

## Development and Evaluation of Oil in Water Nanoemulsions Based on Polyether Silicone as Demulsifier and Antifoam Agents for Petroleum

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**ABSTRACT:** Oil in water (o/w) nanoemulsions were synthesized in order to be evaluated as an alternative to petroleum emulsions destabilization processes and inhibition of foam formed in the crude oil. The nanoemulsions were prepared by the high energy method through High Pressure Homogenizer (HPH), utilizing poly(propylene glycol) (PPG) and xylene solvent as oil phase and different polarity polyether silicone surfactants samples. These nanoemulsions were evaluated in respect to their efficiency in the petroleum demulsification process. The results of these tests showed that nanoemulsions performance on the destabilization of petroleum emulsions is influenced by the utilized surfactant's polarity. The nanoemulsions and pure samples of PPG and xylene solvent were evaluated concerning capacity of formed foam inhibition in petroleum (antifoam test), and the results showed no significant influence of samples on foam stability. Petroleum/saline water added interfacial tension measurements, added or not the nanoemulsions were executed and showed that the additives adsorption in the interface is related to the surfactant's polarity and nanoemulsion drop size.

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### INTRODUCTION

In the petroleum industry, water in oil (W/O) emulsions are found in the production, processing, and transportation phases.<sup>1,2</sup> The presence of this kind of emulsion leads to some problems such as: corrosion of pumps, pipes, and other equipment, caused by the presence of inorganic salts in the produced water.<sup>3</sup>

In petroleum fields, gravitational separation vessels are generally used with the objective of separating petroleum, gas, and water phases, removing emulsifiers present in the phases' interface and allowing coalescence of water drops, that is associated to the crude oil pumped. Although there are many factors that influence the efficiency of these separators, the crucial problem is the formation of foam, for it makes difficult the liquid level mechanical control that can lead to tank and equipment flooding, it occupies great space in the separation vessels, reduces separator capacity and efficiency, it can lead to dragging of liquid phase into the gaseous phase and vice-versa and even cause undesirable and unexpected interruptions of process.<sup>4</sup>

Based on this fact, the development of methods that aim separation of produced water that occurs by the process of breaking (destabilization) of water/oil emulsion is of great importance, as well as those that inhibit or promote the formation of foam.

In the destabilization process of water/oil emulsions, such methods can be physical, like filtration, centrifugation, thermal treatment, and application of electrical field, or chemical, by the addition of additives known as demulsifiers.<sup>5–8</sup> These additives are added in solution, containing from 30 to 40% of active matter, utilizing normally solvents like toluene or xylene/ethanol mixtures.

Methods that aim the reduction of amount of formed foam consist basically on the filtration of solid particles (responsible for the stabilization of foam in petroleum) and on the utilization of chemical agents known as defoamers.<sup>9</sup> These are also added in solution, the solvents, and additives concentrations being similar to the ones used in the demulsification process.

The demulsifiers and defoamers generally feature amphiphilic character, in other words, they possess a hydrophilic portion that interacts preferably with water molecules and another one hydrophobic, of greater interaction with the oil phase.<sup>10,11</sup>

In a previous work,<sup>11</sup> the chemical and physico-chemical properties of commercial antifoam products based on silicone polyethers were evaluated, along with their efficiency in inhibiting foaming. In this work, the formulations were prepared in organic solvent (toluene), in 30 wt/vol % concentrations. It has been verified that compounds that featured good results as

**Table I.** Characterization of Polyether Silicone Samples<sup>a</sup>

	$\bar{M}_w$	% Silicone	% EO <sup>b</sup>	% PO <sup>c</sup>
SP1	8000	20	40	40
SP2	20000	35	29	36
SP3	20000	30	28	42
SP4	30000	20	32	48

<sup>a</sup>Data sent by Empresa Momentive.<sup>b</sup>EO, ethylene oxide.<sup>c</sup>PO, propylene oxide.

antifoam agents did not have the same efficiency as demulsifiers. However, it has been observed that the evaluated additives could be employed on the phase separation of emulsions in petroleum, featuring good efficiency, without causing the formation and stabilization of foams.

With the development of nanotechnology, nanoemulsions are increasingly providing new discoveries in various study fields, whereas properties applied to nanoemulsions are potentiated due to their properties of low interfacial tension, great interfacial area, kinetic stability arising from the small size of their dispersed drops, besides the solubilization capacity of organic compounds.

Emulsions with droplet size in the nanometer range (typically in the range 20–200 nm) are often mentioned in the literature as miniemulsions, nanoemulsions, ultrafine emulsions, submicron emulsions, among others.<sup>12</sup> These systems have low stability, although it may persist for months or years due to the presence of a surfactant that inhibits agglomeration of the droplets of the dispersed phase of the liquid, hindering the formation of larger droplets.<sup>13</sup> Because the nanoemulsions do not form spontaneously, it becomes necessary to supply mechanical energy through devices.<sup>14</sup> A method of forming widely used is called high-energy method and the devices used in this technique are the High Pressure Homogenizers (HPH) and Ultrasound (US).<sup>13,14</sup>

Another important factor that enables the use of nanoemulsions is their low cost, whereas they demand no use of other type of interfacial agent (co-surfactants). Moreover, the amount of surfactant utilized to promote reduction of the system's interfacial tension is low and is in the range of 10–20% of mixture's total mass, and additionally, the oil masses utilized in the nanoemulsion formation processes are also low (5–30 wt %), the remaining being constituted of water (around 58–75% of total formulation mass).<sup>12–15</sup>

With the objective of cost reduction, and also, the incompatibility problem between additives, the development of formulations that can act in more than one specific function has been attracting a lot of interest, mainly in the petroleum industry, in which different types of additives are utilized in various applications. Besides this aspect, the utilization of lower additive and organic solvents content in the prepared formulation can also be of environmental interest.

So, in this work, oil in water (o/w) nanoemulsions, with different oil phases and stabilized by surfactants based on polyether

silicone were developed and evaluated regarding their efficiency for the inhibition of foam formation, formed in petroleum and for the destabilization of emulsions in petroleum. The additives used in this work have been evaluated in previous studies<sup>11</sup> in the toluene solutions and showed good efficiency in breaking oil emulsions. However, we point out that it is the first time that these surfactants are being used for the development of nanoemulsions for application in the separation of W/O emulsions.

## EXPERIMENTAL

### Materials

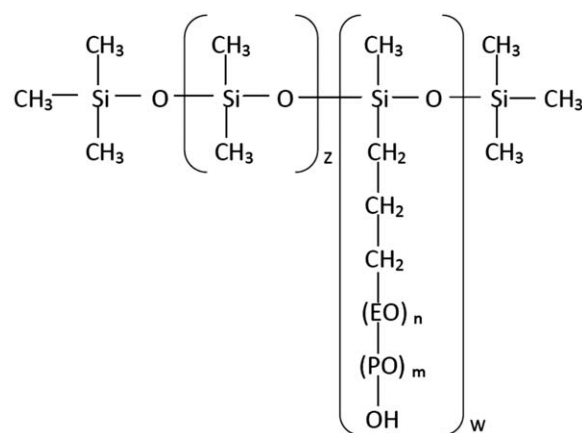
Surfactants based on polyether silicone of different polarities and molar masses were selected to act on the stabilization of the o/w nanoemulsions developed in this work. Previous study<sup>11</sup> showed the high efficiency of these additives in the petroleum emulsions demulsification process, this factor being the preponderant that led to the choice of these compounds. Samples were called SP1, SP2, SP3, SP4, and characterization demonstrated in Table I has been executed by the company providing the additives, Momentive, São Paulo-Brazil.

Yet according to the company, the structure of both compounds is branched, as represented on Figure 1.

Poly(propylene glycol) of molar mass equal to 1000 (provided by the company DOW QUÍMICA S.A., São Paulo-Brazil) and the solvent xylene (provided by the company VETEC, Rio de Janeiro-Brazil) were utilized as oil phase in the o/w nanoemulsions, both being utilized as received.

Petroleum provided and characterized by Centro de Pesquisas da Petrobras (CENPES), Rio de Janeiro-Brazil, was used in the preparation of water/petroleum synthetic emulsions utilized in the W/O gravitational separation tests and for the efficiency evaluation tests of the nanoemulsion as antifoam agents for petroleum. The characterization of the petroleum sample is presented in Table II.

The solvents acetone, alcohol, and toluene were utilized to evaluate the solubility of polyether silicone samples and oil phases. All solvents were provided by the company VETEC, Rio de Janeiro-Brazil and were utilized as received.

**Figure 1.** Polyether silicone branched structure.

**Table II.** Chemical Composition e Density Values of the Oil Samples<sup>a</sup>

Property	Petroleum
Water content (wt %)	0.05
Density ( <sup>o</sup> American Petroleum Institute (API))	21.2
Hydrocarbons saturates (wt %)	40.7
Aromatics (wt %)	34.1
Resins (wt %)	22.9
Asphaltenes (wt %)	2.4

<sup>a</sup>Data provided by CENPES.

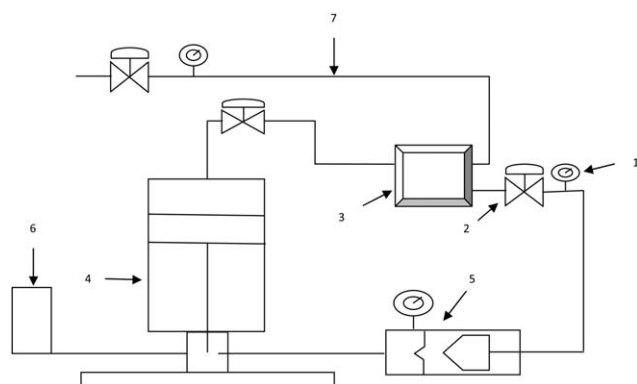
## Methods

**Nanoemulsions Preparation.** Nanoemulsion systems (oil/surfactant/water) were produced in the High Pressure Homogenizer EmulsiFlex C5 Avistin, Ontario, Canada, and the scheme is shown in Figure 2. In this equipment, the (oil/surfactant/water) dispersion is collected (Stage 6) and through a piston located in the pressurizing chamber (Stage 4), the sample is introduced in Stage 5 (cavitation chamber), where it is forced to pass into a very narrow section and, with the fast expansion, brings about the formation of drops in the nanometer scale by the cavitation effect (Stage 5). Due to the lack of homogeneity of the fluid, it is necessary to pass it through the device various times (procedure called processing cycle) until a suitable particle size range is obtained.

This equipment operates in the pressure values comprised between 1000 and 25,000 psi. Based on previous works,<sup>15–17</sup> the selected processing conditions were: 15,000 psi pressure (Stage 1), in four operation cycles. One cycle is defined as the necessary time for a sample to go through the High Pressure Homogenizer interior.

So, the time corresponding to four processing cycles was determined, in seconds, of the passage of a defined volume sample, at a pressure of 15,000 psi.

In order to prepare the dispersions that would be processed at the HPH, initially, the surfactant (polyether silicone) aqueous solutions were prepared, in the concentration of 20 wt %. Afterwards, oil phases selected for the nanoemulsions preparation



**Figure 2.** Scheme of the operation of HPH. (1) Pressure gauge, (2) valve, (3) pressurization control system, (4) pressurization chamber, (5) cavitation chamber, (6) container sample coletagem, (7) compressed air line.

were added to these solutions: PPG or xylene, in the concentration of 5 wt %.

**Determination of Drop Diameter and Nanoemulsion Stability.** The obtained o/w nanoemulsions from the processing conditions described above were characterized with the utilization of a Zetasizer Nano ZS, Malvern (Worcestershire, England) particle size analyzer, in order to obtain the size and size distribution of dispersed drops, its functioning principle being detailed in previous work.<sup>17</sup> This equipment provides the drop size results in tables or percent graphs of scattered light intensity, volume, and number of particles as a function of size (nm), its software operates coupled to a laser reader of 633 nm, positioned in the angle of 173° relative to emitted light beam. The analysis were executed in the temperature of 25°C. Triplicates were executed for all analysis, also being provided standard deviation values.

The obtained nanoemulsions were stored and evaluated through time, in order to verify macroscopic changes visually observed and alteration on average dispersed droplet size by means of the particle size analyzer.

**Petroleum Synthetic Emulsions Preparation.** The water/petroleum emulsions utilized for the demulsification tests were prepared in the lab. Emulsions coming from Petroleum Fields difficult the tests due to their aging process.<sup>15</sup>

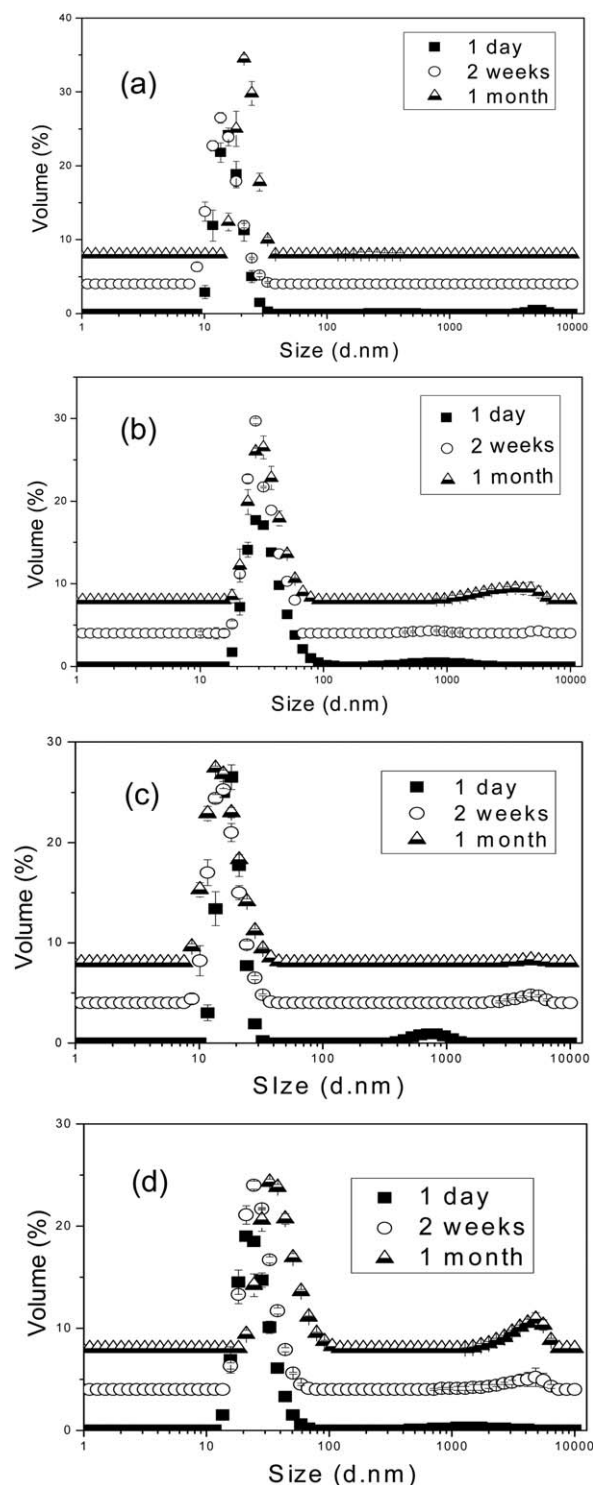
The petroleum synthetic emulsions were prepared containing as the aqueous phase, saline water, constituted of 55,000 ppm of salts (NaCl : CaCl<sub>2</sub> ratio of 10 : 1). The aqueous phase was utilized in a 50% vol/vol content, resulting in the formation of synthetic water petroleum emulsions in a 50/50 proportion. The saline water was initially added to oil with manual agitation, until complete incorporation of water onto the oil phase. The obtained dispersion was then submitted to shearing in the Polyttron PT 3100 D homogenizer in the agitation of 8000 rpm for 3 min, at room temperature.

**Nanoemulsions as Demulsifiers in Petroleum Evaluation Tests.** The evaluation of nanoemulsion performance in the demulsification process was executed by means of water–oil gravitational separation assays (*bottle test*) of petroleum synthetic emulsions prepared according to conditions described in the above section.

In this step, different systems were evaluated:

- o/w stable nanoemulsions;
- surfactant (polyether silicone) aqueous solutions that were utilized in the nanoemulsion preparation. These assays had as an objective evaluate the efficiency of the surfactant as a demulsifier in petroleum when the latter is found in an aqueous solution or present in a nanoemulsion. Due to that, the same surfactant contents were maintained in the aqueous solutions and in the nanoemulsions.

All the assays were executed in a thermostatic bath (70°C) and consist on the vigorous agitation of the petroleum emulsions containing the demulsifying material in the concentration of



**Figure 3.** Drop size distribution of nanoemulsions based on PPG as oil phase and aqueous solutions of surfactants: (a) SP1, (b) SP2, (c) SP3, and (d) SP4.

500 ppm, which are stored inside graduated cylindrical tubes, specific for the execution of water–oil separation assays.

The quantification of separated water was executed in the times of 5, 10, 15, 20, 25, 30, 35, 45, 55, and 65 min. The efficiency of each formulation utilized in these tests was calculated by means of eq. (1)<sup>15</sup>:

$$EF_{AO} = (V_{AS}/V_{AT}) \times 100 \quad (1)$$

where,

$EF_{AO}$  = water–oil gravitational separation efficiency, % in volume;

$V_{AS}$  = separated water volume during the test, mL;

$V_{AT}$  = total water volume present in the interior of the tube, mL.

Duplicates were used for all tests.

**Nanoemulsions as Defoamers for Petroleum Efficiency Evaluation Tests.** The (o/w) nanoemulsions as defoamers for petroleum efficiency evaluation was executed based on the methodology developed in lab and utilized in previous work.<sup>9,11</sup>

In this step, different systems were evaluated:

- stables o/w nanoemulsions;
- oil phase used in nanoemulsions with the objective of oil phase as a defoamer for petroleum efficiency evaluation when the latter is found dispersed in aqueous solution or present in a nanoemulsion.

These tests consist in casting 150 mL of crude petroleum samples, dope with or without the antifoaming material (500 ppm concentration), in a suitably sealed pressurization cell. Then, it was connected to a compressed air line, and with the aid of a manometer, its interior was compressed to a 200 psi pressure for 3 min.

Then, the compression cell was put in a rotary kiln, previously heated to 3°C above the temperature to be employed in these tests (70°C) and kept rotating (conditioning) at a 50 rpm speed, for a period of 2 h.

At the end of these steps, the compression cell was connected to a serpentine where the sample is to be driven through until a decompression cell, in this case, a 100 mL beaker, positioned in the vertical direction with the exit being kept turned face down. Then, the compression cell's blocking valve was lightly opened, and closed when the initial height of the foam formed inside the decompression cell reached the 80 mL value. Immediately, after the closing of the valve, the time count began. The foam level reading was affected in 15 s intervals.

The foam level percent in each time interval was executed according to eq. (2)<sup>9,11</sup>:

$$E_{spuma} (\%vol/vol) = \frac{H - H_F}{H_F} \times 100 \quad (2)$$

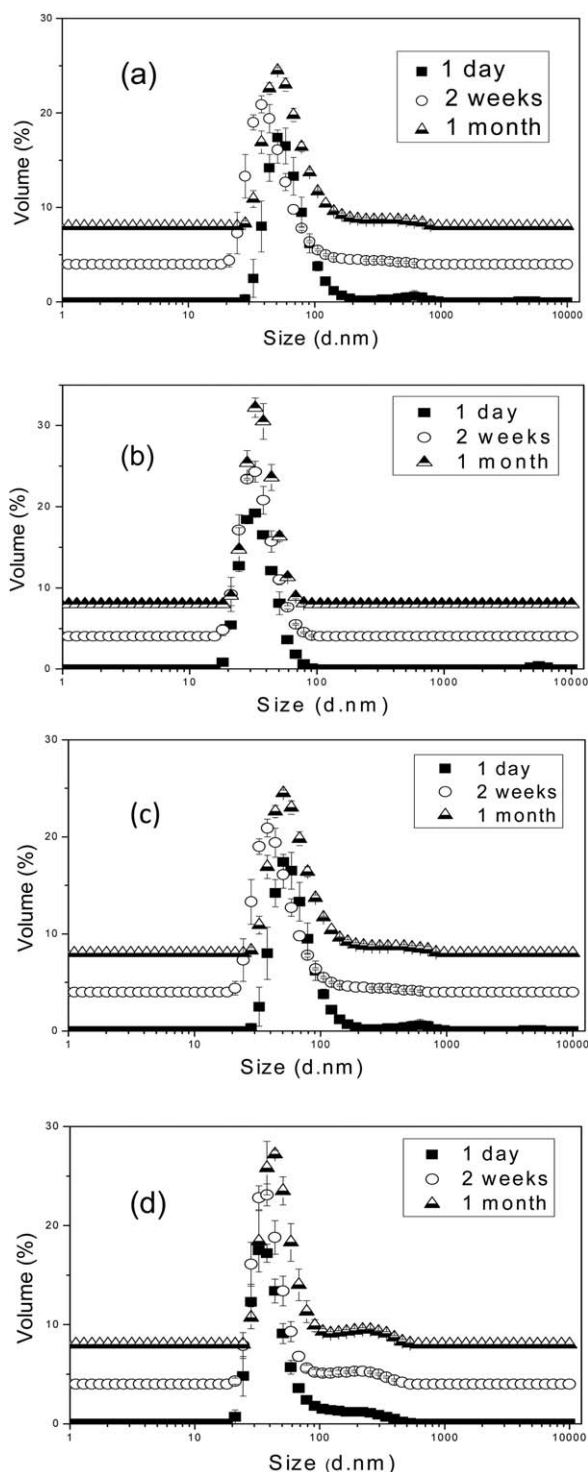
where,

$H$ , initial foam volume

$H_F$ , final foam volume

Duplicates were obtained for all tests

**Determination of Superficial/Interfacial Tensions.** The superficial tension of petroleum measurements as a function of time were executed in a digital Tensiometer Lauda 3D, Baden-Württemberg, Germany, utilizing as an accessory the Du Noüy ring. Interfacial tension measurements of the petroleum/saline



**Figure 4.** Drop size distribution of nanoemulsions based on xylene as oil phase and aqueous solutions of surfactants: (a) SP1, (b) SP2, (c) SP3, and (d) SP4.

water system as a function of time were executed in the same equipment; however, in this case, the Wilhelmy plate method has been utilized.<sup>18</sup> The readings were executed in 5-min intervals, during the period of 1 h.

The superficial tension measurements were executed with the objective of comparing oil phase molecules adsorption to the

petroleum surface when they are found pure or present in the nanoemulsions. Thus, this pure oil content in weight is the same utilized in the nanoemulsions (5 wt %).

The interfacial tension measurements were executed with the objective of comparing the surfactant molecules adsorption in the petroleum/saline water interface when they are found in aqueous solution or present in nanoemulsions. On that basis, the surfactant weight contents were kept the same in the aqueous solution and in the nanoemulsions (20 wt %).

Previous to each executed measurement it was necessary to execute the reading of superficial tension of water, which must be around 72 mN/m, in order to verify the cleanliness of the utilized accessories (Du Nouy ring, plate and cuvette).

All the analyses were executed in triplicate and standard deviations were obtained for each measurement.

## RESULTS AND DISCUSSION

### Development of O/W Nanoemulsions

Initially, the solubility of polyether silicone in water samples was evaluated and all of the samples were soluble in the 20 wt % concentration, which was used for the preparation of nanoemulsions in HPH. In order to evaluate the influence of type of oil phase on the nanoemulsion stability, the solvent xylene or poly(propylene glycol) (PPG) were utilized in the 5 wt % concentration.

Figures 3 and 4 show drop size distribution as a function of preparation time of systems utilizing, respectively, PPG and xylene as oil phases.

By the analysis of graphs in Figure 3, it is possible to observe a unimodal behavior and drop sizes mostly in the range of 10–100 nm, that is comprised in the size range that characterizes the nanoemulsions. It has been observed that there was significant alteration in drops size distribution during the period of analysis, what enables the use of nanoemulsions in other tests described in this work.

Observing Figure 4, it is possible to verify systems with the same unimodal behavior and also with little variation in drop size distribution during the period of 1 month.

The stability of the obtained nanoemulsion systems can be attributed to the insolubility of oil phases in the aqueous phase and the acting of non-ionic surfactants used in this work, which would be promoting the drops' steric repulsion effect, preventing the flocculation process for the formation of bigger drops.<sup>12,15</sup> The main destabilization mechanism of nanoemulsions is known as Ostwald's maturation, which arises from drop size polydispersion of nanoemulsion and from the solubility and/or chemical potentials differences between big and small particles.<sup>15</sup>

### Nanoemulsions Efficiency Evaluation as Demulsifier Agents for Petroleum

The oil/water emulsions formed during the production of petroleum can be very stable due to the presence of compounds with polar characteristics as asphaltenes and resins, that act as

natural emulsifiers and form resistant films at the petroleum/water interface.<sup>19</sup>

Among the properties that are sought in demulsifiers, high adsorption velocities in the water–oil interface, displacement of natural emulsifiers that stabilize the emulsions, and the formation of thin and fragile pellicles in the water–oil interface stand out.<sup>20,21</sup>

Nanoemulsions prepared containing 5 wt % of oil phase and 20 wt % of surfactant and aqueous solutions containing 20 wt % of surfactant were evaluated regarding the efficiency in the demulsifying process of petroleum. Results are shown in Figure 5.

Observing the obtained results, it is possible to verify that all analyzed systems featured good efficiency in the water/petroleum separation (70–90%). This demonstrates that additive molecules, besides migrating to the water/petroleum interface, are acting in the destabilization of the film formed in this interface, favoring the agglutination of water molecules and its posterior sedimentation.

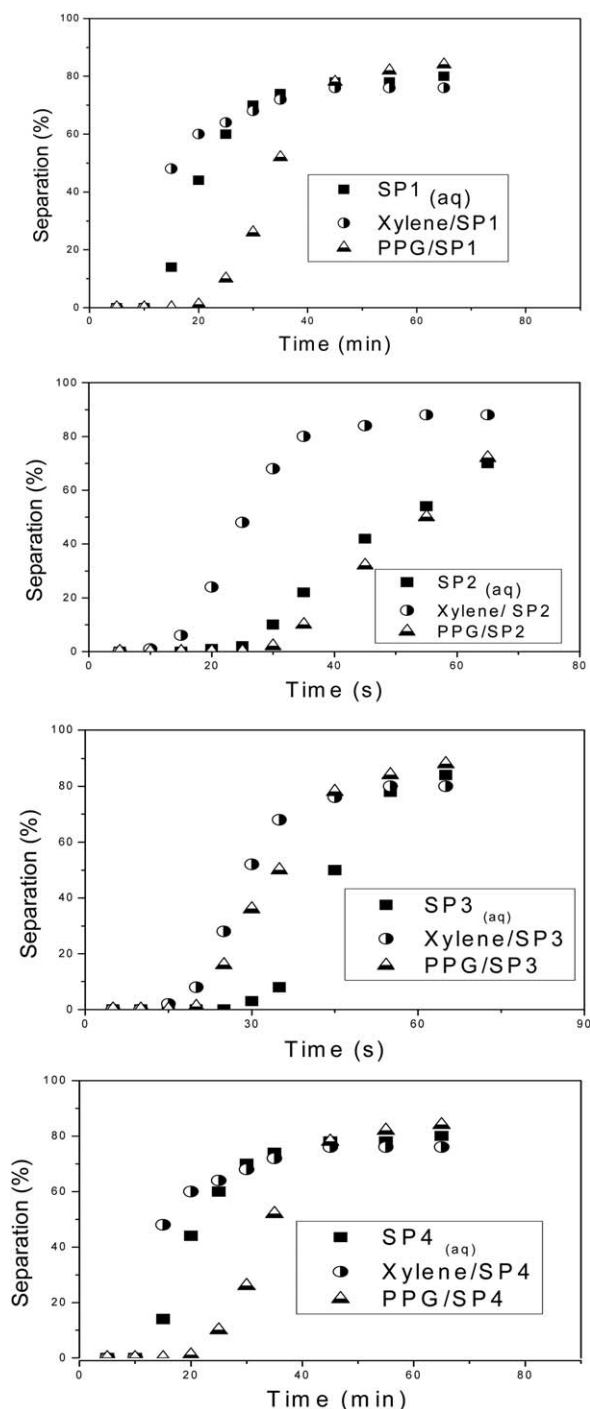
By the analysis of polyether silicone surfactants aqueous solutions, it has been observed the following petroleum emulsion destabilization efficiency order: SP4>SP1>SP3>SP2. These results indicate that the polyether silicone surfactants of greater polarity, attributed to a greater ethylene oxide groups / propylene oxide groups (EO/PO) ratio and to the lower silicone content in their chain (see Table I), have a greater efficiency in the water/petroleum separation. In previous work,<sup>22</sup> it has been verified that more polar surfactants normally feature greater efficiency in the W/O emulsions break down, once the increase in its polarity leads to a greater affinity between surfactant and the disperse aqueous phase, causing this surfactant to faster migration to the interface, leading to a rupture of interfacial film, and, consequently, to the water/oil emulsion destabilization.

In the presence of nanoemulsions oil phases, this migration could be even faster, given that the surfactant micelles are now rich in solvents, which could be assisting this process. This behavior is mainly observed for nanoemulsions prepared with the surfactants SP2 and SP3 and xylene as oil phase, given that the increase in petroleum emulsion break down velocity in the presence of this oil phase.

However, from the results obtained in this work, conclusion can be made that the assistance of oil phases (xylene or PPG) in the surfactant molecules migration to the water/oil interface is influenced by the affinity/solubility in the petroleum medium. In all cases, systems that contain xylene as oil phase possess greater effectiveness in the petroleum emulsions break down velocity. This behavior is attributed to the fact that xylene assists in the diffusion of surfactant micelles through the saline water/petroleum interface due to its good interaction with petroleum. Nanoemulsions that contain PPG as oil phase feature, in general, a lower petroleum emulsion break down velocity.

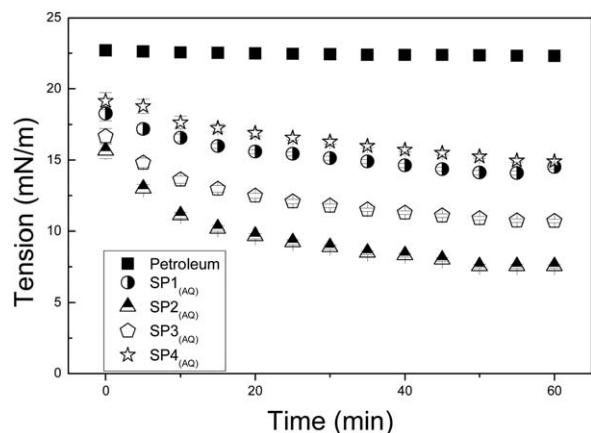
#### Water/Oil Interfacial Tension Measurements

Interfacial tension measurements have been executed to evaluate the adsorption degree of surfactants in the petroleum/saline water interface, and the results have been used as parameters



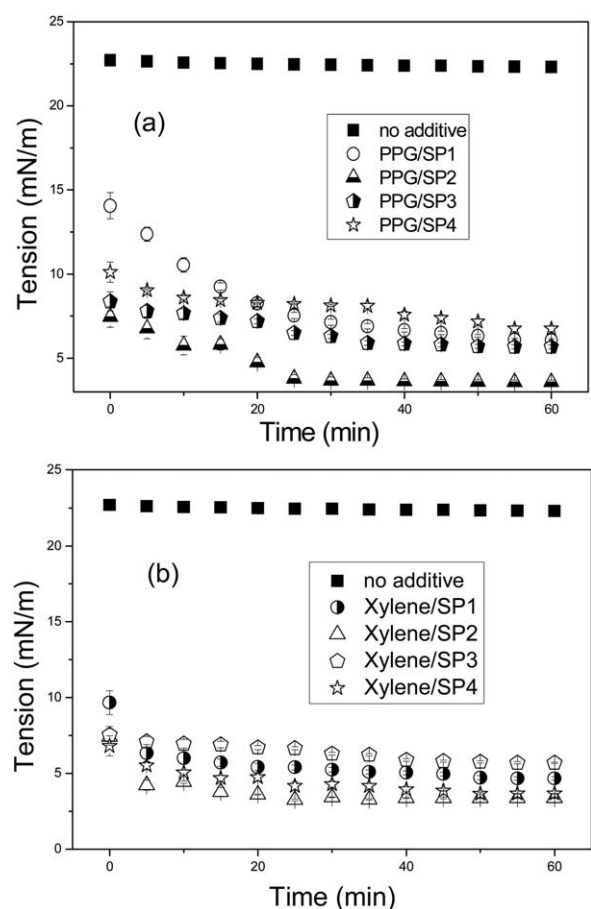
**Figure 5.** Efficiency evaluation in the petroleum emulsions destabilization process for aqueous solutions of polyether silicone surfactants and o/w nanoemulsions (represented as oil/surfactant phase) in a 500 ppm concentration.

for the evaluation of these surfactants as demulsifier agents for petroleum. Figures 6 and 7 show, respectively, interfacial tension measurements, as a function of time, from additive petroleum/saline water systems, or not, with aqueous solutions (20 wt % of polyether silicone samples) and with the nanoemulsions (represented in the form oil phase/surfactant). In both cases, the additive concentration utilized was 500 ppm and the addition was always executed in the oil phase.

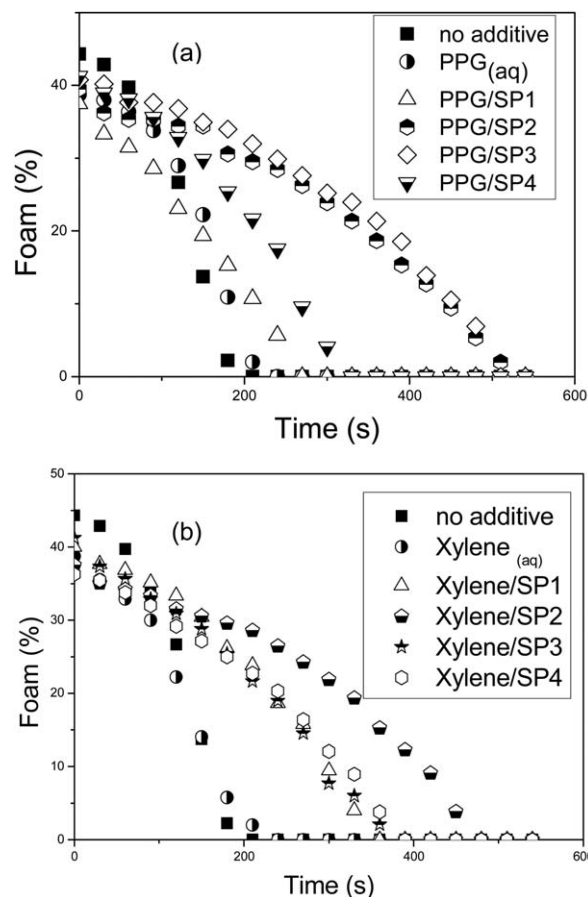


**Figure 6.** Petroleum/saline water interfacial tension measurements with the addition or without polyether silicone surfactants aqueous solutions.

The results presented in these graphs allow the obtainment of a comparison parameter of the surfactants adsorption in the oil/saline water interface when they are present in nanoemulsion systems. It is possible to verify that, for all utilized systems, there occurs a reduction in petroleum/saline water interfacial tension values when compared to this interface without additive



**Figure 7.** Petroleum/saline water system interfacial tension measurements added with or without nanoemulsions containing (a) PPG and (b) xylene solvent as oil phase.

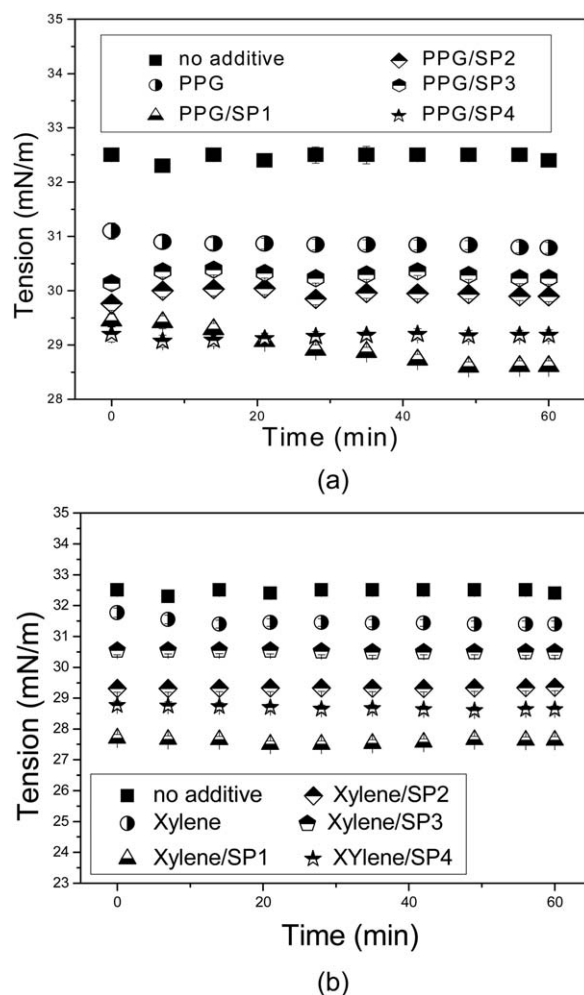


**Figure 8.** Evaluation of defoamer efficiency for petroleum oil phases aqueous solutions and nanoemulsions containing (a) PPG and (b) xylene solvent.

(~22 mN/m). Another behavior that can be observed is that the nanoemulsions featured a greater interfacial tension reduction capacity when compared to surfactants aqueous solutions, which was mainly observed for systems prepared with the xylene solvent.

This observation can be attributed to the fact that the small size of nanoemulsion drops facilitates the diffusion of the system in the medium, and also, the adsorption of surfactant molecules in the petroleum/saline water interface. Therewith, it can be confirmed that nanoemulsified systems will promote the faster break down of petroleum emulsions, given that the faster the interfacial tension minimum values are reached, the greater the diffusion velocity of surfactant molecules to the interface, leading to the formation of thin films, with low elasticity and posterior rupture of this film.

Related to the surfactant aqueous solutions (Figure 6) it is possible to verify that surfactants of lower polarity, in other words, those of lower EO/PO ratio and greater silicone contents in the chain—SP2 and SP3—(Table I), feature greater interfacial tension reduction capacity, despite these surfactants do not feature the best efficiencies in the petroleum demulsifying process (Figure 5). This behavior indicates that the interfacial tension reduction is not the most important parameter for the water/



**Figure 9.** Superficial tension measurements of petroleum, additive or not, with pure oils and with nanoemulsions containing (a) PPG and (b) xylene solvent as oil phase.

petroleum separation. Other factors are also relevant as surfactant molecules diffusion velocity to the interface and the displacement of petroleum natural emulsifiers from the water/petroleum interface.

#### Evaluation of (O/W) Nanoemulsions as Antifoam Agents for Petroleum

The defoamers are being utilized for many years to suppress crude oil foam in gravitational separators, in order to avoid the liquid being dragged with the gas, thereby decreasing phase separation efficiency. For the crude oil to be processed effectively, it is necessary the addition of a chemical agent that can inhibit the formed foam.

Figure 8 shows the results obtained in the executed tests with and without additive petroleum with oils utilized in the nanoemulsions (5 wt %) and with the nanoemulsions (represented in the form oil phase / surfactant). In all analysis, the utilized concentration was 500 ppm.

By the analysis of results shown in Figure 8 it is possible to verify that all systems promoted little reduction on the formation

of foam in the petroleum samples, observed in the initial content formed foam. This behavior is expected to assist in the best efficiency of the systems when added in gravitational separating vessels. On the other hand, the formed foam took around 1–5 min more for its complete destabilization. In spite of that, they can still be considered for application in these equipments, given, mainly, the lowest content of initially formed foam and the stabilization time of this foam being still low.

#### Superficial Tension Measurements of Petroleum

Figure 9 shows superficial tension measurements results, as a function of time, of additive petroleum with 5% m/m of additives utilized as oil phase in the nanoemulsions (PPG and xylene solvent) and with the nanoemulsions (represented in the form oil phase/surfactant). In both cases, the utilized concentration was 500 ppm.

By the graph analysis, it is possible to observe, in a general manner, that all additives had the capacity to reduce petroleum superficial tension related to the obtained value with non additive petroleum ( $\sim 32$  mN/m). It is possible to verify too, that the nanoemulsions brought about greater petroleum superficial tension reduction as compared to the oils, which demonstrate that the small nanoemulsion drop size assist in the adsorption of oil phase molecules in the nanoemulsions in the petroleum/air interface.

The results also show that, regardless of the utilized oil phase, the nanoemulsion particles adsorption to the petroleum/air interface was influenced by the surfactant that stabilize them. Also in both cases, it is possible to verify that the nanoemulsions stabilized by surfactants of greater polarity (SP1 and SP4) adsorb more easily to the interface when compared to those stabilized by surfactants of lower polarity (SP2 and SP3).

#### CONCLUSIONS

The o/w nanoemulsions developed in this work featured good efficiency in the destabilization of petroleum emulsions, confirming the employment of these as a viable alternative for demulsification of petroleum. It was possible to verify that, besides the small drop size, another factor that influences the efficiency of nanoemulsions is the type of surfactant chosen, whereas the nanoemulsions stabilized by surfactants of greater polarity were the ones that featured the greatest efficiencies in the water/petroleum separation process.

The nanoemulsions featured non-effectiveness in the destabilization of foam formed in petroleum regardless of the oil phase and surfactant utilized; however, they did not contribute for a significant increase in stability. This fact, together with results obtained in the water/oil separation tests and the advantages of the use of nanoemulsions presented in this work enable the employment of them in the gravitational separation vessels.

#### ACKNOWLEDGMENTS

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