Isolation and Characterization of Low and High Molecular Weight Acidic Compounds from Cerro Negro Extraheavy Crude Oil. Role of These Acids in the Interfacial Properties of the Crude Oil Emulsions

Sócrates Acevedo,*,[†] Gaston Escobar,[†] María A. Ranaudo,[†] Jose Khazen,[†] Belsay Borges,[†] Juan C. Pereira,[†] and Bernardo Méndez[‡]

Laboratorio de Fisico Química de Hidrocarburos and Laboratorio de Resonancia Magnética Nuclear, Centro de Química Orgánica, Facultad de Ciencias, Escuela de Química, Universidad Central de Venezuela, P.O. Box 47102, Caracas, Venezuela

Two acidic samples, A and B, were isolated from Cerro Negro extraheavy crude oil. Sample A has a relatively low number average molecular weight ($M_n = 480$ Da), low aromaticity ($f_a = 15.2\%$), and low γ (6.8 m Nm^{-1}, toluene−0.1 N HCl), whereas for B, these values were $M_n = 1200$ Da, $f_a = 20\%$, and $\gamma = 14.8$ m Nm^{-1}. These values could be compared to those for Cerro Negro asphaltenes under the same conditions ($M_n = 5000$, in toluene by VPO, $f_a = 47\%$, $\gamma = 20.9$ m Nm^{-1}).

Introduction

Previous studies of toluene solutions of extraheavy crude oil and natural surfactants in contact with water have shown that the interfacial tension has a value of ca. 18 m Nm^{-1}.[1−3] Also at neutral and acidic conditions, the interfacial tension γ changes very slowly, needing several days to reach equilibrium conditions.[2] In part, this behavior has been attributed to the presence of high molecular weight compounds such as asphaltenes at the interface.[2] By contrast, under alkaline conditions (pH > 9), the usual very low equilibrium values are attained within minutes.[4,5] Among other things, these observations suggest that under neutral conditions, carboxylic acids of relatively low molecular weight (compared to asphaltenes) and high interfacial activity could also be adsorbed at the interface.

Reported data has shown that asphaltenes, the high molecular weight components of crude oil, are adsorbed at the crude oil−water interface.[1−3,6,7] Asphaltenes have a relatively low oxygen and nitrogen content, usually less than 5%,[8,9] a very complex structure containing polycyclic ring systems,[10−12] and a high average molecular weight. Thus, it is unlikely that asphaltenes alone could lead to the above, relatively low, γ values under neutral conditions. It is reasonable to expect that asphaltenes (high average molecular weight) and the above low average molecular weight acids are both adsorbed at the interface. Thus, some important interfacial properties of the water in oil (w/o) as well as the oil in water (o/w) emulsions of these crude oils could be accounted for in terms of these low and high molecular weight components. Some of them have been discussed in a preliminary work.[13] For instance, the high stability of the w/o emulsions could be due to strong interfacial films formed by asphaltenes. These films would be very resistant to coalescence.[7,14] On the other hand, the presence of the above carboxylic acids would allow the development of the low γ values needed for emulsion formation.

In this paper, a chromatographic procedure, based on the one reported,[15] has been used to isolate several acidic fractions from Cerro Negro extraheavy crude oil. In agreement with the arguments above, two acidic fractions, hereafter called A and B, were isolated. Fraction A (number average molecular weight $M_n = 480$) has a low aromaticity ($f_a = 15.2$), and fraction B has $M_n = 1200$ and $f_a = 20$. Fraction A was soluble in hexane and heptane, whereas B was not.

* Corresponding author.
† Laboratorio de Fisico Química de Hidrocarburos.
‡ Laboratorio de Resonancia Magnética.
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Table 1. Percentage,[a] Elemental Analysis, H/C Ratios, f_a,[b] H_{ali}/H_{ar},[c] and M_n[d] of Samples Studied

samples	%	C	H	N	S	O	H/C	f_a	H_{ali}/H_{ar}	M_n
acid A	0.74	80.62	10.33	1.79	3.23	4.03	1.53	15.2	22.3	480
acid B	1.53	83.07	7.81	2.3	4.73	2.60	1.12	20	20	1200
fraction C	8.4	82.76	7.83	1.83	5.30	2.28	1.13	38.5	13	2800
CNA[e]	11	81.2	7.7	2.1	5.5	1.9	1.14	47	10.6	5500

[a] Respect to crude oil. [b] Percentage of aromatic carbons. [c] Ratio of aliphatic to aromatic hydrogens. [d] By VPO in toluene at 50 °C. [e] Cerro Negro asphaltenes.

Experimental Section

Cerro Negro Asphaltenes (CNA). Cerro Negro extra-heavy crude oil (API = 8°) was employed. *n*-Heptane asphaltenes from this crude were obtained from a 1:1 (v/v) mixture of crude and toluene by addition of 60 volumes of *n*-heptane as described earlier.[9]

Chromatography. *Fractions A, B, and C.* The acids were separated from the crude oil using an adsorption chromatography procedure with solvent recirculation according to the method described earlier.[15] Briefly, a sample of silica gel (50 g) was activated with a hot solution of potassium hydroxide (5 g) in a solution of isopropyl alcohol (125 mL) and chloroform (100 mL). The column was filled with this mixture, and boiling chloroform was recirculated to remove the alcohol. A solution of crude (20 g) in chloroform (10 mL) was then applied, and the recirculation of chloroform was started. About 72 h was required to remove the neutral−basic fraction (95.2%, average of four runs). The solvent was changed to 20% formic acid−chloroform, and the acidic fractions were obtained (2.3% average of four runs). Asphaltenes from the above neutral−basic fraction, or fraction C, were obtained as described above for the crude oil. Yield: 8.4% of crude oil.

The oil and acidic fraction obtained above was treated with heptane under reflux (1 h) and allowed to cool to obtain a dark solution and a solid. This was filtered, washed with heptane, and dried under vacuum to obtain acidic fraction B (1.53% of crude oil, 66.7% of the acidic fraction). The above washings and filtrate were combined and the solvents removed under vacuum to obtain acidic fraction A (an oil, 0.74% of crude oil, about 30% of acidic fraction).

Characterization. ^{1}H and ^{13}C NMR, infrared, elemental analyses, and VPO measurements were taken in conventional equipment using conventional techniques. The presence of carboxylic acids in samples A and B was confirmed as usual by the ^{13}C signal (183−180 ppm) and the presence of a broad band (3500−3000 cm^{−1}) for OH and the carbonylic band (1705 cm^{−1}) in the infrared spectra. VPO measurements of M_n were performed in toluene at 50 °C. Results are shown in Table 1.

Interfacial Tension (γ) Measurements at the Toluene−Hydrochloric Acid (0.1N) Interface. Interfacial tension measurements were taken in a conventional tensiometer using the ring method at 25 °C. Solutions of materials were prepared in preequilibrated solvents (1 day). Hydrochloric acid (0.1 N) was employed to repress acid ionization. However, no significant changes were observed when this was replaced by water. The toluene solution and the aqueous phase were placed in a glass jar, and γ was measured at the required time. Although about 50% of the change was observed within the first 2 h, apparent equilibrium values were found after 3 days.

Results

Carboxylic Groups, Elemental Analysis, and Molecular Weight. As described in the Experimental Section, the presence of carboxylic groups in samples A and B was confirmed by infrared and ^{13}C NMR spectroscopy. The double bound equivalent (DBE) could be

Table 2. Average Molecular Formula for Samples Studied

sample	formula					DBE[a]
	C	H	N	S	O	
A	32	50	0.7	0.5	1.2	26
B	84	94	2	1	2	45
C	194	220	3.7	4.6	4	46
CNA	344	390	7.8	8.6	6.2	46

[a] Per 100 carbons, see text.

obtained from eq 1

$$DBE = \frac{2C + 2 - H + N}{2} \tag{1}$$

where C, H, and N are the number of carbon, hydrogen, and nitrogen atoms in the formula. For comparative purpose, DBE is referred to 100 carbons, and since N is usually small, it could be neglected to obtain eq 2

$$DBE = \left(1 - \frac{H/C}{2}\right)100 + 1 \tag{2}$$

where the ratio H/C is obtained from the elemental analysis. Equation 2 was used to obtain the values in Table 2.

In Table 1, the elemental analysis and other results of this work are shown. From these it is clear that compared to the other samples, *acid* A has a low M_n and is considerably more aliphatic. Using the results of Table 1, the molecular formula shown in Table 2 were obtained. These, of coarse, are average molecular formula since they correspond to complex mixtures. The differences in M_n and DBE between samples A and B, and with C and CNA, are the most important ones regarding the present work. Sample A has a significantly lower M_n value and is considerably more saturated than the others. In a more detailed NMR study to be published elsewhere, it is shown that sample A has very few, if any, aliphatic unsaturations. This implies the presence of long aliphatic chains that together with the carboxylic acid group account for the ability of this sample to reduce the interfacial tension. The solubility of acids A in heptane and hexane is consistent with the above structural features.

Interfacial Tension. $\gamma-(\ln c)$ plots for samples A, B, and C and the one for asphaltenes (CNA) are shown in Figure 1. Several features are worth commenting on. For instance, the lowest or saturation γ value for sample A (6.8 m Nm[−1], at $c = 6$ g L^{−1}) is interesting. Not only because it reveals that this sample has a high interfacial activity, but because this value is considerably lower than the one obtained for oleic acid under similar conditions ($\gamma = 22$ m Nm[−1], at $c = 10$ g L^{−1}). Also, the saturation values for other samples (see Table 3), although higher than the one for A, are still low when compared to oleic acid. It is expected that oleic acid would produce a close packing of polar heads, leading to γ values significantly lower than the ones for the bulky and less polar samples B, C, and CNA.

Discussion

As described in the Experimental Section, both low and high molecular weight acidic compounds were found in the acidic fraction of the crude oil. It is very interest-
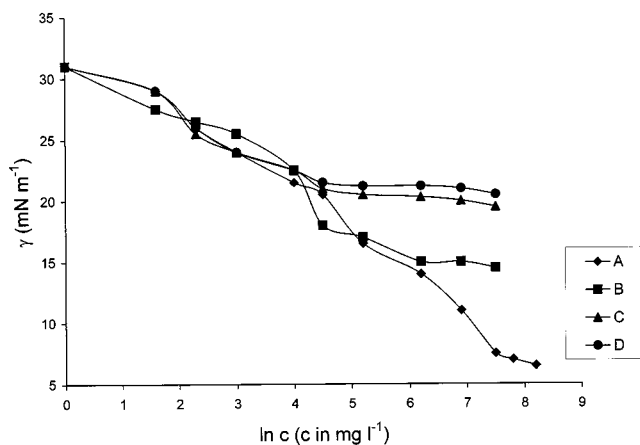
Figure 1. $\gamma - \ln c$ plots: (A) acid A; (B) acid B; (C) acid C; (D) CNA.

Table 3. Solution Concentration Ranges and Interfacial Tension Corresponding to Surface Saturation.

sample	concentration range (mg L^{-1})	γ (m Nm^{-1})
acids A	2000–2500	6.8
acids B	400–600	14.8
fraction C	50–100	19.8
CNA	100–200	20.9

ing that the differences between samples A and other samples are so evident. This strongly suggests different roles for these samples at the interface. For instance, in a diffusion-controlled mechanism, acids A will adsorb at the interface, thereby reducing γ. Then, acids such as B or asphaltenes will be adsorbed, leading to emulsion stabilization. Among other factors, aggregate formations at the interface between A and the other samples would inhibit desorption of acids A from the interface to the water phase. A similar mechanism has been proposed earlier.[13] The above mechanism is consistent with the finding that when a toluene solution of crude oil is contacted with water, γ drops quite rapidly at the beginning and then decreases very slowly during a period of several days.[2] The same behavior was found for samples in this work (see Experimental Section).

It is interesting that in Figure 1 the interfacial tension γ for samples B, C and CNA reach constant values at very low concentrations (see Table 3). For instance, for asphaltenes, this constant value is attained between 100 and 200 mg L^{-1}. This behavior is probably due to aggregate formation in solution. Recently, using a thermal lens technique, the beginning of aggregation for this asphaltene in toluene was detected near 50 mg L^{-1}.[18] If so, the constant γ value observed is either due to no more asphaltene being adsorbed or the fact that A type acids are retained in the aggregates after this point. Similar arguments could be used for the B and C samples.

It should be mentioned that no "break" was found in the γ–(ln c) plot for the asphaltenes case (see Figure 1). Thus, no evidence of a critical micelle concentration (cmc) could be found. This is in agreement with the results obtained in the above-mentioned investigation.[18] Also, cmc values have been reported for asphaltene solutions in toluene and other organic solvents.[19] From the above discussion, it is clear that if small amphiphiles unrelated to asphaltenes are present in these samples, they would be mainly responsible for the γ decrease at the toluene surface.

Conclusions

The isolation from Cerro Negro crude oil of acids A, a relatively low molecular weight and highly aliphatic mixture of carboxylic acids, very strongly suggests that these acids play an important role in reducing γ values of crude oils at the water interface under neutral and basic conditions. It is likely that the main role of the high molecular weight samples, such as the isolated B sample, would be interface stabilization.

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