# ASSESSING THE EFFECTS OF STIRRING INTENSITY AND MIXING TIME ON THE STABLITY OF OLEFIN EMULSIONS

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***Abstract.*** *This work aims to experimentally correlate the effects of stirring speed and mixing time on the stability of olefin emulsions. For this purpose, 40/60 water-in-oil emulsion samples were prepared using olefin as organic base and sodium chloride brine. Only the stirring speed and mixing time were varied on the preparation of the samples, keeping the same products and dosages for all of them. Stability characterization of each sample was performed using gravitational separation tests, microscopic images, viscosity and electrical resistance measurements. The results showed a tendency for improved emulsion stability with increased stirring speed. For emulsification time, it was observed improving in emulsion stability up to the mean value defined for this parameter (10 minutes), so that values higher than this did not show any relevant effects.*

***Keywords:*** *stirring intensity, mixing time, emulsion stability, oil-in-water emulsions, olefin emulsions*

## 1. INTRODUCTION

Emulsions are systems composed of two completely or partially immiscible liquid phases, so that one of the liquids is dispersed as droplets within the other one. These systems have been presented as a basis for the composition of several products, finding a wide range of applications, such as in the chemical, agrochemical, cosmetic, pharmaceutical and food industries (Badolato et al., 2008, Chen et al., 2011).

In oil exploration, invert emulsions have been extensively applied in the formulation of drilling fluids. In these emulsions, organic products compose the continuous phase and water, or brine, constitutes the dispersed phase (Bourgoyne, 1986; Ghalambor et al., 2008; Mohamed et al., 2018). Due to environmental requirements, olefin has been the most widely used organic compound as the continuous phase in this type of emulsion, since it presents low toxicity and good biodegradability. Moreover, lower cost and good stability at high temperatures ensure the possibility of applying this type of fluid in deep and ultra deep wells (Neff et al., 2000; Buckley and Morrow, 2006).

Whatever the application, the effectiveness of the use of emulsions may be hampered by their thermodynamic instability, since these systems have a natural tendency to separate in their two constitutive phases, decreasing the interfacial area and consequently the interfacial energy (Almeida, 2014). Thus, the stability of the emulsions is related to the prevention of the coalescence of the dispersed droplets, which hinders or delays the phase separation, ensuring a successful application.

Improving the stability of the emulsions is usually related to the application of new materials with different dosages in their composition, in particular the emulsifying agents (Maindarkar et al., 2013). However, few studies have turned their attention to the optimization of the operational conditions used in the preparation of the emulsions as a way to guarantee the formation of more stable emulsions.

This study aims to assess the effect of stirring speed and mixing time on the stability of olefin emulsions.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Internal olefin and sodium chloride saturated brine were used as continuous and dispersed phases, respectively, in the preparation of the emulsions. Each sample received the addition of 5 g of hydrated lime and a total of 9 g of primary and secondary emulsifiers, which were added in the ratio 70/30. The emulsions were prepared in 350 ml aliquots, with water/oil ratio of 40/60.

### 2.2 Methods

### 2.2.1 Preparation of emulsions

The olefin emulsions studied in this work were prepared using a Turrax homogeneizer, model T25. The components of the emulsion were added in the order shown in Table 1, with a five-minute interval between the addition of each one.

Table 1 – Formulation of internal olefin emulsions

| Component | Amount |
|---|---|
| Olefin | 203 mL |
| Primary Emulsifier | 6,3g |
| Secondary emulsifier | 2,7g |
| Lime | 5g |
| NaCl brine | 136,5 mL |

The variation of stirring speed and mixing time (after addition of all components) is shown in Table 2. Table 3 shows the combinations of parameters used for each sample.

Table 2 – Velocities and mixing times analyzed

| Variables | | | |
|---|---|---|---|
| Stirring speed (rpm) | 5,000 | 12,400 | 20,000 |
| Mixing time (min) | 5 | 10 | 15 |

Table 3 – Processing parameters for each sample

| Samples | Stirring speed (rpm) | Mixing time (min) |
|---|---|---|
| 1 | 5,000 | 10 |
| 2 | 12,400 | 5 |
| 3 | 12,400 | 10 |
| 4 | 12,400 | 15 |
| 5 | 20,000 | 10 |

### 2.2.2 Stability Tests

The stability of each sample prepared was characterized according to the tests described below.

### Gravitational Separation

The gravitational separation of the phases of the emulsion samples was evaluated by means of bottle tests, based on ASTM D1401-18b. In this procedure, 80 mL of each sample was placed in graduated test tubes and kept at room temperature. The relative volume of the separated phase in each sample was recorded at the following time intervals: 24h, 48h, 72h, 96h e 120h.

### Microscopy

Microscopy images of the emulsions prepared in this work were obtained using the Olympus CX31 Olympus microscope fitted with an LC-30 Olympus digital camera. Images were processed using Stream Essentials software.

### Viscosity

The viscosity of the emulsions was measured on a Brookfield LVDV2T rotational viscometer using spindle SC4-18. Measurements were taken at speeds ranging from 20 to 120 rpm, or up to the maximum value allowed by the equipment. Each reading was performed with relative rotational increases of 2 rpm. The results presented in this work correlate the viscosity and the shear rate for each sample. The conversion of the rotational values to shear rate was performed from a constant presented by the equipment manufacturer, considering the spindle model used.

### Electrical Resistance

Electrical resistance measurements were performed using an ICEL digital multimeter model MD-6130. In this test, the equipment tips were inserted at a fixed distance of approximately 1.5 cm in a 50 ml emulsion sample, heated in a thermal cup to approximately 50°C. Five measurements were performed for each sample. The electrical resistance values considered in this study represent the arithmetic mean of the values obtained for each sample.

## 3. RESULTS AND DISCUSSIONS

### Gravitational Separation

During gravitational separation tests (bottle tests) the stability of an emulsion is checked by observing its homogeneous appearance with a small or no phase separation. On the other hand, emulsion breaking is recognized by observing aspects such as oil phase brightness (indicative of the absence of water), clarity of the water phase and sharpness of the interface presence (Neff et al., 2000).

Figure 1 shows the recording of each emulsion sample 120 hours after the test started. The graphs of Fig. 2 show the separated phase volumes for each sample, recorded during the first five days after preparation.

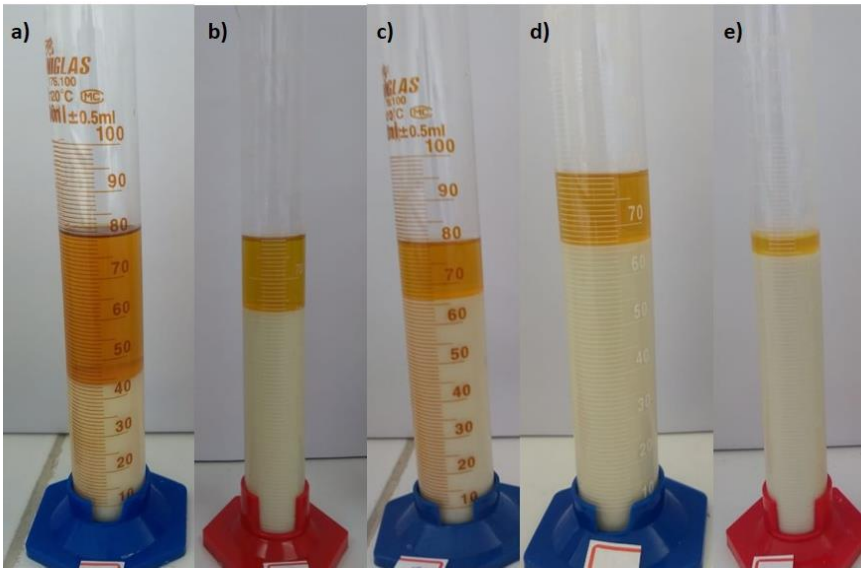


Figure 1. Separated phase for each emulsion after 120 hours for samples 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e)

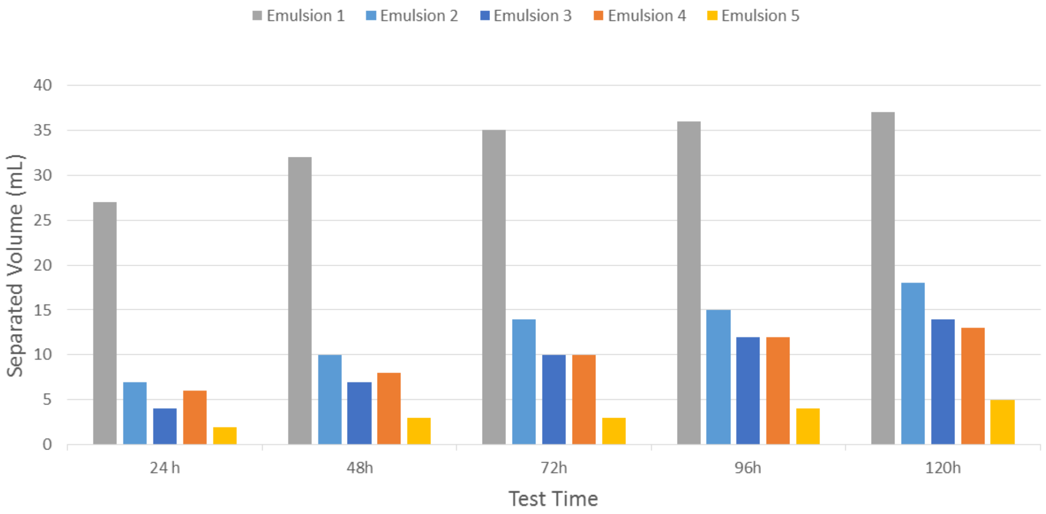


Figure 2. Separated volume during the first 120h after preparation

As can be seen in Fig. 1, for all samples, the separated phase was supernatant to the emulsion and shows a clear appearance. The lower density of the separated phase demonstrates the occurrence of a gravitational separation of the emulsion’s continuous phase, constituted by internal olefin, and for none of the samples was observed the coalescence of the drops of brine, which constitute the dispersed phase. Thus, the separated phase for all samples indicates that the volume of olefin used for the preparation was not entirely emulsified. This non-emulsified volume was markedly higher for emulsion 1, in all times recorded. This emulsion was prepared with the lowest stirring speed (5,000 rpm) and mean emulsification time (10 min). On the other hand, the lowest volume of separated phase was observed for sample 5, for which the highest stirring speed (20,000 rpm) and mean stirring time (10 min) were used.

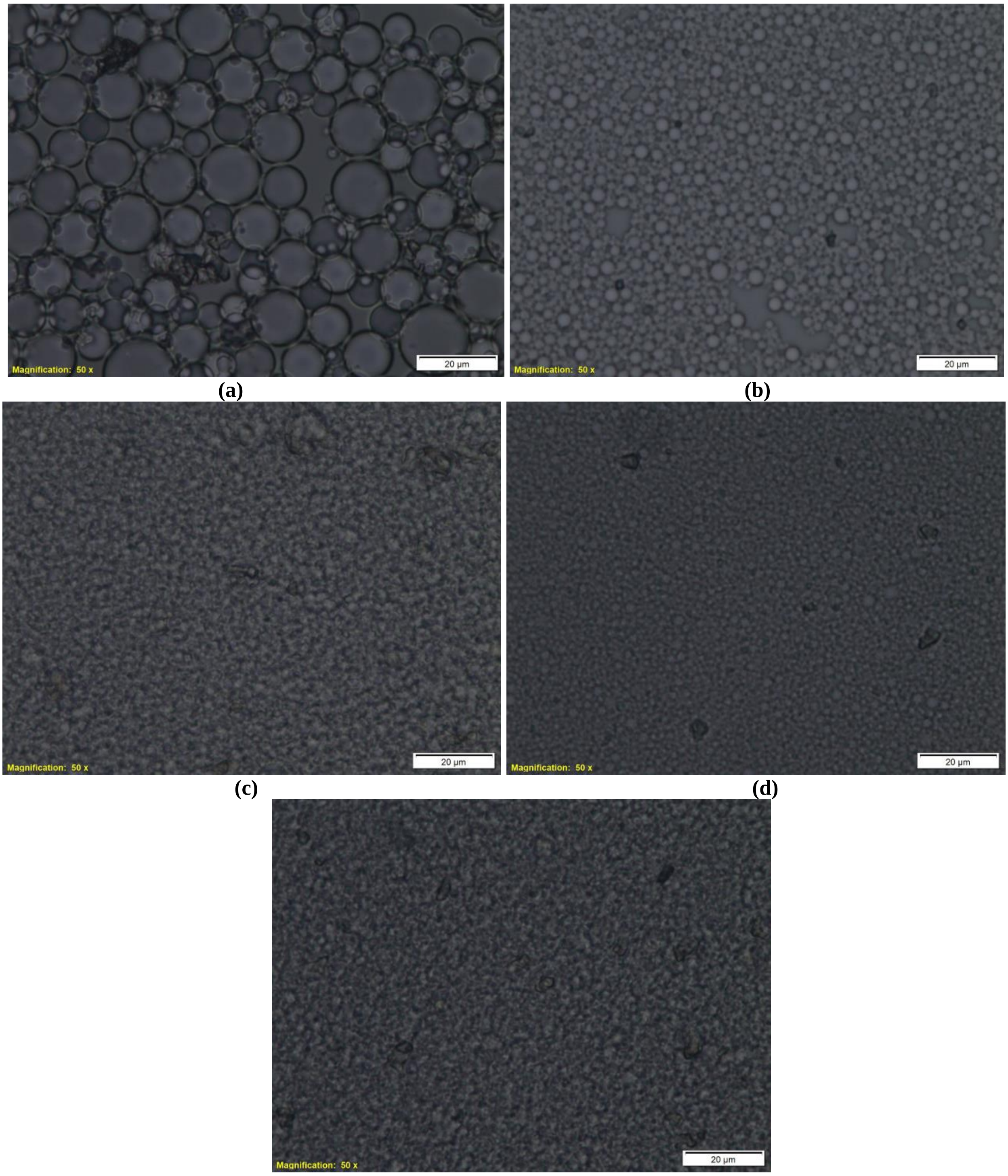
In addition to the separated volume, the difference in color intensity of the separated phase is another aspect to be observed in each sample. The yellowish and orange tones observed for all samples are possibly related to the presence, in a greater or lesser extent, of the emulsifying agent. Once the oil phase is originally colorless, its interaction with the brown coloring emulsifying agents results in the colorations observed during the test. Thus, the sharply more pronounced color of the oil phase observed in emulsion 1 demonstrates the presence of a higher content of emulsifying agent. On the other hand, the clearest color intensity was observed for emulsion 5, which also showed better emulsification of the internal olefin.

Emulsions prepared with medium stirring speeds and different mixing times (Emulsions 2, 3 and 4) have demonstrated a remarkable decrease in the phase volume separated in relation sample 1. This decrease is proportional to the mixing time used, that is, the longer the time, the better the emulsification of the phases that make up the system. However, this improvement is more significant up to the mean value of the analyzed time, since the average and maximum mixing times (10 and 15 minutes) used in the preparation of samples 3 and 4, respectively, presented very close results in the majority of the observations.

Chen and Tao (2005) argue that the application of mechanical energy is the most usual way to obtain the emulsification of two immiscible liquids, since it provides the deformation of the interface of the two liquid phases, leading to the formation of larger droplets, and these are subsequently broken into smaller droplets. The separation of the oil phase, as well as the presence of emulsifier in this phase, observed in this study are indicative that the emulsification process didn´t occurred efficiently. Those results are clearly related to the application of insufficient mechanical energy in the preparation of the emulsion, since the larger volumes of separated oil phase and emulsifier are related to the slower stirring speed. In addition, it is observed that the application of mechanical energy for longer time intervals guarantees a more efficient emulsification process, although the improvements obtained with the increase of this parameter have been, in general, less expressive than those presented through the speed increases.

## Microscopy Images

Optical microscopy is one of the techniques used to characterize an emulsion in terms of droplet size distribution. This parameter is related to the emulsion rheology, besides influencing the destabilization mechanisms of the emulsion, ie, flocculation, coalescence, creaming and sedimentation (Moradi et al., 2010).Figure 3 shows microscopic images of each emulsion sample analyzed in this study.



**(a)** **(b)**

**(c)** **(d)**

(e)

Figure 3. Microscopy images of emulsions 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e). The scale presented for each image is 20 µm

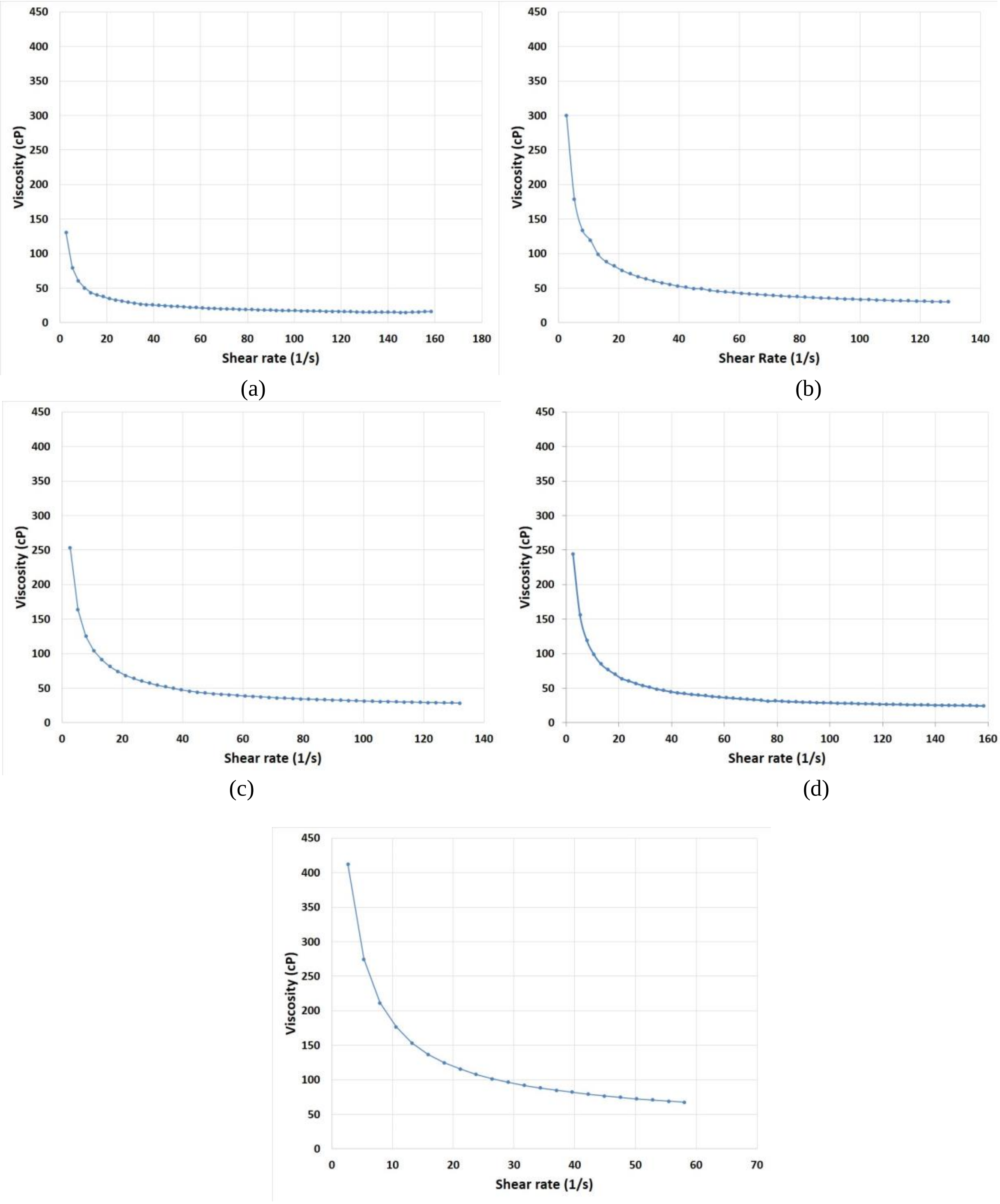
Figure 3 shows droplet sizes substantially larger for emulsion 1, followed by emulsions 2 and 4. This behavior is consistent with the results observed in the bottle test, since, as a rule of thumb, the larger the droplet size, the less stable the emulsion is (Moradi et al., 2011). Thus, microscopic images confirm that low speeds and short emulsification times do not provide sufficient mechanical energy for the system, promoting a less efficient emulsification, and resulting in less stable emulsions and larger droplet sizes.

The low definition observed in the images obtained for emulsions 3 and 5 indicates very small droplet sizes for these systems, which is related to the better emulsification, promoted by the high speeds applied to them.

Considering the mixing time, however, it is observed that averages mixing times used in emulsion 3 provided the formation of a system with droplets smaller than those observed for emulsion 4, in which the maximum time (15 minutes) was used.

### Viscosity

Understanding the rheological behavior of the emulsions provides information about the stability and microstructure of these systems (Pal, 2011). The viscosity curves for the analyzed emulsions in this study are shown in Fig. 4.



(a)

(b)

(c)

(d)

(e)

Figure 4. Viscosity curves for emulsions 1(a), 2(b), 3(c), 4(d) and 5(e)

All the curves presented demonstrate a pseudoplastic behavior of the analyzed samples, since there is a decrease in viscosity values with the increase of the shear stress.

The curves shown in the graphs demonstrate significant variations in the viscosity of each sample. Salager (2000) argues that viscosity increases are related to the decrease in mean droplet size, since the friction between small droplets is higher because of the high surface area. Thus, the behavior observed in the viscosity curves presented in this work confirms the results obtained in the microscopic images, so that the emulsion 5, which presented smaller droplet size in the microscopic images, obtained the highest viscosity values. Emulsion 3, on the other hand, showed the highest droplet sizes, which justifies the significant decrease of the viscosity presented by this emulsion in relation to the other samples.

Intermediate viscosity values were obtained for emulsions 2, 3 and 4, prepared with mean values of stirring speed and different mixing times. The curves presented by these emulsions confirm the viscosity increase with increasing speed, which contributes to the delivery of mechanical energy to the system, and formation of emulsions with smaller droplets. However, the emulsification times used for emulsion 3 (10 minutes) resulted in a lower viscosity of the emulsion, compared to the minimum mixing time (5 minutes) used for emulsion 2.

### Electrical Resistence

The capacity of conduction of electric current of an emulsion is considered as a parameter to predict its stability, since it is influenced by certain characteristics, among which are: liquid type that composes the continuous phase, volumetric fraction and droplet size (Salager, 2000). The graphs of Fig. 5 represent the electrical resistance values obtained for the samples analyzed in this study.

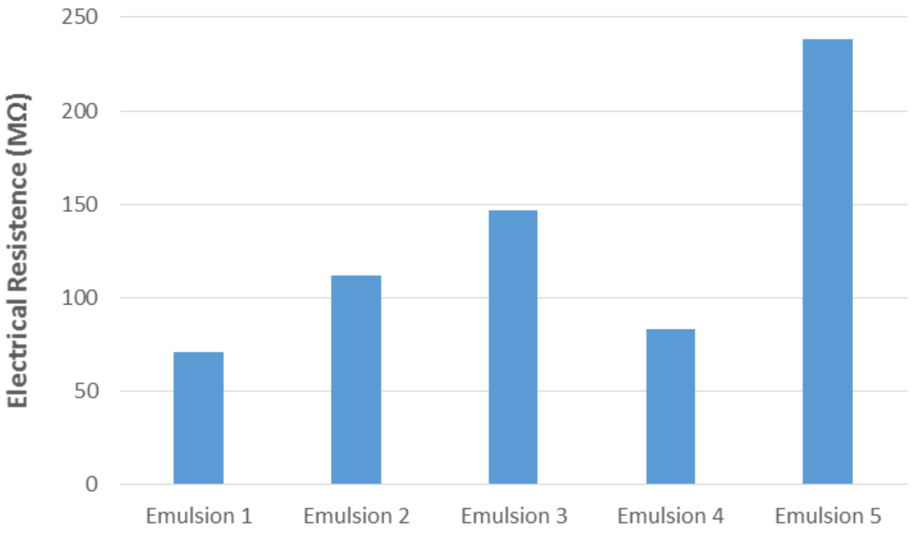


Figure 5. Electrical resistence for the samples anayzed.

The emulsions prepared in this study are water-in-oil type, so that the dispersed phase, consisting of brine, is much more conductive than the olefinic continuous phase. Thus, samples prepared under conditions that favor efficient emulsification are expected to exhibit higher values of electrical resistance. This relationship is clearly observed for emulsion 5, which presented the highest value of electrical resistance, confirming the trend of better stability of this emulsion observed in the other tests performed in this study. The minimum value of electrical resistance observed in the graph also confirms the lower stability presented by emulsion 1 in all tests performed.

The resistance values presented by emulsions 2, 3 and 4 indicated a tendency of greater stability for the emulsion 3, prepared with average stirring time. However, for emulsions 2 and 4, a controversial relationship was observed, since emulsion 4, prepared with maximum stirring time, showed lower electrical resistance than emulsion 2, in which emulsification time was the lowest analyzed.

## 5. CONCLUSIONS

This work aimed to experimentally investigate the effects of stirring speed and mixing time on the stability of olefin emulsions. From the results obtained it is concluded that:

- The separation of the oil and emulsifying phases observed in the bottle tests is related to the low stirring speeds used in the preparation of the emulsions;
- Larger droplet sizes are observed in emulsions prepared with lower stirring speeds;
- The viscosity of the emulsions is related to the droplet size of the dispersed phase, so that emulsions prepared with lower stirring speeds have larger droplets and consequently lower viscosities;
- The electrical resistance tests confirmed the stability trend observed for the emulsion samples;

- Short mixing times provide the formation of less stable emulsions, however, the emulsification obtained using average and maximum times is very similar and;
- Maximum stirring speed values is considered as the best operating conditions for the preparation of emulsions, according to the separated phase volume in the bottle tests, microscopic images, viscosity curves and resistance values.

## 6. ACKNOWLEDGEMENTS

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