



Review article

Essential role of structure, architecture, and intermolecular interactions of asphaltene molecules on properties (self-association and surface activity)



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ABSTRACT

One of the important challenges of the oil industry is the formation of asphaltene deposits and emulsions, which cause many operational and economic problems. Asphaltenes are heavy and polar fractions of petroleum with a mixture of diverse molecules. Their structural complexity makes the understanding of their properties puzzling. The purpose of this review is to understand the self-association and surface activity properties of asphaltenes. There are some popular models for the mechanism of asphaltene aggregation; each alone is not complete and without defects. Experimental studies and molecular dynamics demonstrate that the mechanism of aggregation is influenced by asphaltene' structure, architecture, and intermolecular forces. Factors such as oil composition, temperature, and pressure affect its intensity. In this article, these issues and their impact on the self-assembly of asphaltenes and ways to prevent it, especially chemical inhibitors, have been discussed in detail.

1. Introduction

Because of the industrialization and globalization of the novel world, energy demand has been steadily increasing in the recent century. Statistics shows fossil fuels are still the primary energy for tens or hundreds of years to come. It reach about 80% of global consumption by 2040 (Briefing, 2013) so, investing in newer technologies to optimize the process of oil extraction, production and efficiency is very important (Haji Akbari Balou, 2014). The overproduction of conventional light crude oil, a significant reduction of these reserves has been observed, and many have drained (Hosseini-Dastgerdi et al., 2015; Rashid et al., 2019). Furthermore, despite effective oil recovery methods, refineries face increasing amounts of low-quality crude oil. To compensate for these shortcomings, it is planned to use heavier oils, extra heavy fields, offshore and other unconventional sources of crude oil (Speight, 2009). It is estimated that there are 2.1 trillion barrels of recoverable unconventional oil reserves worldwide (Jaffe et al., 2011). Deposits of organic solids such as wax, hydrate and asphaltene are one of the most problematic issues in the oil industry (Hoepfner, 2013).

The inherent properties of asphaltene, surface activity, and self-association have always troubled the oil industry. By changing the surface hydrophobicity, the initial wetting capability, and reducing oil permeability, the flow phase mobility decreases or, to an extent, increases the mass transfer resistance and prevents the moving phase of

hydrocarbons (Alshareef, 2019; Evdokimov, 2019; Rashid et al., 2019; Sjöblom et al., 2015; Stratiev et al., 2019; Tirjoo et al., 2019; Ungerer et al., 2014; Zheng et al., 2020). Results of this change in properties manifests in the form of emulsion and asphaltene deposits.

- Formation and strengthening of water/oil emulsion are problems in different stages of the oil production chain with the continuous production of oil from the reservoir, especially in the last stages of its life, unfortunately, water content rises, mainly if the reservoir operates by the aquifer. In addition, emulsification flow is a conquering state in pipeline. The perturbation, integration, and agitation through the downhole wellbore, surface hokes, valves, and pump sand pipes will produce emulsions. To improve the quality of oil, the water in oil emulsion must break (usually less than 0.5% by weight of water), which imposes high cost on the industry (Kokal, 2005; Lim et al., 2015; Lima et al., 2017; Wong et al., 2015).
- Asphaltenes can settle precipitate in reservoirs, wells, piping, and equipment that leave many technical and economic problems. Examples of these places: plugging of rock pores, altering congestion, arterial blockage, clogging within pipelines and wellbores, plugging surface facilities, transportation pipelines and settle in transportation tankers, adsorption onto refining equipment, distillation columns, foul heat exchangers (Akbarzadeh et al., 2007; Kraiwattanawong et al., 2009), catalysts deactivation, coke formation (Gonçalves et al.,

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2007), settlement and solidify pending in storage tanks, corrosion, and sinter of production instrument (Gharbi et al., 2017; Keshavarz et al., 2019; Santos Silva et al., 2019).

The precipitation of asphaltenes varies from country to country, area to area, from reservoir to reservoir and, this makes it tough to have a universally unique method for the prohibition and remediation however methods and several techniques were implemented:

1. Asphaltene deposits are cleaned with chemical, physical, mechanical, ultrasonic, thermal, bacterial technologies, etc.
2. Deposition of asphaltenes is prevented by manipulating oil production parameters, using asphaltene inhibitors and dispersants.

The comparison of these methods shows that the removal and cleaning methods of sediments are expensive and time-consuming processes, while sediment inhibition, stabilization of asphaltenes in oil and postponing precipitation are the best techniques to avoid these problems (Ghanavati et al., 2013; Toteva et al., 2020).

After stating the economic importance of crude oil and also the problems caused by properties of asphaltenes, First, weight, structure and architecture describ, then the models and mechanisms of how these properties occur.

2. Asphaltenes

The ancient Sumerians were the first people to use asphalt as an adhesive in the construction of statutes, walls, and buildings in 3000 BC (Abraham, 1920). French Chemist M. Boussingault performed the first bitumen distillation in 1837, and described the separated volatile liquid as "petrolene" and the solid fraction as "asphaltene" (Because of the visual similarity to asphalt) (Boussingault, 1836, 1837). Asphaltenes were introduced in the 1930s as colloidal particles and agents to increase oil viscosity. Asphaltenes are not limited to petroleum sources. Virginal petroleum, Tar sands, Refinery bottoms, Coal, Shale oils, Bitumen, Oil shale, and Coal extracts and Asphalts are named as derivative asphaltenes from fossil fuel.

Crude oil composition: The data set of chemical analyses of crude oils from different sources show that they contain 10^5 - 10^6 distinct chemical species in various amounts (Speight, 2006). These chemical compounds divide into two main classes pure and heteroatomic hydrocarbons. Pure hydrocarbons classify into two main subsets saturated alkanes and aromatics. For example: iso and n-alkanes, cycloalkanes and alkyl-cycloalkanes with rings of the 3 to 8 carbons, alkyl benzenes, alkyl phenanthrenes (Wiehe and Liang, 1996). Heteroatomic hydrocarbons also are classified into two main subsets. The amount of heteroatomic hydrocarbons is much less than pure hydrocarbons and they mainly form asphaltene and resin components. The vast majority of heteroatoms in these compounds include nitrogen, oxygen, and sulfur. A higher percentage of nitrogen is present in aromatic rings. Oxygen finds in aromatic rings, carboxylic acids, and cyclic terpenoids, and the most plentiful sulfur comprising compounds are mono and dibenzothiophene (Marshall and Rodgers, 2008).

Asphaltene definition: Researchers have used different descriptions of asphaltene in different texts in different periods. In fact, asphaltenes are a collection of heavy crude oil molecules and contain compounds with a wide range of molecular weight with the highest polarization and surface activity. Generally, asphaltenes are defined according to two classes: solubility class and molecular structure class.

Solubility class: This classification is that asphaltene is a portion of crude oil that does not dissolve in low carbon/light alkanes. The most famous and functional of these normal alkanes are pentane, hexane, or heptane, while the rest of the oil components are soluble in alkanes (Li and Greenfield, 2011; Speight, 2006).

The conventional and standard SARA method, separates the four main groups of oil based on increasing polarity. The physical appearance

of saturates, aromatics, and resins are liquid, and asphaltenes are dark-some brown or black solid. In the SARA method and analyzes in different countries (Ortega et al., 2015; Sonnenfeld and Canter, 2016; Wiehe, 2012), the length of light alkanes is variable and may be n-pentane or n-heptane (Speight, 2006). The results of molecular weight and chemical compounds extracted from one type of crude oil with two types of solvents are different according to SARA method. Asphaltenes are generally named after the n-alkane solvent applied for their precipitation, such as pentane or heptane asphaltenes (Soleymanzadeh et al., 2019).

The definition of asphaltene based on the solubility class is ambiguous. The most important point is the interaction of the solubility of asphaltene molecules with asphaltene-like molecules in alkanes and aromatics. For example, resin molecules that have a structural similarity to asphaltenes, such as chain lengths, instead of dissolving in alkanes, precipitate with asphaltene and are not considered resins and are considered asphaltene. Asphaltene molecules with small aromatic centers and long-chain lengths dissolve in light alkanes and asphaltene section of the oil reduces and be considered a non-asphaltene fraction (Ghosh et al., 2016; Santos Silva et al., 2019). pass -contamination in traditional SARA analysis has shown in Figure 1 (Bissada et al., 2016).

Molecular structure class: Asphaltines are the heaviest and most polar organic compounds in crude oil. They include Polycyclic aromatic hydrocarbon, alkyl chains, N, O, and S heteroatoms distributed in heterocycles and alkyl chains. Solubility-independent description can be a good guide for researchers who need to define asphaltenes in MD.

Elemental analysis of asphaltene: This shows that asphaltene molecules constructed of carbon, hydrogen, nitrogen, oxygen, and sulfur elements, which have different percentages according to the geographical area of the crude oil source. Elemental analysis has been reported from different oils, with Hydrogen to Carbon proportion (H/C) of 1.14 ± 0.45 % and small amounts of oxygen (0.32%–4.95%), sulfur (0.32%–10.31%) and nitrogen (0.61%–3.31%). Asphaltenes also comprise a few quantities of metals Nickel, Vanadium, and Iron (Ni,V,Fe) in ppm degree that make metal-organic frameworks porphyrin (Speight, 2006; YEN, 1998).

Every oil sample from a particular oilfield will produce a unique collection of asphaltenes. Diversity of asphaltene observe in reservoirs in a geographical area, and even at different times, extraction from a well will not be the same. For this reason, the crude oil sample of each region has a unique elemental analysis. For example, Iraqi crude oil sample lacks N in asphaltene elemental analysis compared to asphaltenes isolated from crude oil of Kuwait and Iran, while they are located in the same geographical area. For other examples, this difference in the oils of Canada and China is well observed to have similar Non-Metals and metals, but their contents change conformity to the origin of crude oil

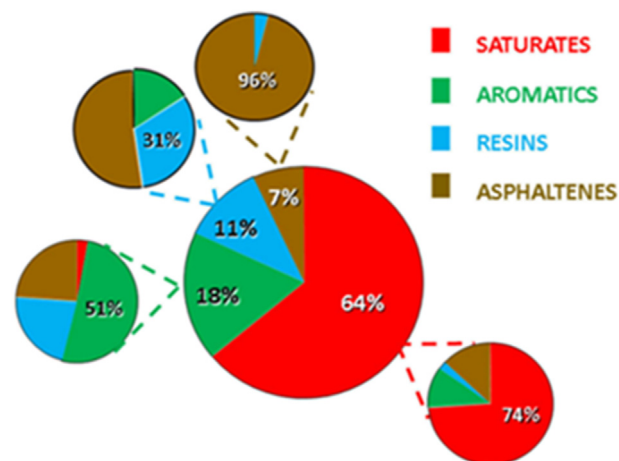


Figure 1. Pass -contamination in traditional SARA analysis (Bissada et al., 2016).

(Ancheyta et al., 2002; Chen et al., 2012; DeCanio et al., 1990; Gharbi et al., 2017; Ibrahim and Idem, 2004; Sato et al., 2005).

2.1. Molecular weight

Determining the weight of asphaltene molecules has been the topic and question of scientific controversy for nearly two centuries and remains a mystery. High molecular diversity and polydispersity of asphaltenes in different oils of the world and the lack of advanced analysis instruments are the reasons for this uncertainty. The results from variant laboratories are not comprehensive and general. Reports of weight results obtained from different laboratories with various techniques vary from several thousand to several hundred (Sjöblom et al., 2015). Some of the reported numbers are 40,000 to 700, 10000 to 7500, >6000, 3200 ± 400 , 800, 300–1400 atomic mass units (AMU) (Li and Greenfield, 2011; Soleymanzadeh et al., 2019). As well as the diversity of the source of oil, the self-aggregation phenomenon of asphaltene molecules is another reason for these different results and molecular weight ranges. Weight measuring devices are usually used at high concentrations of the sample, and at these concentrations, self-aggregation of asphaltene molecules occurs. phenomenon is observed even in much lower concentrations (≈ 10 – 100 mg/L) and suitable solvents such as benzene and toluene (Lundanes and Greibrokk, 1994). For example, Small-Angle X-ray and Neutron Scattering)SAXS and SANS (analysis were usually carried out at concentrations near to 10 g·L⁻¹ for asphaltenes soluble in design solvents (Sjöblom et al., 2015) or vapor-pressure osmometry (VPO) (Sheremata et al., 2004; Stratiev et al., 2019). When the Athabasca asphaltene models solve in ortho dichlorobenzene solvent at above 120 °C, it gives a weight of approximately 4000 g/mol (Stratiev et al., 2019). In the last two decades, techniques of time-resolved fluorescence depolarization (TRFD) (Groenzin and Mullins, 2007), fluorescence correlation spectroscopy (FCS) (Andrews et al., 2006), and laser desorption/ionization mass spectroscopy (L2MS) (Mullins et al., 2008) have helped to solve the problem of weight measurement and reliable results at higher concentrations (Sjöblom et al., 2015). Laser Desorption Mass Spectrometry (LD MS) demonstrates that asphaltenes have molecular weights from 200 to 800 g/mol (Miller et al., 1998). FD information of asphaltenes from the United States, France, and Kuwait outcomes average value for molecular weights of asphaltenes about 750 g/mol,

with a span from 450 to 1200 g/mol (Groenzin and Mullins, 2000; Pomerantz et al., 2009; Sheremata et al., 2004).

Furthermore, Pomerantz, et al. investigated asphaltene samples with L2MS and Surface-Assisted Laser Desorption/Ionization Mass Spectrometry (SALDI-MS) and reported 550 – 750 g/mol (Pomerantz et al., 2015).

2.2. Molecular structure

The chemical structure of asphaltenes has not been definitively determined, but a relative and average understanding of them has progressed through various experimental efforts and molecular models (Ungerer et al., 2014). For example, a few of them have shown in Figure 2 (Groenzin and Mullins, 2000; Headen et al., 2009; Murgich et al., 1996; Speight and Moschopedis, 1979; Ungerer et al., 2014; Zajac et al., 1994).

Polyaromatic units: The central part of the asphaltene molecules constituted of a conjugated carbon core (benzene rings) may also have hetero rings and naphthenic rings (Santos Silva et al., 2019). These molecules, the contribution of aromatic consists of about 40% of the whole molecules (Zajac et al., 1994). Definition of the quantity, size, and position of rings and how to connect them is a troublesome task (Groenzin and Mullins, 2000; Pacheco-Sánchez et al., 2004; Sheremata et al., 2004), to this time, many methods and different techniques have expanded to answer this question example, X-ray scattering (XRD) (Pollack and Yen, 1970; Yen and Chilingarian, 2000), optical absorption (Mullins et al., 1992), fluorescence emission spectroscopy, and fluorescence depolarization (FD) (Albuquerque et al., 2003; Mitra-Kirtley et al., 1996) have applied to determine the number of aromatic rings. Results show they are about 2 – 20 (Pollack and Yen, 1970; Yen and Chilingarian, 2000), and the average number is less than 10 . Ralston et al. investigated fluorescence emission. Their results have shown that the maximum absorption occurs at 450 nm for the asphaltene, with an emphasis on 4 to 10 aromatic rings in asphaltene structure (Mitra-Kirtley et al., 1996). With recent advances in scanning tunneling microscopy (STM), the average number of rings has been reported to be 6 to 7 (Zajac et al., 1994).

After the number, the size of these molecules is essential for researchers and measured by STM, HRTEM, Raman spectroscopy, X-ray

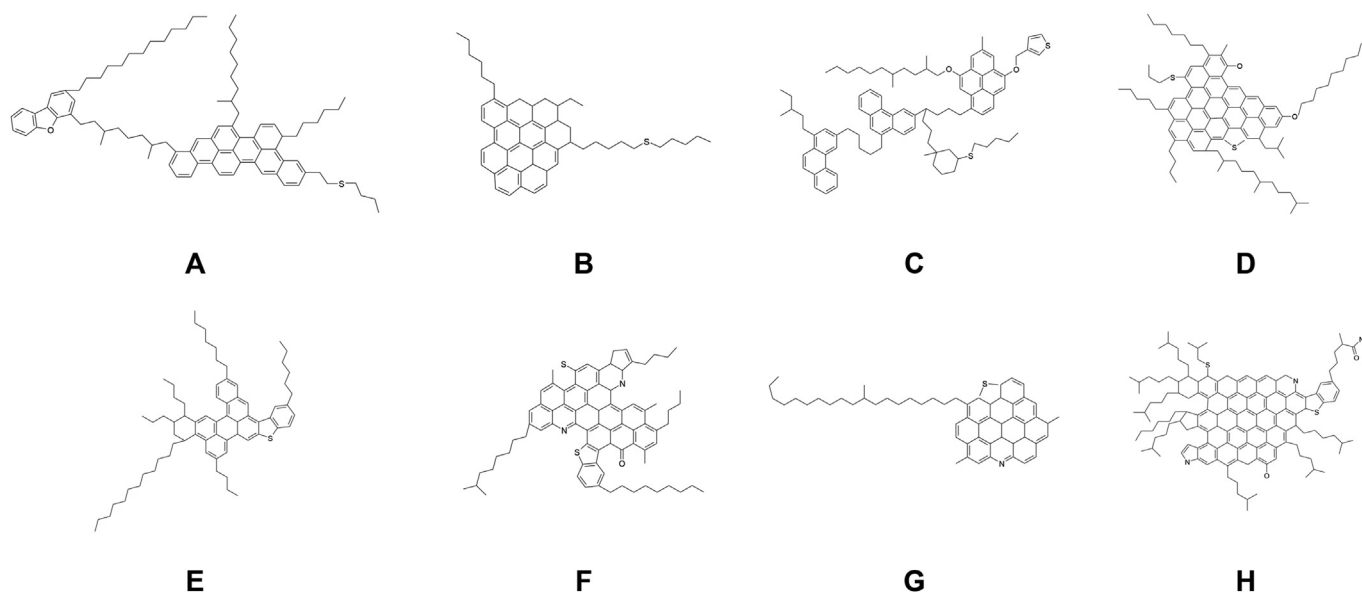


Figure 2. The molecular structures of asphaltenes. A, B Brought from Headen et al. (Headen et al., 2009), C, D for Ungerer et al. (Ungerer et al., 2014), E, F, G, and H are from respectively Groenzin and Mullins et al. (Groenzin and Mullins, 2000), Speight et al. (Speight and Moschopedis, 1979), Zajac et al. (Zajac et al., 1994), and Murgich et al. (Murgich et al., 1996).

Raman, NMR, FCS, and FD techniques. The results of scanning tunneling microscopy (STM) has been shown the molecular size of about 1nm for asphaltenes and corroborated by HRTEM (Sharma et al., 2002). Raman spectroscopy has similar results on asphaltene PAH (polycyclic aromatic hydrocarbons) size (Ruiz-Morales and Mullins, 2009). X-ray Raman results indicated that asphaltenes organize from “sextet” carbon atoms (Zetterberg and Öfverholm, 1999). NMR research disclosed that asphaltene has a considerably smaller PAH size and form of approximately 7–8 fused aromatic rings (Andrews et al., 2011; Djendara et al., 2021; Dutta Majumdar et al., 2013; Majumdar et al., 2017; Schneider et al., 2007). Size can determine by applying FCS and FD techniques. Their outcome demonstrates that the molecular diameter of asphaltenes is approximately 1–2nm (Andrews et al., 2006; Badre et al., 2006; Groenzin & Mullins, 2000, 2001; Guerra et al., 2007; Schneider et al., 2007).

In 2002, Ruiz-Morales did different and more outstanding work theoretically calculating the fluorescence emission for several asphaltenes and evaluated them with experimental results, acquired the most plausible aromatic core in asphaltene structure (Ruiz-Morales, 2002). In this method, the gap between the HOMO and LUMO was noticed as a measure of the size and structure of PAH and then generalized to asphaltene molecules, which is a polyaromatic hydrocarbon calculated value of the HOMO and LUMO distance depends very closely in number and spatial configuration of the fused aromatic rings, the percent of compactness, and the number and location of resonant sextets in the structure these studies show that there are five to ten rings in each core region in asphaltenes outcome lately emphasized by Schuler et al. (Ruiz-Morales, 2002). Shuler et al. investigated the structure of about 100 asphaltenes by combining atomic resolution imaging, AFM, and molecular orbital imaging with STM (Schuler and Meyer, 2015), wondering images and an envoy investigation of the composed of STM and AFM for asphaltene identity illustrated in Figure 3.

The exciting result of this study can be seen and learned about the electronic structure of CA1 in Figure 3f. This is acknowledged by the DFT calculation of the LUMO, applying the structure supposition from AFM, as seen in Figure 3f this exciting study, Schuler et al. made an outstanding contribution to determining the chemical structure of crude oil and coal asphaltene molecules. By direct imaging and physical evidence, they found that the petroleum asphaltenes are bigger than the coal asphaltenes.

Alkyl chains: The other fragment of asphaltene molecules is alkyl chains. They are variable in several long, medium, and short length of hydrocarbons, straight or branch, and attached around the core of molecules at different locations.

Heteroatoms: The third important part of asphaltene is the presence of nitrogen, oxygen, and sulfur elements and how they distribute in the core and alkyl chains of the molecules. Functional groups identified by

these three elements are N: Pyrrolic, Pyridine, Quinoline; O: Hydroxyl, Carbonyl, Carboxyl, and S: Thiophene, Sulfidic, Sulfoxide (Xin et al., 2016). Identification and details of these groups are mainly obtained using FT-ICR MS, NMR, and FTIR, which give information about the aromatic, alkyl, and functional groups fractions, although maybe FT-ICR-MS reveals only a part of the information present in the asphaltene sample (Acevedo et al., 2012; Bava et al., 2019; Goncharov et al., 2019; Liu et al., 2010; Ruiz-Morales, 2007; Schabron et al., 2012; Shi et al., 2010). Different weight percentages of polar heteroatoms have indicated using XPS and XANES groups act as donators or acceptors of protons in the form of intermolecularly and intramolecularly is definite that asphaltenes include both acid and essential parts since they have both total base and acid numbers (TBN and TAN) (Aksenov et al., 1979; Hosseinpour et al., 2013; Mitra-Kirtley et al., 1993; Peng et al., 2009; Rudraka et al., 2009; Simon et al., 2010; Speight, 2004; Zhao et al., 2001).

Metal porphyrins: In elemental analyses from different asphaltene samples have shown that metals such as vanadium, nickel, and iron with PPM concentration metals are often present in the structure of porphyrins as chelating metal structures. Some articles, the role of porphyrins in sediment formation is considered ineffective, and some are considered effective and problematic (Acevedo et al., 2012; Dechaine and Gray, 2010; Fan et al., 2020; McKenna et al., 2009; Zheng et al., 2020).

2.3. Molecular architecture

Another significant subject matter of asphaltene is the architecture (How chemical elements are connected to form different structures and chemical compounds). Essentially, asphaltene molecules are classified into two categories of island or archipelago architecture. Based on polycyclic aromatic cores, if asphaltene has one PAH core per structure's, it names an “Island” or “Continental”, and has a two or more PAH cores with hydrocarbon bridges, it is named an “Archipelago” (Santos Silva et al., 2019).

The first, the “Island” or “Continental” model, usually has a molecular weight in the limited area of ~400–1200 g per mole, with a medium of ~750 g per mole, including 6–7 fused aromatic rings by several functional groups in Figure 2 (B, D, E, F, G, H) and the second, the “Archipelago” has a diverse molecular weight above 1000 g/mol and more than one core which presented in Figure 2 (A, C) (Santos Silva et al., 2019). Many studies suggest the island and archipelago forms are a continuum of asphaltene and that the dominant structure (island or archipelago) depends upon the asphaltene sample (Chacón-Patiñ; o et al., 2017, 2018a).

Diverse techniques have extended to investigation of asphaltene architecture. Such as Fluorescence depolarization (Badre et al., 2006; Borton et al., 2010; Groenzin & Mullins, 2000, 2001; Groenzin et al.,

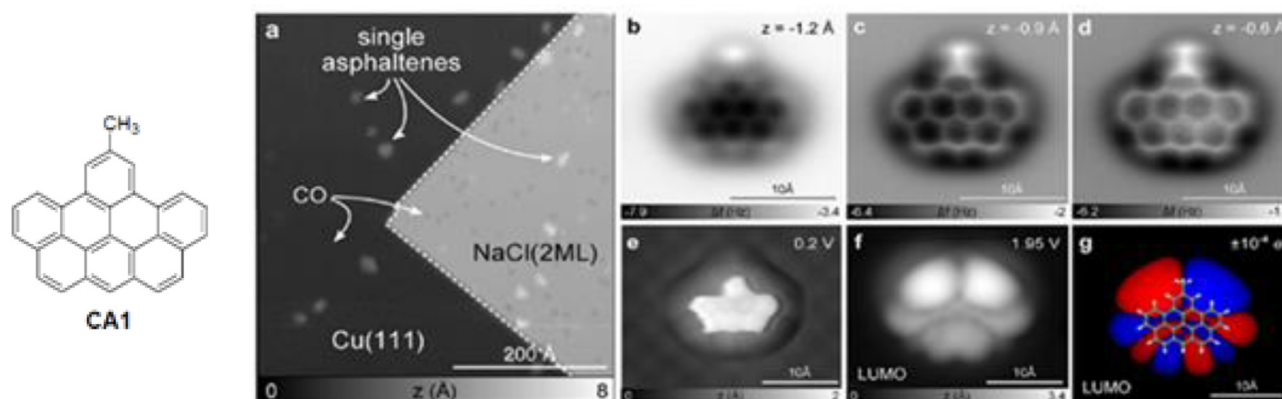


Figure 3. The composed of STM and AFM for coal asphaltene (CA1). (a) STM of CA1 (b–d) AFM of CA1 (e) STM of CA1 (f) STM at the NIR (g) LUMO orbital of CA1 (Ruiz-Morales, 2002).

2003; Sabbah et al., 2011; Wargadalam et al., 2002), Taylor Dispersion (TD) (Wargadalam et al., 2002), MO Calculations (Ruiz-Morales, 2007), Fluorescence Correlation Spectroscopy (FCS) (Andrews et al., 2006; Guerra et al., 2007; Schneider et al., 2007), pyrolysis (Karimi et al., 2011), RICO analyses (Zijun et al., 1997), Fluorescence spectroscopy (Wang et al., 2013), Thermal degradation, and SANS (Sheremata et al., 2004). L2MS and LIAD-MS have helped a lot in this way. Following, the results, different asphaltene compounds show different behaviors against thermal decomposition, so island compounds tend to lose little mass, and archipelago compounds tend to lose large mass.) Heat may break bonds in different parts of the molecule (resistance of various island compounds to fragmentation illustrates the predominance of island versus instability of archipelago compounds (Borton et al., 2010; Sabbah et al., 2011).

2.4. Quantitative molecular representations

The complexity and diversity of asphaltene molecules pose a significant challenge in examining any of their properties (Acevedo et al., 2007; Chacón-Patiñ; o et al., 2017; 2018a; 2018b; Zhang et al., 2014). Quantitative molecular representations incorporate information from different analytical techniques such as MS, NMR, VPO, and elemental analysis to produce a general picture of crude oil (Al Halwachi et al., 2012; Boek et al., 2009). For Example, aromaticity, and degree of substitution from ^1H , ^{13}C NMR dates are the critical information that has facilitated Quantitative molecular representations. Sheremata et al., In 2004 (Sheremata et al., 2004) and Boek et al., in 2009 constructed asphaltene models using the QMR and then widely admitted and used in the literature method has some steps that make it a bit difficult. First stage of this method, by Monte Carlo simulations and using the most common aliphatic groups, aromatic rings, and ordinary hetero atoms, creates asphaltene molecules, and candidate asphaltene molecules must have the best and most adjustment with laboratory results. Number of molecules required in each of these representations ranges from 12 to 10000. The most common use of QMR in MD which can display along with these representations to investigate how asphaltene correlate and interact with solvents (Liu et al., 2015; Sedghi et al., 2013).

QMR has two significant problems. It needs rich library information of fragments to construct the more remarkable structures; consequently, the accuracy of the obtained structures is in query. Collection of molecules that are compatible with the empirical data is usually unmatched, so a large number of structures are acquired, and a level of arbitrariness present when determining which one of these is the most representative of the asphaltene fraction.

3. Asphaltenes properties

3.1. Self-association

The self-association of asphaltene is inherent and is related to their special structure. Asphaltene molecules have been proposed to aggregate in different steps such as destabilization, Nano aggregation, cluster forming, flocculation, and precipitation in the oil. As a result nanometric stable particles of asphaltene become larger and transfer to unstable particles in micron size (Chaisoontornytin et al., 2016, 2018; Tirjoo et al., 2019; Vilas Bôas Fávero et al., 2016).

3.1.1. Aggregation models

Investigations about the self-association mechanism of asphaltene have resulted in several models that even contradict each other (Toteva et al., 2020). The first time, in 1924, Nellensteyn offered his viewpoint about this mechanism; after that, his opinion was expanded by Pfeiffer and Saal in 1940 (Pfeiffer and Saal, 1940). Primitive investigations of aggregate construction were significant progress in many types of research on the mechanism of aggregation for decades (Priyanto et al., 2001; Zhang et al., 2020). The following presents the most popular

theories and models of asphaltene aggregation. Forces of intermolecular and asphaltene architectures are the significant agents of aggregation.

The Colloidal/micelle model. To this model, asphaltene tend to self-aggregate due to their polarity and consequent hydrophilic and hydrophobic interactions between them and other crude oil compounds and have been observed in various forms of micelles such as discs, spheres, and cylinders (Pfeiffer and Saal, 1940; Priyanto et al., 2001; Zhang et al., 2020). Results show that micellization occurs while the concentration of asphaltene oversteps a famous border as critical micelle concentration (CMC) in solvents. In Figure 4 (A and B) how micellization and the formation of the macro-aggregates is shown (Priyanto et al., 2001).

In this model, the growth of micelle restricts by the repulse forces among polar groups. The colloidal/micelle model cannot precisely illustrate the asphaltene aggregation, and a perfect association model is needed.

The steric-colloidal model. This model presents that asphaltene disperse in oil with the surface coating of resin molecules. Adsorbed resin excludes the formation of bigger particles. The power of this deterrent is relevant to interactions between the parts of asphaltene and resins (aromatic and saturated fractions) (Barre et al., 1997; Gafonova and Yarranton, 2001; Priyanto et al., 2001; Spiecker et al., 2003). Figure 5 displays the molecules of asphaltene that make steric-colloidal aggregates in the presence of additional quantities of resins.

Some researchers have collapsed the significant impress of resin in the stability of asphaltene molecules because studies have shown nano-aggregates in aromatic solvents without resins due to weak asphaltene resin interaction (Indo et al., 2009; Zeng et al., 2009), and they can not be able to stabilize them. For these reasons, the steric-colloidal mechanism is confronted with constraints to clarify the aggregation of asphaltene (Zhao et al., 2009).

The Polymeric model. This model is described based on the similarity mechanism of asphaltene aggregation with the polymerization process (Merino-Garcia and Andersen, 2003; Merino-Garcia et al., 2004). To this mechanism, asphaltene assume to have the molecular structure of polymers, and some active sites, such as functional groups and aromatic rings. Asphaltene molecules accumulate through the interaction of these active sites. Asphaltene and resin molecules behave as propagators and terminators in a polymerization-like association interaction. Indeed, Resins frustrate the polymerization by connecting to the interchanging asphaltene molecules. To Agrawala and Yarranton's experimental results, the solvent type and temperature play an essential role in the number and strength of the active sites in polymerization (Agrawal et al., 2012). The schematic of this model shows in Figure 6.

The fractal model. The proposal for this model derives from the analysis of SAXS and SANS information (Duran et al., 2018; Simon et al., 2009). Mechanism was developed based on many studies of asphaltene aggregates applying these methods and discovered that asphaltene in crude oil and heptane creates fractal-like agglomeration. This model, the relation between the aggregate's weight, M , and their radius, R , obeys Eq. (1):

$$M = A \cdot R^{D_f} \quad (1)$$

D_f is the fractal dimension of asphaltene aggregates that expresses the density of the aggregates (as an example, $D_f = 1$: expanded, $D_f = 3$: compressed). Average D_f acquired for asphaltene aggregates can differ from 1.45 to 3.1 (Eyssautier et al., 2012; Headen et al., 2009; Rahmani et al., 2005). Hafner et al. investigated the self-association phenomenon of asphaltene with displaying of SAXS and SANS, and their results led to asphaltene being present in crude oil in different fractions of soluble and insoluble aggregates and as a fractal structure (Hoepfner et al., 2013). Figure 7 shows the instability of asphalt from soluble to insoluble with changes in fractal dimension.

The Yen model. Yen et al. carried out an XRD analysis for the asphaltene of Kuwait visbreaker tar oil (Dickie and Yen, 1967). To these results, asphaltene self-association occurs due to π - π interactions between



Figure 4. A) Asphaltene micellization in polar aromatic solvents. B) Asphaltene aggregation from micelles (Priyanto et al., 2001).

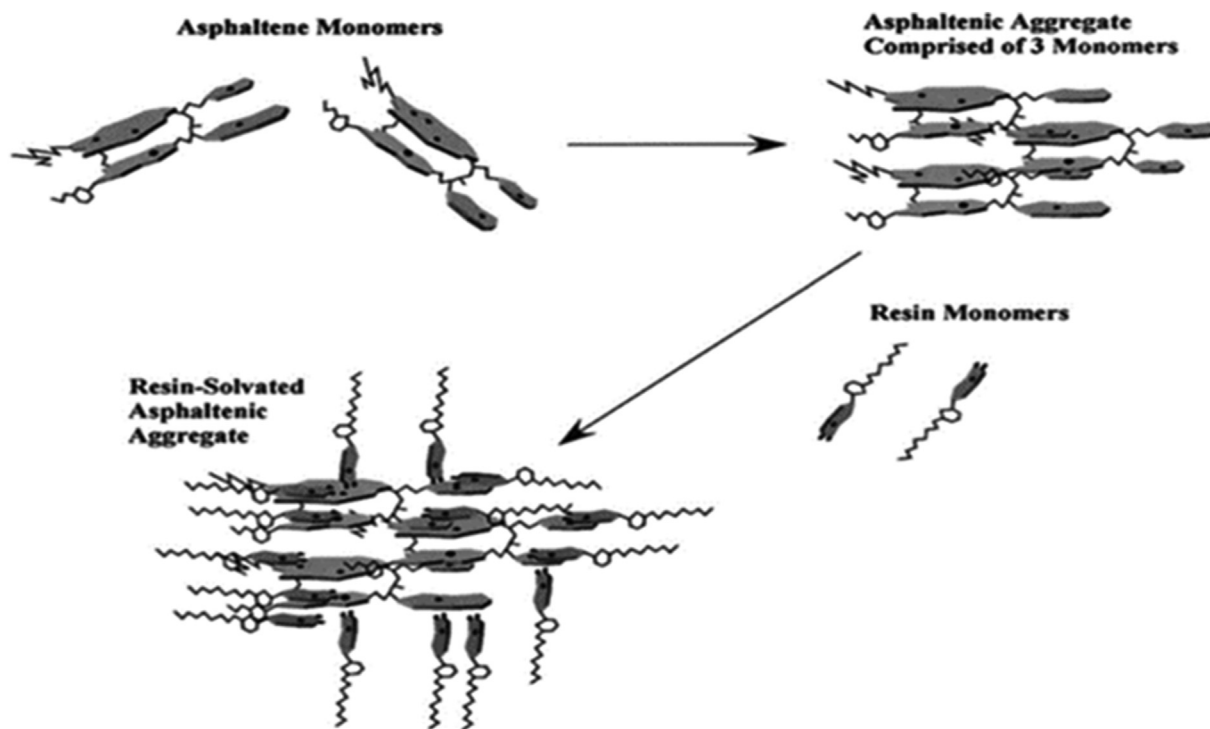


Figure 5. Colloidal aggregation of the archipelago model of asphaltene in the attendance of resins (Spiecker et al., 2003).

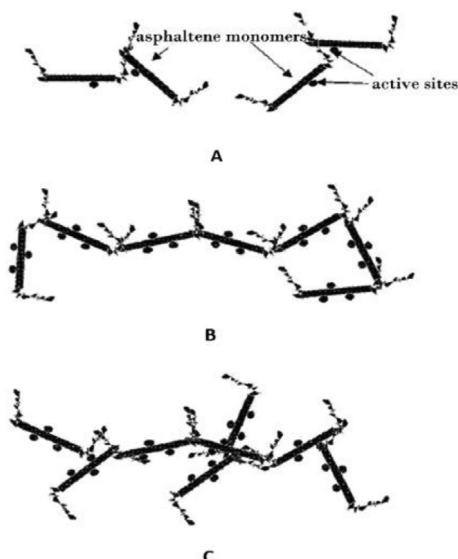


Figure 6. Asphaltene aggregation in the Polymeric model. A) High temperatures, suitable solvent, B) low temperatures and poor solvents (Linear aggregation), C) low temperatures, poor solvents (random, branched aggregation) (Agrawal et al., 2012).

the layers of the molecular sheet and stack on each other (Diamond, 1957; Evdokimov et al., 2003a,b; Pacheco-Sánchez et al., 2004; Wiehe and Liang, 1996). A comprehensive summary of the points made by Yen

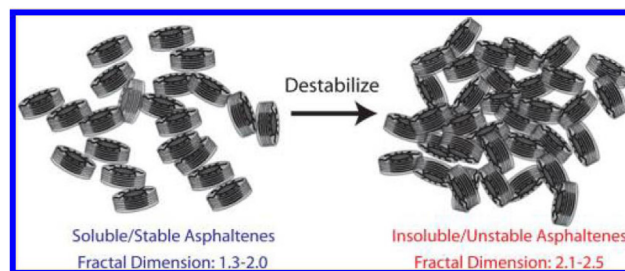


Figure 7. The fractal mechanism of asphaltene (Hoepfner et al., 2013).

et al. are the following: i) 3 to 6 molecules of asphaltene stacked in sheets ii) The distance between the first and last layers of asphaltene molecules is 3.5–3.8 Å iii) Short-range bonding between two molecules in stacked layers are 0.5–20 Å iv) The minimum energy is in the range of 14–20 kcal/mol. The Sum of these conclusions leads us to the fact that asphaltene aggregates are stable. Figure 8 schematically shows the Yen model.

The Yen–Mullins or The Modified Yen model. With more precise analysis techniques Mullin improved the Yen model and expressed the hierarchical continuation of the asphaltene aggregation process model is named the Yen–Mullins or the Modified Yen model (Mullins et al., 2012). Molecules interact with the aromatic cores through van der Waals π – π interactions, that form stacks of less than ten, and an average of 4–9 stacking have been shown in both the island and archipelago structural models, although island stacks are predominant (Dutta Majumdar et al., 2013; Ghosh et al., 2016; Headen et al., 2009; Schuler et al., 2017; Ungerer et al., 2014). The other hand, the alkyl side chains attached to

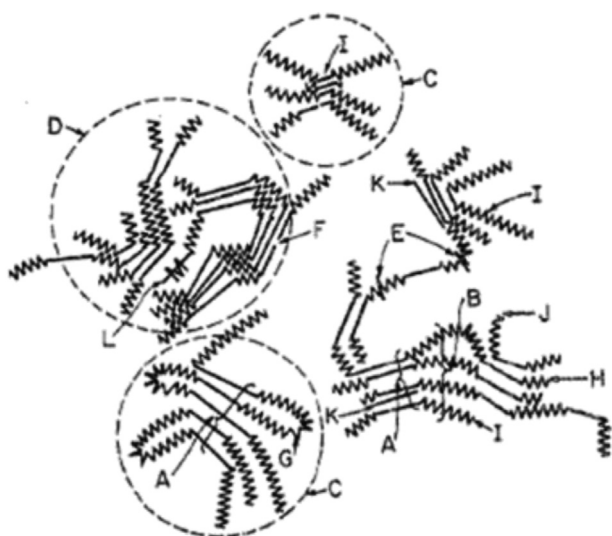


Figure 8. The Yen model of asphaltenes. Straight lines illustrate PAH core, and zigzag lines show alkyl chain with: A. Crystallite, B. Chain bundle, C. Particle, D. Micelle, E. Weak link, F. Gap and hole, G. Intracuster, H. Intracuster, I. Resin, J. Single layer, K. Porphyrin, L. Metal (Dickie and Yen, 1967).

these aromatic cores reduce $\pi-\pi$ interactions by creating a repulsive force with other adjacent alkyl chains. Due to the interactions between the particles of nano-aggregates, micro-aggregate particles form, which are called clusters. It has been observed that the interaction forces for the formation of micro-aggregates are far less than the formation of asphaltene nanoaggregates (Pomerantz et al., 2015). Figure 9 shows this model (Mullins et al., 2012).

The Gray model. Following the proposal of valid scientific models to describe the self-association of asphaltene molecules, Gray et al. (2011) ratiocinate the Yen–Mullins model, which has recently become almost universally accepted, by asking a few essential points and questions based on experimental observations. Example, 1. Ignoring or underestimating functional groups in the complex structure of asphaltene molecules such as porphyrins, nitrogenous and oxygenated compounds. 2. Uncertainty of the vast heterogeneous distribution of asphaltene nano-aggregates size. 3. Uncertainty about the presence of other molecules or nano-aggregates trapped in asphaltene nano-aggregates 4. The cause of porosity of asphaltene nano-aggregates 5. Lack of explanation for the formation of asphaltene film between water and oil interfaces or the surface activity property of asphaltene molecules. 6. Elastic properties of asphaltene nano-aggregates.

For this reason, they proposed a supermolecular model to understand better the self-association behavior of asphaltenes, which includes the above points. In this model, $\pi-\pi$ interactions, which is the predominant force of aggregation in Yen–Mullins model, are considered as a weak and

auxiliary force, and instead, taking into account polar, coulomb-driven interactions as the cumulative effects of some weak physical and chemical interactions (hydrogen bonding, acid/base and metal–organic interactions) in a three-dimensional, porous network are considered as the dominant forces. The practical consequence of this model is to explain the wide range of size distributions of asphaltene nano-aggregates because such molecular interactions cause the diverse growth of nano-aggregates and eliminates the growth and size limit of nano-aggregates. Figure 10 shows the hydrogen, acid/base, and metal–organic bonding networks.

Researchers have conducted numerous laboratory studies to refute or confirm the proposed cumulative models of asphaltene. Many of them have confirmed the colloidal and Yen–Mullins models and vice versa. Some have provided evidence based on the supermolecular Gray model (Schulze et al., 2015; Subramanian et al., 2017; Varadaraj and Brons, 2012). For example, the work of Dutta Majumdar et al. (2017) Proves the aggregation of asphaltene molecules by $\pi-\pi$ interactions in a hierarchical manner, and many experiments and simulations of molecular dynamics prove that acid-base and other polar groups interactions are also involved in aggregation (Headen et al., 2009). Scientists also studied the role of solvents and their penetration into asphaltene nano-aggregates by molecular simulation, which of course shows significant changes depending on the type of solvent, density and number of molecules that make up the nano aggregates (Santos Silva et al., 2019; Toteva et al., 2020).

3.1.2. Aggregation mechanism

Regardless of the model considered, some influential factors such as structure, architecture, diversity of asphaltene molecules, concentration, peripheral chemical composition, pressure, and temperature are responsible for the understanding and intensity of the asphaltenes aggregation mechanism. Among them, structure and, consequently intermolecular forces between asphaltenes molecules in crude oil play a key role in aggregation phenomena. “Structure gives orders to assignment” is an essential principle in materials science that uses macromolecular structural information and nanomaterials to understand their function (Kim et al., 1998; Klebe, 2000; Teklebrhan et al., 2012).

The distribution of electronic charges in the molecule creates the intermolecular forces and, as a result, a different function. General, the most important interactions between molecules divide into four categories: charge transfer, electrostatic, the Van der Waals, and exchange–repulsion interactions (Israelachvili, 2011; Stone, 1996). Essential and determinative intermolecular forces imputed to the aggregation of asphaltenes are 1. $\pi-\pi$ interaction of aromatic cores (the Van der Waals interaction), 2. Steric hindrance between side chains (exchange–repulsion interaction), 3. Electron transfer between functional groups in molecules (charge transfer interaction), Brønsted acid–base interactions, metal coordination complexes 4. Attractive or repulsive interaction between atoms having electric charges (electrostatic interaction/the Van der Waals interactions), hydrogen bonding, etc. Following, the role of each part of the chemical structure and,

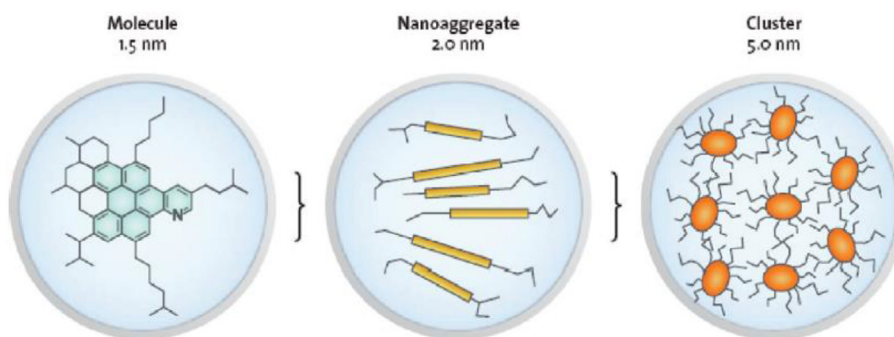


Figure 9. Yen–Mullins model. In this model, at low concentrations, asphaltene molecules form nanoaggregates in the form of a disordered stack of aromatics (<10 numbers). At higher concentrations, nanoaggregates accumulate to form nanoclusters (<10 numbers) (Mullins et al., 2012).

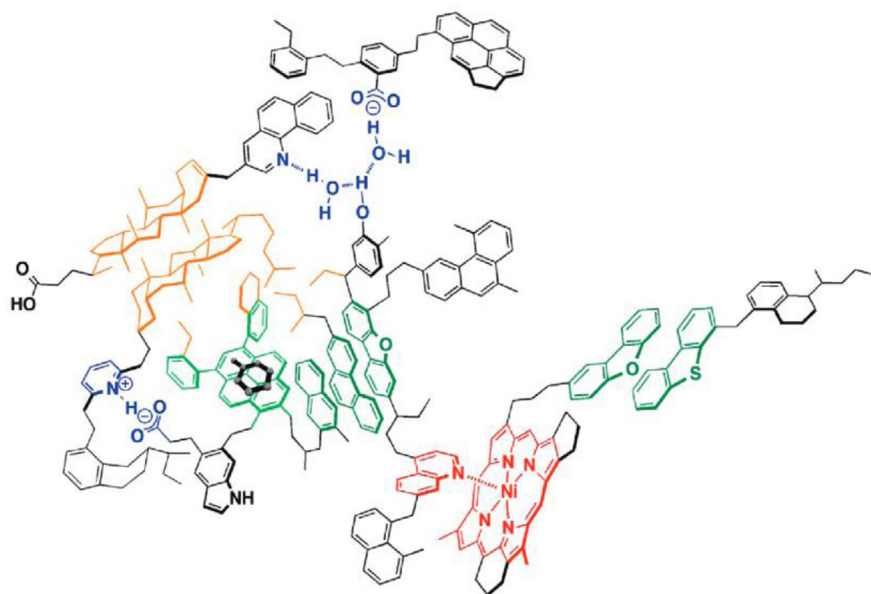


Figure 10. Asphaltene supramolecular contains all the parts and interactions desired in The Gray and other models. Colors represent these interactions: blue) Acid–base and hydrogen bonding, red) Metal coordination complex, orange) A hydrophobic part, green) π – π stacking (Gray et al., 2011).

consequently, the intermolecular forces affecting the self-association phenomenon of asphaltene explained with various examples of molecular simulations of asphaltene.

The π – π stacking effect of aromatic rings: In the aggregation of asphaltene, the most essential of the intermolecular forces involved relate to the π – π interaction. Result of these cumulative interactions, the molecules take different configurations for aromatic interactions (Kertesz, 2019). They are the three states that have the most stable energy: (A) Face-to-face or parallel or (π – π), (B) Face-to-Edge or T-shape or (π – σ), Edge-to-Edge or offset parallel or (σ – σ). The aggregation of significantly

large polycyclic molecules, the face-to-face or edge-to-edge configurations are set off as more desirable than the T-shape configuration. In these two cases, more vital Van der Waals forces apply due to the flatness of the aromatic part and more overlap (Rashid et al., 2019). Pacheco-Sanchez et al., in 2003, By molecular simulation of a hypothetical asphaltene model, observed three types of conformations in its dimers, trimer, and tetramer. as shown in Figure 11 (Pacheco-Sánchez et al., 2003).

Structural and molecular particularities such as the size and shape of aromatic cores play a decisive role in the morphological properties of asphaltenes (Jian et al., 2013; Sedghi et al., 2013). This fact

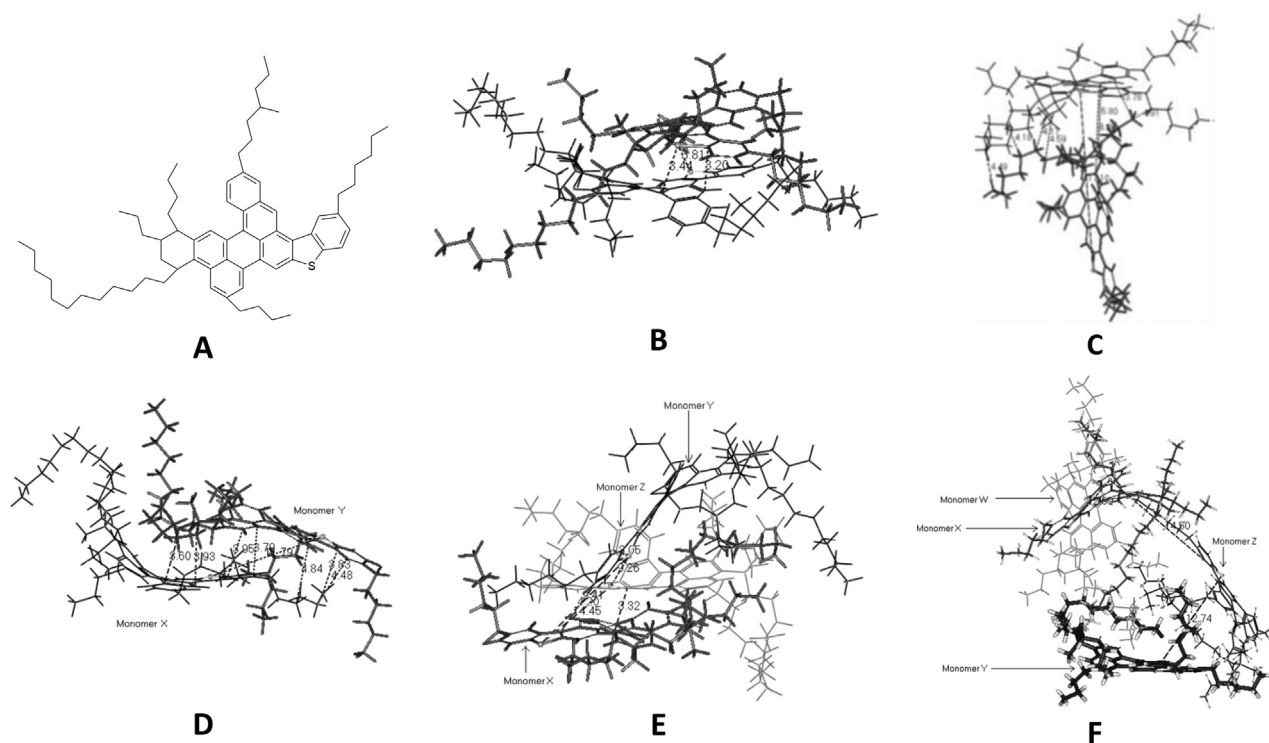


Figure 11. Symbolic visualization conformation of (A) An asphaltene model, proposed by Groenzin H and Mullins et al. (B, C, D) Dimers of Face-to-Face, Face-to-Edge, and Edge-to-Edge, (E) Trimer in a mixture of Face-to-Edge and Edge-to-Edge, (F) Tetramer in a mixture of several forms of T-shaped (Pacheco-Sánchez et al., 2003).

demonstrated by measuring the aggregation energy of asphaltene molecules. For example, whenever the number of rings increases from 8 to 11, the accumulation energy also increases from -14 to -19.4 kJ/mol.

The steric hindrance of aliphatic side chains: As the π - π stacking is the operating force of self-association, the steric hindrance is the limiting force of self-association. Evidence for this is the changes in melting point and solubility of alkyl aromatics compounds with different alkyl chains, demonstrating steric interference to attractive interaction between cores. Indeed, these experimental results show the effect of disturbing repulsive forces of alkyl chains as a destructive agent in the attractive forces between the aromatic cores (π - π stacking) (Jian et al., 2013). One of the exciting works that can be exemplified the effect of alkyl chain repulsive forces on the accumulation of cores is the study of perylene bisimide compounds (polyaromatic surfactants) with different alkyl chain length and polarity as asphaltene-like models by Teklebrhan et al. Table 1 (Teklebrhan et al., 2012).

They found that the attractive force of the π - π stacking was one of the most vital self-association propulsive forces in perylene bisimide surfactants. Contrast, the repulsive forces of alkyl chains (which depend on their polarity) are among the most potent inhibitory forces. The higher and more robust the steric barriers by the alkyl chains in the molecule, the less and weaker the self-association by the aromatic rings, course, depends on the environment around the molecules, ie, the type of solvent and their polarity. Figure 12 shows conformation and steric hindrances and π - π stacking of these compounds.

In this regard, Zhang et al. investigated the effect of steric hindrances on alkyl chains by choosing the different ratios of the length of the alkyl chain to the size of the aromatic core. They performed experiments on two types of asphaltene molecules, one long chain with a small aromatic core and the other a short chain with a larger aromatic core. Results showed a difference in the possibility density, which they attributed to the relative orientation of these molecules in neighboring polyaromatic cores and the difference in the degree of steric repulsion between the alkyl chains (Zhang and Greenfield, 2007).

For better understanding of steric repulsion effect on the self-aggregation of asphaltene, Cuiying Jian et al. investigated molecules of Violanthrone-78 (VO-78), (C70H84O6) (Figure 13-A) with different chain lengths in water with MD (Jian et al., 2013). They found that the self-association of polyaromatic molecules had no monotonic relationship with their chain length. Surprisingly, they observed that very short and very long chains (C4, C16) formed denser aggregates than the chains between the two (C8, C12) (Figure 13-B). They concluded that the balance between the aromatic cores (π - π) on the one hand and the interactions between the aromatic cores with the aliphatic chains (π - σ) and the aliphatic chains with each other (σ - σ) on the other hand caused such different aggregations.

Charge Transfer or Electrostatic Interactions of heteroatoms: As mentioned earlier, the atoms of oxygen, nitrogen, and sulfur relative to carbon and hydrogen have identified in asphaltene molecules as heteroatoms. These heteroatoms scattered in places such as aliphatic chains, aliphatic saturation rings, aromatic cores, and bridges between aromatic cores. Heteroatoms in the asphaltene molecule cause permanent or partial charge density imbalances not see in non-polar compounds such as pure hydrocarbons. Heteroatoms generally participate in hydrogen bonds or act as electron donors (Sedghi et al., 2013; Silva et al., 2016). The contribution of heteroatom polar interactions in the self-association of asphaltene molecules is significant and has well studied by molecular dynamics simulations and dielectric spectroscopy. Example, to investigate the effect of heteroatoms in the aromatic and aliphatic sections on self-association, pyridine compounds were selected. The results of free aggregation energy calculations showed that heteroatoms inside the aromatic ring were significantly more effective in aggregation than outside the aromatic ring (da Silva Oliveira et al., 2014; Durand et al., 2010; Qiao et al., 2017; Rajagopal and Silva, 2004; Subramanian et al., 2016; Wang et al., 2011; Waters, 2013).

3.1.3. Effective factors on asphaltene aggregation

After the role of the chemical structure, which is the primary source of intermolecular interactions in self-association of asphaltene molecules, there are other factors that have different impact coefficients on it, which are The composition surrounding asphaltenes in oil matrix (the nature of maltene fraction), Temperature and Pressure (Carbognani et al., 1999; Guzmán et al., 2017).

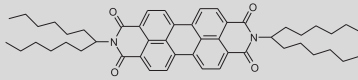


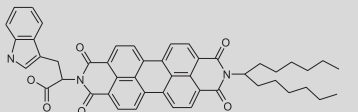
Effect of crude oil composition: Numerous studies have performed experimentally and operationally to evaluate the stability of asphaltene in the event of changes in compositions and predict asphaltene precipitation, such as the Colloidal instability index (CII), Stability index, and Stankiewicz plot (Asomaning and Watkinson, 2000; Guzmán et al., 2017).

Colloidal instability index (CII): In this index, oil is defined as a colloidal system with the composition of asphaltenes, resins, aromatics, and saturates. The stability of asphaltene is a function of them, and It is mathematically expressed in the dividing flocculants into peptizers, so that flocculants (the sum of asphaltenes and saturates) cause the instability of asphaltene and peptizers (the sum of resins and aromatics) stabilize asphaltene (Wiehe and Kennedy, 2000) (Eq.2):

$$CII = \frac{(Asphaltenes \text{ in wt}\%) + (Saturates \text{ in wt}\%)}{(Resins \text{ in wt}\%) + (Aromatics \text{ in wt}\%)} \quad (2)$$

Asomaning et al. measured the stability of asphaltene in crude oil by liquid chromatography and reported the results: If $CII \geq 0.9$, asphaltenes

Table 1. The polyaromatic surfactant molecules (Teklebrhan et al., 2012).

PA Compound (Abbr.)	Formula	Molecular structure
N, N'-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylicbisimide (BisA)	C ₅₀ H ₆₄ N ₂ O ₄	
N-(1-hexylheptyl)-N'-(2-phenylpropanoic acid)-perylene-3,4,9,10-tetracarboxylicbisimide (PAP)	C ₄₆ H ₄₆ N ₂ O ₆	
N-(1-hexylheptyl)-N'-(5-carboxylicpentyl)-perylene-3,4,9,10-tetracarboxylicbisimide (C5 Pe)	C ₄₇ H ₄₈ N ₂ O ₆	
N-(1-hexylheptyl)-N'-(2-indol-3-yl-propanoic acid)-perylene-3,4,9,10-tetracarboxylicbisimide (TP)	C ₄₈ H ₄₇ N ₃ O ₆	

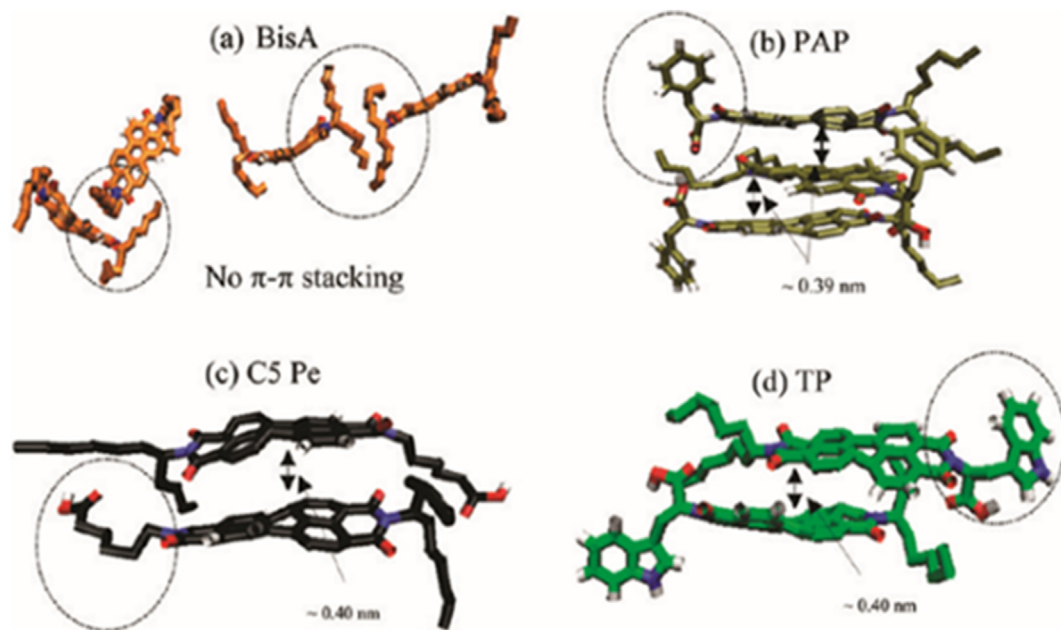


Figure 12. Stereochemistry of two polyaromatic surfactants and their interactions: (a) No π - π stacking, (b, c, and d) π - π core stacking. The snapshots took at the 20 ns MD time (Teklebrhan et al., 2012).

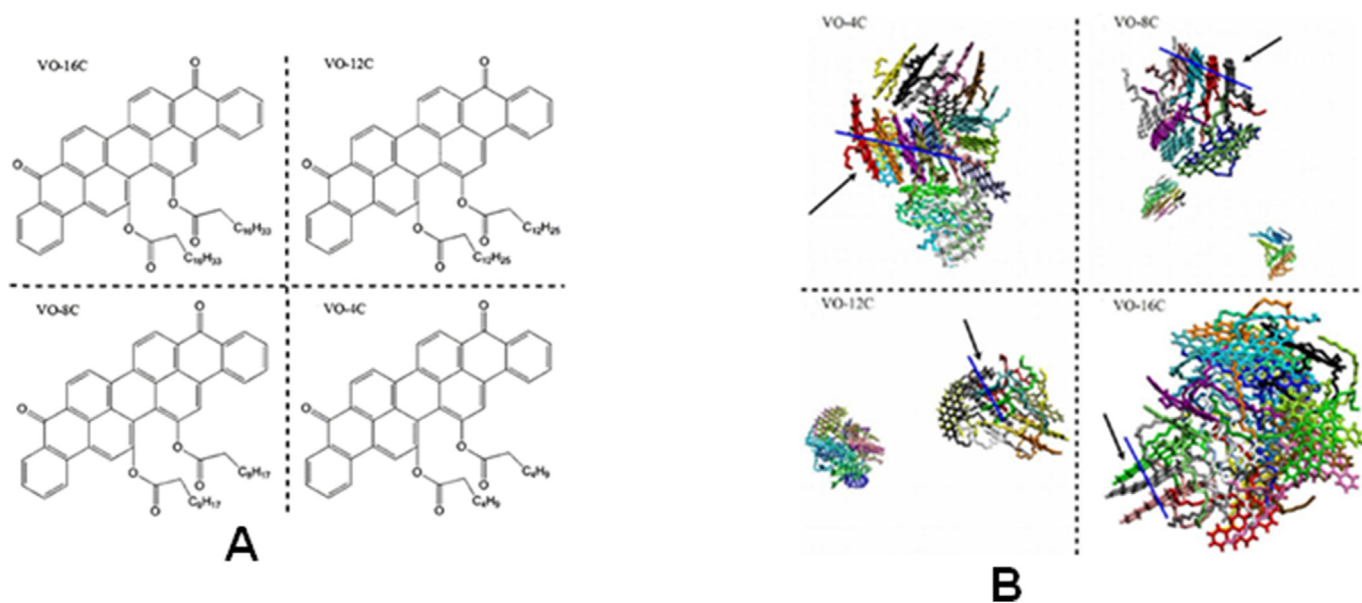


Figure 13. (A) Molecular structures selected from Violanthrone-78, VO16C, VO-12C, VO-8C, and VO-4C for MD. (B) Snapshots of the final simulation stages of systems for them. Molecules shows in 24 different colors for better display. Molecules of water deleted for clarification (Jian et al., 2013).

join to be unstable. If $CII \leq 0.7$, the asphaltene is stable when $0.7 \leq CII \leq 0.9$, asphaltene stability is indistinct (Asomaning and Watkinson, 2000).

Stability index: In this index (A/R ie, Asphaltenes/Resins) ratio, the stability of asphaltene in crude oil define as the division of asphaltene into the resin. Despite its simple appearance, this index is very efficient and widely used. Because both fractions used in this equation are heavy and non-volatile components of oil and measure with reasonable accuracy. Resins act as the natural peptizers of asphaltene molecules in petroleum. This is how Asomaning et al. defined the numerical value of the index: If the A/R ratio is lower than 0.35, then the crude oil will be stable (Asomaning and Watkinson, 2000).

Stankiewicz plot: This method is known as the fractions of SARA components, ie, S(Saturates)/A_r(Aromatics) and A (Asphaltenes)/R

(Resins). Matching these fractions with the graph, the stability of asphaltenes in crude oil can predicted, but if this method combines with the CII index, more reliable results obtaine. Figure 14, two well-defined regions, stable and unstable are identified (Gaona et al., 2010; Stankiewicz et al., 2002).

Effects of pressure and temperature: Most studies on the effect of temperature and pressure on the aggregation of asphaltene have performed in operational areas, ie, oil reservoirs and wells. Results show that reducing the pressure, aggregation, and deposition of asphaltene in crude oils with high-asphaltene content occurs significantly (Demir et al., 2016; Hu et al., 2015; Kuznicki et al., 2008; Tan et al., 2009). Effect of temperature is slightly more complex than pressure because various factors have identified. A) As the temperature increases, the solubility of

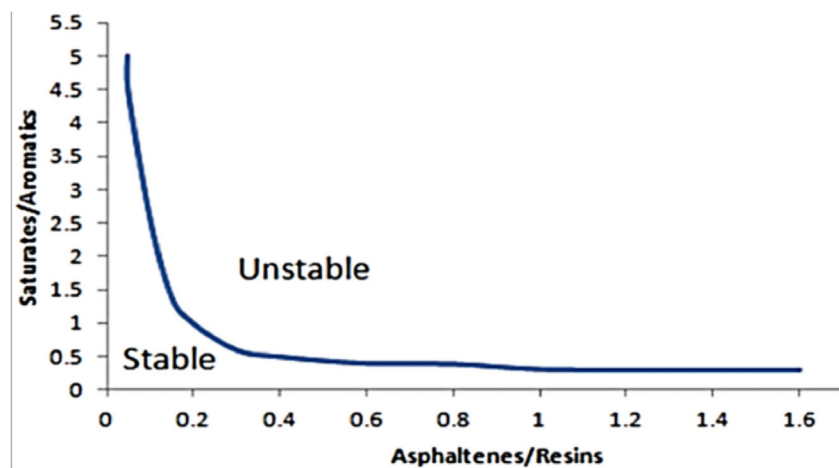


Figure 14. Stability criterion of Stankiewicz (Stankiewicz et al., 2002).

asphaltene increases, and aggregation occurs less frequently. B) With increasing temperature, the chemical composition of crude oil changes with the escape of light fractions, mainly the alkanes, and reduces the solubility of asphaltene in oil and will lead to quick aggregation. C) As the temperature rises, the viscosity of the oil decreases. moreover, the diffusivity of asphaltene particles increases and leads to faster aggregation (Maqbool, 2011; Moradi et al., 2012). In general, the effect of crude oil composition and pressure on the self-association of asphaltenes has reported to be greater than temperature.

3.1.4. Asphaltenes aggregation inhibitors

Several physical and chemical methods use to manage asphaltenes aggregation and solve the problems caused by it. Traditional and physical techniques as jetting, coil tubing, drilling, milling, etc., are generally tricky and sumptuous, while new and chemical methods are more accessible, less expensive, and more economical (Chang and Fogler, 1994; Tirjoo et al., 2019). As chemical inhibitors (Barcenas et al., 2008; Keshavarz et al., 2019; Kraiwattanawong et al., 2009) that allow the production, operation, and transfer of oil to take place without separation of the asphaltene phase or with a delay. If the inhibitors play their full role, they can act as dispersants to stabilize in the crude oil.

Factors such as the structural properties of asphaltene, the chemical structure of the inhibitors, and the type of solvent have a significant role on the performance of the inhibitors (Alhreez and Wen, 2019; Barcenas et al., 2008; Chang and Fogler, 1994; Ibrahim and Idem, 2004; Leon et al., 1999, 2000; Wang et al., 2009). Figure 15 shows mechanism of inhibitors adsorption on surface of nanoaggregates and prevent them from joining together and growing (Alhreez and Wen, 2019)..

Kheira Gharbia et al. have collected several inhibitors in the papers from 2005 to 2016. Some of the most commonly used are n-butylisoquinolinium chloride [C₄iq⁺] [Cl⁻], 1-allyl-3-hexadecylimidazolium Bromide, coconut essential oil, sandalwood oil, Boscan resins, DBSA, dodecyl trimethyl ammonium bromide, TiO₂ nanoparticles, Nanofluids of Al₂O₃, Propoxylatedpolydodecyl Phenol, Octylphenol, Dodecyl phenol, Salicylic acid, Non-Ionic polymeric surfactants (Gharbi et al., 2017).

3.2. Surface activity

The second inherent property of asphaltene molecules is their surface and interfacial activity. They have an excellent ability to adsorb the interfaces oil-air, gas-oil, solid-oil, and water-oil and make very constant foams and emulsions (Andrews et al., 2011; Fan et al., 2010; Ortiz et al., 2010; Rashid et al., 2019). Asphaltene, compared to other surface-active agents in petroleum, plays the crucial stabilizer in the water/oil emulsions and acts as natural surfactant (Jestin et al., 2007; Zhang et al., 2005). Researchers show the performance of them depends on

physicochemical properties of the system, for example pH of the aqueous solution (Poteau et al., 2005) asphaltene solubility, polarity and aromaticity of the organic phase (Nenningsland, 2012; Nenningsland et al., 2014).

Of the biphasic systems mentioned, the water-oil emulsion is more critical in the oil industry because these types of emulsions not only cause many problems in reservoirs and, production facilities, transmission lines but also due to the spread of oil on the surface of the oceans and seas, it also creates problems for cleanup and environmental effects (Akbarzadeh et al., 2005). Although compounds such as resins, clay, carboxylic acid, naphthenic acids, and their additives; drilling fluids, chemicals, and corrosion inhibitors, play a role as a surfactant in oil at stabilizing the emulsion, the surface activity of asphaltene is more than theirs and has a major share in altering the interfacial tension (IFT) of the oil-water phase (Fang et al., 2008; Ortiz et al., 2010; Zhang et al., 2018). The stability of the water in oil emulsion increases the density of crude oil. Also, heavy crude oil emulsions that contain more asphaltene are much more stable than light crude oil emulsions.

Many experiments and studies have done on the mechanism of interfacial activity of asphaltene molecules. Overview is that the asphaltene molecules align themselves parallel to the interface from the flat part of the poly-aromatics rings, creating a two-dimensional monolayer layer structure and the side chains of the asphaltene molecules enter the oil phase (Zhang et al., 2005, 2007). Gradually, this layer re-arranges to create a steric hindrance that prevents the surface from rupturing between the two phases. Recent studies show three-dimensional structures of molecules on an interface that stabilizes the surface (Kuznicki et al., 2008; Yarranton et al., 2000). Figure 16 is a hypothetical image that shows this mechanism (Rane et al., 2013).

As shown in the figure, asphaltene monomers are adsorbed on the water-oil interface in the form of “flat on” while asphaltene nanoaggregates not adsorbed on the surface (Rane et al., 2012; Yang et al., 2015). It may be due to two different intermolecular interactions in different environmental conditions. According to the Yen–Mullins model, in the oil phase, the interaction of aromatic cores and side chains leads to the formation of nano-aggregates, while the interaction of asphaltene molecules at the water-oil interface is on one side, the aromatic cores are in contact with the water surface. On the other side, the aromatic cores and aliphatic chains are in contact with the oil phase. Asphaltene nanoaggregates may interact with lateral aliphatic chains with aliphatic side chains of asphaltene monomers. It seems that suchlike nanoaggregate will have more significant affliction in adsorption than monomers. Only monomers have the power of interfacial absorption and stabilize the water-oil emulsion (Keshavarz et al., 2019; Mullins et al., 2012).

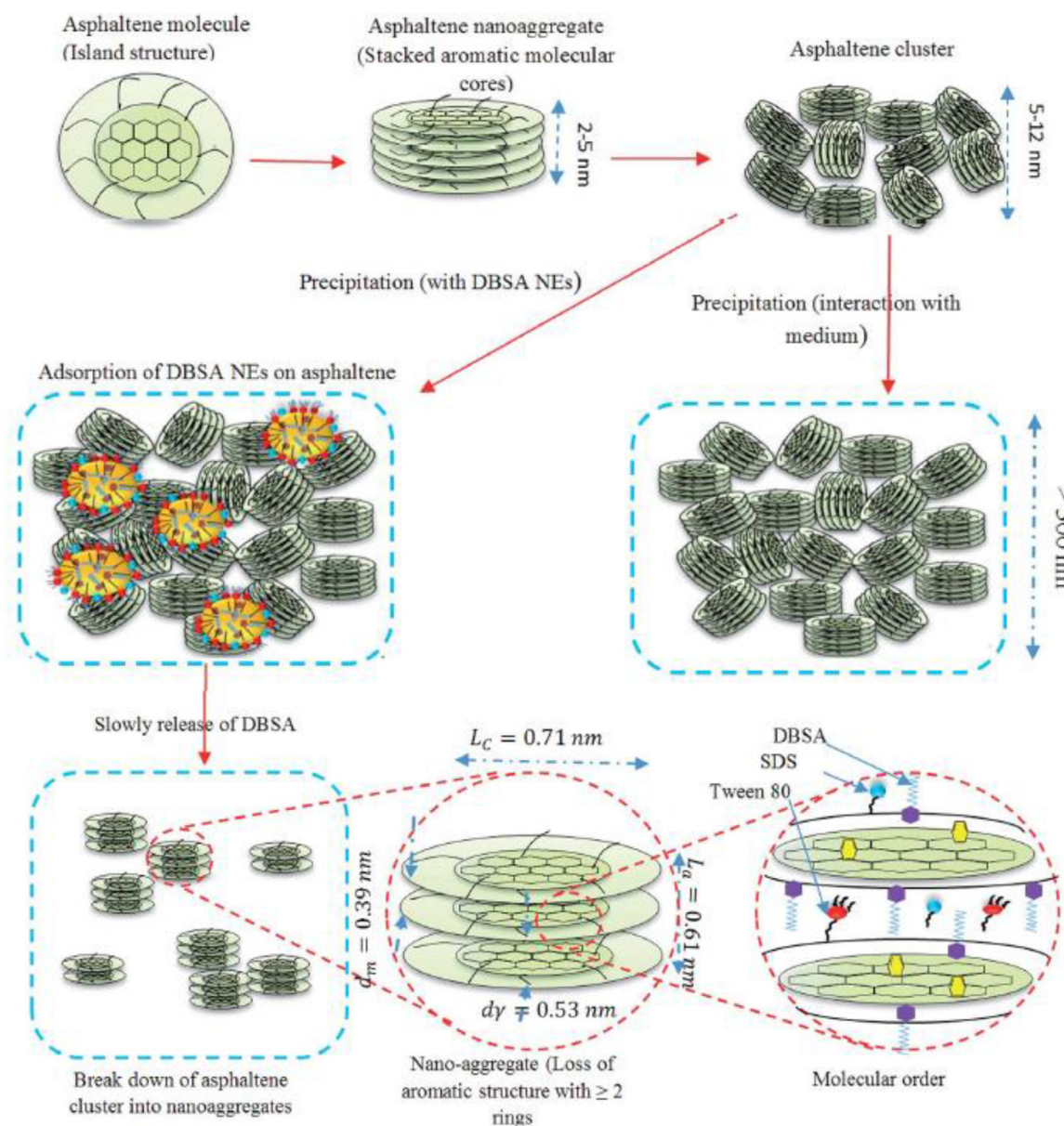


Figure 15. Illustration of the formation of nanoaggregates to clusters over time and penetration of surfactants into the stacked layers of aromatic cores and creating a distance between them and preventing aggregation (Alhreez and Wen, 2019).

Yang et al. performed experiments with polar asphaltene with heterogeneous oxygen and sulfur atoms. Results showed that polar asphaltene molecules behave differently in the interface of two phases of water and oil than asphaltene molecules with lower polarity (Yang et al., 2015). Therefore, the molecular structure and architecture of asphaltene molecules play an essential role in the stability of water and oil emulsions, too (Ruiz-Morales and Mullins, 2015).

In parallel with laboratory work, the study of the interfacial activity of asphaltene molecules in two phases has been done by molecular dynamics simulation (MD) in abundance. Example, Kuznicki et al. selected different models of asphaltene and asphaltene-like and studied the aggregation and interfacial activity properties in water, heptane, and toluene (Kuznicki et al., 2008). They first observed that in pure solvents alone, the self-association of asphaltene molecules occurs through the stacking of their polyaromatic rings then simulated these molecules in a mixture of water and toluene to study the interfacial activity. Result was

that the non-charged asphaltene molecules did not form any clusters at the toluene-water interface. In contrast, the asphaltene molecules with charged terminal groups had a considerable affinity in interfacial activity. Figure 17 shows the interfacial activity of four different types of asphaltene molecules with non-charged and charged terminal groups (Kuznicki et al., 2009).

The first result was that the accumulation of asphaltene molecules is always in the toluene phase. Second point of this study was that asphaltene molecules with charged terminal groups (COO^-) (b and c) had self-aggregation and surface activity between the water and toluene interface. It is most likely due to the intramolecular hydrogen bonding of the asphaltene molecules with each other (self-aggregation) and the hydrogen bonding of the asphaltene molecules with water (surface adsorption). While non-charged molecules (a and d) had only self-aggregation of molecules in toluene and did not show any activity at the water-toluene interface.

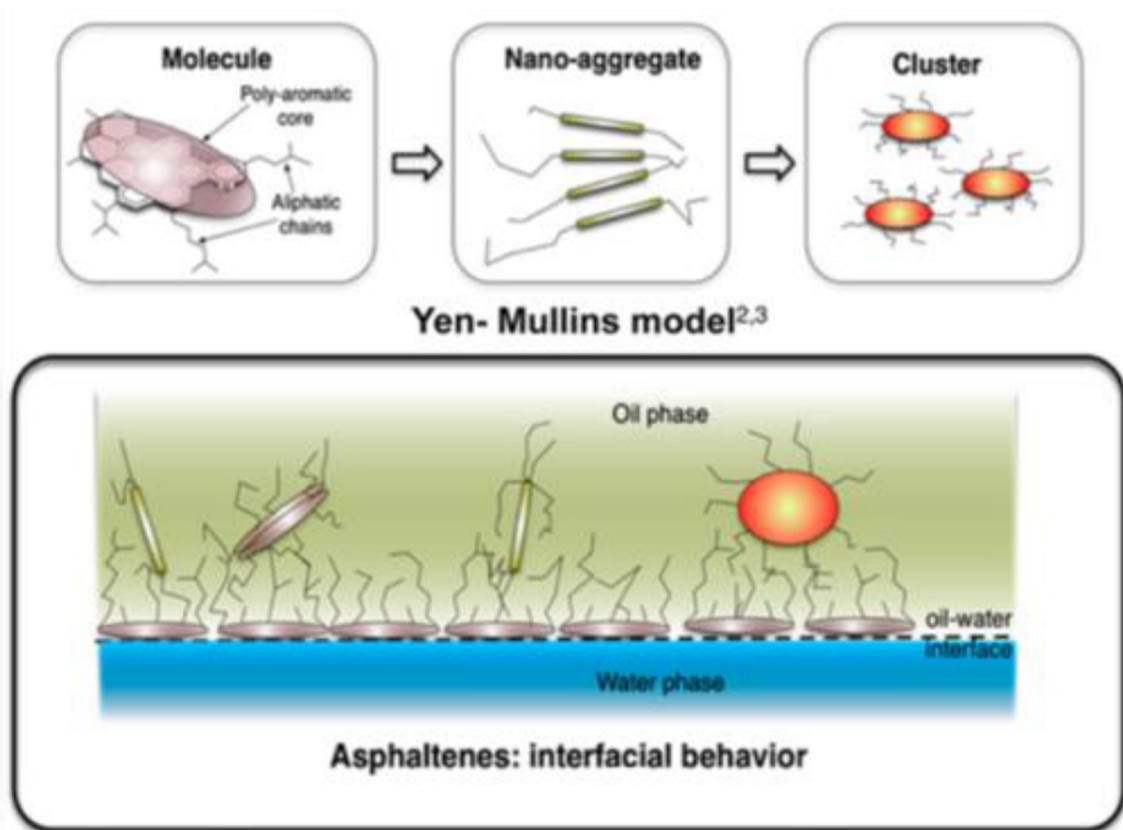


Figure 16. Schematic asphaltene adsorbing at oil–water interface (Rane et al., 2013).

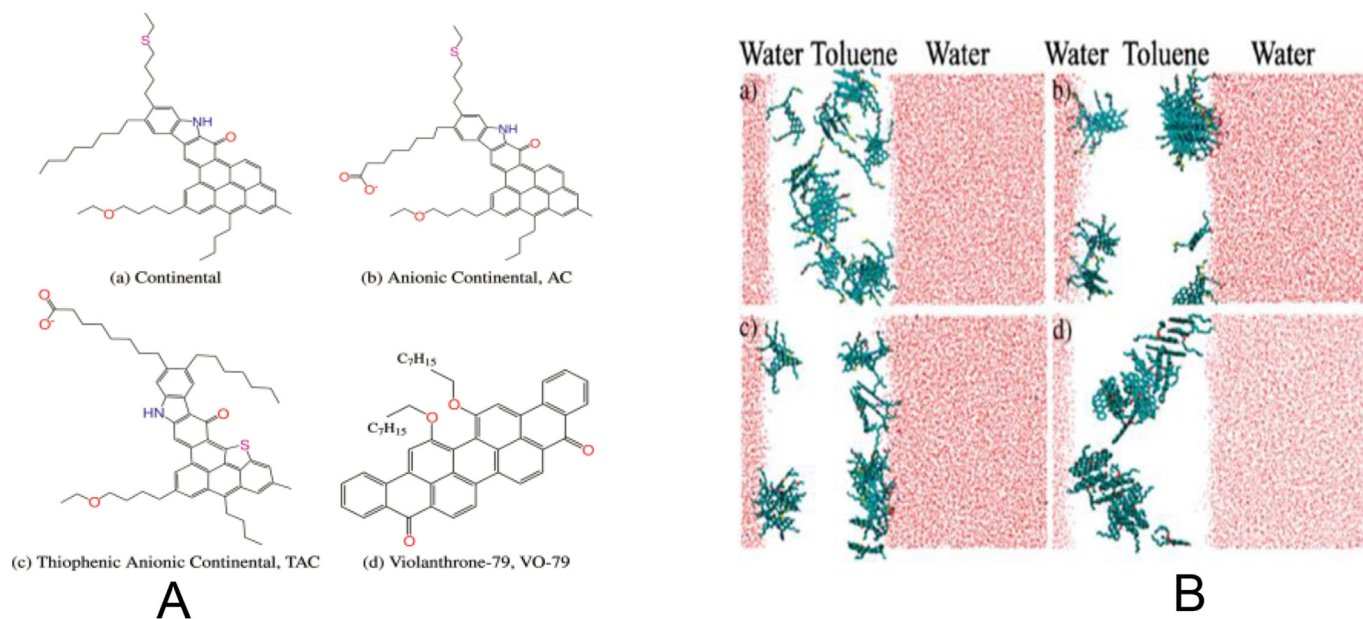


Figure 17. A) Model compounds proposed by Kuznicki et al. B) Snapshots taken after seven ns showing the aggregation and interfacial activity of the model compounds in toluene–water mixtures (Toluene molecules were removed) (Kuznicki et al., 2009).

4. Conclusion

This article is a comprehensive review of asphaltene from different angles. Critical look at the technical and economic problems of asphaltene in the oil industry and a thorough study of the important issues of asphaltene, including molecular weight, chemical structure, molecular

architecture, and aspects of intermolecular interaction, discussed. Various proposed models reviewed with the limitations of each. Although each model is compatible with some laboratory results, it does not cover all observations and cannot fully implement in a particular model. The structural diversity and architectural complexity of asphaltene molecules in the crude oil of the world and The weakness or lack of

advanced nanoscale techniques/methods have led to a scientific puzzle in understanding their properties, specifically aggregation. Property of self-association of asphaltenes is highly dependent on intermolecular forces, which derived from the chemical structure and architecture of the molecule. Asphaltenes have three essential parts in their molecular structure: Aromatic core (fused rings), Side aliphatic chains, and Heteroatoms. As a result, they encounter intermolecular forces such as the π - π interaction between aromatic sheets, the steric hindrance of aliphatic side chains and hydrogen bonds, acid-base interaction, electron transfer, etc. between functional groups. These are the main factors in the phenomenon of self-association, and other factors such as the percentage and type of non-asphaltic compounds of crude oil, temperature, and pressure affect and stimulate the self-aggregation process. The help of laboratory and computational methods, good progress has made in finding puzzle pieces of the aggregation phenomenon and providing a solution to prevent it.

The authors make the following recommendations or suggestions for future research:

1. So far, there is no single comprehensive method for presenting the accurate molecular structures of asphaltene in an oil sample due to their structural diversity and molecular weight range. It has been enough to provide models close to laboratory results with speculation, and further research in this field is necessary.
2. Structure plays an essential role in developing physicochemical properties of asphaltenes. structural Impact factor should have considered in the presentation of thermodynamic and computational models in addition to temperature, pressure, and chemical compounds around asphaltene molecules.
3. For design, synthesize, and select appropriate anti-aggregation inhibitors and demulsifiers to their reversibility mechanism, it is necessary to know the exact molecular structure of asphaltene and the type of intermolecular interactions between inhibitors and asphaltenes. Further research needs in this field, especially in molecular dynamics simulation.

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Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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