# Aggregated Structure of Flocculated Asphaltenes

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*Many petroleum processing problems are related to asphaltene flocculation. A detailed understanding of the colloidal structure of asphaltenes in oil can play a decisive role in improving processing facilities and/or operating conditions. The structure of the flocculated part of the asphaltenes of a crude oil far above the flocculation threshold was studied to understand its links with macroscopic phase separation. Asphaltene filtrations were performed using filter pore sizes from 0.025 to 10 μm. According to small angle X-ray scattering (SAXS) spectra and density measurements, these extracted asphaltenes in toluene solutions did not have any physical differences. Measurements of nanometric sizes for the dispersed particles after dissolution in toluene show that micron-size flocculated asphaltenes are strongly aggregated structures. Therefore, filtration experiments separate asphaltenes corresponding to various aggregates of similar entities using electron micrographs of asphaltene powders show spherically shaped aggregates of micron size. SAXS and USAXS techniques were used to investigate the internal structure of the asphaltenes powder. The aggregates are clearly a compact organization of asphaltenic material. This dense structure explains why flocculated asphaltenes are subject to sedimentation, which induces the visible macroscopic phase separation.*

## Introduction

Organic deposition, flocculation and plugging can occur during heavy oil production in the reservoir, near the wellbore (Park and Mansoori, 1988) during pipeline transportation (Escobedo and Mansoori, 1992), during refining, in the coking process, and during combustion. The economic implications can be important as the production efficiency is severely affected by the heavy components of the crude oil which self-associate (Pfeiffer and Saal, 1940; Sheu et al., 1992), flocculate or even polymerize at certain temperatures and pressures (Janardhan and Mansoori, 1993).

Asphaltenes are the heaviest components of a crude oil defined as the insoluble fraction in light normal alkanes (*n*-heptane according to AFNOR standard) (AFNOR, 1982). This fraction contains aliphatic (or naphtenic) and aromatic structures (Yen et al., 1961), as well as small amounts of heteroatoms: sulfur, oxygen, nitrogen (Moschopedis et al., 1976). Because of their definition, asphaltenes are generally incompatible with light petroleum fractions leading to undesirable effects in many stages of the petroleum industry.

Significant advances in our understanding of colloidal aggregation have been made over the past several years. Some models (Fleischmann et al., 1989; Weitz et al., 1984; Meakin and Family, 1987) have been proposed in order to explain the structure of the colloidal aggregates allowing a more detailed study of the process, as well as to clarify the relationship between fractal cluster structure and aggregation kinetics. Asphaltene aggregates have already been recognized to follow a fractal pattern with a fractal dimension $D_f \approx 2$ in solutions in good solvents before flocculation occurs when a flocculant is added to these solutions (Janardhan and Mansoori, 1993; El Mohamed et al., 1988; Liu et al., 1995; Anisimov et al., 1995; Fenistein et al., 1998; Yen, 1994; Winniford, 1963; Altgelt, 1968; Andersen et al., 1991; Al Jarrah and Apilian, 1987; Speight et al., 1985). Some authors relate the self-similarity of asphaltenes to theoretical aggregation models (DLCA or RLCA) (Al Jarrah and Apikian, 1987; Janardhan and Mansoori, 1993; El Mohamed et al., 1988).

A key to the understanding of colloidal aggregation is the energy of interaction between two approaching particles which is assumed to be divided in a short-range attractive part and in a repulsive part which behaves as a barrier. If the height of the repulsive energy barrier $E_b$ is sufficiently large compared to $k_bT$ (attractive part), the particles will be unable to stick to each other when their diffusive motion causes

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them to collide, and then they will be stable without aggregation. Aggregation can occur when the height of the barrier is reduced. If $E_b$ is reduced to much less than $k_bT$, every collision will result in the particles sticking together, leading to a very rapid aggregation, limited only by the rate of diffusion-induced collisions between the clusters. This regime is therefore called diffusion limited colloidal aggregation. In contrast, if $E_b$ remains comparable to or larger than $k_bT$, many collisions must occur before two particles stick to each other. In this case the aggregation rate is limited by the probability of overcoming the repulsive barrier $P \sim \exp(-E_b/k_bT)$, thus leading to a much slower aggregation. This regime therefore is called reaction limited colloidal aggregation. In each case, however, as particles stick together to become clusters, the clusters themselves continue to diffuse, collide, and aggregate. Thus, both regimes are examples of cluster-cluster aggregation. In any case the interaction range is short compared with the particle radius while the strength of the resultant bonds are much larger than $k_bT$, so the aggregation is irreversible and the clusters formed are rigid. A fast aggregation (only limited by diffusion) leads to an open structure ($D_f = 1.7–1.8$) while an aggregation that must overcome an energy barrier (limited by reaction) gives rise to more dense ones ($D_f = 2.0–2.1$).

The addition of *n*-heptane, which is a known flocculant for petroleum products, induces an aggregation process between asphaltene particles. Petroleum products are characterized by the existence of a flocculation threshold that corresponds to the minimum *n*-heptane proportion necessary to induce asphaltenes phase separation. Above this threshold, the addition of *n*-heptane increases the quantity of separated fraction up to a certain proportion.

The main objective of this article is to investigate the structure of the asphaltenes flocculated part of a crude oil far above the flocculation threshold in order to understand its links with the macroscopic phase separation.

## Experimental Studies

Three petroleum fluids have been examined: a vacuum residue already reported elsewhere (Fenistein et al., 1988; Ravey and Espinat, 1990; Herzog et al., 1988; Barre et al., 1997) named **G** and two asphaltene rich crude oils from different geographic origins named **M** and **K**. The usual procedure to extract asphaltenes is described by AFNOR standard NF T60-115, using 40 cm$^3$ of n-heptane per gram of crude oil to flocculate the asphaltenes and further filtrating the liquid plus the flocculated asphaltenes with a filter of "appropriate pore size." As this size is not precisely defined for the extraction of asphaltenes, we used filters of a wide range of pore sizes (Millipore made of ester of cellulose: 0.025 $\mu$m, 0.05 $\mu$m, 0.1 $\mu$m, 0.3 $\mu$m, 0.45 $\mu$m, 0.65 $\mu$m, 1.2 $\mu$m, 3 $\mu$m, 5 $\mu$m, 10 $\mu$m). The extracted fraction was dried overnight and weighted, with the percentage of asphaltenes in the crude oil then being calculated. Filters of a different material (teflon) have also been used in order to verify that there were not any interactions between the material and either the filtrates or the deposits. The results of the characterization procedures described hereafter did not show any fractionation of either the filtrates or the deposits resulting from such interactions.

The asphaltenes extracted from these filtrations for each crude oil examined have been analyzed in dilute toluene solutions. Densities have been measured using an Anton Paar DMA45 vibrating tube densitometer at ambient temperature. The specific volume (inverse of the density) of the solutions is linear with asphaltenes concentration in the range 0 to 15 wt. %. We extrapolated to the density of pure asphaltenes assuming this linearity over the entire concentration range. The values obtained are 1.195, 1.2, 1.2 g/cm$^3$ for asphaltenes ***G***, ***M*** and ***K***, respectively.

### *SAXS measurements on asphaltenes in toluene solutions*

SAXS has been performed using a Huxley-Holmes camera with a sample to detector distance of 0.82 m. The investigated wave vector $q$ [$q = (4\pi/\lambda)\sin 2\vartheta$] ranges from $10^{-2}$ to $2.10^{-1}$ Å$^{-1}$, the scattering wavelength being $\lambda = 1.544$Å. Intensities have been converted to an absolute scale by measuring the attenuation coefficient for the incident beam. The Lake method (Lake, 1967) has been used for collimating corrections. Dilute solutions (less that 2%v/v) of asphaltenes in toluene have been placed in a 2 mm glass capillary.

Scattered intensity can be expressed for a solution of particles by the equation

$$I(q) = \Phi \Delta \rho^2 V P(q)\, S(q) \tag{1}$$

In dilute asphaltene solutions, the structure factor $S(q) \rightarrow 1$, with the assumption that the interactions between particles are negligible.

All the spectra presented a Guinier plateau in the low $q$ range (Guinier and Fournet, 1955). In this range, $P(q = 0)$ can be expressed in the limiting form as

$$P(q \rightarrow 0) = \left(1 - \frac{q^2 R_g^2}{3} + \ldots\right) \tag{2}$$

We analyzed the spectra in this domain using a Zimm approximation (Zimm, 1948)

$$\frac{1}{I(q)} = \frac{1}{I(q=0)}\left(1 + \frac{q^2 R_g^2}{3}\right) \tag{3}$$

The zero q intensity can be related to the asphaltenes molecular weight, $M_w$, through the relation

$$\frac{I(q=0)}{\Phi \Delta \rho^2} = \frac{M_w}{N_a d} \tag{4}$$

$\Delta \rho^2$ is the contrast term ($8.1 \times 10^{-4}$ cm$^{-1}$·Å$^{-3}$, $7.3 \times 10^{-4}$ cm$^{-1}$·Å$^{-3}$ and $7.3 \times 10^{-4}$ cm$^{-1}$·Å$^{-3}$ for ***G***, ***M*** and ***K*** oils, respectively), $\Phi$ is the volume fraction of asphaltenes in toluene, $d$ is the asphaltenes density, and $N_a$ is the Avogadro number.

### *Structure determinations on asphaltenes powder*

SAXS spectra of an asphaltenes powder have been recorded using the same apparatus as previously described. USAXS measurements have been conducted in the

'Laboratoire de Chimie Moléculaire' in CEA (Saclay, France) using a Bonze-Hart camera. The investigated wave vector $q$ for USAXS ranges from $5\times10^{-4}$ Å$^{-1}$ to $5\times10^{-2}$ Å$^{-1}$. The contrast term for an asphaltenes powder is $\Delta\rho^2 = 1.18\times10^{-2}$ cm$^{-1}$·Å$^{-3}$. To complete this set of structure determinations, scanning electron micrographs have been also taken. In the following section, experimental results are given for one asphaltenes powder. However the observations made and the conclusions drawn are supported by other data relative to asphaltene deposits recovered from different crudes coming from various geographical origins, whatever is the pore size of the filter used to separate them.

### *Kinetics of asphaltenes aggregation and sedimentation*

Asphaltenes flocculation is also ruled by kinetics. Indeed, an evolution of the mass of asphaltene aggregates occurs with time. There is also an increasing possibility of incorporation to these aggregates of lighter fractions of the crude oil.

## Results

The evolution of the asphaltenes amount recovered as a function of filters pore size is presented in Figure 1.

As it is seen from Figure 1, the asphaltenes content is not constant when the pore size of the filters changes. Thus, the polydispersity of asphaltene aggregates in an excess of n-heptane is clearly shown.

The experimental data have been fitted using a power law equation

$$Q = AR^b \tag{5}$$

$R$ is the pore size and thus the minimum size of asphaltene particles retained by the filter, $A$ and $b$ are fitting parameters, and $Q$ is defined as the mass (g) of asphaltenes extracted from 100 g of crude.

The values of the fitting parameters $A$ and $b$ calculated for the oils examined can be seen in Table 1.

These results raise questions concerning the definition of asphaltenes according to a standard separation procedure while the comparison of data from literature when asphaltenes are separated using different filters should be reconsidered. According to our results, these differences on asphaltene quantities are less important for heavy petroleum products (for which the variation range is within the experimental uncertainty for titration experiments) and more important for light petroleum products (for which the relative variation can be of the same order of magnitude than the measured asphaltenes content). Although the AFNOR standard has been proposed mainly to characterize asphaltene rich products, heavy crudes and bitumen, and that usually filters with pore sizes greater than 10 $\mu$m are used, a more precise definition of the filters pore size is needed to obtain more accurate results.

SAXS and density measurements have been conducted on asphaltenes recovered by filtration and redissolved in toluene. The Small Angle X-ray Scattering spectra presented in Figure 2 as well as density measurements (1.195, 1.2 and 1.2 g/cm$^3$ for asphaltenes ***G***, ***M*** and ***K*** respectively) reveal that there are not any significant differences for the different fractions recovered.

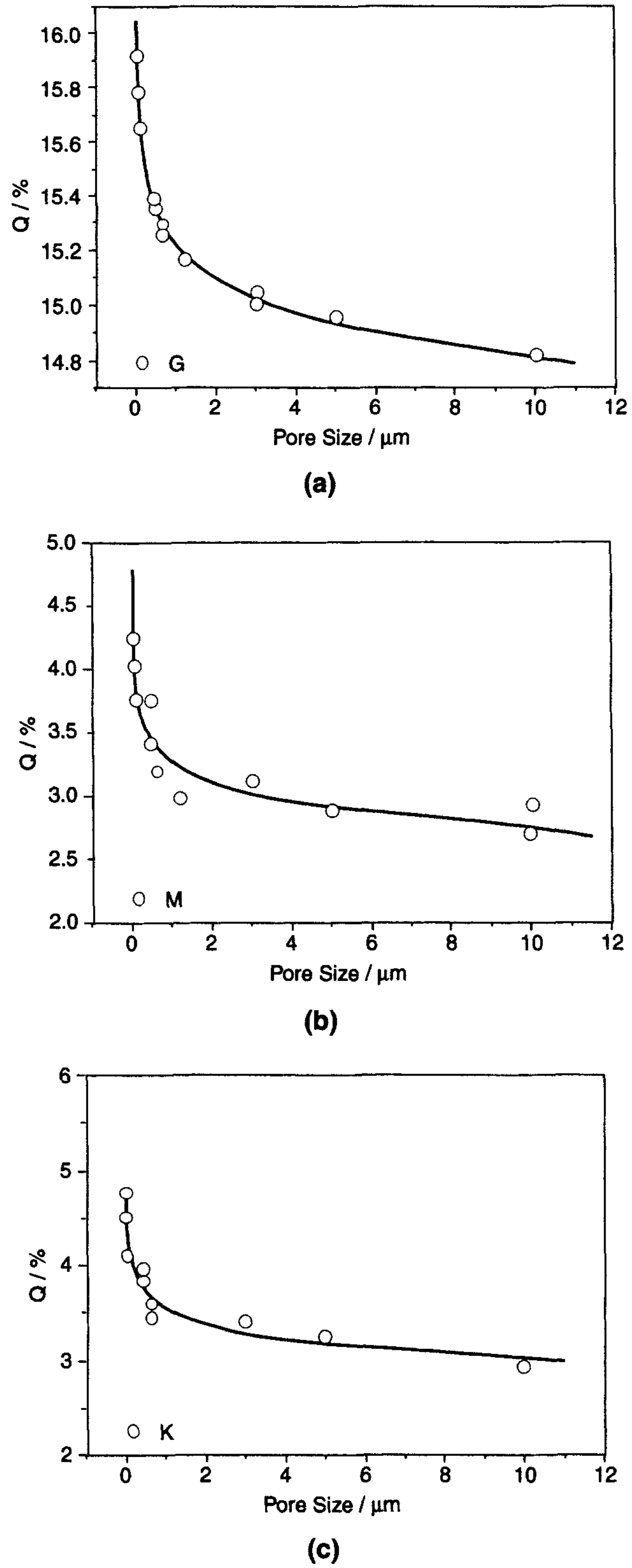

**Figure 1. Asphaltenes quantity evolution as a function of filters pore size.**

The values of the radius of gyration and of the molecular weight computed from the SAXS spectra are presented in Table 2 for the three asphaltenes examined.

Table 1. Values of A and B in Eq. 5

| Oil | A | b |
|---|---|---|
| ***G*** | 15.22 | −0.01192 |
| ***M*** | 3.242 | −0.06950 |
| ***K*** | 3.545 | −0.06714 |

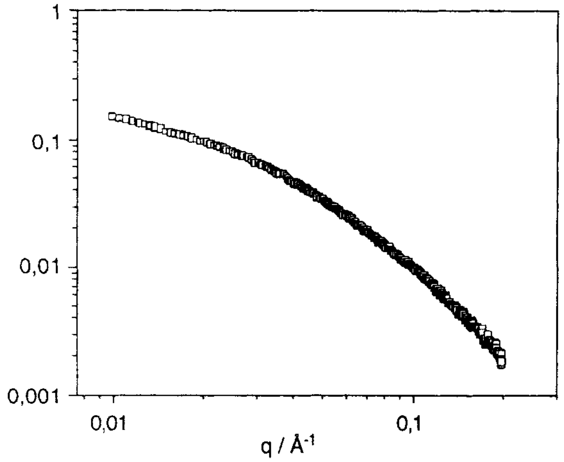

**Figure 2a. Small angle X-ray scattering spectrum of asphaltenes *G*.**

Filter pore size: ■ 10 μm; ● 0.45 μm; Δ0.025 μm.

These observations show that flocculated asphaltenes recovered by filtration are strongly aggregated structures since after their dissolution in toluene, the measured sizes of the dissolved entities are orders of magnitude smaller than the sizes of the former ones. For each crude oil, the different amounts of asphaltenes recovered by filtration are thus related to the different extent of aggregation of similar entities.

Asphaltenes flocculation is also ruled by kinetics. As crude oils flow continuously for very long periods in wells, pipes and surface facilities, the buildup of an asphaltenic deposit resulting from aggregation and further sedimentation has been observed over an arbitrarily fixed period of four months. The time dependence of the amount of asphaltenes recovered may be seen in Figure 3.

As flocculated asphaltenes are aggregates of micron size, we wanted to investigate the structures involved. SAXS and USAXS spectras of an asphaltenes powder, as well as scanning electron micrographs (SEM) of this powder, can be seen in Figures 4 and 5, respectively.

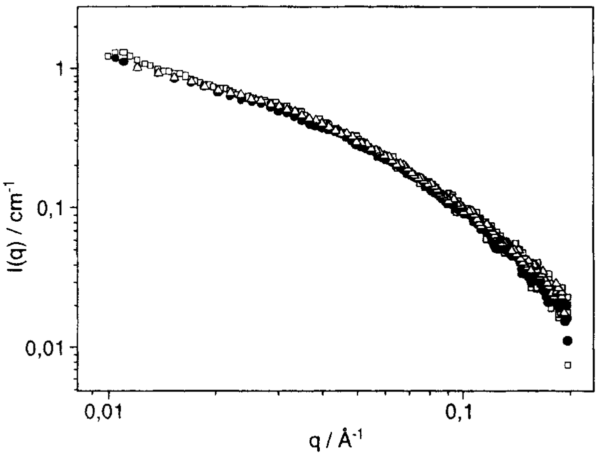

**Figure 2b. Small angle X-ray scattering spectrum of asphaltenes *M*.**

Filter pore sizes: ■ 10 μm, ● 0.65 μm, Δ0.025 μm.

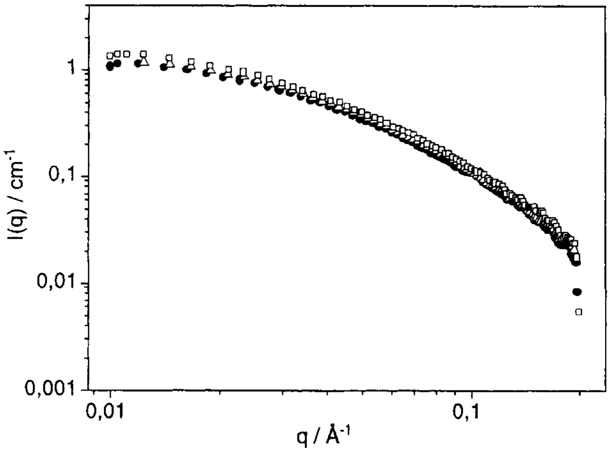

**Figure 2c. Small angle X-ray scattering spectrum of asphaltenes *K*.**

Filter pore sizes: ■ 10 μm, ● 3 μm, Δ0.025 μm.

Table 2. Molecular Weight $M_w$ and Radius of Gyration $R_g$ for Asphaltenes *G*, *M*, and *K*

| Oil | Molec. Wt. g·mol$^{-1}$ | Radius of Gyration Å |
|---|---|---|
| ***G*** | 115,000 | 65.5 |
| ***M*** | 75,000 | 55 |
| ***K*** | 103,000 | 60 |

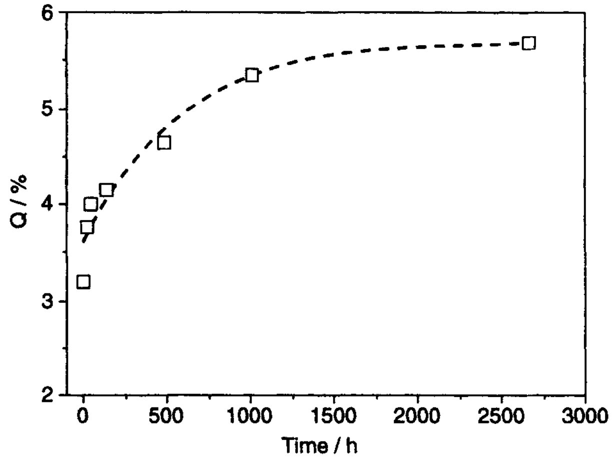

**Figure 3. Kinetics of asphaltenes aggregation and sedimentation.**

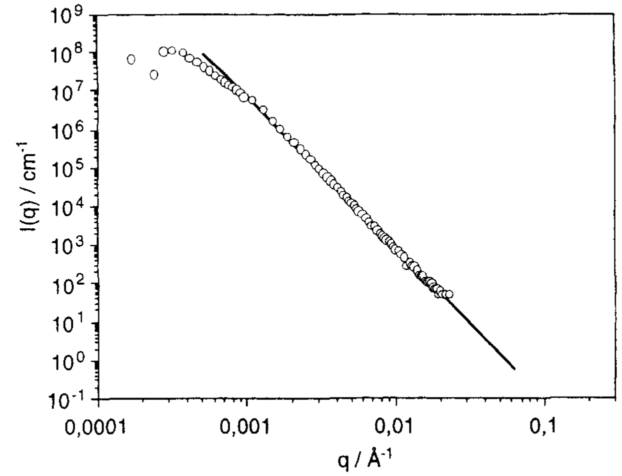

Figure 4. SAXS and USAXS of an asphaltenes powder.

A great scattered intensity for the $q$ vectors ranging from $q_{\min} = 3 \times 10^{-4}$Å$^{-1}$ to $q_{\max} = 4 \times 10^{-2}$Å$^{-1}$ can be easily observed in Figure 4. The slope(s) of the curve for the examined $q$ range is $s = -3.94 \pm 0.01$. This high value is characteristic of dense objects (compact aggregates), the order of size of which can be given by $(1/q_{\min}) \approx 1\,\mu$. The value of $q_{\max}$ can express the scale of the smallest heterogeneity inside this compact structure which is very small compared to the radius of the aggregate ($(1/q_{\max}) \approx 25$Å). According to the equation $s = -2D_f + D_s$ (Fleischmann et al., 1989; Auvray and Auroy, 1991), a slope of $-4$ does not only mean a dense structure in the mass fractal organization but also implies a smooth surface in the related size range.

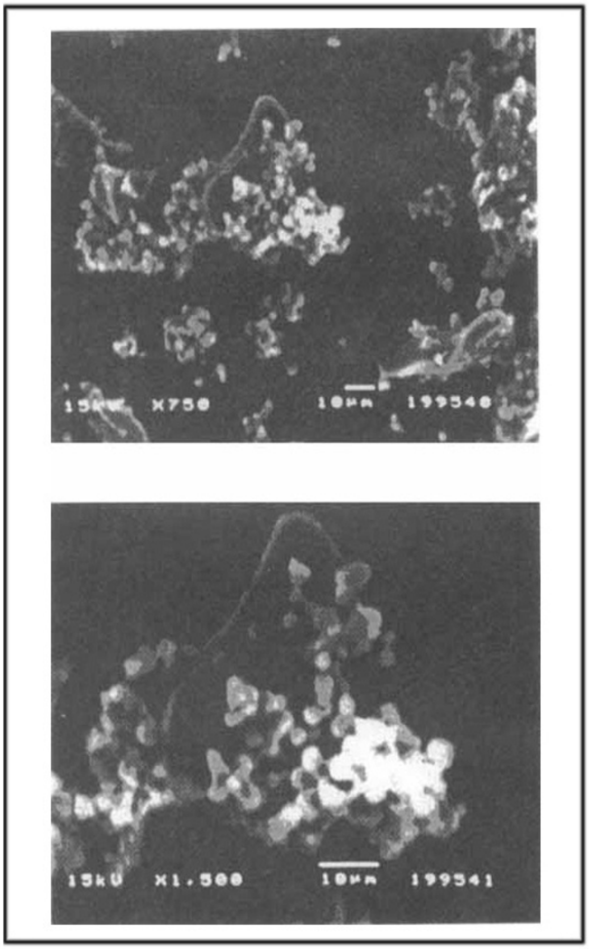

Figure 5. Scanning electron microscopy of asphaltenes powder.

Scanning electron micrographs of the asphaltenes confirmed the presence of dense spherical structures of which the polydispersity in size is in a good agreement with the results already presented (one up to a few tens of microns). The structure of flocculated asphaltenes is clearly a compact organization of entities ranging from nanometers to microns. The larger objects are sensible to sedimentation and, thus, visual macroscopic observation of phase separation above flocculation threshold is possible. It is interesting to note that the results obtained from the literature for asphaltenes aggregation before the flocculation threshold showed an open structure of these aggregates. A phenomenon such as structure reorganization is not predicted by theoretical models of colloidal aggregation such as DLCA or RLCA.

We argue that attractive interactions between asphaltene particles can become quite intense, but also that the interaction range can increase up to a level that models of short-range interactions are not capable to fully represent, thus not being able to explain the asphaltenes behavior in an excess of n-heptane.

## Conclusions

The addition of a light alcane (n-heptane) to a petroleum oil induces the growing of asphaltene aggregates as well as the compaction of their internal structure over a wide range (2.5 nm to 1 $\mu$m). The compact organization of the large clusters permits the gravitational forces to induce a fast sedimentation, resulting in a visible macroscopic phase separation. The adding of a flocculant decreases the solvent capacity of the asphaltenes environment thus increasing the intensity, as well as the range of the attractive interactions between asphaltene molecules. Therefore, a mass reorganization of the aggregates from an open to a dense structure can occur.

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## Notation

$A$ = fitting parameter, $\mu$m$^{-1}$
$b$ = fitting parameter

$D_f$ = mass fractal dimension
$D_s$ = surface fractal dimension
$E_b$ = repulsive energy barrier, J
$I(q)$ = scattered intensity, cm$^{-1}$
$k_b$ = Boltzmann constant, J·K$^{-1}$
$M_w$ = molecular weight, g·mol$^{-1}$
$N_a$ = Avogadro number
$P(q)$ = form factor
$q$ = wave vector, Å$^{-1}$
$Q$ = mass (g) of asphaltenes extracted from 100 g of crude
$R$ = filter pore size, $\mu$m
$R_g$ = radius of gyration, Å
$S(q)$ = structure factor
$T$ = absolute temperature, K
$V$ = volume of aggregate, Å$^3$
$\lambda$ = scattering wavelength, Å
$\rho$ = density, g·cm$^{-3}$
$\Delta\rho^2$ = contrast term, cm$^{-1}$·Å$^{-3}$
$\vartheta$ = angle between scattered and incident beam, °
$\Phi$ = volume fraction

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