Article

The Influence of Asphaltenes Subfractions on the Stability of Crude oil Model Emulsions

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O petróleo é produzido na forma de emulsão água em óleo e os asfaltenos são considerados os principais responsáveis pela estabilização dessas emulsões. O objetivo deste trabalho foi avaliar a influência de diferentes frações asfaltênicas sobre a estabilidade de emulsões modelo de petróleo (salmoura em asfaltenos/tolueno) e sobre a eficiência de desemulsificantes. A estabilidade das emulsões foi acompanhada pelo ensaio de garrafa, com e sem a adição de desemulsificante. Os resultados mostram que a amostra de asfaltenos com larga distribuição de polaridade promove maior estabilidade da emulsão do que a amostra com distribuição mais estreita e polaridade intermediária. Além disso, a eficiência do desemulsificante na separação das emulsões está diretamente relacionada à estabilidade original da emulsão. Resultados de tensão interfacial evidenciaram a eficiência de deslocamento dos asfaltenos pelos tensoativos desemulsificantes, o que ocorreu com maior eficiência para as emulsões contendo frações de asfaltenos com distribuição estreita e polaridade intermediária.

Crude oil is produced as water-in-oil emulsion, and asphaltenes have been considered the main responsible by their stabilization. The aim of this work was to evaluate the influence of the asphaltenes subfractions on the stability of petroleum model emulsions and on the efficiency of demulsifiers. Model water-in-oil emulsions were prepared: aqueous phase of brine and oil phase of asphaltenes in toluene. Different asphaltenes fractions were used. The emulsions' stability was assessed by the bottle test, with and without adding demulsifier. The results show that a sample of asphaltenes with broad polarity distribution promotes greater emulsion stability than a sample with narrow distribution and intermediate polarity. Besides this, the efficiency of demulsifiers in separating the emulsions is directly related to the original stability of the emulsion. Measurements of the interfacial tension revealed the efficiency of displacement of the asphaltenes by the demulsifiers, which occurred more efficiently for the emulsions containing asphaltenes fractions with narrow distribution and intermediate polarity.

Keywords: water-in-oil emulsion, stabilization, demulsification, asphaltenes subfractions

Introduction

During production of crude oil, a large amount of water is also produced, coming from the reservoir itself and/or return of the water injected to enhance the oil recovery. In the presence of sufficient shear force when the oil and water are produced, stable emulsions can be formed at practically all steps of production and processing, such as in reservoirs, risers, treatment installations, pipelines and refineries. Once formed, the water-in-oil (W/O) emulsion can: hamper the petroleum treatment; cause changes in gas-oil separation units; affect the size of the pumping systems; and produce

scaling and corrosion of equipments. W/O emulsions must be treated to remove the associated water and inorganic salts, to obtain oil with proper specifications for transport, storage and exportation and to reduce the corrosion and contamination of catalyzers at processing plants.[1,2]

W/O emulsions are stabilized by emulsifiers (surfactants), which tend to migrate and concentrate at the W/O interface, forming a film that reduces the interfacial tension between the phases, promoting the dispersion of water droplets in the continuous phase and inhibiting their coalescence. Some natural emulsifiers are present in crude oil, such as asphaltenes, resins and organic acids and bases. Others are injected for some type of operation/treatment, such as wax deposition inhibitors, asphaltenes stabilizers

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and anti-corrosive agents. Fine solids can also promote mechanical stabilization of emulsions.[3-6]

The literature[7-9] shows that the molecular aggregates formed by asphaltenes, more so than the molecules in free form, help to stabilize W/O emulsions by forming a film or barrier at the interfaces.

Asphaltenes have macromolecular characteristics and are present in the heaviest fraction of crude oil. The asphaltenes fractions are also the most polar in the oil. The structure of asphaltenes is formed by aromatic polycondensate nuclei linked to the cyclical and aliphatic chains, containing heteroatoms like oxygen, nitrogen and sulfur along with metals such as iron, vanadium and nickel. Their exact structure is unknown due to the variety and complexity of their chemical structure. Several structural models have been proposed, such as archipelago and island.[10] During crude oil refining in a fractioning column, the asphaltenes are not distilled and remain solidified with the resins, receiving the name asphaltic residue. The asphaltenes are separated from the resins by the addition of an apolar (paraffinic) solvent such as n-pentane or n-heptane, forming precipitates, and are dissolved in aromatic compounds such as toluene.[11,12]

Emulsion destabilization can be achieved by different methods.[13-15] Crude oil can be demulsified by adding chemical compounds (normally at concentrations of 10 to 1000 ppm) to improve the separation rate of the W/O emulsion. These additives cause thinning of the interfacial film, allowing the droplets to coalesce more easily, thus allowing the phases to separate.[5,16,17] These chemical compounds have nonionic character, with relatively high molar mass (normally above 3,000 Da) and have one part that is hydrophilic and another hydrophobic.[18] The hydrophilic part includes the oxyethylene, hydroxyl, carboxyl or amine groups, while the hydrophobic parts are composed of alkyl, alkylphenol or oxypropylene groups.[19,20] Among the commercial demulsifiers are ethoxylated phenol-formaldehyde resins and poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers.[21-24]

Among the properties desired of demulsifiers are high adsorption speed at the water-oil interface, displacement of the natural emulsifiers that stabilize the emulsions and formation of thin and fragile films at the water-oil interface, facilitating coalescence of the droplets.[16,25,26]

The aim of this work was to study the influence of crude oil asphaltenes subfractions, obtained and characterized previously,[27] on the stability of water-in-oil (W/O) emulsions. The measurements were performed by the bottle test, with and without the addition of a demulsifier.

Experimental

Materials

The asphaltic residue (ASPR) was supplied by Petrobras (Rio de Janeiro, Brazil). The asphaltenes fractions and subfractions obtained from this residue and utilized in this work were: fraction C5, subfraction C5-C6, subfraction C8-C9 and fraction C10. Such (sub)fractions were obtained in a previous work as following.[27] The asphaltic residue and n-pentane (proportion of 15g:1L) were placed under stirring for 24 h. The insoluble fraction was placed in a Soxhlet extractor with n-pentane (proportion of 1g : 45mL). This extraction step continued until the paraffinic solvent appeared clear in the extractor. The solvent in the extractor was then replaced with dry toluene (proportion of 1 g of precipitate:35 mL of solvent) and the extraction process was repeated until this new solvent appeared clear. The dissolved asphaltenes (fraction C5) were recovered after evaporation of the toluene in a rotary evaporator and dring for 3 days in a chapel to evaporate the residual solvent. Successive extractions were performed from the C5 asphaltenes to obtain different subfractions, separated by the difference in solubility in various solvents (n-hexane, n-heptane, n-octane, n-nonane and n-decane). The subfraction C5-C6 corresponds to that extracted by solubilization in n-hexane, starting from the C5 asphaltenes. The remaining precipitate was then subjected to another extraction, this time with n-heptane, to obtain the subfraction C6-C7 dissolved in the n-heptane. The remaining precipitate was again submitted to extraction, this time using n-octane, to obtain the subfraction C7-C8. Next, the undissolved solid was placed in n-nonane in the extractor to obtain the subfraction C8-C9. Finally, the remaining precipitate was subjected to extraction with n-decane to obtain the dissolved C9-C10 subfraction, leaving a precipitate which was called C10 asphaltenes. All the dissolved subfractions were dried for around 3 days and weighed to calculate the yield. Figure 1 shows the fractioning carried out and the yield of the asphaltenes (sub)fractions.
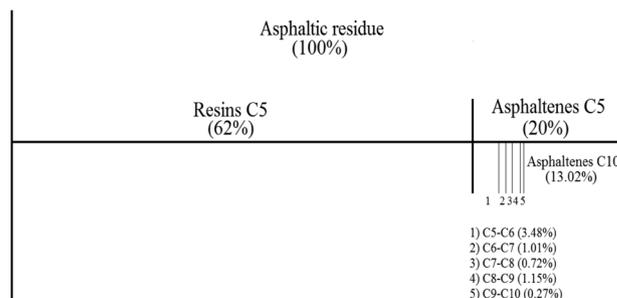
Figure 1. Yield of the asphaltene fractions.

Table 1. Molar mass, EO/PO* ratio and chemical structure of demulsifiers[28,29]

Additives	$\overline{M}_n$ [(a)]	$\overline{M}_w$ [(a)]	$\overline{M}_w/\overline{M}_n$ [(a)]	EO/PO ratio[(b)]	Molecular structure
Copolymer B	11600	12000	1.03	0.19	$CH_2(PO)_{58}(EO)_{11}OH$ | $CH(PO)_{58}(EO)_{11}OH$ | $CH_2(PO)_{58}(EO)_{11}OH$
Copolymer L	3000	4100	1.37	0.51	$CH_3(PO)_{37}(EO)_{19}OH$

*Ethylene oxide/propylene oxide; [(a)]by size exclusion chromatography (SEC); [(b)]by hydrogen nuclear magnetic resonance (^{1}H-NMR).

Toluene, acquired from Vetec Química Fina (Rio de Janeiro, Brazil), was distilled and dried in alumina. HPLC-grade toluene was supplied by Tedia Brasil (Rio de Janeiro, Brazil). Sodium chloride and calcium chloride were also acquired from Vetec Química Fina.

The poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers (branched, B; and linear, L) were donated by Dow Química Ltda. (São Paulo, Brazil). The characterization data are in Table 1.[28,29]

Preparation of the model water-in-oil emulsions

First 500 mL of dispersions were prepared containing 0.25% (m/v) of one of the following samples dissolved in dry toluene: asphaltic residue, asphaltene fraction C5 (extracted with n-pentane), subfraction C5-C6, subfraction C8-C9 and fraction C10.

The model emulsions containing these dispersions as the oil phase were prepared so as to contain 30.0% synthetic brine at a concentration of 55,000 ppm of salts ($NaCl:CaCl_2$ ratio of 10:1). To prepare each emulsion, 70.0 mL of this dispersion was placed in a 250-mL beaker and submitted to shearing in a Polytron PT 3100D homogenizer under stirring of 8,000 rpm with slow addition of 30.0 mL of the brine. Then the system was kept under stirring for an additional 3 min, at room temperature.

Gravitational water-oil separation measurement by the bottle test

The gravitational separation of the water from the oil was measured by the bottle test. The tests were conducted initially to assess the stability of the model emulsions without the addition of a demulsifier (blank test). Afterwards, 100 ppm solutions of the PEO-PPO block copolymers in toluene (at 40% m/v) were added to the model emulsions to perform the tests with the demulsifiers added. The test procedure was described in a previous publication.[29]

The efficiency of gravitational separation of each formulation used in these tests was calculated by applying equation 1:

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

In equation 1, EF_{WO} is the efficiency of gravitational separation of water and oil, in % by volume; V_{WS} is the volume of water separated during the test and V_{WT} is the volume of total water inside the test tube, both in mL. All measurements were taken in triplicate.

Determination of the size distribution of the saltwater droplets in the model emulsions

An Axiovert 40 MAT optical microscope was used to study the size of the saltwater droplets in the emulsions. One minute after preparing each emulsion, a small aliquot was diluted in spindle oil, placed on a slide and examined under the microscope. This was done at room temperature, with a total of 140 to 200 droplets, to obtain their average diameter by using AxioVision 4.4 imaging software.

Determination of the interfacial tension between the brine and asphaltene dispersions

The interface tension measurements were determined by the Du Noüy ring method using a Krüss K10ST digital tensiometer, at 25 ºC. All the measurements were performed in triplicate, and only the values with variation less than 1 mN m^{-1} were considered.

Results and Discussion

Water-oil gravitational separation tests

The bottle test technique was used to assess the water-oil gravitational separation of the model emulsions, composed of brine as the aqueous phase and asphaltenes dispersed in toluene as the oil phase. The types of asphaltenes employed were: asphaltic residue (ASPR), fraction C5, subfraction C5-C6, subfraction C8-C9 and fraction C10. The other subfractions were not used in these tests because of the low yield during their extraction.[27]

The concentration of ASPR and the asphaltene fractions/subfractions in the oil phase was in all cases 0.25% m/v, because this was the lowest concentration tested that produced sufficiently stable emulsions to conduct the study.

All the tests were performed in triplicate and in the presence or absence of the demulsifiers (linear and branched PEO-PPO block copolymers) at a concentration of 100 ppm.

Tests without the demulsifier additives

Table 2 summarizes the maximum separation values attained for each type of emulsion.

Table 2. Maximum separation efficiency of model water-in-oil emulsions

Model emulsion	Maximum separation efficiency / % (min)*
ASPR	100 (35)
Fraction C5	18 (65)
Subfraction C5-C6	100 (10)
Subfraction C8-C9	60 (25)
Fraction C10	0

*Time required to achieve maximum efficiency.

The synthetic emulsions prepared without any demulsifier (blank tests) containing the ASPR dispersions as the oil phase were highly unstable. The presence of resins in the composition, which are less polar than asphaltenes, reduced the emulsifying action of this mixture of resins/asphaltenes, permitting faster coalescence of the water droplets and total separation of the aqueous phase.

The demulsification test with the oil phase composed of the C5 asphaltenes fraction presented only a small phase separation (approximately 20%), which was expected since the asphaltenes separated from resins tend to leave the solution and migrate to the interface, where they act to stabilize the emulsion.

In the blank test performed with fraction C10, the emulsion was very stable, without any phase separation during the test period (65 min). As shown in a previous work,[26] this fraction has higher polarity, so a more rigid interfacial film is generated, impeding the coalescence of the dispersed phase.

The first subfraction isolated from the asphaltenes, called subfraction C5-C6, is constituted of a portion of the C5 asphaltenes with lower polarity, leading to a less stable emulsion. Subfraction C8-C9 has higher polarity than subfraction C5-C6 and the result of the blank test showed, as expected, a more stable emulsion, with no total phase separation observed during the test.

Comparing all the results, the instability of the model water-in-oil emulsions was in the following decreasing order in terms of type of asphaltenes added:

C5-C6 > ASPR > C8-C9 > C5 > C10

It is interesting to note that the most unstable system was that containing the subfraction C5-C6. The system containing ASPR, despite the presence of the resins, was more stable than that containing C5-C6. This can be attributed to the fact that the ASPR sample contains a much wider distribution of molecular structures than the subfraction C5-C6. In other words, the ASPR sample contains the same molecules as the subfraction C5-C6, and also more apolar and more polar molecules. The presence of more polar molecules makes the system more stable, despite the presence of less polar molecules (resins) in a much higher quantity, which tend to stabilize the asphaltenes in the oil phase. The stability result leads to the conclusion that the asphaltenes fraction with narrower distribution and intermediate polarity, in this case subfraction C5-C6, has less capacity to stabilize emulsions than does a mixture of various components with varied polarities, whose more polar molecules can migrate to the interface.

Similar behavior was observed when comparing the stability results obtained for the C5 asphaltenes fraction, with wider distribution of structure types with distinct polarities, and those for the subfraction C8-C9, with narrower distribution. The subfraction C8-C9, which belongs to half of asphaltenes fraction C5 (see Figure 1) of which has lower polarity, leads to more unstable emulsions than the C5 fraction. Therefore, the difference in stability was much more accentuated: 60% separation efficiency for C8-C9 *versus* 18% for C5.

Furthermore, the influence of the C5 and C10 fractions on the emulsions' stability is very significant: the separation efficiency of 18% for fraction C5 and 0% for C10.

Tests in the presence of the demulsifier additives

The linear (L) and branched (B) PEO-PPO block copolymers used here were employed in a previous work[28] as demulsifiers, and it was observed that the branched copolymer was more efficient in breaking the synthetic water-in-oil emulsions tested. This efficiency was associated with: (*i*) their branched structure, where the EO and PO groups are more distributed in the chains, thus facilitating their dispersion between the phases of the W/O emulsion, and (*ii*) their average molar mass, since too long chains cannot diffuse through the oil phase because they form agglomerates and too short polymer chains diffuse too slowly, so requiring a molar mass near to an optimal value.[30]

In this work it was also observed in the gravitational separation tests that the branched PEO-PPO block copolymer tended to be more efficient.

The separation efficiency percentages are presented in Table 3. In all the systems there was 100% separation efficiency, with only the time required to reach this result varying. This also reflects the stability of the emulsion. This complete efficiency result was to a certain extent expected, since model systems are more easily separated than petroleum emulsions.[6] The initial stability of the model emulsion is reflected in the performance of the demulsifier: the more unstable emulsions (subfractions C5-C6 and C8-C9) were broken down faster by the demulsifiers (5 and 10 min), while it took longer (15, 20 and 30 min) longer for the demulsifiers to break down the more stable emulsions (fractions C5 and C10).

Table 3. Percentage of efficiency of phase separation

Model emulsion	Maximum separation efficiency / % (min)*		
	Without additive	PEO-PPO B	PEO-PPO L
ASPR	100 (35)	100 (5)	100 (10)
Fraction C5	18 (65)	100 (15)	100 (30)
Subfraction C5-C6	100 (10)	100 (5)	100 (10)
Subfraction C8-C9	60 (25)	100 (5)	100 (5)
Fraction C10	0	100 (20)	100 (20)

*Time required to achieve maximum efficiency.

Determination of the size of the water droplets dispersed in the model emulsions

Table 4 shows the average sizes, the standard deviation and the size range detected. The results show that the mean diameters of the water droplets, as well as the size distributions, were very similar in the four cases, indicating there is no influence of the water droplets' size and size distribution on the stability differences of the emulsions. This means that the differences in stability observed here really came from the type of asphaltenes molecules added to the systems.

Table 4. Mean diameter and standard deviation for different asphaltene fractions and subfractions

	Asphaltenes C5	Subfraction C5-C6	Subfraction C8-C9	Asphaltenes C10
Diameter / μm	12.28	18.91	15.76	12.66
Standard deviation	5.98	14.62	12.35	5.51
Detected range / μm	0-40	0-120	0-130	2-32

It is important to highlight that the continuous phase in model emulsions is not as complex and viscous as that in real petroleum emulsions, so micrometer emulsions were formed and detected by optical microscopy. Literature shows that in crude oil very small drops, with sizes of some nanometers, have been detected. In this case, calorimetric measurements can be used.[31]

Determination of the saltwater/asphaltene dispersion interfacial tensions

For the interfacial tension measurements (Table 5), each sample was placed in a cuvette and left at rest for 1 h so as to allow similar measurement conditions for all the samples. After adding the surfactant, its molecules should migrate to the W/O interface, displacing the asphaltenes molecules and promoting demulsification.

The blank system was composed of only brine with toluene, without the addition of any asphaltenes. In this system the interfacial tension was 30.5 mN m^{-1}, a figure that declined to 14.8 and 11.4 mN m^{-1} with the addition of the branched and linear surfactant, respectively. As expected, in both cases the samples showed the effects of the surfactant, with the molecules migrating to the interface and reducing the interfacial tension. The linear surfactant was slightly more efficient in reducing the tension, probably due to its more hydrophilic character (EO/PO ratio = 0.51) in comparison with the branched surfactant (EO/PO ratio = 0.19): The more hydrophilic the surfactant dissolved in the organic phase is, the greater is its tendency to migrate to the interface and interact with the aqueous phase.

Table 5. Interfacial tension of brine/asphaltene dispersions

Asphaltenes	Interfacial tension / (mN m^{-1})		
	Without surfactant	With surfactant B	With surfactant L
Blank*	30.5 ± 1.1	14.8 ± 0.7	11.4 ± 0.4
ASPR	20.5 ± 0.4	15.6 ± 0.4	11.2 ± 0.2
Fraction C5	21.4 ± 0.1	16.3 ± 0.3	11.1 ± 0.6
Subfraction C5-C6	26.9 ± 0.6	13.5 ± 0.8	11.3 ± 0.0
Subfraction C8-C9	21.9 ± 0.4	15.6 ± 0.5	11.0 ± 0.4
Fraction C10	20.3 ± 0.1	16.0 ± 0.4	10.3 ± 0.1

*Brine/toluene.

The first column of Table 5 contains the results of the emulsions without surfactant addition. As expected, the surfactant character of the asphaltenes can be noted, since they were able to reduce the interfacial tension of the brine/toluene system. In this case, the more accentuated the polar character of the fraction is, the greater the reduction

in the interfacial tension. Subfraction C5-C6 by itself presented the highest tension value, due to its less polar character and a lesser tendency to migrate to the interface, related to the greater instability in the emulsions formed with this subfraction (Table 3). Except for the emulsion containing ASPR, the correlation between the reduction of the interfacial tension, imposed by the presence of the asphaltenes, and the stability of the emulsions remained steady: the more stable the emulsion, the lower the interfacial tension value.

It is believed that the demulsification process occurs by removal of the asphaltenes from the interface, with their place taken by the surfactant additive. This surfactant forms a less rigid interfacial film than that formed by the asphaltenes, making the emulsion more fragile, i.e., allowing the water droplets to coalesce more easily.[6,9]

The action of the branched surfactant (B) in displacing asphaltenes from the interface was greatest in the emulsion containing the least polar subfraction, C5-C6. The interfacial tension values were higher in all the other emulsions. This behavior is likely to be related to the presence of asphaltenes molecules at the interface together with the branched surfactant molecules. Therefore, the higher interfacial tension values of the systems containing the C5 and C10 fractions than in any of the other systems was probably associated with the fact that the branched surfactant was less effective in displacing these kind of asphaltenes from the interface. This hypothesis is supported by the results on maximum efficiency presented in Table 3, where it can be seen that the systems that needed the longest time to reach 100% efficiency were those containing the C5 and C10 fractions. This correlation of results leads to the conclusion that the separation efficiency is directly related to the facility of displacing the asphaltenes molecules from the interface.

For the linear surfactant (L), all the interfacial tension values were similar to each other and to that of the system without the presence of asphaltenes. It appears that after one hour all the asphaltene is removed from the interface by the linear surfactant. None of these emulsions took more than 30 min to separate completely.

Comparison of the separation efficiency results (Table 3) with those on interfacial tension shows that lowest tension values corresponded to the lowest separation efficiencies. In other words, the systems containing the linear surfactant presented lower tension values and also less efficient separation.

Conclusions

The stability of the emulsions, as expected, was the greatest in the presence of more polar asphaltenes fractions.

However, this work presents the first verification that a sample of asphaltenes with wide polarity distribution promotes greater stability than a sample with much narrower distribution and intermediate polarity. This means that even the presence of a large quantity of less polar molecules is not sufficient to stabilize the more polar molecules in the dispersion, causing these molecules to migrate to the emulsion's interface.

The efficiency of demulsifiers in separating emulsions is related to the original stability of the emulsion, i.e., more unstable emulsions are broken down by demulsifiers more quickly. In this work, all the emulsions containing demulsifiers were completely separated, due to the greater facility of separating the model emulsions (which are composed of brine and a dispersion of asphaltenes in toluene) than petroleum emulsions. The greater efficiency of the branched surfactant over the linear one was confirmed.

The size and size distribution of the water droplets in the model emulsions were similar, indicating the effect of the type of asphaltenes molecules on the stability of emulsions.

The interfacial tension measurements revealed the efficiency of the demulsifier surfactants in displacing the asphaltenes, which occurred more efficiently for the emulsions containing fractions with narrow distribution and intermediate polarity.

Acknowledgments

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