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Small-angle X-ray scattering study of oil- and deposit-asphaltene solutions

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Abstract Two different asphaltenes, separated from a crude oil and a deposit both from the same well, were solubilized in toluene and in tetrahydrofuran, at several contact times. The concentration of asphaltene was below 0.03% w/w, which was assumed to be the critical micelle concentration. Small-angle X-ray scattering measurements provided the structural parameters, which indicate that the shape, the particle size and the fractal dimension are determined by the duration of the contact time between asphaltenes and the solvent.

Keywords Asphaltene · Micelles · Small-angle X-ray scattering · Fractal dimension

Introduction

Asphaltenes are operationally defined as pentane- or heptane-insoluble and toluene-soluble organic materials of crude oil, bitumen, vacuum residues or deposits [1]. They are considered to be a mixture of polydisperse and chemically heterogeneous species. Moreover, asphaltenes have a natural tendency to self-associate in solution, which makes it difficult to determine their molecular weight [2], as well as their shape and size [3, 4, 5].

Solubility of asphaltenes in crude oil has been modeled following two approaches. Pfeiffer and Saal [6] proposed the first structural model, referred to as the steric-stabilization model, assuming that asphaltene has a micellar core surrounded by resin molecules. If the resin concentration decreases, the asphaltene micelles flocculate, causing them to precipitate [7]. In the second approach, referred to as the solubilization (lyophilic)

model [8], asphaltenes are assumed to be nonassociated molecules, solvated in a hydrocarbon medium. Thus, the difference between the steric-stabilization and solubilization models lies in the issue of whether the asphaltene colloids are suspended or dissolved in a hydrocarbon medium.

In previous works, the effect of temperature, asphaltene concentration and type of solvents on the asphaltene solution behavior has been widely studied by different techniques, and most of the works suggest a strong dependence on these parameters [8]. Specifically, the dimension of the asphaltene particles has been related to the nature and efficiency of the organic solvents, which have been classified from poor to good solvents following the order benzene, toluene, *o*-xylene, tetrahydrofuran (THF), pyridine, nitrobenzene, etc. As the solvent power increases, asphaltene-solvent interactions tend to dominate over the asphaltene-asphaltene interactions [9]. However, the same effect occurs when the

asphaltene concentration is below the critical micelle concentration (cmc), i.e. a very dilute regime ensuring that only dissociation effects take place [10].

Bardon et al. [11] have estimated, from small-angle X-ray scattering (SAXS) measurements, a cmc of 0.015% w/w in toluene and 0.03% w/w in pyridine, for the Safanya vacuum residue. Bouhadda et al. [12] have reported a cmc value of 0.17% w/w for a deposit recovered from the Hassi Messaoud field (Algeria), from surface tension measurements. From other measurements, the asphaltene cmc has been determined to be below 0.35% w/w [10]. Consequently, the cmc values depend on the asphaltene origin. Moreover, the effect of the asphaltene origin on the size of the asphaltene particles was demonstrated by Ravey et al. [13]. The size of the asphaltene micelle obtained by SAXS or small-angle neutron scattering (SANS) can reach as much as 800 Å [5, 11, 13, 14, 15, 16]. The asphaltene particle shapes have been modeled from the SAXS or SANS data as disklike or sheetlike [13, 14], spheres [3, 12, 15] or open aggregates or micelles [17]. It seems that the differences between the reported sizes and shapes may also be often related to a nonstandard time of dissolution. In most of the experimental procedures, the time to reach the complete dissolution of the solid matrix of asphaltene and the equilibrium of the solution is mentioned only as a minor factor [4]. Nevertheless, an asphaltenic matrix should dissolve slowly, similar to a polymeric system [8].

In this work, a study of the size- and shape-related parameters determined by SAXS as a function of time is presented. In order to understand the asphaltene-solvent interactions in the highly diluted regime, the asphaltene solutions were prepared below 0.03% w/w concentration, assumed to be the cmc. To determine the influence of the asphaltene origin, the asphaltene samples used in this work were prepared from a crude oil and from a deposit from the same petroleum well. Finally, to establish the power of solvents, the asphaltene solutions were prepared with toluene and THF.

Experimental

Sample preparation

Samples of a crude oil and of a deposit adhered to the tubing well surface were collected from a well located in a south-eastern Mexican field.

The deposit was fractionated following the ASTM D473 procedure and the toluene-insoluble fraction was first separated. Afterwards, the deposit-asphaltene fraction was obtained following the ASTM D4124 procedure with *n*-heptane.

The oil-asphaltene fraction was prepared from crude oil following the ASTM D2007 method with *n*-pentane (40 cm³/g oil). The oil- and deposit-asphaltene fractions were dissolved in toluene (analytical grade) and tetrahydrofuran (high-performance liquid chromatography grade) at room temperature and the concentrations of these solutions are presented in Table 1.

Table 1 Concentration of the asphaltene solutions (% w/w)

Solvent	Oil asphaltene	Deposit asphaltene
Toluene	0.016	0.020
Tetrahydrofuran	0.017	0.019

Characterization

SAXS measurements were performed with the fresh samples, after 1 week and after 1 month of contact, and the solutions were stirred vigorously before each measurement. SAXS experiments were performed using a Kratky camera coupled to a copper anode tube whose K α radiation was selected with a nickel filter. The collimated X-ray beam was linear and corresponded to an "infinitely high" beam. The SAXS data collected with a proportional linear counter were processed with the ITP program [18, 19, 20, 21], where the angular parameter, h , in reciprocal angstroms, is defined as $h = 4\pi\sin\theta/\lambda$, where θ and λ are the scattering angle and the wavelength of the X-rays, respectively. The samples in solution were introduced into a capillary tube. The temperature (25 °C) was controlled with the help of a circulating water bath (Anton Paar sample holder). To obtain good-quality statistics, the measurement time was 9 min.

The radius of gyration was obtained from the slope of the curve $\log I(h)$ versus h^2 of the Guinier plot [22]. The form of the particles was estimated from the Kratky plot, i.e. $h^2 I(h)$ versus h , as follows. If the Kratky curve presents a broad peak, the scattering particles most probably present a globular conformation, whereas if the curve approximates to a plateau the particles most probably have a fiberlike shape [23].

If the shape is known, it is possible to calculate the distance distribution functions [20]. These distributions provide a criterion to estimate the solution polydispersity. In SAXS experiments, the $\log I(h)$ versus $\log h$ plot provides the fractal dimension [25, 26], which is a useful number to differentiate the degree of aggregation and the internal structure of the scattering object.

Results

The gyration radius, R_G , is a size-dependent parameter determined at very small angles without any hypothesis on the shape of the scattering objects, corresponding to the average of the whole sample. The gyration radii obtained from the solutions examined in this study are compared in Table 2. Independently of asphaltene origin or solvent type, all the gyration radii turned out to be 161 ± 2 Å after a contact time of 1 month; however, such is not the case for the freshly prepared asphaltene solutions, as the aggregates are clearly larger. Within

Table 2 Gyration radii, R_G , obtained for the oil-asphaltene and deposit-asphaltene solution (Å)

Contact time	Oil asphaltene		Deposit asphaltene	
	Toluene	Tetrahydrofuran	Toluene	Tetrahydrofuran
Fresh	255	192	190	181
1 week	182	173	194	187
1 month	163	161	160	162

error range, the 1-week samples are intermediary between these two extremes. Therefore, for short contact times, the solvent power and the sample origin determine the gyration radii, whereas after 1 month of contact the values are the same, i.e. R_G is independent of these two parameters.

The Kratky plots of the asphaltene solutions in toluene and in THF are compared in Figs. 1 and 2, respectively, and the configurations are summarized in

Table 3. All the samples start as fibers, spheres or micelles and rapidly tend to a micellar shape. Still, the deposit-asphaltene solution in THF starts as large micelles ($R_G = 181 \text{ \AA}$); this shape and size are not stable and the scattering objects turn into spheres after 1 week and after 1 month turn into micelles again but smaller ($R_G = 162 \text{ \AA}$).

The calculated particle size distributions of the oil- and deposit-asphaltene solutions assuming the shape

Fig. 1 Evolution in time of the Kratky plots of **a** oil asphaltene and **b** deposit asphaltene in toluene

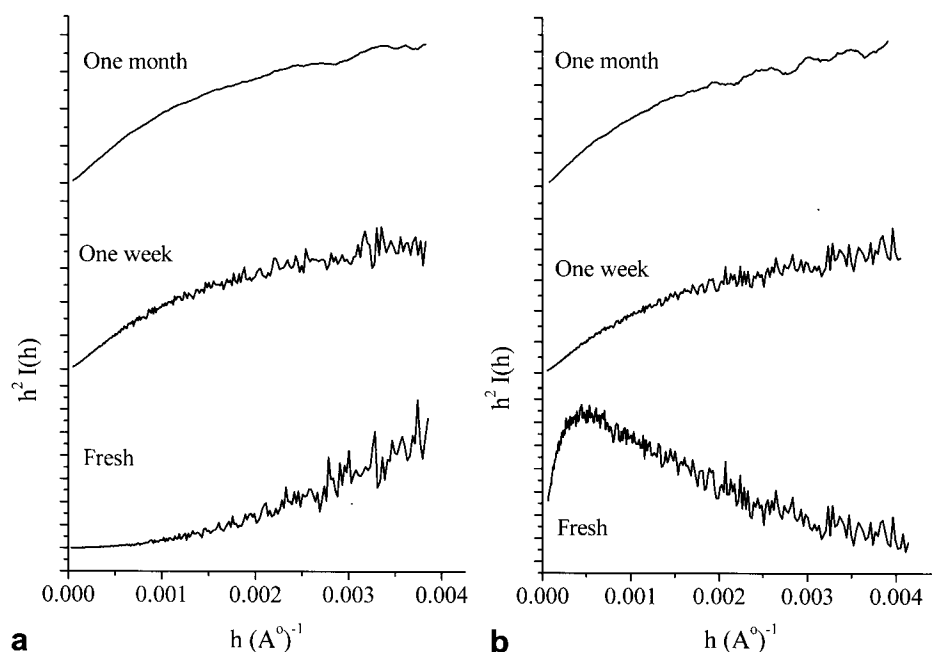


Fig. 2 Evolution in time of Kratky plots of **a** oil asphaltene and **b** deposit asphaltene in tetrahydrofuran (THF)

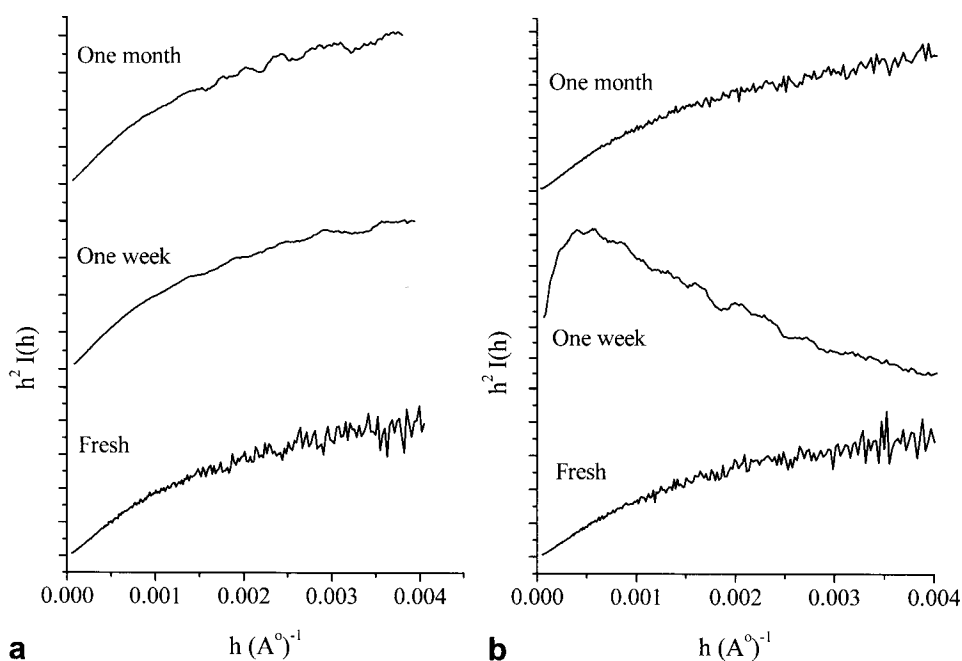
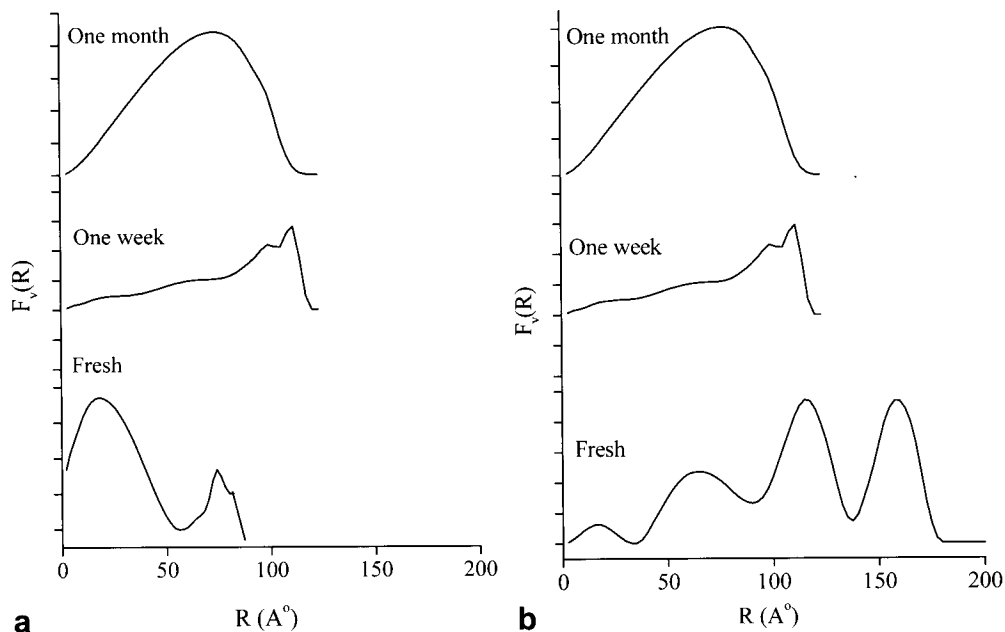
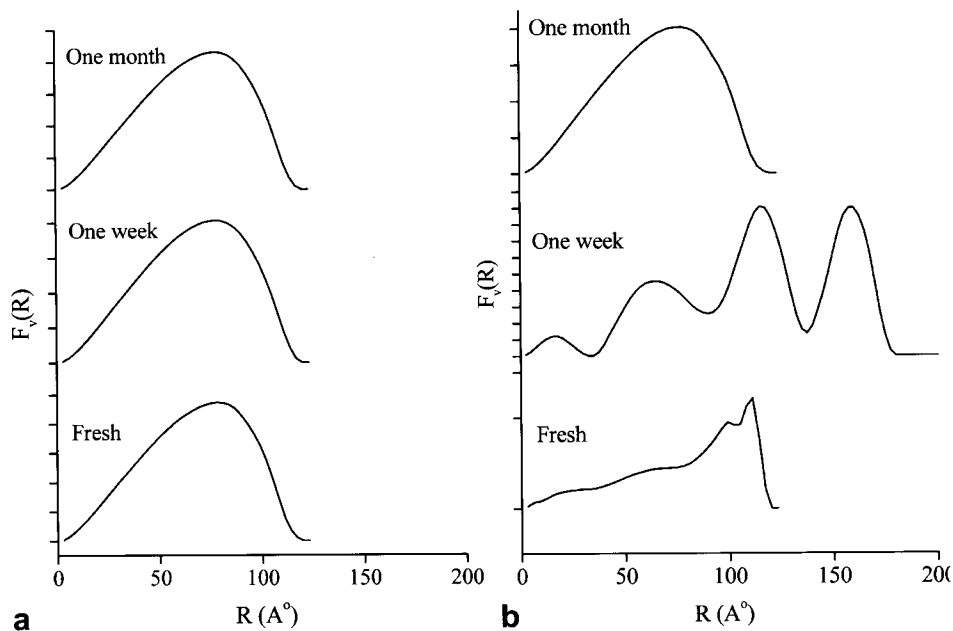


Table 3 Shape of the oil-asphaltene and deposit-asphaltene particles in solution

Contact time	Oil asphaltene		Deposit asphaltene	
	Toluene	Tetrahydrofuran	Toluene	Tetrahydrofuran
Fresh	Fibers	Micelles	Spheres	Micelles
1 week	Micelles	Micelles	Micelles	Spheres
1 month	Micelles	Micelles	Micelles	Micelles

determined from the Kratky plots (Table 3) are shown in Figs. 3 and 4. These particle size distributions are obtained from the aisle of the curve, which corresponds to the smaller scattering entities. In toluene (Fig. 3), both asphaltenes reach monomodal distributions after 1 month. Moreover, in both samples, the peak is found for a radius of about 80 Å. Nonetheless, the size distributions of the freshly prepared solutions in toluene are different for oil asphaltene and for deposit asphaltene.

Fig. 3 Evolution in time of particle size distribution in toluene of **a** oil asphaltene and **b** deposit asphaltene**Fig. 4** Evolution in time of particle size distribution in THF of **a** oil asphaltene and **b** deposit asphaltene

The distribution of the oil-asphaltene particles represents the radius of the fiberlike particles, whereas the distribution of the deposit asphaltene particles is the radius distribution of the spherelike particles. The oil asphaltene fiber radii are either 20 or 75 Å. The spheres that constitute the deposit-asphaltene solution are mainly 115 or 160 Å, although particles close to 20 and 65 Å are also found. The micelle particles turn to be smaller than 110 Å, after 1 week of contact, independently of the asphaltene origin.

If the solvent is THF (Fig. 4), the oil asphaltene is instantaneously dissolved (the freshly prepared solution). Thus, the equilibrium is obtained from the beginning of the experiment, and the initially monomodal distribution with a peak at about 80 Å is the same after 1 week or 1 month. The deposit-asphaltene solution in THF presents a very broad distribution for radii between 20 and 110 Å where most particles are 80–110 Å even after 1 month of contact. Note how the very broad distribution of the freshly prepared solution found initially becomes a distribution of spheres with four well-defined sizes after 1 week of contact.

Apparently, the dissolution of the deposit-asphaltene sample in both solvents follows a more complex mechanism than the oil-asphaltene sample. The liberation of small fragments of asphaltene (radius 20 Å) and large agglomerates (radius about 160 Å) are observed during the dissolution of deposit asphaltene. However, although the sample is constituted by micelles, the solution does not seem to be homogeneous after 1 month.

The evolution with time of the fractal dimension of the two asphaltenes studied is compared in Fig. 5 as a function of solvent type. If toluene is used, the interface between the deposit-asphaltene particles remains unaltered, as the fractal dimension is constant.

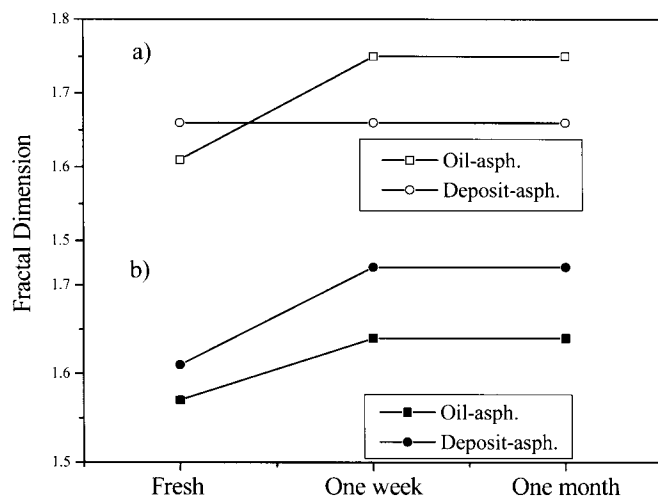


Fig. 5 Evolution in time of fractal dimension of oil asphaltene and deposit asphaltene: a in toluene and b in THF

contrast, THF promotes in the deposit-asphaltene a variation of fractal dimension from 1.61 to 1.72, which is already reached after 1 week. This last behavior is reproduced by the oil-asphaltene sample, which in both solvents, toluene or THF, increases the fractal dimension after 1 week, and this value is maintained up to 1 month.

Discussion

From the study of the gyration radii or the shape, the asphaltene-solvent diluted solutions are metastable systems which evolve in time to a state of equilibrium, independent of the solvent or asphaltene origin; however, if the fractal dimensions or the size distributions are compared, each sample can be distinguished even after 1 month.

The effect of contact time is evident for the oil asphaltene in toluene, as the gyration radius diminishes by 36% after 1 month, while for the deposit asphaltene in the same solvent, the R_G reduction is only 16%. The reduction of R_G of the oil asphaltene is only 16%, while for the deposit asphaltene it is 10%, both in THF.

The effect of the asphaltene origin is evident for the fresh solutions, as R_G of the oil asphaltene is 25% larger than R_G of the deposit asphaltene, both in toluene; however, in THF, this difference is about 6%, which is within the error range being insignificant. After 1 week, the differences between the gyration radii are not significant. This is in accordance with the observations of Storm and Sheu [5], which indicated that the role of the surrounding solvent in determining the size of the asphaltene particles is not crucial if the contact time is long enough.

As far as the shape of the particles is concerned, the same effect is observed. After 1 month all the shapes are those of micelles independent of solvent or asphaltene origin. However, in a fresh solution, both asphaltenes are micelles in THF, but the oil-asphaltene shape in toluene is fiberlike and the deposit-asphaltene particles are spherelike.

Such behavior is similar to the behavior of a polymeric solution, which experiences a time-dependent tendency to transform into a state of lower free energy when particles become totally dispersed [8]. However, in the present work, the particles do not seem to be completely dispersed as the R_G values are far from the values observed in the particle size distributions. Thus, the particle size distributions correspond to heterogeneities within the large asphaltene aggregates or to fragments of these aggregates, which point to a structure disruption. This feature is clearly shown by the fractal dimensions, which are between 1.57 and 1.75. These values are lower than the value of about 2

reported by Roux et al. [10] or than the value of 2.0–2.2 reported by Fenistein et al. [17], but they correspond to the expected value for a diffusion-limited colloidal (DLC) process [26]. With time, the fractal dimension increases toward 2, which is considered to be a characteristic value of a reaction-limited colloidal (RLC) process [26]. It is likely that both mechanisms are present: time favors first the DLC process, but slowly the RLC process becomes more probable. These mechanisms depend on the dissolution of asphaltene aggregates, being initially limited by the entrance of solvent into the aggregate structure, and consequently, the initial fractal dimension values are related to a DLC process. As the contact time increases, the asphaltene aggregate breaks apart, as shown by most of the size distribution patterns. The fractal dimensions of these new objects are larger than the original asphaltene aggregates and they are related to a RLC process, conditioned by the adhesion forces among asphaltene fragments.

Conclusions

Asphaltenes in solution are dynamical systems, which change with time. The gyration radius, however, tends to a common value of 161 Å, after a contact time between asphaltene and solvent of 1 month, independent of asphaltene origin or solvent type. In contrast, the shape of the aggregates, the size distributions and the fractal dimensions are variables depending on asphaltene origin and solvent type and change with the dissolution process.

Asphaltene colloids may be described as a polymeric system evolving with time and experiencing structure disruption. Thus, for the fresh solution, asphaltene dissolution tends to follow the steric-stabilization model, a micelle core surrounded by resin molecules. Still, the solutions are better described by the solubilization model, i.e. by non associated molecules in a hydrocarbon medium after 1 month of contact time.

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