Isolation and characterization of natural surfactants from extra heavy crude oils, asphaltenes and maltenes. Interpretation of their interfacial tension–pH behaviour in terms of ion pair formation

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Natural surfactants (NS) have been isolated from extra heavy crude oils and from their asphaltene and maltene fractions. The elemental analyses and molecular weight (M_w) properties and the molecular weight distribution (*MWD*), as well as the interfacial tension (γ) behaviour (toluene solutions) with pH have been measured. The NS of crude oils (NSC) and those from asphaltenes (NSA) presented properties similar to those of asphaltenes (high M_w, low H/C ratio, heteroatom content and γ–pH behaviour) whereas the NS isolated from maltenes (NSM) resembled neither asphaltenes nor resins. The γ–pH behaviour of the crude oil systems were not reproduced by their fractions (asphaltenes, maltenes, NSC, NSA or NSM). A chemical equilibrium, based on ion pairs formed between carboxylic acids and amines, is proposed to account for the observed γ–pH changes.

Due to their importance in production and in other processes in the petroleum industry, the native tensoactive compounds, referred to here as natural surfactants (NS), present in crude oils have been the subject of many studies. Reisber and Doscher[1] were among the first to determine the presence of such compounds in crude oils. As reported here (see below) and elsewhere[2], these authors[1] found a bell-shaped curve when the interfacial tension (γ) of their light crude oils was plotted against aqueous pH in a pendant drop experiment. Seifert and Howells[3] reported the isolation of carboxylic acids from a light California crude by means of a long extraction procedure. According to these workers, such acids are responsible for the very low γ values (~ 0.01 mN m^{-1}) found in the alkaline region. Moschopedis et al.[4] used a solvent sequence to separate surface active materials from Athabasca bitumen. In contrast to the present study (see below), the M_n values (benzene, v.p.o.) reported by these authors were low (<1000) and the H/C ratios were >1.38.

Strassner[5] reported that in water in crude oil (W/O) emulsions, the water droplets are surrounded by a film made up of resins and asphaltenes. This author proposes that the solid character and mobility of the film are due to asphaltenes and resins, respectively. Jones et al.[6] found that the adsorption of NS at the water–crude oil interface gives rise to viscoelastic films and proposed that the high stability of the W/O emulsions is due to low compressibility values for such films, since coalescence requires compression of the interface. In fact, Eley et al.[7] have reported low compressibility values for such films

and also suggested that their viscoelastic character is a consequence of a three-dimensional network of asphaltenes adsorbed at the interface.

The importance of low γ values and their obtention by means of alkaline flooding has long been recognized in enhanced oil recovery. Jennings[8], after the examination of 164 crudes, concluded that the γ values of water–crude oil interfaces could be reduced to <0.01 mN m^{-1} after the addition of KOH. Babu et al.[9] working with heavy crude oils reported low values of γ ($0.01 < \gamma < 0.06$ mN m^{-1}) for the system crude oil–water–NaOH. They found that γ reached a minimum at short contact times and then increased with temperature. Chan and Yen[10] proposed a model to predict γ behaviour in the alkaline region, in which they suggested that the sudden drop in γ and the later increase with NaOH concentration are due to carboxylic acid dissociation and sodium carboxylate precipitation, respectively.

In this paper the NS isolated from three extra heavy crude oils (Cerro Negro, Zuata and Tia Juana) and from their asphaltenes and maltenes (Cerro Negro and Zuata) have been characterized. A chemical equilibrium, based on the formation of acid–base ion pairs, is proposed to describe the γ–pH behaviour of NS.

EXPERIMENTAL

Materials

Cerro Negro and Zuata extra heavy crude oils (8.3° and 9.5° API gravities) came from the Orinoco oil basin. Hexane asphaltenes and maltenes were obtained from

these crudes by a previously reported procedure[11]. Tia Juana (10° API) was obtained from Lake Maracaibo.

Natural surfactants

The NS of the crude oils were isolated using the method reported previously[2]. The following modification to this method was employed to isolate the NS of maltenes (NSM) and asphaltenes (NSA): NSM were isolated from a W/O emulsion formed by stirring, in a commercial blender, a mixture of 100 ml of maltenes, 200 ml of a xylene–heptane (3:1) solution and water (200 ml, 40%). After stirring for 3 min, the brown mixture was allowed to settle and the mousse-like W/O emulsion was separated from the supernatant oil and washed several times with the xylene–heptane solution until the washing mixture became clear. After breaking the emulsion with ethanol, the separated solid was centrifuged, filtered and dried under vacuum. The NSM so isolated were insoluble in hexane. The NSA were obtained after stirring a 3.2% w/v solution of asphaltenes in xylene with water (40%), with work-up as described for NSM. The NSC from Tia Juana crude oil were also obtained at acidic and basic conditions (pH 2.5 and 11.2, respectively) by adjusting the pH of the aqueous phase, before making the above W/O emulsion.

Molecular weights

A Corona–Wescan instrument (model 210) was employed for the M_n (v.p.o.) measurements. Benzil was used as the standard for calibration. Measurements in benzene and pyridine were obtained at 50°C in the range of 1–5 g l^{-1}. G.p.c. results [M_n, M_w and molecular weight distribution (MWD)] were obtained using the h.p.l.c. equipment described earlier[11]. Tetrahydrofuran (THF) was used for a mobile phase. A Dupont 60-S column was employed and calibrated with polystyrene standards (M_w = 30000, 15000, 8000, 800 and 200). A u.v. detector set at 253 nm was used.

Elemental analyses

These were carried out by Mikroanalytisches Laboratorium, Germany.

Interfacial tension

The Wilhelmy plate method was employed and the measurements performed with a Rovalt Micropore mark II microbalance from C.I. Electronics Ltd. The samples were dissolved in 50 ml of toluene (0.01–0.1% w/v) and transferred to a flask containing tridistilled water adjusted to the required pH. The flask was flushed with nitrogen, stoppered and then opened again at the required time (2 h, 1, 3 or 7 days). The pH was readjusted and the measurements carried out as usual.

RESULTS

The yields, elemental analyses and atomic ratios of the samples are given in *Table 1*. The elemental analyses of asphaltenes, NSA and NSC are similar with regard to atomic ratios and percentage of nitrogen plus oxygen. The H/C ratio of NSM is lower than those corresponding to resins and maltenes showing their greater degree of unsaturation. As expected, this H/C ratio is higher than that observed for asphaltenes. Interestingly, the nitrogen plus oxygen percentage was found to be around 4 for asphaltenes and all NS (N + O = 4.0 ± 0.3%). The percentage was lower for resins.

Molecular weights

The v.p.o. M_n values, measured in pyridine M_n (P) and toluene M_n (T), as well as the M_w and M_n values determined by g.p.c. in THF, are shown in *Table 2*. As reported by Acevedo et al.[11], the M_n (T) values are higher than the M_n (P) values due to the greater capacity of pyridine to break intermolecular associations. A plot of M_n values in both solvents leads to equation (1) suggesting that all samples have similar tendencies to form intermolecular associations.

$$M_n (T) = 1.17 M_n (P) + 2600 \qquad (1)$$

It is interesting that whereas the NSA resemble asphaltenes in the above properties, the NSM resemble neither resins nor maltenes. Besides, the NSM were insoluble in hexane and soluble in toluene and benzene, as were the asphaltenes. Thus, although the NSM maintain some similarities to asphaltenes (solubility, high

Table 1 Percentage yields (w/w), elemental analyses and atomic ratios of asphaltenes, maltenes, resins, NSC, NSA and NSM
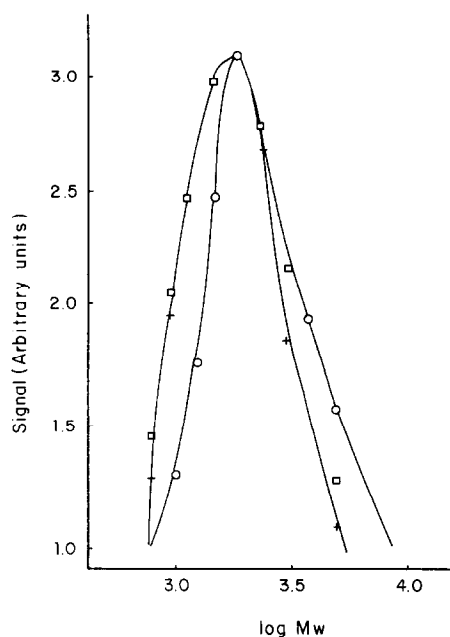
| Crude oil | Fraction | Percentage | Elemental analyses (%) | | | | | | | Atomic ratios | | |
			C	H	O	N	S	N + O	H/C	O/C	N/C	S/C
Cerro	NSC	1.1	82.1	8.1	2.3	1.9	4.3	4.3	1.18	0.021	0.020	0.020
Negro	Asphaltenes	13.8	82.3	8.1	1.9	1.9	5.9	3.8	1.18	0.017	0.020	0.027
	NSA	0.9	80.5	7.9	2.2	1.8	4.8	4.1	1.18	0.020	0.019	0.022
	Maltenes	82.0	83.6	10.8	0.9	0.6	3.9	1.5	1.55	0.008	0.007	0.017
	NSM	0.9	80.6	9.2	3.2	1.2	4.3	4.5	1.37	0.030	0.013	0.020
	Resins[a]	66.0	80.7	9.8	1.3	0.8	4.1	2.2	1.46	0.012	0.008	0.020
Zuata	NSC	0.9	81.5	8.5	2.4	1.5	4.7	4.0	1.25	0.022	0.016	0.022
	Asphaltenes	11.6	82.5	7.9	3.7	2.1	5.2	3.8	1.15	0.034	0.022	0.024
	NSA	0.6	82.6	7.9	1.9	1.6	5.2	3.5	1.15	0.017	0.017	0.024
	Maltenes	80.6	84.2	11.9	1.2	0.5	3.4	1.7	1.70	0.011	0.005	0.015
	NSM	0.6	80.1	9.3	2.9	1.1	4.0	4.1	1.40	0.027	0.012	0.019
	Resins[a]	58.0	81.0	9.6	1.4	0.7	4.5	2.2	1.42	0.013	0.007	0.021

[a]Data from reference 11 included for comparison

Table 2 Average molecular weight values of the samples studied

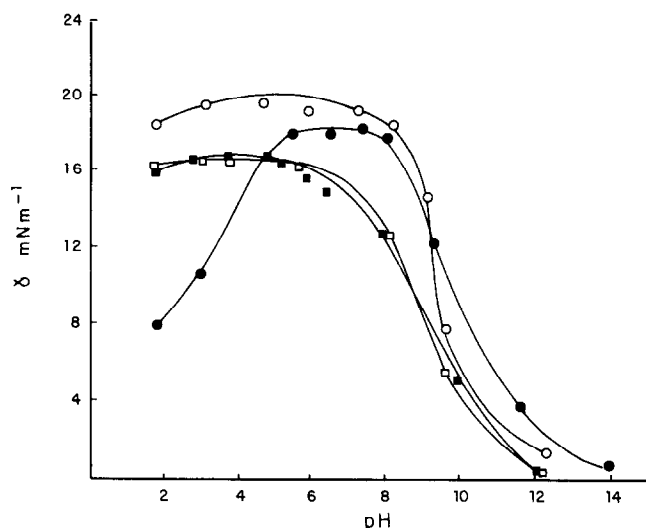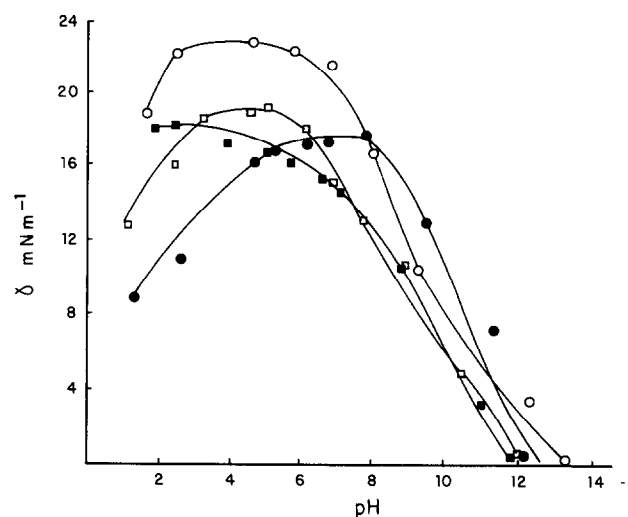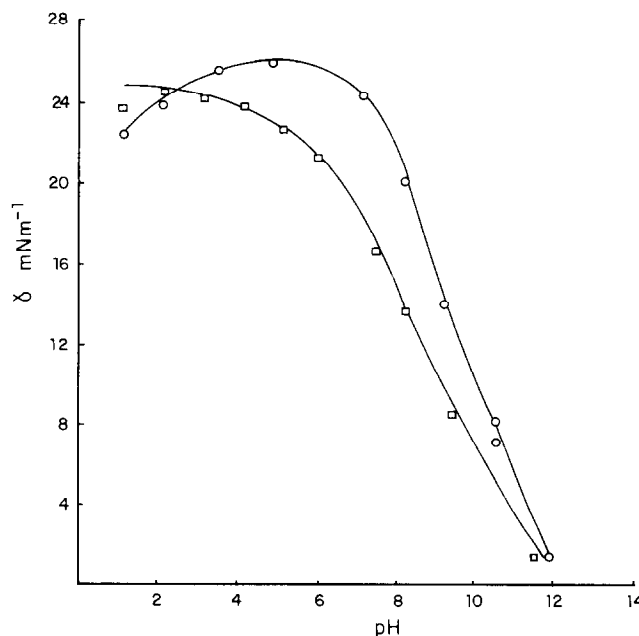| Crude | Fractions | V.p.o. $(M_n)^a$ | | G.p.c.^{b} | |
		Toluene	Pyridine	M_n	M_w
Cerro	SNC	6600	3900	1400	4300
Negro	Asphaltenes	5000	2500	1700	5700
	SNA	9000	4300	1400	4000
	SNM	4600	1600	1300	3500
Zuata	SNC	7000	4600	1300	2300
	Asphaltenes	7500	2100	1500	3500
	SNA	7700	4000	1500	3500
	SNM	4600	1600	1300	2400

^{a}At 50°C. Errors = ~10%
^{b}Low values due to adsorption problems (see text)

Figure 1 *MWD* of NS isolated from Zuata crude oil: +, NSC; ○, NSA; □, NSM

Figure 2 γ-pH curves for Cerro Negro samples: ●, crude; ■, NS; ○, asphaltenes; □, NSA. Conditions: tridistilled water; samples diluted in toluene; $T = 25°C$

Figure 3 γ-pH curves for Zuata samples: ●, crude; ■, NS; ○, maltenes; □, NSM. Conditions as in *Figure 2*

molecular weight, percentage of nitrogen plus oxygen), the H/C ratio and the γ-pH behaviour (see below) are quite different.

The *MWD* of NSC, NSA and NSM samples isolated from Zuata crude oil are shown in *Figure 1*. Similar plots were obtained for samples obtained from Cerro Negro. It can be seen that the *MWD* of these samples, as well as those obtained for asphaltenes (not shown), are similar. Note that the M_n values measured by g.p.c. are lower than those measured by v.p.o. Presumably, part of this difference could be due to adsorption effects on the g.p.c. columns, leading to longer retention times and artificially lower M_n values. Hence, the g.p.c. data were used only for comparative purposes.

Interfacial tension

The γ-pH curves were found to be dependent on sample nature (*Figures 2-4*), time (*Figure 5*) and the aqueous pH used in the extraction of the NS from the crude oil (*Figure 6*). In general, the γ-pH curves were bell-shaped for crude oils and maltenes (*Figures 2-4*). For the NSC, NSA and asphaltenes the value of γ' ($\gamma' = d\gamma/dpH$) in the acidic region was either zero or

Figure 4 γ-pH curves for Tia Juana samples: ○, crude; □, NS. Conditions as in *Figure 2*
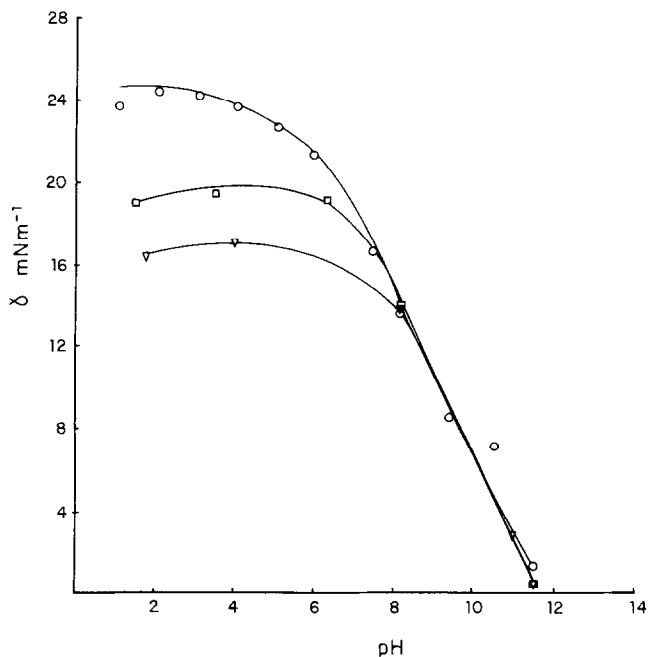
Figure 5 γ–pH curves for NS from Tia Juana crude at different contact times: $\bigcirc$, 2 h; $\square$, 3 days; $\triangledown$, 7 days. Conditions as in *Figure 2*
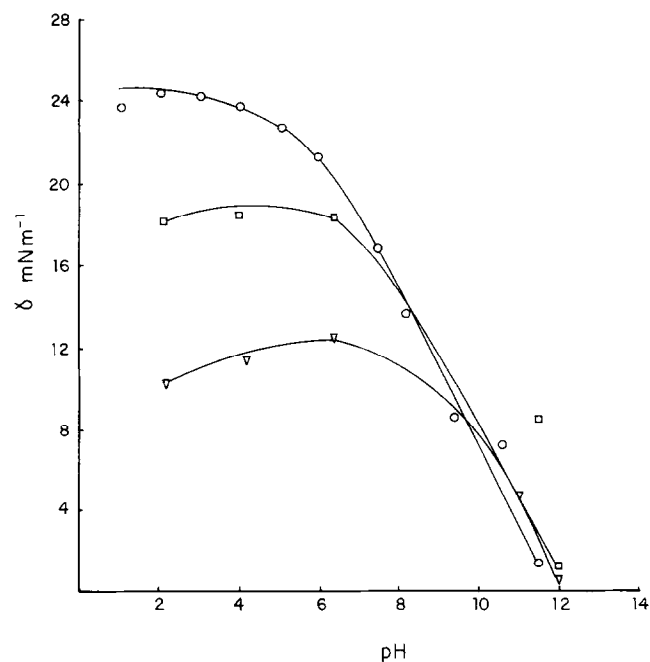
Figure 6 γ–pH curves for NS from Tia Juana crude extracted at different pH values of the aqueous phase. pH values: $\bigcirc$, 6.5; $\triangledown$, 2.5; $\square$, 11.2. For conditions see text and *Figure 2*

approached zero upon ageing (*Figure 5*). According to the data reported in the literature[9,10], the γ–pH behaviour is such that γ rapidly approaches a minimum below 1 mN m^{-1} when the pH nears 10, and then increases with higher pH values. Although we have found this to be the case for Cerro Negro dilutions[12] using the spinning drop method, the results shown in the above figures were obtained with the plate method and thus no reliable data below 1 mN m^{-1} could be measured. Therefore it should be understood that the continuous line drawn in these figures in the alkaline region below pH 10 only reflects the limitations of the plate method.
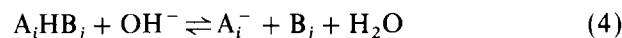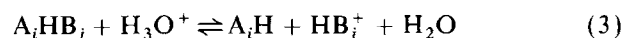
As shown in *Figure 5*, the γ values approach equilibrium very slowly, reaching constant values after 7 days. However, the γ–pH curves maintained their general shape over this time; that is, the relative values of γ' (negative or positive) did not change significantly during this period. Therefore, comparisons between different γ–pH curves were made after 2 h of contact.

It should be mentioned that part of the difference observed in the γ–pH curves could be accounted for in terms of differences in surface concentration (cf. *Figure 6*). This could be seen, for instance, by plotting γ/γ_0 in each case instead of γ, where γ_0 is the highest value of γ. As far as the present work is concerned, we are interested only in relative changes rather than absolute values of γ (see below).

DISCUSSION

None of the NS fractions isolated from the crude oils reproduced the complete γ–pH behaviour found for the crude oil dilutions. This suggests that such behaviour should not be attributed to asphaltenes or resins alone but, instead, to a combination of both. The similarity between the NSC and asphaltenes, with regards to the structural features (elemental analyses and molecular weights) and γ–pH behaviour could be due to selective desorption of the more soluble resins during the extraction procedure (see Experimental). Note that a relatively high nitrogen plus oxygen percentage and a high M_w value are common features of all the NS samples studied.

The wide range of pH values over which $\gamma' \sim 0$ suggests the presence of ion pairs. Such ion pairs could be formed between carboxylic acids and amines as shown in equation (2), where A_iH and B_j represent the carboxylic acid and the amine, respectively.

$$A_iH + B_j \rightleftharpoons A_iHB_j \tag{2}$$

$$A_iHB_j + H_3O^+ \rightleftharpoons A_iH + HB_j^+ + H_2O \tag{3}$$

$$A_iHB_j + OH^- \rightleftharpoons A_i^- + B_j + H_2O \tag{4}$$

In principle, dissociation of A_iHB_j will depend, among other factors, on the nature and concentration of the samples, pH and temperature, and of course, on the interfacial energy balance. If both A_iH and B_j are asphaltenes, the intermolecular association leading to acid–base aggregates (A_iHB_j) is expected and more so if it reduces hydrophobic interactions. As shown elsewhere[6,7], asphaltenes do form quite strong multilayer films at the oil–water interface. When the pH is increased above seven, the γ value drops due to the dissociation of ion pairs [equation (4)] and a net charge appears. The electrostatic repulsions due to the accumulation of negative charges at the interface leads to its expansion, resulting in low viscoelastic parameters[12]. Presumably, in the acidic region the interfacial energy liberated in equation (3) is not enough to break the asphaltene ion pairs and therefore γ' is approximately zero in this zone.

When the compound in the above interface is the crude oil or NSM, the γ–pH curve is bell-shaped. The dependence of γ on pH in the acidic region ($\gamma' > 0$) could be due to the dissociation of aggregates [equation (3)] or to the presence of an excess of basic compounds. In the present case, such aggregates are not expected to be as stable as those for asphaltenes, and therefore their dissociation in the acidic zone can be expected. The
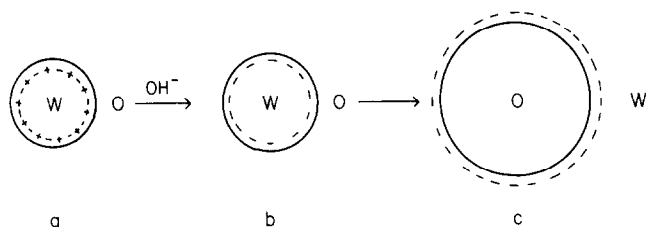
Figure 7 Schematic model for emulsion inversion. a, Water droplet in W/O, stabilized by acid–base aggregates. b, Increasing the pH leads to neutralization of positive charges and increased electrostatic repulsion. c, As a consequence of the above repulsion, the emulsion is inverted to an O/W emulsion where the mean distance between charges is now greater

positive value of γ' observed in this zone for the NSC isolated at pH 2.5 (*Figure 3*), suggests that this result could be due to an excess of amines. However, the slow change in γ near the maximum suggests the presence of the acid–base aggregates mentioned above.

It is well-known that carboxylic acid ionization in water occurs at about pH 4. Thus, if these acids alone occupy the interface, the γ drop would occur around this pH value. Although some evidence of early ionization is apparent in our results (c.f. *Figure 3*), in our view, this only means that an excess of carboxylic acid is present at the interface, and the ion pair formation provides a valid model for the drop in γ at the higher pH values observed. As mentioned above, Chan and Yen have proposed a model for the γ–pH behaviour in the alkaline region[10]. However, their model is not satisfactory in the present case since it neither makes provision for the acidic behaviour of γ nor for the drop in γ at high pH values.

We have found that the W/O emulsions formed with extra heavy crude oils in the region $1 \leqslant \text{pH} < 10$, suffer inversion to O/W emulsions when the pH is increased above 10. Also, γ, measured by means of the spinning drop method, affords values[12] below 0.1 mN m^{-1}. Such a phase change is consistent with the abrupt changes in γ in this zone[9]. These findings can be explained by the presence of ion pairs at the interface. This is illustrated in the oversimplified model in *Figure 7*. Here, the W/O

emulsion is stabilized by a film of NS ion pairs. As the pH is increased the positive charges are neutralized, leading to an increase in electrostatic repulsions as mentioned above. A further increase in pH leads to emulsion inversion wherein the more expanded and mobile films allow a decrease in electrostatic repulsions.

CONCLUSIONS

All NS isolated presented high molecular weight values and MWDs similar to asphaltenes. In particular the NSC and NSA properties (M_w and γ–pH behaviour) were essentially those found for asphaltenes. However the NSM presented a lower M_n value and different γ–pH behaviour when compared to asphaltenes. The γ–pH behaviour of all systems studied, as well as the emulsion inversion in the alkaline zone, can reasonably be accounted for in terms of the formation of ion pairs between the carboxylic acids and amines present in these extra heavy crude oils.

ACKNOWLEDGEMENT

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