Properties of Venezuelan Asphaltenes in the Bulk and Dispersed State

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Abstract: The properties of asphaltenes derived from Venezuelan vacuum residues have been investigated using several techniques. X-ray diffraction and Differential Scanning Calorimetry (DSC) and infrared spectrometry results indicate that asphaltenes are complex mixtures that form nanostructures with some (low) degree of ordering, probably consistent with a sheet-like arrangement of aromatic nuclei. Nanostructures seem to be also present in solutions of the asphaltenes in toluene, and an increase in their concentration can induce phase separation by flocculation. Asphaltene aggregates show an isoelectric point at around pH=4 and their charge is highly negative at high pH. This is attributed to the presence of ionisable acidic groups that also are responsible of low water/toluene interfacial tensions at basic conditions. A decrease in interfacial tension is also induced by increasing asphaltene concentration or the addition of electrolyte. The results are correlated with the stability of water-in-oil emulsions, which seems to be determined by interfacial adsorption.

Key words: asphaltene, X-ray diffraction, interfacial tension, zeta potential, crude oil emulsion

1 Introduction

High oil prices have renewed the interest not only in new sources of energy but also in using more efficiently the available oil reserves, which are mostly of the heavy or bituminous type. Many of the problems associated with processing of heavy crude oils come from asphaltenes, roughly defined as fractions which are soluble in aromatic solvents such as toluene and benzene and insoluble in alkanes such as pentane or heptane

(1,2). This scientifically vague definition makes difficult a precise characterization of asphaltenes, which composition and structure depends on the source and it is therefore a matter of discussion. In general, the chemical structure consists of an aromatic nucleus with several benzenic rings surrounded by alkyl chains and heteroatoms (1). However, it is difficult to estimate a precise molecular weight due to association among molecules (3).

The behavior of asphaltenes in solution has also

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attracted attention since it is related to precipitation phenomena that are undesirable during production and processing. To explain the mechanism of precipitation, several models have been proposed, some of them based on liquid-liquid or solid-liquid equilibria (4,5). A good deal of research follows the idea of the self-aggregation of asphaltenes in oil, in which micelles are stabilized by the adsorption of polar compounds (resins) on the interface (6-8). These micelles form coacervates that can precipitate (4). Several experimental techniques were used as a support for the existence of micelles, but results diverge concerning size and shape. These conflicts were addressed in a recent paper by Porte *et al.* (9). In fact, micellar aggregation of asphaltenes is again being questioned (10).

Asphaltenes are also held responsible of the emulsification of water in the crude oil (11), which is a subject of concern in the processing of crude oil. In view of their relevance for applications, the surface and interface properties of asphaltene solutions have been a subject of study (12-17).

Due to the complex nature of asphaltene mixtures, it is very important to increase the amount of experimental data that supports further developments in the field.

In this context, we present a report on the properties of bulk and dispersed Venezuelan asphaltenes using several experimental techniques.

2 Experimental

2.1 Materials

Boscán vacuum residue ($^{\circ}\text{API} = 1.1$) was supplied by

Fig. 1 Asphaltene Yield as a Function of the Solvent/feed Ratio (R).

PDVSA-INTEVEP. (Venezuela). Toluene (99.7%), n-heptane (99%) and double distilled water were used in the experiments.

2.2 Asphaltene Extraction

To 100 g of Boscan vacuum residue, n-heptane was added in a volumetric ratio 1:40. The mixture was agitated for 24 h at 25°C and then left to settle for additional 24 h. The precipitate was filtered under vacuum through porous glass, washed several times with n-heptane until the solvent became colorless, and then dried at 90°C.

The resins were separated from the asphaltenes by Soxhlet extraction using hot n-heptane until the solvent became colorless. The recovered asphaltenes were dried at 90°C, ground with a mortar and stored under nitrogen to prevent oxidation.

Samples contained no clay or other inorganic solids.

Defining the solvent/feed ratio (R) as the volume of heptane (cm^3) per unit weight (g) of vacuum residue used in the extraction procedure, it can be seen in **Fig. 1** that the asphaltene yield first increases with solvent/feed ratio (R) and then becomes constant at around $R \approx 10$, so that the maximum yield of the Boscan vacuum residue is about 30wt%.

The FTIR bands assignment for asphaltene samples (measured with a Shimadzu FTIR-8900 spectrometer equipped with a ZnSe internal reflection element) are summarized in **Table 1**. The spectra show common features of asphaltenes (18-20), namely, a peak around 3050 cm^{-1} corresponding to aromatic double bonds, and peaks around 2930 (very strong) and 2850 corresponding to CH_3 and CH_2 groups (aliphatic C-H stretching). A band at 3080 cm^{-1} also appears, probably related with the presence of amino groups.

Table 1 FTIR Bands of Asphaltenes.

Band ν (cm^{-1})	Structural features
3142-3063	N-H stretching
3063-3022	Aromatic C-H stretching
2990-2880	Aliphatic C-H stretching
1605	Carbonyl C=O stretching
1460	Aliphatic C-H bending
1029	S-O stretching
728	C-H rocking

X-ray elemental analysis gave the following composition (weight) for the asphaltenes: S = 5.91% ; Ni = 398.5 ppm; V = 2971.5 ppm

2.3 X-ray Scattering Measurements

Small Angle X-ray Scattering (SAXS) measurements were performed on a Rigaku Nanoviewer equipped with a CCD detector at an applied voltage and filament current of 40 kV and 20 mA, respectively. Ni-filtered Cu- K_{α} radiation ($\lambda = 1.541 \text{ \AA}$) was used.

Wide Angle X-ray Scattering (WAXS) measurements were carried out at Yokohama National University (Japan) using a SAXSess camera (Anton Paar, Austria), equipped with a focusing multilayer optics, a block collimator for a slit collimation, and a transparent beam stopper. The reported scattering vectors are calculated from $q = 4\pi\sin(2\theta)/\lambda$, where θ is the scattering angle.

2.4 Viscosity Measurements

Viscosities were measured with a temperature controlled RHEOMETRIC SCIENTIFIC SR-5000 using Couette geometry with 26 mm bob diameter and 28.5 mm cup diameter.

2.5 Differential Scanning Calorimetry

A differential scanning calorimeter (Seiko Instrument, DSC6200) equipped with an automatic sample changer was used. The samples (about 10 mg weight) were introduced in aluminum pans and then tightly sealed to avoid evaporation of any volatile compound by an electric sealer. DSC traces were recorded using a heating rate of $2.5^{\circ}\text{C}/\text{min}$.

2.6 Electrophoretic Measurements

Zeta -potential and particle diameters were measured with a COULTER DELSA 440 Doppler Electrophoretic Light Scattering Analyzer (Beckman & Coulter, USA) using quartz cells. The instrument uses laser light, four photodiodes, and four 256-channel autocorrelators to detect zeta potential differences by electrophoretic mobility measurement. For the measurements, 30 mg of asphaltenes were dispersed in 20 mL of distilled water and the pH was adjusted using either HCl or NaOH.

2.7 Interfacial Tension Measurements

Interfacial tension was measured by the du Nouy ring method with a FISHER SURFACE TENSIO-MAT model 21 instrument using Platinum-Iridium rings. The

ring was placed in the water phase prior to adding the organic phase and pulled through the interface. The precision is $\pm 0.1 \text{ mN/m}$.

2.8 Emulsion Stability Measurements

Emulsions were prepared by mixing components with a 6-blade (1.6 cm each) propeller mixer at 2000 rpm for 20 s. A cylindrical flask (diameter = 3.7 cm, height = 5.9 cm) was used as mixing container. The propeller was placed a height of 3.1 cm from the bottom of the flask. 30 mL samples were prepared. The weight fraction of aqueous phase was 0.3 for all samples.

Emulsion stability was determined by placing the samples in cylindrical tubes (diameter = 1 cm, height = 27.5 cm) and measuring the amount of separated (resolved) water as a function of time under the effect of gravity. Each experiment was repeated three times to check for reproducibility.

3 Results and Discussion

3.1 X-ray Diffraction Analysis

Figure 2 shows the SAXS patterns for bulk solid asphaltenes. There are no well-defined peaks, indicating the absence of long range order. The curves, however, show a non-monotonic variation with respect to the scattering angle, indicating some (low) degree of correlation between scattering points. At 25°C there is maximum around $2\theta = 1.7$ degrees ($q = 1.2 \text{ nm}^{-1}$), consistent with previous data on asphaltenes of different origin (21-23). This maximum can be attributed both to the

Fig. 2 SAXS Patterns of Bulk Solid Asphaltenes at Different Temperatures.

existence of supramolecular aggregates or clusters dispersed in an amorphous medium, or to some inhomogeneities in the electron density such as those caused by polar groups surrounded by an apolar background (10). In the case of asphaltenes, inhomogeneities are quite possible due to existence of aromatic nuclei surrounded by aliphatic chains, as well as other chemical groups. Defining roughly the average distance between scattering points as $d = 2\pi/q_{\max}$, where $q_{\max}$ is the value of the scattering vector at the peak maximum, the broad peak in **Fig. 2** would correspond to $d \approx 5$ nm. As temperature is increased, the correlation is lost and almost disappears at 150°C, indicating that aggregates have vanished due to the entropy contribution, although changes in the electronic density can not be ruled out.

When plotted against the scattering vector q (plot not shown), the scattered intensity in **Fig. 2** at $T = 25^\circ\text{C}$ tends to follow a scaling behavior $I(q) \propto q^{-d}$ in the low q range, with $d = 1.5$. d is sometimes related to the fractal dimension of clusters (24,25), which has been reported to be close to 2 (as it would correspond to sheets) for some asphaltene samples (26). The presence of asphaltene layered structures has also been reported in emulsion films (27).

The WAXS pattern for an asphaltene sample at 25°C is presented in **Fig. 3**. There is a broad peak with a maximum around $2\theta = 18$ degrees ($q = 12.8 \text{ nm}^{-1}$) and a shoulder around $2\theta = 25$ degrees ($q = 17.7 \text{ nm}^{-1}$), which are assigned to the so called γ and graphene bands, respectively. The γ band is associated aliphatic compound whereas the graphene band comes from the aromatic portion of the asphaltene (26). Interestingly, the features of this pattern are quite similar to those of lamellar liquid crystals of amphiphilic compounds bear-

Fig. 3 WAXS Pattern of Bulk Solid Asphaltenes at 25°C .

ing a polycyclic (cholesterol-type) moiety (28,29), which gives support to the assignment of one of the bands to benzenic rings in a fluid-like state. γ and graphene bands indicate the existence of correlation distances at sub-nanometer scale, i.e. between close molecules. Assuming a microstructure formed by aromatic sheets such as that depicted in **Fig. 4**, the distance between those sheets can be estimated as

$$d_m = \lambda / \sin(\theta_{\text{graphene}}) \quad (1)$$

where $\lambda = .154$ nm (wavelength of X-rays) and θ_{graphene} is the scattering angle at the maximum of the graphene band. From data of **Fig. 3**, d_m is estimated to be 3.6 nm, in agreement with previous reports on asphaltenes of different origins (26,30).

Although a slightly different equation has been proposed to calculate the distance between alkyl chains of asphaltene molecules (30,31), we have used Eq. 1 to obtain $d_\gamma = 5$ nm, a value similar to other reported data (26,30).

3.2 DSC Measurements

Results from DSC measurements are shown in **Fig. 5**. There is no clear base line within the experimental temperature range, probably attributed to the presence of a glassy transition at lower temperatures (32). Poor resolved DCS curves are characteristic of asphaltenic systems, due to the complex chemical nature of the samples, which might contain entrapped compounds in the liquid state (33). However, a broad endothermic peak centered at around 60°C can be identified. The position of the peak is similar to those previously reported for asphaltene samples by Masson *et al.* (32), who related the peak to the presence of an amorphous

Fig. 4 Schematics of the Arrangements of Asphaltene Molecules in the Sheet Model (adapted from Ref. 31).

Fig. 5 DSC Curve of Bulk Solid Asphaltenes.

mesophase, although this is not a conclusive result. The absence of a clear base line in **Fig. 5** prevented us to estimate the associated enthalpy, but it should be pointed out that the transition enthalpy of polyaromatic mesophases can be relatively high when compared to that of hydrocarbons in which the chains are in a liquid state (28,29).

The complexity of the thermal curve suggests the occurrence of several molecular processes, probably due to variations of the microstructure of asphaltenes, which are inhomogeneous systems and contain microdomains differing in structure and composition, as inferred from X-ray measurements. On the other hand, thermal effects may correspond to aggregation-dissociation of certain components of the asphaltene. The step-like variation of the baseline testifies for the occurrence of second-order transitions (34). However, calorimetric results alone cannot explain mechanisms of observed

Fig. 6 Viscosity as a Function of Asphaltene Concentration (C_A) in Toluene at $T=25^\circ\text{C}$.

phenomena.

3.3 Viscosity of Asphaltene Solutions

Figure 6 shows the variation of Newtonian viscosity (shear rates = $30\text{--}200\text{ s}^{-1}$) with asphaltene concentration in toluene. Below 8 wt%, the viscosity of the system is close to that of the solvent, indicating little influence of interparticle interactions (35). Back scattering DLS measurements (not shown) indicated that the correlation length of asphaltene aggregates remains almost constant around 30 nm up to 0.1%, within the same order of magnitude of the values reported for some asphaltenes of different source (36). The viscosity curve shows a break around 8 wt%, which contrasts with the monotonic increase found in polymers in the absence of phase transitions (25). The discontinuity probably indicates the formation of coacervates or larger aggregates that might flocculate resulting in a macroscopic precipitation (6,9,13,37).

3.4 Zeta Potential

Figure 7 presents the zeta potential of asphaltene samples as a function of pH. The zeta potential of asphaltene changes from positive to negative with increasing pH and becomes zero at the isoelectric point of the material. It is known that asphaltenes contain pH-dependent ionisable functional groups, acidic and basic, that can undergo dissociation and protonation (38,39). The negative surface charge on asphaltenes comes from the dissociation of acidic surface functional groups such as carboxylic (40), whereas a positive surface charge is induced by the protonation of basic nitrogen-containing functional groups such as amines (40). The pH value

Fig. 7 Variation of Zeta Potential with pH for Asphaltene Samples at $T=25^\circ\text{C}$. The Asphaltene Concentration is 1.5 g/L.

for the isoelectric point of asphaltenes is about 4, which is close to the pKa of carboxylic acids, and similar to that found for asphaltenes of different origin (38). The highly negative surface charge at high pH suggests that asphaltene dispersions would be stable under alkaline conditions.

3.5 Interfacial Tension

The interfacial tension (σ) between toluene solutions and water as a function of pH is shown in **Fig. 8**. σ is reduced by molecular adsorption at the interface, which is favored when the asphaltenes are charged. In fact, asphaltenes behave as amphoteric compounds (12). At very low pH, the nitrogen-containing (basic) groups in the asphaltene should be protonated, hence σ is slightly lower than in neutral conditions. Above pH=8, there is a sharp decrease in σ probably related to the dissociation of carboxylic groups of asphaltenes, which makes them more surface active. The interfacial tension is reduced up to 2 mN/m when pH=13, namely, the effect of acidic organic compounds on interfacial tension at high pH is stronger than the presence of basic organic compounds at neutral to low pH. The data of **Fig. 8** agrees with reports on coal tars (41), crude oils (42,43) and other asphaltenes (12,17). According to these results, emulsification of asphaltene-containing oils would be favored under alkaline conditions. In fact, at oil well conditions, saponification must be favored due to the high temperatures. We found (results not shown) that when asphaltenes are subjected to alkaline treatment at 90°C before the measurement (pre-saponification), lower σ values are obtained.

Fig. 8 Interfacial Tensions between a 0.5wt% Solution of Asphaltenes in Toluene and Water at Various pH (T=25°C).

Figure 9 shows the variation of σ with asphaltene concentration at pH=12 for different salt concentrations. σ decreases almost monotonically with asphaltene content, without any breaking point in the trend, hence there is no clear indication of aggregation processes (44,45). The slopes of the curves, proportional to the adsorption at the interface, are steeper than those reported at neutral conditions (45); namely, the adsorption increases with pH, due to the dissociation of carboxylic groups and the consequent increase of the polarity of asphaltene molecules (46). This is equivalent to a decrease in asphaltene solubility, which is known to increase the surface activity of asphaltene particles (27,45).

The effect of NaCl addition on σ could be relevant from the point of view of practical operations, since the water originally present in oil fields (which may come out together with crude oil) usually contains a considerable amount of salts. As can be seen in **Fig. 9**, NaCl addition results in lower σ values. Electrolytes tend to shield charges in amphiphilic compounds, producing a decrease in the surface area per molecule and facilitating the packing at the interface; this would cause an increase in adsorption, but there is no evident difference in the data trends (slopes) with or without electrolyte.

3.6 Emulsion Stability

The stability of asphaltene-containing water-in-toluene emulsions (as models of water-in-crude oil

Fig. 9 Interfacial Tensions between Solution of Asphaltenes in Toluene and Water (pH=11, T=25°C) at Different Concentrations of NaCl. No added NaCl (×); 30 g dm⁻³ (◆); 300 g dm⁻³ (■). C_A is the concentration of asphaltenes in toluene.

emulsions) were monitored as function of pH and asphaltene concentration. As shown in **Fig. 10**, emulsions are very stable at high pH, and a considerable amount of water remains dispersed in droplets one day after preparation. It has been reported (46) that asphaltene films become more rigid as pH increases.

Emulsion stability also increases with asphaltene concentration (see **Fig. 11**), in agreement with previous reports (47). The coalescence rate seems to be fast at the first 10 min, but then substantially decreases. This behavior is similar to that of **Fig. 10** and might indicate the presence of two different mechanisms of droplet coalescence.

Fig. 10 Stability Curves of Asphaltene-Containing Water-in-Toluene Emulsions at 25°C for Different Values of pH ($C_A = 10 \text{ g dm}^{-3}$). The total concentration of aqueous phase in the samples is 30 wt%.

Fig. 11 Stability Curves of Asphaltene-Containing Water-in-Toluene Emulsions at 25°C for Different Asphaltene Concentrations (C_A). Squares: 0.1 g dm^{-3} ; Triangles: 1 g dm^{-3} ; Circles: 10 g dm^{-3} . The total concentration of water in the samples is 30 wt% (pH = 12).

The effect of pH and asphaltene concentration on emulsion stability is more clearly seen in **Fig. 12(a)** and **(b)**, where the amount of resolved water after 1000 min has been taken as stability parameter. Interestingly, there is a maximum in resolved water (i.e. a stability minimum) as function of pH (12). The results of **Fig. 12(a)** correlates with those of interfacial tension (**Fig. 8**), namely, the lower the interfacial tension the higher the emulsion stability. As mentioned previously in the text, the ionization of asphaltene molecules at high pH decreases their solubility in toluene and hence promotes adsorption at the interface, which prevents droplet coalescence (48). A proposed mechanism (27) consists in the formation a layered structure, acting as repulsive barrier, inside the thin oil film between water droplets.

The increase in emulsion stability with increasing asphaltene concentration at constant pH observed in **Fig. 12(b)** can also be related to improved interfacial adsorption, as indicated by the σ curves in **Fig. 9**.

Fig. 12 Stability of Asphaltene-Containing Water-in-Toluene Emulsions at 25°C as a Function of (a) pH ($C_A = 10 \text{ g dm}^{-3}$) and (b) Asphaltene Concentration (pH=12). The total concentration of water in the samples is 30 wt%.

4 Conclusions

It has been found that asphaltenes are complex mixtures that show a tendency to form sheet-like structures with low degree of order at a nanometer scale. This tendency is also present in solution, and might be related to a flocculation-induced phase separation. The dispersion properties are highly influenced by the presence of acidic groups in the asphaltene molecules that undergo dissociation at high pH and promote interfacial adsorption. This behavior seems to be determinant in the stabilization of asphaltene-containing water-in-toluene model emulsions.

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