

INTERFACIAL PROPERTIES OF THE PRODUCTS OF OZONOLYSIS OF HAMACA CRUDE OIL

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ABSTRACT

A sample of extra-heavy Hamaca crude oil, dissolved in carbon tetrachloride, was oxidated with ozone for a few minutes. The reaction mixture was washed with a concentrated solution of HCl, neutralized with sodium carbonate, and the products were extracted from the aqueous phase. The products were characterized by using gel permeation chromatography (GPC), elemental analysis, ^1H nuclear magnetic resonance (NMR), and Fourier transformed infrared (FTIR) techniques. The results of the analyses show that the products have lower molecular weights, lower aromatic character, and higher oxygen content than the original sample. They also indicated that these products were mainly carboxylic acids, aldehydes, and/or ketones, with a higher affinity for water than for carbon tetrachloride, the organic solvent that was used. Interfacial tension γ measurements (water–toluene) performed with these products showed a linear dependence with concentration, where γ dropped from 32 to about 7.7 dinas/cm at the apparent critical Micelle concentration (cmc) (2 g/L). Larger quantities of a commercial sample of nonylphenol ethoxylated were needed for an equivalent γ drop. In another experiment the above oxidated product was mixed with

Furrial asphaltene in toluene, and γ measurements were performed as above and compared with the values obtained for the same experiment using the ethoxylated surfactant. In this case, the γ values for the oxidated product were higher, suggesting a better adsorption on the asphaltene colloids. These preliminary results suggest that these oxidated products could be employed as general surfactants in the oil industry.

1. INTRODUCTION

Venezuela has the largest heavy and extra-heavy oil deposits in the world. Over 70% of the Venezuelan oil resources are comprised of these type of crudes (1). Due to the low commercial value of these materials and processing difficulties, these oils present a big challenge for Venezuela regarding production, transportation, and refining. The development of *Orimulsión*[®], a crude oil-in-water emulsion, and some refining catalytic processes are among the exploitation technologies used in Venezuela with these crudes.

The *Orimulsión*[®] is employed as combustible in some places as a substitute for carbon. However, *Orimulsión*[®] demand is very low, aside for the environmental regulation limiting its use.

Aqueous conversion is a relatively new process now in the development stage in refineries, and some results at the bench scale are encouraging (2). The needed hydrogen is obtained from the catalytic conversion of water.

The usual catalytic processes are expensive due to the sophisticated equipment needed and the use of high pressures and temperatures (3,4). Improving these methods will require large investments, and therefore alternative routes are sought. In this sense ozonolysis is a possibility.

Ozonolysis has been used previously in the treatment of Hamaca asphaltene solutions in carbon tetrachloride (5). The results obtained suggest that asphaltenes could be converted to a mixture of small compounds ($M_n \sim 400$), mainly formed by carboxylic and carbonylic compounds. This treatment was also employed with the Hamaca crude yielding products of potential commercial value (6,7). In this work, the interfacial properties of the ozonolysis of the Hamaca crude oil are analyzed, and its possible use as a surfactant is discussed.

2. EXPERIMENTAL

A 500-ml solution of crude oil (5000 mg/l) in CCl_4 was prepared and 645 mg of ozone were added using commercial equipment (O_3 Associates) with a capacity

of 100 mg/min as determined by the iodine method (8). During ozone addition the solution was sonicated, 100 ml of HCl 6 M were added, and the mixture was stirred for one hour, leaved until the clear separation of the two layers. Then the mixture was neutralized with NaHCO₃ and the organic layer (OL) was separated and the aqueous layer (AL) was extracted with dichloromethane. After working up the yield of product from the OL was 290 mg and the AL was 585 mg.

Obtained products were characterized by using gel permeation chromatography (GPC), elemental analysis, ¹H nuclear magnetic resonance (NMR), and Fourier transformed infrared (FTIR) techniques.

Mean molecular weights were measured for both the ozonated products and their respective blanks. This was done by means of GPC, on a Perkin Elmer model 3-B Pro chromatograph, coupled to a model LC-75 UV detector. Calculations were performed by using a program supplied by Perkin Elmer Co.

IR spectra were recorded on a Perkin Elmer FTIR model 1760X spectrometer, fitted with a Spectra-Tech 'collector' diffuse reflectance accessory and employing an accumulation of 10 scans at 4 cm⁻¹ resolution.

¹H NMR spectra were obtained on a Jeol model Eclipse 270 spectrometer operating at 270 MHz. Measurements of carbon, hydrogen, and nitrogen contents were performed by means of a Perkin Elmer model 2400 analyzer.

Interfacial tension measurements were carried out at the toluene–aqueous interface using a Lauda, TE1CA-M, model which allows measurements above 1 mN m⁻¹ at 25°C.

3. RESULTS AND DISCUSSION

Some of the most important properties of the ozonated samples and their respective blanks are compared in Table 1, where the mean molecular weights obtained by GPC are shown. The aliphatic hydrogen content and elemental analysis are also shown. It is observed that the molecular weight of the aqueous layer of the ozonated sample is substantially lower than that of its respective blank. This suggests that the ozonolysis products have smaller mean size than the original sample, thus indicating that fragmentation occurs during the process. On the other hand, the differences among the Mn values of the products in the organic layer and those of their blanks are within the error of the method, i.e., less than 10%. Therefore, we can say that they have the same mean molecular weight. This result suggests that most of the ozonated products have high affinity for water and hence the most relevant changes will be observed when comparing the properties of the aqueous products with their blanks. That is the case for the aliphatic hydrogen content of every sample shown in Table 1, this value being systematically higher in the AL compared to the OL and the blank. This indicates that ozone reacts with

the aromatic fraction of the sample producing compounds with higher polarity than the original ones, which favors its solubility in water. Similar results were observed by Lugo when treating solutions of asphaltenes in CCl_4 (5).

Another important aspect observed in Table 1 is the (S + O) content. This was calculated by subtracting the (C + H + N) content from the total. The observed values are higher in the ozonated products compared to the blanks. This is an expected result due to the fact that there will be two oxygen atoms for every C=C bond, once the reaction takes place (9). It is remarkable that the higher content of (S + O) is observed in the products of the aqueous fraction, in agreement with the comments about the higher polar character of this sample.

A final observation on Table 1 concerns the content of nitrogen; it has not been detected in the AL and is observed in both, the original sample and the organic fraction after the ozonation process. Between these two, the latter is smaller than the former. This result is similar to the observations of Escobar in his study, "Degradación Oxidativa del Crudo Hamaca por Ozonolisis" (7). Nevertheless, Escobar reports total elimination of nitrogen in the organic layer and its presence in the aqueous fraction; in our study the content of nitrogen decreases in the organic phase, but it is not detected in water. This could be due to the shorter time of reaction in our study compared to his. If we accept this argument, the decrease in the amount of nitrogen can be related to the addition of oxygen to the molecules of the sample. These results, together with those obtained by Escobar, suggest that in ozonolysis, the elimination of nitrogen does not occur as much as observed in other processes utilized to convert crude oils (10,11).

As a whole, the results of Table 1 show that the most relevant changes are observed in the aqueous fraction. This is more evident when the ^1H NMR spectra of the different samples are compared to each other. Figure 1 shows the spectra of the ozonated organic layer (a) and its blank (b). Although there are some differences, they are not remarkable. The signals due to aromatic protons are slightly stronger and those of the aliphatic protons appear overlapped to each other.

The spectra of the ozonated aqueous layer (a) and its blank (b) are shown in Figure 2. There are relevant differences between them. The ozonated sample shows several signals between 2 and 5 ppm that can be readily assigned to H atoms

Table 1. Some of the Most Important Properties of the Ozonated Samples and Their Respective Blanks

Muestra	Mn (Daltons)	% Hal	C	H	N	(S+O) ^a
ALB	500	93.64	80.85	9.89	—	9.26
AL	300	96.69	72.71	8.36	—	18.93
OLB	280	93.63	81.50	9.83	0.57	9.10
OL	320	90.24	76.95	9.60	0.31	13.14

^aDetermined by difference.

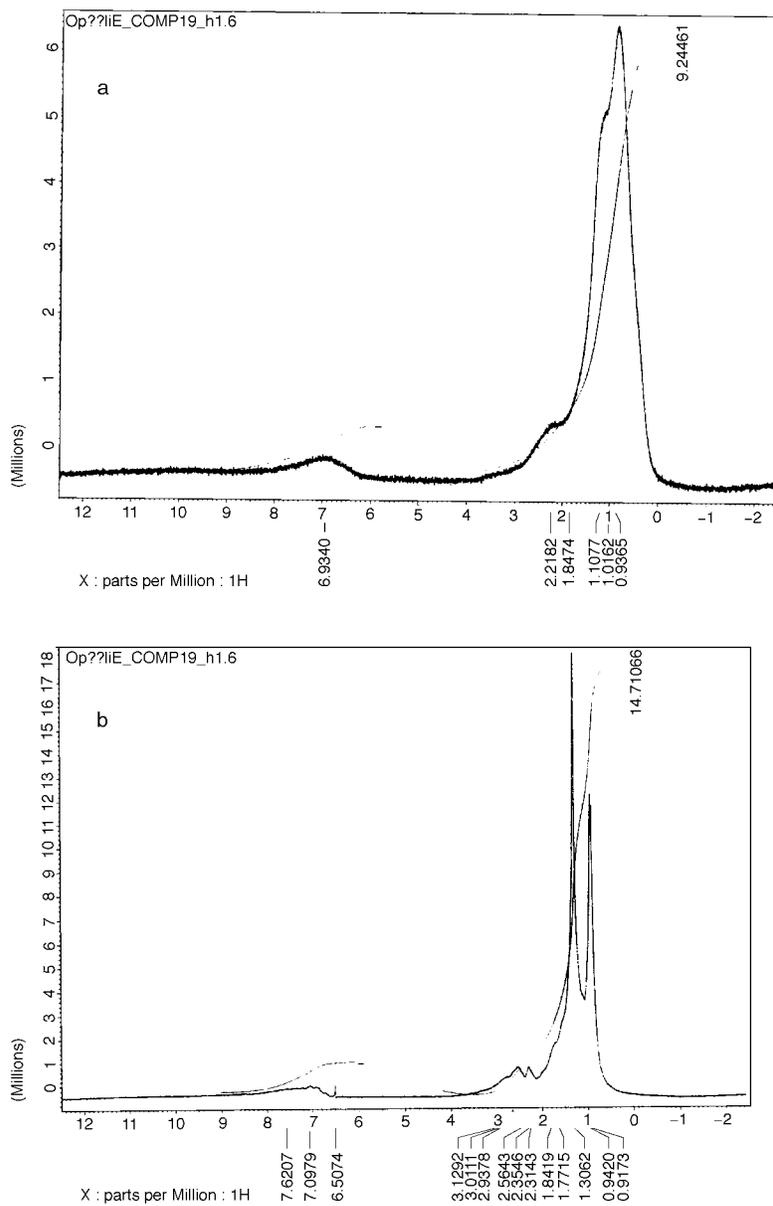


Figure 1. ¹H NMR spectra of the ozonated organic layer (a) and its blank (b).

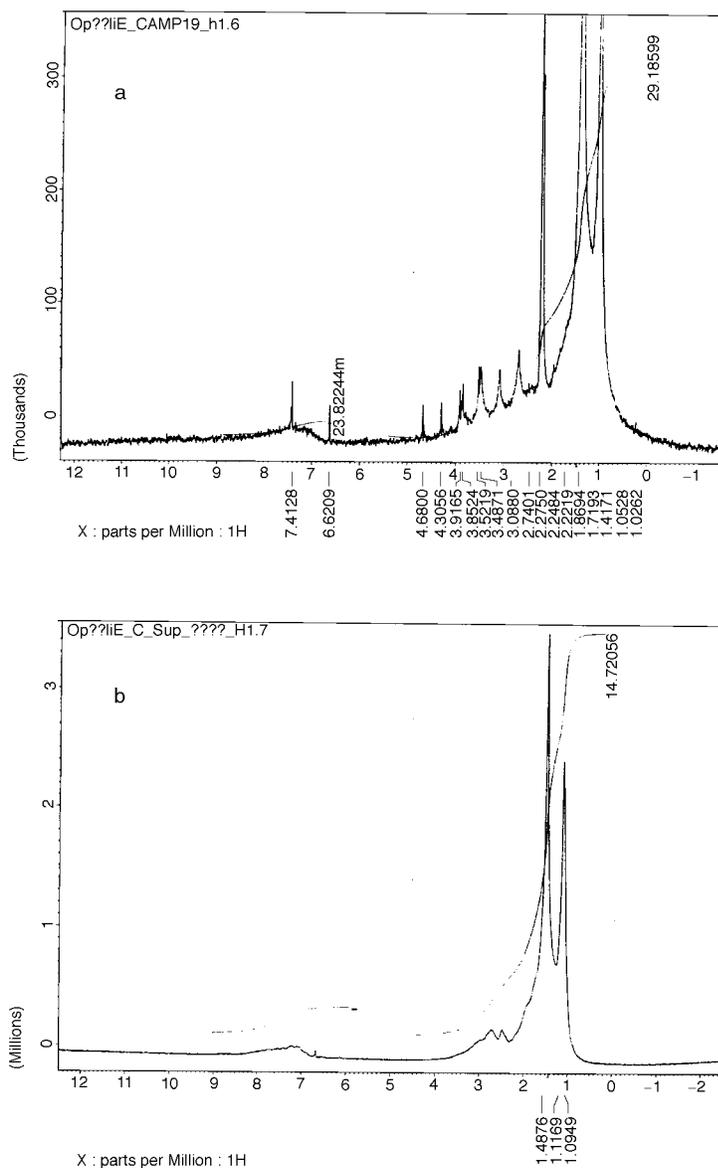


Figure 2. ^1H NMR spectra of the ozonated aqueous layer (a) and its blank (b).

bonded to C—O, i.e., H—C—O. These signals are not observed in the spectrum of the blank, thus confirming that the compounds with higher polar character are mainly contained in the aqueous fraction after ozonation.

3.1. Analysis of the FTIR Spectra of the Ozonated Samples and Their Blanks

Figure 3 shows the IR spectra of the ozonated products in the aqueous layer (a) and its blank (b). Bands at 2924 cm^{-1} and 2853 cm^{-1} , respectively assigned to aromatic and aliphatic C—H stretchings, are observed in the latter. Additional

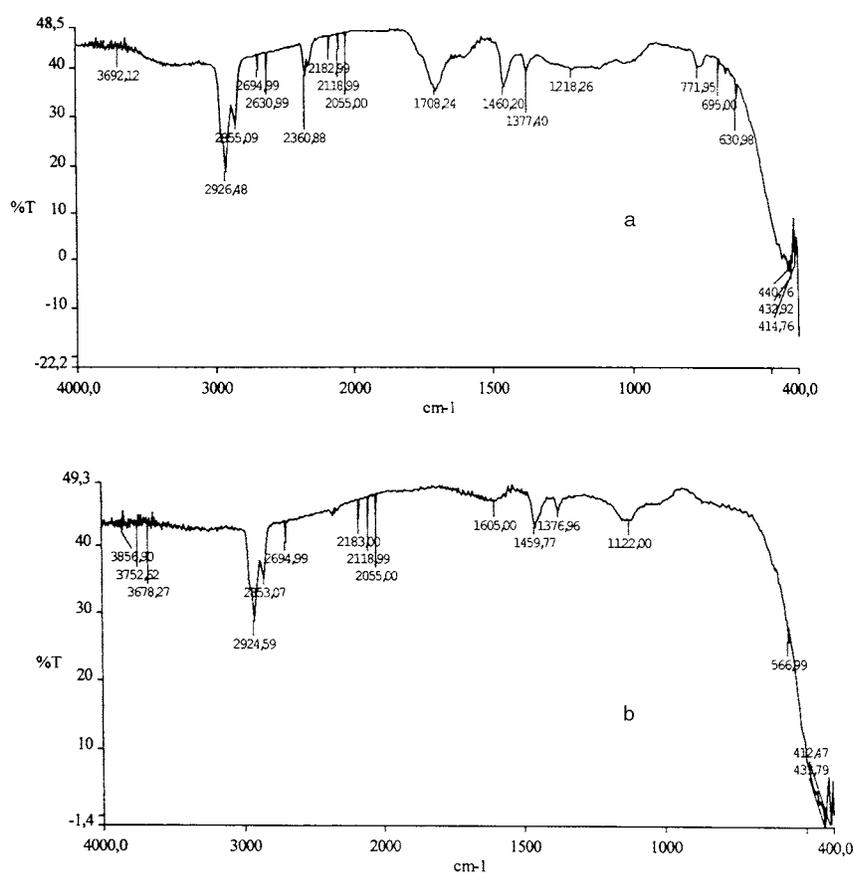


Figure 3. FTIR spectra of the ozonated aqueous layer (a) and its blank (b).

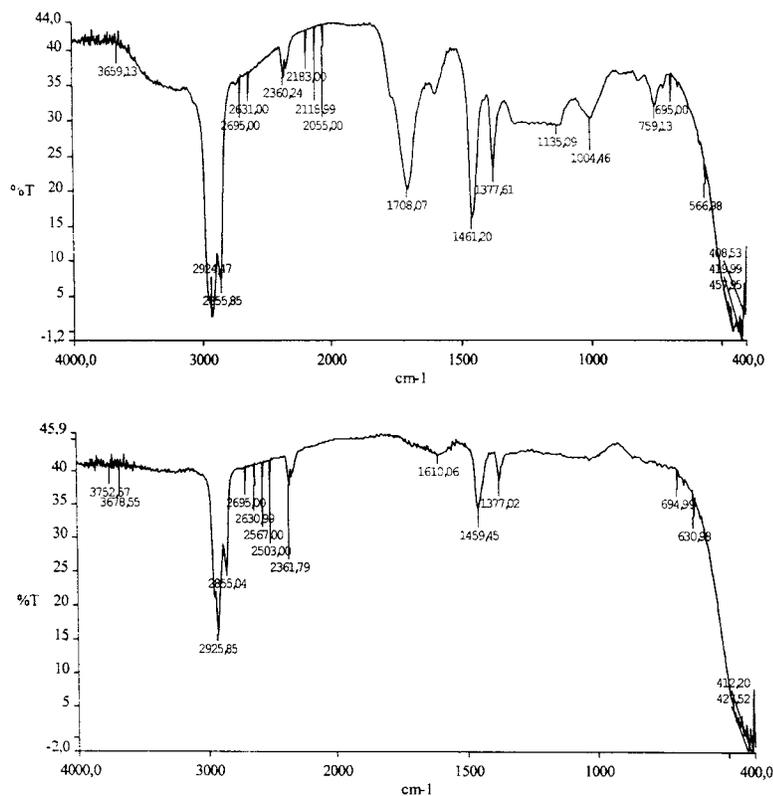


Figure 4. FTIR spectra of the ozonated organic layer (a) and its blank (b).

important features are the bands at 1605, 1460, 1378, and 1120 cm^{-1} , respectively corresponding to the aromatic C—C stretching, the asymmetric flexion of the aliphatic C—H, the symmetric flexion of the aliphatic C—H, and the symmetric flexion of the aromatic C—H (Silverstein et al., 1973). Conversely, the IR spectrum of the AL confirms the presence of carboxylic acids. It shows the stretchings of O—H and C=O at 3430 and 1708 cm^{-1} , respectively.

Figure 4 shows the IR spectra of the ozonated products in the organic layer (a) and its blank (b). The bands in Figure 4b are practically the same as for the blank of the aqueous fraction, except for a band at 1122 cm^{-1} , assigned to the symmetric flexion of the aromatic C—H. The spectrum of the organic fraction is similar to that of the aqueous layer. The only difference is the higher intensity of the O—H and C=O bands at 3430 and 1708 cm^{-1} , respectively. This is due to the fact that the sample was more concentrated in the organic phase.

As a general conclusion, GPC, elemental analysis, $^1\text{H NMR}$, and FTIR spectroscopies have shown that the ozonated products have lower molecular weight, lower aromatic character, and higher oxygen content than the original samples. Carboxylic acids and carbonyl compounds are the main products, with higher affinity for water than CCl_4 .

3.2. Comparison of the Tensio-Active Potential of Ozonolysis Products with the One for a Synthetic Surfactant

With the objective of comparing the tensio-active properties of ozonolysis products with the one for nonylphenol ethoxylated (NFE), a synthetic surfactant, we measured the changes in interfacial tension γ_c with concentration in the presence and absence of an asphaltene from Furrial crude oil, a crude with precipitation problems. The results are shown in Figures 5–8.

Figure 5 is a plot of interfacial tension water–toluene against concentration of NFE, where at 5000 mg/l the interfacial tension is 7.3 dinas/cm. Besides a linear relationship is obtained in this case.

A similar study was carried out with the ozonolysis product obtained from the aqueous layer (see above). These results are shown in Figure 6, where it is shown that the interfacial tension falls with concentration up to 7.7 dinas/cm for a concentration of 2000 mg/l, and after a slight increase it remains constant

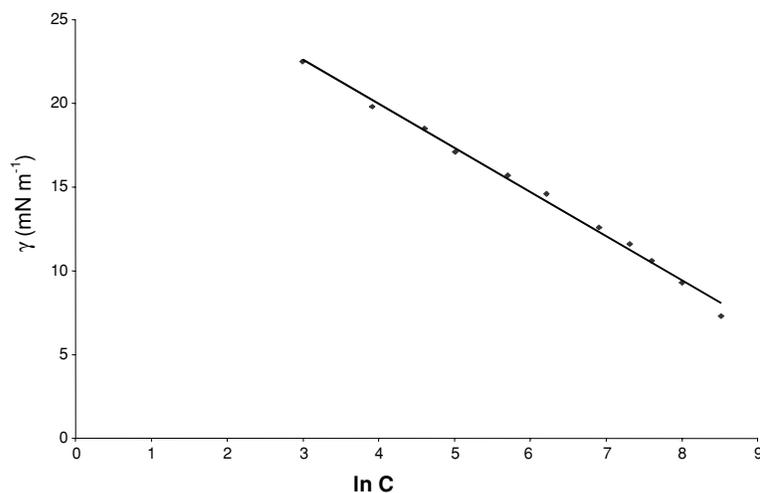


Figure 5. γ vs $\ln C$ curve for nonilphenoethoxilate. Condition: acidificated distilled water, samples diluted in toluene at 25°C .

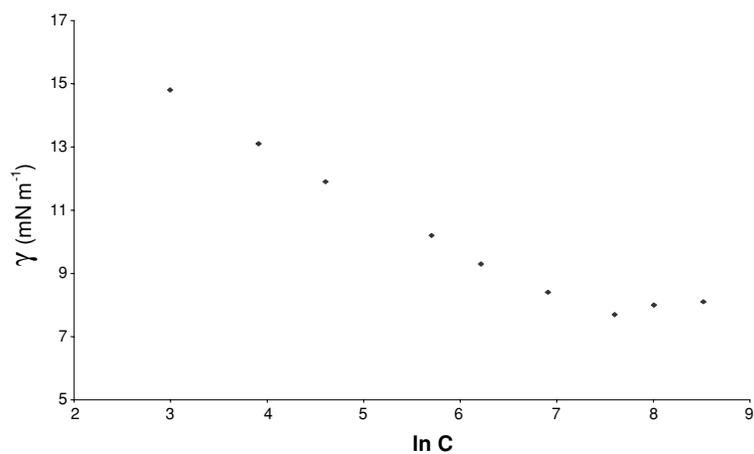


Figure 6. γ vs $\ln C$ curve for ozonolysis products (AL). Condition: acidificated distilled water, samples diluted in toluene at 25°C.

with concentration, suggesting the formation of micelles and a CMC value near 2000 mg/l.

The above study was also performed in the presence of Furiial asphaltenes. In both cases asphaltenes solutions of 5000 mg/l were used. The results for NFE and the ozonolysis products are shown in Figures 7 and 8, respectively.

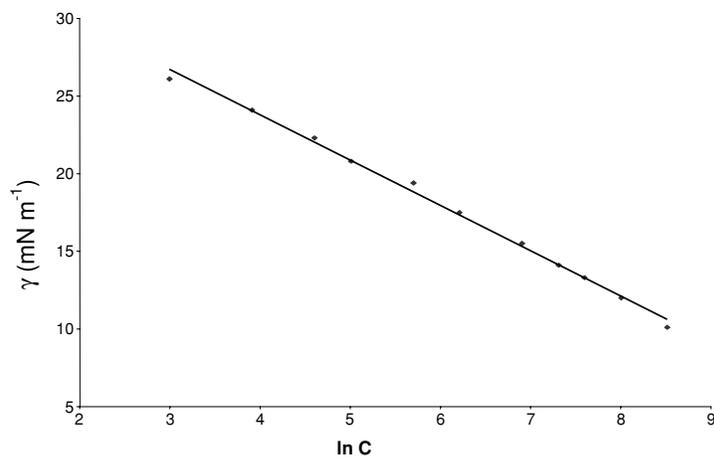


Figure 7. γ vs $\ln C$ curve for nonilphenoethoxilate + asphaltene (5000 ppm). Condition: acidificated distilled water, samples diluted in toluene at 25°C.

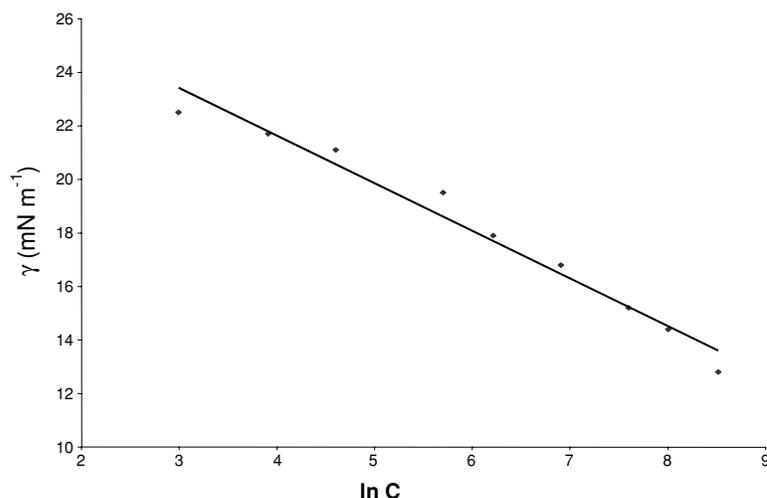


Figure 8. γ vs $\ln C$ curve for ozonolysis products (AL) + asphaltene (5000 ppm). Condition: acidificated distilled water, samples diluted in toluene at 25°C.

A linear plot was obtained in Figure 7 with the interfacial tension falling up to 10 dinas/cm, whereas for the ozonolysis product a reduction to 12.8 dinas/cm was observed (Fig. 8). These results show that the interfacial activity of NFE is similar to the ozonolysis products, suggesting that the commercial surfactant could be substituted.

It should be mentioned that when the results in Figure 8 are plotted as interfacial tension vs $\ln C$, a linear relationship was found with no evidence of a CMC.

CONCLUSIONS

As a general conclusion, GPC, elemental analysis, ¹H NMR, and FTIR spectroscopies have shown that the ozonated products have lower molecular weight, lower aromatic character, and higher oxygen content than the original samples. Carboxylic acids and carbonyl compounds are the main products, with higher affinity for water than CCl₄.

Treatment of asphaltenes with ozone leads to the formation of two layers, one soluble in CCl₄, or organic layer, and the other insoluble, or aqueous layer.

The compounds obtained in this process have significant interfacial activity, and a lower concentration of them, compared to NFE, is required to reduce the interfacial tension to the same value.

Comparison of the interfacial activity of the ozonolysis products with the one for NFE in the presence of Furrial asphaltenes obtained from a crude oil with precipitation problems shows that the difference is small. This suggests a potential for the use of these products to solve industrial problems, such as asphaltene precipitation and emulsion formation.

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