AGGREGATE STRUCTURE ANALYSIS OF COLOMBIAN HEAVY CRUDE OIL-DERIVED ASPHALTENES USING SMALL ANGLE X-RAY SCATTERING

ANÁLISIS DE LA ESTRUCTURA DE AGREGADOS DE ASFALTENOS DERIVADOS DE PETRÓLEO CRUDO PESADO COLOMBIANO USANDO DISPERSIÓN DE RAYOS-X A BAJO ÁNGULO

ANÁLISE DA ESTRUTURA DE AGREGADOS DE ASFALTENOS DERIVADOS DE PETRÓLEO BRUTO PESADO COLOMBIANO USANDO DISPERSÃO DE RAIOS-X DE BAIXO ÂNGULO

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ABSTRACT

Small-Angle X-ray Scattering (SAXS) technique was used to characterize the structure of Asphaltene aggregates as a function of its concentration in Toluene solutions. Asphaltene concentration ranged from 0.01 to 1% w/v. Solid Asphaltenes were obtained from a Colombian heavy crude oil following the ASTM D6560-12 standard method by precipitation with *n*-heptane. Structural properties were interpreted in terms of the radius of gyration (R_g) and the power-law exponents (d). The obtained spectra for Asphaltene-Toluene systems allowed us to explore two regions. At low values of the scattering vector q ($q < 3 \times 10^{-2}$), we found that Asphaltenes self-associate to form aggregates with fractal properties. These structures exhibit a particular transition from surface fractals to mass fractals as concentration increased. In the second one ($q > 3 \times 10^{-2}$), scattering curves showed that Asphaltenes form small dense regions, in which the intensity of the scattered radiation rises with increasing concentration. The observed results demonstrate that Asphaltenes in Toluene solutions coexist as large scale aggregates and nanoaggregates, likewise these structures are conditioned by the Asphaltene concentration and self-association processes.

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RESUMEN

Se utilizó la técnica de dispersión de rayos X a bajo ángulo (SAXS) para caracterizar la estructura de agregados de Asfaltenos en función de su concentración en soluciones de tolueno. La concentración de Asfaltenos osciló entre 0,01 y 1% p/v. Se obtuvieron Asfaltenos sólidos a partir de un petróleo crudo pesado colombiano siguiendo el método estándar ASTM D6560-12 por precipitación con *n*-heptano. Las propiedades estructurales se interpretaron en términos del radio de giro (R_g) y de los exponentes de ley de potencia (*d*). Los espectros obtenidos para los sistemas asfaltenos-tolueno nos permitieron explorar dos regiones. A valores bajos del vector de dispersión q (q < 3 x 10^{-2}), encontramos que los Asfaltenos se auto-asocian para formar agregados con propiedades fractales. Estas estructuras exhiben una transición particular de fractales de superficie a fractales de masa a medida que aumenta la concentración. En la segunda región (q > 3 x 10^{-2}), las curvas de dispersión mostraron que los Asfaltenos forman pequeñas regiones densas, en las que la intensidad de la radiación dispersada aumenta con el incremento de la concentración. Los resultados observados demuestran que los Asfaltenos en soluciones de tolueno coexisten como agregados a gran escala y nanoagregados, asimismo estas estructuras están condicionadas por la concentración de Asfaltenos y por procesos de auto-asociación.

Palabras clave: *Asfaltenos Colombianos, Propiedades estructurales de agregados, Rayos X de Ángulo Reducido de Dispersión, Efecto de concentración.*

RESUMO

Utilizou-se a técnica de dispersão de raios-X de baixo ângulo (SAXS) para definir a estrutura de agregados de asfaltenos em função da sua concentração em soluções de tolueno. A concentração de asfaltenos variou entre 0,01 e 1% p/v. Asfaltenos sólidos foram obtidos a partir de um petróleo bruto pesado colombiano seguindo o método padrão ASTM D6560-12 por precipitação com *n*-heptano. As propriedades estruturais foram interpretadas em termos do raio de giro (R_g) e dos expoentes de lei de potência (*d*). Os espectros obtidos para os sistemas asfalteno-tolueno possibilitaram explorar duas regiões. A valores baixos do vetor de dispersão q (q < 3 a 10^{-2}), descobrimos que os asfaltenos se unem por auto-associação para criar agregados com propriedades fractais. Essas estruturas mostram uma transição particular de fractais de superfície para fractais de massa enquanto aumenta a concentração. Na segunda região (q > 3 a 10^{-2}), as curvas de dispersão mostraram que os asfaltenos formam pequenas regiões densas, nas quais a intensidade da radiação dispersa aumenta com a elevação da concentração. Os resultados observados demostram que os asfaltenos em soluções de tolueno coexistem como agregados em grande escala e nanoagregados, do mesmo modo, essas estruturas estão condicionadas pela concentração de asfaltenos e por processos de auto-associação.

Palavras-chave: *Asfaltenos Colombianos, Propriedades estruturais dos agregados, Dispersão de Raios-X a Baixo Ângulo, Efeito da concentração.*

1. INTRODUCTION

Heavy crude oils are becoming an increasingly important energy resource worldwide. These crudes are characterized by extremely low mobility due to high viscosity at reservoir conditions and high content of undesirable components, such as Asphaltenes, heavy metals and sulfur (Speight, 2010). Asphaltenes are recognized as the least comprehended compounds of the petroleum industry; however it is well-known that Asphaltenes exhibit a colloidal structure in crude oils (Nellensteyn, 1938; Pfeiffer & Saal, 1940). The great significance of Asphaltenes in the petroleum industry is through its negative impact on several operations, such as oil production, transporting, and refining. Flocculation and subsequent precipitation of Asphaltene colloid particles under changes in thermodynamic conditions (Temperature, Pressure, Composition) in the crude oil matrix cause serious problems in all steps of the production chain. From a practical point of view, clarifying how the colloidal structure relates to Asphaltene precipitation is considered to be one of the main challenges in this field because, in the light of such knowledge, effective mitigation strategies will be optimized in petroleum industry.

For many years it has been proposed that Asphaltene precipitation is the result of colloid aggregation (Leontaritis & Mansoori, 1987). Within this approach, the initial molecular aggregation occurs when the aromatic cores of Asphaltene molecules interact by π-π stacking to form colloidal nanoaggregates, which then further associate into larger structures called "fractal clusters" (Figure 1) (Yen, Erdman, & Pollack, 1961; Dickie & Yen, 1967; Mullins, 2010; Eyssautier *et al.*, 2011; Hoepfner, Vilas Bôas FáVero, Haji-Akbari, & Fogler, 2013). It is generally agreed that Asphaltene aggregates are in the colloidal length scale between 5

and 1000 Å (Sheu, 2006). Typical aggregates, depending on the type of their intermolecular interactions, are assumed to associate according to certain general models reported in the literature as Diffusion-Limited Custer Aggregation (DLCA) or Reaction-Limited Cluster Aggregation (RLCA) (Weitz, Huang, Lin, & Sung, 1984; Meakin & Family, 1987).

Various of the properties of scientific and industrial interest (e.g. phase behavior, viscosity and microstructure) are strongly influenced by the physical dimension of colloidal particles (Hiemenz & Rajagopalan, 1997). Nowadays, the size distribution of Asphaltene monomers and aggregates continue to be discussed. Besides the size, establishing other parameters such as the shape, structural factors, and polydispersity of Asphaltenes is required to develop phase behavior models in order to predict the thermodynamic conditions where Asphaltene precipitation takes place. To quantitatively characterize these colloidal parameters, small-angle scattering techniques have been applied on Asphaltene systems as a function of thermodynamic conditions (Tanaka *et al.*, 2003; Sheu, 2006; Headen, Boek, Stellbrink, & Scheven, 2009; Amundaraín, Chodakowski, Long, & Shaw, 2011).

In this work we used SAXS to characterize, for the first time, the aggregated structure of Colombian Asphaltenes in Toluene solutions at a dilute concentration regime from 0.01 to 1 % w/v. Results showed large changes in the scattering behavior of Asphaltenes as a function of its concentration, mainly at low values of the scattering vector q. The key point of this article is the way as fractal morphology of the large scale aggregates change from surface-to-mass structures as concentration is increased. Besides, we demonstrated that Asphaltenes are under an aggregate form as a continuum of fractals and nanostructures in the concentration range studied.
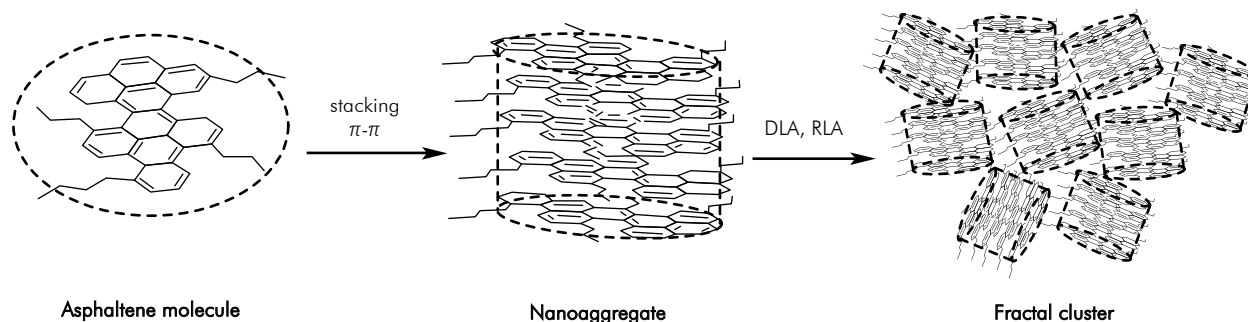

Figure 1. Representation of the hierarchical structures for Asphaltenes.

2. SAXS DATA ANALYSIS

In the analysis of the SAXS spectra some typical regions and laws are identified: i) in the low-q region, a Guinier or Zimm behavior is common, from which the radius of gyration can be calculated and ii) for intermediate and large q a scaling dependence of type $I(q) \approx q^{-d}$ from which a structural model is chosen. The Radius of gyration (R_g) is defined as the root mean squared distance from the center of the mass of the particle to the position of all atoms and is given by the formula, according to Guinier approximation (Guinier & Fournet, 1955):

$$I(q)=I(0)exp(-\frac{q^2 R_g^2}{3})$$ (1)

The radius of gyration, R_g, is obtained from the slope of a line given by $\ln I(q)$ vs q^2 in the q region where $qR_g \leq 1$. Similarly, the Zimm approach (Zimm, 1948), defined by equation 2, has been found to be more appropiated than the classical Guinier formalism because its validity can be extended for complex samples as Asphaltene aggregates up to $qR_g \leq 2$. The $1/I(q)$ versus q^2 plot gives directly the radius of gyration R_g of the particles:

$$\frac{1}{I(q)} = \frac{1}{I(o)}(1+\frac{q^2 R_g^2}{3})$$ (2)

For Polydispersed Systems, R_g corresponds to the z-average-squared radius of gyration:

$$R_{gz}^2 = \frac{\sum_i n_i M_i^2 R_{gi}^2}{\sum_i n_i M_i^2}$$ (3)

Where ni, Mi and R_{gi}^2 are the number per unit of volume, the molecular weight and the radius of gyration of aggregate i, respectively. R_g can be used to quantify the particle dimensions once the structure of the particle is known. Otherwise, the intensity of scattered radiation $I(q)$ by aggregates usually behaves as a power law over the intermediate range of the scattering vector, q:

$$I(q) \propto q^{-d}$$ (4)

Where d is the power-law exponent and can be measured directly from the negative slope of the linear region of a log-log plot of $I(q)$ vs q (Sakai, Alba-Simionesco & Chen, 2011). The power-law exponent is directly related to the fractal dimension of the particles. If $1 < d < 3$, then a mass-fractal scaling is observed

and $d=d_m$, where d_m is the mass fractal dimension. If $3 < d < 4$, then a surface-fractal scaling is observed and $d=6-d_s$, where d_s is the surface fractal dimension (Martin & Hurd, 1987; Avnir, 1989). Different power-law exponents, though diversely interpretable, have been elucidated from small-angle scattering measurements at the low-q region. For example, an exponent of -4 refers to a dense structure (compact aggregates) in the fractal organization and also represents a smooth surface of the fractal objects. On the other hand, power-law exponents that are less than 3 are related to mass fractal aggregates that tend to become more porous and larger in size (Martin, J. E. & Hurd, A. J., 1987; Narayanan, 2008).

3. EXPERIMENTAL SECTION

Sample Preparation.

Asphaltenes were extracted from a Colombian heavy crude oil following the ASTM D6560-12 standard method. Initially, a portion of the crude was mixed with n-heptane in a 1:25 ratio (g/mL) and the mixture heated under reflux. The precipitated Asphaltenes were collected on a filter paper and then Soxhlet-washed with hot *n*-heptane to remove the waxy substances co-precipitated. After removal of the waxy matter, the Asphaltenes were separated from the inorganic material by dissolution in hot Toluene in a Soxhlet extractor. Finally, the extraction solvent was roto-evaporated and Asphaltenes were weighed, ground and stored. The yield of Asphaltenes (precipitate) was 15% w/w.

Elemental analysis for C, H, N and S was carried out using a Thermo Finnigan elemental analyzer. Metal content (V, Ni) was analyzed using a XRF Bruker S8 TIGER spectrometer (Karlsruhe, Germany) with an X-ray tube with rhodium target (Kα_1 0.6136 Å) on finely ground powder of Asphaltenes. Results are presented as percent by weight (%w.) for each element in Table 1.

A 1% w/v Asphaltene solution was prepared by dispersing the appropriate amount of solid Asphaltenes in the solvent (Toluene) by sonication and subsequent magnetic stirring during 24 h. Then, less concentrated solutions of Asphaltenes (0.1 and 0.01% w/v) were prepared from the 1% solution by successive dilutions. All samples used in the SAXS studies were allowed to stand overnight before any experiment.

Table 1. Elemental Analysis of Asphaltenes

	Nom metals				Metals*	
	C	H	N	S	V	Ni
%wt.	84.27	7.12	0.58	4.47	0.19	0.05

* Measured from XRF analysis.

Small-Angle X-ray Scattering

The SAXS work presented here was performed using the Small Angle X-Ray facility at the Laboratory of Universidad Autónoma Metropolitana (Iztapalapa, Ciudad de México, México). The analysis was conducted by loading 2 mm quartz capillaries with aliquots of the 1, 0.1, and 0.01 w/v % Asphaltene solutions in Toluene. Data were collected at the laboratory conditions, room temperature and atmospheric pressure, by using a high resolution small-angle X-ray scattering, Xeuss (SAXS) equipment from XENOCS, with radiation Kα(Cu) with a wavelength of (λCu = 0.1541 nm) and a detector in two dimensions (2D, Pilatus 300 K). We used a sample-to-detector distance of 1.14 m, covering a q (scattering vector) range from 7.7×10^{-3} to 0.25 $Å^{-1}$.

Fit2D® software was used for image analysis and processing (Hammersley, 1997). The total scattered intensity from a liquid solution (Asphaltene-solvent) is a contribution of the camera background, cell or capillary background, and the solvent signal. To obtain the scattering arising from the Asphaltene particles alone, a subtraction must be performed: data from the sample minus data from the pure solvent. The effect of background scattering was evaluated using SAXS intensity for empty sample tubes and solvent-filled tubes. In this way, all dispersion data from each sample were corrected before being converted to an absolute scale [cm^{-1}].

4. RESULTS AND DISCUSSION

SAXS technique was used to obtain structural information of Asphaltene aggregates in model systems (Asphaltene solutions in Toluene) as a function of its concentration. Figure 2 shows the SAXS profiles for all the solutions at 25 °C as a double-logarithmic plot of $I(q)$ versus q. A qualitative analysis of the scattering data in Figure 2 is enough to conclude that all of the samples are colloidal systems with aggregates having

polydisperse sizes. Although solutions at 0.01 and 0.1 w/v % present very similar scattering curves, the derived structural parameters are slightly different when both samples are compared as will be discussed later. In these spectra two regions can easily be distinguished: a first one corresponding to small q-values ($q < 3 \times 10^{-2}$ $Å^{-1}$) in which the scattered intensity is a fastly decreasing function of q (or power-law scattering), and a second one at large q-values ($q > 3 \times 10^{-2}$ $Å^{-1}$) where the scattered intensity shows a plateau (or Guinier region) followed by a slight decrease of the intensity at higher q. Similar scattering profiles have been obtained previously in small angle scattering studies for some concentrated Asphaltene solutions and crudes (Espinat *et al.*, 1998; Roux, Broseta, & Deme, 2001; Sheu, 2006; Gawrys, Blankenship, & Kilpatrick, 2006; Zielinski, Saha, Freed, Hürlimann, & Liu, 2010).

In a different way, the SAXS profile for the 1% Asphaltene solution just exhibits a power-law scattering behavior in which the scattered intensity decays as q^{-d}, and therefore, only the structure parameter d can be extracted from the data. This particular scattering behavior is typical of particles with fractal dimensionality in which the power-law exponent (d) provides an insight into the highly complex structural morphology giving rise to the scattering (Beaucage, 1996). We will discuss this behavior at the end of this section.
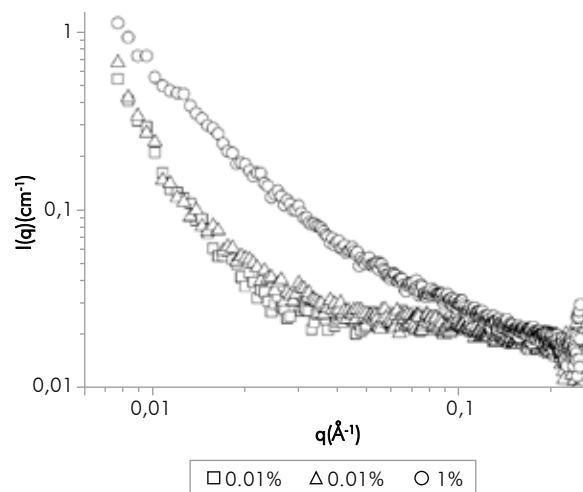

Figure 2. SAXS spectra of Asphaltene solutions at different concentrations.

Low-q region ($q < 3 \times 10^{-2}$ $Å^{-1}$). According to the literature, a large upturn in the scattering intensity at very low-q is related to density fluctuations of small

aggregates or coexistence of large aggregates with smaller ones in the solution (Espinat, 1998). In our opinion, the power-law scattering at low-*q* for all samples indicates the presence of large scale aggregates with fractal dimensionality whose radius of gyration could not be established with the present experimental setup (the Guinier region was not accessible in this q range). This *q*-dependence is proof of structures are much larger than $1/q_{min}$ (i.e., $R_g \gg 13$ nm).

As mentioned earlier, the fractal dimension d is related to the nature of the structures present in the medium. If these structures are interacting in the solvent through any association process, they could form a mass fractal structure or they could have fractal surfaces. Our measurements showed that for the 0.01 and 0.1 % (w/v) Asphaltene solutions, the power-law scattering is derived from a surface-fractal scaling characterized by fractal dimensions around 2.8 and 2.6, respectively. However, for the most concentrated solution (1% w/v), the fractal dimension dropped off to ~1.9 which corresponds to a mass-fractal scaling. The fractal dimension of aggregates was estimated from the fitting of power-law exponents in the spectra and the results are given in Table 2. Results show a decreasing of the fractal dimension as Asphaltene concentration is increased. This result is attributed to morphological changes of the Asphaltene aggregate structures due to a singular surface-to-mass fractal transition probably controlled by the increase of the inter-particle interactions. We have to emphasize that this type of fractal evolution has not been previously reported for Asphaltenes in solvents. Also, the decrease in the fractal dimension indicates that the aggregates formed at the highest Asphaltenes concentration (1% w/v) have a substantially less dense structure, whereas aggregates formed at lower concentrations (0.01 and 0.1 w/v %) are more compact in its fractal organization. Such concentration-dependent structural effects are summarized in Figure 3.

Table 2. Fitted parameters of power-law regime at low-*q*

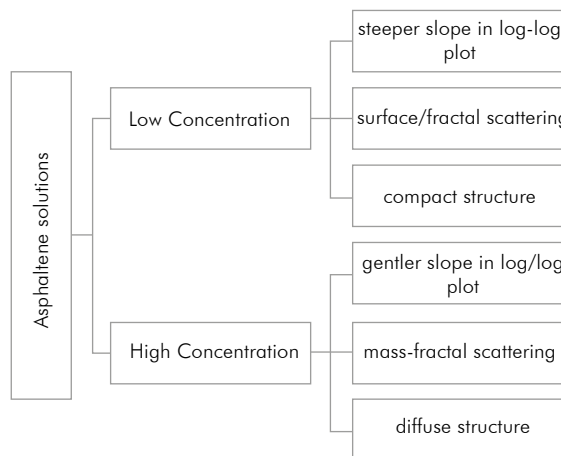|	Low-q region		
c (w/v %)	0.01	0.1	1
d	-3.18	-3.44	-1.86
d_s	2.82	2.56	---
d_m	---	---	1.86

Figure 3. Scheme of Asphaltene concentration effects in the low-q region

High-q region ($q > 3 \times 10^{-2}$ Å^{-1}). We have observed in Figure 2 that in this region the intensity levels drop off to a (quasi)plateau followed again by power-law behavior at the largest q. These features are due to the presence of small heterogeneities with a size in the order of a few nanometers corresponding to the primary Asphaltene aggregates known as "nanoaggregates". Note that there are not robust changes in the scattering intensities when Asphaltene concentration raises up to 0.1% w/v, indicating that this concentration is not sufficiently high to modify the aggregation state of nanoaggregates. We suggest that this specific behavior is because these small aggregates behave as independent particles (i.e., uncorrelated objects) probably due to packing constraints, however, when the Asphaltenes concentration is increased up to 1% w/v, the scattering intensity is strongly modified because of nanoaggregates are increasingly in contact favoring some type of interaction.

As a first step in the data treatment, we have used the Zimm approximation (*Eq. 2*) from a lower limit where scattering from large scale aggregates comes to be significant to an upper limit defined by $q_{max}R_g \leq 2$. From this analysis, the scattering intensities at $q = 0$ and the radii of gyration (R_g) were calculated. However, for the 1% Asphaltene solution, the extraction of these structural parameters was rendered difficult due to the quasi-plateau corresponding to the Guinier region overlaps with the intense scattering at low q. The fitted parameters are given in Table 3. Our results are not completely in agreement with previous studies, where higher radii of gyration for Asphaltene aggregates in solvents were obtained. For example, Roux, J. N.,

Broseta, D. & Deme, B., (2001) studied the structure of Asphaltene aggregates in Toluene solutions by SANS (small-angle neutron scattering) observing radii of gyration larger than 30 Å in a dilute concentration regime (from ~0.3 to ~3%) at 20 °C. (Morimoto, Morita, Takanohashi, & Nishikawa, 2013) also reported SAXS measurements on Asphaltene solutions in Toluene finding aggregates with radii of gyration between ~30–60 Å for concentrations as low as 20 mg/L. Other reports, on the other hand, showed a range of ~20–23 Å for R_g from SAXS measurements on Asphaltene/Toluene systems (Sheu, 2006; Yarranton *et al.* 2013). The discrepancies in the gyration radii derived from several small-angle scattering measurements could be ascribed to the diverse compositions of Asphaltenes.

In a second step, Asphaltene nanoaggregates were assumed to be spherical particles. Several small angle scattering studies of Asphaltenes from different geological sources have reported that Asphaltene colloids form more-or-less spherical aggregates (Sheu, 1998; Sheu & Acevedo, 2001). Therefore, it is acceptable to use a spherical shape to derive the particle dimension from SAXS data. In this sense, the average radius R of the sphere can be calculated from the following equation:

$$R = \sqrt{\left(\tfrac{5}{3}\right)R_g} \qquad (5)$$

Where R_g is the radius of gyration obtained from the Zimm analysis. R values are also given in Table 3. As one can see, the results confirm that Asphaltenes assemble to form colloidal structures conforming to the hierarchical aggregation model proposed by Mullins (Mullins, 2010) in which particle dimensions range between 50–100 Å for nanoaggregates. Additionally, we proved the Asphaltenes nanoaggregates are fully formed in a solvent such as Toluene at concentrations similar to the previously reported "critical nanoaggregate concentration" (CNAC ~100 mg/L) (Andreatta, Bostrom, & Mullins, 2005)

Table 3. Fitted parameters at high-q region.

c (w/v%)	Zimm		Spherical model	
	I(0)(cm⁻¹)	R_g(Å)	R(Å)	D(Å)*
0.01	0.024 ± 0.006	28.5 ± 3.0	36.8	73.6
0.1	0.033 ± 0.007	27.3 ± 1.4	35.2	70.4
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*Particle dimension D inferred from the sphere radius

As we mentioned at the beginning of this section, the scattering curve for 1% Asphaltene solution is characterized by the appearance of a crossover between two successive power-law regimes which correspond to mass fractals. Evidence for succession of power-law regimes on Asphaltenic Systems from SANS data have been earlier reported (Headen, 2009). This type of scattering is commonly related with a complex multi-level structure, i.e. a large-scale particle composed of smaller sub-particles. From the values of the scattering exponents of both power-law regimes (see Figure 4), we have inferred that this complex structure is formed by one mass fractal embedded into another mass fractal. However, a more accurate description of this fractal system should also involve the size polydispersity of the aggregates. On the other hand, as the mass fractal dimension decreases the structures appear sparser until at $d = 1$ (the lowest possible value for a '*connected*' fractal) the object essentially becomes a line (Martin & Hurd, 1987). According to the mass-fractal morphologies defined by Beaucage (1996), the large-scale structure may be assumed as a multi-particle diffusion limited aggregate, whereas the substructures may be described like randomly oriented rods. Thus, we suggest that structures present in the 1% Asphaltene solution are low-dimensional subunits that form a large-scale structure by some growth process.
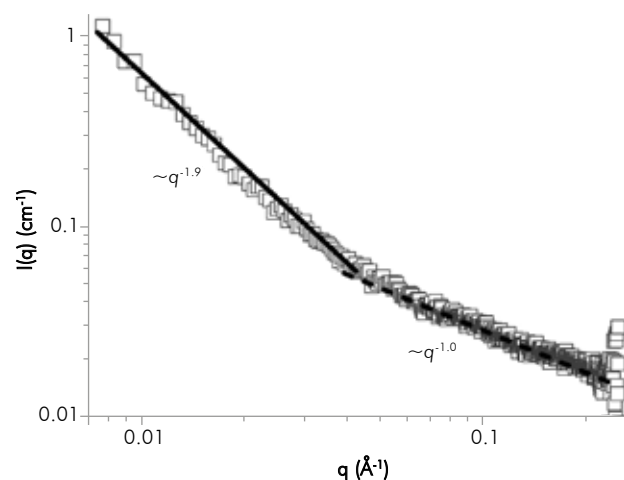

Figure 4. Power-law fits of the SAXS data for Asphaltenes in Toluene at 1% w/v.

5. CONCLUSIONS

- Asphaltene-Toluene solutions were investigated by SAXS as a function of Asphaltene concentration. Scattering curves were separated in two regions to be analyzed: low-*q* values and high-q values.

In the low-*q* range studied, Asphaltenes displayed power-law scattering indicating the presence of large aggregates with fractal properties. We demonstrated the structural evolution of these large heterogeneities as concentration was increased. The most consistent interpretation of this evolution is the modification of the aggregation state of Asphaltenes due to some fractal association processes, resulting in the transition from surface aggregates to mass aggregates. Besides, Asphaltenes showed to form loosely structured aggregates (porous or diffuse) at the highest concentration (1% w/v), whereas aggregates that formed at lower concentrations (0.01% and 0.1% w/v) are denser.

- At high-*q* values, we proved that in a solvent such as Toluene, large scale aggregates coexist with Asphaltene nanoaggregates in the order of a few nanometers at relatively low concentrations ($\leq$ 1% w/v), i.e. that not all nanoaggregates are part of the larger aggregates. These results are in agreement with the general view of the modified Yen model. On the other hand, the scattering intensity for the 1% Asphaltene solution is described by the presence of two successive mass fractal regimes with two different power law exponents ($q^{-1.9} \rightarrow q^{-1.0}$) which is consistent with a multi-phase system of mass fractals. Finally, we expect that Asphaltenes in Colombian heavy crude oils or the various industrially processed petroleum fractions also exhibit a similar concentration dependence from which the hydrocarbon phase behavior can be explained.

ACKNOWLEDGEMENTS

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