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An Electron Microscopy Study of Crude Oils and Maltenes

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An electron microscopy study of four Venezuelan crude oils and their corresponding maltenes has been performed, using the combine freeze fracture–transmission electron microscopy (FFTEM) technique. All samples showed the presence of spherical primary colloidal particles, with average diameters in the range of 7–9 nm and an apparent Gaussian distribution. Large aggregates of primary particles, with the longest length being ~200 nm or more were observed in some crude oils. These aggregates could be broken down to smaller aggregates or to primary particles by stirring and/or heating the crude oil. This indicates that the binding energy of these aggregates is weak, on the order of kT . Dilution with benzene up to 80 times does not dissolve the colloids completely but does reduce its diameter. On the other hand, the addition of heptane (up to 3 volumes) leads to an increase in diameter, which suggests the adsorption of resins upon dilution. In agreement with previous findings,³ these results were observed to be consistent with the model for the colloidal particle, where low-solubility fractions are mainly located at the core and soluble fractions prevail at the periphery.

Introduction

The colloidal nature of crude oils is thought to be responsible for many problems in the production and processing of petroleum. Thus, many studies related to this aspect have been reported.^{1–20} Perez-Hernández et

al.¹ reported a scanning electron microscopy (SEM) and transmission electron microscopy (TEM) study of vacuum residues and observed very large asphaltene aggregates (50 nm in size). Aquino-Olivos et al.² tested commercial asphaltene inhibitors at high pressures on bottom-hole samples, and these authors found that a large concentration of inhibitors was needed to observe any effect. Gutierrez et al.³ used the PNP method to isolate fractions A1 and A2 with very different solubility in toluene (where fraction A1, which is practically insoluble, is solubilized by fraction A2). According to these authors,³ the colloidal nature of asphaltenes was due to the low-solubility fraction A1. Acevedo and co-workers^{4,6} found that silica promotes quantitative asphaltene flocculation. Using small-angle X-ray scattering (SAXS), Sheu and Acevedo⁵ reported colloidal diameters of ~7 nm for Furiel crude oils (see below). Wu and Prausnitz⁷ and Victorov and Firoozabadi¹¹ used several theoretical platforms (SAFT and others) to study asphaltene flocculation within a thermodynamic framework.

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(1) Perez-Hernández, R.; Mendoza-Anaya, D.; Mondragón-Galicia, G.; Espinoza, M. E.; Rodríguez-Lugo, V.; Lozada, M.; Arenas-Alatorre, J. *Fuel* **2002**, *82*, 977–982.

(2) Aquino-Olivos, M. A.; Buenrostro-Gonzalez, E.; Andersen, S. I.; Lira-Galeana, C. *Energy Fuels* **2001**, *15*, 236–240.

(3) Gutierrez, L. B.; Ranaudo, M. A.; Méndez, B.; Acevedo, S. *Energy Fuels* **2001**, *15*, 624–628.

(4) Acevedo, S.; Ranaudo, M. A.; Escobar, G.; Gutierrez, L. B.; Gutierrez, X. In *Asphaltenes: Fundamentals and Applications*; Sheu, E. Y., Mullins, O. C., Eds.; Plenum Press: New York, 1995.

(5) Sheu, E. Y.; Acevedo, S. *Energy Fuels* **2001**, *15*, 702–707.

(6) Castillo, J.; Fernández, A.; Ranaudo, M. A.; Acevedo, S. *Pet. Sci. Technol.* **2001**, *19* (1&2), 75–106.

(7) Wu, J.; Prausnitz, J. M. *AIChE J.* **1998**, *44*, 1188–1199.

(8) Fenistein, D.; Barré, L.; Broseta, D.; Espinat, D.; Livet, A.; Roux, J.-N.; Scarcella, M. *Langmuir* **1998**, *14*, 1013–1020.

(9) Barré, L.; Spinat, D.; Rosenberg, E.; Scarcella, M. *Rev. Inst. Fr. Pet.* **1997**, *52*, 161–175.

(10) Fotland, P. *Fuel Sci. Technol. Int.* **1996**, *14* (1&2), 313–325.

(11) Victorov, A.; Firoozabadi, A. *AIChE J.* **1996**, *42*, 1753–1764.

(12) Bardon, Ch.; Barré, L.; Espinat, D.; Guille, V.; Li, M. H.; Lambard, J. C.; Ravey, J. C.; Rosenberg, E.; Zemb, T. *Fuel Sci. Technol. Int.* **1996**, *14* (1&2), 203–242.

(13) Storm, D. A.; Barresi, R. J.; Sheu, E. Y. *Fuel Sci. Technol.* **1996**, *14* (1&2), 243–260.

(14) Sheu, E. Y.; Storm, D. A. In *Asphaltenes: Fundamentals and Applications*; Sheu, E. Y., Mullins, O. C., Eds.; Plenum Press: New York, 1995; Chapter 1, p 1.

(15) Storm, D.; Sheu, E. Y. *Fuel* **1995**, *74*, 1140–1145.

(16) Acevedo, S.; Ranaudo, M. A.; Escobar, G.; Gutierrez, L. B.; Ortega, P. *Fuel* **1994**, *74*, 595–598.

(17) Thawer, R.; Nicoll, D. C. A.; Dick, G. *SPE Prod. Eng.* **1990**, *5*, 475–480. (Also given as SPE Paper 18473.)

(18) Leontaritis, K. J.; Mansoori, G. A. Asphaltene Deposition during Oil Production and Processing: A Thermodynamic Colloidal Model. Presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, TX, February 4–7, 1987, SPE Paper 16258.

(19) Haskett, C.; Tartera, M. J. *Pet. Technol.* **1965**, 387–391.

(20) Kants, D. L. *Ind. Eng. Chem.* **1945**, *37*, 195–200.

A minimum in the intrinsic viscosity was observed by Fenistein et al.⁸ when diluted toluene solutions of asphaltenes were treated with heptane. According to these authors,⁸ the intrinsic viscosity increased again near the flocculation point. Barré et al., using small-angle neutron scattering (SANS), analyzed several asphaltene solutions in toluene and determined an average radius in the range of 0.63–1.8 nm.⁹ Fotland¹⁰ reported a conductivity method for detecting asphaltene precipitation under high pressure and high temperature. Bardon et al.,¹² using SAXS and SANS, and toluene solutions of asphaltenes and resins, determined ratios of 0.8–20 nm for asphaltene particles considered as thin disks (0.8–1 nm thick). Those authors¹² reported that the maximum ratio decreased as the resins content increased. Storm¹³ reported particle sizes on the order of 10 nm for a VR analyzed via SAXS. They¹³ found that asphaltene particles are stabilized at <200 °C against the attractive dispersion forces between asphaltenes by an adsorbed layer of non-asphaltenic molecules (NAMs). These authors estimated that the binding energy holding these NAM to the particle is $\sim 3kT$.

Colloidal flocculation during crude oil production is a high-impact problem. Because of changes in temperature, pressure, and composition, as well as contact with adsorbing surfaces, colloidal stability may be perturbed, leading to a separation of organic colloids as a solid phase. This solid is then deposited on well pores or on the production facilities, leading to severe reduction or a complete halt in production.

Relevant to this problem are colloidal size, colloidal composition, and colloidal stability. The emphasis of the present study is the measuring of colloidal size of crude oils and their change with different conditions such as stirring, temperature, presence of active surfaces, and dilution. To our knowledge, it is the first systematic study of this type performed using combine freeze fracture TEM (FFTEM).

As described in detail below, the results obtained compare well with those reported using SAXS,^{5,12,13} and they could be related to important colloidal aspects such as colloidal structure, composition, and stability.

Experimental Section

Materials. Crude oils were obtained from different locations in Venezuela. Furrial and Ceuta have serious asphaltene coagulation problems, whereas Cerro Negro and DM-153 are stable crude oils.

Asphaltenes were precipitated from crude oils, according to routine methods that have been reported elsewhere.⁴ For extra-heavy Cerro Negro, a 1:1 (v/v) dilution with toluene was used before the addition of 40 volumes of *n*-heptane. In this case, dilution with toluene was used to reduce the viscosity of the extra-heavy oil. No such dilution was needed in the other three cases. Resins that were coprecipitated with asphaltenes during the precipitation procedure (hereafter called R_C) were obtained after thoroughly washing the precipitated material with boiling *n*-heptane in a Soxhlet extractor. These materials were dried under high vacuum, weighed, and added to the filtrate.

Maltenes were obtained from the filtrate of the aforementioned asphaltene precipitation, after the evaporation of *n*-heptane under vacuum.

Equipment. A freeze fracture apparatus (JEOL, model JFD 9010C) was used. A TEM system (JEOL, model JEM-1220)

Table 1. Properties of Crude Oil Studied

crude oil	API gravity (°)	asphaltene content (%) ^a	coagulation problems
Furrial	21	7	+
Ceuta	21	2	+
DM-153	14	10	–
Cerro Negro	8	12	–

^a With respect to the crude oil.

with an accelerating voltage of 110 kV was used to visualize, analyze, and photograph the replicas.

Methods. Samples for freeze fracture were prepared by placing a tiny amount of sample material on the sample holder. This was placed in contact with liquid–solid nitrogen that was contained within the freezing chamber (–150 °C) under high vacuum (10^{–6} Torr). Therefore, freezing occurs very quickly and no change in the system is expected. The sample thus prepared was then shadowed with the platinum/carbon powder at an angle of 45°, with respect to the sample holder, and covered with carbon powder at 90°. The sample then was fractured, withdrawn from the chamber, and placed in tetrahydrofuran (THF) to dissolve the sample. The floating replica was then placed in a copper grid for observation via TEM.

Microphotographs were taken under a magnification of 25 000 or 50 000. This augmentation was increased twice after the photographs were developed. Particle size and other properties (e.g., size distribution and particle density) were determined using the program Scion Image for Windows with the capability of an additional 3-fold enlargement. This program transforms the bright areas of the microphotography to bands and the dark areas to valleys. By an adequate calibration, the width of the band is then converted to a particle diameter.

Using a commercial colloidal gold suspension with a certified size of 5 nm, the aforementioned methods were validated, by submitting this water suspension to the same process as that used for the samples studied. Thus, we determined that our resolution was better than 5 nm.

All diameter measurements performed were highly reproducible, within a deviation of 2.2% or better. Average properties, such as diameters and particle densities, were obtained after averaging 10 measurements performed on different sections of the replicas. For convenience, these densities were measured by counting the number of particles in an area of 10 000 Å². These densities were somewhat difficult to measure in the Cerro Negro case; here, overlapping of the contrast bands was very common and, thus, the density measured in this case could be considered to be a good estimate.

Before application of the FFTEM method, some samples were subjected to the following series of tests, to obtain information under different conditions. Crude oils were heated at 80 °C for 8 h under stirring and a nitrogen atmosphere. Furrial oil was also heated and stirred in a Parr reactor at different temperatures (50, 100, 150, 200, and 250 °C) and constant pressure (20 psi).

With silica gel, two tests were performed. In the first test, a drop of Furrial oil was placed in contact with a silica plate for 24 h, and then a small sample was taken from the top of the drop for analysis. In the other test, the crude was stirred for 6 h with silica powder in a 7:1 w/w oil/silica ratio and then centrifuged and analyzed. A similar silica plate experiment was performed with the DM-153 crude oil. Both the silica plate and the silica powder were commercial samples that are used for chromatography.

FFTEM studies were also performed on diluted crude using toluene, benzene, and *n*-heptane as solvents. Dilution with large volumes of toluene (more than five volumes) led to bad fractures. Presumably, these bad fractures are the consequence of the very low melting point of toluene (–93 °C). Thus, when large dilution was required, benzene was used.

Table 2. Saturates, Aromatics, Resins, and Asphaltenes (SARA) Composition of Crude Oils^a

crude oil	Composition (%)					S/As	Ar/As	Res/As	R _C /As
	saturates, S ^b	aromatics, Ar ^b	resins, Res ^b	resins coprecipitated with asphaltenes, R _C ^b	asphaltenes, As ^c				
Cerro Negro	15	38	35	5.6	12	1.25	3.16	2.9	0.47
DM-153	17	44	30	3.5	10	1.7	4.4	3	0.35
Furrial	42	34	18	1.8	7	6	4.9	2.6	0.26
Ceuta	41	45	12	0.7	2	20.5	22.5	6	0.35

^a Percentages given with respect to the crude oil. ^b Errors estimated to be <10%. Determined by the SAR method. ^c By precipitation from the crude oil.

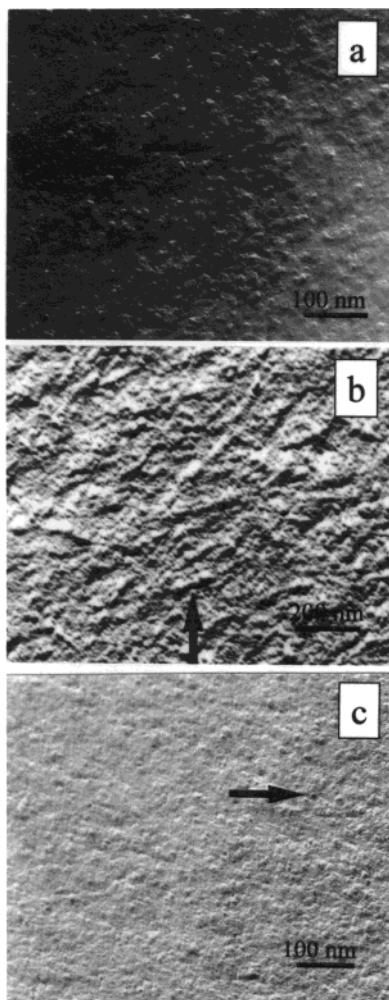


Figure 1. Microphotographs of crude oils measured using the combined freeze-fracture transmission electron microscopy (FFTEM) technique: (a) DM 153 oil, (b) Furrial oil (as received), and (c) Furrial oil (after stirring). Arrows are used to facilitate observation.

Determination of saturates, aromatics, and resins (SAR analysis) was performed on maltenes on silica bars, using an Iatroscan equipment. A solvent gradient, from heptane to toluene to dichloromethane and to dichloromethane–methanol (9:1), was used.

Results

Some properties of crude oils are shown in Table 1. These span a wide range of asphaltene contents and API gravities. Both Furrial and Ceuta have flocculation problems during oil production.

Table 2 shows the SARA composition of crude oils. Here, S, Ar, Res, and As represent saturates, aromatics, resins, and asphaltenes, respectively. R_C denotes resins

Table 3. Diameters and Other Parameters for Crude Oils Measured Using the FFTEM Technique^a

crude oil	D_p (nm) ^b	σ (nm) ^c	Diameter Observed (nm)		density ^d
			maximum, D_M	minimum, D_m	
Cerro Negro	9.2	1.0	11.7	5.4	24 ^e
DM 153	7.1	1.4	10.8	5.0	20 ± 2
Furrial	7.1	2.3	12.1	5.0	17 ± 1
Ceuta	8.8	2.0	11.5	5.8	6.0 ± 0.9

^a Errors are <2%, unless indicated otherwise. ^b Average value observed. These values were determined to be equal to those fitted to Gaussians, within 2.2% or better. ^c Standard deviation of the Gaussian distribution. ^d Density of particles in 10 000 Å². ^e Good estimate; see text.

that have been coprecipitated with asphaltenes. Apparently, both the S/As and the R_C/As ratios are related to the colloidal stability of the crude oils. Ceuta and Furrial are both crude oils with flocculation problems. These have the highest and lowest values of S/As and R_C/As, respectively, which is a somewhat expected result. Interestingly, the ratio that is related to colloidal stability in the present case is the R_C/As ratio, rather than the Res/As ratio.

Figure 1a corresponds to a microphotograph of DM 153 oil, whereas Figures 1b and c corresponds to microphotographs of Furrial oil before and after shearing. The arrows in these figures are used to facilitate the observation. Scale bars in these photographs denote a length of 100 or 200 nm. In Figure 1a, spheroidal particles can be easily observed. A comparison of Figure 1b and c shows that, after shearing, the large flocks present in the oil are broken down into single particles or smaller aggregates.

In Tables 3–9, the diameters and other parameters measured for different samples and different conditions are shown. The measured average diameter (D_p ; see Table 3) was within 2% of that obtained by fitting the data to a Gaussian distribution. The D_p value for Furrial oil was almost identical to that reported using SAXS⁵ (6.8 nm). The observed maximum and minimum diameters (D_M and D_m , respectively) are also shown in this and other tables. It is likely that the samples contain particles with diameters lower than D_m , and, because of the limiting low resolution, we were unable to see them.

On the other hand, the D_M values could be measured with high precision, and, except for the silica gel experiments, the highest D_M value measured was ~13 nm.

As expected, particle density is related to asphaltene content. This is shown in Figure 2, where a reasonably straight line could be drawn through the points. Note that the stable crude oils (Cerro Negro and DM 153) are those with the highest density.

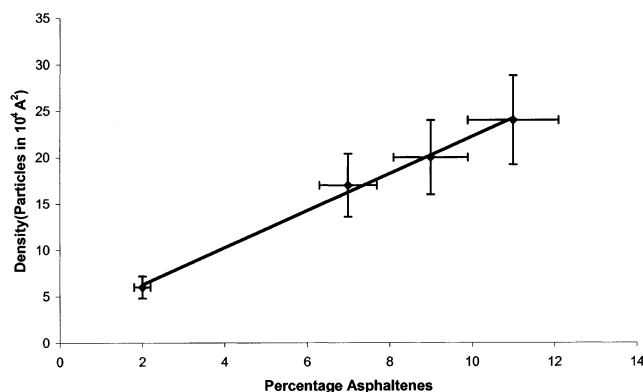


Figure 2. Plot of density versus asphaltene percentage in crude oils (see Table 3).

Table 4. Diameters and Other Parameters for Maltenes, Measured Using the FFTEM Technique^a

maltene	D_p (nm) ^b	σ (nm) ^c	Diameter Observed (nm)		density ^d
			maximum, D_M	minimum, D_m	
Cerro Negro	6.5	1.1	11.5	5.4	7 ± 2
DM 153	6.4	1.2	8.8	5.5	5.0 ± 1.5
Furrial	6.5	1.1	9.4	5.7	5.3 ± 1.5

^a See comments in Table 3. ^b Average value observed. ^c Standard deviation of the Gaussian distribution. ^d Density of particles in $10\,000\text{ Å}^2$.

Resolution was good enough to see clearly that the unitary or single particles were spherically shaped (spheres or low-asymmetry ellipsoids). Although particle diameters of $>4\text{ nm}$ could be measured without any problems in all cases, for Cerro Negro, we found no clear separation between the particles. This result is consistent with the extra-heavy nature of this crude (very high viscosity).

Except for the Ceuta case, the presence of colloids was also detected in maltenes, where lower D_p and lower density values were observed. The corresponding measurements are shown in Table 4. The presence of colloids in maltenes clearly indicates that asphaltene separation is not 100% effective, which is a fact that has been known for a long time. When diluted with toluene (in a 2:1 toluene–maltenes ratio), the D_p values remain

Table 5. Diameters and Other Parameters for Crude Oils after Heating at 80 °C ^a

crude oil	D_p (nm) ^b	σ (nm) ^c	Diameter Observed (nm)		density ^d	δD_p ^e
			maximum, D_M	minimum, D_m		
Cerro Negro	7.8	1.9	12.2	5.6	24 ± 2	-1.4
DM 153	6.8	1.3	11.3	5.2	19 ± 2	-0.3
Furrial	6.7	1.2	12.9	5.6	16 ± 1	-0.4
Ceuta	7.9	1.6	10.5	5.7	5.5 ± 0.6	-0.9

^a Using the FFTEM technique. See comments in Table 3. ^b Average value observed. ^c Standard deviation of the Gaussian distribution. ^d Density of particles in $10\,000\text{ Å}^2$. ^e Change relative to the values at room temperature.

Table 6. Diameters and Other Parameters for the Furrial Oil, Measured at Different Temperatures Using the FFTEM Technique^a

temp. T (°C)	D_p (nm) ^b	σ (nm) ^c	D_M (nm) ^d
25	7.1	2.3	12.1
50	6.9	2.0	13.4
80	6.7	1.2	12.9
100	6.5	1.9	11.1
150	6.3	1.7	10.8
200	5.9	1.6	10.6
250	5.8	0.9	8.5

^a See comments in Table 3. Minimum diameters were $\sim 5\text{ nm}$ and densities were ~ 17 in all these measurements. ^b Average value observed. ^c Standard deviation of the Gaussian distribution. ^d Maximum diameter observed.

almost constant. In other words, in this case, particle density was the only parameter affected (halved) by dilution.

As may be expected, a reduction in D_p was observed when the crude oils were heated. A similar trend was observed using the SAXS technique.⁵ No significant change in density was observed. The results are shown in Tables 5 and 6. As shown in Figure 3, for Furrial oil, a steady reduction in D_p with temperature was observed. A similar reduction, using SAXS, has been reported earlier for the same oil.⁵ As a result of heating, significant changes in the standard deviation σ and the particle diameter distribution (PDD) were detected in most cases. This is illustrated in Figure 4 for the Ceuta case.

Experiments where oils were contacted with silica or clay lead to different results, depending on the oil.

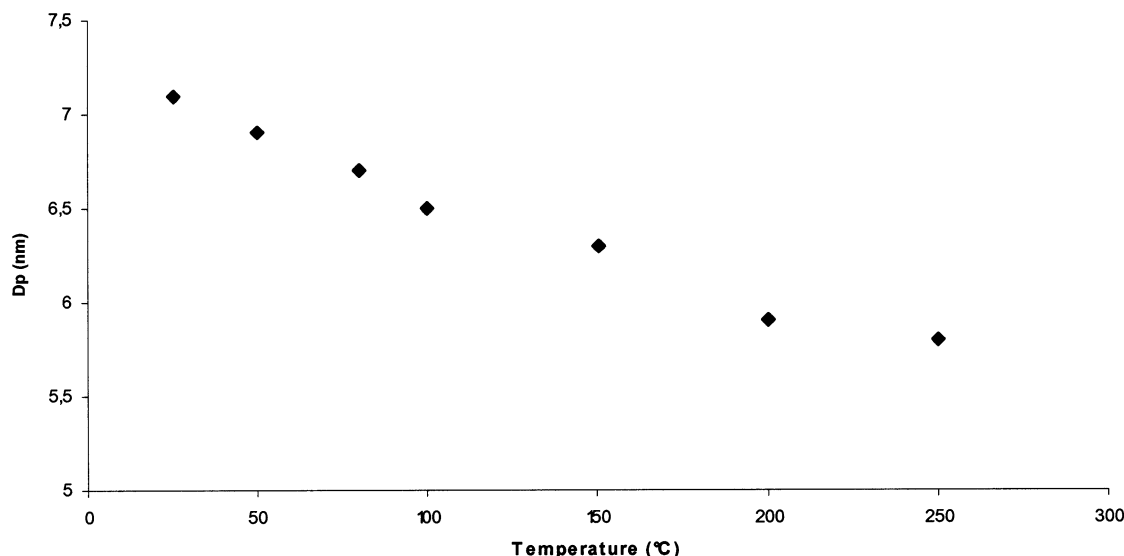


Figure 3. Plot of measured average particle diameter (D_p), as a function of temperature, for the Furrial oil.

Table 7. Diameters and Other Parameters, Measured Using the FFTEM Technique, for the Furrial Oil and the DM 153 Oil in Contact with Silica^a

conditions	sample	D_p (nm) ^b	σ (nm) ^c	Diameter Observed (nm)		density ^d
				maximum, D_M	minimum, D_m	
contacted with a silica plate	Furrial	12.4	2.5	19.6	8.2	14 ± 1
contacted with silica powder and centrifuged	Furrial	8.8	1.4	14.8	6.6	11 ± 2
contacted with silica plate	DM 153	7.5	2.3	11	5.1	13 ± 2

^a See comments in Table 3. ^b Average value observed. ^c Standard deviation of the Gaussian distribution. ^d Density of particles in 10 000 Å².

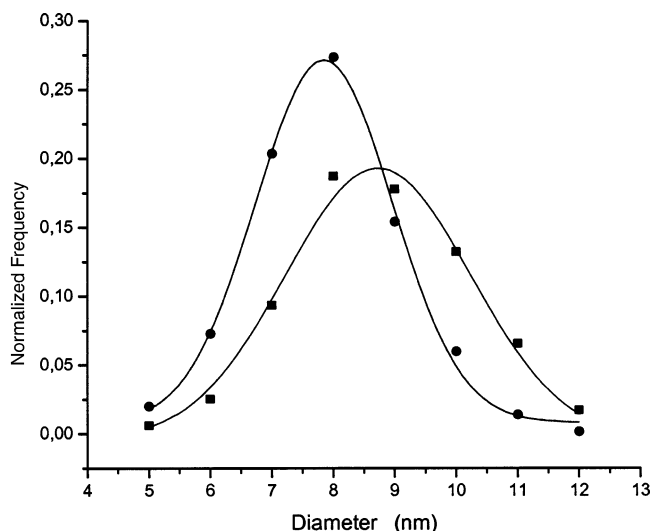


Figure 4. Fittings to Gaussian curves of the particle diameter distribution (PDD) for Ceuta oil. Gaussian curves were observed by fitting to the experimental PDD (datapoints). Curve to the left (plotted data represented by filled circles) represents data collected at 80 °C, whereas the curve to the right (plotted data represented by filled squares) represents data collected at room temperature (also see Tables 3 and 5).

Table 8. Diameters and Other Parameters, Measured for Diluted Oils (with Five Volumes of Toluene), Using the FFTEM Technique^a

crude oil	D_p (nm)	σ (nm)	Diameter Observed (nm)		density	δD_p ^b
			maximum, D_M	minimum, D_m		
DM 153	6.1	1.2	7.9	4.9	8.2	-1.0
Furrial	5.7	1.3	8.9	5	4.5	-1.4
Ceuta	6.5	0.7	8.7	6	2.4	-2.3

^a See comments in Table 3. ^b Reduction with respect to the crude oil (see Table 3).

Whereas significant changes in all parameters were observed for Furrial oil, only modest changes in D_p were observed for the DM 153 oil (see Table 7). The presence of very large flocks was observed in the microphotographs of the Furrial oil. This was not the case for the DM 153 oil, the photography of which seemed similar to that of the untreated oil. The reduction in density in both cases is due to asphaltene separation by the silica surface.

As shown in Tables 8 and 9, and Figure 5, oil dilution with toluene or benzene leads to a significant decrease in D_p and D_M . As shown in Figure 5, for the Cerro Negro case, for D_p , this effect stabilizes for a 20/1 v/v relationship.

On the other hand, as shown in Figure 6, dilution with *n*-heptane led to quite a significant increase in D_p for the Cerro Negro oil.

Table 9. Diameters and Other Parameters, Measured Using the FFTEM Technique, for Benzene/Cerro Negro Oil Mixtures^a

oil/benzene composition (v/v)	D_p (nm)	σ (nm)	D_M (nm)	density	δD_p ^b
1/0	9.2	1.0	11.7	24	0
1/5	7.5	1.4	11.5	9	-1.7
1/20	7.1	1.8	10.1	4	-2.1
1/80	7.0	0.7	9.0	ND	-2.2

^a See comments in Table 3. ^b Change with respect to the crude oil.

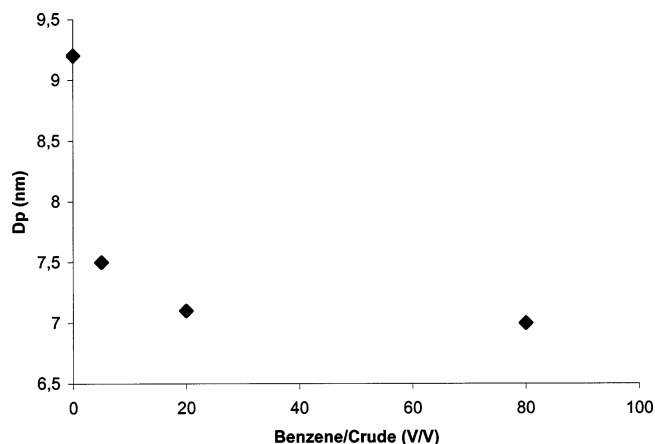


Figure 5. Plot of D_p as a function of the benzene/Cerro Negro crude ratio (v/v).

Discussion

According to the results in Table 2, the combine S/As and the R_C /As ratios seem to be related to colloidal stability, at least for the four cases studied here. Also interesting is the fact that R_C rather than the total amount of resins is the amount that seems to be related to colloidal stability. If so, some type of specific interaction between the resins in R_C and the asphaltenes may be occurring here. However, similar studies with a large number of oils are required before reaching a final conclusion in this regard.

There is no doubt that the major contribution in the present paper comes from the D_p results in Table 3. Although indirect techniques such as SAXS have been used to study colloidal size in crude oil,^{5,8,9} the present methodology involves direct measurement, independent of any model used to represent the colloids. The excellent agreement between the two techniques, which is observed for the Furrial case⁵ (see the experimental section), is, no doubt, very good news.

The results in Tables 5–9, and in Figure 6, should be relevant to colloidal composition and structure. It has been reported that asphaltenes are a mixture of two fractions A1 and A2 that differ widely in regard to solubility.³ Thus, for Furrial asphaltene, it was found

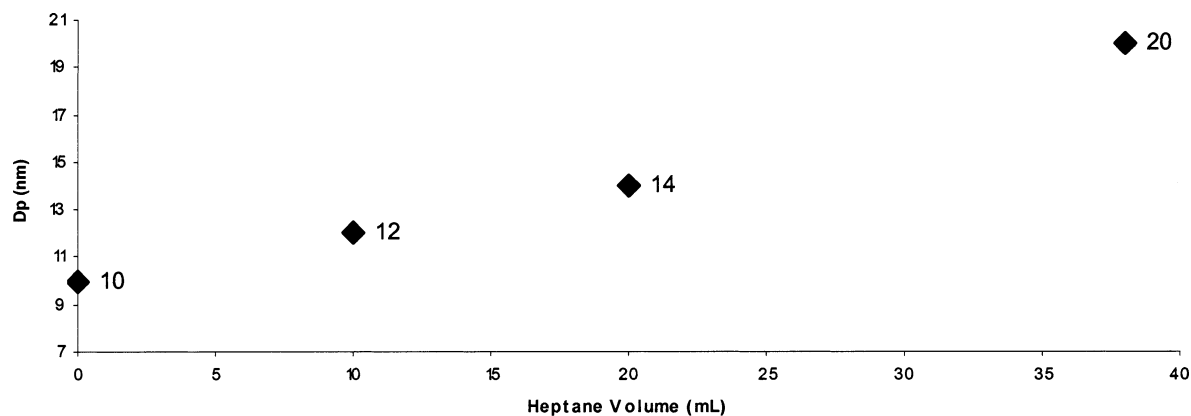


Figure 6. Plot of D_p as a function of the *n*-heptane/Cerro Negro crude ratio (v/v).

that solubility of A1 (toluene, room temperature) was observed to be ~ 0.09 mg/L, whereas that for both asphaltene and the fraction A2 is ~ 57 g/L. On the basis of this observation, a model for asphaltene colloids was proposed that had a core rich in A1-type molecules and with a periphery rich in A2-type molecules. In this way, in aromatic solvents, the fraction A1 is co-solubilized by the fraction A2. As has been discussed previously, the effect does not seem to be a simple surfactant effect; rather, it is related to the ability of these fractions to form solid solutions.³

Using parallel arguments, the solubility of crude oil colloids could be taken into account in similar terms, with resins and other oil components playing the role of fraction A2 in asphaltene colloids. That is, asphaltenes are expected to be in the core and resins are expected to be in the periphery. Thus, when crude oil is diluted or heated, this periphery is dissolved and the D_p is reduced to a point where the insoluble portion (asphaltenes) is exposed to the medium. This would account for the stabilization shown in Figure 5.

On the other hand, diluting with *n*-heptane increases D_p , presumably because of the adsorption of resins on the surface colloids (see Figure 6). This is an important result for two reasons. First, according to some resin adsorption reports, an increase in resin adsorption on asphaltenes is expected when the surface tension of the medium (γ_m) is reduced.¹³ For instance, when the medium changes from toluene ($\gamma_m = 28$ dynes/cm) to *n*-heptane ($\gamma_m \approx 19.28$ dynes/cm). Second, as a basis for a well-known flocculation mechanism, it has been proposed that, during dilution with a nonsolvent, such as *n*-heptane, desorption of resins is the cause of flocculation.¹⁸

Instead, the aforementioned results suggest a process whereby, after the addition of the first volumes of *n*-heptane, the adsorption of resins would prevail. This adsorption will, in turn, reduce the colloid surface tension, thus delaying flocculation. This is consistent with the usual large *n*-heptane volume required to reach the flocculation threshold in most crude oils. In the case of Cerro Negro, more than 3 volumes are required, whereas at least one is needed with the Furrial and Ceuta oils. Although some desorption could be expected with a large excess of *n*-heptane, this will occur when flocculation is over.

Asphaltene colloids in maltenes could be considered as a crude oil that has been highly diluted with a good

solvent. Hence, according to the aforementioned arguments (see Figure 5), the observed low D_p values are expected, with a low tendency to change upon dilution (see results and Table 4).

Microphotography of the Furrial oil, taken of the crude as received from the field, showed the presence of large particle aggregates with the largest length being ≥ 200 nm (see Figure 1b). Most of these aggregates were converted to single entities (primary particles) after stirring or heating the crude oil (see Figure 1c). This means that, for dead oil at least, the energy holding these particles is weak (on the order of kT). As a consequence, random aggregation was observed in these oils.

Another interesting thermal effect is shown in Figure 4, where a very significant change in diameter distribution was observed after the Ceuta oil was heated. Similar changes were observed for the other samples (compare Tables 3, 5, and 6). According to Table 6, a steady reduction in σ with increasing temperature was observed for the Furrial oil. Thus, the reduction in diameters with temperature is accompanied by changes in diameter distribution. We believe that further research is needed to account for these PDD changes properly.

It has been reported that quantitative precipitation of asphaltenes could be achieved by treatment of crude oils with silica.⁶ In this case, two possible mechanisms for asphaltene flocculation in the presence of silica could be envisioned: (i) removal of asphaltene dispersants by the surface, followed by flocculation and flock deposition, or (ii) direct adsorption of particles on the surface, without any other intervening path. Floc formation and diameter increase (see Table 7) seem to be the case for the Furrial oil. In this case, removal of the dispersant promotes flocculation. On the other hand, the small changes that are observed with the DM 153 oil suggest a direct adsorption of colloids.

These results strongly suggest that, in the Furrial case, the adsorbed dispersant layer is weakly bound to the colloid and, hence, is easily removed by the silica surface. On the other hand, for the DM 153 case, the aforementioned layer is strongly bonded and cannot be easily removed by the silica surface. These results and arguments are consistent with the colloidal stability of these oils.

Conclusions

Colloidal particles in crude oils were observed to be spherical, with measured average particle diameter (D_p) values in the range of 7–9 nm, with maximum diameters of <13 nm. The colloidal particle model that has been proposed, where low-solubility asphaltene molecules occupy the core and soluble compounds, which allow for the colloid dispersion, occupy the periphery, was determined to be consistent with the thermal, dilution, and adsorption experiments that have been performed on the four examined oils. Thus, a decrease in D_p after heating or after dilution with a good solvent was consistent with an increase in the solubility of

compounds in the periphery. Experiments with silica strongly suggest that the colloidal instability of some crude oils is due to a periphery weakly bonded to the core of the colloidal particle. Increases in D_p , after the addition of *n*-heptane to the crude, were observed, which is consistent with adsorption of the resins.

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