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Mechanisms of Asphaltene Aggregation: Puzzles and a New Hypothesis

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ABSTRACT: In petroleum science, asphaltenes are well-known as the most refractory fraction of crude oil and remain infamous for problems in production, transportation, and refining processes. Hence, they have been continuously analyzed and modeled over more than half a century. Defined only by solubility and characterized by an extremely complex and diverse molecular composition, asphaltenes lack discriminative molecular descriptions and definitive chemical characteristics. Most of the historic research has focused on representative structures in an attempt to yield physical and chemical models of asphaltenes, and thus, conflicting theories of bonding structures and aggregation interactions remain. This review focuses on the aggregation behavior of asphaltenes and attempts to rationalize a structure−property relationship to asphaltene aggregate thermal stability. Herein, the chemical and physical bonding properties of asphaltenes and the contradictory interpretations of their nature and composition are examined, particularly as they impact formation and stability of asphaltene aggregates. We propose a new hypothesis involving free radical interactions, i.e., pancake bonding, as an additional significant contributor to the bonding structure and formation of aggregates in asphaltenes that is consistent with the latest findings based on Fourier transform ion cyclotron resonance mass spectrometry and non-contact atomic force microscopy techniques. Various structural features of polycyclic aromatic hydrocarbons contributing to this interaction involving a stable free radical are highlighted, and suggestions for future research are presented.

1. INTRODUCTION

Petroleum asphaltenes are known as the most refractory molecules in petroleum and are responsible for detrimental effects in numerous industrial processes that span production, transportation, and refining of crude oils.[1−3] The mysterious nature of asphaltenes has been continuously researched and intensively debated over half a century.[4−7] In this review, a critical analysis of the concepts, models, and propositions will be presented with a historic perspective. By pointing out the limitations of the proposed models in the context of the structural information known at the time, we attempt to reinterpret the archived information and consolidate the historical understanding within the context of recent research advances. While looking for a general trend and consistencies, we pay attention to irregularities and highlight a few contradictory reports in the literature. We raise questions on the aggregation mechanisms of asphaltene interactions and identify gaps in the current understanding. We propose a new hypothesis based on evolving chemical bonding concepts termed pancake bonding that are not generally considered by petroleum chemists. This hypothesis addresses knowledge gaps, and we conclude with suggestions for future studies.

1.1. Problematic Definitions of Asphaltenes.

Despite continuous research into the chemical composition and physical properties of asphaltenes over many decades, significant controversies remain.[4−6] Since the outcry raised in "Asphaltenes, Where Are You?" by Boduszynski in 1980 that has been reiterated by many papers and reviews since,[8−11] it is clear that much of the confusion is caused by the imprecise definition of asphaltene, an ill-defined term based solely on solubility. Asphaltenes are simply the fraction of petroleum insoluble in *n*-alkanes (usually *n*-heptane) but soluble in toluene.[1−3] In chemistry, solubility is a relative qualifier (high or low), as measured by the saturated concentration of a solute in a solvent, rather than a dichotomous attribute (yes−no, as indicated by soluble or insoluble). Hence, thresholds are required to define the solubility of asphaltenes in *n*-heptane (e.g., less than 100 or 10 ppm). Furthermore, even as jargon in petroleum science, solubility is a collective term for bulk behavior and, hence, is problematic at the molecular level, where the line between solute and solvent is blurred for a highly diverse molecular mixture, such as crude oil. This lack of clarity is further exacerbated by the fact that asphaltenes are often isolated via precipitation by the addition of a large volume of *n*-alkane to a crude oil (e.g., ASTM method D6560).[12] This simple method requires little laboratory skill and would appear to be easily replicated; however, in practice, it is predisposed to many problems, such as a lack of specificity on (a) isolation methods, (b) operation temperature and sedimentation time, (c) criteria of clean separation (e.g., coloring) and size limit detected by light or electron microscopy (micrometer- or nanometer-sized monomers,

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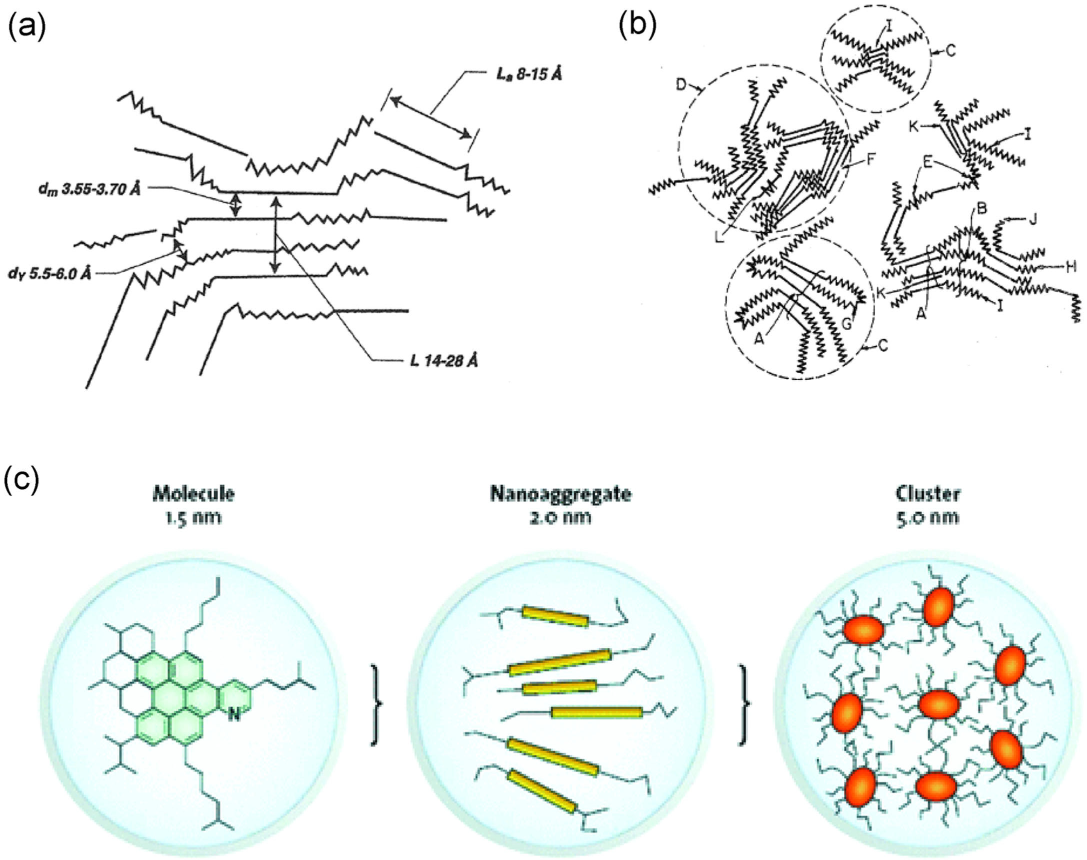
Scheme 1. A Few Physical Models for Asphaltenes[a]



[a](a) The side view of the original Yen model proposed in ca. 1961.[15] The zig-zag structure represents a saturated carbon chain or loose net of naphthenic rings, and the straight line represents flat sheets of condensed aromatic rings. (b) The macrostructure model proposed by Yen in 1967.[18] The letter designations are as follows: A, crystallite; B, chain bundle; C, particle; D, micelle; E, weak link; F, gap and hole; G, intracluster; H, intercluster; I, resin; J, single layer; K, petroporphyrin; and L, metal. (c) The Yen−Mullins model proposed ca. 2010 composed of three scale regimes, including monomers, nanoaggregates, and clusters.[19] These figures were reused with permission from refs 15, 18, and 19. Copyrights 1961, 1967, and 2010 American Chemical Society.

micelles, nanoaggregates, or clusters), and (d) penetration of the solvent and the entrained solvent/solute molecules (non-asphaltenic) in the precipitated or suspended solids. Soxhlet extraction and ultracentrifugation provide an arbitrary criteria for clean separation judged by color changes and are thus preferred, but they are still plagued with some of these issues (such as thorough solvent−solid exchange). Most asphaltene fractions contain a small amount of inorganic particles (clay) and waxes (paraffins) that are often considered as "impurities" and can be removed by purification, but many studies have shown that no asphaltene is "pure". There are always solvent or non-asphaltene molecules trapped or occluded in asphaltenes, regardless of how much effort is put into purification; however, at the same time, more and more "asphaltenes" are leaching out or solubilized in the solvent.[8,10,13] Therefore, after reviewing the evolution of the asphaltene definition in "Asphaltenes, What Art Thou?", Moir pointed out that the concept of "pure" asphaltenes is an oxymoron.[4]

Despite the problematic definition based on solubility that does not provide much insight into molecular structures, asphaltenes are generally associated with molecules or fractions that are enriched in polar species with heteroatoms (mostly N, S, and/or O) or metals, highly aromatic (H/C of ∼1.0−1.3), or with a high boiling point and/or high molecular weights (hence "heavier" molecules).[4,13] However, while these characteristics are generally true, none is unique to asphaltenes and allows for a clear distinction between asphaltenes and non-asphaltenic fractions in petroleum. The classification of asphaltenes as macromolecules of high molecular weight is especially problematic, because their molecular masses are not as high as polymers, as was once believed.[4,5,14] The nature of asphaltene isolated from petroleum is further complicated because the parent feedstock is often a blend of crude oils of different origins or different process streams that may also contain chemicals added during production or refining. Hence, petroleum asphaltene is a highly complex and diverse molecular mixture, and the chemical characteristics of asphaltenes remain difficult to define. This is not to deny the existence of refractory molecules in petroleum that cause numerous problems in field production and refineries, which can be colloquially known as asphaltenes, but a complete consensus on exactly what asphaltenes are may never be reached. Recognizing these factors, we focus this review on certain properties or behaviors manifested by asphaltenes and then rationalize their underlying structure−property relationships, instead of focusing on molecular structures for asphaltenes confined by their solubility definition. Specifically, we explore the aggregation behavior of asphaltenes and provide insight into specific structural motifs or features that potentially affect aggregation interactions.

1.2. Critical Analysis of Asphaltene Models from a Historical Perspective.

The structure of asphaltenes has a long history of controversy. Although aromatic and aliphatic moieties were evident from early studies from infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies, the size of polycyclic aromatic hydrocarbons (PAHs) and their spatial arrangement in asphaltenes were initially tackled by Yen, Erdman, and Pollack in 1961 using powder X-ray diffraction (XRD),[15] a then primary and advanced technique to characterize molecular structures that is still widely used today.[16] The (002) and γ bands of asphaltene XRD patterns were first attributed to aromatic and aliphatic moieties through comparison to amorphous carbon black[17] and the aliphatic chains of polyethylene, respectively. On the basis of the assumed crystalline behavior, a stack of five aromatic sheets with sizes of 0.85−1.5 nm in diameter separated by an interlayer spacing of d_M of 3.6 Å (002 bands) was deduced and illustrated with a schematic model, which later became known as the Yen model (Scheme 1a).[15] Although an interchain distance of d_γ of 5.5−6.0 Å was deduced from the smaller γ bands, neither the chain length nor its position relative to aromatic core structures was specified, except for some indications of limited branching.

It should be noted that, in this pivotal study, Yen and colleagues mainly portrayed a physical picture for asphaltenes (constructed with particles, disks, and rods) rather than chemical structures, because it was based on the assumption of a crystallite and used Bragg scattering and the Scherrer equations to approximate the lattice size (or correlation length). Several years later, this model was modified by accommodating a chemical parameter, the molecular weight, which at the time was reported to range from 1000 to 500 000 Da from several methods [XRD, mass spectrometry (MS), gel permeation chromatography (GPC), vapor pressure osmometry (VPO), ultracentrifugation, and electron microscopy].[18] A macrostructure model (Scheme 1b) was proposed by Yen in 1967 that was composed of the aromatic disk weight (300−800 Da), unit (or sheet) weight (800−3500 Da), particle (or unit cell) weight (2500−10 000 Da), and micelle weight (37 000−10 000 000 Da). For example, the unit sheet weight (800−3500 Da) obtained from XRD was attributed to the ultimate or minimal molecular weight of asphaltenes, several of which are subsequently associated (stacked together) to become a unit cell or particle measured by XRD and VPO. This hierarchical macrostructure model likely reflected a popular view at the time or was inspired by the tertiary structures of proteins and DNA just resolved by XRD, both recognized with Nobel Prizes in 1962.[16] It is in this model that the weak links between aromatic core structures were first introduced, which later became known as the archipelago model.[18] It should be noted that the weak links are not evidence-based but rather a consequence of the very high molecular weight species believed to exist. It was unclear at the time whether these links were inter- or intramolecular connections by nature.

1.3. Puzzles on the Connections in Asphaltene Bonding Structures.

The physical models (or pictures) by Yen inspired several generations of researchers and prevailed in the petroleum field for the next several decades and up to the present day, despite the fact that the assumptions and quantification method were shown to be inaccurate by Ebert in the 1980s.[20−22] The other side of the picture by the chemists, however, was only tentatively sketched, and significant challenges were presented to attest to the chemical structures of molecules in these models. Tremendous analytical advances were made in the next few decades in characterizing asphaltenes,[9] yielding gains in the understanding of the average molecular structure with NMR,[23] chemical types by fractionation [e.g., saturate, aromatic, resin, and asphaltene (SARA)],[24] functional groups by pyrolysis[25,26] or chemical cleavage, and compositional analysis (e.g., hydrocarbons, S-containing compounds, and metalloporphyrins) by mass spectrometry.[1,27] One significant advance is the structure continuity model by Boduszynski, which clearly argues against the basic principles of crystallinity in XRD (lack of repeating units or lattice).[28,29] Another is the molecular weight distribution of asphaltenes, because it is now accepted that most species range from a few hundred up to a thousand, indicating that the assumptions in the macrostructure model were incorrect.[2,30,31] On the basis of the advances in understanding of chemical structures, interactions, and reactivities, numerous models were proposed through modification or extension of the original Yen model.[32−34] For example, the model by Sirota treated asphaltene association as a continuum, invoking concentration fluctuation approaching phase separation.[132,133] On the other hand, the hierarchal macrostructure model by Yen was modified by Mullins in 2010 to accommodate the fact that asphaltenes form nanoaggregates at low concentrations (~0.2 g/L), which may further form clusters or even flocculates and precipitates at higher concentrations. This new model includes three scale regimes, monomers (1.5 nm), nanoaggregates (2.0 nm), and large clusters (5.0 nm), and today is referred to as the Yen−Mullins model (Scheme 1c).[35,36] The advent of ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) MS over the last two decades provided tremendous insights into petroleum composition and enabled petroleomics as a new field in structure determination.[30] The astonishing molecular complexity of asphaltenes was recently exemplified by up to 500 resolved mass peaks within one nominal mass unit by FT-ICR MS at 21 T,[37] and evidence for the chemical composition of asphaltenes and heavy petroleum fractions confirmed and extended the original Boduszynski continuum model.[38−45] More recently, non-contact atomic force microscopy (nc-AFM) emerged as a powerful tool by providing a glimpse of structural information on individual asphaltene molecules.[46−53]

One of the key unanswered questions concerns the nature of the weaker bond linkages between PAH core structures, first proposed in the Yen macromolecular or archipelago model. The chain length and/or the presence of heteroatoms (such as sulfidic linkages) was unclear, although their presence is evidenced from refining operations, such as coking and hydrocracking,[33] and supported by fragments formed in pyrolysis studies.[34,54−58] Recent evidence of archipelago motifs was gleaned from the collision-induced dissociation (CID) and infrared multiphoton dissociation (IRMPD) combined with FT-ICR MS, as indicated by the reduction of both the carbon number and double bond equivalent (DBE) upon dissociation or fragmentation,[40] which showed the presence of both single and multiple aromatic core structures.[40,44] However, recent results suggest that selective ionization limits the compositional information attainable by subsequent mass spectral analysis,[39,40,59] which underscores the importance of its combination with fractionation to yield a more comprehensive picture. Recently, a series of synthetic dumbbell structures composed of two aromatic core structures were investigated with nc-AFM as a first-order approximation of archipelago architecture, showing that a covalent hydrocarbon chain of C_{20}, C_{10}, and C_2 linkers can be imaged.[52,60] The absence of such structural types in nc-AFM studies of natural asphaltenes suggests that they are likely to be in low abundance in the samples examined. However, while model compound studies are essential to understand the nuances of sample introduction and nc-AFM imaging, a direct extrapolation to complex petroleum mixtures is not straightforward and is thus unadvised. While nc-AFM provides precious structural information for real molecules in the petroleum mixture at the level of details not attained by any other means, the quantitative aspects of the imaged species as representative of the molecular diversity in asphaltenes is still unclear.

1.4. Puzzling Mechanisms in Petroleum Asphaltene Aggregation. One of the main behaviors of asphaltenes is their propensity to aggregate,[61] which caused the confusion in molecular weight measurements.[18] Although it has been long established that asphaltenes form stable and strong aggregates, the mechanisms underlying the process remain puzzling.[62,63] For example, a finite crystal size was calculated from XRD data by Yen et al.,[15] with an average stack of five molecules. Tanaka et al. studied asphaltene aggregates with XRD and small-angle X-ray scattering and showed that the average number of stacks decreased from 8 to 5 as the temperature increased from 30 to 300 °C.[64] The high temperature stability of asphaltene aggregates indicates cumulative bond strengths equivalent to covalent bonds (mostly $> \sim 90$ kcal/mol) that quickly break above ∼350 °C. These findings were recently supported by a hydrodemetalation and hydrodesulfurization study that revealed that the largest aggregates remained intact after hydroprocessing.[65]

Various non-covalent interactions have been suggested for the interactions within aggregates, including $\pi-\pi$ stacking, van der Waals (vdW) interaction,[66] hydrogen-bonding interaction,[62] electrostatic (or ionic) interaction, polar−polar (dipole−dipole) interaction, π−cation interaction, charge-transfer interaction, and metal coordination.[34,67] Most of these interactions depend upon heteroatoms and/or transition metals that are known to be enriched in petroleum asphaltenes. For example, it has been recently shown that oxygen-containing compounds possibly drive asphaltene aggregation through hydrogen bonding.[62] For the roles of hydrocarbons in asphaltenes, $\pi-\pi$ stacking has been attributed as the dominant interaction, mostly as a result of the predominant presence of PAH structures.[5,19,62,68] However, the importance of $\pi-\pi$ stacking between asphaltene molecules has been continuously challenged by many researchers because these are not strong.[66,69] Moir suggested that London forces are a driving force for the self-assembly of large PAH molecules, and the interaction energy is proportional to the size of molecules, analogous to a refrigerator magnet.[5] Although it is a reasonable hypothesis and seems to be supported by theoretical calculations, it is unclear if most asphaltenes have a sufficiently sized aromatic core structure to confer strong interactions in the presence of solvents and why a population of smaller molecules in the asphaltene fraction would not start to dissociate, considering the wide distribution in molecular size. Another widely used analogy for collective cooperative interactions is the DNA duplex, which is bound by a large number of hydrogen bonds (and base pair stacks). However, isolated DNA can be easily unwound or denatured at mild temperatures (>70 °C).

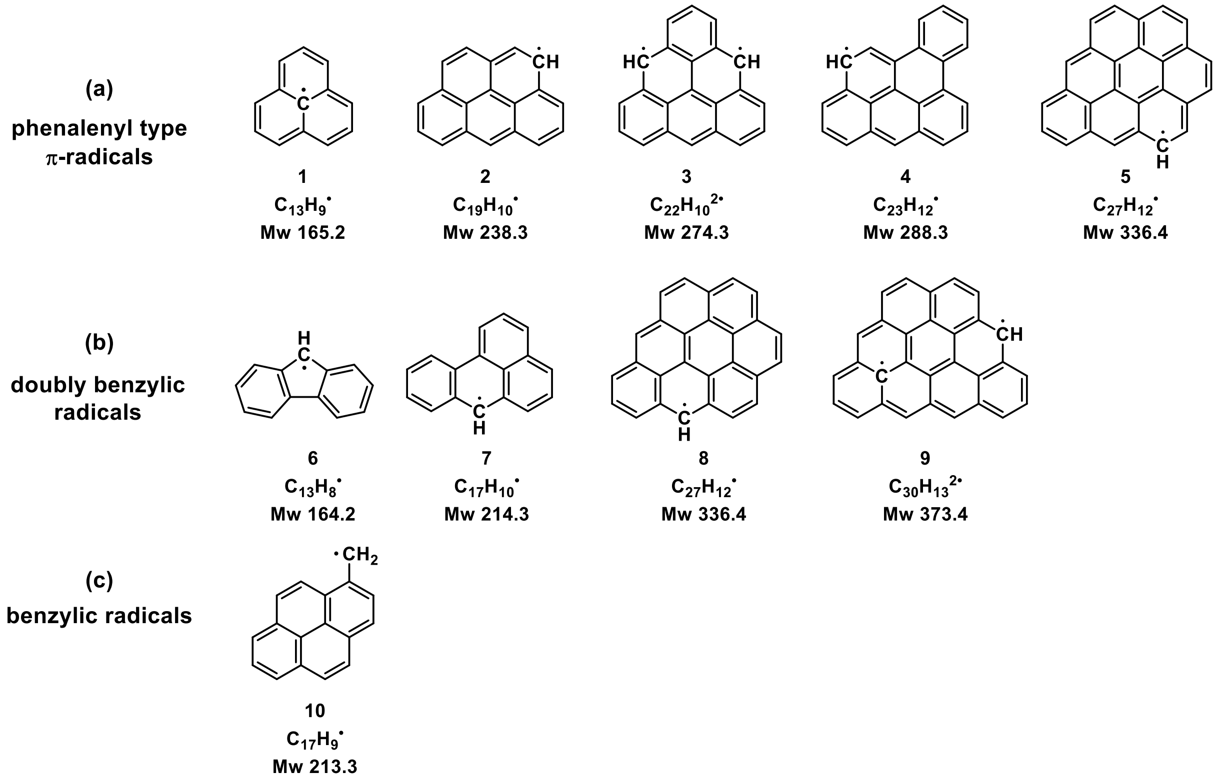
There is a lack of synthetic systems that can mimic asphaltene aggregation and be used to test the responsible forces. For example, Akbarzadeh et al. found that pyrene and alkylpyrene compounds exhibited little aggregation in toluene.[70] Classic archipelago structures composed of PAHs connected by aliphatic linkers are also unlikely to exhibit strong aggregation in strong aromatic solvents, such as toluene. Metals and petroporphyrins have been widely believed to participate in asphaltene aggregation through π−cation interactions. However, a study by Yin et al. showed that associative $\pi-\pi$ interactions of condensed aromatic compounds with vanadyl or nickel porphyrins were not evident in the presence of an organic solvent.[71]

Therefore, the question remains, what is so special about asphaltenes and their aggregation interactions?

2. NEW HYPOTHESIS FOR ASPHALTENE AGGREGATION VIA PANCAKE BONDING INTERACTIONS

Two of the most peculiar properties of asphaltenes are their strong propensity to aggregate and the persistence of stable radical species. Here, we propose that pancake bonding, a new concept emerging from physical organic chemical studies of organic conductors,[72−74] can be applied to petroleum asphaltenes and used to potentially explain both properties. In particular, we will focus on the widely accepted $\pi-\pi$ stacking interaction in asphaltenes and take one step further by considering the potential role of persistent free radicals. Before introduction of this hypothesis, the necessary basic components, including free radical PAHs, will be reviewed and their key structural features will be described. The background on pancake bonding will be introduced and applied to asphaltene aggregation, followed by a critical analysis of existing evidence that supports this hypothesis. Lastly, future studies that could provide a better understanding of pancake bonding and their significance in asphaltene aggregation are proposed.

2.1. Presence of Persistent Free Radicals in Asphaltenes and Their Possible Structures. Free radicals are generally known in organic chemistry as reactive intermediates with lifetimes from nanoseconds to microseconds. However, some organic radicals are long-lived, even shelf-stable, and commercially available, such as (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) and α,γ-bisdiphenylene-β-phenylallyl (BDPA). The presence of radical species in petroleum has been known since their detection using electron spin (or paramagnetic) resonance (ESR or EPR) in the late 1950s[75−78] and remains a subject of active research today.[79−88] They are carbon-centered free radicals based on the g value of 2.0034 ± 0.0004, indicating that a free electron is delocalized in a π system (g is a spectroscopic splitting factor dependent upon the orbital, and the electronic environment of the electron, g_e, is 2.0023 for the free electron). This is easily distinguished from paramagnetic metals, such as the septet peaks, as a result of vanadyl (VO^{2+}) petroporphyrins.[89,90] The presence of organic radicals in petroleum is unquestionable, but the featureless single EPR signal does not readily reveal information about their structures.[77,85] Much of the structural information that can be provided by EPR on individual radical species is lost, apparently as a result of overlapping signals from a mixture of diverse radicals. Recent AFM studies revealed the presence of radicals in petroleum fractions.[46,47,50,52,60,91] While the structures of most radical species in petroleum remain largely unknown, we can draw inspiration from AFM studies, Scheme 2. Three Prototypical Types of Free Radical Species Expected in the Petroleum[a]



[a](a) Phenalenyl-type π radicals (**1**−**5**) have electrons delocalized into aromatic systems, with simple examples including phenalenyl radical (**1**) and other non-Kekulé PAHs (**4** and **5**). (b) Doubly benzylic radicals (**6**−**9**) are predominantly σ radicals, but with a significant degree of delocalization to neighboring aromatic rings. (c) Benzylic radicals (**10**) are σ radicals located on an α carbon attached to an aromatic system. Some radicals, such as compound **9**, are mixed types containing both a π radical and a doubly benzylic radical center. The molecular formula and molecular weight were shown to indicate larger PAH systems expected for petroleum.

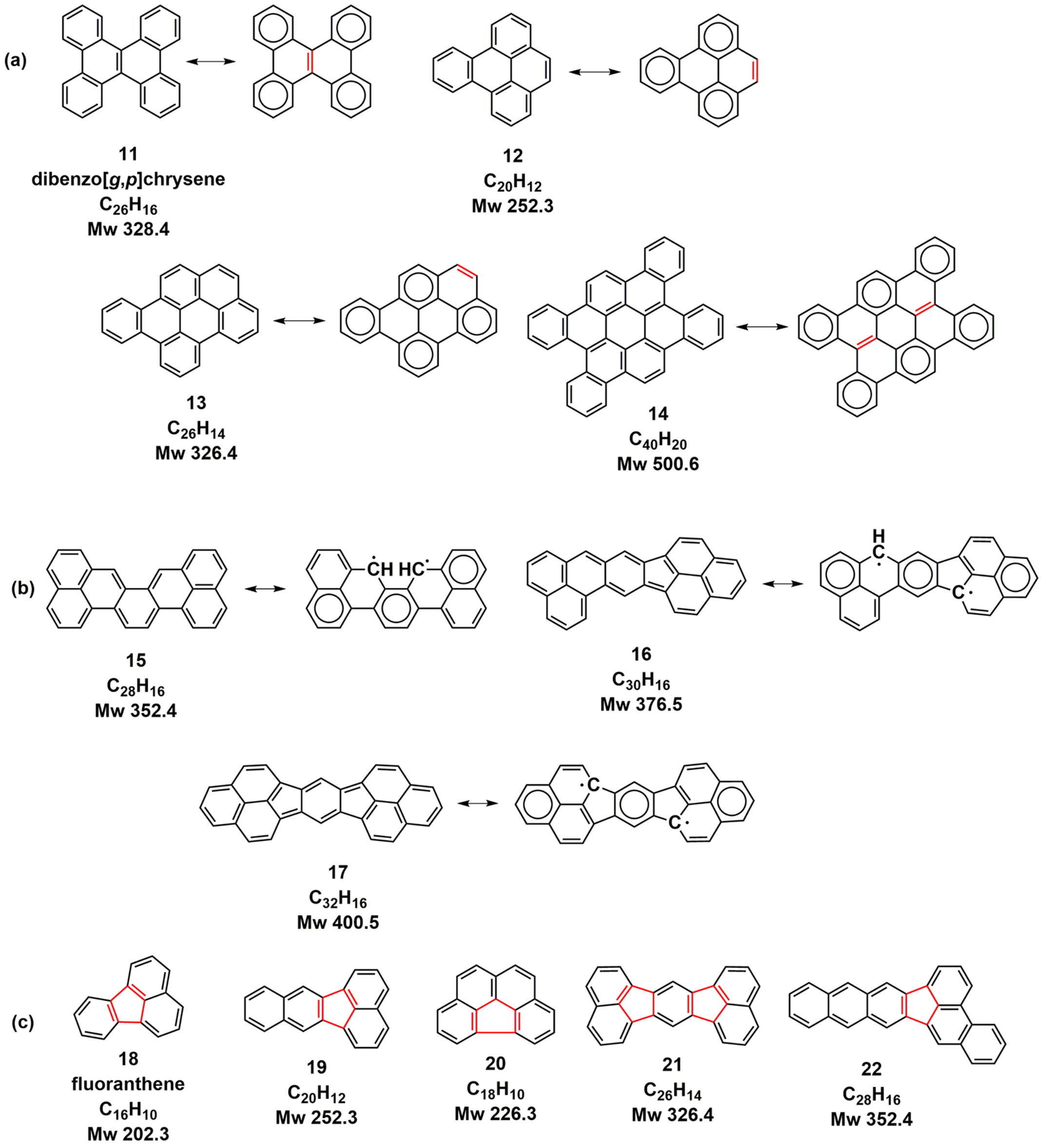
canvass what structures are possible, and rank them by their stability based on chemical principles. Using this approach, three types of free radicals are proposed and classified, as shown in Scheme 2.

The first type of radicals consists of a large delocalized π system with phenalenyl as a prototype, first known to form pancake bonding (Scheme 2a, **1**).[92] These odd alternant PAHs have non-Kekulé structures with an odd number of carbons, or an even number of carbons could arise from diradicals (such as triangulene) or polyradicals. While the phenalenyl radical (**1**) has been suggested as the potential radical in bitumen,[93] we think larger multiple ring aromatic systems (>5−7 rings, >250−500 g/mol) are more reasonable, because they are consistent with larger molecular weights of asphaltenes (**2**−**5**). These large π radicals will be even more stable than the phenalenyl radical because the unpaired electron can be delocalized over many carbons, with the multiple possible resonance structures having similar stability. The existence of these kinds of stable π radicals can be rationalized by aromatization of odd carbon number hydrocarbon precursors, because aromatization is the main pathway leading to increased stability for molecules during formation of asphaltenes in petroleum from kerogen catagenesis. Therefore, this type of non-Kekulé PAH radical is inevitable under geological conditions and over geological time scales. A few free radicals observed thus far by nc-AFM on various coal and petroleum asphaltenes fall into this category.[47] Additional radicals of this type were also found in jet fuel,[94] marine diesel,[88] coal tar,[95] petroleum pitch,[91] and soot[96] samples and inferred to be present in high-ranked coals[97] and petroleum mass spectra.[98,99]

The second type of doubly benzylic radicals is σ radicals that are significantly stabilized by delocalization into two aromatic systems confined by a five- or six-membered ring (Scheme 2b, **6**−**9**). This radical is largely localized on carbon in a five- or six-membered ring but can be delocalized to two aromatic systems as a result of a favorable coplanar configuration. These types of radicals can be formed (at least in theory) by losing a H atom from the CH_2 between two aromatic systems, with a prototypical example being the fluorenyl radical (**6**), which is readily found in nc-AFM images.[100] This radical can be present in either crude oil or thermally processed hydrocarbons because the C−H bond is quite weak (~80 kcal/mol),[101] probably one of the weakest chemical bonds in a hydrocarbon. Most C−H bonds are >100 kcal/mol, and C−C bonds are >90 kcal/mol.

The third type of benzylic radicals are σ radicals attached to only one aromatic system (Scheme 3c) and, hence, are stabilized by less delocalization than seen in doubly benzylic radicals that are stabilized across two aromatic systems. A prototypical example is the benzylic free radical (**10**), although the aromatic ring systems in asphaltenes would contain primarily multiple rings. Benzylic-type free radicals are more reactive than the other types of radicals and are less likely to be present in high concentrations in petroleum. Such a small probability can be compensated for by the incidental removal of a hydrogen atom from a large number of precursor molecules over geological time scales.

Scheme 3. Different Structural Features in PAHs May Contribute to Aggregation Interactions with Free Radicals[a]



[a](a) PAHs (**11**−**14**) with hidden double bonds (highlighted in red) stabilized by maximal Clar's sext structures. (b) PAHs (**15**−**17**) with diradical characters stabilized by Clar's sextets.(c) PAHs (**18**−**22**) expected in petroleum with five-membered rings, which can confer partial anti-aromatic or non-aromatic characters and, hence, charge separation. The molecular formula and molecular weight were shown to be consistent with PAHs expected in petroleum.

These three types of Radicals may be present with different probabilities in petroleum asphaltenes or involved in various processes to different degrees. π radicals are the most stable type and, hence, are most likely to be persistent radicals present in unprocessed petroleum asphaltenes. Benzylic σ radicals are the most reactive species among the three types and are significant under thermal conditions of refinery operations (T > 350 °C). Beyond the neutral free radical species, radical ions are also possible and should be considered because they can be produced by one electron oxidation or reduction of highly delocalized PAHs at various conditions, although some studies have indicated that most radicals in asphaltenes are neutral rather than radical ions.[102]

The abundance of stable free radicals in petroleum can be estimated from EPR spin concentrations. Levels of free radical have been reported in the range from 3 to 9 × 10^{18} spins/g of aphaltenes.[85,102] Assuming one spin per molecule (mono-radical) for asphaltenes with a reasonable average molecular weight of 600−900 g/mol, radicals could account for 0.3−1.3 mol %. A recent study that estimated about 1−2 free radicals per 100 asphaltene molecules[102] is consistent with this estimate. If aggregates consist of 5−8 molecules on average, then radicals should be present in up to 10 mol % of asphaltene aggregates. This fraction would increase depending upon the proportion of the asphaltene molecules, which do not participate in nanoaggregates. More studies will be needed to characterize radicals from petroleum asphaltenes to confirm the extent that the proposed structures occur and to determine their distribution.

2.2. Structural Features of PAHs of Asphaltenes.

Aromatic hydrocarbons are the main structure motifs of asphaltenes and heavy petroleum molecules as evident by their low H/C ratio and from the distinctive aromatic H and C NMR chemical shifts. FT-ICR MS combined with extrography readily identified species with high degrees of unsaturation (DBE) that are consistent with highly aromatic species with few alkyl substitutions that span a wide number of aromatic rings (from 4 to greater than 10).[39] PAHs are conjugated systems with highly delocalized electrons, and these electron-rich species are expected to have favorable interactions with free radicals. More importantly, these π electrons in PAHs, although fully conjugated, are not evenly distributed in local aromaticity, which can be predicted by Clar's sextet theory as a guiding principle.[103] Asphaltenes are also known to be enriched with heteroatoms, especially S, with a lesser degree in N and O, which are mostly incorporated in PAHs as heterocyclic compounds. Although not the focus of this discussion on hydrocarbon molecules, heteroatoms can be considered perturbations of the electronic structures of PAHs and are likely to play important roles in asphaltene solubility and aggregation.

Although numerous structures are possible for PAHs, their exact structure has recently been directly imaged by nc-AFM.[46,47,50,53] Many different kinds of aromatic structures are observed, such as alternant and non-alternant PAHs.[50] One of the significant findings in nc-AFM is that most PAHs observed thus far in petroleum are *cata*-condensed instead of *peri*-condensed as one would expect because *peri*-condensed PAHs are often more stable, with a higher degree of unsaturation. More significantly, those *cata*-condensed molecules contain many reactive sites, known as the K region (Scheme 3a, **12** and **13**), that have an enhanced double bond nature and, hence, can participate in some olefinic-type reactions, such as preferred hydrogenation and oxidation at the 9 and 10 positions of phenanthrene.[50,53,104] C═C Bonds in PAHs can range widely, from true "aromatic bonds" in benzene (bond index of 1.4) to as high as the true double bond in ethylene (bond index of 2.0), or as low as a single bond in ethane (bond index of 1.0, such as in triphenylene).[50] Most C═C bonds with the highest bond orders in PAHs have bond indices of ∼1.5−1.7 (e.g., phenanthrene has a bond index of 1.65 at 9 and 10 positions).[50] Because petroleum has a wide range of PAHs, it is reasonable to assume that a fraction of PAHs has hidden "double bonds", with a prototypical structure as in dibenzo[*g*,*p*]chrysene (**11**) and compound **14** shown in Scheme 3, similar to a molecule recently demonstrated by the Wu group.[104] These localized double bonds, hidden in PAHs, are expected to be reactive, similar to olefins, and participate in numerous reactions. In the presence of persistent radicals or more reactive transient radicals, these double bonds will prefer to react with radical centers by acting as a radical "trap" and produce a more stable radical, which can further react with other PAHs with a hidden double bond. This mechanism is analogous to polymerization of styrene, but a full polymerization of the incomplete double bonds in PAHs will be severely inhibited by the aromatic stability and steric effects. Therefore, it is likely to result in an incomplete or reversible process, resulting in an oligomer or aggregate composed of a few PAHs. The final oligomer/aggregate is still a radical species but much more stabilized from delocalization and steric effects, because it is unlikely capped by an H atom extracted from another molecule in the reservoir fluid (otherwise, it would necessarily produce a more reactive radical). Thus, it is conceivable that an oligomer or aggregate can be formed by a free radical with a number of PAHs with various degrees of double bond character, and the bond formed between the monomer PAH could be dynamic or reversible, because the oligomer or aggregate contains a radical that can be delocalized across multiple molecules and become even more stable.

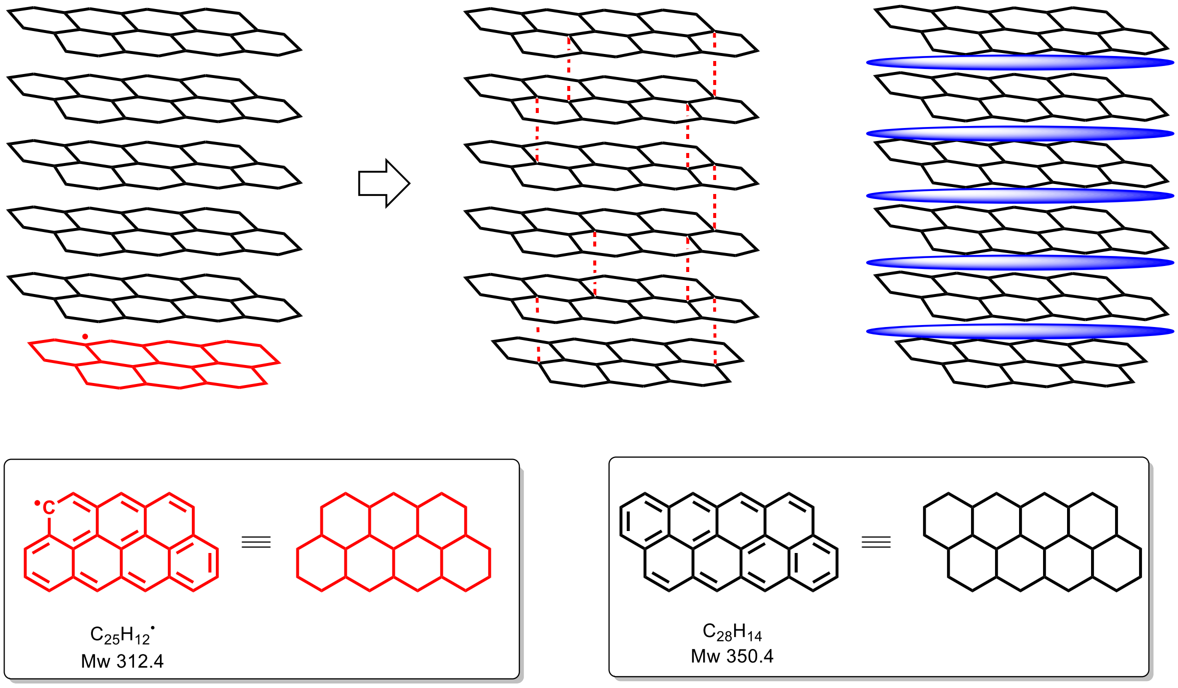
Another important factor to consider is that many PAHs are polyradicals (Scheme 3b).[105] As shown above, many non-Kekulé PAHs are true diradicals, such as the π radical triangulene. Besides these, many Kekulé PAHs demonstrate various degrees of diradical character, with a typical example shown in compound **15**, where aromatic stabilization from the maximal number of sextets leads to an open-shell radical, as recently demonstrated by the Kubo group.[105,106] There is abundant literature predicting that the radical character is increased with an increase in larger ring systems.[105] Most experimental studies are confined to small aromatic molecules as a result of the challenge of synthesizing larger species of the size expected in petroleum asphaltenes. For example, it has been predicted in the late 1990s that, starting with heptacene (seven linear rings), polyacenes adopt a diradical triplet state as their most stable ground state,[107] which has been recently found to be an open-shell diradical singlet by advanced calculations.[108,109] While we think heptacene or larger linear polyacenes are unlikely to be in petroleum PAHs because of their high instabilities,[110] recent studies have shown no more than three linear rings in petroleum PAHs (rule of three),[50] and many PAHs in petroleum are expected to have certain degrees of diradical character.[111] For example, π stacking of zethrene (**15**) was formed as a result of its hyperpolarizability and diradical character.[112] We predict that these radical centers will likely have even more favorable interaction with free radicals.

A third potentially contributing factor to be considered in the aggregation of PAHs is anti-aromatic or electron-deficient centers in PAHs (Scheme 3c, **18**−**22**), despite being generally known as electron-rich species. Many non-alternant PAHs were observed to have localized sextet rings, and the five-membered rings have decreased aromaticity, becoming non-aromatic or even of anti-aromatic character, such as fluoranthene (**18**).[50,53] Not only will these uneven distributions contribute to $\pi-\pi$ stacking through matched charge separations, they may have favorable interactions with radicals, because free radicals are both electrophilic and nucleophilic.

2.3. Pancake Bonding.

Pancake bonding is an unusual type of parallel π stacking interaction that occurs between radicals with highly delocalized π electrons.[96] First coined by Mulliken in 1969,[113] interest in pancake bonding has revived in the past decade and is being actively studied in the crystal structures of organic conductors.[114] It is differentiated from $\pi-\pi$ stacking, because it is characterized by a stabilized bonding interaction between the singly occupied molecular orbitals (SOMOs) of delocalized radicals, resulting in a stronger interaction, closer contact distances in the π-stacking direction, and preferred orientation for direct atom-to-atom overlapping. In contrast to $\pi-\pi$ stacking that generally adopts a displaced parallel "herringbone" arrangement or T-shaped geometry separated by the vdW distance (3.6 Å), pancake bonding adopts a preferred orientation, such as a columnar geometry and a much closer binding distance of 3.1−3.2 Å. The binding energy is from −9.5 to −11 kcal/mol for a prototypical phenalenyl dimer in solution,[115] significantly stronger than vdW interactions (1−3 kcal/mol) or even 3−5 hydrogen bonds (∼3−5 kcal/mol). Furthermore, the attractive dispersion energy as a result of the SOMO−SOMO interaction

Scheme 4. Schematic To Show the Potential Aggregation of Petroleum Asphaltenes through Pancake Bonding[a]



[a] Only one persistent π radical is present (shown in red) to interact with multiple PAHs (shown in black) that have different degrees of double-bond, radical, and aromaticity characters. Upon interaction, the radical center is delocalized across the oligomer or aggregate formed and is stabilized. The radical-initiated pancake-bonding interaction is a dynamic process, with fluxional bonds forming and breaking between all of the PAHs (indicated by the red-dashed lines), resulting in an extended interaction that is stronger than the $\pi-\pi$-only interaction (indicated as the general blue cloud). Possible substituents and heteroatoms are omitted for clarity.

is quite strong (−80.2 kcal/mol) and is countered by a significant Pauli repulsion (+51.7 kcal/mol) because of shortened distances, resulting in a smaller total interaction energy (−28.5 kcal/mol) for certain molecules as predicted by calculations.[114] In pancake bonding, a fluxionality between π- and σ-bonded aggregates or a covalent-like multi-electron/multi-center intermolecular interaction can occur,[116] similar to fluxional molecules, such as bullvalene, which has no permanent covalent bonds with rapid bond forming and breaking. The rings of a pancake bonded dimer become more aromatic than that of the monomer.[92] Examples of pancaking bonding in solution phase are scarce but exist, such as the TCNE radical anion dimer, dipyridyl biradicals, or viologen cation.[117] Pancake bonded dimers can be isolated by high-performance liquid chromatography (HPLC) and studied with NMR in solution and are detected by cold-spray ionization MS.[92] π-Stacked columns composed of trioxotriangulene neutral radicals has been reported.[118] Heteroatomic species, especially S- (thiophene and thiazyl) and N-containing compounds have also been reported to be involved in pancake bonding,[114] providing another potential link to heteroatom- and aromatic-rich asphaltene molecules. We predicted that this kind of interaction can be extrapolated to other intermolecular interactions among radical or ionic species between donors and acceptors, such as charge-transfer complexes, and excimers from photoexcitation of PAHs.[119]

2.4. Applying Pancake Bonding to Asphaltene Aggregation. This concept of pancake bonding emerging from physical chemistry can be applied to interactions in the aggregation of petroleum molecules. Here, we hypothesize that radicals play a key role in asphaltene aggregation as a result of the ubiquitous presence of delocalized π radicals and PAHs in asphaltenes and heavy oil fractions (Scheme 4). Although most previous studies on conductive organic materials investigated pancake bonding between homoassociated radicals or diradicals, asphaltene aggregation through pancake bonding is more likely to be a heteroassociation between a radical species and multiple diverse PAHs and/or heteroatom-containing PAHs. Because the vast majority of asphaltene molecules are closed-shell PAHs and free radicals are only present in trace amounts (0.3−1.3 mol %), radicals could account for up to 10−20 mol % of asphaltene aggregates, assuming 5−10 units for each nanoaggregate. At first glance, the interaction between a radical and closed-shell PAHs may seem to not be as strong as pancake-bonded free radical dimers (e.g., phenalenyl dimer), because the formal bond order is reduced to half and can be considered as "half pancake bonding".[120] However, we think that the larger sizes of both PAH and the delocalized π radicals expected for petroleum asphaltenes (~300−700 Da) would provide stronger interactions than that of the radical−radical interaction of smaller molecules (note that a phenalenyl radical is only 165 Da). In addition, we envision that pancake-bonded asphaltene aggregates should be enhanced by the diradical, double bond, and anti-aromatic character of PAHs and heteroatoms (especially S). We believe that pancake bonding and $\pi-\pi$ stacking interactions should be complementary rather than exclusive to the overall interaction in asphaltene aggregation.

We propose that pancake bonding is a critical element in the formation and stabilization of asphaltene aggregation. Again, pancake bonding and $\pi-\pi$ stacking interactions should be complementary rather than exclusive to the overall interaction, with the former amplifying aggregation in the presence of stable free radical PAHs, while the latter dominates in their absence. Other interactions, such as hydrogen-bonding, electrostatic, and π−cation interactions, are likely of secondary importance.

This hypothesis requires that only a small portion of the species that constitute the asphaltene fraction are PAHs that are stable free radicals. Despite their established presence, the involvement of free radicals and the potential roles that they play in asphaltene aggregation has been largely overlooked or discounted.[121] This is mostly due to the presumed irreconcilable dichotomy between the thermodynamic stability expected for persistent radicals over geological times and kinetic reactivities expected for short-lived reactive intermediates in thermal chemistry. A few previous studies have tried to address one or both sides of this dichotomy. For example, it was rationalized that caging effects or steric protection play a role in stabilizing these radicals and account for their persistence.[86,122] The second overlooked hurdle is their presumed presence in trace amounts in petroleum. However, on the basis of analysis of the literature and our own understanding, these radicals are about 0.3−1.3 mol % of the asphaltene molecules.

Building upon numerous studies on radicals and especially inspired by structures imaged from nc-AFM, we hypothesized three different types of free radicals and rationalized their relative stabilities and the potential mechanisms of their formation in petroleum. While the structures of radicals in petroleum are still largely unknown and we cannot rule out new types of radicals to be discovered in petroleum that may fall outside of the radicals discussed, we reasoned that these three types of radicals, especially π radicals and stabilized σ radicals, are the most reasonable candidates to be present.

Because stable free radicals are unequivocally and ubiquitously present at concentrations up to 1.3 mol % in petroleum asphaltenes, it seems reasonable to assume that radicals participate in aggregation at the basic level. Petroporphyrins and metals have been suggested to contribute to aggregation,[34] and their concentrations are at a similar level as free radicals. Moreover, like pancake-bonding interactions between π radicals in organic conductors, large π radicals in petroleum are expected to interact favorably with large PAHs, through their polyradical character, double-bond character, and uneven local aromaticity. Similarly, pancake bonding may further stabilize these radicals through delocalization, in addition to the caging or steric effects from aggregation. Furthermore, pancake bonding provides a more solid rationale for the preferred stacked overlap of aromatic core structures in asphaltenes than π−π stacking, in which a stacking geometry is often less preferred. Therefore, the presence of π radicals provides an alternative and likely preferred explanation over π−π stacking, although π−π stacking and other interactions are also present and will contribute to aggregate stability.

3. DISCUSSION

We rationalize the structures of stable free radicals based on their existence in petroleum and their stability over geological time and predicted that these persistent free radicals will play a role in a variety of intriguing properties in asphaltenes, especially aggregation via pancake bonding as a result of the co-existence of free radicals with a myriad of different PAHs in the mixture. Hence, pancake bonding can be considered as a special π−π stacking involving free radicals; however, the difference is that pancake-bonded nanoaggregates can be overlapped stacking columns without the π−π repulsion, and the resulting interaction is stronger.

There is circumstantial evidence that supports asphaltene molecules exhibiting pancake bonding. For example, Rogel et al. found the addition of radical initiator (benzoyl peroxide) led to a ~21 wt % increase in the precipitated asphaltene content.[134] If pancake bonding promoted by radicals is a key contributor to asphaltene aggregation, we would expect that it would result in a shorter packing distance. The packing distance in π−π stacking is bound by a vdW distance of 3.6 Å.[4,123] Packing distances of 3.55−3.70 Å were reported in the original XRD study by Yen,[15] and a wide range of distances (3.3−3.7 Å) has been reported by several subsequent works on asphaltenes.[64,69,124,125] Some report that asphaltene stacking approached that of graphite (3.34−3.35 Å), and pancake bonding has been invoked in interactions in graphite or graphenes.[114] Electron diffraction studies of asphaltene aggregates generally report shorter distances. For example, Dorset and Siskin found a distance of 3.4 Å for asphaltenes and various coke products.[126] A much shorter distance of 3.10 Å was directly measured using transmission electron microscopy (TEM), which is supported by 3.26 Å determined by XRD in the same study.[67] A packing distance of 30% less than the vdW distance (3.5−3.6 Å) strongly indicates that a greater association mechanism, likely pancake bonding, is at play in asphaltene aggregation. Therefore, it is important to reexamine the XRD patterns of asphaltenes with proper calibration compounds and with advanced techniques. Future studies should provide cross validation of the packing distance using different techniques.

It should be noted that a crystalline behavior for asphaltenes was assumed in Yen's original and many subsequent XRD studies. Since then, corrections for the contributions from amorphous disordered aromatic carbons were proposed by Ruland,[127] which have become a standard method for correcting the amorphous halos in XRD. Ebert showed that the aromaticity quantification by Yen via aromatic and aliphatic carbons from diffraction was likely oversimplified,[20,21] and the assumption of crystalline behavior is questionable for asphaltenes and vacuum resids based on a comparison to model compounds.[22] Later, Andersen et al. pointed out that the interpretation of broad diffraction peaks in asphaltenes is highly affected by a few parameters, including curve-fitting and baseline corrections.[69] Modern approaches to interpret broad diffuse signals in X-ray scattering data in soft materials are described in a recent review.[128] In addition, it is important to understand to what extent the results from a solid state can be applied to a liquid state, because most XRD studies on asphaltenes were reported on the isolated solid (or coagulated) state rather than the liquid phase or solution state occurring in crude oils.

On the basis of previous studies on smaller molecules, pancake bonding, although much stronger than vdW interactions and even stronger than the sum of 3−5 hydrogen-bonding interactions, is about ~10−20 kcal/mol for a homodimer of phenalenyl radicals. It seems unlikely that this binding interaction would withstand the temperatures associated with covalent bond breakage. One potential explanation is provided by analyzing the nature of interaction. The smaller net interaction is a consequence of a rather strong associative interaction by SOMO−SOMO (on the order of a covalent bond) counterbalanced by a strong Pauli repulsion as a result of a closer distance. It seems reasonable to assume that, when the distance increases during dissociation, the attractive interaction is reduced as well as the Pauli repulsion, with a net interaction that remains more or less unchanged. This indicates that interactions through pancake bonding are rather broad on the potential energy surfaces, and computations have suggested a broad range as well.[114] Pancake bonding, thus, is important over a long distance, longer than vdW or even dispersion forces alone, especially in the presence of an organic solvent.

To confirm this hypothesis on pancake-bonded asphaltene aggregation and quantify the interactions, more studies are needed comparing model compounds to petroleum asphaltenes. The structures of free radicals are challenging to characterize, and EPR is the most powerful current tool to do so. Not only does EPR provide definitive evidence for the presence of radicals but also provides quantitative concentrations of these radicals. More advanced high-frequency EPR[102] and pulsed EPR techniques [e.g., electron nuclear double resonance (ENDOR)] can also be used to study the structure of these free radicals.[129] Higher resolution MS could also provide a clue on the presence of radicals in petroleum from the presence odd masses or odd carbons, although neutral free radicals themselves cannot be directly detected and only ions (or radical ions) can be detected by MS. A closer look of these species using MS will be helpful in this context, by understanding ionization mechanisms and susceptibility of monomeric free radicals or their aggregated form. The effect of paramagnetic radical species on NMR data should be considered when applying NMR to characterize structures or to study $\pi-\pi$ stacking and aggregation of asphaltene samples.[130] The presence of pancake bonding in π dimers has been studied by NMR, although prudent analysis as a result of the presence of paramagnetic radicals should be re-examined carefully as well as in interpreting the traditional liquid- or solid-state NMR results. Techniques that take advantage of both electron and nuclear spins, such as ENDOR or chemically induced dynamic nuclear polarization (CINDP), should be considered.

Direct molecular imaging using nc-AFM will continue to provide direct and credible structural information on free radical species. Of particular note is the orbital imaging via scanning tunneling microscopy (STM) that can distinguish free radicals by their distinguished SOMO compared to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for closed-shell molecules. One of the major limitations is that only one to two free radicals can be expected to be found in 30−50 molecules imaged; nc-AFM methods are currently time-consuming, and such a study approaches the practical limit. This could be improved by developing a preparation method that yields a radical enriched fraction. Further development in the instrumentation and automation of image acquisition and analysis will be needed to provide a more comprehensive survey of asphaltene molecular structures.

Computational studies will also be helpful to understand the significance of pancake bonding in asphaltene aggregation based on PAH structures proposed in Schemes 2 and 3 and previously published AFM structures.[46,50,53,91] Considerable theoretical calculations have been performed on prototypical phenalenyl radicals in studying pancake bonding,[72,73,114,131] although applying these methods to larger PAH systems that are relevant to petroleum asphaltenes are expected to be computationally challenging. Previous studies also showed that advanced methods, such as coupled cluster calculations, are required to accurately predict intermolecular interactions between closed-shell structures,[5] and hence, their applications to open-shell structures or between open- and closed-shell structures would be important and worth exploring.

4. CONCLUSION

We reviewed various concepts and models of asphaltenes focused on the bonding structure and interactions that result in aggregate formation. Several non-covalent interactions, including hydrogen-bonding, electrostatic, $\pi-\pi$ stacking, vdW, and dispersion forces, have all been evoked to explain the behavior exhibited by asphaltenes. We proposed a new hypothesis that geologically stable PAH radicals are present in sufficient proportion to be a significant contributor to asphaltene aggregation via pancake bonding. This hypothesis is consistent with petroleum asphaltene structures derived from EPR, ultrahigh-resolution FT-ICR MS, and AFM imaging as well as the thermal stability of asphaltene aggregates. It does not exclude other interactions contributed from heteroatoms (such as hydrogen bonding), and all of these should work in concert. Future studies are needed to confirm and quantify these various interactions, and we propose various ways to experimentally or computationally advance this hypothesis and our fundamental understanding on the structure and properties of asphaltenes.

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Notes

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