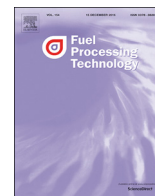




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Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Effect of solvents on the microstructure aggregation of a heavy crude oil

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ARTICLE INFO

Keywords:

Asphaltenes
Intrinsic viscosity
Huggins coefficient
Clusters
Rheology

ABSTRACT

We study the asphaltene microstructure in a heavy crude oil in response to the addition of solvents of different qualities by measuring the intrinsic viscosity and the Huggins coefficient. Dilution with good solvents (xylene and cyclohexanone) causes the native asphaltene clusters swelling, while that with poor solvents (a diesel oil and a C11-C14 alkanes mixture) may induce different microstructural rearrangements. The mixture of C11-C14 alkanes induces the aggregation of clusters, while the diesel oil their shrinkage. Moreover, if the diesel is added in small quantities instead of cluster shrinkage it may induce cluster aggregation thus forming larger “macro-clusters”. These structures survive after further dilution in both poor and good solvents and their formation is always accompanied by a reduction of the Huggins coefficient that implies the better solubility of these self-aggregated structures in the used solvent. Finally, an unusual negative Huggins coefficient is measured, when the macro-clusters are formed and the solution is diluted in a good solvent. This might be due to a prevalence of the intra-macro-cluster interactions on the inter-macro-cluster ones.

1. Introduction

Nowadays unconventional oils represent the vast majority of the world oil reserves and this justifies the increasing interest on their exploitation. Based on their density and viscosity, unconventional oils are divided in bitumen, extra-heavy crudes, and heavy crudes [1], the latter have an API gravity between 10° and 20°, the formers have API < 10° and viscosity at 15,6 °C smaller than 10⁴ cP, the extra heavy crudes, and larger than 10⁴ cP, the bitumen [2].

The crude oil is a mixture of several components, mostly hydrocarbons: Alkanes, cycloalkanes and aromatics, and other organic compounds containing heteroatoms like nitrogen, oxygen, sulfur and traces of metals. A traditional way to determine a crude oil composition is the SARA fractionation [3] that, on the basis of a different solubility in solvents of different polarities, separates the oil in four fractions: Saturates, Aromatics, Resins, and Asphaltenes. In heavy crudes the saturates usually amount to 5–20% in weight and are colorless or lightly colored liquids, aromatics are yellow to red colored liquid amounting to about 15–35%, resins form a black solid at room temperature and constitute about the 20–45% of the heavy crude, and asphaltenes form a black powder at room temperature, when eluted with short n-alkanes, and are largely responsible for the black color of the crudes. They typically amount to 5–20% of the whole heavy crude oil [4,5]. A crude oil is a “chemical continuum”, with a gradual increase of molar mass, aromatic content and polarity from saturates to asphaltenes, which

consequently makes the SARA fractionation problematic [6]. It is then often considered more convenient to group saturates, aromatics and resins into a single class. This class of components is called maltenes that can be indeed separated via solvent extraction typically with n-pentane or n-heptane from the crude oil. The fraction, insoluble in heptane or pentane, constitutes the asphaltenes, whose definition is then very similar to the classical one given by Boussingault [7]: Asphaltenes are operationally defined as the crude oil components soluble in toluene and insoluble in n-heptane. They are the heaviest and most polar fraction of the oil and are made of polycyclic aromatic hydrocarbon rings with peripheral alkane chains [8].

Asphaltenes are the main responsible for the high viscosity and the eventual non-Newtonian behavior of unconventional oils and thus for the difficulties encountered in heavy oil production, transportation and refining [9]. It is indeed well known that the non-Newtonian behavior of a fluid affects the flow through a porous medium [10–12], and that asphaltenes precipitation can cause well bore plugging and pipe clogging. In the literature, great attention has been paid on the structure and aggregation of asphaltenes. The most accepted model is the Yen-Mullins hierarchical structural model [13] where two colloidal structures are recognizable: The nanoaggregate and the cluster of asphaltenes (Fig. 1a). First the asphaltene molecules, constituted of about seven fused aromatic rings disposed according to the “island” architecture with peripheral alkane substituents, form the nanoaggregates where about six asphaltene molecules stack up in disordered piles

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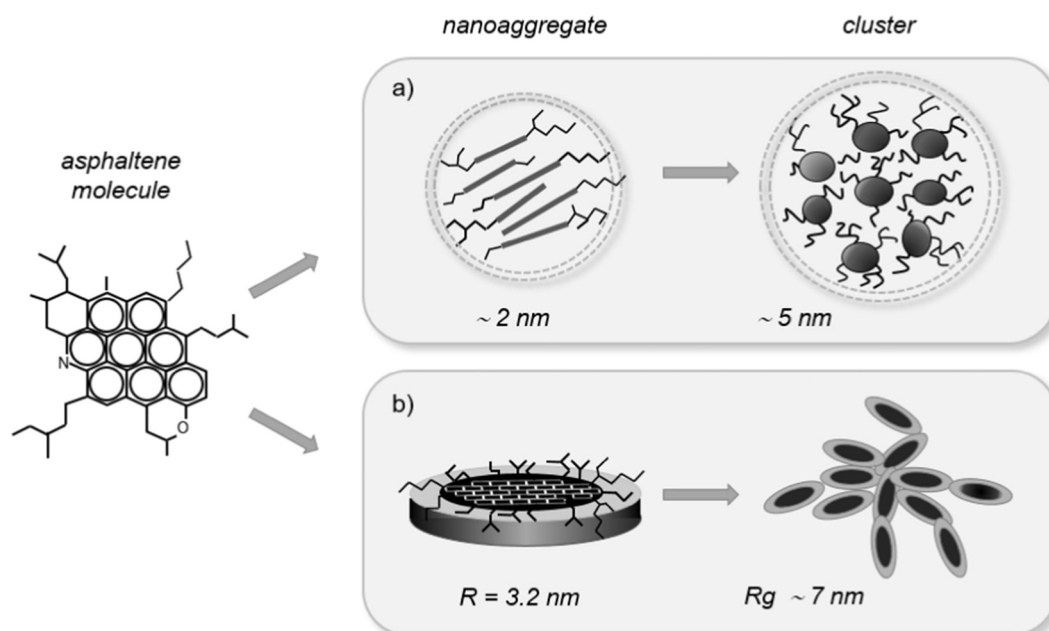


Fig. 1. a) Yen-Mullins hierarchical structural model; b) fractal structural model.

leaving to the exterior mostly the alkane substituents. Successively, increasing the asphaltene concentration, about eight nanoaggregates can form globular clusters that are not much bigger than the nanoaggregates themselves. This model can explain the vast majority of the experimental evidences, but appeared incompatible with small angle X-ray and neutron scattering data that brought to a new model that is, however, very consistent with Yen-Mullins one [14]. Two colloidal structures are also individuated: The nanoaggregates and the clusters (Fig. 1b). The formers have the asphaltenes geometrically organized so to have an aromatic core and an alkane shell, the latters are formed by nanoaggregates that are joined with a fractal structure with a small fractal exponent of about 2. There are various differences between the two models that, to the opinion of Mullins et al. [14], are secondary to the overall similarities. In the literature there are theories, the so-called lyophobic models, for which the asphaltenes colloidal structures, being essentially insoluble in the oil, are peptized by resins to form a stable colloid, and opposite theories, the lyophilic models, which postulate that asphaltene aggregates are solvated by the surrounding medium to form a stable phase [15].

The dynamics of asphaltene aggregation, under the action of different solvents, is a key factor in understanding and predicting asphaltenes precipitation and thus attracted a lot of interest in the literature, from a theoretical [16], numerical [17] and experimental [18] point of view. The vast majority of the papers is focused on the behavior of a synthetic oil where the asphaltenes extracted from a crude oil are re-dissolved in a model solvent, formed by a mixture of a good and a poor solvent, as toluene and heptane. The synthetic oil mimics the behavior of the maltenes with a solubility power tunable by changing the ratio toluene/heptane. This approach has the advantage of dealing with a simplified system where several parameters can be independently investigated so to have insights on fundamental, and hopefully, universal characteristics of the crude oils. However, it is well known that not only the asphaltenes extracted from different oils may be quite different, but also that their interactions with maltenes can be so specific that asphaltenes extracted from one oil might not be dissolved into the maltenes of a different one [19]. Moreover, e.g., Sanière et al. [20] showed that a heavy crude oil with its native colloidal microstructure (i.e. with well dispersed asphaltenes) exhibits a viscosity three times larger than that of the corresponding “reconstituted” crude oil obtained by re-mixing, after the fractionation, the asphaltenic and

the maltenic phase. The reconstituted oil showed a slurry morphology, with precipitated asphaltene aggregates suspended in the maltenes. However, the reconstituted slurry gradually evolved toward the original colloidal microstructure and the viscosity also increased reaching that of the original oil when the colloidal microstructure was not yet entirely reformed. This shows how tricky may be the investigation of the oil microstructure in a reconstituted oil and thus it highlights a possible warning on the applicability of the results coming from the investigation of a model oil to real crude ones [21]. Recently, efforts have been dedicated to study the asphaltene aggregation in crude oils and in live oils [22,23] paying some attention to the process reversibility [15,24].

The vast majority of the papers investigate the asphaltene aggregation with scattering techniques, while fewer papers are concerned with rheological measurements, which are known to be very effective to investigate the unperturbed material microstructure [25–27], and in particular effort has been paid to the derivation of a constitutive equation that relates the oil viscosity to the asphaltene concentration. Starting from the idea of a colloidal stable structure, the model of Pal and Rhodes [28] has been widely used assuming the flocculation factor to be unity, more recently, Pal and Vargas [29] modified the model to account for the possibility of a viscosity divergence in correspondence of a maximum packing of the asphaltenes nanoaggregates and derived a master curve based on Krieger-Dougherty equation [30,31] capable of describing several data of suspensions of asphaltenes in toluene. In 2015, Pal [32] derived a more general model valid for solution of asphaltenes in toluene and maltenes. Rheology was also used to investigate the asphaltene microstructure already in 1975 when Altgelt and Harle [33] studied the effect of the asphaltene concentration, molecular weight and solvent quality on the intrinsic viscosity of solutions of asphaltenes. They observed that the solvent quality plays a major role on the intrinsic viscosity only for asphaltenes (or clusters of asphaltenes) with high molecular weight, and they concluded that the poorer the solvent, the more pronounced the asphaltene aggregation. Rheological and scattering measurements were compared by Fenistein et al. [34] who studied solution of asphaltenes in mixture of heptane and toluene (heptol) showing that in toluene the asphaltenes possess an open structure that upon addition of a small amount of heptane becomes slightly denser and, as soon as heptane exceeds the 15% of the solvent, the structure grows, and the molecular weight increases, up to

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