



Historical perspective

# Thermodynamic modelling of asphaltene precipitation and related phenomena



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## ABSTRACT

Asphaltenes are considered to be the heaviest and most polar fractions of crude oils and are frequently implicated in problems encountered during production and refining as a result of phase separation. In recent years, considerable effort has been given to understanding the phase behaviour of these structurally heterogeneous materials from both experimental and computational perspectives. Various experimental studies have confirmed the long-advanced colloidal behaviour of asphaltenes in organic media, and this has inspired a number of modelling strategies. The present review is specifically concerned with advances in modelling asphaltene phase behaviour with emphasis on the use of the statistical associating fluid theory (SAFT), which it attempts to place into the wider context of thermodynamic treatments.

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## 1. Introduction

Asphaltenes have attracted much research curiosity for many years. Interest has ranged from their chemical characterisation in order to define their molecular structure, to understanding their solution and interfacial behaviour, including their aggregation and precipitation tendencies. However, even today, many of these aspects are still open questions where further research is needed. The main reasons for this stem from the limited or ambiguous knowledge concerning their characterisation.

Crude oils are complex mixtures of thousands of components [1], which are difficult to analyse and therefore characterise [2]. The vast amount of components existing in crude oil has led to comparison

with the amount of genes in the genome, giving rise to the use of the words “petroleome” and “petroleomics”. The difficulties in characterising the crude oil are also evident in the case of asphaltenes, the heaviest nondistillable fraction in crude oil, where the characteristics of this fraction will also depend on the source of the crude oil [3]. Generically, they are classified solely on their solubility properties, typically as the fraction of oil that is soluble in toluene and insoluble in n-heptane.

In the oil industry upstream and downstream operations could each benefit from a comprehensive understanding of asphaltene-related phenomena. Over the years, many studies have shown asphaltenes to be active at water-oil interfaces, resulting in the stabilization of oil/water emulsions, and solid-oil interfaces, causing modifications to rock wettability (refs. [4,5] and references therein). On the other hand, a number of problems also result from their flocculation and sedimentation caused by changes in solvency [6,7].

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The phase behaviour of reservoir fluids is intricate. Regions of up to four phases in equilibrium (solid-liquid-liquid-vapour) have been identified in asymmetric oil mixtures containing asphaltenes, resins and light hydrocarbons as constituents [8]. Asphaltenes and other petroleum fractions also exhibit complex path-dependent phase behaviour, which implies an added difficulty in the prediction of asphaltene precipitation. In particular precipitated asphaltenes have been observed to undergo a complex transition from solid to liquid in a temperature range of  $\sim(300\text{--}500)$  K [9–12] and additionally to present amphotropic [13] liquid-crystal domains [14].

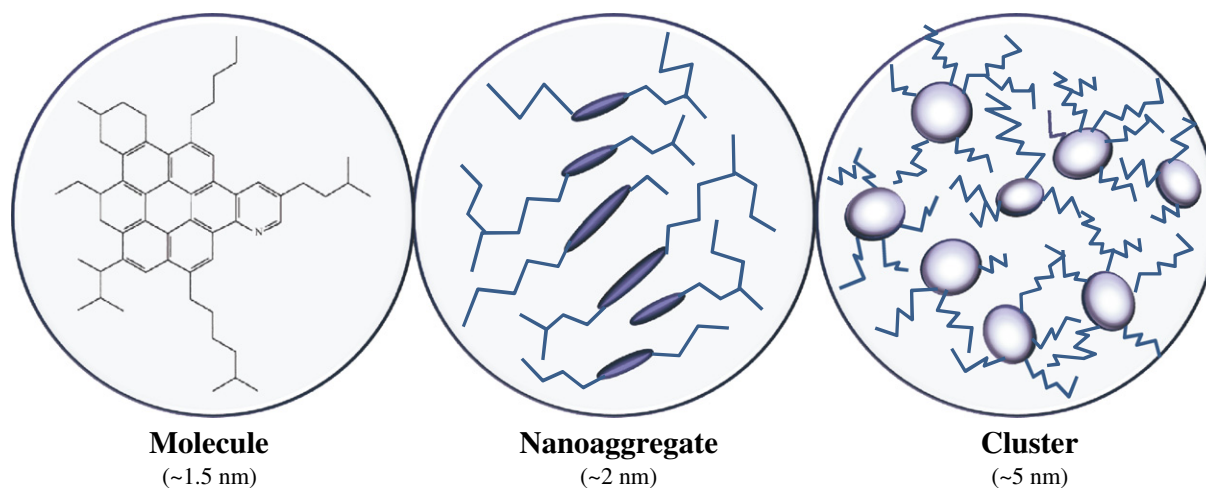
From a physicochemical viewpoint, asphaltenes have presented a very interesting research topic, not least because of their colloidal nature in crude oils [15–18] with the earliest theories based on interactions with structurally-similar resins. Asphaltenes are known to contain a high proportion of polycyclic aromatic groups and aliphatic chains. Two different molecular architectures have been proposed which are consistent with established atomic compositions and supported by a range of analytical techniques. The first is an “archipelago” structure wherein differentiated aromatic groups are linked together through alkyl bridges; the second is an “island” or “continental” structure wherein the core of the molecule is based on a single polycyclic aromatic hydrocarbon ring that contains peripheral alkane substituents. Different authors have suggested models with one or the other being predominant for different asphaltene samples (*e.g.*, refs. [19–25] favour the archipelago architecture and [26–31] favour the continental) or asphaltene fractions [32], notwithstanding that the reliability of some common experimental methods may be a matter of concern [33–35]. A predominant molecular structure for asphaltenes supporting the continental archetype has been identified in the Yen-Mullins model [36–38] (*cf.* Fig. 1); these structures can further assemble in the form of *nanoaggregates* at low concentrations ( $\sim 100\text{ mg L}^{-1}$ ) and *clusters* at higher concentration ( $\sim 3\text{ g L}^{-1}$ ). In the past, self-aggregation leading to the formation of aggregates has led to much disagreement regarding asphaltene molecular weights; over the years values have ranged from a few hundred to several million (see refs. [26,39–41] and references therein). In turn, from a modelling perspective this has led to different representations of the basic structural unit in the model (*i.e.*, ranging from molecular to aggregated).

However, the lack of a comprehensive understanding of the nature of asphaltenes as well as their interactions with other components of crude oil has motivated the development of a variety of different approaches to model their behaviour in solution and mechanisms

involved in their aggregation and subsequent precipitation. Central to the modelling discussions is the question of the intermolecular forces involving the asphaltenic constituents and other components in crude oil, which affect their solubility and aggregation properties. Perhaps one of the most systematic studies is that of Wiehe [42], who studied the dominant interactions in asphaltenic fractions through a solubility analysis in a wide range of solvents arranged on the basis of their “complexing” and “field force” solubility parameters. These parameters provide indications of whether directional (hydrogen-bonding or electrostatic) or nondirectional (van der Waals and other polar) interactions dominate their solubility. Those with high field force but low complexing solubility parameters were found to be the best solvents, supporting the idea that non-polar van der Waals interactions play a major role. The importance of van der Waals dispersion interactions in aggregates of asphaltenes and resins has also been supported by several other authors [43–45], although electrostatic interactions have been additionally suggested [44,46]. However, the contribution from hydrogen-bonding interactions should not be disregarded in the case of asphaltenes with a high proportion of polar functionality or heteroatom content, as these are likely to promote their propensity to stabilise water-oil emulsions [47].

Of particular interest from a modelling perspective is the nature of the instability responsible for the precipitation of asphaltene-rich phases for which both solid-liquid [48,49] and liquid-liquid [50] immiscibilities have been suggested, which has given rise to some disagreement in the approach to model these systems.

Furthermore, two different conceptual descriptions of the mechanism by which asphaltenes are considered as being stable in crude and residual oils have provided the basis for modelling asphaltene stability over the years. As alluded to earlier, the first supports the notion that the phase behaviour of these systems is governed by their colloidal nature, in which it was originally considered that asphaltenes are dispersed in the oil matrix in the form of aggregates that are stabilised by structurally similar resins which possess a slightly greater affinity for the bulk oil. In this case, asphaltene precipitation is assumed to be the result of a loss in the stabilising effects of the resin molecules. The resulting colloidal picture led Nellensteyn [51] to introduce the concept of a “micelle” for the first time by in petroleum science. Later, Pfeiffer and Saal [52] further developed the resin-stabilised asphaltene micelle model. Within this first perspective, most attention is paid to asphaltene-asphaltene and asphaltene-resin association based on  $\pi$ - $\pi$  stacking of the aromatic units. At that time, no specific details were



**Fig. 1.** Conceptual view of the modified Yen-Mullins model. The proposed molecular structure is seen in the left image. The polycyclic aromatic hydrocarbon of the molecules is represented by a flat oval in the middle image; these can form nanoaggregates with aggregation numbers of about six which contain a single aromatic disordered stack in the interior (*cf.* middle image). The latter can form clusters with aggregation number of about eight; this is represented in the right image, where the spheres depict the aromatic disordered stack in a nanoaggregate. The lines are the (mainly) alkane substituents. Adapted from ref. [36].

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