With the visualization of the drop without interface aging it is possible to note that the drop elongates as it flows through the throat and regains its shape without losing mass. On the other hand, for the drops with aging time of the interface there are an amount of microdroplets on the interface, then the elongation of the drop with its flow through the constriction increases the surface area, disrupting the interface structure. Moreover, the flow leads to a strong shear stress along the interface. These two phenomena contribute to more the small drops formed during the interface aging step from the interface towards the back of the large drop. Downstream of the throat, the drop interface is clean (it is clear in the

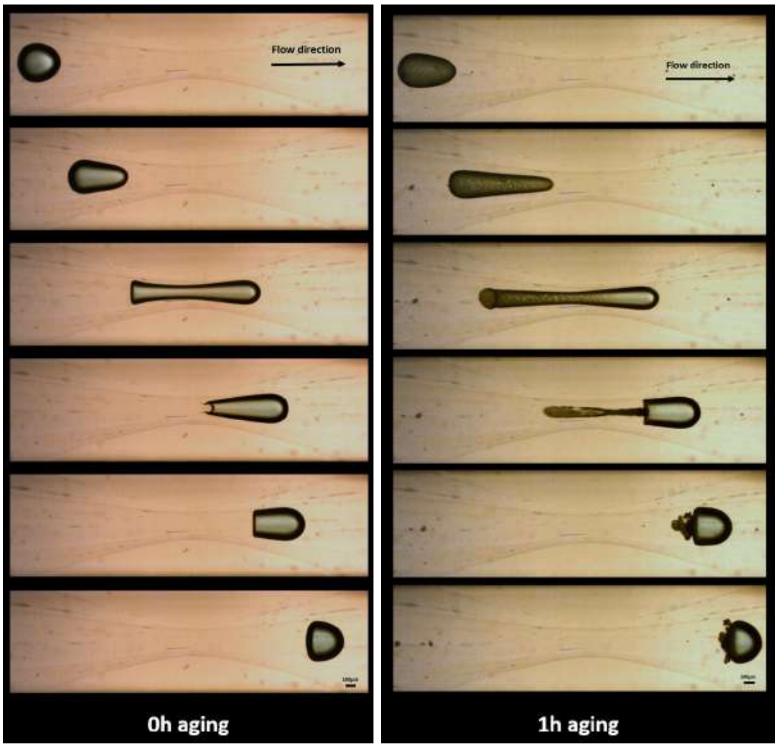

Figure 4. Evolution of the drop position and behavior as it flows through the constriction. Surfactant concentration of $0.5\%wt.$ and different drop interface aging.

images) and cloud of small drop is observed on its trailing edge. The apparent size of the drop falls, as the mass associated with the small drops was removed from the interface.

### 3.2.2 Evaluation of interface cleanliness for produced emulsions

Finally, by observing the possibility of promoting the cleaning of the interface by passing the drop through a constriction, some tests were performed trying to destabilize a w/o emulsion. Monodispersed emulsions were produced with drop diameters between 350 and 450 $\mu m$ and with different surfactant concentrations. We analyzed the stability of the produced emulsions at different interface aging times and whether or not the drops passed through a constricted capillary before collecting them in a vial. All experiments presented in this section were repeated three times and showed the same behavior.

Images of the emulsions produced with the surfactant concentration of 0.5 $\%wt.$ and evaluated using the three cases presented in the Experimental Section are shown in Fig 5. Case A represents the emulsion with drops produced and collected shortly thereafter. On the bottom part of the vial there is a layer of water that is the result of coalescence of the drops. Above this free water layer there is a w/o emulsion, both segregated of the oil phase. To allow the aging of the interface before the contact between the drops and thus avoid coalescence, the drops were produced and collected only 1 hour later (Case B). This was possible by the addition of a meter-long collection hose, as shown before. Drops remain stable over time once there is no appearance of a layer of water at the bottom of the vial. Above this w/o emulsion layer there is also a stable w/o emulsion but with micro water drops. In Case C, the drops traveled in the line, allowing the aging of the interface, but before being collected, they passed through a constriction that allowed the removal of the small droplets that formed spontaneously, as seen in the previous section. Once the interface is clean again, after being collected, it is possible to observe the formation of a free water phase on the bottom of the vial, which characterizes coalescence. It is noted that in Case C the oil layer above the emulsion is whitish. This is due to the small droplets that have detached from the interface of the larger drops and that, due to their size, remain suspended in the oil phase.

The results for tests performed with a surfactant concentration of 0.25 $\%wt.$ presented similar behaviors with results obtained for the concentration of 0.5 $\%wt.$. The only difference observed was in the speed of destabilization of the samples. The emulsions produced with the smallest surfactant concentration destabilized faster than the emulsions produced with 0.5 $\%wt.$ of surfactant concentration, as expected. Again, the interface structure was removed by flowing the drops through the constricted capillary leading to destabilization of the emulsion and the appearance of a water free phase.

Finally, the highest concentration was evaluated (2.0 $\%wt. =$ 40 times CMC). As cited before, at this concentration, interfacial phenomena occur faster than at other concentrations due to the great availability of surfactant to act at the

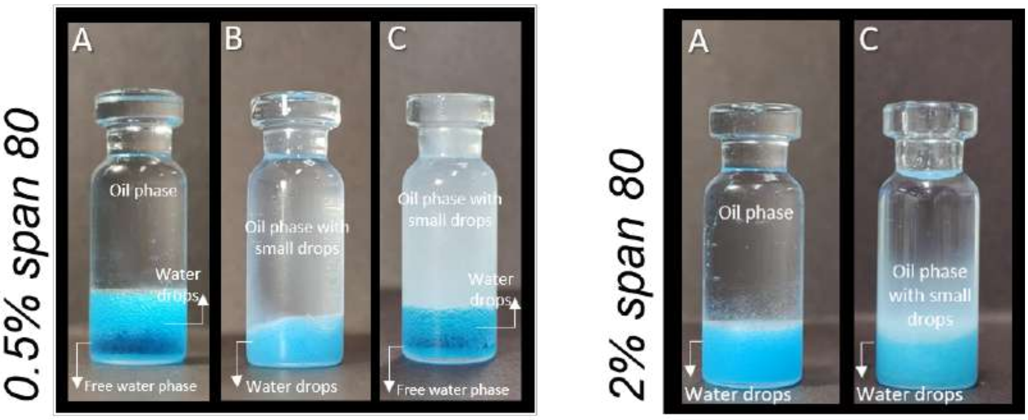

Figure 5. Emulsions produced with different surfactant concentration. (A) represents the collection of the drops right after the production. (B) represents the condition of drop interface aging of one hour. And (C) is a continuation of case B, but drops pass through by a constriction before being collected.

interfaces. Case A in Fig. 5 shows the drops produced and collected with short aging time. For this case the drops remained stable for more than 1 day. Due to the high stability of the system, case B was not evaluated. Case C was evaluated but for the drops with short aging time. We observed that, even going through the constriction the drops did not coalesce when collected. Although, one observes a whitish region above the water drops on the bottom. It corresponds in this case to the small drops removed from the large drop during the passage through the constriction. We believe that the spontaneous emulsification happens so fast that probably droplets with nano size growing up at the interface are enough to hindering the coalescence. A suggestion would be to vary the size and assess whether the stability is related to this parameter, once there are studies at the literature that found a strong dependence on the drop stability with its size (Politova *et al.*, 2017; Basheva *et al.*, 1999).

## Conclusions

The investigation of the morphology and the phenomena that lead to the interfacial structure formed at the oil-water interfaces was performed in this work. Firstly, the interface aging of a water drop was evaluated and it was observed the appearance of small droplets along the interface of the large drop. As the experiment occurred without any external energy input, we can conclude that these water droplets are the result of spontaneous emulsification at the oil-water interface. Nevertheless, the kinetics of appearance of these small droplets on the interface depends on the surfactants concentration, which can go from a few minutes to a few hours and somehow they interact with each other forming a network that maintains the stability of the interface of the larger drop. Although the self emulsification process and the resulting interfacial structure formed are directly related to the system analyzed (mineral oil Primol 352 and Span 80), similar phenomena has been observed with other systems, including different crude oils containing natural surfactants (Wu and Firoozabadi, 2021; Bochner de Araujo *et al.*, 2019). Secondly, it was evaluated the behavior of a single drop passing through a constriction whereby it was confirmed the possibility of cleaning of the drop interface. Finally, it was proposed a new method to destabilize an water-in-oil emulsion by disrupting the interface structure that is formed along the water-oil interface, which hinders coalescence and leads to very stable emulsions. For this, different surfactant concentrations were tested, all above the CMC (5, 10, and 40 times). The results showed that for the two lowest concentrations, emulsions with less than 1 minute of aging time showed instability, with phase separation being observed already after collection time. Differently when the drops of these emulsions had time to age (1 hour at least). In these cases, the emulsions showed stability after production and for days afterwards. As a way to promote phase separation, for these emulsions with longer aging time, the drops were subjected to pass through a constriction, which allowed a cleaning of the interfaces and, consequently, a rapid phases separation after production. Emulsions produced with the highest concentration evaluated (40 times of the CMC) were stable with short aging time before the contact between the drops. Although these drops were subjected to passage through the constriction, the residence time before collection was enough to stabilize this new drop interface formed, consequently the emulsions were stable. During all this study, it was seen that the Span 80 concentration plays an important role on the dynamic of the interfacial rheology and consequently on the coalescence process. This observation is in concordance with studies at the literature that evaluating the amount of asphaltenes on the crude oil and presenting that the stability of emulsion will increase with the increase in the concentration of asphaltenes in the crude oil (Zaki *et al.*, 2000; Aguilera *et al.*, 2010).

## 4. ACKNOWLEDGEMENTS

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