Evaluation of nanoemulsions based on silicone polyethers for demulsification of asphaltene model emulsions

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ABSTRACT: Asphaltenes are considered the main agents responsible for stabilizing petroleum emulsions. However, due to the complex chemical nature of crude oil, it is necessary to extract these molecules and prepare model solutions to investigate the effects of the various asphaltenes separately. In this study, the demulsification efficiency of oil-in-water (O/W) nanoemulsions based on silicone polyethers was evaluated using asphaltene model emulsions. The interfacial properties of the model emulsions were evaluated, with and without the presence of the nanoemulsions, by interfacial tension and inerfacial rheology measurements and correlating them with the ability and/or speed of diffusion to the interface. Dispersion/flocculation tests of the asphaltenes were performed to assess whether the nanoemulsions were modifying the aggregation state of the asphaltenes during the process of destabilizing the model emulsions. Through the interfacial rheology tests of the model asphaltene/saltwater system, with or without addition of the systems used in the demulsification tests, it was possible to determine the influence of the nanoemulsions on the mechanical properties of the interfacial film. The results of the water/oil gravitational separation tests showed that the nanoemulsions had separation efficiency between 80 and 95%, depending on the composition of the water/surfactant/oil/asphaltene system. The nanoemulsions containing xylene as the oil phase destabilized the emulsions the fastest. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44174.

INTRODUCTION

The formation of emulsions in crude oil is attributed to the presence of water droplets (dispersed phase) in the oil (continuous phase), associated with the constant sheer forces imposed during the production process.[1] These emulsions are stabilized by the presence of native compounds of the oil, such as solid particles, resins, and asphaltenes.[2]

Various factors affect the stability of emulsions. The most important are pH, water droplet size, oil viscosity, oil/saltwater ratio, interfacial tension, and phase density differences.[3,4]

Asphaltenes are considered the main agents responsible for stabilizing emulsions in petroleum.[5,6] The word asphaltenes designates the petroleum macromolecules, with high molar mass and polarity. They are described as amorphous solids, with color ranging from dark brown to black. They are precipitated by the addition of an excess of n-heptane and are soluble in toluene and benzene. Their structure is composed of polynuclear aromatic rings, with the presence of heteroatoms (N,O,S) and metals (Ni, V, Fe) in their chemical composition.[7–9]

Resins, although their structure is similar to that of asphaltenes, are less polar fractions with lower molar masses. They are defined as molecules soluble in light alkanes (pentane, hexane, or heptane), but insoluble in liquid propane. They are mainly composed of naphthenes, aromatic ring systems and acyclic chains.[10] They act to disperse asphaltenes in petroleum.[11]

The asphaltene molecules interact chemically by means of superposition of the π-π bonds between the aromatic rings and by hydrogen bonds between functional groups, among other interactions.[5] This causes the formation of aggregates that migrate to the water-oil interface where they form a strong and highly elastic film, which acts as a barrier impeding coalescence of the water droplets.

The process of destabilizing emulsions is not fully clarified in the literature. The initial hypothesis was that the molecules of the demulsifier can partly or totally substitute the asphaltene molecules, adsorbing them reversibly at the water-oil interface.[12] Ramalho et al.[13] proposed a mechanism in which the performance of demulsifiers is related to the voids left by the

Table I. Characteristics of O/W Nanoemulsions

Nanoemulsion	Characteristics of surfactant[a]					Oil phase[b,c]	Droplet size range (nm)
	Surfactant	$\bar{M}_w$	% Silicone	% EO	% PO		
NSP1-xylene	SP1	8000	20	40	40	Xylene	20–100
NSP1-PPG						PPG	10–30
NSP2-xylene	SP2	20,000	35	29	36	Xylene	20–80
NSP2-PPG						PPG	20–100
NSP3-xylene	SP3	20,000	30	28	42	Xylene	20–100
NSP3-PPG						PPG	10–30
NSP4-xylene	SP4	30,000	20	32	48	Xylene	20–140
NSP4-PPG						PPG	20–60

[a] Surfactant content = 20 wt %.
[b] Oil phase content = 5 wt %.
[c] PPG, poly(propylene glycol).

asphaltene aggregates at the interface. In other words, the smaller these aggregates are, the larger the free spaces will be, facilitating adsorption of the demulsifier molecules.

The demulsifiers normally used are composed of polymers, such as poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers, ethoxylated phenols, alcohols, ethoxylated resins, ethoxylated nonylphenols and sulfonic acid salts.[14,15]

Searching for new systems, recently our group has carried out studies,[16,17] involving development of stable oil-in-water (O/W) nanoemulsions that are efficient in phase separation of O/W emulsions. These systems contained nonionic surfactants based on polyoxides, at concentrations from 10 to 20 wt % of the total mixture, along with low oil masses used in the process of forming nanoemulsions (5 to 15 wt %), with the remainder composed of water (65–85 wt %).

Nanoemulsions are oil-in-water dispersions, stabilized by a surfactant, in which the dispersed droplets have diameters ranging from 1 to 100 nanometers.[18] To form these systems, it is necessary to apply energy.[19] One of the most common ways to obtain nanoemulsions is called the high-energy method, in which the necessary energy is provided by mechanical devices, such as ultrasound or high-pressure homogenizers (HPH).[20–22]

Fraga and collaborators[17] prepared O/W nanoemulsions based on silicone polyethers using a high-pressure homogenizer that remained stable for at least one month (the period of the experiment), with size distribution in the range of 10–100 nm. They verified that these systems were effective in destabilizing petroleum emulsions, with gravitational water separation efficiency of 70–90%, depending on the composition of the particular nanoemulsion. The polarity of the surfactant and type of oil phase present in the nanoemulsions evaluated as demulsifiers had a significant effect on demulsification speed, and at the same time influenced the adsorption speed of the surfactant molecules at the water-oil interface.

Because it is hard to analyze the isolated effect of asphaltenes on the stability of oil emulsions, due to the complex chemical nature of petroleum, an alternative for this purpose is to form water-oil emulsions in model systems, in which the oil phase consists of a dispersion of asphaltenes in aromatic solvents, sometimes with small quantities of a flocculant (aliphatic solvent).

The objective of this study was to evaluate the performance of O/W nanoemulsions prepared in a previous experiment[17] as demulsifiers in asphaltene model systems and to relate the results with the interference of these nanoemulsions in the aggregation state of the asphaltenes, to note whether or not they facilitate adsorption of the molecules present in the nanoemulsion systems at the water-asphaltene solution interface.

In this work, we evaluated the stability of the emulsion by means of the rheological properties of interfacial film. This describes the functional relationship between the deformation of an interface, the stresses exerted on it and upon it, and the flows resulting from adjacent faces of the fluid, which can be carried out by dilatation and shear methods.[23]

In the present study, it was proposed to use the interfacial rheology tests in rotational rheometer with Du Noüy ring, which applies oscillatory shear forces at the interface. It is able to measure the properties of the interface with high precision, without its inertia prevailing and interfering in the results.

EXPERIMENTAL

We evaluated as demulsifiers O/W nanoemulsions stabilized with surfactants based on silicone polyether with different polarities and molar masses, developed in a previous study.[17] Two nonionic silicone polyether surfactants with different quantities of ethylene oxide (EO) and propylene oxide (PO) units in their chains were used, donated by the Brazilian subsidiary of Momentive (São Paulo, SP - Brazil). According to the company, the structure of both compounds is branched. The characteristics of the nanoemulsions produced are presented in Table I.

The nanoemulsion systems (oil/surfactant/water) were produced in an Avistin EmulsiFlex C5 high-pressure homogenizer (Ontario, Canada), according to the processing conditions reported in Ref. 17. These nanoemulsion systems remained stable, that is, without significant changes in the average droplet size and size

distribution, for at least one month, the period chosen for their use in the tests.

The asphaltene samples used were extracted from petroleum P1, supplied and characterized by the Petrobras Research Center (CENPES, Rio de Janeiro, Brazil). This crude oil has the following properties: water content = 0.05 wt %; density (^{0}API) = 21.2; saturated hydrocarbons = 40.7 wt %; aromatics = 34.1 wt %; resins = 22.9 wt %; and asphaltenes = 2.4 wt %.

The solvents n-heptane and toluene were used to prepare the asphaltene model solutions. All solvents were supplied by Vetec (Rio de Janeiro, RJ - Brazil) and were used as received.

Extraction of Asphaltenes from the Crude Oil Sample

About 30 mL of the petroleum P1 sample was placed under the action of the precipitating agent of the paraffinic solvent (n-heptane) in the proportion of 1 L to 30 mL for one week under agitation. Then the mixture was filtered twice through filter paper at room temperature (25 °C). The precipitate was passed through a Soxhlet extractor to separate and dissolve the impurities (mainly resins) adsorbed on the asphaltene molecules. The asphaltenes that remained precipitated in the cartridge were extracted with the use of an aromatic solvent (500 mL of dry toluene).

Finally, the solubilized asphaltenes were recovered by evaporating the toluene in a rotary evaporator, and then were left at rest at room temperature for evaporation to the residual solvent.

Preparation of the Asphaltene Model Emulsions

To evaluate the influence of the nanoemulsions in systems containing only asphaltenes dispersed in solvent mixtures as the oil phase, model emulsions were prepared with the asphaltenes. The oil phase was composed of 0.5 m/v of asphaltenes in a mixture of the solvents heptane/toluene (heptol) in the proportion of 25:75.

The aqueous phase of these emulsions consisted of saltwater containing 55,000 ppm of salts (NaCl:CaCl$_2$ ratio of 10:1). The aqueous phase concentration used was 50% v/v, resulting in model oil phase/aqueous phase emulsions in the proportion of 50:50.

These emulsions were prepared by first adding saltwater in the oil phase with manual stirring until complete incorporation. The dispersion obtained was submitted to shear in an Ultra-Turrax homogenizer at rotation of 11,000 rpm for 3 min, with permanent circulation of the entire emulsion around the device's shaft.

Determination of the Interfacial Tension of the Saltwater/Asphaltene Solutions

The interfacial tension values of the systems as a function of time were measured with a Lauda TD 3 digital tensiometer (Baden-Württemberg, Germany), using the Wilhelmy plate method. The readings were taken at five-minute intervals during one hour.

The interfacial tension values were measured to compare the adsorption of the surfactant molecules at the interface of the asphaltene/saltwater solutions and to determine whether these were present in the aqueous solutions or nanoemulsions.

Because of this, the same proportion by mass of surfactant in the aqueous solution and nanoemulsions was maintained (20 wt %). The concentration used was 500 ppm of the same additives employed in the demulsification tests, always added in the oil phase.

Before each measurement, it was necessary to read the surface tension of the water, which must be near 72 mN/m, to verify the cleanliness of the accessories used (Wilhelmy plate and cuvette).

All the analyses were conducted in triplicate and the means and standard deviations of each measure were calculated.

Evaluation of the Efficiency of the O/W Nanoemulsions in Demulsifying the Asphaltene Emulsions

The demulsification tests of the water-oil emulsions were carried out in a water bath at room temperature. The amount of water separated was quantified at intervals of 5, 10, 15, 20, 25, 30, 35, 45, 55, and 65 min. Before the observation at each time, the emulsion was gently swirled for one minute.

The efficiency of each formulation in these tests was calculated by eq. (1):

$$EF_{WO} = (V_{WS}/V_{WT}) \times 100 \tag{1}$$

where,

EF_{WO} is the water-oil gravitational separation efficiency, in % v/v;

V_{WS} is the volume of water separated during the test, in mL;

V_{WT} is the total volume of water inside the tube, in mL.

These demulsification tests were conducted by first evaluating the stability of the emulsions without addition of the demulsifier (blank). Then the emulsions were evaluated after adding the following substances (always at concentration of 500 ppm):

- stable water/surfactant/oil nanoemulsions;

- aqueous solutions of the surfactants that were utilized to prepare the nanoemulsions. The aim of these tests was to compare the action of these additives when in solution and/or present in the nanoemulsions.

All the tests were run in triplicate and the means and standard deviations were calculated to obtain the experimental error.

Evaluation of the Precipitation of Asphaltenes with or without the Presence of the O/W Nanoemulsions

The flocculation or dispersion of the asphaltenes was evaluated by the asphaltene precipitation test,[24] using a Varian Cary 50 ultraviolet spectrometer (Palo Alto, CA), equipped with an external probe containing two tips, with the optical path of each one being 2 or 5 mm.

Before performing the tests, a standard curve of adsorption intensity versus asphaltene concentration was plotted. For this purpose, a 100 mL round-bottom beaker was used to prepare a stock solution of 1000 mg of asphaltenes extracted in toluene from the petroleum P1 sample, from which solutions with different concentrations were prepared (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09%). The absorbance data to construct the

standard curve were measured at 850 nm in the ultraviolet spectrometer.

Asphaltene Precipitation Test. A 10 mL round-bottom beaker was used to prepare a 5 wt/v % solution of asphaltenes in toluene, to which a sample of each of the systems used in the water-oil demulsification tests was added (concentration of 500 ppm). The solution was left at rest for 24 h to allow complete solubilization of the sample.

Eight 1 mL aliquots were removed from this solution and placed in eight test tubes. Then, 9 mL of a mixture of solvents containing toluene and n-heptane, in varied proportions, was added to each tube, so as to obtain final mixtures of 0, 15, 30, 40, 50, 60, 70, 80, and 90% of n-heptane in relation to the total volume. A blank test (no addition of nanoemulsion system) was also performed. These samples were left at rest for 24 h and then centrifuged at 30,000 rpm for 30 min. The absorbance value of the supernatant from each tube was read in the spectrometer at 850 nm and converted into percentage from the standard curve.

Evaluation of the Rheological Properties of the Interfacial Films of the Asphaltene/Saltwater System

The interfacial rheology tests were performed with a Haake MARS III rotational rheometer. This apparatus works by imposing torque on the measurement instrument (Du Noüy ring), which applies oscillatory shear forces at the interface. The data collected are used to calculate the properties of the fluids, which are inserted with a specific geometry.

The purpose of these tests was to ascertain the influence of the nanoemulsions and the aqueous surfactant solutions used to form them on the storage (or elastic) modulus and loss (or viscous) modulus (G' and G'' respectively) of the interfacial film formed in the saltwater/asphaltene solutions. The additives were always introduced in the oil phase, at the same concentrations used in the water/oil gravitational separation tests (bottle tests).

The Du Noüy ring is highly sensitive and has delicate geometry. Due to its sensitivity, the ring must be cleaned after every experiment with a suitable solvent (here toluene), and at the start of every round of experiments it must be flame cleaned. We used a glass cuvette as the recipient of the system because it has geometry that enables identifying the interface points, and its dimensions assure that the effects of the wall are negligible during the tests. To assure the thermal homogeneity of the system and avoid evaporation of the solvents, we developed an acrylic coating with water passage at the same temperature at which the tests were conducted (25°C) and with geometry adaptable to the glass cuvette and the rheometer's base (Peltier plate).

RESULTS AND DISCUSSION

Analysis of the Interfacial Tension of the Asphaltene/Saltwater System

The interfacial tension tests were performed first to determine the tension between saltwater and 25/75 heptol mixture and between the saltwater and asphaltene dispersion in heptol (0.5% m/v of asphaltenes dissolved in heptol 25/75), to evaluate the
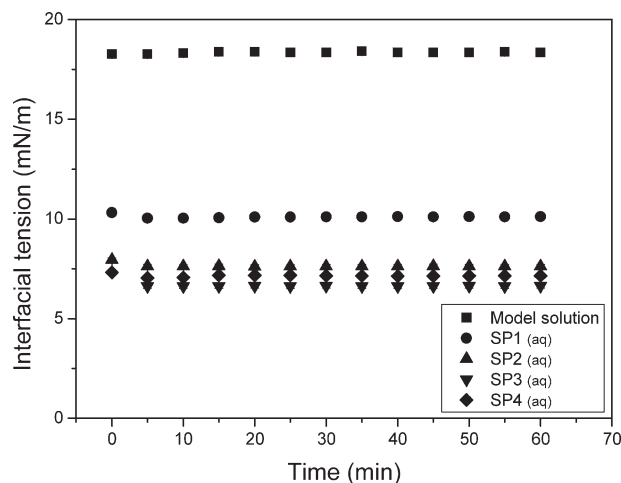

Figure 1. Model solution/saline water interfacial tensions in the presence or not of aqueous surfactants solutions (SP$_{aq}$).

adsorption kinetics of the asphaltenes at the respective interfaces. Then the systems used in testing the saltwater/petroleum interfacial tension, at the same concentrations, were added to the water/asphaltene dispersion systems.

The initial analyses showed that the interfacial tension values were reduced from 25.0 mN/m in the heptol 25/75 mixture to approximately 18 mN/m after adding the asphaltenes to the system, demonstrating their interfacial activity.

Figures 1 and 2 show, respectively, the interfacial tension results of the water/asphaltene dispersion systems with or without addition of the aqueous solutions of silicon polyether surfactants and with the nanoemulsions (oil phase/surfactant), at a concentration of 500 ppm.

The results presented indicate that sample SP1, in the presence of the oil phases, was able to reduce the interfacial tension slightly more than the aqueous solution of the surfactant SP1 (SP1$_{aq}$). These results were expected and show that the oil phases help the adsorption of the molecules of this surfactant at the interface, as discussed in a previous article.[17]

On the other hand, the interfacial activity of sample SP3 was similar in both the aqueous solution (SP3$_{aq}$) and in the presence of the oil phases utilized (xylene or PPG), while sample SP4 caused a slight reduction in the interfacial tension values in the presence of xylene [Figure 2(b)] and a slight increase in the presence of PPG [Figure 2(a)], compared to the results for the aqueous solution of these surfactants (SP4$_{aq}$). For sample SP2, the interfacial tension values increased in the presence of both oil phases in comparison with the corresponding aqueous solution (SP2$_{aq}$).

This unexpected decline in the interfacial activity of some surfactants in the presence of a determined oil phase can be attributed to the interference caused by these oil phases in the formation of asphaltene aggregates. What might be happening in these cases is that the presence of the oil phase favors the formation of larger asphaltene aggregates, hindering the adsorption of the surfactant molecules at the water/asphaltene solution interface. That behavior will be discussed better when
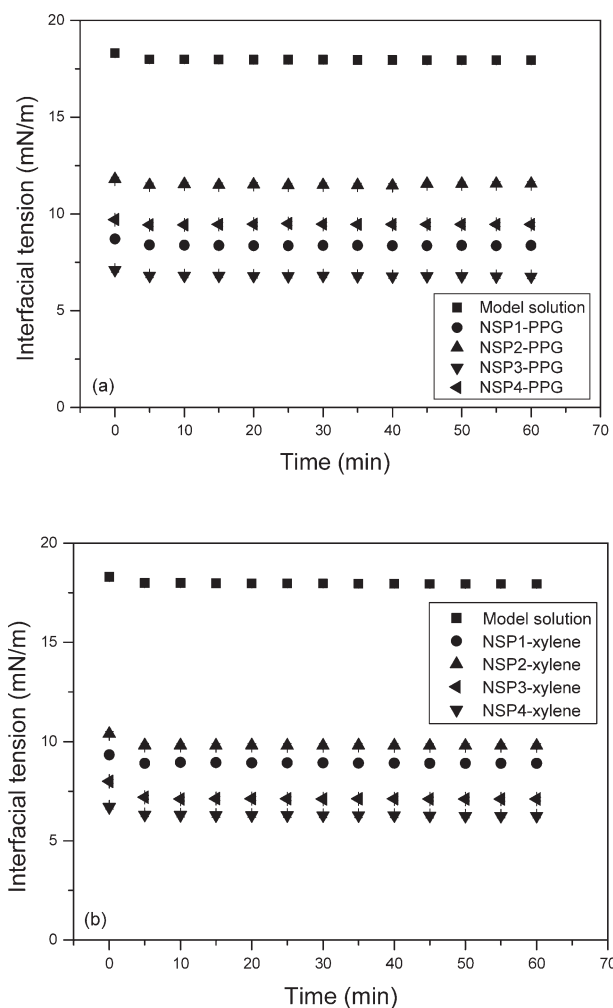
Figure 2. Model solution/saline water interfacial tensions in the presence or not of nanoemulsions at concentration of 500 ppm.

presenting in the results of the analyses of asphaltene precipitation in the presence of the nanoemulsions.

Application of O/W Nanoemulsions for Demulsification of the Asphaltene Emulsions

As stated previously, it is difficult to analyze the effect of asphaltenes on the stability of crude oil emulsions, so an alternative is to form water/oil emulsions in model systems in which the oil phase consists of a dispersion of asphaltenes in aromatic solvents, also possibly containing small amounts of a flocculant (aliphatic solvent).

Based on this idea and with the objective of better understanding the mechanism by which O/W nanoemulsions act to destabilize water/oil emulsions, we performed demulsification tests using asphaltene model emulsions (Figure 3).

We first evaluated the stability of the emulsions without adding the demulsifier (blank). The asphaltene emulsion remained stable, that is, without water/asphaltene solution separation during the entire experimental period (65 min), assuring that any water/oil separation would be due only to the action of the additive used.

The results show that all the systems analyzed presented high speed and good efficiency in separation (80–95%).

For sample SP1, the interfacial activity was slightly stronger in the presence of PPG as the oil phase compared to the respective aqueous solution, a factor explaining the greater separation velocity of this nanoemulsion in relation to the surfactant's aqueous solution. On the other hand, the activities for sample SP3 were similar (Figures 1 and 2) with or without the presence of the oil phase containing xylene or PPG, which was confirmed by the water/solution gravitational separation results, which were similar for all the systems evaluated.

In contrast, for sample SP2, the presence of PPG inhibited the interfacial activity of this surfactant [Figure 2(a)], so that it resulted in slower gravitational separation compared to the corresponding aqueous solution. The same results were obtained for sample SP4.

In general, in all the water/oil separation tests the gravitational separation was slower when using the nanoemulsion systems containing the solvent PPG as the oil phase. These results indicate that the oil phase present in the nanoemulsions evaluated as water/oil demulsifiers might interfere in the size of the asphaltene aggregates, and consequently in the results of overall efficiency of the process.

Evaluation of the Nanoemulsions as asphaltene Dispersants/Flocculants

The asphaltene precipitation test consists of adding aliphatic solvents (n-pentane, n-heptane, etc.) in an asphaltene dispersion for the purpose of reducing the solubility parameter of the medium to a critical point, at which the solvation power becomes insufficient to keep the asphaltene aggregates dispersed, thus promoting the precipitation of these aggregates. The concentration of the dispersed asphaltenes (not precipitated) was obtained by measuring the absorbance with an ultraviolet-visible spectrometer and comparing the results with a response curve.

The nanoemulsion systems analyzed were the same as those in the water/asphaltene solution separation tests. We also evaluated the aqueous solutions of the surfactants used to prepare the nanoemulsions.

Construction of the Response Curve of Absorption Intensity versus Asphaltene Concentration. The asphaltene precipitation studies were carried out at a wavelength of 850 nm, where the absorption intensity values in function of the concentration of asphaltenes remain within the scale of the equipment and follow the Beer-Lambert Law.

Test of Asphaltene Precipitation in the Presence of the Nanoemulsions.. The asphaltene precipitation tests in the system containing 0.50% m/v of asphaltenes in the heptol mixture were performed to determine the concentration of dispersed asphaltenes in function of the varied quantities of n-heptane added (0, 10, 20, 30, 40, 50, 60, 70, 80, 90%).

We used the results of these tests to construct the graphs of dispersed asphaltene concentration (i.e., the percentage of non-precipitated asphaltenes dispersed in the solvent medium) versus heptane concentration (% v/v) in the heptol mixture (% v/v), shown in Figure 4.
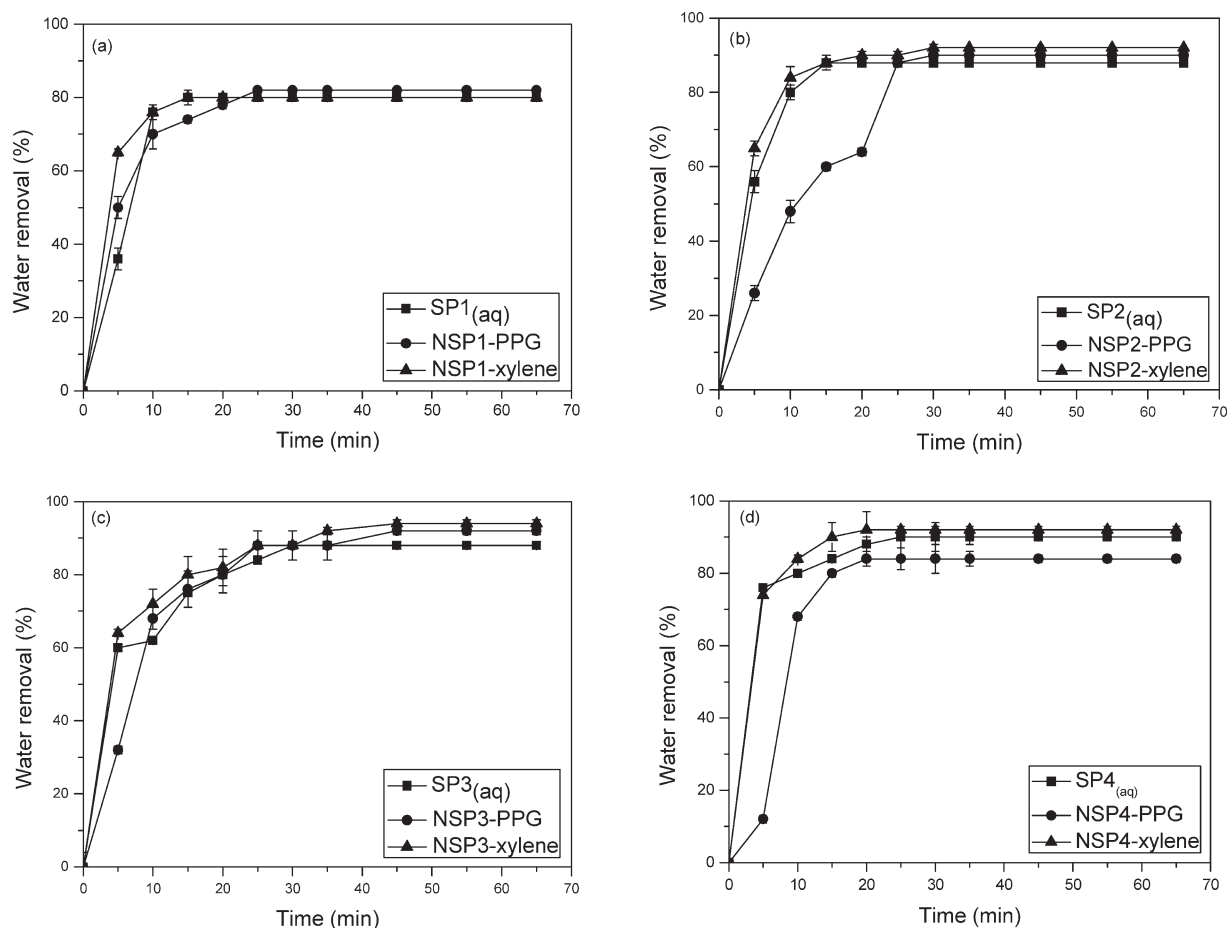
Figure 3. Tests of the efficiency in demulsifying asphaltenes model solutions of aqueous surfactants solutions (SP aq) and the nanoemulsion systems (NSP-oil phase) at concentration of 500 ppm.

Figure 4 presents a typical solubility diagram of asphaltenes in toluene/heptane mixtures (blank), where a reduction can be seen in the concentration of asphaltenes dispersed in the solvent medium starting at a determined proportion of heptane, added to the asphaltenes/toluene mixture. The results of this test showed that in the concentrations analyzed, the onset of precipitation occurred at heptane/toluene ratio of 50/50.

It can be seen that for all the tests, the aqueous solutions of the surfactants used to prepare the nanoemulsions presented asphaltene dispersion efficiency: the concentrations of asphaltenes dispersed in the solvent medium at the precipitation onset point were higher than those obtained in the reference test. The contrary happened with the nanoemulsions containing surfactant SP2, where a larger quantity of asphaltenes precipitated for all the heptane/toluene ratios compared to the reference test.

The nanoemulsions containing surfactant SP4 presented different behaviors according to the oil phase. Only the oil phase containing xylene caused a change in the aggregation of the asphaltenes in solution, increasing the quantity precipitated for all heptane/toluene ratios in relation to the reference test.

Based on these results, which show modifications in the asphaltene aggregation level promoted by adding the nanoemulsions and that nanoemulsion systems containing the same surfactant

but different oil phases cause different aggregation levels, we can suggest that the type of oil phase influences the size of the asphaltene aggregates, favoring the precipitation process or not.

The results obtained also help explain the differences in the destabilization speed of the asphaltene emulsions. The nanoemulsions containing xylene as the oil phase promoted faster gravitational separation. This occurred even in the presence of the systems containing surfactants SP2 and SP4, causing an increase in the size of the asphaltene aggregates, suggesting that this increase could be slowing down the adsorption of these surfactants' molecules at the interface, as can be observed in the analyses of water/asphaltene solution interfacial tension. We also believe that in the presence of the nanoemulsion containing SP4 and xylene, the asphaltene aggregates precipitated (i.e., left solution), leaving more voids at the water/asphaltene solution interface. This suggestion is based on the higher precipitation observed in Figure 4(d).

Study of the Interfacial Rheology of the Asphaltene/Saltwater Solution

Interfacial rheology tests have important and interesting applications, such as control of emulsions' stability, control of foam formation and study of surfactant compounds.
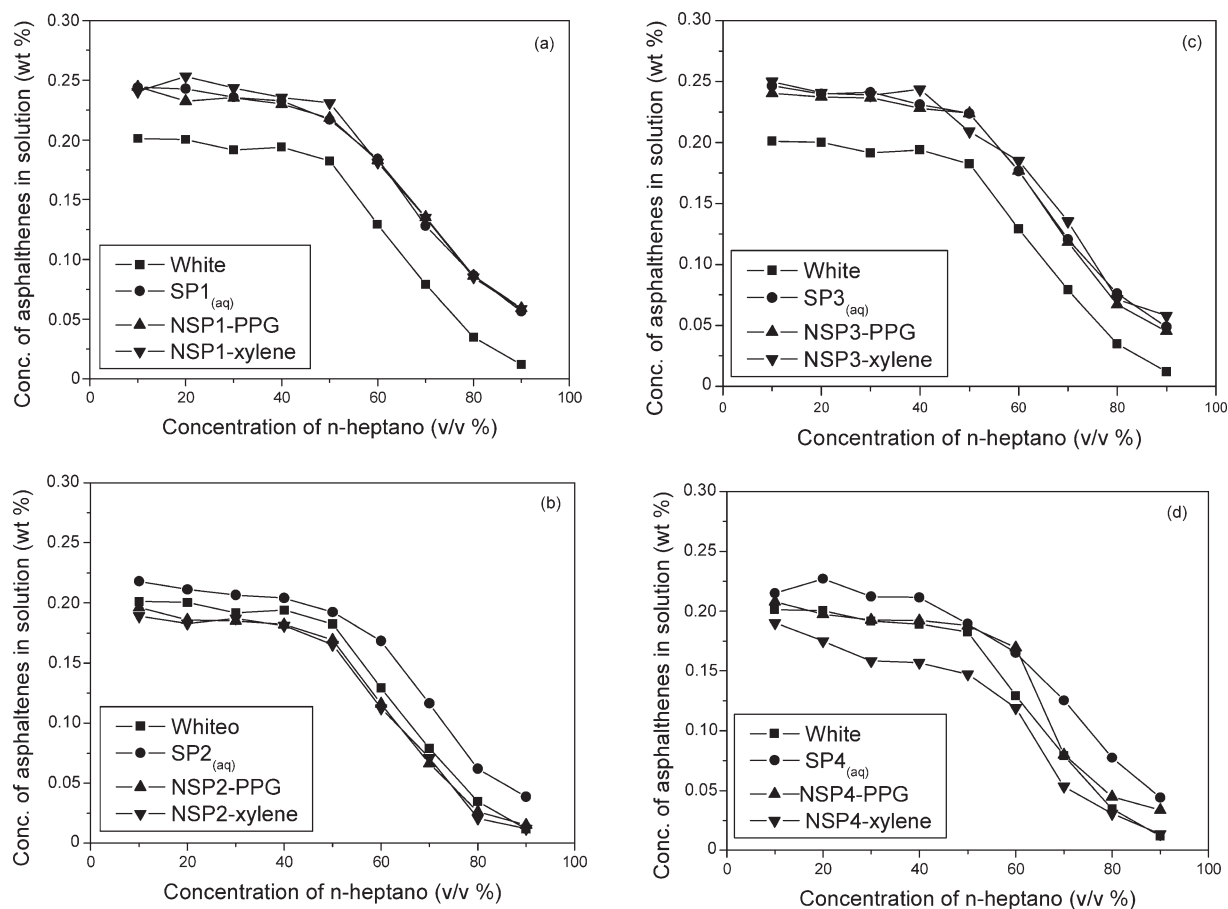
Figure 4. Tests of asphaltenes precipitation in toluene/heptane mixtures in presence or not of aqueous surfactants solutions (SP aq) and the nanoemulsion systems (NSP-oil phase).

Rheological tests with variation of sheer force provide information about the structure formed at the interface, by analyzing the storage modulus and loss modulus (G' and G'', respectively), and viscosity.[25] Here we tested the rheological properties of the interfacial films through the deformations caused by rotation (torsion). In this process, the rotor does not turn continually in one direction. Instead it alternates direction between clockwise and counterclockwise, in a sinusoidal function with small angle. This enables separately analyzing the contribution of the viscous and elastic parts of the film. A method widely described to measure the interfacial rheological properties in response to shear force relies on a biconical disk or bob.[5,12,26,27] We used a Du-Noüy ring as the measurement accessory.

The interfacial rheology tests of the asphaltene/saltwater solution (containing 0.5% asphaltenes in a heptane/toluene mixture in proportion of 25/75) were performed with the same systems and same concentration used in the demulsification tests, to establish a correlation and help understand the efficiency of the O/W nanoemulsions as demulsifiers when using asphaltene model emulsions.

We developed a method consisting of scanning in function of tension and frequency applied to the interfacial systems, with or without additives. The aim was to discover the region of linear viscoelasticity, i.e., the tension and frequency range where the

values of the storage and loss moduli (G' and G'', respectively) remained constant. This means that at this tension and frequency range, no change occurs in the three-dimensional configuration of the interfacial film, so that possible alterations in these parameters are caused only by the action of the additives.

Initially we carried out scans using the asphaltene/saltwater systems after different resting times (10 min, 30 min, 2 h, 14 h), with the objective of verifying whether the resting time influences the linear viscoelasticity range. The results did not indicate significant differences in this range in function of resting time.

Therefore, we chose the resting time of 10 min for the other tests. Figures 5 and 6 show, respectively, the scans in function of tension and frequency with this resting time.

Afterward, we added the nanoemulsions and aqueous solutions used in the water/oil gravitational separation tests to verify whether the presence of the additives would alter the system's linear viscoelasticity range. The results obtained for all the systems showed that the presence of the additives did not affect this range, both for the measures with scans in function of tension and in function of frequency.

The next procedure was to choose a suitable time for analysis. For this purpose we conducted tests with the asphaltenes/saltwater solutions at time intervals from 1 to 4 hours, with
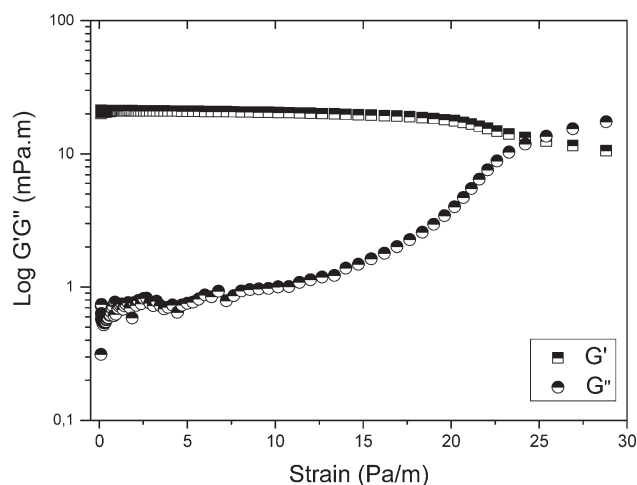
Figure 5. G' and G'' as a function of strain variation for the system: asphaltenes model solution/saline water. Frequency: 1 Hz.

Figure 7. G' as a function of time for the system: asphaltenes model solution/saline water, containing or not aqueous surfactant solutions at 500 ppm. Frequency: 1 Hz and Strain: 0.5 Pa/m.

defined tension and frequency values (0.5 Pa/m and 1 Hz). No significant changes occurred in the storage and loss moduli in function of time, so we chose 1 h for all the ensuing tests.

In all the analyses presented in Figures 7–9, significant changes only occurred in the values of G', making it possible to explain the effect of the additives on the mechanical properties of the interfacial film. All the additives utilized reduced the G' values, so both additives reduced the rigidity of the water/asphaltene solution interfacial film. This behavior, together with the ability to decrease the interfacial tension of the water/asphaltene solution demonstrated for all the systems, explains the fact that the additives destabilized the asphaltene model emulsions used in the demulsification tests.

It is important to note that this reduction of the value of G' might have happened through two mechanisms. The first is that the surfactant molecules adsorbed at the interface displace the asphaltene aggregates. The second hypothesis is that the oil phase of the nanoemulsions (together with the surfactants) alters the dispersion state of the asphaltenes so as to promote
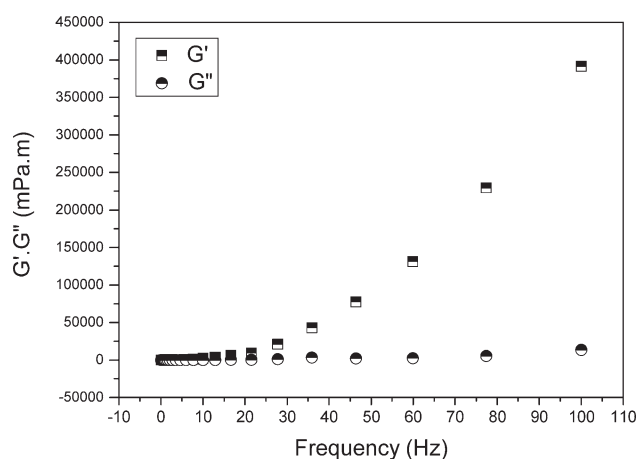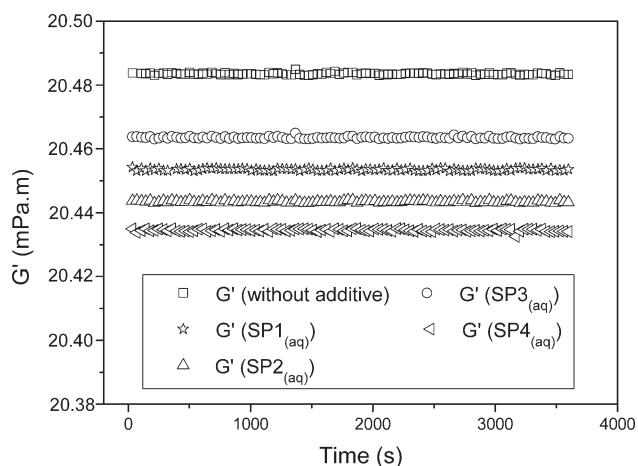
the formation of smaller aggregates, leading to the formation of interfacial films with less mechanical resistance.

From the results for the systems containing the aqueous surfactant solutions (Figure 7), it is possible to suggest that the reduction of the G' values for all the systems might be due to the ability of all these solutions to disperse the asphaltenes in solution, thus contributing to the formation of smaller aggregates, as discussed earlier. For these systems, this effect appears to be preponderant, since the aqueous solution of surfactant SP1 presented the weakest ability to reduce the interfacial tension (Figure 1), meaning a smaller quantity of surfactants at the interface acting to displace the asphaltene aggregates, but still caused a reduction in the G' values similar to those of the aqueous solution of surfactant SP2, which presented a slightly greater reduction in the tension values for this interface. Further support for this conclusion is that sample SP3 caused the smallest reduction of the G' values, even though it was the sample with the lowest level of surfactants adsorbed at the interface (Figure 1).
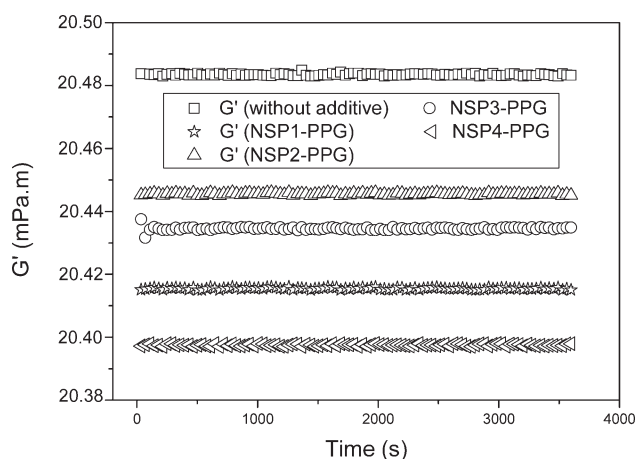

Figure 6. G' and G'' as a function of frequency variation for the system: asphaltenes model solution/saline water. Strain: 0.5 Pa/m.

Figure 8. G' as a function of time for the system: asphaltenes model solution/saline water, containing or not aqueous nanoemulsions based on PPG, at 500 ppm. Frequency: 1 Hz and Strain: 0.5 Pa/m.
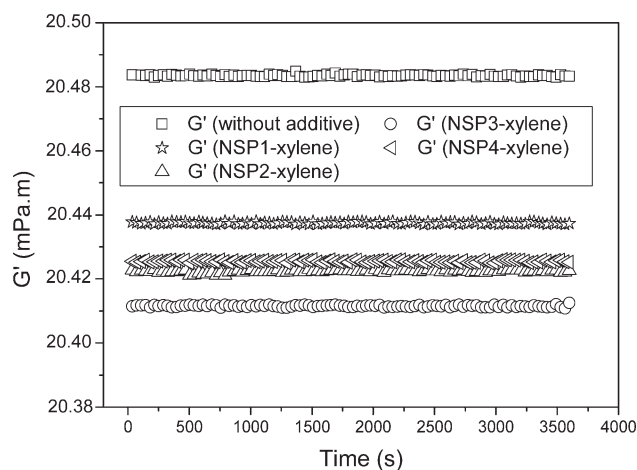
Figure 9. G' as a function of time for the system: asphaltenes model solution/saline water, containing or not aqueous nanoemulsions based on xylene, at 500 ppm. Frequency: 1 Hz and Strain: 0.5 Pa/m.

In relation to the systems containing PPG as the oil phase (Figure 8), the samples containing the surfactants SP1 and SP4 promoted a greater reduction of the G' values. For the system PPG/SP1, the reduction appears to be associated with the dispersion of the asphaltenes caused by the presence of this nanoemulsion. In turn, for the nanoemulsion PPG/SP4, the effect of displacing the asphaltene aggregates appears to prevail, since this system showed good ability to reduce the interfacial tension of the water/asphaltene solution and did not significantly promote the formation of larger asphaltene aggregates. For the systems containing the surfactant SP3, the reduction can also be attributed to the ability to promote formation of smaller asphaltene aggregates, while for that containing SP2 it can be attributed to the ability to displace the asphaltene aggregates by the molecules of this surfactant, since the addition of the nanoemulsion also favored the formation of larger asphaltene aggregates.

The same reasoning can be applied to the nanoemulsions containing xylene as the oil phase (Figure 9). For the samples containing SP1 and SP3, the reduction of the G' values can be attributed to the ability to form smaller asphaltene aggregates in the presence of these systems. In turn, the nanoemulsions in the presence of SP2 and SP4 appear to have reduced the G' values by their ability to displace the asphaltene aggregates, since larger asphaltene aggregates formed in the presence of both, causing an increase in the G' values.

CONCLUSIONS

In the water/oil demulsification tests with asphaltene model emulsions, the fastest demulsification was obtained using xylene as the oil phase of the nanoemulsions.

The type of oil phase used in the nanoemulsions had an important influence on the speed of destabilizing the model emulsions, since the presence of nearly all the nanoemulsion systems had a significant influence on the dispersion/flocculation state of the asphaltenes, thus altering the size of their aggregates at the interface, influencing the adsorption speed of the surfactant molecules at the saltwater/asphaltene solution interface.

All the O/W nanoemulsions studied caused a reduction of the G' values of the interfacial film, demonstrating that the presence of the nanoemulsions causes the formation of interfacial films with weaker mechanical resistance. This explains the good efficiency of the O/W nanoemulsions used to test the destabilization of the asphaltene model emulsions. These changes in the physical properties of the interfacial film occur either by alteration of the size of the asphaltene aggregates or the nanoemulsions' ability to displace the surfactant molecules adsorbed at the interface.

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