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“ISOLATION AND CHARACTERIZATION OF NATURAL SURFACTANTS PRESENT IN EXTRA HEAVY CRUDE OILS”

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"ISOLATION AND CHARACTERIZATION OF NATURAL SURFACTANTS PRESENT IN EXTRA HEAVY CRUDE OILS"

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ABSTRACT

Natural surfactants have been isolated from two Venezuelan crudes using a novel procedure. These compounds were analysed and their interfacial tension against pH were measured. The results were compared with those obtained for resins and asphaltenes isolated from the crudes by conventional methods.

1. INTRODUCTION

The Venezuelan Orinoco Oil Belt is probably the largest heavy and extra heavy crude oil field in the world. Estimates of the reserves in this area suggest the presence of up to $2x10^{12}$ barrels in place (1). Unfortunately, it is difficult to produce, transport and dehydrate, owing to its high viscosity, and the development of

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non-conventional techniques is of paramount importance. Before any non-conventional techniques can be developed. However, it is important to understand how crude oil components influence the interfacial chemistry governing the three processes mentioned above. This is our main objective in the paper we present here.

The presence of natural surfactants in crude oils has been acknowledged for many years and carboxylic acids (2-6), phenols (7), porphyrins (8), resins and asphaltenes (9) and waxes (10) have all been shown to play a role in emulsion stabilisation. For example, Reisberg and Doscher (2) showed that the interfacially active compounds present in Ventura (California) crude oil are acidic in nature. Seifert and Howells (4) also described the extraction of interfacially active carboxylic acids from a Californian crude oil, together with an inactive phenolic fraction. When the two were mixed together, however, the interfacial activity of the carboxylic acid increased, the reason for which were more fully explained in a later publication (11). Unlike Seifert and Howells, Newmann (6) found that the phenols extracted from a West German crude oil were interfacially active. Synergistic effects brought about by the molecular interaction between uncharacterised crude oil waxes and indigenous surfactants have also been noted (10). In this case, the effects ibserved were found to be a function of crude oil thermal history. Baltell and Niederhauser (8) demonstrated that resins and asphaltenes were then main interfacially active component in Rio Bravo (Californian) crude oil, whereas Dunning et al (7) reported porphyrins to be the major contributors to the interfacial activity of crude oils.

In the current study we describe a technique for isolating natural surfactants from Zuata and Cerro Negro heavy crude oils The compounds isolated have been subjected to thorough analyses and to physicochemical characterization at the oil/water interface. The results obtained have also been compared with those for different classes of compounds such as saturates, aromatics, resins and asphaltenes fractionated from the heavy oils by an alternative method to the novel method herein described. This has enabled us to determine the class of compound to which natural surfactants belong.

2. EXPERIMENTAL METHODS

a. Materials

Crude oil: Cerro Negro, CN-36 (8.3 °API) and Zuata, (9.5 °API)
Water: Tri-distilled
Solvents: All solvents used were analytical grade and distilled before use.

b. Isolation and Natural Surfactants from the Heavy Crude Oil

The extra heavy crude oil was dissolved in a mixture of heptane/xylene (3:1 v/v). Water was then added to this mixture and a water-in-oil emulsion was prepared using a Waring blender. The emulsion was centrifuged at 1500 rpm for 10 minutes and the oil/heptane/xylene mixture decanted from the creamed emulsion.

A fresh batch of heptane/xylene was added to the creamed emulsion to remove the remaining crude oil from between the water droplets. The emulsion was centrifuged once again to effect rapid creaming and the oil/heptane/xylene mixture was decanted from the creamed emulsion once more. The whole process was repeated several times until no crude oil was observed in the upper layer of the tube. The only remaining components of the crude oil are those responsible for stabilising the emulsion i.e the surfactants indigenous to the crude oil and present at the water/oil interface. Therefore, in order to extract these interfacially active compounds the emulsion was destabilised by the addition of benzene followed by the distillation of the water and solvents.

c) Heavy Crude Oil fractionation

Asphaltenes were precipitated by adding to one volume of 1:1 mixture of crude oil and benzene, sixty volumes of heptane. This procedure ensures that a minumum amount of resins will coprecipitate with asphaltenes (12). The mixture was left overnight, filtered and the asphaltenes were placed in a Soxhlet extractor. Resines I were dried under vacuum (10 mm Hg) at 60°C and analysed as described in the next section.

The compounds present in the maltenes were separated using silica gel column chromatography. The silica was activated at 120 °C for 24 hours. The saturates were eluted with hexane, the aromatics with 4% ethylacetate-hexane and Resins II were stripped from the column with ethylacetate followed by methanol.

d) Analysis and physico-chemical characterization

Each of the above series of compounds was subjected to the following analyses.

Infrared: using a Perkin Elmer model 257 spectrophotometer.
Carbon tetrachloride and carbon disulphide were used to prepare 5% w/v solutions

NMR: H-1 and C-13 NMR were obtained with a Bruker wp 80 spectrometer using Fourier transform. The compounds were dissolved in dichloromethane-d_2 for H-1 and in deuterochloroform for C-13. Analyses were carried out using Inverse Gated Decoupling and chromiun acetyl acetonate as a relaxing agent.

Elemental analyses: these were carried out in the laboratories of F. Pascher, Bonn, West Germany

Molecular weight (MW) analysed: A Corona Wescan model 210 was used the. Equipment was calibrated with Benzyl using benzene as the solvent and in one case (Zuata asphaltenes) pyridine as well as benzene was used. For both solvents, parall lines were obtained for benzyl by ploting $\Delta V/C$ vs C where ΔV is the voltage and C the concentration.

The temperature was set at 40 ° C. For checking purposes the MW of maltenes (620 daltons) was measured and compared with the one predicted by equation 1.

$$Mn = \frac{Ws + Wa + Wr}{Ws/Ms+Wa/Ma+Wr/Mr} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

In this equation Mn, Ms, Ma, Mr, Ws, Wa, are Mw and weights of maltenes, saturates, aromatics and resins. The calculated value (600 daltons) was equal to the observed one within the experimental error (10%).

Methylation with diazomethane: The sample (asphaltene or resin) was dissolved in tetrahydrofuran and the mixture was chilled at 5 ° C. An ethereal solution of diazomethane was added and the mixture was stirred for two days. After this time a further portion of diazomethane was added and the mixture stirred for another two day period. The reaction was controlled by monitoring the reduction of the -OH infrared absorbance at 3500-3000 cm. The excess of diazomethane was removed by bubbling nitrogen into the reaction mixture and the solvents were distilled off in a rotary evaporator. The residue was dried under vaccum (10^{-6}mm Hg) at 60°C. Blank experiments were carried out with the resins and asphaltenes by stirring these samples in a ether-tetrahydrofurane mixture for 4 days. No changes were detected in the MW and elemental analyses of these samples when compared to those of the starting materials.

Interfacial tension measurements: These were obtained using the Wilhelmy plate method (microbalance C.I.Electronics Model Mark II). The compounds under investigation were dissolved in nitrobenzene. Tridistilled water at various pH's was added to these solutions and both phases were left in contact for 48 hours before taking measurements.

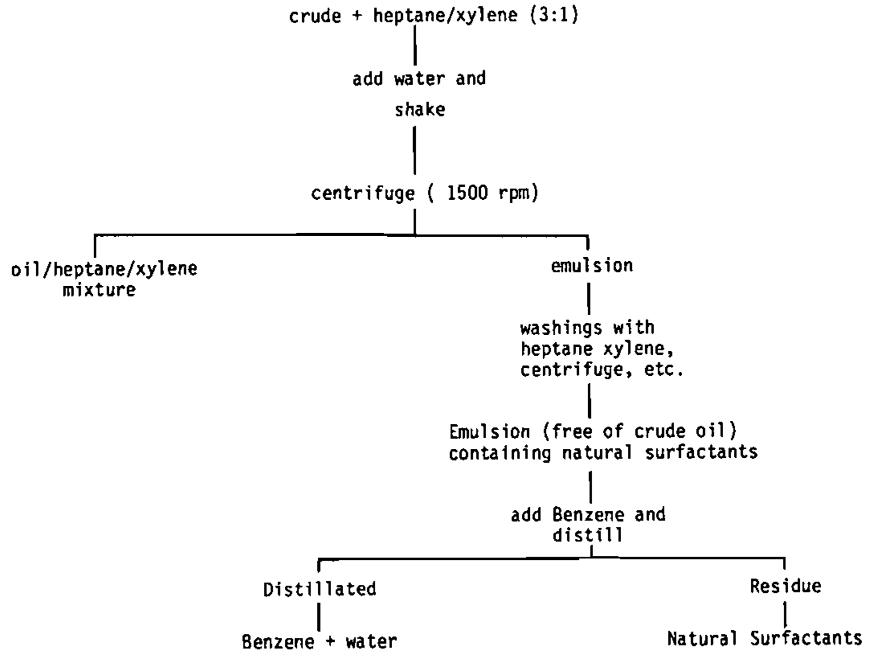

FIGURE 1

Scheme for the Isolation of Natural Surfactants from Crude Oils

3. RESULTS AND DISCUSSION

a) Interfacial Behaviour

In figures 2 and 3 we have plotted the interfacial tensión versus pH for various solutions of natural surfactants or crude oil in nitrobenzene against water. Thus, we have compared the interfacial activity of the natural surfactants isolated from Cerro Negro and Zuata crude oil respectively, with the two crude oils per se. Whilst the two sets of data illustrated in each figure do not correspond exactly, their broadly similar shapes indicate that the procedure adopted to isolate the natural surfactants from the two crude oils has worked satisfactority.

In figure 4 and 5 we have plotted the interfacial tension versus pH for natural surfactants isolated at different aqueous phase pH and for natural surfactants

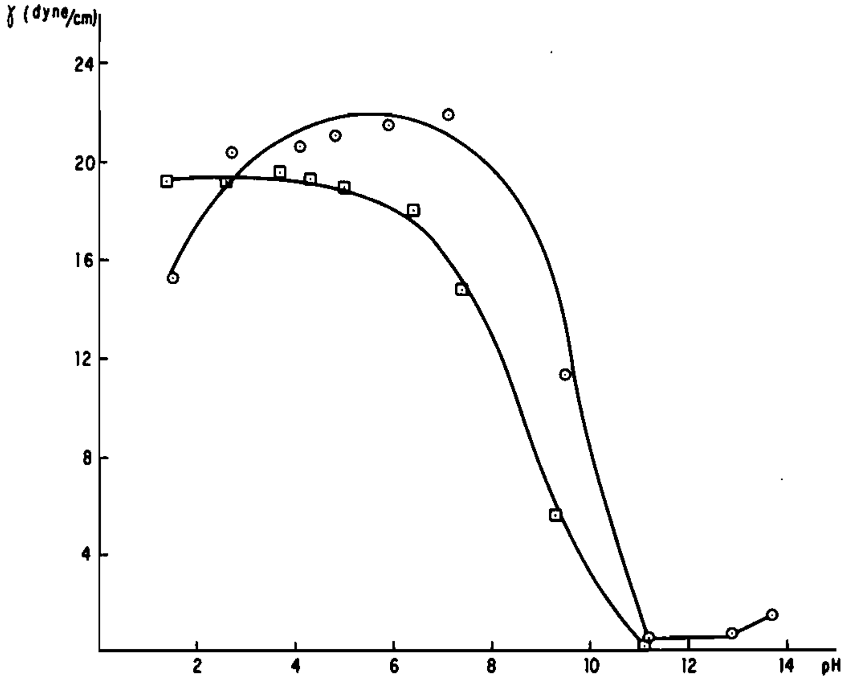

FIGURE 2. INTERFACIAL TENSION Vs pH FOR CERRO NEGRO CRUDE OIL (⊙⊙⊙) AND NATURAL SURFACTANTS EXTRACTED FROM IT (⊡⊡⊡)

isolated using different amounts of water in the emulsion making process. Again we have included data for the Cerro Negro and Zuata crude oils per.se. As in Figures 2 and 3 the data obtained with the natural surfactants do not correspond exactly to those obtained with the crude oils. This is most likely due to the adsorption of different chemical species at different pH. For example, the compounds isolated at intermediate and high pH do not show significant interfacial activity at low pH, whereas those isolated at low pH do.

In figures 6 and 7 we have plotted interfacial tension versus pH for the compounds isolated by the alternative technique described in the experimental section. Thus, we have plotted the interfacial activity of the saturates, aromatics, resins and asphaltenes, isolated fromn Cerro Negro and Zuata respectively, versus pH. Only the two types of resins and asphaltenes possess interfacial activity, with the former possessing more activity than the latter.

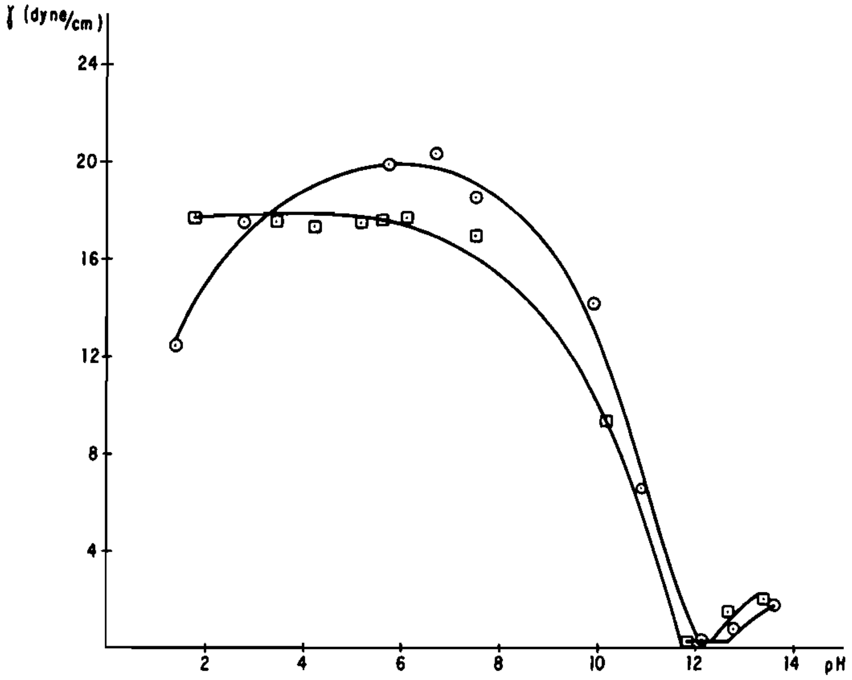

FIGURE 3. INTERFACIAL TENSION Vs pH FOR ZUATA CRUDE OIL (⊙⊙⊙) AND NATURAL SURFACTANTS EXTRACTED FROM IT (⊡⊡⊡)

This indicates that the majority of natural surfactants are present in the resin fraction, particularly the heavier resins of the crude oil.

Figures 1-6 indicate that acid species, most likely carboxylic acids, are responsible for most of the interfacial activity observed with the crude oils. In view of theis relatively low pk in water (4) the ionisation of carboxylic acids might be expected to occur at lower pH values than those observed (see Figures 1-6 where the onset of ionisation occurs at pH values between 5 and 7). However, these values correspond to the pH of the bulk water and not of the water in close proximity to the interfacial region. In fact, in one or two experiments we observed a decrease in the pH values as measurements were made closer and closer to the interface. This is extremely interesting because it suggests the development of a doublelayer effect in which localised pH values are lower than bulk pH values. So it is likely that the onset of ionisation does indeed occur at lower pH than is indicated in Figures 1-6 but

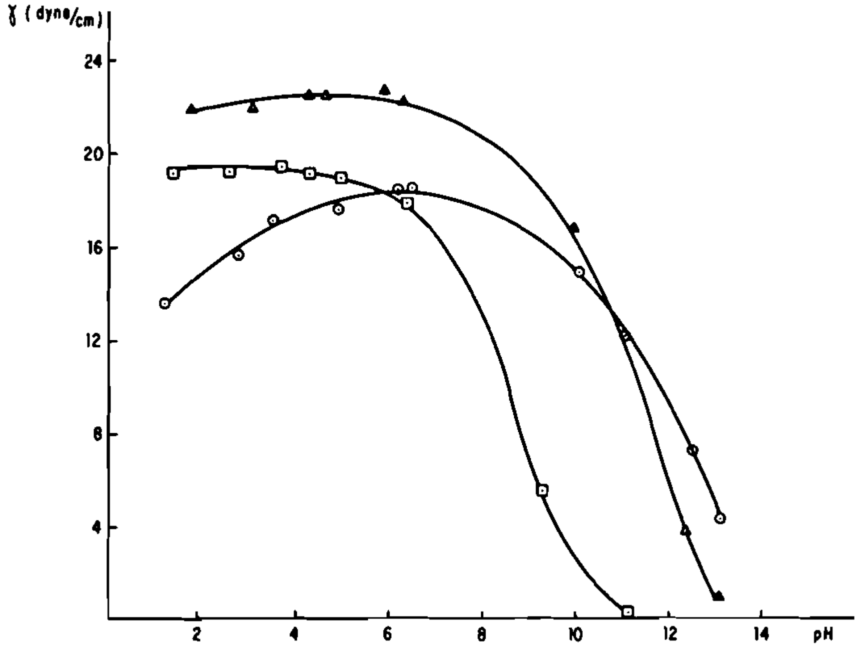

FIGURE 4. INTERFACIAL TENSION Vs pH FOR NATURAL SURFACTANTS EXTRACTED FROM CERRO NEGRO OIL AT pH's 2.7 (⊙⊙⊙), 6.0 (⊡⊡⊡) AND 11.7 (△△△)

because of the masking effect of the double-layer the ionisation process is not recorded until higher pH values are reached. As shown in the Figures, the crude, as well as the other fractions show little interfacial activity below pH 6. Since proteins show a symetrical bell shaped curve when is plotted against pH (13), that behaviour can not be attributed to a larger activity for the carboxylic funtional group compared with the amino group. It is likely that the lower activity at acidic pH might be due to an over crowding effect by alkyl substituents near or on the basic nitrogen that prevent a closer aproach of the latter with the interface. It has been shown, that phenolic material isolated from a Californian crude oil has no interfacial activity (4) and since most phenols ionize below pH 10 this fact might also be a consequence of the steric hindrance effect mentioned above. These arguments are supported by the NMR data (Table 5) which shows a very high aliphatic to aromatic relationship.

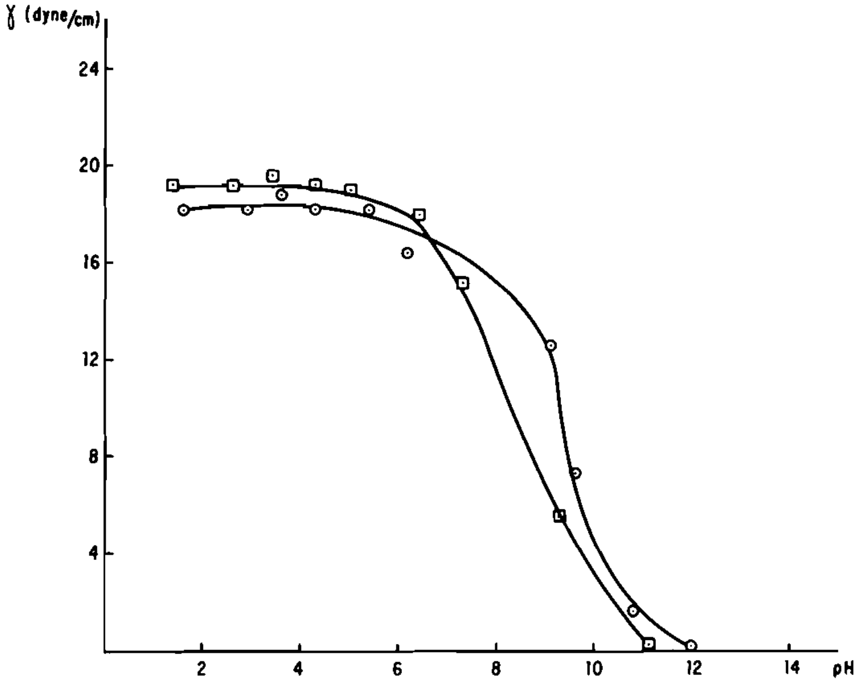

FIGURE 5. INTERFACIAL TENSION Vs pH FOR NATURAL SURFACTANTS EXTRACTED WITH 10% WATER (○○○) AND 40% WATER (□□□) AT pH 6.0 FROM CERRO NEGRO CRUDE OIL.

b) Analysis and Physicochemical Characterisation

ia) Natural surfactants isolated by Emulsion Technique

In table 1 we have listed the data for the elemental analyses, molecular formulae, molecular weights, double bond equivalents and atomic relatioships of the natural surfactants isolated by the emulsion technique described in the experimental section. It is interesting to note the relatively small amounts of natural surfactants isolated (0,2%). However, the technique used assures a true reflection of the interfacial concentration of natural surfactants present. From the data gathered in this work same calculations can be made to illustrate the type of structure likely to be present in the natural surfactants.We will take the case of Zuata surfactants as an example

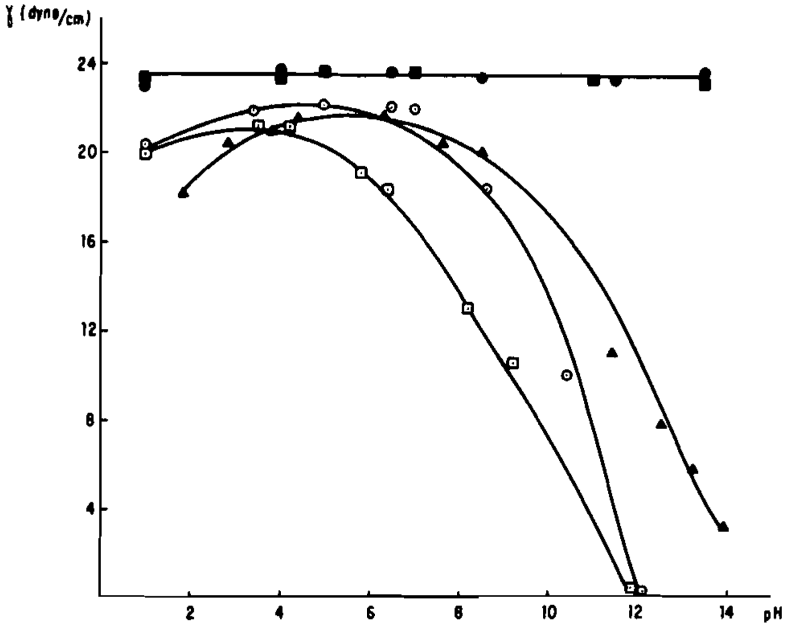

FIGURE 6. INTERFACIAL TENSION Vs pH FOR AROMATICS COMPOUNDS (●●●), SATURATED COMPOUNDS (■■■),ASPHALTENES (△△△),RESINS 1 (○○○) AND AND RESINS 2 (□□□),EXTRACTED FROM CERRO NEGRO CRUDE OIL.

Aliphatic Carbons = 107 x 0.84 = 90 (see tables 1 and 5)
Aromatic Carbons = 107 - 90 = 17

Since 17 aromatic carbons should lead to about 13 unsaturations this leaves 27 unsaturations to be accounted for. Since olefins are present in Zuata crude only in trace quantities (14) these non-aromatic unsaturations should be aliphatic rings. Hence, about 60% of the total carbons present in the natural surfactant are located on aromatic or aliphatic rings and consequently, the type of compounds we are dealing with are rather rigid ones. So it is not surprising that once the films made for these compounds are formed, as happens in pendant drop experiments, these films could be isolated by retracting the oil contained within the drop.

2. Compounds isolated by the fractionation process

In table 2 and 3 we have listed similar data for the saturates, aromatics, resins and asphaltenes to those data shown in Table 1 for the natural

TABLE 1: Some molecular parameter for the natural surfactants (NS) Isolated from Zuata and Cerro Negro crudes

Crude Cerro Negro	Elemental Analyses					MW	Molecular Formulas					DBE
	C	H	N	O	S		C	H	N	O	S	
NS_1 (pH= 2.07)	79.91	9.02	1.64	4.52	3.73	957	63.7	86.3	1.3	2.7	1.1	20
NS_2 (pH= 7.12)	79.46	8.28	1.67	4.92	4.28	1060	70.2	87.8	1.3	3.3	1.4	26.
NS_3 (pH= 11.73)	77.07	8.41	1.28	7.65	3.95	1488	95.6	125.1	1.4	7.1	1.9	33.
Zuata												
NS_4 (pH= 7.00)	81.17	8.26	1.57	4.1	4.17	1579	107	130	2.0	2.0	4	41

Natural Surfactant	Atomic Relationships			
NS_1	1.35	0.02	0.04	0.02
NS_2	1.25	0.02	0.04	0.02
NS_3	1.31	0.01	0.07	0.02
NS_4	1.22	0.02	0.04	0.02

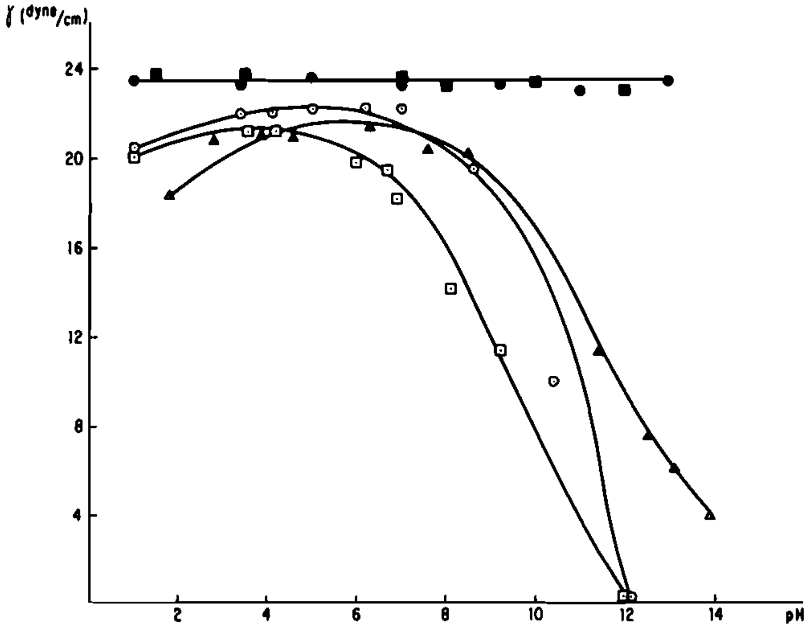

FIGURE 7. INTERFACIAL TENSION Vs pH FOR AROMATICS COMPOUNDS(●●●), SATURATED COMPOUNDS(■■■), ASPHALTENES (▲▲▲), RESINS 1 (○○○) AND RESINS 2 (▣▣▣) EXTRACTED FROM ZUATA CRUDE OIL.

surfactants. These will now be discussed in two sections entitled Maltenes and Asphaltenes.

a) Maltenes

The data obtained for elemental analyses and molecular weight determinations are similar to those found with other crude oils from the Orinoco basin (14). Predictably, the saturated fraction contains heteroatoms in trace amounts only, the porcentage of C and H adding up to 99.5 and 99.3 for Cerro Negro and Zuata crude oils respectively. A value of 3 double bond equivalents could be assigned to the saturated fraction of each crude oil, probably due to the presence of cyclohexane rings. As discussed in a earlier section, the saturate fraction did not possess interfacial activity.

The presence of small amounts of sulphur in the aromatic fraction and the absence of interfacial activity of these compounds leads us to assume that the sulphur is present in the form of thiophenes and benzothiophenes.

The value of 6 double bond equivalents indicates that the aromatic fraction is composed mainly of mono- and di-aromatics. As described in the experimental section two types of resins, labelled I and II, were found to be present the former co-precipitating with the asphaltenes, the latter being separated from the maltenes by chromatography. Both resins and asphaltenes were methylated with diazomethane, and the products (ethers and esters) were of a lower MW (see table 2). Extreme care was taken to ensure that these MW changes were not artificial (see experimental). The molecular weight reduction upon methylation has been reported before and has been interpreted as being due to the blocking of hydrogen bonding points, established in the reactants, by methyl groups (16). Hence, specific intermolecular associations between asphaltenes and resins I is a possibility and this was examined by comparison with resins II. However, except for higher oxygen content in resins II all properties examined were very similar (see Tables 2-5) apparently ruling out any major structural differences between resins I and II.

Asphaltenes

Results obtained in the present study agree very well with earlier studies of crude oil asphaltenes from the Orinoco region (14), particulary with elemental analyses, MW of methylated products and C-13 analyses. The atomic relationships found to agree well with those found for asphaltenes from elsewhere (15). As found earlier, the high carbon aromatic/aliphatic relationship and the large number of double bond equivalents points to polyaromatic structures. These aromatic rings must be highly substituted with aliphatic chains in view of the large proton aliphatic to aromatic ratio (see Table 5).

c) Comparison of natural surfactants extracted by the emulsion technique and resins and asphaltenes extracted by fractionation.

As shown on figures 2 and 3 reaches very low values (1 dynes/cm) at pH's around 12 for both Cerro Negro and Zuata crudes and their natural surfactants. Similar behaviour is presented by resins I an II (see figures 6 and 7). However at this pH, the interfacial tension of asphaltenes is about 9 dynes/cm suggesting that at alkaline pH's the interfacial activity of both crude and natural surfactants is due to the resins. By contrast, at acidic pH's the values for asphaltenes are lower than those exhibit by resins I and II and similar to those shown by the crude oils and natural surfactants isolated at acidic pH's. The behaviour at alkaline pH could be due to a more rapid migration of resins to the interface in view of their lower MW (difusion control process). Moreover, the O/C relationship might be larger for the adsorbed resins than for the asphaltenes. The behaviour at acidic pH is probably due to a combination of two facts: 1. The nitrogen content of asphaltenes is twice that of the resins on a percentage basis (see table 4) 2. Nitrogen atoms ion resins may be more sterically hindered than in asphaltene in

TABLE 2: Elemental analysis, percentages and molecular weights of the Different fractions of Zuata and Cerro Negro crudes.

			Elemental Analyses				
Fractions	% (W/W)	MW	C	H	N	S	O
Saturates							
Zuata	21.8	334	85.90	13.43	-	-	-
Cerro Negro	14.2	350	86.2	13.4	-	-	-
Aromatics							
Zuata	8.9	277	85.64	10.74	-	-	-
Cerro Negro	6.7	325	85.88	11.02	0.2	2.6	0.2
Resins 1							
Zuata	6.6	503	83.07	10.08	0.77	1.13	3.89
Cerro Negro	9.0	800	82.07	9.90	0.76	4.13	1.26
Resins 2							
Zuata	48.6	593	80.84	9.63	0.67	3.54	4.45
Cerro Negro	57.1	820	79.18	9.70	0.71	4.74	4.88
Asphaltenes							
Zuata	12.5	15700	82.82	7.70	2.05	5.03	2.05
Cerro Negro	9.9	12400	81.16	7.68	2.12	5.52	1.90
Methylated Asphaltenes							
Zuata	-	2100	-	-	-	-	-
Cerro Negro	-	2100	-	-	-	-	-

a. Methylated

TABLE 3: Some molecular parameters of the fractions isolated from the crudes Zuata and Cerro Negro

	Molecular Formula					DBE	Atomic Relationships			
Fraction	C	H	N	O	S		H/C	N/C	O/C	S/C
<u>Saturates</u>										
Zuata	23.9	45.0	-	-	-	3	1.8	-	-	-
Cerro Negro	25.1	46.7	-	-	-	3	1.85	-	-	-
<u>Aromatics</u>										
Zuata	20.0	30.1	-	-	-	-	1.51	-	-	-
Cerro Negro	23.2	35.8	-	-	-	6	1.54	-	-	0.01
<u>Resins 1</u>										
Zuata	34.8	50.7	0.3	0.4	0.6	11	1.46	0.01	0.01	0.020
Cerro Negro	54.1	79.5	0.4	2.4	1.2	16	1.45	0.01	0.01	0.02
<u>Resins 2</u>										
Zuata	39.9	57.1	0.3	1.3	0.8	13	1.39	0.01	0.03	0.02
Cerro Negro	54.1	79.5	0.4	2.4	1.2	15	1.47	0.01	0.05	0.02
<u>Asphaltenes</u>										
Zuata	145	161.7	3.1	2.7	3.3	63	1.12	0.02	0.02	0.02
Cerro Negro	114.0	161.3	3.2	2.5	3.6	61	1.14	0.02	0.02	0.03

TABLE 4

	H	N	O	S[a]	DBE
Zuata					
Natural Surfactant: (pH= 6.5)	122	2	4	2	30
Resin I	146	1	1	2	32
Resin II	139	1	3	2	33
Asphaltene	112	1	3	2	43
Cerro Negro					
Natural Surfactant (pH= 2.1)	135	2	4	2	33
Natural Surfactant (pH= 7.1)	125	2	4	2	38
Natural Surfactant (pH= 11.7)	131	1	7	2	35
Resin I	145	1	1	2	29
Resin II	147	1	5	2	27
Asphaltene	114	2	2	3	43

a. These values are calculated relative to 100 carbons atoms

view of the larger aliphatic content of the former compound (see Table 5.) Hence it appears that the interfacial behaviour displayed by the crudes examined in the acidic region of pH (2-5) is due to the asphaltenes and the activity shown at alkaline pH's is due to resins.

The versus pH curve for natural surfactants isolated at pH= 6.0 resembles the curve shown by the resins. However, when these indigenous surfactants are isolated at pH 2.7 and 11.7 the interfacial behaviour changes radically (see Figure 4) in spite of similarities in average composition (see Table 4). As shown on this Figure, the natural surfactants isolated at acidic pH's demonstrate amphoteric behaviour, while the other two show a typical carboxylic acid type of curve. Pressumably at pH 6 only the more active carboxylic acids are capable of migrating to the interface whereas at alkaline pH these most

TABLE 5

Percentages of aliphatic protons and carbons for the compounds studied

Compound	H	C
NS_1	97	-
NS_2	94	-
NS_3	96	-
NS_4	95	-
Resins I (CN)	95	84
Resins II (CN)	95	71
Resins I (Zuata)	96	67
Resins II (Zuata)	93	40
Asphaltenes (CN)	90	53
Asphaltenes (Zuata)	91	42

active carboxylic acids are probably lost due to solution into the aqueous phase (see experimental), and so only the heavier, more hydrophobic less active carboxylic acids are adsorbed at the interface.

CONCLUSIONS

The natural surfactants isolated from the crudes investigated reflect the interfacial behaviour of the crudes, particulary at alkaline pH's At acidic pH's the asphaltenes are probably adsorbed at the interface whereas the lower interfacial tension found at alkaline pH's are due to the more active and lighter resins. The structural study of these compounds showed that the natural surfactants are polycyclic molecules which once adsorbed at the interface will lead to the formation of rigid films

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