

Evaluation of the Influence of Polyoxide-Based Surfactants on the Separation Process of Model Emulsions of Asphaltenes Using the FTIR-ATR Technique

Janaina I. S. Aguiar, Jéssica S. G. Neto, Sarah M. Almeida, Claudia R. E. Mansur

Federal University of Rio de Janeiro, Institute of Macromolecules, Laboratory of Macromolecules and Colloids for the Petroleum Industry—Av. Horácio Macedo, 2030, Cidade Universitária, 21941598, Rio de Janeiro, RJ, Brazil

Correspondence to: C. R. E. Mansur (E-mail: Brazil celias@ima.ufrj.br or aguiar.jis@ima.ufrj.br)

ABSTRACT: During extraction of crude oil, water is generally present in the oil. This water-in-oil (w/o) mixture undergoes turbulent flow that promotes sheer forces, resulting in the appearance of emulsions. These emulsions can be highly stable due to the presence of compounds with polar characteristics such as asphaltenes, which act as natural emulsifiers and form resistant films at the oil–water interface. Nonionic surfactants based on polyoxides are widely used to prevent the formation or to break down w/o emulsions. To shed more light on the destabilization mechanism of w/o emulsions promoted by these surfactants, in this study the techniques of tensiometry and Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) were applied to study the interface formed by poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers and asphaltenic petroleum fractions. Initially, the critical micelle concentration of the copolymers in aqueous solution was determined. The results agreed with those found by tensiometry. The bottle test was used to evaluate the break-down of the w/o emulsions in the presence of the PEO-PPO block copolymers, and the results presented good agreement with those obtained by tensiometry and FTIR-ATR. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: copolymers; micelles; oil and gas; surfactants; spectroscopy

Received 27 February 2012; accepted 30 June 2012; published online

DOI: 10.1002/app.38292

INTRODUCTION

During the extraction of crude oil, the mixture of water and oil is subjected to turbulent flow, promoting the dispersion of the water in the form of small droplets and resulting in the formation of emulsions. The emulsification of water in oil occurs due to the immiscibility of the two liquid phases, the sheer forces imposed during flow, and the existence of natural emulsifiers present in the oil. Substances such as asphaltenes and resins, with polar characteristics, form resistant films at the oil–water interface.^{1–3}

Resins correspond to the oil fraction composed of polar molecules, which often contain polycondensates with aromatic rings linked to aliphatic chains of varied sizes. Their structure contains heteroatoms such as nitrogen, oxygen, and sulfur and metals such as nickel, vanadium, and iron. Resins are insoluble in ethyl acetate and soluble in aliphatic hydrocarbons with low molar mass and in aromatic solvents such as benzene and toluene.

Asphaltenes have a structure similar to resins, but they also have higher molar mass and aromaticity. Besides this, asphal-

tenes contain a greater quantity of heteroatoms and metals. This fraction is insoluble in aliphatic solvents with low molar masses and soluble in aromatic solvents.⁴

In a petroleum fractionating column, the asphaltenes are not distilled and remain solid together with the resins, generating the petroleum fraction called asphaltic residue.^{2,3}

Asphaltenes' structure contains a large quantity of polar functional groups, with low affinity for the organic phase. Because they do not interact well with the surrounding medium, asphaltene molecules associate with each other and form aggregates. This association occurs due to the interactions of the π electron clouds of the aromatic rings of the asphaltenes and the acid–base interactions between functional groups, with transfer of loads and hydrogen bonds between the functional groups.^{5,6}

Rheological studies indicate that in water-in-oil (w/o) emulsions, the interfacial film is highly viscoelastic and is formed by a three-dimensional network of asphaltene molecules that interact through intermolecular forces, forming aggregates or micelles at the water–oil interface.^{7,8}

Midttun et al.⁹ evaluated the stability of model emulsions in the presence of mixtures of asphaltenes and resins. They observed that for short periods, the stability of the systems was between that of systems composed exclusively of asphaltenes and of those composed only of resins. But for longer periods, the stability increased, associated with the interaction between the asphaltenes and resins at the interface. In some cases, these emulsions were more stable than those composed of higher asphaltene concentrations but without the presence of resins.

McLean and Kilpatrick¹⁰ also analyzed the influence of the solvency of asphaltenes on the stabilization of emulsions. They noted that asphaltenes act to stabilize w/o emulsions when they are at or near the precipitation point. The results showed a reduction in the stabilization of the emulsions tested when the solvency degree of the asphaltenes was altered from the aggregate state to the molecular state. Asphaltene aggregates are adsorbed at the water–oil interface by the hydrogen bonds or other interactions between the water and polar portions of the aggregates.

Among the methods developed to destabilize w/o emulsions, the use of chemical additives (demulsifiers) is very common. In general, they are amphiphilic substances that have strong interfacial activity. It has been proposed that these additives are capable of migrating to the w/o interface, where they displace the emulsion's natural stabilizing agents. Therefore, demulsifiers break or weaken the rigid film that acts as a barrier, facilitating the coalescence of the water droplets in the dispersed phase.¹¹

Demulsifiers are products composed of one or more active ingredients and solvents. They reduce the viscosity and facilitate the handling and dosing of emulsions. Normally, the active components are nonionic polymeric surfactants such as poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers. The PEO portion of these compounds' structure is hydrophilic and tends to interact with water, while the PPO portion is lipophilic and tends to interact with the oil phase. The formulations can also contain other compounds, such as esters, polyester amines, and phenols. Each of these components has a different action, so that demulsifiers have different properties depending on their composition.¹¹

Understanding the mechanisms for demulsification of w/o emulsions is difficult. Therefore, studies aiming to elucidate the demulsification mechanism are important for application to development new technologies.

To shed more light on the destabilization of w/o emulsions promoted by PEO-PPO block copolymers, this work applied tensiometry and Fourier transform infrared spectrometry with attenuated total reflectance (FTIR-ATR) to study the interface formed by these copolymers and the asphaltenic fractions of crude oil.

EXPERIMENTAL

Materials

The asphaltenes used in this study were extracted from a crude oil sample from the Campos Basin, donated by the Petrobras Research Center (CENPES). The characterization of this sample was shown in an earlier article¹²: water content = 0.05 wt %;

density = 21.2 gravity of American Petroleum Institute (API); and concentrations of saturates, aromatics, and asphaltenes = 40.7, 34.1, 22.9, and 2.4 wt %, respectively.

The PEO-PPO block copolymers used in this study as demulsifier additives were of the branched (*B*) and linear (*L*₁ and *L*₂) monofunctional types, donated by Dow Química, Brazil. The characterization of these samples was also shown in previous works,^{13,14} in which it was shown that the branched copolymer has an average molar mass of 11,600 Da and an EO/PO ratio of 0.19, while the linear copolymers have average molar masses of 3000 and 3600 Da and EO/PO ratios of 0.51 and 0.84, respectively, for samples *L*₁ and *L*₂.

The solvent *n*-heptane (P.A. purity, 99.5%) was used as received, and toluene was distilled and dried in alumina. Both solvents were obtained commercially from Vetec Química Fina, Brazil.

Methods

Extraction of the C7 Asphaltenes. Approximately 20 g of crude oil was placed in contact with 1 L of the asphaltene flocculant solvent (*n*-heptane) for 24 h under stirring and then filtered twice through filter paper at room temperature (25°C). This produced a solution of resins in paraffinic solvent, which was saved, and asphaltenes, denominated C7 for having been extracted with *n*-heptane as the solvent, as precipitates in the filter paper.

The asphaltenes that remained precipitated in the filter paper were placed in a cartridge and dissolved with the aromatic solvent dry toluene, in a proportion of 1 : 35 (g of oil/mL of solvent) in a balloon flask. Then, the solution was processed in a Soxhlet extractor until the solvent appeared clear. The dissolved asphaltenes were recovered after evaporation of the toluene in a Gerhardt Soxtherm rotary evaporator at a temperature of 80°C.

The concentrated solution of asphaltenes obtained from the Soxtherm evaporator was placed in a Pyrex beaker inside a hood for ~ 3 days to evaporate the residual solvent. The asphaltenes were then placed in closed flasks covered with aluminum foil to prevent their oxidation by the action of light.

Preparation of the Model Emulsions. The model emulsions, containing the dispersion of the C7 asphaltenes at 0.25% v/v in toluene, were prepared so as to contain 30.0% synthetic salt water. This water was formulated with a concentration of 55,000 ppm of salts (NaCl : CaCl₂ ratio of 10 : 1). The procedure to prepare the emulsions is described below.

- 70.0 mL of the asphaltene dispersion was placed in a 250-mL beaker.
- Then, the fluid was subjected to shear in a Polytron PT 3100 homogenizer at 8000 rpm with slow addition of 30.0 mL of salt water. After all the salt water was added, the system was left under stirring for 3 min at room temperature.

Preparation of the Solutions of 40% v/v Surfactants in Dry Toluene. A volume of 50 mL of a 40% v/v surfactant solution in dry toluene was prepared for each of the three demulsifiers. The solution was left to stabilize for a period of 24 h.

Measurement of Gravitational Water–Oil Separation by the Bottle Test. The gravitational separation of water from oil in

the model emulsions was measured by the bottle test. The tests were initially performed to evaluate the emulsions' stability without addition of the demulsifier (blank test), after which their stability was evaluated after addition of 100 ppm of each demulsifier evaluated.

For this purpose, 100.0 mL of each model emulsion was placed in graduated test tube suitable for the bottle test and swirled vigorously by hand for 1 min. Then, each tube was placed in a water bath at 25°C, and the water separation was read at intervals of 5, 10, 15, 20, 25, 35, 45, 55, and 65 min.

Next, the same procedure was performed after the addition of 25 μL of each demulsifier solution before the vigorous swirling at the start of the test.

The phase-separation efficiency was calculated by eq. (1):

$$EF_{A0} = (V_{AS}/V_{AT}) \times 100 \quad (1)$$

where EF_{A0} is the gravitational water–oil separation efficiency, in % by volume, V_{AS} the volume of water separated during the test, in mL, and V_{AT} the total volume of water in the tube, in mL.

Determination of the Water–Oil Interfacial Tension Values. The water–oil interfacial tension tests were performed in a Krüss K10T digital tensiometer, which works on the Du Noüy ring method, at a temperature of 25°C. Each test was performed in duplicate or triplicate, initially to evaluate the interfacial tension between the salt water and dispersion of asphaltenes alone, and subsequently the tension between the salt water and the asphaltene dispersions containing 100 ppm of each demulsifier.

Distilled and deionized water was used as a reference before each test to verify that all the instruments used in the test were clean, so as not to influence the results. All the tests involved addition of 12 mL of the denser phase (salt water) and 12 mL of the lighter phase (dispersion of asphaltenes), after which the system was left to stabilize for 30 min. Then, the same procedure was followed for each demulsifier solution, this time adding 6 μL of that solution (40% v/v) to the 12 mL of the asphaltene dispersion before its addition to the salt water.

Determination of the Refraction Index of the Aqueous Surfactant Solutions. The refraction index of a medium (n_m) is the ratio between the speed of electromagnetic radiation in a vacuum (c_0) and the speed of the same radiation in the medium (c_m), according to eq. (2).¹⁰

$$n_m = c_0/c_m \quad (2)$$

The refraction index was obtained in a Baush & Lomb refractometer, which calculates the deviation of a light ray as it passes from one medium to another with different density. By Snell's Law, the relative refraction index of the second medium in relation to the first is given by eq. (3),¹⁵ where i is the angle of incidence measured from the normal and r is the angle of refraction in relation to the normal.

$$n_m = \sin(i)/\sin(r) \quad (3)$$

To obtain the refraction index measurements, a circulating bath was coupled to the refractometer to maintain the temperature at 25°C. The branched (B) PEO-PPO block copolymer solutions were prepared in distilled water at concentrations of 0.00001, 0.003, 0.01, 0.03, 0.05, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.00% v/v, by means of successive dilutions.

FTIR-ATR Analyses. The aqueous copolymer solutions and solutions of asphaltenes in toluene were analyzed by FTIR using an ATR accessory.

Two crystals were used in this accessory: polycrystalline zinc selenide (ZnSe) and germanium (Ge).

The operating conditions of the FTIR-ATR apparatus were 2 cm^{-1} resolution and 100 scans.

Initially, aqueous solutions of each copolymer (B , L_1 , and L_2) were prepared at concentrations of 2, 1, 0.9, 0.7, 0.5, 0.3, 0.1, 0.05, 0.03, 0.01, 0.003, 0.001, 0.0003, and 0.0001% v/v by means of serial dilutions, to ascertain whether the technique was able to discern the start of micelle formation.

To determine the proper wavelength to evaluate the behavior of the surfactants in solution with toluene and in the asphaltene dispersions, solutions were prepared of the three block copolymers (B , L_1 , and L_2) at concentrations of 2.0, 1.0, 0.5, 0.1, 0.01, and 0.001% v/v by means of serial dilutions.

To analyze the spectra generated by the solutions of asphaltenes in toluene and later to perform the mixtures with the copolymers, asphaltene solutions were prepared at concentrations of 0.5, 0.25, and 0.05% v/v by means of serial dilutions.

Finally, to assess the influence of the variation of the copolymer concentration on the crystal/asphaltene dispersion interface, concentrations of these asphaltenes were prepared of 0.05, 0.1, and 0.25% v/v with copolymer concentrations of 1.0, 0.5, 0.1, 0.07, 0.05, 0.01, 0.001, and 0.0001% v/v.

RESULTS AND DISCUSSION

Water–Oil Gravitational Separation Tests

The water–oil gravitational separation measurements were performed by the bottle test, with the w/o model emulsions, where the aqueous phase was composed of salt water and the oil phase by the asphaltenes dispersed in toluene.

The asphaltene concentration in the oil phase was 0.25% v/v, the lowest concentration in the earlier tests that allowed obtaining sufficiently stable emulsions. All the tests were run in triplicate, with and without the presence of demulsifying additives based on linear and branched PEO-PPO block copolymers (Table II), at a concentration of 100 ppm.

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

The water separation efficiency results of the tests performed with the emulsions prepared without adding any demulsifier (blank tests) are shown in Figure 1. It can be seen that at the end of the test, the water separation was 18% v/v, allowing the use of this emulsion for study of the behavior in the presence of the additives.

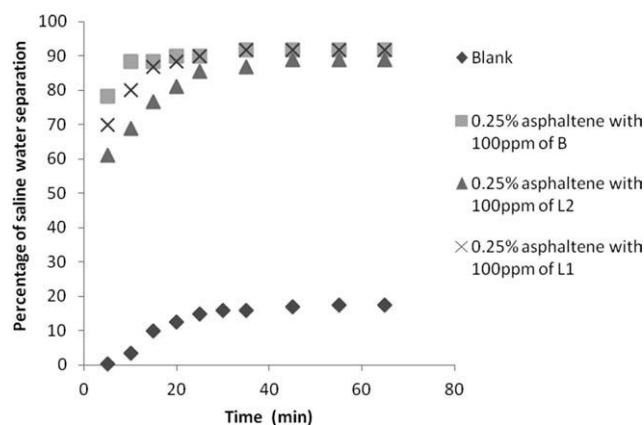


Figure 1. Gravitational separation of water from the model emulsion vs. time in minutes.

Of the three surfactants used, the branched copolymer broke down the emulsion the fastest: after 5 min the water separation was 78% v/v. Copolymer L_2 was slowest, only separating 60% v/v of the water after 5 min, while the speed of copolymer L_1 was intermediate between the other two surfactants.

Despite the differences in speed, the efficiency of the phase separation at the end of the test was virtually the same for all three surfactants studied: about 91.7% of the salt water was separated from the model emulsions.

These surfactants were used in earlier studies,^{13,14} where it was observed that the branched copolymer breaks down the emulsion faster and is also more efficient in breaking down synthetic w/o emulsions. This behavior is associated with its branched structure, where the EO and PO groups are more widely distributed in their molecular chains, thus facilitating the copolymer's dispersion between the phases of the w/o emulsion.

Water–Oil Interfacial Tension Tests

The interfacial tension between the oil phase (without asphaltene) and salt water phase was measured (blank tests) and compared with the values obtained between the salt water and this oil phase containing 100 ppm of surfactant (6 μ L of the 40% v/v surfactant solution in dry toluene). This procedure was performed in triplicate for each surfactant studied. The results are presented in Table I.

It can be seen that the interfacial tension between the salt water and toluene (emulsion without surfactant) was 30.5 mNm^{-1} ,

which declined to 14.8, 12.1, and 11.1 mNm^{-1} with the addition of the surfactants B , L_1 , and L_2 , respectively. These surfactants work by migration of their molecules to the interface, where they reduce the tension. The linear surfactants (L_1 and L_2) were slightly more efficient in reducing the interfacial tension, probably due to their linear structures, which might favor the packing of their molecules at the interface.

As expected, analysis of the salt water/oil phase emulsion (solution of 0.25% asphaltene in toluene) without the addition of any surfactant showed the surfactant character of asphaltene, which were able to reduce the interfacial tension of the salt water/toluene system.

We believe that the demulsification process occurs by removing asphaltene from the interface, with their place being taken by the added surfactant. This surfactant forms a less rigid interfacial film and thus facilitates the coalescence of the water droplets.

In the case of the systems analyzed, the interfacial tension results indicate the interface is basically composed of surfactant molecules, with some asphaltene molecules as well, as the interfacial tension values after the surfactant's addition were slightly higher than those observed for the systems without asphaltene.

Finally, despite the reduced interfacial tension of the systems with addition of the surfactants, these were not capable of stabilizing the w/o emulsions, behavior expected for products considered to be good demulsifiers.

Determination of the Refraction Index of the Aqueous Surfactant Solutions

To evaluate and select the most suitable crystal for the FTIR-ATR analyses (between zinc selenide and germanium), we measured the refraction index of the aqueous solutions of the branched surfactant to calculate the radiation penetration depth in the solution, by means of eq. (4),¹⁵ where λ_c is the wavelength in the crystal, θ is the angle of incidence, and n_s and n_c are the refraction indices of the sample and crystal, respectively.

$$d_p = \frac{\lambda_c}{\sqrt{2\pi[\sin^2\theta - (n_s/n_c)^2]}} \quad (4)$$

In this technique, which is based on the total radiation reflected when it reaches the crystal–sample interface, it is necessary to know how far the radiation manages to penetrate in the sample so that the spectrum can be correctly analyzed, as the

Table I. Results of the Interfacial Tension Between Salt Water and Dispersions of Asphaltene

Sample	Interfacial tension ± 0.1 (mN m^{-1}) ^a			
	Emulsion without surfactant	Emulsion with surfactant B	Emulsion with surfactant L_1	Emulsion with surfactant L_2
Blank ^b	30.5	14.8	12.1	11.1
C7 Asphaltene	23.4	15.2	12.6	11.5

^aTests performed in triplicate; results are the mean \pm the respective standard error.

^bSalt water/toluene system.

Table II. Refraction Index of the Branched Copolymer Solutions and Penetration Depth According to the Crystals Chosen

Concentration (% R)	Solution (n_2)	δ Ge ($n_1 = 4.0$)	δ ZnSe ($n_1 = 2.4$)
0.00001	1.3321	0.1023	0.8664
0.00003	1.3322	0.1023	0.8667
0.00010	1.3320	0.1023	0.8661
0.00030	1.3320	0.1023	0.8661
0.00100	1.3321	0.1023	0.8664
0.00300	1.3320	0.1023	0.8661
0.01000	1.3317	0.1022	0.8652
0.03000	1.3330	0.1025	0.8690
0.05000	1.3332	0.1025	0.8696
0.10000	1.3332	0.1025	0.8696
0.30000	1.3335	0.1026	0.8705
0.50000	1.3337	0.1026	0.8711
0.70000	1.3341	0.1027	0.8723
0.90000	1.3347	0.1028	0.8740
1.00000	1.3344	0.1027	0.8731

δ , penetration depth; n_1 , refraction index of the crystal; n_2 , refraction index of the solution.

concentration of substances that absorb light can vary according to the distance from the crystal.

Table II shows the refraction indices of the branched copolymer solutions and the radiation penetration depth for each solution and each crystal.

The results show that even with a variation on the order of 10^5 in v/v % in the concentration of the branched surfactant in the solution, the refraction index only varied in the third decimal place and the medium became more refracting as the copolymer's concentration increased. Also, the higher the solution's refraction, the greater was the radiation's penetration in this medium. In relation to the crystals, germanium only allowed about one-eighth the penetration of zinc selenide, besides being less sensitive to the variation in the sample's refraction index. As the aim of this study was to elucidate whether the copolymers act at the interface with asphaltenes and also to validate the FTIR-ATR technique for this purpose, the less the penetration the better the efficiency.

FTIR Analyses

We studied two aspects with this technique: determination of the critical micelle concentration (CMC) of the aqueous solutions of the PEO-PPO block copolymers and evaluation of the interface of the solutions containing asphaltenes and these copolymers.

Determination of the CMC Values. Initially, we analyzed the aqueous solutions of the three copolymers (L_1 , L_2 , and B) at various concentrations with the intent to validate the FTIR-ATR technique for the study of crystal/aqueous copolymer solution interfaces and thus to verify whether it is possible to observe

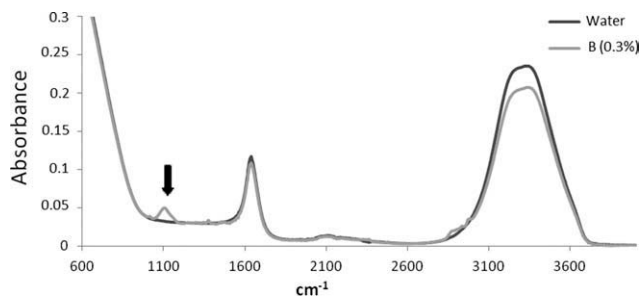


Figure 2. Spectrum of water and the branched copolymer solution with the zinc selenide crystal.

the behavior of the copolymers in solution, that is, to determine the CMC values.

To study the spectra generated (absorbance \times wavelength of incident radiation) of the PEO-PPO block copolymers, we evaluated the ratio of the absorption band at $\sim 1106 \text{ cm}^{-1}$, corresponding to the absorption of the C—O—C group of the copolymers, with the absorption at 1640 cm^{-1} , related to the O—H group of the water. The purpose of calculating the ratio of these absorbances is to remove the effect of the optical path, according to the Lambert–Beer law.¹⁶ We chose the absorption band of 1106 cm^{-1} because water does not interfere at this frequency, as can be observed in Figure 2. The same behavior was observed for all the surfactants.

As can be seen in Figure 3, the absorption band at 1106 cm^{-1} was not detected until a certain copolymer concentration, from

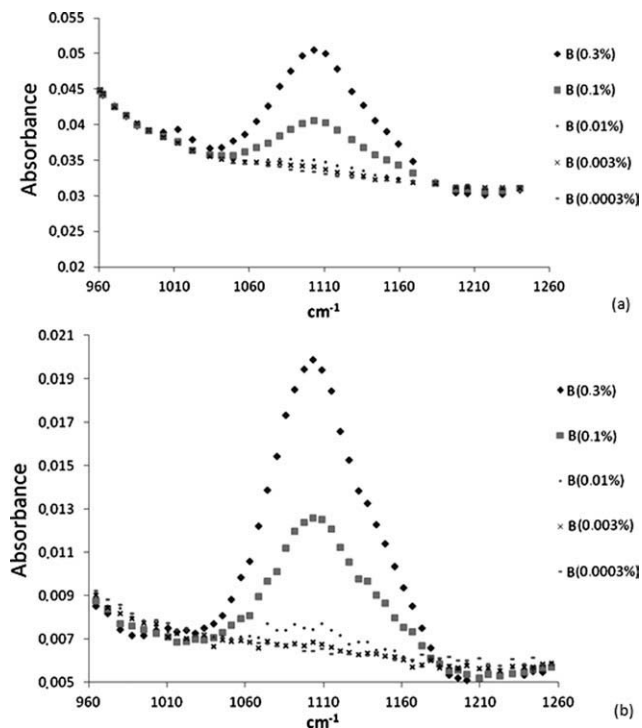


Figure 3. Enlarged spectra containing analyses of the aqueous solution of the branched copolymer by FTIR-ATR: (a) with the zinc selenide crystal and (b) with the germanium crystal.

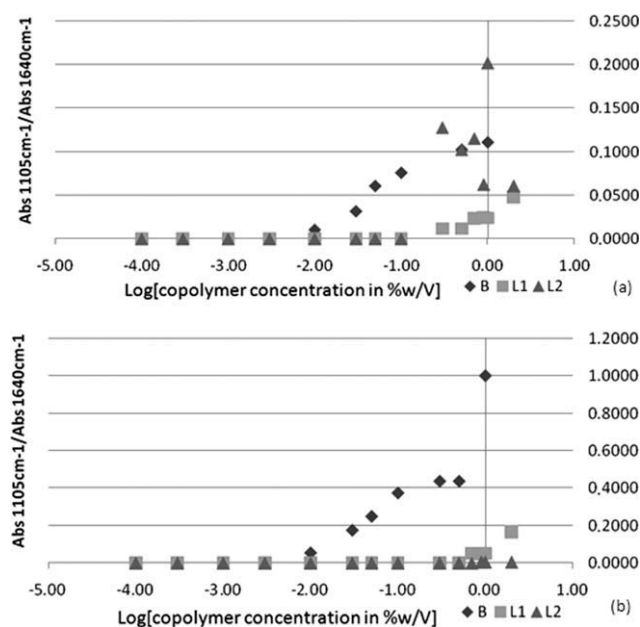


Figure 4. Ratio of the absorbances of the copolymers (L_1 , L_2 , and B) with the logarithm of their concentrations obtained by FTIR-ATR: (a) with the zinc selenide crystal and (b) with the germanium crystal.

which point the absorbance started to increase with rising concentration. This behavior was observed for all the copolymers and with both crystals. Figure 4 allows better observation of the relation between intensity of the absorption bands and the copolymer concentrations.

CMC values measured by the FTIR-ATR technique were obtained when the ratio of the absorption bands located at 1105 and 1640 cm^{-1} was different from zero, indicating that the apparatus was capable of capturing the signal of each copolymer. The CMC values obtained by FTIR-ATR and tensiometry¹⁷ are shown in Table III. It can be seen that the results of the two techniques agree. Copolymer L_2 did not present a curve similar to those of the other copolymers, i.e., with an increase in its concentration, there was an increase in the absorption band ratios. This result confirms what was observed previously by tensiometry: the study of the surface of the aqueous phase of copolymer L_2 does not permit observation of the formation of micelles.

This behavior indicates a good correlation in the observation of the solid–liquid interface (by FTIR-ATR) and the liquid–air interface (by tensiometry). Besides this, the germanium crystal

Table III. Comparison Between the Values Obtained by FTIR and Tensiometry

Copolymer	FTIR—crystal :		Tensiometry ¹⁷
	zinc selenide	germanium	
	CMC (%)	CMC (%)	CMC (%)
B	0.01	0.01	0.01
L_1	0.3	0.7	0.7
L_2	–	–	–

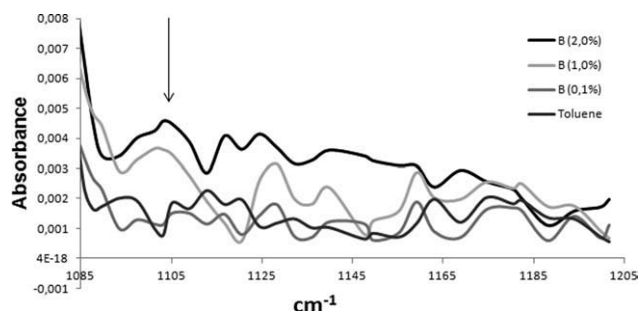


Figure 5. Enlarged spectrum of the solution of copolymer B in toluene with germanium crystal.

is more effective. This coherent because, as already discussed, with its use the radiation only penetrates in the solution about one-eighth as much as when using the zinc selenide crystal. Therefore, the analysis with asphaltenes and copolymers was performed with the germanium crystal.

Study of the Interface of the Solutions Containing Asphaltenes and the PEO-PPO Block Copolymers.

In the study of the interface of the solutions of asphaltenes and PEO-PPO block copolymers, all the solutions were prepared with toluene as the solvent. Therefore, the spectra were analyzed of the solutions with different concentrations of the branched copolymer for the purpose of identifying the absorption band that could be used in this study. Figure 5 shows that the absorption band located at 1106 cm^{-1} can be used to discern the presence of copolymers in this solution, due to the increase of its intensity with increasing copolymer concentration. This behavior was similar for the two linear copolymers as well (L_1 and L_2).

The concentration of asphaltenes in toluene was also varied, but it was not possible to observe an absorption band that stood out in relation to the solvent, as shown in Figure 6. Thus, it was not possible to observe an absorption band in the solution of asphaltenes that stood out in relation to the solvent, so it was not possible to use a specific band for the asphaltenes, as was the case of the copolymer, to directly assess their behavior at the interface.

To calculate the ratio with the absorption band at 1106 cm^{-1} , we chose the absorption band located at 2923 cm^{-1} , which is related to the axial deformation of the CH_2 and CH_3 groups that are present in all the compounds in the solutions analyzed: asphaltenes, surfactants and to solvent toluene itself. This allows monitoring the adsorption of the surfactant at the crystal/surfactant solution interface in the presence of asphaltenes.

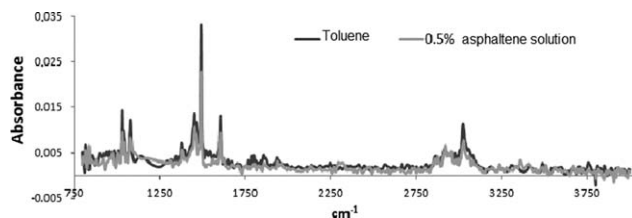


Figure 6. FTIR-ATR spectrum obtained with the crystal germanium of toluene and 0.5% asphaltene solution.

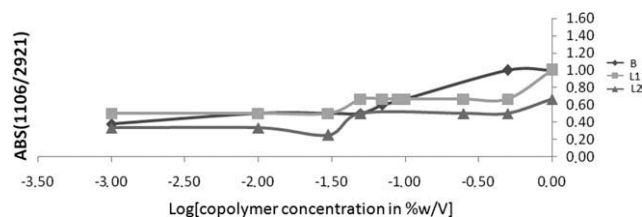


Figure 7. Graph of the ratio of absorbance bands (1106/2921) in function of the logarithm of the copolymer concentration at a fixed asphaltene concentration of 0.05%.

After preliminary analyses, we studied the effect of increasing the concentration of the copolymers with a determined concentration of asphaltenes.

From the graph shown in Figure 7, which was obtained for the lowest concentration of asphaltenes analyzed, it can be seen that the curves have the same shape: the ratio of the absorption bands selected increases with increasing surfactant concentration in the solution to a certain concentration, after which this ratio remains practically constant. It can also be seen that the concentration of the branched copolymer at the interface has the greatest variation, followed by the linear copolymer L_1 . For higher concentrations of asphaltenes (Figures 8 and 9), an increase in the ratio of absorbances for the branched copolymer was only observed at the highest concentrations of this copolymer. For the other copolymers, no significant increase in these values was observed when comparing the final and initial concentrations of these copolymers, suggesting that at high asphaltene concentrations, copolymers L_1 and L_2 are not effective in removing these compounds from the interface analyzed.

It can therefore be concluded that although the surfactants L_1 and L_2 were adsorbed at the interface composed by the asphaltenes (as shown by the results in Table I), they were not able to remove the asphaltenes as was the case of the branched surfactant, which has greater volume.

A possible explanation why copolymers L_1 and L_2 were efficient at low concentrations, but not at high ones is that at high concentrations, the asphaltenes, through their intermolecular interactions, could be forming a more rigid film at the interface, impeding removal of the asphaltenes even more.

This indicates that at first, copolymer B should be more effective in the process of demulsifying crude oil emulsions. These results are coherent with those obtained earlier in the study of the destabilization of the model emulsions prepared with the

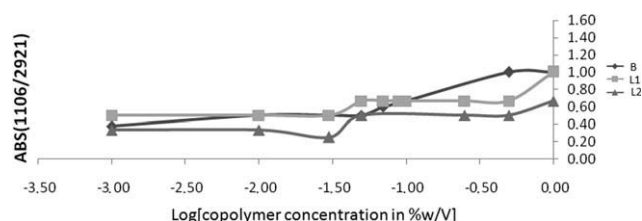


Figure 8. Graph of the ratio of absorbance bands (1106/2921) in function of the logarithm of the copolymer concentration at a fixed asphaltene concentration of 0.10%.

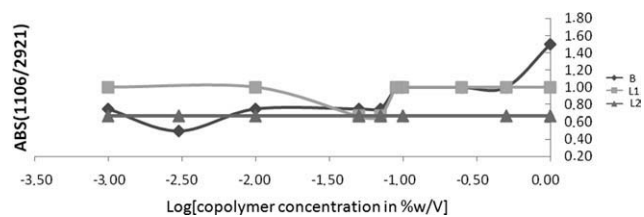


Figure 9. Graph of the ratio of absorbance bands (1106/2921) in function of the logarithm of the copolymer concentration at a fixed asphaltene concentration of 0.25%.

asphaltenes, where copolymer B obtained the efficiency of 92% more quickly than the other two copolymers.

In a previous study,¹⁴ it was also shown that copolymer B was more effective in separating the phases of w/o emulsions, by promoting this separation more quickly and efficiently.

The fact that the three copolymers presented the same efficiency at the end of the demulsification tests (Figure 1) can be explained by the fact that the model emulsion prepared already was unstable, and any alteration at its interface provoke phase separation.

CONCLUSIONS

Among the three surfactants investigated in this study, the PEO-PPO block copolymer with a branched structure (B) worked fastest in breaking down the emulsion. But overall, the efficiency in separating the phases of the model emulsion composed of salt water dispersed in asphaltenes in dissolved in toluene was the same for the three surfactants: 91.7% of the salt water was separated from the model emulsion.

The measures of the interfacial tension between the saline solution of surfactants and solution of asphaltenes in toluene indicate that the interface is composed of asphaltene molecules together with molecules of the surfactants.

The measurement of the CMC of the aqueous solutions of the PEO-PPO block copolymers evaluated in this study by the FTIR-ATR technique presented results that agreed with those obtained by tensiometry. This indicates a good correlation of the results obtained when evaluating water/air (tensiometry) and water/crystal (FTIR-ATR) interfaces.

The best results of the FTIR-ATR technique were obtained using the germanium crystal in the ATR accessory.

The FTIR-ATR technique was effective in studying the interface of the solutions composed of block copolymers based on poly(ethylene oxide)-poly(propylene oxide) and asphaltenic fractions of crude oil, showing that for the surfactant with greatest demulsification efficiency (copolymer B), a greater variation in the copolymer concentration was obtained at this interface.

ACKNOWLEDGMENTS

The authors thank the Brazilian National Research Council (CNPq), Carlos Chagas Filho Foundation for Research Support (FAPERJ), and PETROBRAS for financial support, and the Dow Chemical and PETROBRAS companies for providing the samples.

REFERENCES

1. Kokal, S. Crude-oil emulsions-a state-of-the-art review. Society of Petroleum Engineers, SPE Production & Facilities: Houston, Texas, USA, February **2005**.
2. Speight, J. G. *SPE Journal* **2004**, *59*, 467.
3. Santos, R. G.; Mohamed, R. S. Avaliação da molhabilidade de oleodutos através de medidas de ângulo de contato. Efeitos de asfaltenos e ácidos naftênicos do petróleo. 2° Congresso Brasileiro De P&D em Petróleo e Gás: Hotel Glória, Rio de Janeiro, **2003**.
4. Mullins, O.; Groenzin, H.; Buch, L.; Gonzalez, E. B.; Andersen, S. I.; Galeana, C. L. *Fuel* **2003**, *82*, 1075.
5. Chang, C. L.; Fogler, S. H. *Langmuir* **1994**, *10*, 1749.
6. Chang, C. L.; Fogler, S. H. *Langmuir* **1994**, *10*, 1758.
7. Kokal, S.; AL-Juraid, J. Quantification of various factors affecting emulsion stability: Watercut, temperature, shear, asphaltene content, demulsifier dosage and mixing different crudes. *Society of Petroleum Engineers*: Houston, Texas, USA, **1999**, 56641.
8. Kokal, S. Crude oil emulsions: A state-of-the-art review. SPE Annual Technical Conference and Exhibition, 77497, San Antonio, Texas, USA, September 29, **2002**.
9. Midttun, Ø.; Kallevik, H.; Sjoblom, J.; Kvalheim, O. J. *Colloid Interface Sci.* **2000**, *22*, 262.
10. McLean, J. D.; Kilpatrick, P. K. *J. Colloid Interface Sci.* **1997**, *196*, 23.
11. Daniel-David, D.; Pezron, I.; Dalmazzone, C.; Noik, C.; Clause D.; Komunjer, L. *Colloids Surf. A* **2005**, *270-271*, 257.
12. Fraga, A. K.; Santos, F. R.; Mansur, C. R. E. *J. Appl. Polym. Sci.* **2012**, *124*, 4149.
13. Mansur, C. R. E.; Aparecida, F. C. L.; Mauro, C.; González, G.; Lucas, E. F. *J. Appl. Polym. Sci.* **2007**, *106*, 2947.
14. Pacheco, V. P.; Spinelli, L. S.; Lucas, E. F.; Mansur, C. R. E. *Energy Fuels* **2011**, *25*, 1659.
15. Bueno, W. A. Manual de Espectroscopia Vibracional; McGraw-Hill, Ltda: São Paulo, Brazil, **1900**.
16. Stuart, B. H. Infrared Spectroscopy: Fundamentals and Applications; Wiley: Chichester, UK, **2004**.
17. Silva, P. R. S.; Mauro, A. C.; Mansur, C. R. E. *J. Appl. Polym. Sci.* **2009**, *113*, 392.