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Review article

Review on aggregation of asphaltene vis-a-vis spectroscopic studies

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ABSTRACT

Both petroleum and coal derived asphaltene finds important place on the present research areas of hydrocarbon based liquid and solid fuels. It has earned a name of 'unwanted' fame for its deleterious impacts arising mainly due to its self aggregational phenomenon. Over the period of time the asphaltene aggregation has been seriously investigated worldwide even at the molecular scale. Besides several methods, the spectroscopic findings (UV Vis and Fluorescence), in this regard, contribute to substantial meaningful data. The major spectroscopic researches on the aggregation of asphaltene over the last ten years have been reviewed in this present study. A brief discussion on the asphaltene molecular structure and molecular weight also comes as a prelude. Asphaltenes derived from both petroleum and coal have been considered.

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1. Introduction

The uninterrupted supply of crude oil has become pivotal for every country to sustain in today's modern times. Although presently there is a slump in the crude oil prices, this trend may be transient as it originates from non renewable sources. In fact, our country India is the third largest importer of crude oil. About 70% of India's electricity generation capacity is from fossil fuels, with coal accounting for 40% of India's total energy consumption followed by crude oil and natural gas at 28% and 6% respectively. India is largely dependent on fossil fuel imports to meet its energy demands — by 2030, India's dependence on energy imports is expected to exceed 53% of the country's total energy consumption. In view of the above it is imperative that we must strive for alternative sources of energy but on the top of it we must strengthen our research on fossil fuel. In this context asphaltene and asphaltene aggregation is a significant area to deal with. Asphaltenes are not limited to petroleum origins. Asphaltenes can be derived from any fossil fuel sources. These sources include the virgin component, all the intermediate leading to a finished commodity, and to the processed products. A few of the fossil fuel derived

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asphaltenes are as follows: virgin petroleum, refining bottoms, coal liquids, tar sands, bitumens, oil shale extracts, shale oils, coal extracts, and a great number of naturally-occurring asphaltoids, asphaltites, and asphalts [1].

Since, it is pretty clear that the world's reliance on crude oil will have to end sooner or later. In that case the wide variety of carbonaceous materials – including shale, coal, and bitumen – may be upgraded to produce so-called 'synfuels'. The synthetic fuels thus produced may in principle be processed using the same infrastructure that is already in place for crude oils [2]. The role of asphaltene and its unique properties such as self-aggregation requires special attention in order to explore the above manifest energy from the above mentioned sources. However in this review we will concentrate our discussion on the asphaltene that are derived from petroleum and coal.

Asphaltenes, typically considered as the non-volatile fraction of crude oils consist of many different molecules of different molecular weight and polarity having the same solubility properties in the oil or precipitation solvent [3,4]. It may contain some resins as well adsorbed on their surface [5]. Since, asphaltenes can be derived from any fossil fuel sources. Hence, asphaltene is broadly defined as solids soluble in aromatic solvents and insoluble in paraffinic solvents. This definition is actually quite useful and not arbitrary as it captures the most aromatic component of crude oil.

1.1. Asphaltene structure and molecular weight

The molecular architecture and PAH ring size remain subjects of debate. Both nanoaggregates and clusters are very small and are formed in solvent systems that provide only small contrast to the colloidal asphaltenes. Indeed, there appears to be no single methodology that provides complete and definitive characterization of these species. It is preferred to treat the many different studies in terms of a single framework, if applicable.

The molecular and colloidal structures of asphaltenes have been the subject of widespread investigation (Fig. 1) [6,7]. Early work gave birth to the structure of asphaltenes specifying corresponding types of chemical moieties, the "Yen model" [8]. However, major uncertainties about asphaltenes including asphaltene molecular weight, molecular architecture, aggregation species, aggregation numbers, concentration of formation – and very importantly – the relationship between laboratory species and those that prevail in crude oils, especially in the subsurface remained somewhat unresolved [6,7]. In recent years, there has been a substantial convergence of extensive studies that has enabled to propose much more specific model of asphaltene molecular and colloidal structure. This model shown in Fig. 1 has been referred as the modified Yen model [6,7] and at the same time the "Yen-Mullins model" (Fig. 1) [9–11].

The fundamental features of the Yen-Mullins model are illustrative in Fig. 1. First, the petroleum asphaltene molecular weights are ~750 amu, with most of the population being between 500 and 1000 amu. In the present scenario, the mass spectral methods [12–16] and the diffusion measurements [17–21], also yield equivalent results on this issue. With this the molecular weight issue is now more than resolved. The number of fused rings in asphaltene polycyclic aromatic hydrocarbons (PAHs) has been addressed by direct molecular imaging [22,23] and by optical absorption and emission analysis coupled with molecular orbital (MO) calculations [9,24,25], and Raman spectroscopy also obtained close results on asphaltene PAH size [26]. These studies indicated that the most probable number of fused rings is seven for petroleum asphaltenes. X-ray Raman studies show that the type of aromatic carbon which dominates asphaltenes is the more stable 'sextet' carbon, not the isolated double bond [27]. Chemical stability is not a surprising attribute of asphaltenes. However, NMR studies indicated substantially smaller PAHs dominated asphaltenes [28]; thus, uncertainty exists here and demands closer investigation. For the known asphaltene molecular weights only one PAH of seven rings can comfortably fit within this constraint, the so-called island architecture. The first studies that proposed the island architecture were the time resolved fluorescence depolarization (TRFD) studies [17,18,29,30].

Recently, by solution-state ^{1}H NMR relaxation measurements and 2D HSQC-NMR spectroscopy [31], the ^{1}H T_1 and T_2 relaxation behaviors of specific sites in petroleum asphaltene molecules have been studied, and it is shown that the relaxation behavior is in agreement with the hierarchical molecule-nanoaggregate-cluster model proposed by Mullins [6]. The NMR parameters obtained from the deconvolution analysis indicate an average of 6–7 pericondensed aromatic rings present in each molecule, in agreement with the island model. The average molecular weight was determined at ~720 g/mol, which would be typical for island model structures, hence lending strong support for the Yen–Mullins model. Further, Pomerantz et al. have examined the spectrometry-volatilization, ionization and the overall analysis mechanism of asphaltene in two forms of laser-based mass spectrometry: laser desorption laser ionization mass spectrometry (L^2MS) and surface-assisted laser desorption/ionization mass spectrometry (SALDI) [32]. These observations add credibility to conclusions from L^2MS and SALDI that petroleum asphaltenes typically have an average molecular weight in the range of 600–700 amu with an upper mass limit near 1500 Da, asphaltenes are dominated by the island geometry, asphaltenes form stable nanoaggregates containing approximately seven molecules, and

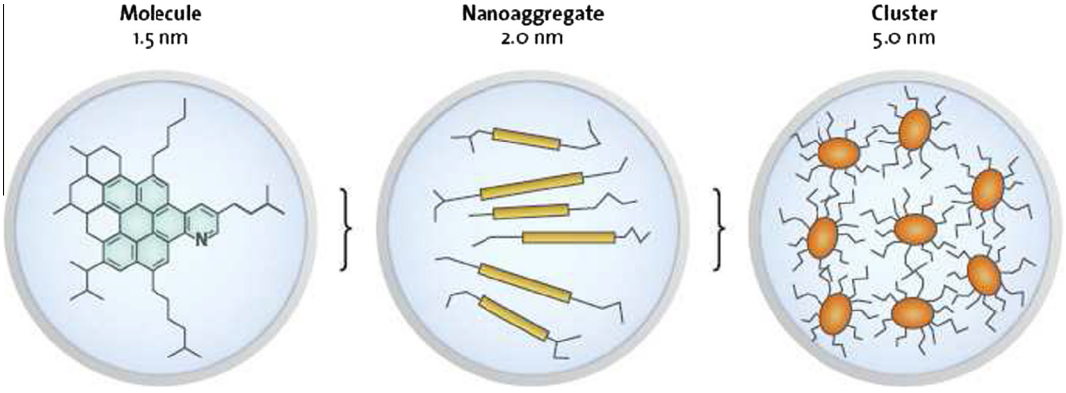

Fig. 1. The Yen-Mullins model [6,7,9–11]. This model shows the dominant molecular and colloidal structures for asphaltenes in laboratory solvents and in crude oils. The most probable asphaltene molecular weight is ~750 g/mole (Da.) and the "island" molecular architecture dominates with one aromatic ring system per molecule.