

Aging of water-in-crude oil emulsions: Effect on water content, droplet size distribution, dynamic viscosity and stability

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ABSTRACT

The production of crude oil containing emulsified water presents problems, for example the corrosion of transport systems and the poisoning of catalysts during the refining stage. The ease of separating water from petroleum varies with the aging of the emulsion; however, this issue has not been explored extensively in the literature. This study aims to evaluate the relationship between aging and stability of emulsions, to assess the contribution of certain variables such as asphaltene content and the variation in the size of water droplets in the emulsion, as well as the dynamic viscosity of the oily phases and emulsions. The effect of aging on the performance of a commercial demulsifying product was also evaluated. To this end, synthetic emulsions were prepared from Brazilian crude oil and from the dispersion of asphaltenes in different oily phases. The emulsions were evaluated immediately after preparation and every 15 days for a 60 days period. It was found that a high performance demulsifier can become inefficient in the treatment of aged emulsions causing serious damage to the petroleum treatment. The most significant effect of aging probably occurs because of changes in the internal structure of the emulsion, more specifically in the interfacial film, since there are no significant changes in the emulsified water content, in the droplet size distribution and in the dynamic viscosity of emulsions with the aging of the emulsion. The influence of the asphaltene content on the stability of emulsions was confirmed by the variation of the properties of the model emulsions containing different asphaltene contents.

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1. Introduction

Petroleum is produced as water-in-oil (W/O) emulsions [1]. The emulsification of water in oil is due to the immiscibility between these two liquid phases, to the shear imposed on the fluids during the production flow and to the existence of natural surfactants in the petroleum's composition [2,3].

These natural surfactants are adsorbed on the surface of water droplets and create a physical barrier (interfacial film with viscoelastic properties), which prevents coalescence between the water droplets [3]. According to Kilpatrick et al., the main species responsible for the stabilization of these emulsions are asphaltenes [4]. Even though asphaltene molecules do not have clearly identifiable hydrophilic polar heads and hydrophobic tails, they present surface activity [5].

Asphaltene is a term that was used to refer to the heaviest and most polar components that can be extracted from petroleum.

More recently results, however, show that the average molecular weight of asphaltenes extracted with n-heptane is about 750 g/mol [6]. Even lower values (~400 g/mol) have been found [7]. In terms of solubility, asphaltenes is defined as the crude oil molecules that are insoluble in n-heptane (and other linear alkanes such as n-nonane, n-pentane or n-propane) and soluble in toluene [8].

Emulsified water may cause problems at several stages of the production of crude oil, such as: (a) increased viscosity, (b) higher cost of transport and storage, (c) corrosion and salt deposits in the refining equipments and (d) poisoning of catalysts [9]. The emulsion destabilization, an essential step for the efficient operation of separating water from petroleum, can be carried out by the addition of chemical substances, named demulsifiers [1,3,10–13]. Such substances include block copolymer based on ethylene oxide and propylene oxide (PEO-b-PPO), which have been extensively studied by our research group [14–19].

In addition to aspects related to the formation of the interfacial film, the adsorption and the solubility of natural emulsifiers, one must also consider the characteristics of the emulsified system (droplet size distribution, content of the dispersed phase, viscosity, chemical nature of the phases and so forth), the temperature, the

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pressure and the aging time, because these are equally important for the stability of the emulsions [20].

In recent decades, numerous papers on petroleum emulsions and treatment technologies have been published [12,21–30], however hardly any studies have been carried out to investigate the effect of aging on the characteristics of emulsions [20,31–34]. These papers highlight the relevance of studying aging and indicate that the properties of petroleum emulsions change over time, and that these changes may influence their stability and separation processes.

One of the first studies about how aging influences the stability of emulsion was published by Rønningsen et al. [31] who found that the properties of petroleum and, consequently, the emulsion formed from it under certain conditions, can undergo changes with aging. These studies were later complemented by the study of Midittun et al. [20], which assessed emulsions of petroleum and asphaltene model emulsions, and observed the effect of increased stability due to the aging of the emulsions. This effect was attributed to the migration of asphaltenes and resins to the interface of the droplets over time, and the extent of the aging effect was related to the nature of the petroleum and the ratio of resins to asphaltenes. One of the few papers on the subject with Brazilian petroleum was published by Ramalho; this showed a large increase in stability and viscosity in petroleum emulsions as a function of aging. According to the author, when an emulsion ages, there is an increase in stability due to oxidation, loss of light fractions, precipitation of some components, and, especially, higher adsorption of natural emulsifiers at the interface, which facilitates the formation of more elastic interfacial films [32]. Based on such studies, Aske suggests, as a matter of security, that the process of petroleum emulsions destabilization should be carried out as soon as possible. This would prevent the emulsion from becoming stable and more difficult to treat [33].

Therefore, a better understanding of the aging effect on the characteristics and the stability of emulsions extracted from a given well can help producers understand how to treat the petroleum more efficiently. Such studies may enable, for example, to identify how long the emulsion can be stored or transported before being submitted to the primary treatment for water separation. Such knowledge will help in planning logistics. These researches may also elucidate the mechanism of emulsification, which is an important premise for the development of new technologies, development of demulsifying formulations and optimization of operational variables of existing treatment processes at various stages of petroleum production [34].

For the purposes of this study, a petroleum emulsion and asphaltene model emulsions were prepared and the effect of aging on their main characteristics was discussed. The study assessed the influence of time on the content of emulsified water, dynamic viscosity, the droplet size distribution and stability of emulsions. For the latter study, a commercial demulsifier was used.

2. Experimental

2.1. Materials

The Brazilian petroleum, supplied by Petrobras, presents °API of 28.3, water content of 0.090% m/m and SARA (saturates, aromatics, resins and asphaltenes) composition of 58.4, 26.2, 14.6 and 0.79 wt%, respectively. From this petroleum sample, asphaltenes (fraction C7) were extracted by the solubility difference: the asphaltenes precipitation was promoted in a soxhlet extractor with an excess of n-heptane (99.5% PA purity), followed by vacuum filtration at room temperature.

The demulsifying surfactant, supplied by Clariant (Macaé) and based on a copolymer of poly(ethylene oxide-b-propylene oxide), presents number average molecular weight of 2330 g/mol, polydispersity of 4.9 and EO/PO ratio of 0.49.

2.2. Methods

2.2.1. Preparation of emulsions

Seven emulsions were prepared, one of which was produced from petroleum and the other 6 model emulsions were prepared at different oily phases, containing different concentrations of the asphaltene fraction extracted from the petroleum (Table 1). The water-in-oil emulsions, containing 40.0% (v/v) aqueous solution at 50 g/L NaCl, were prepared at room temperature, using a Polytron PT 3100 homogenizer, at 10,000 rpm for 3 min.

2.2.2. Effect of the aging of emulsions

The aging study consisted of analyzing the stable emulsions which were formed through assays conducted over 60 days, at 15-day intervals. The study analyzed: water content, droplet size distribution (DSD), dynamic viscosity and demulsifying performance in water-in-oil separation.

2.2.3. Emulsified water content

The measurement of emulsified water content was carried out using potentiometric titration with Karl Fisher reagent, using a Metrohm potentiometric titrator, model Titrando 841. This method is based on the chemical reaction between alcohol, sulfur dioxide, a nitrogenous base, iodine and water. The methodology is based on the ASTM D 4377 [35].

2.2.4. Size and size distribution of droplets

The size and size distribution of water droplets in the emulsions were measured at room temperature, using a Mastersizer 2000 (Malvern Instruments) which allows the measurement of droplet diameters in the range of 0.02–2000 µm. The results were shown in volumetric distribution, and the average diameter of water droplets was calculated as the mean volume-weighted droplet sizes $D[0.5]$.

2.2.5. Dynamic viscosity

To determine the dynamic viscosity of emulsions and oily phases, a DV III Ultra viscometer (Brookfield) was used. A spindle shear element was adapted and a thermostatic bath SC 18 TC-502 (Brookfield) was also used, in line with the ASTM D 341 [36]. The measurements were carried out at 40 °C according to the schedule for the aging study, i.e., over two months at every 15 days.

2.2.6. Natural phase separation

The separation of water from the emulsions was evaluated without the addition of demulsifier, every 15 days during 60 days of aging at 40 °C. Emulsion (50 mL) was placed in a graduated bottle test tube and the percentage of water separation was visually quantified.

2.2.7. Demulsification test (bottle test)

The evaluation procedure of the natural separation of water from emulsions was also applied to the separation phase assays in the presence of demulsifier. The water separation index (WSI), which is a quantification of the efficiency of the demulsifier to promote phase separation, was calculated using Eq. (1) [3].

$$WSI (\%) = \frac{\sum SW \times (SW_f/100)}{n} \quad (1)$$

where $\sum SW$ is the sum of the percentages of separated water at each reading time; SW_f is the final percentage of separated water and n is the number of readings. For the petroleum emulsion, a

Table 1
Emulsions that was prepared and evaluated.

| Emulsion | Oil phase 60% | Aqueous phase 40% |
|----------|---|---------------------|
| #1 | Petroleum containing 0.79% m/m of asphaltenes | Brine (50 g/L NaCl) |
| #2 | 0.79% m/v of asphaltenes in 18% of toluene in mineral oil | |
| #3 | 0.79% m/v of asphaltenes in 18% of toluene:n-heptane 1:1 in mineral oil | |
| #4 | 0.79% m/v of asphaltenes in 40% of toluene in mineral oil | |
| #5 | 0.10% m/v of asphaltenes in 18% of toluene in mineral oil | |
| #6 | 0.05% m/v of asphaltenes in 18% of toluene in mineral oil | |
| #7 | 0.005% m/v of asphaltenes in 18% of toluene in mineral oil | |

100 ppm dosage was used and for the model emulsions, 100, 200, 1000, 2000 and 4000 ppm dosages were used.

3. Results and discussion

The petroleum emulsion was stable over two months. From this result, model systems were prepared to investigate the effect of asphaltenes on the formation of emulsions and their properties along aging. The oily phase of the model emulsions consisted of: (1) petroleum-extracted asphaltenes (the concentration of 0.79 wt/wt% represents the same concentration of asphaltenes in petroleum); (2) n-heptane, to simulate the aliphatic characteristics of petroleum; (3) mineral oil, which represents the non-polar compounds and raises the viscosity of the model emulsion; and (4) toluene, to simulate the aromaticity.

During the preparation of the model emulsions, the agitation of the phases provoked the incorporation of the aqueous phase into the oil phase, so that no phase separation occurred. The same behavior was observed for the petroleum emulsion. The exception was the Emulsion #7, which had the lowest asphaltene content; it presented immediate phase separation: 87.5% of water separation in 5 min. These results highlight the role of asphaltenes in the stabilization of emulsions and are in agreement with results obtained by other authors, who believe that asphaltenes are responsible for the formation of a viscoelastic film in liquid–liquid interface, which prevents the coalescence of droplets [3,4].

3.1. Effect of aging on water content

All emulsions were prepared by dispersing 40% water in their oily phases (Table 1). The water content of the stable emulsions (#1–6) was measured over time and the results revealed that the amount of emulsified water remained fairly constant over time in all emulsions.

3.2. Effect of aging on size of droplet and droplet size distribution

The results of size and size distribution of water droplets in Emulsion #1, before and after aging, are shown in Fig. 1a and b, respectively. The profile of the histogram of size distribution was maintained constant, except for a shift for slightly larger droplets for the aged emulsion, when compared with the non-aged one. This variation is due to the coalescence phenomena and Ostwald ripening effect: the intrinsic thermodynamic instability of emulsions and the polydispersity of droplet size means the larger droplets grow in detriment of the smaller ones [37].

The model systems, on the other hand, did not present any changes in the DSD histograms. This lower sensitivity to aging can be interpreted as evidence of greater stability of the model systems, most likely due to differences in the aromaticity degree. The model emulsions with the same content of asphaltenes do not reproduce exactly the same conditions found in the petroleum emulsion. There are probably differences, such as the aromaticity degree and the resins/asphaltenes ratio.

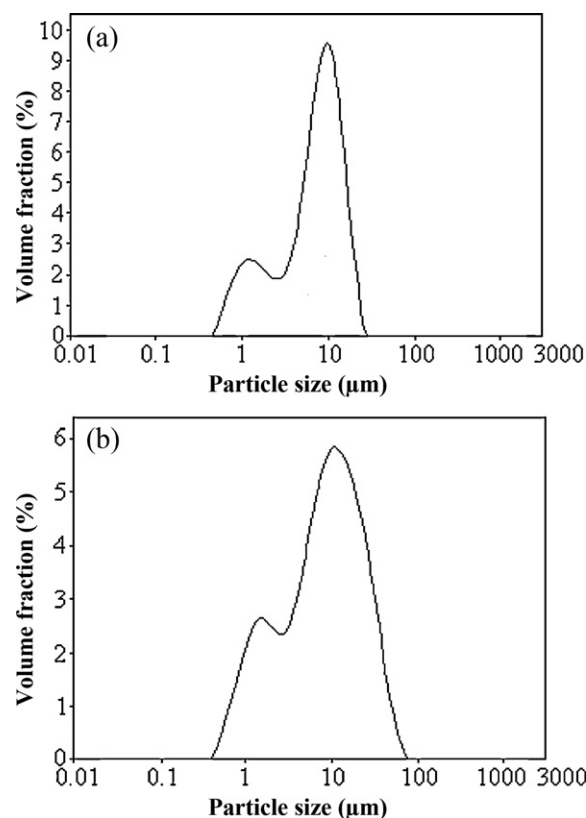


Fig. 1. Water droplets size and size distribution of petroleum emulsion (#1): (a) fresh and (b) 60 days of aging.

The $D[0.5]$ values were determined for all emulsions from the curves, and are shown in Fig. 2 as a function of aging time of the emulsions. Excepting by Emulsion #6, the model emulsions had a constant distribution of droplet size over time.

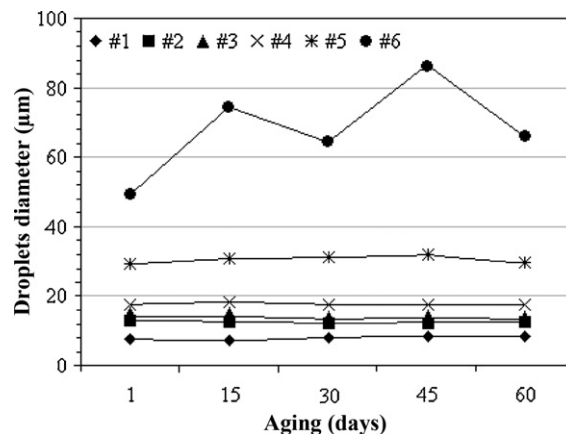


Fig. 2. Water droplet size ($D[0.5]$) as a function of aging of emulsions.

Table 2

Performance of commercial demulsifier on breaking fresh petroleum emulsion (Emulsion #1).

| Aging (days) | Separated water (%) | | | | | | WSI (%) |
|--------------|---------------------|--------|--------|--------|--------|--------|---------|
| | 5 min | 10 min | 15 min | 20 min | 25 min | 30 min | |
| 0 | 40.0 | 85.0 | 90.0 | 90.0 | 90.0 | 90.0 | 72.7 |
| 15 | 0 | 9.0 | 24.2 | 43.3 | 65.0 | 75.0 | 27.1 |
| 30 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 45 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 60 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

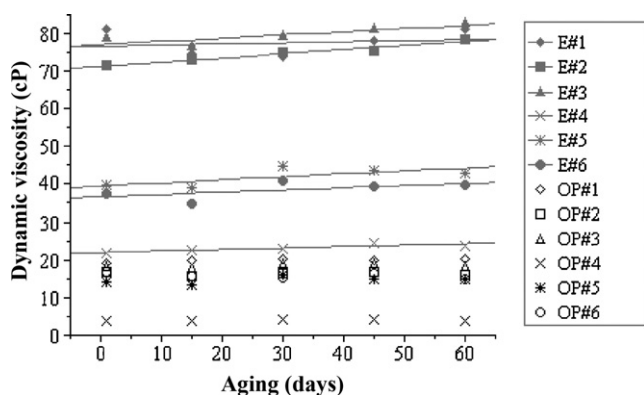
The petroleum emulsion had a droplet size in the range of micrometers ($D[0.5] = 8.0 \mu\text{m}$), which is the typical diameter of water droplets in water-in-petroleum emulsions [38]. Although a shift of the distribution curve was observed, its profile and the median of the distribution were practically constant over the 60 days of analysis, i.e., there was no significant influence of time on this variable for Emulsion #1. The model systems prepared with oily phases of different polarities, but with the same asphaltene content as petroleum (Emulsions #2–4), had $D[0.5]$ close to those obtained with the petroleum emulsion. For such model emulsions the aging did not influence this variable either.

The small differences in $D[0.5]$ found for these three model emulsions show the influence of the composition of the dispersant phase on the droplet size. Among these systems, Emulsion #4 had the highest $D[0.5]$, probably due to the high proportion of toluene, which can affect the emulsion under two aspects: (1) low toluene viscosity, which provides higher coalescence rates and higher diffusion rates of droplets in the external phase during the application of shear, resulting in a greater droplet size; (2) high aromaticity character of toluene, which favors the solubilization of asphaltenes, and this can probably interfere with the structure of the interfacial film and the stability and size of water droplets.

In the model systems prepared with oily phases of the same composition containing different amounts of asphaltenes (Emulsions #2, #5 and #6), the droplet size decreased as the asphaltene content increased. The size of water droplets in Emulsion #6, which had the lowest asphaltene concentration, oscillated over time. This behavior can be attributed to the natural instability of the system due to the low concentration of emulsifier (asphaltenes).

3.3. Effect of aging on the dynamic viscosity

The dynamic viscosity (μ) as a function of aging time is shown in Fig. 3 for the emulsions and their oily phases. The addition of mineral oil to the model emulsions achieved our objective: a viscosity level similar to petroleum in the oily phases of the model emulsions. The viscosities of all oily phases were similar to each other, excepting Oily Phase #4, which had the lowest viscosity due to the high

**Fig. 3.** Dynamic viscosity as a function of time (40 °C). E = emulsion. OP = oil phase.

toluene content (solvent with low viscosity). The slightly lower values of Oily Phases #5 and #6 when compared to #1–3 are probably associated with the lower asphaltene content, which contributes to a slight reduction in flow resistance. As expected, the emulsions' viscosities were higher than those obtained for the respective pure oily phases and, moreover, varied significantly from each other. The effect of dispersant type and asphaltene content on the viscosity of emulsions seems to follow the same trend observed in the results of the oily phases, but with much more pronounced differences. Among the emulsions produced with the same oil phase composition, but with different amounts of asphaltenes (Emulsions #2, #5 and #6), the viscosity increased with increasing content of asphaltenes ($\mu_{E\#2} > \mu_{E\#5} > \mu_{E\#6}$).

Regarding the effect of aging, all systems only varied slightly over time (the largest percentage change during the 60 days was a viscosity increase of around 10% for Emulsion #2). The straight slopes were all positive. The small variations in viscosity observed for these systems suggest that the aging effect on the viscosity depends on the petroleum source, because much more pronounced effects were published in the literature for other petroleum samples under the same conditions of analysis [32].

3.4. Effect of aging on the demulsification process

As mentioned earlier, Emulsions #1–6 were relatively stable, so that there was no natural layer of free water for at least two months after preparation. To further evaluate the stability of the emulsions, a bottle test was carried out to observe the phase separation by adding a demulsifier.

First, the performance of commercial demulsifier in the phase separation of the non-aged petroleum emulsion (Emulsion #1) was evaluated. The action of 100 ppm of the product was evaluated at 40 °C for 30 min, and phase separation was monitored at every 5 min. The phase separation of the petroleum emulsion is shown in the first line of Table 2. There was a progressive increase in the percentage of separated water from 5 min (40%) to 15 min (90%), and the maximum efficiency of the demulsifier for the emulsion under test was 90%.

The assays with the aged emulsions presented a reduction in efficiency of the demulsifier, due to the rise of the stability of Emulsion #1 with time. The WSI values of Emulsion #1 fell significantly from 72.7% of the non-aged emulsion to 0.0% at 30 days of aging. These results confirm that the storage of petroleum before primary processing can cause serious damage to the treatment [22].

The demulsification tests of the model emulsions were carried out under the same conditions. However, no phase separation occurred by adding the demulsifier, not even when the dose was 40 times higher than that used to observe phase separation of the petroleum emulsion (Emulsion #1). The higher stability of model emulsions, compared with petroleum emulsion, is consistent with the results for droplet size and size distribution. The model systems #2–4, despite having the same content of asphaltenes and similar dynamic viscosity and droplet size, did not simulate the exact same behavior found in petroleum emulsion. The differences in the stability and sensitivity to aging are probably due to differences in

chemical characteristics of the continuous phase of emulsions, such as the aromaticity degree and resins content that can interfere with the aggregation of asphaltenes and the properties of the interfacial film.

4. Conclusions

Asphaltenes plays an important role in stabilizing water-in-petroleum emulsions: model emulsions, with an essentially aromatic oily phase, present a decrease in water droplet size and a slight increase in dynamic viscosity with increasing asphaltene content.

The asphaltenes behavior in petroleum is closely related to their interactions with other oil fractions. Synthetic emulsions were much more stable, and therefore less sensitive to aging, than the petroleum emulsion, even for the model emulsion containing the same amount of asphaltenes as petroleum.

The petroleum emulsion's stability is dramatically affected by aging. It is suggested that the most important effect of aging occurs in the changes of the interfacial film of the emulsions since certain characteristics of the emulsion, such as emulsified water content, distribution of droplet size and dynamic viscosity, undergo insignificant variations.

Furthermore, aging can cause serious damage to the process of oil–water separation: demulsifying additives with excellent performance in the newly formed emulsion may become ineffective in the treatment of emulsions with less than thirty days of aging.

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