COLLOIDAL STRUCTURE OF HEAVY CRUDES AND ASPHALTENE SOLUTIONS

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STRUCTURE COLLOÏDALE DES BRUTS LOURDS ET DES SUSPENSIONS D'ASPHALTÈNES

L'industrie pétrolière est souvent confrontée a des problèmes industriels importants liés, entre autre, à la présence d'une forte concentration d'asphaltènes dans les fluides traités. Une meilleure connaisssance de la composition de ces molécules et de l'évolution de leur structure colloïdale en solution ou dans leur milieu naturel est d'une grande importance pour mieux comprendre les mécanismes mis en jeu, et ainsi, pouvoir agir et limiter les problèmes rencontrés. Les asphaltènes correspondent à la fraction insoluble dans le n-heptane. Les molécules solubilisées dans l'alcane sont appelées maltènes et peuvent à leur tour être fractionnées par chromatographie en phase liquide; on obtient alors trois nouvelles fractions appelées résines, aromatiques et saturées. La plupart des travaux de recherche réalisés sur ces molécules complexes concernent la détermination de la composition chimique obtenue à l'aide de diverses techniques d'analyse telles la spectroscopie infrarouge et la résonance magnétique nucléaire. En revanche, peu d'informations sur la macrostructure colloïdale des asphaltènes sont disponibles dans la littérature.

La détermination de la masse moléculaire a été le premier objectif: plusieurs méthodes, comme l'osmométrie à tension de vapeur, ont été appliquées. La conclusion principale de ces déterminations est la grande variation de la masse moléculaire mesurée suivant la technique employée. Nous avons fait appel à la diffusion des rayons X et des neutrons aux petits angles afin de mesurer la polydispersité en taille et la masse moléculaire moyenne en poids des macromolécules d'asphaltènes. Nous avons étudié différents systèmes constitués, soit par les asphaltènes ou les résines en solution dans différents solvants, soit par le mélange asphaltènes et résines en solution dans de plus ou moins bons solvants. Nous avons également suivi l'effet de la température sur ces systèmes. Les résultats obtenus montrent que l'agrégation, en d'autres termes, le nombre d'entités élémentaires formant la molécule, peut fortement varier en fonction de la nature du solvant et de la température. Les résines apparaissent comme un très bon solvant des asphaltènes. Les mesures de diffusion montrent une forte intensité diffusée à petites valeurs du vecteur de diffusion; elle traduit la présence dans le milieu d'hétérogénéités de taille assez étendue probablement dues à des fluctuations de la concentration en asphaltènes. Ainsi, il existe dans la suspension des régions plus ou moins étendues où la concentration en asphaltènes est supérieure à la concentration moyenne. La microscopie en mode cryogénique a permis de confirmer l'inhomogénéité du système. Un milieu composé de deux phases a clairement été visualisé. La diffusion des rayons X aux petits angles s'avère être une technique importante pour étudier les milieux non fractionnés, comme les bruts ou les résidus de distillation, pour lesquels aucune séparation

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au n-heptane n'a été réalisée. Nous avons pu mettre en évidence, pour ces systèmes, l'existence de fluctuations de densité à grande échelle.

COLLOIDAL STRUCTURE OF HEAVY CRUDES AND ASPHALTENE SOLUTIONS

Many industrial problems that arise during petroleum processing are related to the high concentration of asphaltenes. A good knowledge of the chemical composition of these macromolecules and a detailed understanding of the evolution of the colloïdal structures present in oil and its derivatives can play a decisive role in improving processing facilities. Asphaltenes are defined by their insolubility in n-heptane. Soluble molecules are called maltenes which can be fractionated by liquid chromatography in so-called resins, aromatic and saturated fractions. The major part of the research carried out on these complex molecules concerned the chemical composition determination from powerful techniques measurements as for instance IR or NMR methods. Nevertheless, very little information on the colloidal structure of asphaltenes or resins in pure solvent or in real systems is accessible.

The molecular weight determination was the first objective; several techniques, as vapour pressure osmometry (VPO), were used. The main conclusion of these determinations was the huge variation of the molecular weight measured by different methods. We used X-ray and neutron small angle scattering techniques in order to deduce the size polydispersity and the weight average molecular weight. Different systems as (i) asphaltenes or resins in solution with different solvents, or (ii) asphaltene and resin mixtures in suspension with good or bad solvents were investigated as a function of temperature increase. We have exhibited that the aggregation number, i.e. the number of smaller entities, can strongly vary with solvent composition and temperature. Resins appear as very good solvent for asphaltene molecules. Scattering measurements often exhibit strong scattered intensity at small scattering vector, showing the presence in the suspension of large heterogeneities in diluted solutions of asphaltenes and resins. We can suggest that these heterogeneities are due to concentration fluctuations. It exists in the diluted suspension regions more or less extended, where the asphaltene concentration is greater than the average asphaltene concentration. Cryo-scanning electron microscopy has confirmed the system inhomogeneity. A two phase system was clearly highlighted. The flocculation process was followed during n-heptane addition by scattering measurements and microscopy observations. Small angle X-ray scattering (SAXS) appears as a powerful tool for non-fractionated systems, as crude oil or other heavy derivatives. Density fluctuations were observed for a vacuum residue.

ESTRUCTURA COLOÍDAL DE CRUDOS PESADOS Y DE SUSPENSIONES ASFALTÈNICAS

La industría petrolera está llamada a solucionar problemas industriales importantes relacionados, entre otras cosas con la presencia de una elevada concentración de asfaltenos en los fluidos tratados. Un mejor conocimiento de la composición de estas moléculas y de la evolución de su estructura coloídal en solución o en su medio natural es sumamente importante para poder comprender de mejor modo los mecanismos que entran en acción y, de este modo, poder actuar y limitar los problemas con que se tropieza. Los asfaltenos corresponden a la fracción insoluble en el n-heptano. Las moléculas que se solubilizan en el alcano reciben la denominación de maltenos, que pueden a su vez ser fraccionados por cromatografía en fase líquida; en este caso se obtienen tres nuevas fracciones denominadas resinas, aromáticos y saturados. La mayor parte de los trabajos de investigación que se han llevado a cabo con relación a estas moléculas complejas se refieren a la determinación de la composición química obtenida por medio de diversas técnicas de análisis, como por ejemplo la espectroscopia infrarroja y la resonancia magnética nuclear. En cambio, la literatura únicamente contiene muy pocas informaciones acerca de la macroestructura coloídal de los asfaltenos.

La determinación de la masa molecular ha constituido el primer objetivo: se han aplicado varios métodos, como por ejemplo la osmometría con tensión de vapor. La conclusión principal de estas determinaciones es la gran variación de la masa molecular medida según la técnica aplicada. Hemos recurrido a la difusión de los rayos X y de los neutrones en los pequeños ángulos, con objeto de medir la polidispersidad en dimensión y la masa molecular de promedio en peso, de las macromoléculas asfalténicas. Hemos estudiado diversos sistemas compuestos ya sea para los asfaltenos o las resinas en solución en distintos disolventes, también hemos procedido al seguimiento del efecto de la temperatura en estos sistemas. Los resultados obtenidos permiten demostrar que el número de agregación, y en otros términos el número de las entidades elementales que forma la molécula, puede variar en grado sumo en función de la naturaleza del disolvente y de la temperatura. Las resinas aparecen como un disolvente muy correcto de los asfaltenos. Las mediciones de difusión muestran una gran intensidad difusa con pequeños valores del vector de difusión; ello refleja la presencia en el medio de heterogeneidades de dimensiones bastante amplias, debidas probablemente a las fluctuaciones de la concentración en asfaltenos. Así, existe en la suspensión de las regiones más o menos amplias en las cuales la concentración de asfaltenos es superior a la concentración de promedio. El microscopio en modo criogénico ha permitido confirmar la inhomogeneidad del sistema. Un medio compuesto por dos fases se ha visualizado claramente. La difusión de los rayos X en los pequeños ángulos demuestra constituir una técnica importante para el estudio de los medios no fraccionados, como ocurre con los crudos o los residuos de destilación, para los cuales no se ha realizado ninguna separación mediante n-heptano. Hemos podido así evidenciar, para estos sistemas, la existencia de fluctuaciones de densidad a gran escala.

INTRODUCTION

The high asphaltene concentration in crude oils or in heaviest cuts obtainable at atmospheric or vacuum distillation is responsible of many problems which are encountered during production, transportation, refining processes. Asphaltene flocculation and deposition can block pore throats in the near wellbore zone; the deposition can strongly modify wettability properties and relative permeabilities giving rise to a huge reduction of oil production. It's then necessary to inject good aromatic solvents, as toluene or xylene, often in combination with dispersant agents, in order to remove the deposits rich in asphaltenes. Flocculation behaviour can appear during secondary oil recovery or gas injection, water flooding or naphta injections. During storage or transportation, sedimentation can occur and the high viscosity of the products mainly due to the high asphaltene concentration causes important problems. The upgrading of heavy petroleum feed stocks becomes more and more difficult as the amount of unstable molecules such as asphaltenes or resins increases. It is well known that the heaviest fractions are often responsible for the catalyst deactivation.

The strong motivation in developing a more accurate description of crude oils and heaviest products is a better understanding of the mechanisms of what occurs during industrial problems which were previously highlighted.

A detail examination of the literature concerning asphaltenes or resins characterisation shows that the major part of the studies which have been carried out concern their chemical characterisation:

- determination of the chemical composition, the amount of the component elements such as carbon, hydrogen, oxygen, sulphur, or metals such as nickel or vanadium;
- analysis of the organic structure; identification of different types of carbon environment existing in naphtenic, aromatic, or paraffinic molecules, existence of specific functionalities such as pyroles, indoles, esters and carbonyl functions;
- structural characterisation using 13C NMR or infrared spectroscopies which can lead to an average model for asphaltene or resin molecules, and wide angle X-ray scattering for describing interactions between several elementary molecules.

Yen and co-workers [1], proposing a general model for asphaltene aggregation made a very nice synthesis of all the data which were collected on asphaltene molecules. According to this model, the asphaltene organisation can be described by three different entities: sheets, micelles and aggregates.

The chemical description is very useful for classifying crude oils and is important in the context of catalytic conversion. Nevertheless, it seems that this information is not sufficient to explain some frequently observed unusual behaviour. We have practical evidence that crude oils having the same composition may or may not produce deposits in the field. Quite similar feed stocks can exhibit very different catalytic behaviour.

In addition to the chemical characterisation, we proposed to investigate the colloidal macrostructure of (i) asphaltenes or resins in solution and (ii) crude oils and heaviest fractions without any prior fractionation. It's straightforward that macroscopic structural data on a much larger scale are necessary for studying crude instability, even if they are mainly governed by local interaction forces, strongly influenced by the chemistry of the molecules.

All the investigations were carried out on asphaltenes which were extracted from crude oil. Very few works deal with characterisation of asphaltenes or resins in the crude. The only model proposing an overview of the crude structure was proposed long time ago by Pfeiffer and Saal [2]. This model emphasises the important role of resins which act as peptizing agents of asphaltenes.

The objective of this paper is to present results obtained by the use of scattering techniques, electron microscopy, in order to give an accurate description of the system in a large range of sizes [3] and [4]. Scattering methods (X-ray and neutron) are well known techniques for colloidal systems investigations. Low-temperature scanning electron microscopy can provide information at much larger scale, from 50 nm to 10 microns.

1 EXPERIMENTAL

1.1 Techniques

1.1.1 Small angle X-ray and neutron scattering (SAXS and SANS) [5] and [6]

SAXS and SANS measure the scattered intensity $I(Q)$ at small angles 2Θ [5]. The scattered intensity per unit volume for a two-phase system (asphaltene and solvent) in dilute conditions is given by:

$$I(Q) = C_i \cdot n_e \cdot v \cdot (\rho_1 - \rho_2)^2 \cdot F(Q) \cdot S(Q) \quad (1)$$

where Q is the scattering vector defined as $Q = \frac{4\pi \sin(\Theta)}{\lambda}$, λ is the wavelength, C_i is a constant which depends on the radiation used, n_e is the number of particles (asphaltene molecules) per unit volume and v is the volume of a single elementary particle. ρ_1 and ρ_2 are the scattering densities of the particle and the surrounding medium, respectively. $F(Q)$ is the particle form factor ($F(Q) = v$ for $Q = 0$); it is Q-dependent and provides information about the shape, particle size and, consequently, the molecular weight of a single asphaltene or resin particle. $S(Q)$ is the structure factor which depends on the inter-particle interactions. It explicitly depends on the distribution of particles in the suspension. From the slope of $S(Q)$ one can tell if the solution is diluted or if the aggregation occurs. $S(Q)$ is large at small Q-values and becomes equal to unity as Q increases. For a diluted system, the scattering curve directly provides data on the average molecular weight, M_w. In this case the scattered intensity at $Q = 0$ is proportional to M_w (c is the asphaltene concentration):

$$\left(\frac{I(Q)}{c}\right)_{(Q = 0,\, c \to 0)} \propto M_w \quad (2)$$

The scattering form factor $F(Q)$ depends on the shape and size of molecules in solution. The most general way to analyse SAXS or SANS data is to try and find an adequate structural model, calculate the scattering curve corresponding to this model and, finally, fit the model parameters to the experimental data using, for instance, a least-square procedure.

All our recorded spectra were absolutely calibrated. The fitting procedure needs the calculation of the contrast term $(\rho_1 - \rho_2)^2$ (equation 1), which is not very well known due to the uncertainty on the density of the molecule in suspension. The particle volume is related to the particle dimension, which is a fitting parameter, and n_e depends on (i) the particle volume, (ii) the concentration of asphaltenes or resins and (iii) the solvent as well as asphaltene molecular density.

X-rays are sensitive to the electron density whereas neutrons interact with the nuclei. In particular, there is a strong difference between hydrogen and deuterium neutron scattering. Therefore, by dissolving the asphaltenes in deuterated solvents one strongly increases the neutron scattering intensity.

The form factors for various structural models are well known. For systems of randomly oriented spheres, cylinders or ellipsoids; the form factor $F(Q)$ has been given by Guinier and Fournet [6]:

(i) spheres of radius R and volume v:

$$F(Q) = v \cdot \left(3.\frac{(\sin(QR) - QR\cos(QR))}{(QR)^3}\right)^2 = v \cdot \Phi^2(QR) \quad (3)$$

(ii) cylinders of axial length 2H, cross-sectional radius R and volume v:

$$F(Q) = v \int_0^{\frac{\pi}{2}} \frac{\sin^2(QH\cos\alpha)}{(QH\cos\alpha)^2} \frac{4J_1^2(QR\sin\alpha)}{(QR\sin\alpha)^2} \sin\alpha \, d\alpha \quad (4)$$

where J_1 is the first order Bessel function and the integration variable α is the angle between the scattering vector Q and the cylinder axis. Expression (4) is rather complex. For very flat, disk-like cylinders ($R >> 2H$) or rod-like particles, formula (4) can be simplified [6].

(iii) ellipsoids of axes lengths ($2a$, $2a$, $2xa$) and volume v:

$$F(Q) = v \cdot \int_0^{\frac{\pi}{2}} \Phi^2 \left(Q \cdot \mathrm{a} \cdot \sqrt{\cos^2(\alpha) + x^2 \sin^2(\alpha)}\right) \cdot \cos(\alpha)\, d\alpha \quad (5)$$

where Φ is the function defined by formula (3) and the integration variable α is the angle between the scattering vector Q and the ellipsoid.

The size distributions of heavy molecules tend to exhibit polydispersity. We have treated our data using a standard polydispersity model represented by a log-normal size distribution:

$$f(R) = \frac{1}{\sqrt{2\pi}\sigma R} \exp\left(-\frac{1}{2}\left[\frac{Ln(R) - Ln(R_0)}{\sigma}\right]^2\right) \quad (6)$$

where R is the disk radius, and σ and R_0 are the standard deviation and the average radius of the log distribution, respectively. The general formula for the scattering intensity of a polydisperse system is:

$$I(Q) = C_i \sum_k n_k v_k (\rho_1 - \rho_2)^2 F_k(Q) \quad (7)$$

where n_k and v_k are the number of particles per unit volume and volume of the particle k, respectively.

We can define the volume average and the weight average molecular weight according to the following formulae:

$$<V> = \frac{\sum_k n_k \cdot v_k}{\sum_k n_k} \tag{8}$$

$$M_w = \frac{\sum_k n_k \cdot M_k^2}{\sum_k n_k \cdot M_k} \tag{9}$$

The experiments were performed using two X-ray arrangements: a Huxley-Holmes type camera for SAXS and a double crystal camera especially designed for ultra small angle X-ray scattering, USAXS [7]. The total Q-range accessible with these instruments was $6.10^{-4} - 0.5\ A^{-1}$. A high-temperature cell has been developed for both cameras in order to perform experiments at elevated temperatures up to 673 K.

SANS experiments were performed using a neutron spectrometer (PAXE) at the *Leon Brillouin Laboratory* (*LLB, CE Saclay*, France). The Q-domain accessible with neutron spectrometer was $3.10^{-3} - 2.10^{-1}\ A^{-1}$.

1.1.2 Cryoscanning electron microscopy [8], [9] and [10]

When a hydrated sample is left at ambient temperature inside the high vacuum chamber of a scanning electron microscope, water is rapidly lost causing a shrinkage and distortion of the sample. By rapidly cooling the hydrated specimen and maintaining it at a temperature below 113°K one preserves it in such a condition that it can be examined in vacuum for an extended period of time without the loss of water. The macrostructure of the quenched specimen can be exposed by fracturing at low temperature and the structural details can be often revealed and/or enhanced by carefully raising the temperature up to a point at which water begins to sublime at a slow, controlled rate. This process can be halted when necessary by lowering the temperature. This approach was applied for asphaltene suspensions investigation.

An Oxford-Hexland cryotrans system fitted to a JEOL JSM6300F scanning electron microscope was used in our experiments.

The studied suspension is introduced into a drilled copper stub (1 mm diameter cavity), covered with a thin copper plate (in contact with the liquid) and, finally, rapidly frozen by plunging into a nitrogen slush at a temperature of about 63 K. The stub is then transferred into a cryopreparation vacuum chamber, which is a cold stage maintained at 108 K. The copper plate is then removed in vacuum in order to cleave and expose a fresh fracture plane of the sample. The cleaved sample is then transferred into the cold stage of the microscope which is maintained at 83 K. A heater in the stage enables the temperature to be raised to any preset value from 83 K to 323 K. The sublimation process is controlled by the SEM image observation. For the vacuum of the microscope chamber (typically 4.10^{-6} torr) the appropriate sublimation temperature of toluene is 158 K. Our observations have been made at this temperature, and the sublimation process was followed as a function of time. The porous texture of the sample corresponding to an etching depth of several micrometers was typically revealed after about 40 minutes. If necessary, the sublimation process can be stopped and the sample coated with gold in order to improve the image quality.

1.2 Samples

We have studied asphaltenes extracted from several crude oils and the Safaniya vacuum residue. They were prepared according to the AFNOR T60-115 method. Maltenes, i.e. the fraction soluble in n-heptane, was fractionated by liquid chromatography in order to obtain resins. We used a column filled with silica and alumina. The different crude oils investigated are listed in table 1 and we give the chemical composition of the corresponding asphaltenes.

TABLE 1

Composition of the various asphaltenes which were investigated and the asphaltene concentration in these crude oils

Crude oils Asphaltene contents (% w/w)	**Asphaltene chemical composition**
A - 0.6%	$C_{7.27}\ H_{8.0}\ N_{0.055}\ O_{0.2}\ S_{0.023}$
B - 14%	$C_{6.79}\ H_{8.02}\ N_{0.13}\ O_{0.1}\ S_{0.215}$
C - 4%	$C_{7.35}\ H_{8.57}\ N_{0.112}\ O_{0.08}\ S_{0.011}$
D - 1%	$C_{7.36}\ H_{7.9}\ N_{0.095}\ O_{0.13}\ S_{0.008}$
E - 24%	$C_{6.73}\ H_{6.88}\ N_{0.005}\ O_{0.06}\ S_{0.357}$
F - 1.5%	$C_{6.96}\ H_{7.2}\ N_{0.078}\ O_{0.07}\ S_{0.228}$
G - 9%	$C_{6.68}\ H_{7.69}\ N_{0.005}\ O_{0.08}\ S_{0.337}$
H - 4%	$C_{6.825}\ H_{6.5}\ N_{0.093}\ O_{0.11}\ S_{0.159}$
Safaniya vacuum residue - 15%	$C_{6.87}\ H_{7.49}\ N_{0.072}\ O_{0.08}\ S_{0.236}$

2 RESULTS

2.1 Asphaltene solutions in toluene

The X-ray scattering data for a 5 % w/w asphaltenes (E) in toluene are presented on Figure 1. We can distinguish two different domains corresponding to Q-values larger and smaller than 2.5 10^{-3} A^{-1}. For large Q-values we observe a near constant intensity which is followed by a more pronounced decrease of the intensity at very large Q-values. As detailed in a previous paper [4] this Q-range is used for the shape and size determination of the asphaltene molecules. For small Q-values, a strong increase of the scattered intensity is observed which corresponds to the presence of very large particles in the suspensions; this particular behaviour will be discussed later. We can mention that the general aspect of the scattering curve is very similar to the one which was obtained for asphaltenes of Safaniya vacuum residue in solution in toluene [4]. Neutron scattering experiments were carried out on several asphaltene samples (Fig. 2). As mentioned in the technical presentation, SANS spectrometer enables the scattering measurement only for large Q-values, greater than 3.10^{-3} A^{-1}. The concentration of asphaltenes in toluene was close to 4% w/w for each solutions; nevertheless, the scattered intensity was divided by the exact concentration value. Thus, if we assume that the contrast term between the different asphaltenes molecules and deuterated toluene doesn't vary too much, and according to formula (2), we can yet classify the asphaltene with their molecular weight. We can see that the highest average molecular weight is for C asphaltene, and the smallest one is measured for A asphaltenes.

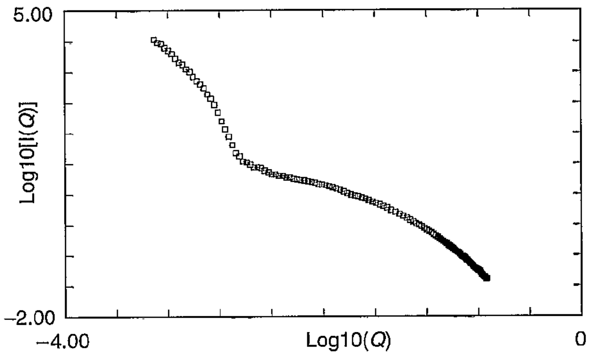

Figure 1

X-ray scattering for E asphaltenes solution in toluene (5% w/w).

Using the curve fitting procedure, the average asphaltene molecular weight and the size polydispersity have been calculated. We have tested different models of simple particle shape, as spheres, ellipsoids and disks. In order to obtain a good fit, it was necessary introduce polydispersity. For ellipsoid and disk model, we only consider a polydispersity on the larger axis for ellipsoids and on the radius for the disk model. Figure 3 shows the comparison between experimental data and simulations for the different models for asphaltenes F; we can notice the very good agreement between experimental and calculated data. We can confirm that several models can fit experimental values. Characteristic

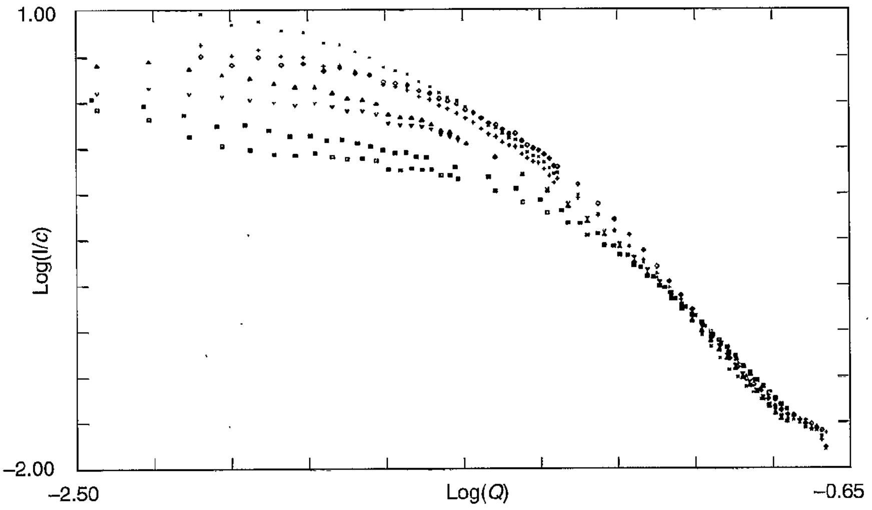

Figure 2

Small angle neutron experiments for several asphaltene solutions: (×) C, (+) B, (◇) D, (▲) E, (▷) F, (■) G, (□) A. The asphaltene concentration was close to 4% w/w and the intensity is divided by the exact concentration.

parameters of the polydispersity for the different models are gathered in Table 2. As we measured the asphaltene density in toluene solution equal to 1.19, it is possible to calculate the average molecular weight M_w. We can remark that the average volume $<V>$ is not too different by using fitting with sphere, ellipsoid models; higher value is obtained using disk model.

Neutron scattering data presented in Figure 2, were treated considering asphaltenes molecules as spheres and size parameters were deduced for different crude oil asphaltenes previously mentioned (Table 3).

Asphaltene size polydispersity, obtained with sphere-like particles model, is presented in Figure 4. We have plotted the volume size polydispersity and we can notice huge differences between different asphaltenes investigated. If we compare the distribution calculated for D, F and A (Fig. 4a), we can see that D asphaltene particles are much larger than F and A asphaltene molecules. Size polydispersity can vary strongly for several asphaltenes as shown on Figure 4b. This behaviour has a huge influence on the average molecular weight which depends on the amount of big particles in suspension.

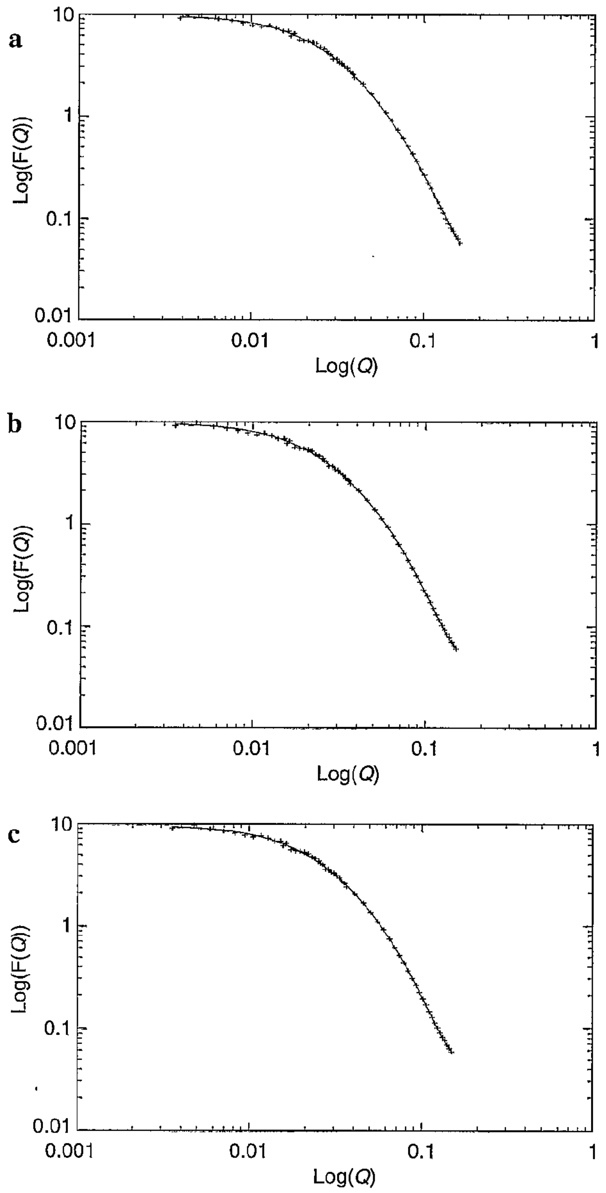

Figure 3

Curve fitting results for F asphaltene solutions in toluene with three different particle models:
(a) spheres, (b) polydispersed disks,
(c) ellipsoids with constant thickness and variable radius.

TABLE 2

Parameters of the polydispersity obtained by curve fitting for F asphaltenes: spheres, R_0 is the average radius of the log-normal distribution, σ the standard deviation as defined by formula (6); ellipsoids, R_0 is the average larger axis and σ the standard deviation and H is the length of the smallest axis which is fixed during the curve fitting; disks, as for ellipsoid model, R_0 is the average radius of the disk and σ the standard deviation, H is the height of the disk which is constant

Shape	R_0(A)	σ	H(A)	$<V>(A^3)$	$<M_w>$
Spheres	8.4	0.6		340 000	243 000
Ellipsoids	25.5	0.56	20	370 000	260 000
Disks	28	0.53	33	440 000	320 000

TABLE 3

Size parameters (sphere model) for several asphaltenes extracted from different crude oils and Safaniya vacuum residue (R_0 is the average radius of the log-normal distribution, σ the standard deviation as defined by formula (6), $<V>$ is the volume average)

Asphaltene	R_0(A)	σ	$<V>(A^3)$
A	6.3	0.6	130 000
B	9.6	0.62	700 000
C	11	0.64	1.200 000
D	18	0.48	550 000
E	4.6	0.72	480 000
F	12.1	0.54	370 000
G	5.7	0.63	180 000
H	8	0.57	170 000
Safaniya vacuum residue	8.5	0.6	340 000

2.2 Asphaltenes and resins suspensions in toluene

Resins extracted from Safaniya vacuum residue were investigated by SAXS [3] (Fig. 5). We can observe for two different concentrations (6 and 10% w/w) spectra which are very similar to those carried out for asphaltenes solutions. At large Q-values ($Q > 10^{-2} A^{-1}$), a near plateau is detected followed by a strong decrease of the intensity proportional to Q^{-2}. For small Q-values, lower than 10^{-2}, a huge increase of the scattered intensity is observed which indicates the occurrence of large entities. The average molecular mass was calculated according to curve fitting procedure [3], and was found much smaller than the asphaltene molecular weight (M_w = 2700 by SAXS and M_w = 4500 by SANS). We have investigated the effect of resin addition into asphaltene suspension. We have plotted in Figure 6 the large Q X-ray scattering intensity for a pure asphaltene solution and a mixture of asphaltenes plus resins in toluene. We can remark a more intense scattering for higher Q when resins are present in solution. This can be easily interpreted by the presence in toluene suspension of small entities (resins) which contribution is higher at large scattering vector. On the contrary, we can observe a decrease of the intensity for small

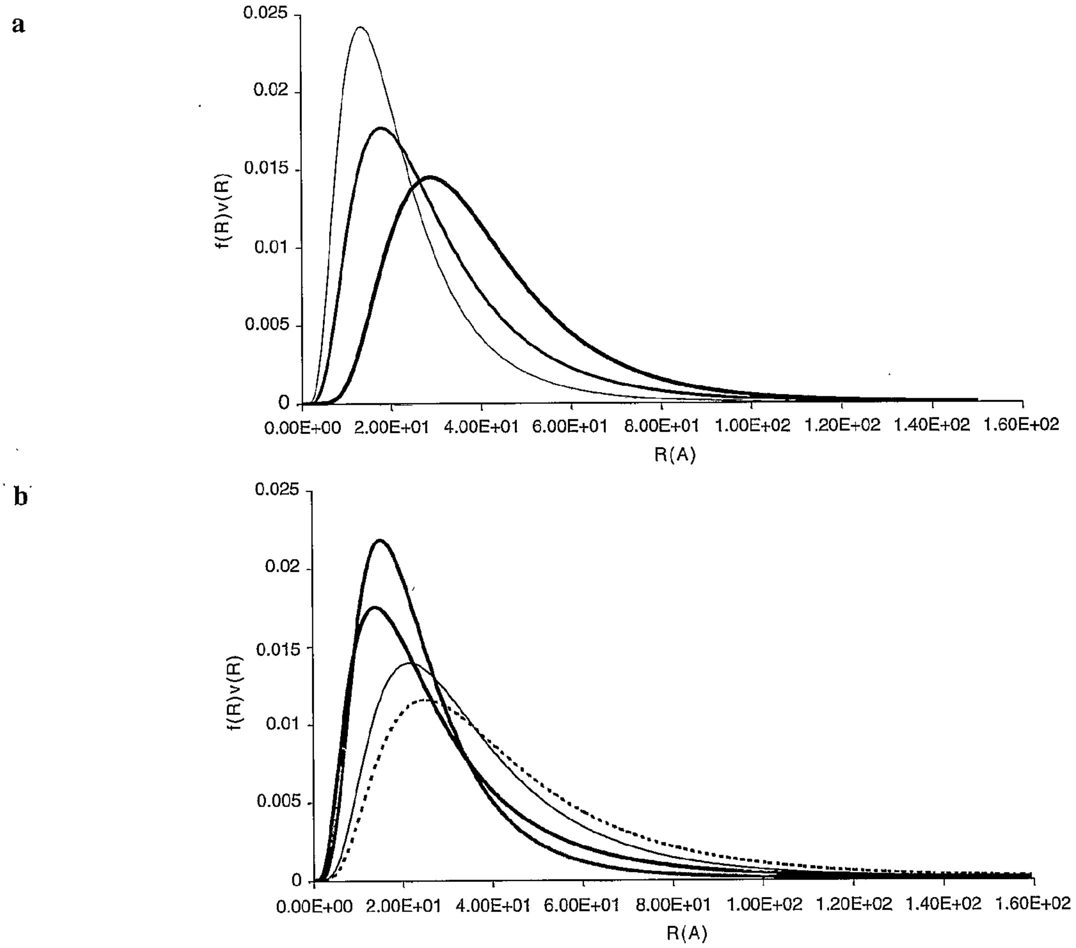

Figure 4

Size distribution carried out using a sphere-like particle model: (a) size distributions for A (__), D(__) and F (__) asphaltenes in toluene, (b) size distributions for asphaltenes E(__), B(__), C(...), H(__).

Q values which traduces some changes of the solution organisation. In order to precise this point, we have compared the scattering curve of the mixture asphaltenes plus resins with the sum of the intensities which were measured for pure asphaltenes and pure resins (Fig. 7). The sum is larger than the intensity of the mixture, which indicates a decrease of the asphaltene molecular weight. These observations confirm that resins are good solvent of asphaltenes.

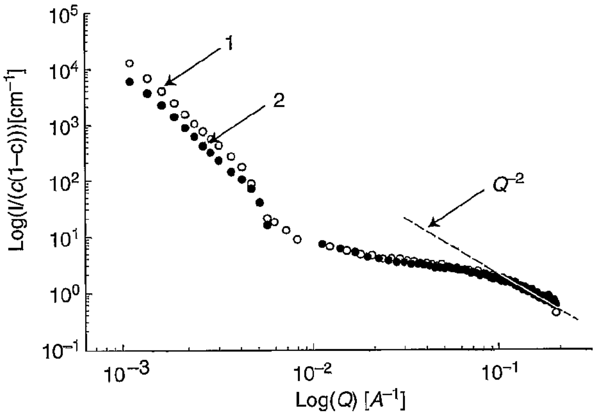

Figure 5

Small angle X-ray data for Safaniya vacuum residue resins dissolved in toluene at different concentrations c:
(1) 6% w/w, (2) 10% w/w.

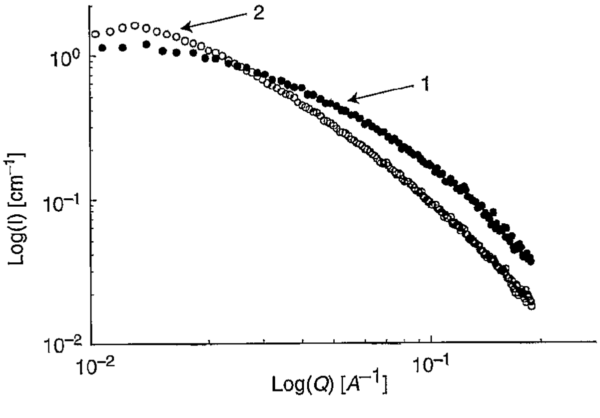

Figure 6

X-ray scattering for a mixture Safaniya vacuum residue asphaltenes (2% w/w) and resins (4% w/w) in toluene (1), and comparison with the SAXS diagram for a 2% w/w Safaniya vacuum residue asphaltene solution in toluene (2).

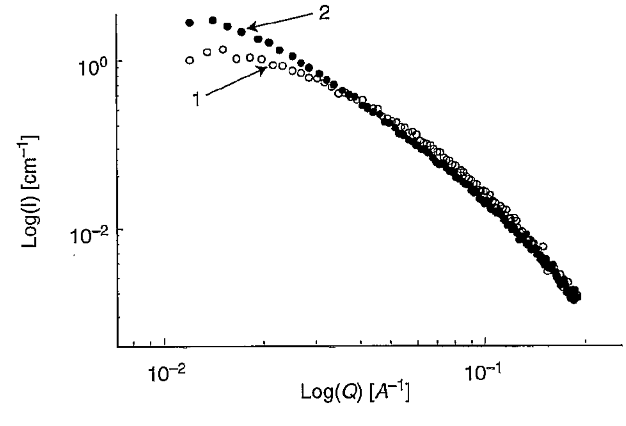

Figure 7

SAXS data for a mixture of Safaniya vacuum residue asphaltenes and resins: (1) 2% w/w asphaltene + 4% w/w resins in toluene, (2) the sum of scattering intensity for pure asphaltenes (2% w/w) and pure resins (4% w/w) in toluene.

2.3 Small Q-values behaviour of SAXS data

Figure 1 exhibits huge scattered intensity at small Q-values for E asphaltene solutions. We have confirmed this general behaviour for several asphaltenes which have different origins. X-ray scattering data obtained for three asphaltene toluene suspensions of Safaniya vacuum residue, C and E crude oils are presented in Figure 8. The separation between the two domains, large and small Q-values, is not very different. As previously mentioned, this behaviour indicates that large entities exhibiting high density contrast (formula 1) or large density fluctuations are present in these asphaltene suspensions. We have suggested two different models (Fig. 9):

- asphaltenes molecules form complex aggregates by van der Waals and/or hydrogen bonds which can be created by polar molecules. In these extended regions, the asphaltene concentration (C2) is higher than the average one and of course much higher than C1 (Fig. 9a). This density fluctuation can explain an increase of the scattered intensity;
- asphaltene molecules or micelles, whose size polydispersity is deduced from large Q-values data fitting, are present close to much bigger aggregates which give a huge scattering contribution at small Q-values (Fig. 9b).

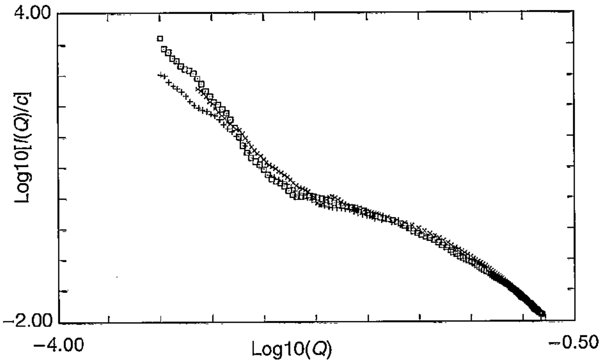

Figure 8

Small angle X-ray scattering of three different asphaltene suspensions in toluene: (□) C, (X) E, (+) Safaniya vacuum residue (see Table 1).

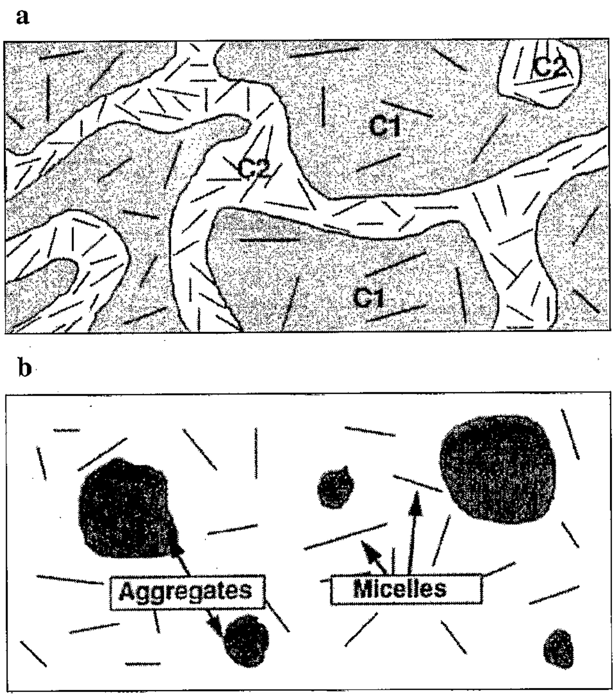

Figure 9

Aggregation models for asphaltene solutions. (a) the concentration (density) fluctuations, (b) a mixed system of high molecular weight aggregates and elementary asphaltene micelles.

In order to clarify these descriptions, we performed cryoscanning electron microscopy experiments (Cryo-SEM). Figure 10 shows the aspect of a 2% w/w Safaniya vacuum residue asphaltene in toluene. We observe a kind of porous system, which pores are related to low-concentrated asphaltene regions of the solution. In these zones, toluene was sublimated at lower temperature. Bright regions correspond to more concentrated parts of the suspension; toluene is not yet sublimated. If the asphaltene concentration was constant in each elementary volume of the suspension, the toluene sublimation into the microscope will occur at one temperature and it would be impossible to observe the macrostructure shown in Figure 10.

These observations tend to confirm the model which was proposed in Figure 9a.

2.4 Effect of n-heptane addition

Cryosem technique was used for describing the macrostructure evolution with n-heptane addition. We have prepared a 35% w/w n-heptane Safaniya vacuum residue asphaltene solution. The observation is presented in Figure 11. Two morphologies can be observed: (i) the first one is very similar to the one previously shown in picture 10 without any n-heptane addition, (ii)

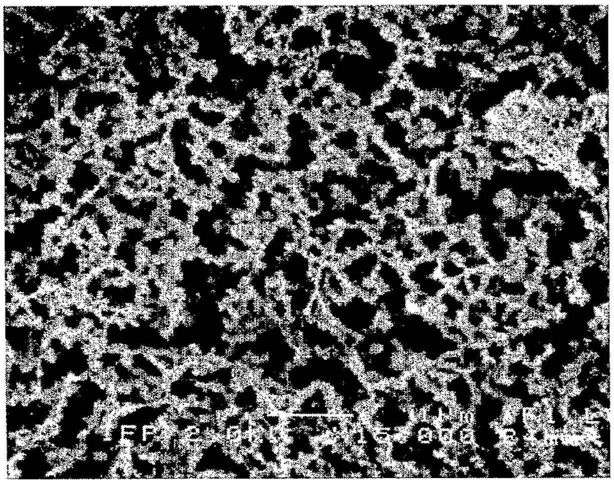

Figure 10

Cryo-SEM image of 2% w/w Safaniya vacuum residue asphaltene solution in toluene.

the second one seems denser, more homogeneous, and traduces the beginning of the flocculation. We must point out that this solution didn't show any huge aggregates which could be detected by the naked eye.

A new Safaniya vacuum residue asphaltene suspension (2% w/w) was prepared with 65% w/w n-heptane in toluene. Huge aggregates can be easily observed, the suspension being flocculated. We have collected, on a carbon grid used for transmission electron microscopy analysis, one of these large aggregates which was observed by cryomicroscopy (Fig. 12). We can see in some parts of the picture the carbon of the grid which exhibits well defined holes. Small asphaltenes aggregates which size is close to a fraction of micron form a fractal-like structure. The increase of the n-heptane concentration (80% w/w) gives a similar macrostructure of the asphaltene aggregates (Fig. 13). On these last pictures, we can remark that the network made by highly concentrated regions (Fig. 10) disappears giving rise to an aggregated structure where the concentration of asphaltene molecules is much more higher than the average asphaltene concentration. Figure 13b illustrates this aggregation at much higher magnification.

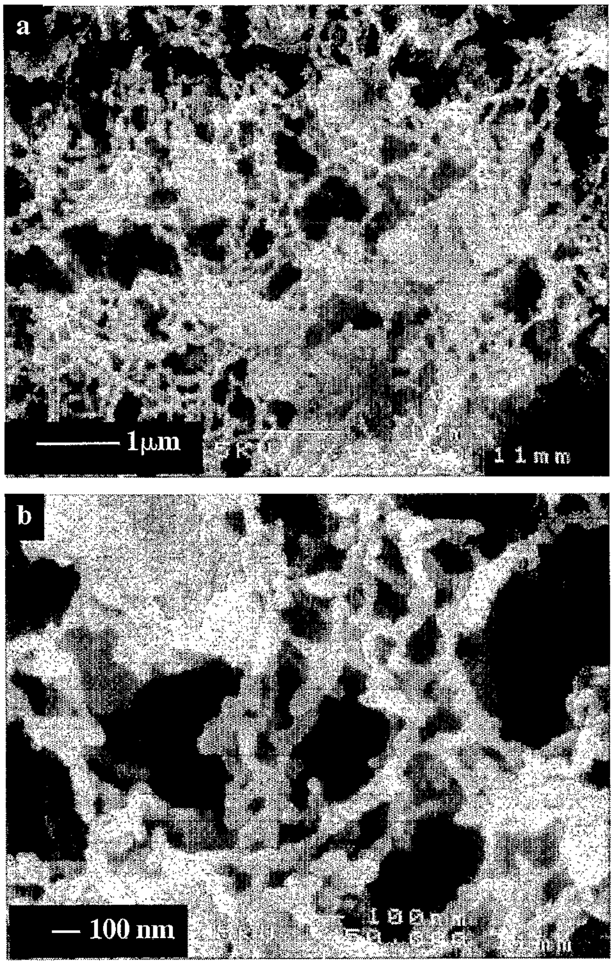

Figure 11

Cryo-SEM image of 2% w/w Safaniya vacuum residue asphaltene solution in toluene with n-heptane (35% w/w) (a) low magnification, (b) high magnification.

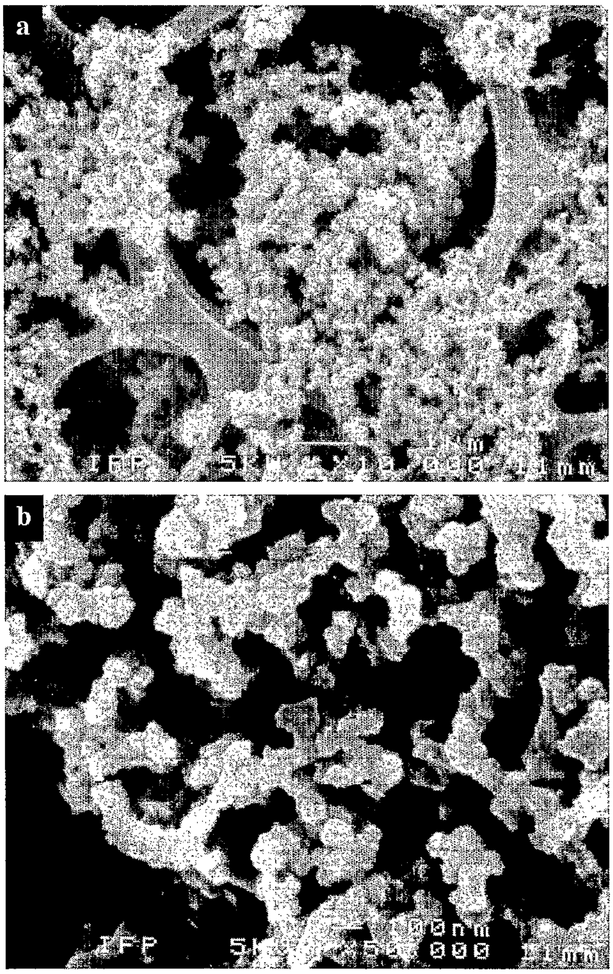

Figure 12

Cryo-SEM image of 2% w/w Safaniya vacuum residue asphaltene solution in toluene with n-heptane (65% w/w) (a) low magnification, (b) high magnification.

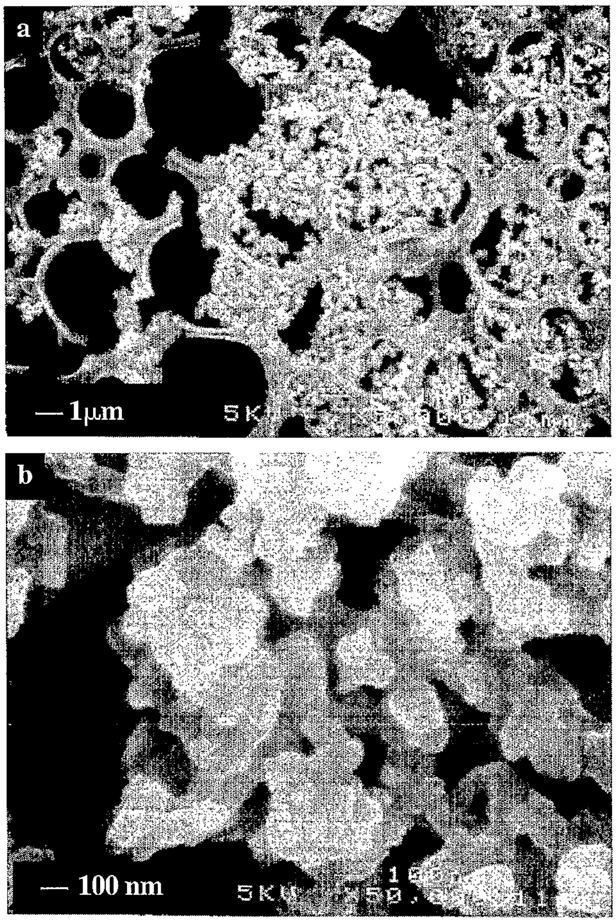

Figure 13

Cryo-SEM image of 2% w/w Safaniya vacuum residue asphaltene solution with n-heptane (80% w/w) and toluene: (a) low magnification and (b) high magnification.

2.5 Investigation of pure crude oils

In Figure 14, we have plotted the X-ray scattering intensity for two different crude oils E and H and the Safaniya vacuum residue. We can conclude that these materials are not homogeneous. As for asphaltene suspensions in toluene, we can distinguish two domains:

- For large Q-values ($Q > 9.10^{-3}\,\text{A}^{-1}$), a more or less pronounced plateau is detected, followed by a decrease of the scattered intensity for higher Q-values. This domain corresponds to the scattering of small dense regions probably made by the stacking of aromatic entities which are present in the different fractions of the crude oil (asphaltenes, resins, aromatic fraction).
- At smaller Q ($Q < 9.10^{-3}\,\text{A}^{-1}$), a strong increase of the intensity is observed for Safaniya vacuum residue and H crude oil but not for E crude oil. We didn't plot any point of the scattering curve for E crude oil for Q-values lower than 4.5 $10^{-3}\,\text{A}^{-1}$ because no signal was detected, indicating very low intensity really scattered in this domain. The intense signal is due to the presence of large density fluctuations. They are probably related to the aggregation of aromatic molecules, rich in electrons, which are consequently not homogeneously distributed in the suspension. Looking at the shape of the high Q-values scattering intensity we can conclude that small heterogeneities are larger for E crude oil than for H crude or Safaniya vacuum residue. Nevertheless no large heterogeneities which sizes will be smaller than about one micron are detected. If bigger heterogeneities would exist, the corresponding X-ray scattering will be measurable at much smaller Q-values which are not accessible with the double crystal camera used for our experiments. The curve fitting procedure was applied in order to extract some information on the volume average of the smaller heterogeneities whose scattering region is at high Q-values ($Q > 9.10^{-3}\,\text{A}^{-1}$). Results are presented in Tables 4, 5 and 6, respectively for Safaniya vacuum residue, E and H crude oils. We have used the sphere model and data concerning crude oils are compared to those carried out for asphaltenes in toluene investigated with SAXS and SANS techniques.

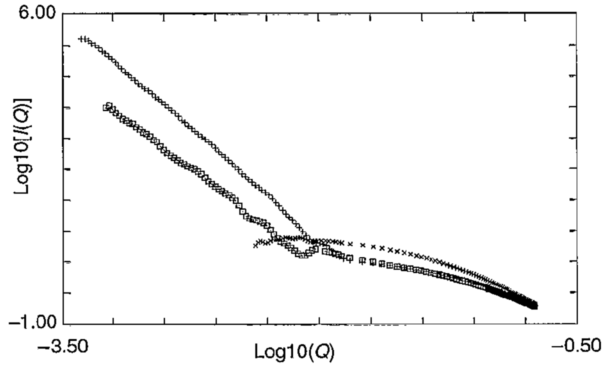

Figure 14

SAXS data for three different oils (xxx) E, (+++) Safaniya vacuum residue and (□□□) B.

We can see that the average entities in crude oil is much smaller than particles which can be measured in toluene by SAXS or SANS techniques. We can notice that asphaltene molecule size measured by SAXS is smaller than the one obtained by SANS treatment. This can be explained [6] by the fact that X-ray are more sensitive to aromatic regions which are rich in electrons, instead of neutron scattering which is sensitive to hydrogen and then to paraffinic regions which are extended at the periphery of the asphaltene molecules according to Yen model [1].

TABLE 4

Comparison of the size distribution and the average volume for Safaniya vacuum residue and its asphaltenes in toluene characterised by SAXS and SANS (R_0 is the average radius of the log-normal distribution, σ the standard deviation as defined by formula (6), $<V>$ is the volume average)

Oils and asphaltene Technique used	R_0(A)	σ	$<V>(A^3)$
Safaniya vacuum residue - SAXS	1.6	0.75	30 000
Asphaltenes in toluene - SAXS	2.6	0.7	62 000
Asphaltenes in toluene - SANS	8.4	0.6	240 000

TABLE 5

Comparison of the size distribution and the average volume for E crude oil and its asphaltenes in toluene characterised by SAXS and SANS (R_0 is the average radius of the log-normal distribution, σ the standard deviation as defined by formula (6), $<V>$ is the volume average)

Oils and asphaltene Technique used	R_0(A)	σ	$<V>(A^3)$
E crude oil - SAXS	1.5	0.78	52 000
Asphaltenes in toluene - SAXS	1.8	0.8	220 000
Asphaltenes in toluene - SANS	4.6	0.7	480 000

TABLE 6

Comparison of the size distribution and the average volume for H crude oil and its asphaltenes in toluene characterised by SANS (R_0 is the average radius of the log-normal distribution, σ the standard deviation as defined by formula (6), $<V>$ is the volume average)

Oils and asphaltene Technique used	R_0(A)	σ	$<V>(A^3)$
H crude oil - SAXS	1.9	0.78	120 000
Asphaltenes in toluene - SANS	8	0.57	170 000

CONCLUSIONS

This work has demonstrated that scattering techniques (SAXS and SANS) can help us in order to highlight a better description of the colloidal state of asphaltene and/or resin suspensions and, last but not least, of pure crude oils and their heavy fractions obtained for instance by distillation process. We have shown that the behaviour of asphaltenes and resins in solution of more or less good solvents is governed by an aggregation equilibrium [4]. Our present results show that the molecular weight can vary strongly for several kind of asphaltenes. The size polydispersity also depends of the asphaltene type. The maximum of the distribution varies from 0.5 nm to 1.8 nm, and the value of σ is always very large in comparison to the values generally obtained in the literature concerning other colloidal systems. Asphaltenes obtained from n-heptane precipitation exhibits a huge polydispersity. Looking at the size polydispersities, we can nevertheless remark that the number of small entities whose size is lower than 2 nm are in majority. Larger particles are of course less numerous but can greatly influence the colloidal stability of the suspension. Recent results [11] have shown by *n*-heptane fractionation that the most unstable fraction is formed by large molecules which are more aromatic and rich in heteroelements.

We have tested several models for the curve fitting of large *Q*-values data. We have shown that several classical models, used for scattering data interpretation and considering single shape for particles, as spheres, disks or ellipsoids, can fit experimental data. This comparison will probably close the discussion opened about the shape of asphaltene molecule. Monodisperse disk model was proposed for SANS data interpretation [12]. Sphere model was used by Sheu *et al.* [13] for X-ray data interpretation and Thiyagarajan [14] has found rod-like particle shape. It's obvious that all these models are too simple for asphaltene shape description. According to chemical representations given in the literature [1] and [15], the aromatic core surrounded by aliphatic chains having a more or less complex geometry, it seams difficult to reduce asphaltene molecules to a simple shape entity.

Another difficulty is the sensitivity of each technique to different parts of the molecule; we have shown that X-ray is more sensitive to aromatic regions whereas neutron scattering strongly depends on the hydrogen concentration. The polydispersity contributes to smooth the scattering curve which becomes less sensitive to the shape of the particles.

Whatever the particle model chosen, the average molecular weight must be independent and obtained according to formula (2). Consequently, the simple observation of the large Q-values scattering intensity evolution can provide, after concentration correction, interesting information on the aggregation of different types of asphaltene molecules. It's obvious that the most important problem concerns the aggregation state behaviour from the microscopic to macroscopic scale.

We have demonstrated that resins play an important role for decreasing the aggregation of asphaltenes. A better understanding of the resin action is a decisive issue. In particular, it remains unanswered how asphaltenes and resins are in interaction.

We have shown that all the solutions we have investigated are heterogeneous systems. Both X-ray scattering and cryomicrospy confirm the existence of large concentration fluctuations which are probably the onset of a flocculation process. It would be interesting to better understand why such fluctuations occur. Are they due to the presence of specific chemical functions like aromatics or hetero-elements giving rise to special interactions between molecules as π-π or hydrogen bonds?

It was possible by cryomicroscopy to follow the flocculation process by n-heptane addition. It appears that this process can be considered as a phase separation where two phases characterised by different asphaltene concentration are produced. As the amount of n-heptane increases, large aggregates grow; solvent is still present inside these huge particles but asphaltene concentration and density progressively increases. We don't obtain a pure asphaltene solid phase as it's in general the case for classical salt precipitations. Pictures obtained for *n*-heptane highly concentrated suspensions, exhibits a fractal-like structure of asphaltene aggregates.

We have demonstrated that a large amount of natural products as crude oils or of course vacuum residue are heterogeneous systems. We can conclude that electronically large dense regions exist in these materials. We only didn't find density fluctuations in crude oil E; if they exist, their sizes should be very large and no accessible to SAXS experiments. We must remark that E crude oil contains the biggest particles in comparison with other crude oils. As the huge heterogeneities at large scale are probably due to the aggregation of the particles we can understand that some very large fluctuations may be developed whose sizes will be bigger than those present in other products. This point could be further investigated by using other technique as electron microscopy which was already applied to heavy products as bitumen [16, 17, 18].

The origin of these large density fluctuations is another important issue. We have suggested the gathering of dense particles made by the stacking of aromatic part [1] of asphaltene entities more or less developed depending on the aromaticity of the molecule. Several of these stakings can be connected by hydrogen bonds or covalent links; we can imagine that several aromatic nuclei belong to the same asphaltene molecule and participate to different stackings. We have show [4] that huge heterogeneities, corresponding to small Q scattering, are very stable as a function of temperature increase. The size of these elementary stackings is probably not very large, in the range of 1 to 2 nm, as was observed by Yen and co-workers [1] and may correspond to a domain of the size distribution of which we have given some illustrations.

In conclusion, we are now able to apply various complementary techniques in order to describe the colloidal state of asphaltene solutions and crude oils. This is a new progress for asphaltenic crude oils and heavy fractions investigation; the majority of the previous works dealt with asphaltene solutions. We could expect to improve our description of these complex fluids and establish correlation between this macrostructural description and their stability, their rheological or catalytic properties. It will be possible to further investigate the role of additives during flocculation process and the system evolution at high temperature and pressure.

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