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Full Length Article

# The influence of the polarity of fractionated asphaltenes on their Langmuir-film properties

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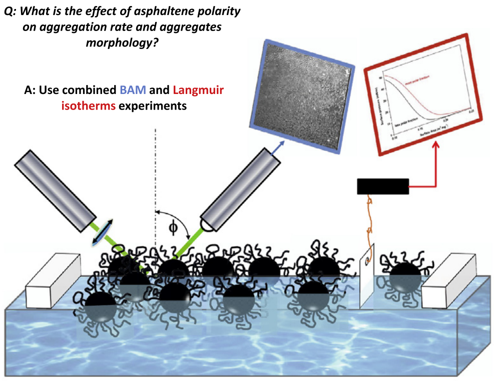
## GRAPHICAL ABSTRACT



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## ABSTRACT

The amphiphilic and aggregation properties of fractionated asphaltenes have been studied using Langmuir trough experiments and Brewster angle microscopy (BAM). In particular, two fractions from three different crude oils have been extracted by using two *n*-pentane:crude oil volume *ratios* (3:1 and 18:1) in a two-step precipitation procedure. The concentration dependence of the surface properties and the variations in their ability to form true monolayers at the air–water and liquid–liquid interfaces are investigated. The shape of the resulting isotherms are decidedly different. The greater amphiphilic character of the second fraction provides more expanded isotherms and well-behaved hysteresis cycles with more homogeneous domains in comparison with the first one. These results inferred from interface experiments corroborated previous experiments carried out with the pendant drop method. Finally, high contrast BAM images revealed a different aggregation state of the two fractions. The first fraction presents lower surface activity as derived from the air–liquid and liquid–liquid interface experiments and forms aggregates separated by empty spaces at low surfaces pressures according to BAM images. The second fraction show a more homogeneous film structure even at higher surface pressures.

## 1. Introduction

Asphaltenes are commonly defined in a solubility class scale as the *n*-heptane-insoluble, toluene-soluble fraction of crude oil or coal. Since a large number of molecules fit into this practical definition, the physicochemical characterization of this product has

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promoted an increasing number of experimental works appearing daily in the literature as a clear reflection of this complexity (see for instance the classical Refs. [1,2]). In this sense, although the experimental evidences collected through the years are smartly comprised in a functional prototype for the asphaltene "monomer" called the Yen-Mullins model [3], the heterogeneous results derived from the polydispersity of this fraction and supported on the pioneering work of Pfeiffer and Saal [4] have promoted a long-lived discussion on the nature, structure and composition of asphaltene molecules (see for instance Refs. [5–11]). From a chemical viewpoint, an island-like core of condensed polyaromatic rings sided by aliphatic chains that eventually contains heteroatoms (oxygen, nitrogen, and sulphur), hydrophilic moieties (–OH, –COOH, and NHO-groups) and associated metals (primarily nickel and vanadium) are hypothesized to be the skeletal molecular architecture of the paradigmatic component of this material [1–3,12–16]. In spite of some evidences that seem to confirm the molecular architecture of the asphaltene monomers that has been recently reported in Ref. [17], the debate is far from being closed. Particularly, given the practical importance of the asphaltene tendency to aggregate and stack that interferes in heat transfer, lubrication, transport and efficiency in the combustion of the fuel [18], the aggregation model proposed in the Yen-Mullins model in a polymer-like based idea can be reinterpreted from a micellar theory founded in the original work of Rogacheva et al. theoretically explained by Pacheco-Sánchez and Mansoori [19,20].

This aggregation together with the existence of amphiphilic groups control the surface activity and the formation of stable films at the air–water and liquid–liquid interfaces [15,21–36]. Moreover, along with resins and particles, asphaltenes are also commonly considered to be responsible of the stabilization of water-in-oil emulsions [15,37,38]. These emulsions are undesirable for a number of reasons, including pipeline and reservoir corrosion, additional cost of recovery and transport and a greater environmental damage in oil spillage on the sea. The balance between hydrophobic and hydrophilic interactions (i.e. the global polarity) and the consequent aggregation state are the intrinsic leading contributions to the surface properties of asphaltene films. In order to get a better understanding of asphaltene effect on emulsion stability, many investigations were carried out in the field of interfaces in the last years. For instance Leblanc and Thyrion [21] studied asphalts, asphaltenes and deasphalted oils at the air–water interface obtaining multilayers structures when these compounds were spread onto the water subphase. Mohammed et al. [22] deduced the formation of solid films in the asphaltene-water interface by studying the shape and properties of isotherms obtained by spreading a mixture of asphaltene with several resin proportions at the air–water interface. Moreover, using high resin *ratios*, isotherms with smaller collapse pressure were obtained. Ese et al. [23] studied the film forming properties of resins and asphaltenes from North Sea, European continent and Venezuela. They found that asphaltenes form less compressible and polar films than resins because of the higher intermolecular aggregation of the former during the compression process. This behavior is strongly influenced by the spreading solvent and the asphaltene bulk concentration. Zhang et al. [24,25] studied asphaltene Langmuir films at the air–water and toluene-water interfaces. They investigated fractions with high and low molecular weight at the air–water interface finding a very similar behaviour characterized by the close resemblance of their surface pressure-area, hysteresis and relaxation isotherms. At the liquid–liquid interface, they showed how the asphaltenes do not migrate from the monolayers toward toluene or water subphases. Subsequently, more experiments with the Langmuir trough were carried out by Díaz et al. [26], Cadena et al. [27], Vieira et al. [28], Orbulescu et al. [29] and Fan et al. [36] with very similar results about the behaviour of the asphaltenes at the air–water-interface. Lobato et al. [33,34] showed the importance of aggregation processes in the asphaltene behaviour at the air–water interface, concluding that the spreading concentration is a key aspect that must be controlled in surface studies. In particular, they proved that the nanoaggregate-to-cluster transition described in the Yen-Mullins model [3] can be observed at the interface when milligram per liter and gram per liter spreading concentrations are used respectively. These findings where well supported by *in situ* Brewster angle microscopy (BAM) images. Afterwards, Álvarez et al. [30,35] corroborated our BAM images [34] with similar conclusions about the asphaltene aggregation.

Finally, the effect of the polarity/aggregation on the interface behavior has been described by using the fractionation of asphaltenes. This procedure consists in the separation of asphaltene portions using different solvents or different solvent/crude oil volume *ratios* [1,39–42]. So, the chemical properties of the obtained fraction lead to different amphiphilic character as a consequence of the different polarity of the constituents. In this way, Fossen and coworkers [42,43] obtained two fractions by applying a two-step precipitation procedure with increasing *n*-pentane-to-crude oil *ratios*. They performed a combined experimental work in which interfacial tension measurements (IFT), small angle neutron scattering (SANS) and near infrared spectroscopy (NIR) are used to determine the interfacial activity and aggregation properties of the two fractions. They found that the fraction soluble in a low *n*-heptane/crude oil *ratio* exhibited a higher interfacial activity when compared to the first (insoluble) one. SANS experiments also demonstrated the formation of bigger aggregates in the first fraction, by comparing the radius of gyration in both cases. These results were further supported by nuclear magnetic resonance (NMR) and Fourier Transform Infrared spectroscopy (FTIR) indicating that the less *n*-pentane soluble fraction exhibits a larger and more polar aromatic core while the more soluble fraction posses more branched aliphatic side chains with a larger degree of hydroxylic and carboxylic groups. In this work we have used the same method than Fossen et al. [43] to obtain asphaltene fractions. Subsequently, the fractions have been investigated at different interfaces using methods as Langmuir through and Brewster Angle Microscopy. We demonstrate here that these two fractions with different surface activity and tendency to aggregate also exhibit different film forming properties that can be directly related to their *n*-pentane solubility. Hence, we provide evidences that the optical and mechanical techniques employed here (Langmuir isotherms and BAM) give insight into the importance of the aggregation state of the asphaltene in bulk solutions by observing a differentiated behavior in the surface activity of each fraction that is hardly conditioned by the chemical nature of the spreading solution [3,34]. It should be mentioned that we will refer to "aggregation" in the most general sense. Although the existence of spherical and symmetrical micelles at the air–water interface (without the existence of solvent) seems difficult to be conceived and the existence of nanoaggregates or anisotropic hemi-micelles is more likely, in the liquid–liquid experiments their presence cannot be discarded. Since our results are of mainly phenomenological character, they do not need of any specific molecular model for asphaltene to be properly discussed. The microscopic or mesoscopic descriptions of the asphaltene nature are far from our goals, and it is further to reopen the long-lived discussion regarding this matter. In fact, our techniques are not able to discern the intrinsic molecular structure of the asphaltene but provide interesting information for practical purposes.