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AN EXPERIMENTAL STUDY OF ASPHALTENE PARTICLE SIZES IN n-HEPTANE-TOLUENE MIXTURES BY LIGHT SCATTERING

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Abstract - The particle size of asphaltene flocculates has been the subject of many recent studies because of its importance in the control of deposition in petroleum production and processing. We measured the size of asphaltene flocculates in toluene and toluene - n-heptane mixtures, using the light-scattering technique. The asphaltenes had been extracted from Brazilian oil from the Campos Basin, according to British Standards Method IP-143/82. The asphaltene concentration in solution ranged between 10^{-6} g/ml and 10^{-7} g/ml. Sizes was measured for a period of about 10000 minutes at a constant temperature of 20°C. We found that the average size of the particles remained constant with time and increase with an increase in amount of n-heptane. The correlation obtained for size with concentration will be useful in asphaltene precipitation models.

Keywords: asphaltene particle sizes in n-heptane-toluene, light scattering.

INTRODUCTION

Asphaltenes belong to a class of soluble compounds found in petroleum fluids and are functionally defined as a precipitate obtained from petroleum by adding an excess of n-heptane. They are usually the heaviest components of the fluid and are very refractory. They may separate from the oil phase due to variations in pressure, composition and temperature and may clog the reservoirs, tube lines and process equipment. On heating, asphaltenes form coque, which can deactivate cracking catalysts. These properties of asphaltenes have an impact on petroleum processing and can affect the entire supply chain, from oil production to refining and storage. An understanding of the physical behavior and the chemical activity of asphaltene particles is necessary to alleviate operational problems and to optimize different unit operations in petroleum processing.

To be able to control the deposition of asphaltenes in reservoirs and process equipment, it is necessary to study the composition, structure, solubility and size of the particles and other factors that are important for achieving a comprehension of the mechanism of flocculation and deposition of asphaltenes. Deposition is usually preceded by flocculation of asphaltene particles, mainly caused by variations in compositions of crude oil. The physical and chemical properties of asphaltenes depend on the origin of the petroleum as well as the extraction procedure. Caldas et al. (1997) studied experimentally the flocculation properties of several European crude oils and compared their behavior with those of typical Venezuelan and Brazilian oils. Ramos et al. (2001) extensively studied the interfacial colloidal behavior of asphaltenes obtained

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*To whom correspondence should be addressed from Brazilian crude oils. Rajagopal et al. (1998) evaluated several inhibitors of flocculation for an unstable Brazilian crude oil.

Several researchers have proposed models of asphaltene flocculation adapting the original view of Nellensteyn (1933) that crude oil is a colloidal system asphaltene forming the dispersed phase, protected by adsorbed resin and hydrocarbon materials. Leontaritis et al. (1987) developed a colloidal model for predicting the onset of asphaltene flocculation. They also proposed a fractal aggregation model for organic deposition, which takes into account the dual nature of asphaltenes (partly colloidal and partly dissolved)(Park and Mansoori, 1988). The deposition mechanisms of asphaltene and other heavy organics were reviewed by Mansoori (1997).

More recently, Rajagopal et al. (2001) proposed a polydisperse flocculation model for predicting the onset and size of asphaltene particles. They also applied this model for simulating formation damage in reservoirs, using a tangent plane criterion for the stability of reservoir fluid (Monteagudo et al. 2001). In all these models, it is necessary to know how the average size of asphaltene particles varies with concentration and the composition of the solvent. The objective of this work was to measure the size of asphaltene flocculates at low concentrations in toluene and in solutions of toluene plus n-heptane.

Many recent studies utilize the light-scattering technique for determining sizes of colloidal particles in solution. Of the existing techniques, light-scattering offers the advantage of not destroying or disturbing the samples, because they are simply illuminated by a light beam. On the other hand, the disadvantage of this technique is that it cannot be readily used on opaque systems. Using photon correlation spectroscopy (PCS) adapted to opaque systems, Yudin et al. (1998) studied the size of asphaltene flocculates of different origins during the process of aggregation. The sample concentration ranged between 10^{-2} and 10^{-3} g/ml. The authors found different behaviors above and below a critical molecular concentration.

Burya et al. (2001) studied the colloidal properties and the size of asphaltenes during aggregation for three types of oil using the PCS technique adapted to opaque systems. The results were correlated with the type of oil.

Fenistein and Barré (2001) studied the distribution of the molecular mass of asphaltenes in solutions of up to 3% (v/v) of asphaltene in toluene. They found that the light-scattering technique can be applied only to more dilute fractions in order to obtain the molecular mass and radius by Zimm approximation.

In the present work, we measured the size of asphaltene flocculates in very dilute solutions of toluene and in mixtures of toluene–n heptane, during a long period of time, using the light-scattering technique. Asphaltene concentration in solution ranged between 10^{-6} g/ml and 10^{-7} g/ml and the sizes were measured for a period of about 10000 minutes at a constant temperature (about 20°C). For the concentration range tested, the variation in refractive index with solution concentration was also measured experimentally to improve precision.

EXPERIMENTAL METHODOLOGY

A Brazilian crude oil from the Campos Basin in Brazil was selected for this work, as a significant amount of Brazilian production comes from this basin. The asphaltenes were extracted according to British Standards Method IP-143/82. The reagents used were HPLC grade, acquired from Tedia. Whatman syringe-type filters, an inorganic membrane with a nominal pore size of 0.02 μm, were utilized in this work. The 0.02 μm porosity filter was selected after previous work on the size distribution of asphaltene aggregates utilizing a set of filters (Rajagopal and Silva, 2002).

The asphaltenes and resins in the crude oil were well characterized. Structural parameters and aromaticity were determined by ^{13}C NMR experiments. The functional groups were identified by IR spectroscopy. The classical element was analyzed using the ASTM D1552 method in order to determine weight percentages of C, H, N, O and S. The amount of sulfur present was also determined by X-ray fluorescence as well as the nickel and vanadium contents. All the solvents used were of certified reagent grade. The results are shown in Tables 1, 2 and 3.

The asphaltene particles were dispersed in pure toluene and in mixtures of toluene and n-heptane, using the following experimental procedure. A solution of asphaltene in toluene at a concentration of 10^{-4} g/ml was prepared. The toluene had been previously filtered through a syringe-type filter, with openings of 0.02 μm in order to remove any suspended particles in the solvent. The solution was then homogenized in a thermostatic bath for 5 minutes and stabilized for 24 hours in a dark ambient.

Table 1: Analysis of Nuclear Magnetic Resonance

Analysis	Results	Analysis	Results
Unsaturated C	24% M	Gama H	19.9% M
Saturated C	76% M	Saturated H	92.5% M
Alkyl aromatic C	10.2% M	CH ratio	0.568
Aromatic C, H	13.2% M	Linear alkanes	19.9% M
Aromaticity factor	0.240	Average chain size Linear alkanes	
Aromatic H	7.5% M	Terminal methyl C	19.0%
Olefin H	0.0% M	Branched methyl C	2.1% M
Alpha H	17.3% M	chain	2.7% M
Beta H	59.4% M		

Table 2: Organic analysis

Atom	%
Carbon	86.1
Hydrogen	8.6
Nitrogen	1.4

Table 3: Quantitative analysis of RX

Atom	%
Sulfur	10
Nickel	< 0.5
Vanadium	< 0.5

From that stock solution, four other solutions were prepared and diluted to concentrations of around 10^{-6} g/ml. These samples were then put in an ultrasound bath for 5 minutes to ensure perfect homogenization. Then the light-scattering measurements with the Dawn multiphotometer were started, at time intervals of less than 10 minutes between one measurement and the next.

The solutions of asphaltene in toluene-n-heptane mixtures were prepared from an initial solution of asphaltene in toluene with known concentrations around 10^{-3}g/ml, following the procedure described above. Afterwards, n-heptane was added to the toluene solution at defined weights to reach the exact proportion of n-heptane, i.e., 40%, 50%, 60% and 70% (v/v). Both toluene and n-heptane had been previously filtered through the Whatman´s syringe-type filter with microholes of 0.02 μm. After the toluene and n-heptane had been added the samples were again placed in an ultrasound bath for 5 minutes for homogenization. From that point on, multiphotometer measurements were taken at equally spaced intervals. The intensity of the scattered beam was measured at different angles simultaneously as a fraction of the intensity of the incident beam. All the experiments were carried out in a dark ambient and at a temperature of 20º C.

The light-scattering measurements were taken in a Dawn- DSP Laser Multiphotometer from Wyatt Technology Corporation. Figure 1 shows a diagram of the multidetector used to in the measurements the radii. The Dawn instrument was used in the batch mode and the collimated detectors were arranged at fixed angles (θ) around the cell that contained the sample.

In order to evaluate the molecular mass, it was necessary to measure the variation in the refractive index with concentration of solution $\left[{}^{dn}\!/_{dc}\right]$, which was done using the Dawn interferometer with a P2 cell and an optical path of 2 mm. The experimental procedure for measuring the ratio $\left[{}^{dn}\!/_{dc}\right]$ started with the preparation of nine solutions for each solvent with a concentration range the same as that which had been used with the multiphotometer. These measurements were also carried out in a dark ambient and at a constant temperature of 20ºC.

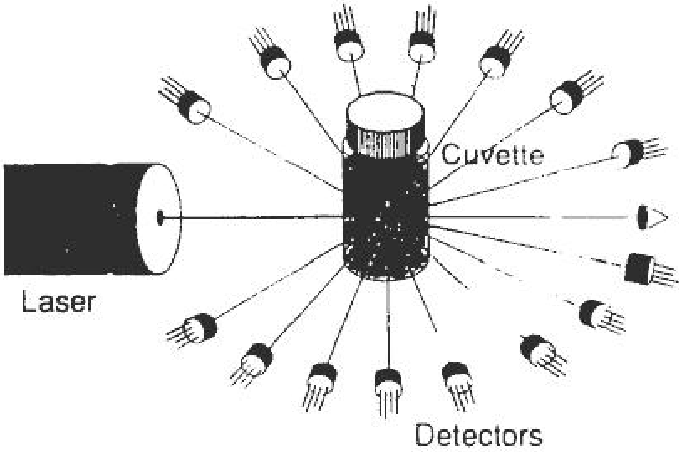

Figure1: Diagram of the Multiphotometer Dawn DSP

Size of Particles from Light Scattering

When the incoming light is vertically polarized, we can use the well-known Zimm equation for any given value of concentration of solute in the solvent.

$$\frac{R_\theta}{K^* c} = M_w P(\theta) - 2A_2 c M_w^2 P^2(\theta)\sqrt{a^2+b^2} \qquad (1)$$

where

$$R_\theta = \frac{(I_\theta - I_{\theta,solvent})r^2}{I_0 V} \qquad (2)$$

$$K^* = 4\pi^2 n_0^2 \left(\frac{dn}{dc}\right)^2 \lambda_0^{-4} N_A^{-1} \qquad (3)$$

$P(\theta)$ can be related to the distances between the molecular scattering centers by

$$P(\theta) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left[1 - \frac{\mu^2 h_{i,j}^2}{3!} + \frac{\mu^4 h_{i,j}^4}{5!} - .....\right] \qquad (4)$$

where

$$\mu = \frac{4\pi}{\lambda}\text{sen}\left(\frac{\theta}{2}\right) \qquad (5)$$

The average of the squares of the radii of the molecules in relation to their centers of gravity can be defined as

$$\left\langle r^2 \right\rangle = \frac{1}{2N^2}\sum_{i=1}^{i=N}\sum_{j=1}^{j=N} h_{i,j}^2 \qquad (6)$$

Substituting equation 6 in to equation 4, we have

$$P(\theta) = 1 - \frac{2\mu^2\left\langle r^2\right\rangle}{3!} + ... \qquad (7)$$

That is the relationship between $P(\theta)$ and $< r^2>$ of a molecule independent of the molecular conformation at the limit when $\mu^2 \left\langle r^2 \right\rangle << 1$.

Zimm Diagram

To create the Zimm diagram, the values of $\frac{K^* c}{R_\theta}$ versus the values of $\text{sen}^2\left(\theta/2\right) + kc$ are plotted, where *k* is an arbitrary constant used to scale the graph and generally has a value equal to the inverse of the highest concentration of solute used in the experiment. At the limit of the scattering angle tending to zero, the points obtained by extrapolation of Raleigh ratios at several scattering angles at a constant concentration should describe a line given by the following equation:

$$\lim_{\theta \to 0} \frac{K^*c}{R_\theta} = \frac{1}{M_w} + 2A_2c \qquad (8)$$

By linear regression, the value of the intercept, the reciprocal of the molecular weight $\frac{1}{\overline{M}_w}$, and the value of the slope and the second virial coefficient, ($\overline{A_2}$), can be estimated.

At the limit of infinite dilution,

$$\lim_{c \to 0} \frac{K^*c}{R_\theta} = \frac{1}{M_w P(\theta)} \qquad (9)$$

the concentration is zero, and in the curves for each angle at different concentrations, the intersection is, as in the previous case, equal to $\frac{1}{\overline{M}_w}$ and the slope is related to the radius, r_g . Figure 2 shows a Zimm diagram for 10^{-6} g/ml asphaltene solution in 40% n-heptane-toluene mixture at 3150 minutes. About 300 such diagrams were drawn to plot the change in size with time.

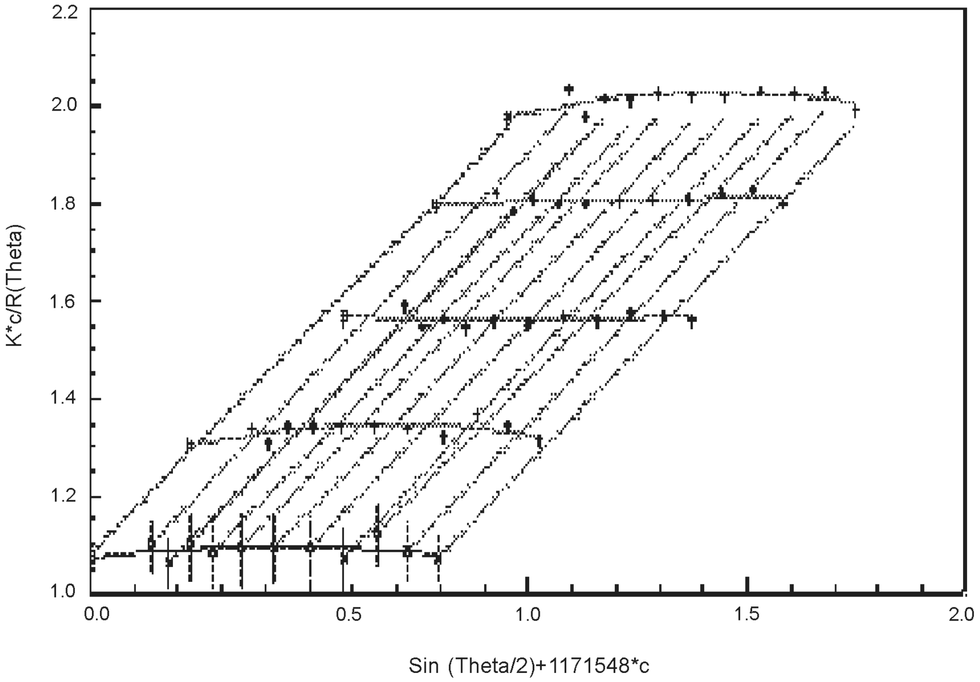

Figure 2: Zimm diagram for 10^{-6} g/ml asphaltene solution in 40 % n-heptane-toluene mixture at 3150 minutes.

RESULTS AND DISCUSSION

Using the light-scattering technique described above, we measured the size of asphaltenes in a very dilute solution of toluene with a concentration of 1 g/m3 for a period of 100 hours. The measurements were taken every 15 minutes during the daytime. The sizes are shown in Figure 3. The average size of the asphaltene was 23 nm and varied very little with time. The maximum size found was 28 nm and the minimum was about 14 nm. The dispersion around the average remained more or less the same. Priyanto et al. (2001) indicate an average size of 25nm for asphaltene micelles in toluene; the dispersion in size is attributed to the reversible nature of micellization and the disorderly growth of the particles. The early studies of Rogacheva, as cited by Mansoori et al. (2001), indicated formation of micelles and coacervates for asphaltene concentrations above 1mg/g of toluene. Recently, Acevedo et al. (1999) and Castillo et al. (2001) confirmed the presence of stable aggregates, even in very dilute solutions, as in the present case, with concentrations of 10^{-6} to 10^{-4} g/ml of toluene.

Next we studied the effect of paraffin, by adding different amounts of n-heptane to the dilute solution of asphaltenes in toluene. In each case we measured the size of asphaltene particles for 170 hours and in each case the average size of the particles decreased for about 6 hours and stabilized at a stationary value (e.g. when the continuous phase is 60% n-heptane and 40% toluene). The average size decreased from 151.9nm to 111nm during the first 6 hours and remained constant thereafter. The stationary size of the particles are plotted as a function of n-heptane concentration in Figure 4. The average size of the particles increased with an increase in the amount of n-heptane. The average size increased from 30.3 nm for 40 % n-heptane solution to 131.7 nm for 70% n-heptane solution. The initial sizes were similar in all cases. These results are in agreement with those of Burya et al. (2001). In particular, the behavior of marlin asphaltenes in toluene was similar to the Mars A-12 oil tested by Burya et al. (2001); the size of the particles remained constant with the addition of n-heptane.

The results can be correlated in a form suitable for formation damage models.

$$\langle r \rangle = r_0 \cdot (1 - x)^{-1,5} \tag{10}$$

This variation is more important than the variation in average size with the concentration of solvent and is as important as the density of the solvent. According to Leontaritis et al. (1987) the mean radius increases with the cube root of the concentration. Monteagudo et al. (2001) correlated the average radius with the density of the solvent as

$$\langle r \rangle = A \cdot (\rho_L)^{-1,6} \tag{11}$$

The process of flocculation is similar to that induced by addition of polymer in water treatment (Adachi, 1995). In the present case, large aggregates were also initially formed by bridging. The resin molecules adsorbed in two or more asphaltene molecules acted as connecting links. Over time some of the links were dissolved, the surface became stable and the size remained constant until the end of the experiment.

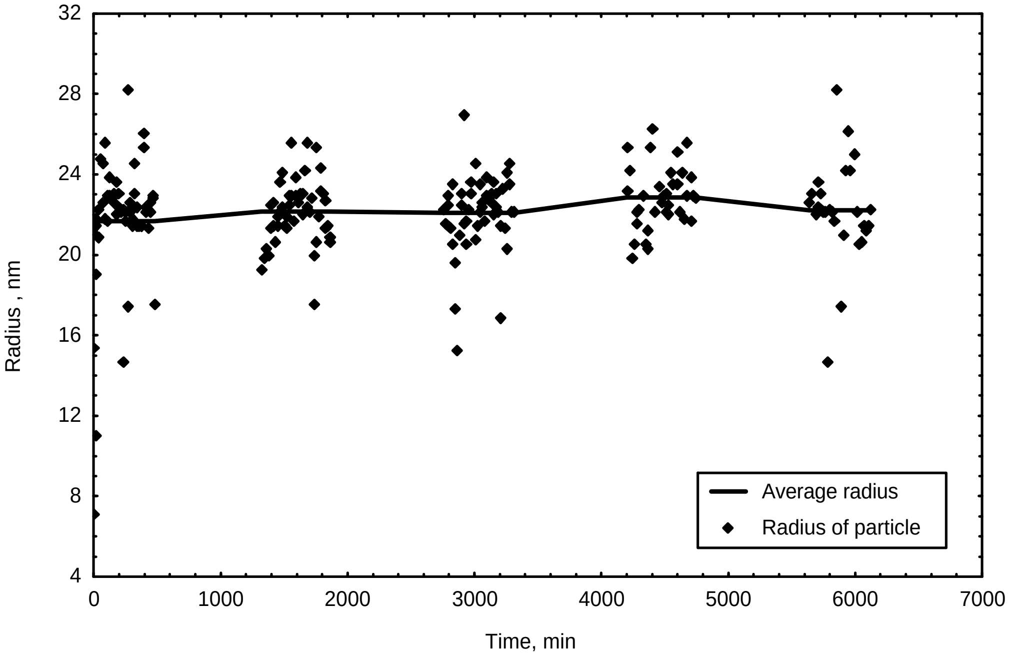

Figure 3: Size of asphaltene particles in toluene solution versus time.

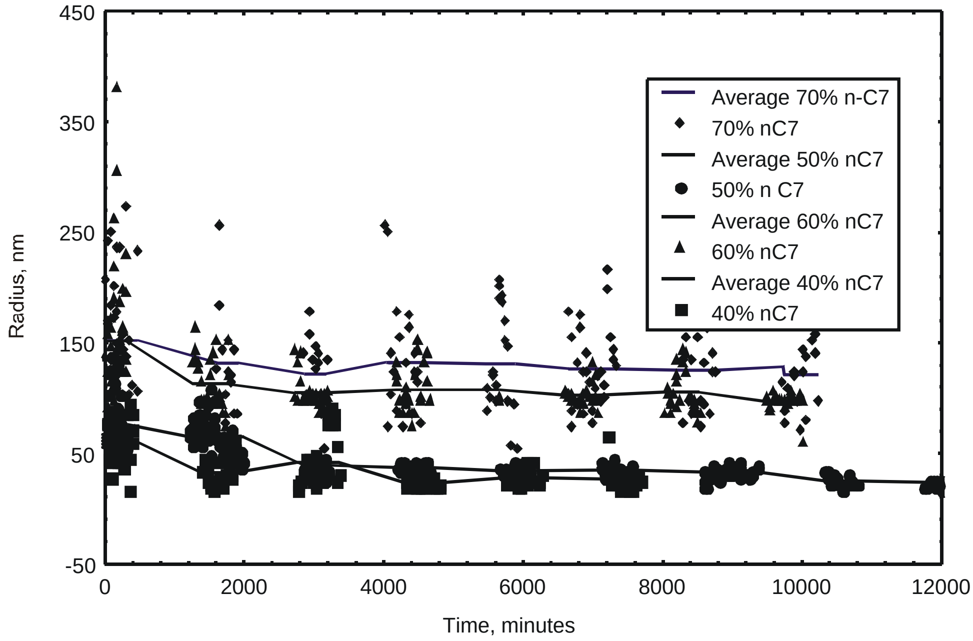

Figure 4: Size of asphaltene particles in several mixtures of toluene and n-heptane versus time.

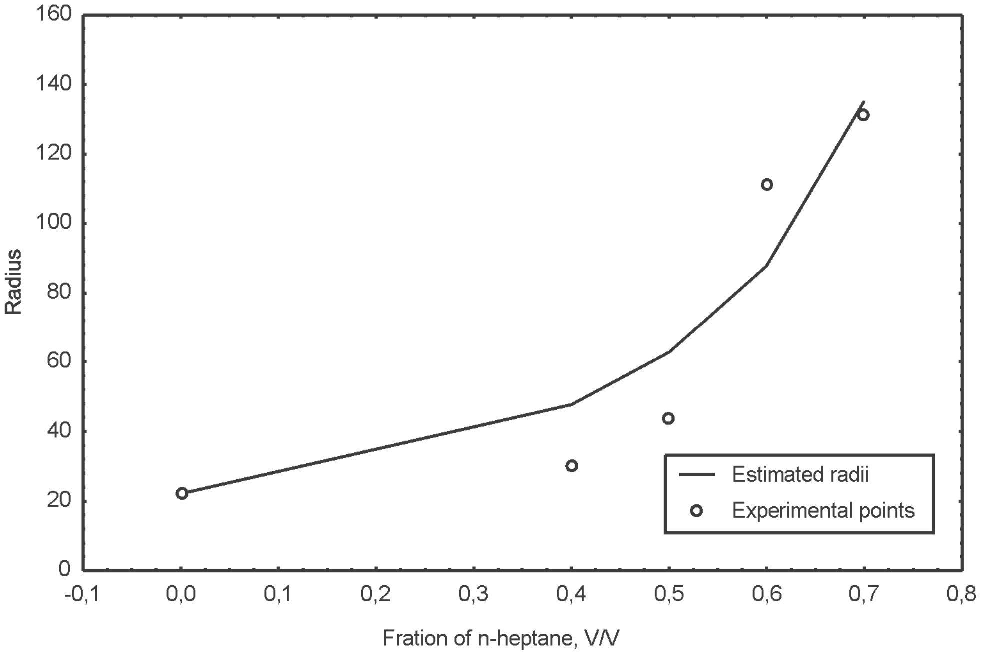

Figure 5: Variations in radius of asphaltene particles of with concentration of n-heptane.

CONCLUSIONS

From our experimental study we can conclude that asphaltene flocculates are of a specific size in solutions of toluene. The steady-state size of the particles increases with the amount of flocculating agent n-heptane. This increase is more important than the variation in asphaltene concentration.

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NOMENCLATURE

R_θ	excess Rayleigh ratio, i.e., excess of scattering of the solution over that scattered by the solvent itself, all divided by the incident intensity,
θ	angle between the incident and the scattered beam,
I_θ	scattered intensity of the sample,
$I_{\theta,\text{solvent}}$	scattered intensity of the solvent,
I_0	intensity of the incident beam,
R	distance between the scattering volume and the detector,
V	volume of the scattering medium,
C	concentration of solute in the solvent,
M_w	average molecular mass,
A_2	second virial coefficient,
K^*	optical constant,
n_0	refractive index of solvent for radiation wavelength in vacuum,
λ_0	wavelength of the incident light in vacuum, in nm,
N_A	Avogadro number,
$\left(dn/dc\right)$	differential increment of the refraction index of the solution in relation to the variation in concentration of solute, value obtained with another instrument,
$P(\theta)$	form factor,
N	total number of scattering centers,
$h_{i,j}$	distance between the i^{th} and j^{th} centers,
k	arbitrary constant used to scale the graph; generally of a value equal to the inverse of the highest concentration of solute used in the experiment,
$\langle r_0 \rangle$	average radius of particle of asphaltene in solution of toluene,
$\langle r \rangle$	average radius of particles of asphaltene in solvent mixtures,
x	concentration of n-heptane.

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