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Supramolecular Assembly Model for Aggregation of Petroleum Asphaltenes

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ABSTRACT: The components of petroleum asphaltenes exhibit complex bridged structures comprising sulfur, nitrogen, aromatic, and naphthenic groups linked by alkyl chains. These components aggregate in crude oil and toluene over a wide range of concentrations and temperatures, exhibit strong adhesion to a wide range of surfaces, occlude components that are otherwise soluble, are porous to solvents, and are elastic under tension. None of these properties is consistent with an architecture dominated only by aromatic stacking by electrostatic and/or van der Waals forces, often called $\pi-\pi$ stacking. We propose an alternate paradigm based on supramolecular assembly of molecules, combining cooperative binding by Brønsted acid–base interactions, hydrogen bonding, metal coordination complexes, and interactions between cycloalkyl and alkyl groups to form hydrophobic pockets, in addition to aromatic $\pi-\pi$ stacking. A range of architectures are suggested, which almost certainly occur simultaneously, including porous networks and host–guest complexes. The latter may include organic clathrates, in which occluded guest molecules stabilize the assembly of a cage, as methane does in gas hydrates. This model has a number of implications for analysis of asphaltene mixtures and predicting asphaltene phase behavior and transport properties.

INTRODUCTION

For almost 90 years, the dominant conceptual model for aggregation of petroleum asphaltenes has been based on clusters of aromatic components in a surrounding medium of less aromatic components. Drawing on the then recent work on surfactant micelles, Nellensteyn¹ and Pfeiffer and Saal² suggested segregation of highly aromatic species from the bulk of the oil, with polar components serving to promote the dispersion of these colloidal aggregates in the oil. Later elaboration of these ideas by Dickie and Yen³ and Mullins and co-workers^{4–6} stressed the formation of clusters of molecules by $\pi-\pi$ stacking of aromatic rings.

We challenge this paradigm for asphaltene behavior, because it is unable to predict or reconcile a disparate range of experimental observations, from the molecular to the macroscopic scale. Drawing on recent research in materials chemistry, on inclusion compounds and organic clathrates, we propose that supramolecular assembly of petroleum components provides a much more powerful context for understanding, modeling, and predicting asphaltene behavior. The driving forces for this assembly includes molecular recognition and host–guest interactions in three-dimensional porous networks. In this conception of asphaltene behavior, the $\pi-\pi$ stacking of aromatic rings is a contributing factor rather than the dominant motif. This paper presents a brief review of asphaltene behavior, presents new data on the behavior of an alkyaromatic model compound as a test, and then draws on the recent literature to propose a new view of the physical structure of asphaltene aggregates.

CANONICAL BEHAVIOR OF PETROLEUM ASPHALTENES

The composition and behavior of petroleum asphaltenes has been studied by diverse experimental methods, giving rise to

rapidly growing literature. Here, we list the most important experimentally determined attributes of the petroleum asphaltenes that must be consistent with any model for aggregation. (1) Molecular complexity: Crude oil compounds contain a number of functional groups that can give associative interactions in the liquid phase, including carboxylic acids, nitrogen bases, aromatic rings, carboxylic esters, and porphyrins.⁷ Attached groups, such as alkyl chains and steranes (i.e., polycyclic naphthenes) modify and direct these interactions. Because of the aggregation of the asphaltenes, complete molecular analysis by mass spectrometry has not yet been achieved. Pyrolysis of asphaltenes demonstrates a complex range of attached pendant groups, including aromatics and naphthenes.^{8–12} Recent work has demonstrated that addition reactions under catagenic conditions yield alkyl-bridged polycyclic aromatic species¹³ that can easily contain more than one functional group. (2) Heterogeneous aggregation and coagulation behavior: The precipitation of the asphaltenes by the addition of a *n*-alkane solvent generates a mixture that separates from the oil because of both coagulation of colloidal aggregates and simple insolubility. We use the term coagulate to indicate direct contact between the aggregates. The aggregated material in the asphaltenes, which we define as multicomponent structures that are aggregated in the original crude oil and in solvents, such as toluene, will always be a subset of the total precipitated asphaltene sample, in combination with species that do not associate at all¹⁴ but are simply insoluble. The coagulation of the aggregates is consistent with a change from repulsive interactions between the aggregates in toluene to attractive

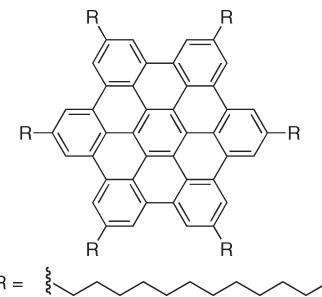
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interactions in *n*-heptane. Among the various aggregates, there is a wide range of stability, which precludes applying concepts of critical concentration.¹⁵ Many of the aggregates dissociate as the concentration is decreased⁵ or as the temperature is increased,¹⁶ but to date, the complete deaggregation of natural asphaltene has not been verified. Consequently, we must allow for a wide range of aggregate stability in solvents, such as toluene, and in the original petroleum. Similarly, we must be cautious about assigning a size to the heterogeneous population of aggregates, but a range of analytical techniques put the mean aggregate size in the range of 2–20 nm.^{5,14,17–20} Evidence suggests a range of sizes in a polydisperse distribution;²¹ therefore, we need to be cautious about stressing mean values too much. The interpretation of data from scattering methods has been questioned,²² but the physical separation of aggregates from crude oil by filtration²³ and from dilute solution by centrifugation⁵ and dialysis²⁴ suggests the presence of aggregated material with very slow kinetics of dissociation. (3) Occlusion in asphaltene aggregates: The precipitation of asphaltenes always results in the entrapment of material that is normally soluble in *n*-pentane or *n*-heptane. Dissolution and reprecipitation will give less and less recovery of asphaltene solids with each cycle because the amount of occluded material is decreased. For example, Strausz et al.²⁵ found that six successive cycles of dissolution and reprecipitation with *n*-pentane gave mass loss at each step, to a cumulative amount of 22%. No steady state was reached. Some loss of material would be expected because of simple partitioning of the asphaltenes with the solvent, but in this case, the aggregates can occlude saturated compounds, such as sterane biomarkers, which are otherwise miscible with heptane.²⁶ In the most extreme example, reactive biomarkers were so effectively protected in the asphaltene aggregates that they were stabilized over geological time.²⁷ (4) Porosity of asphaltene aggregates: On the basis of the work with deuterated solvents, portions of the asphaltene aggregates are porous enough to enable exchange with surrounding solvents. For example, Verruto and Kilpatrick²⁸ used neutron scattering of asphaltenes in binary solvents to probe which solvents entered the aggregates. They found enrichment of toluene inside the aggregates in preference to decalin or *n*-heptane. Measurements of relaxation times and diffusion rates for asphaltenes and maltenes by nuclear magnetic resonance (NMR) spectrometry also suggest that the aggregates are porous and readily admit mobile species.²⁹ Models that combine scattering experiments with viscosity measurement suggest that an open fractal structure best describes aggregate structure in strong solvents, such as toluene, implying a porous structure.²¹ (5) Adhesion to surfaces: Asphaltenes adhere avidly to a range of surfaces,³⁰ particularly to oxides, such as alumina and silica. This adhesion was the reason why asphaltenes must be precipitated before column chromatography analysis by the saturates, aromatics, resins, and asphaltenes (SARA) method. Both adhesion of aggregates and adsorption of molecular components would contribute to the total amount of asphaltene on a given surface. The irreversible adhesion and adsorption of the asphaltenes interferes with the chromatographic separation of the resins, aromatics, and saturates. The adhesion and adsorption of asphaltenes to silica can be suppressed by incorporating alkyl chains on the silica surface;³¹ attachment is insignificant on low-energy surfaces, such as polytrifluoroethylene.³² (6) Formation of films at oil–water interfaces: Asphaltenes combine with surface-active components of crude oil and colloidal mineral particles to form viscoelastic films at oil–water interfaces, playing

Scheme 1. Hexa-dodecyl-hexa-*peri*-hexabenzocoronene (C_{12} -HBC)



a critical role in the stabilization of water-in-oil emulsions.^{33–37} In this case, aggregation of molecules at the interface is difficult to distinguish from attachment of preformed aggregates with subsequent interactions and restructuring, but the resulting films are stabilized by incorporation of water and can be highly resistant to dispersion in solvents.³⁴ (7) Mechanical properties: Asphaltene aggregates deposited on mica will adhere to the probe tip of an atomic force microscope.³⁸ The elastic extension of the aggregates is consistent with a long-chain polymer under pulling by an external force. The rigidity of the aggregates in water was dependent upon the water chemistry, so that lower solution pH values and the presence of divalent cations reduced the bending rigidity of the aggregates. Similarly, aggregates on silica in solvent behaved like polymers, with properties that depended up on the solvent composition.³⁹ (8) Interactions with resins and surfactants: Agrawala and Yarranton⁴⁰ found that the apparent molecular weight of asphaltenes in toluene, as measured by vapor-pressure osmometry, depended upon both the concentration of the asphaltene and the concentration of resin components in the solution. This behavior is consistent with assembly of aggregates by stepwise addition of propagator components (i.e., asphaltenes) with the termination of the addition sequence by the addition of smaller resin components. Petroleum resins can also alter the rheology of crude oil when the volume fraction of asphaltenes is high,⁴¹ and surfactants, such as aromatic sulfonates, can completely suppress the coagulation and precipitation of the asphaltenes when solvents, such as *n*-heptane, are added.⁴²

Even a cursory examination of this list will demonstrate that these properties are inconsistent with a model of aggregation only by stacking of alkyl-aromatic components. Readers who are familiar with the literature may want to add further to this list of requirements, as necessary tests for a comprehensive model for molecular organization in asphaltenes. To emphasize the limited ability of aromatic π – π -stacking to serve as the dominant organizing force for asphaltenes, we consider the case of a very large alkyl-aromatic compound.

■ TEST OF THE π – π STACKING PARADIGM: ALKYL HEXABENZOCORONENE

The hexabenzocoronenes have been thoroughly investigated by Müllen and co-workers as interesting graphene fragments with novel electrical and optical properties.^{43–45} These 13-ring condensed aromatics give strong association in solution based on electrostatic and van der Waals forces through face-to-face stacking of the large planar aromatics, commonly called π – π stacking. We have investigated solutions of the hexa-dodecyl-substituted version of this compound (Scheme 1; C_{12} -HBC) in

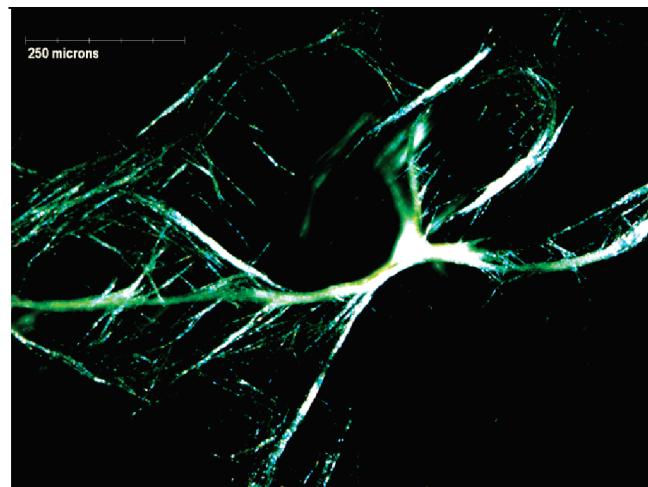


Figure 1. Microscopic images of the C_{12} -HBC organogel in toluene.

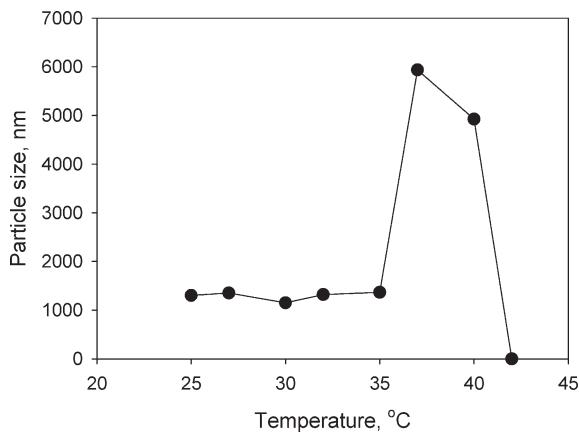


Figure 2. Apparent particle size of $30 \mu\text{M}$ C_{12} -HBC in toluene by dynamic light scattering. From $25\text{--}35^\circ\text{C}$, C_{12} -HBC formed a fibrous network, and the length scale (*y* axis) from light scattering is dominated by the cross-section of the fibers. At 37 and 40°C , the mixture gave short fibers in suspension, giving much larger apparent dimensions. At 42°C , no aggregation was detected down to a size of $<1\text{ nm}$.

toluene. At low temperatures, this compound forms a weak organogel at a concentration of $30 \mu\text{M}$ (46 mg/L). The gel structure resembles cotton wool, with a network of fibers as illustrated in Figure 1, with toluene solvent in the open volume between the fibers. These fibers do not adhere to glass surfaces, and they completely dissolve at 42°C (Figure 2). At 70°C , measurement of the apparent molecular weight of the C_6 -HBC analogue in toluene by vapor-pressure osmometry revealed only the presence of dimers in toluene solution.⁴⁶

The fibers imaged in Figure 1 and measured in Figure 2 consist of stacks of HBC groups, with the alkyl side chains radiating outward,⁴⁷ based on X-ray diffraction, X-ray scattering, and modeling;⁴³ therefore, C_{12} -HBC presents an extreme example of the type of stacking proposed by Dickie and Yen.³ The linear side chains on this compound enable stable aggregates in solution, because analogous compounds with attached $C_4\text{--}C_{24}$ branched alkyl groups give weaker aggregation. Despite the large size of the aromatic group and the lack of steric interference from the peripheral side chains, the association of this compound was much weaker than the observed association of asphaltene

compounds. Even C_{96} core structures, comprising 34 aromatic rings, are soluble when substituted with suitable alkyl groups.⁴⁸

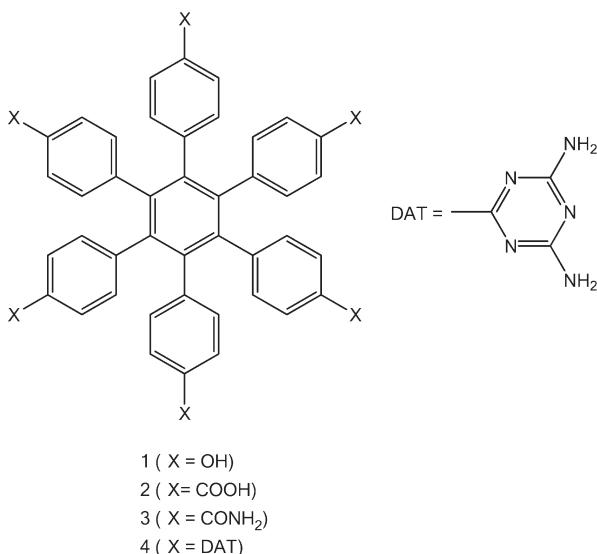
Active assembly of asphaltenes to give multimers was detected in toluene at 70°C by Agrawala and Yarranton,⁴⁰ conditions that give at most dimers for C_6 -HBC and no detectable particles (down to $<1\text{ nm}$) for C_{12} -HBC (Figure 2). In a melt, C_6 -HBC forms liquid crystals by $\pi\text{--}\pi$ stacking that persisted to well over 300°C ,⁴⁶ but toluene competes successfully for adsorption to the planar aromatic ring, so that stacking in solution is weak and equilibrating at room temperature. Similarly, liquid crystals in maltenes and asphaltenes are effectively disrupted by exposure to toluene vapors.⁴⁹ These results show that the $\pi\text{--}\pi$ stacking of even very large aromatics is too weak in toluene solutions to account for aggregation of asphaltenes in highly dilute solution or at elevated temperature.

Asphaltenes exhibit strong adhesion to surfaces, such as silica and alumina (property 5 above). In contrast, our studies using C_{12} -HBC fibers show no significant adhesion to glass in toluene solution. The purification of C_6 -HBC after synthesis was accomplished using column chromatography on silica gel to elute the purified product, using $\text{CH}_2\text{Cl}_2/\text{hexanes}$ (1:1) as eluent, following the synthetic method used to prepare C_{12} -HBC. On this basis, the hexa-alkyl HBC series of compounds adsorbs on silica gel in hexane but desorbs in stronger solvents; therefore, they would be classified as resins. A large aromatic group does not give strong adsorption on silica, and the alkyl side chains have minimal interaction. Indeed, appending alkyl chains to a silica surface suppresses the adhesion and adsorption of asphaltenes.³¹ Consequently, alkylated aromatics, as a class, fail to model the interactions of asphaltenes with oxide surfaces like silica.

SUPRAMOLECULAR ASSEMBLY OF ASPHALTENES INTO NANOAGGREGATES

The construction of molecular assemblies by noncovalent interactions of smaller components or building blocks is referred to as supramolecular chemistry. The range of molecular weight in petroleum, up to 10^3 Da, fits in the scope of supramolecular chemistry, although most work to date has been on components of <500 Da. The results of supramolecular assembly include a wide range of structures, such as micelles, fibers (e.g., Figure 1), tubes, porous materials, and designed functional molecules for

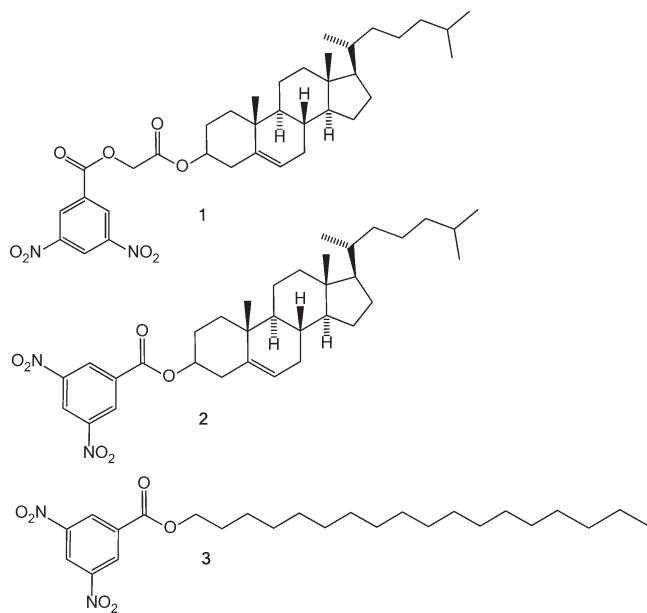
Scheme 2. Hexaphenyl Benzene Derivatives for Porous Crystals⁵⁹



self-assembly. In petroleum asphaltenes, we have an extraordinarily complex mixture of diverse components; therefore, any supramolecular assembly will be randomized, resulting in very limited length scale of structure. Long-range ordering, such as the fibers in Figure 1, is unlikely in such mixtures. Supramolecular assembly can result from a wide range of noncovalent interactions that give thermodynamically stabilizing association; in petroleum, we would expect such supramolecular assemblies to represent at least local energy minima. The subset of intermolecular interactions relevant to petroleum is well-known and has been elaborated by Murgich⁵⁰ and others to include the following. (1) Acid–base interactions: Brønsted acidic species, such as carboxylic acids, can interact directly with bases, such as pyridine groups, forming salts.^{51–54} In our opinion, ionic association represents the strongest interaction driving asphaltene aggregation. (2) Hydrogen bonding: Groups such as hydroxyls and carboxylic acids can participate in hydrogen bonding with weak nitrogen bases, and nitrogen bases can associate with each other through mutual hydrogen-bonding interactions with water.⁵⁵ (3) Coordination complexes: The concentration of vanadium and nickel is low, but these species can contribute by axial coordination to bases,⁵⁶ as well as hydrogen bonding to the vanadyl oxygen. (4) The association of apolar, cycloalkyl, and alkyl groups in hydrophobic pockets driven by van der Waals interactions, similar to the behavior of steroidal or lipid bilayers. (5) π – π stacking: This interaction is rather controversial and ill-defined,⁵⁰ but it is commonly used to describe van der Waals and induction-type interactions between parallel aromatic ring systems.^{57,58} Arenes containing electronegative nitrogen or oxygen atoms can serve as acceptors, resulting in complementary interactions with electron-rich arene groups.

Each of these interactions is relatively weak in isolation, but a crucial principle of supramolecular chemistry is that strongly associated structures arise from the cumulative effects of multiple weak interactions. At the other extreme are weaker forces between molecules that exhibit only a single mode of interaction, such as the association of toluene with C₁₂-HBC in the example above.

Scheme 3. Compounds Based on 3,5-Dinitrobenzoate (1, Intermediate Flexibility; 2, Rigid; and 3, Flexible) Assemble with Anthracene To Form Fibers in Solution⁶⁰



The literature on supramolecular chemistry is growing exponentially, although only a subset is of interest for petroleum behavior. Rather than presenting a review of this literature, we instead offer selected case studies of interactions in pure, well-characterized systems that we believe are instructive for petroleum.

Porous Organic Networks with Significant Accessible Volume. Crystallization of derivatives of hexaphenyl benzene (Scheme 2) gives hydrogen-bonded networks with significant open volume for penetration of small molecules.⁵⁹ The accessible pore volume in these hydrogen-bonded networks can range up to 75% of the total volume, depending upon the specific methods of forming the crystals. Less porous but very robust networks have been observed because of salt-forming interactions between pyridine bases and carboxylic acids.^{51–54}

Recruitment of Aromatic and Naphthenic Structures. Two-component assembly in solution was reported by Siccis et al.,⁶⁰ mediated by donor–acceptor complex formation between electron-deficient esters of dinitrobenzoic acid (1–3) and anthracene (Scheme 3). The acceptor ester by itself is insufficient to yield ordered structures; polycyclic aromatic diluents are required to yield visible fibrous structures in solution. In this work, the ratio of the components could be as high as 15 mol of aromatic compound/1 mol of acceptor. This model system indicates that large quantities of aromatic material, engaged in weak π – π stacking, can be aggregated cooperatively with low concentrations of a strong electron acceptor, while neither component by itself gives rise to aggregation. Another interesting aspect of this model mixture is the participation of appended naphthenic groups, in this case, cholesterol, in forming stable structures. Such structural elements are ubiquitous in petroleum, and their potential role in stabilizing aggregated structures has not been discussed previously.

A second example of aromatic–naphthenic aggregation was reported by Abdallah and Weiss,⁶¹ who observed aggregation of the anthracene–cholesterol derivative illustrated in Scheme 4.

Efficient formation of self-aggregated fibers (similar in appearance to Figure 1) in organic solvents results in gelation, where the liquid solvent is retained in the pores between the fibers. Although bulk gelation is important in wax deposition in petroleum, the complexity of the asphaltenes precludes the formation of such large aggregates from long-range association of repeat units. The literature on organogels is useful instead in demonstrating motifs for aggregation of building blocks in a solvent environment. The anthracene–steroid conjugate is particularly compelling because it is a feasible component in heavy petroleum, comprising anthracene and cholestanone joined by ester functionality. Aliphatic and aromatic esters have been found in the asphaltene fraction of bitumens.¹⁰

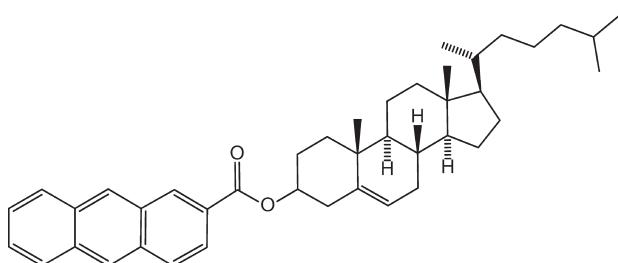
Host–Guest Inclusion Compounds and Clathrates. Dependent upon the organization of the organic framework, the size of the cavities can be small enough to promote specific molecular interactions with additional component(s) in solution. The interaction between the host network or aggregate and the guest compound can be highly cooperative, so that the two species interact synergistically to give a more stable structure than either of the components separately. One example of this interaction occurs in gas hydrates, which trap compounds, such as methane and hydrogen sulfide, in a solid lattice of water molecules at temperatures well above the freezing point of the gas. A clathrate is the combination of a closed cage and a guest compound. The terms inclusion compound, inclusion complex, clathrate, and host–guest complex are used interchangeably in the literature. These aggregates are commonly studied in pharmaceutical chemistry because they give rise to polymorphs during crystallization.⁶² One potentially relevant clathrate comprises a pyrene derivative that organizes ordered complexes with benzene solvent (structure H2 in Scheme 5). The host–guest stoichiometry

is 1:3, and the occluded benzene molecules begin to escape from the lattice only at 150 °C, i.e., well above the boiling point of pure benzene. The clathrate is stabilized by C–H···O hydrogen bonding and by C–H···π hydrogen bonds. When the same compound H2 is crystallized from dimethyl ether in the presence of naphthalene, it forms a lattice with four molecules of the host and four naphthalene and four dimethyl ether solvent molecules in each unit cell. This example nicely illustrates that cooperative interactions in host–guest complexes can involve the simultaneous and spontaneous assembly of multiple molecules with different structures.

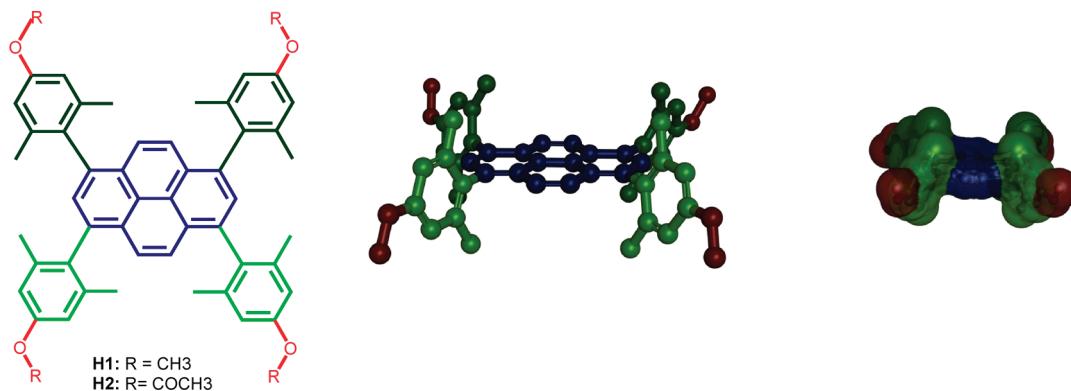
Role of Water in Aggregation. Water plays a significant role in the aggregation behavior of asphaltenes, because of its ready participation in hydrogen-bonding networks and its ubiquitous presence in crude oil systems. Association because of water has been observed in asphaltene solutions by calorimetry⁶⁴ and with pyridine model compounds.⁵⁵ In the broader context, self-assembly of steroids into superstructures based on hydrophobic effects is a common motif in supramolecular chemistry,^{65–67} while encapsulating small water clusters within hydrogen-bonding networks is also well-documented.^{68–71} Water is a ubiquitous presence in petroleum, but its role in driving asphaltene aggregation has received little attention.

Representative Asphaltene Aggregate. We suggest that the general motifs of supramolecular assembly observed in simple mixtures are equally relevant to asphaltene aggregation and that the stoichiometry and thermodynamics of aggregation in complex petroleum mixtures will follow the trends discussed by Agrawala and Yarranton.⁴⁰ Strong donor–acceptor interactions, such as illustrated in Scheme 3, will be absent in petroleum, but the large asphaltene molecules will engender multiple cooperative associations, combining acid–base interactions, hydrogen bonding, metal coordination, hydrophobic pockets, and aromatic π–π stacking, as embodied by the “representative structure” shown in Figure 3. These aggregates must be considered as at least ternary complexes that arise from the mutual interactions of host molecules, guest molecules, and solvent(s). We view host molecules as components that have at least two centers for interaction with other components, so that, following the terminology of Agrawala and Yarranton,⁴⁰ they can propagate an extended supramolecular network. Guest molecules may include a range of small and large alkyl aromatics, as demonstrated by Sicsic et al.⁶⁰ and Natarajan et al.,⁶³ and naphthenes, as observed by Yang et al.²⁶ and Zhao et al.²⁷ Low-molecular-weight species, including solvents, can serve as terminators of the assembly

Scheme 4. 2-Cholesteryl-antranilic Acid Assembles To Form Fibrous Networks in Organic Solvents⁶¹



Scheme 5. Tetraaryl Pyrene Crystallizes To Give Clathrates with Benzene and Naphthalene



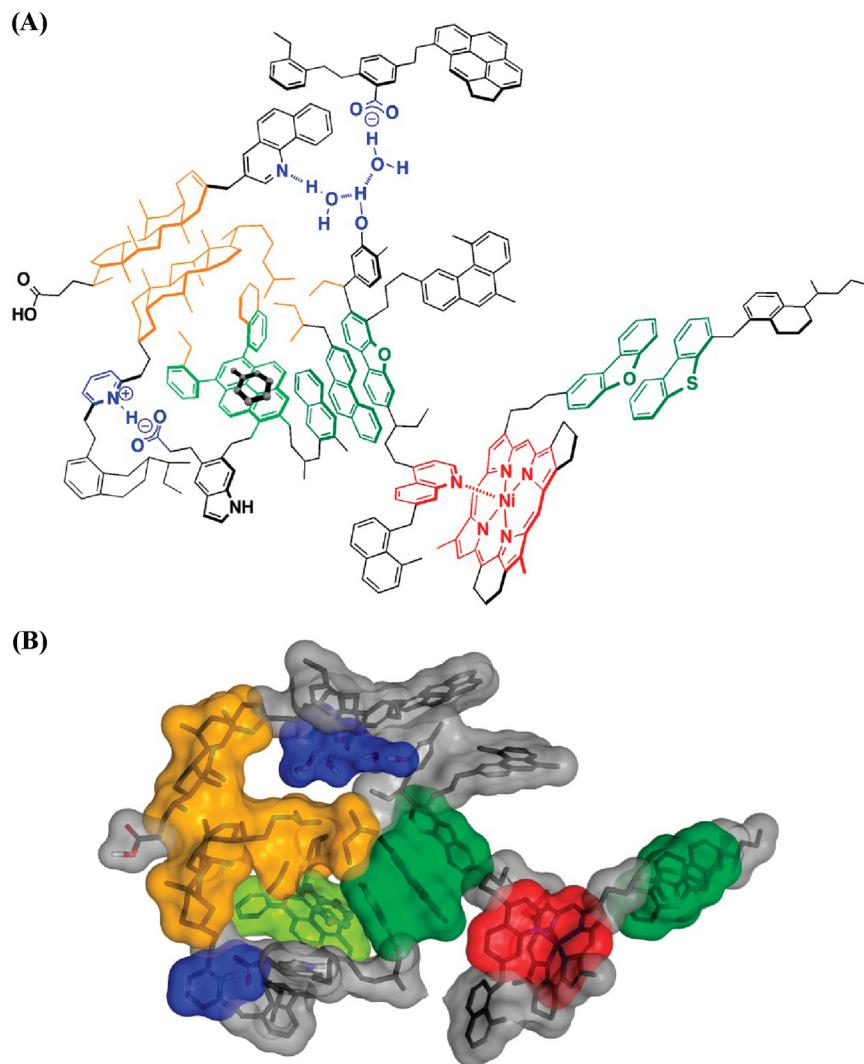


Figure 3. Schematic representation of a supramolecular assembly composed of host and guest species in a representative asphaltene aggregate. Associations between molecules are color-coded in (A) the molecular depiction and (B) the space-filling version: acid–base interactions and hydrogen bonding (blue), metal coordination complex (red), a hydrophobic pocket (orange), π – π stacking (face-to-face dark green; within a clathrate containing toluene, light green).

process if they have only one site for interaction with the supramolecular network.⁴⁰

We suggest that multicomponent assemblies of this type are consistent with the known chemistry of petroleum and are consistent with the canonical properties of the asphaltene fraction listed above. No specific molecular motif is required, but clearly bridged aromatic groups with multiple sites for association will be the main host compounds, while simpler components will be guests. The size and shape of the aggregates will be highly variable, giving significant polydispersity in the population. The stability of the aggregates will be broadly distributed in terms of concentration and temperature thresholds, depending upon the local thermodynamic minima attained by the assembly of randomly combined components, driven by individual cooperative interactions. Although π – π stacking contributes to this representative structure, the size of these domains is much smaller than the overall size of the aggregates, consistent with recent high-contrast scattering studies.⁷² Occlusion of a range of components inside the aggregates and sufficient porosity to enable solvent access are intrinsic to

this type of assembly, as depicted in Figure 3B. Strong adhesion to surfaces and interaction with smaller molecules in solution are facilitated by exposed functional groups on the exterior of the assembly. In contrast to an exterior of alkyl chains, as proposed by Dickie and Yen,³ these supramolecular aggregates can express a wide range of groups to interact with solid surfaces and oil–water interfaces. Agglomerates with multiple groups on the surface are consistent with irreversible binding to surfaces, such as silica, while polar or charged groups on the surface would favor oil–water interfaces. As a network structure, the supramolecular assemblies can respond to external forces by compressing or undergoing elastic elongation, consistent with the mechanical properties of the asphaltene aggregates. Given the assembly of building blocks in solution, this type of aggregation process is entirely consistent with the dependence of the apparent molecular weight upon both composition and concentration. We expect that the polymerization model of Agrawala and Yarranton⁴⁰ can be extended to represent the development of the aggregate network and the incorporation of guest compounds.

■ COLLOIDAL INTERACTIONS OF ASPHALTENE NANOAGGREGATES

As noted in point 2, the precipitation of asphaltenes from crude oil upon dilution with *n*-alkane solvent is a definitive property. This precipitation is generally induced at modest temperatures and high concentrations, conditions under which a significant population of asphaltene aggregates are already present in the crude oil. The precipitation of asphaltenes can be viewed in two self-consistent ways: as a phase separation to form a fluid that is below its glass transition temperature²² or as coagulation of a colloidal suspension. The colloidal paradigm is more convenient when we describe the behavior of molecular aggregates, especially under dilute conditions,⁷³ on surfaces and at oil–water interfaces, therefore, we use this framework for analyzing the interactions between the aggregates. Following the colloidal paradigm, the addition of a *n*-alkane solvent has three principal effects on the mixture: (1) The net force interactions between the aggregates change from repulsive to attractive. (2) Changes in the aggregate population occur in response to the shift in the solvation strength of the hydrocarbon medium. (3) Low solubility components, such as vanadyl porphyrins and other highly aromatic species, will precipitate from solution. Pre-existing aggregates likely serve as nucleation sites for this precipitation.

Recent work by Wang et al.³⁹ illustrates how the addition of *n*-heptane gives coagulation and precipitation of asphaltene aggregates primarily by changing the colloidal interactions in solution. They used atomic force microscopy to measure forces between a film of asphaltene and a probe coated with asphaltene. When the liquid medium was >80 vol % toluene, balance *n*-heptane, the force between the asphaltene films was repulsive. For <20 vol % toluene (balance *n*-heptane), the forces were attractive. The attractive forces in pure *n*-heptane were completely consistent with van der Waals forces.

The second important observation from Wang et al.³⁹ is that the distances of interaction between the asphaltene surfaces are strongly dependent upon the solvent medium. In pure toluene, the films begin to repel at a separation of ca. 60 nm (relative to the final minimum separation). In contrast, the same films in *n*-heptane do not interact until the separation is only 5–7 nm. In a strong solvent for aromatic material, therefore, the asphaltene films swell and likely extend attached groups into the solution. In a weak solvent, the structure collapses to give a minimal distance. Wang et al.³⁹ attributed the difference to extension of bridged aromatic groups into the solution in toluene, giving interactions similar to a polymer brush over a significant distance. Clearly, the type of assembly depicted in Figure 3 is consistent with this behavior. A flexible network that admits solvent can swell or contract in response to the solvent strength, much like a polymer material. Similarly, solvation of groups on the surface of an aggregate will determine whether they extend into solution or lie close to the aggregate surface.

Many studies have found that Hildebrand or Hansen solubility parameters are useful for correlating the onset of asphaltene coagulation, expressed through *P* values, *S* values, or compatibility index.⁷⁴ These useful relationships would seem to imply that asphaltenes are soluble initially then precipitate when the solvent medium changes. This assumption of phase separation underlies thermodynamic models for asphaltene coagulation⁷⁵ and is supported by measurement of properties of asphaltenes, such as swelling,⁷³ surface tension, and viscosity.⁷⁶ However, as

demonstrated by Wang et al.,³⁹ changes in repulsive forces and the strength of van der Waals interactions between asphaltenes also change in response to the composition of the liquid medium.

The two paradigms for asphaltene precipitation, i.e., phase separation and colloidal coagulation, have an intersection in the use of solubility parameter. The concept of cohesive energy density or solubility parameter and derived measures, such as *S* value, *P* value, and compatibility index, work just as well for stability of colloidal suspensions in non-aqueous media as for true molecular solubility. The application of solubility parameters has included many studies on colloidal suspensions in paints and pigments.⁷⁷ An extreme example illustrates this point. Machula and Dekany⁷⁸ investigated the stability of hydrophobic silica particles (20 nm in diameter) in mixtures of *n*-heptane and benzene. On the basis of rheology and light scattering, the silica particles were stable in benzene-rich mixtures but flocculated in *n*-heptane. The explanation was that benzene adsorbed onto the silica surfaces, reducing the van der Waals attractive force and giving a stable suspension. At high heptane concentrations, the surfaces were not coated with aromatics and the particles flocculated. In a second example, Zahabi et al.⁷⁹ dispersed 1 μm silica spheres in a solution of asphaltenes in toluene. Asphaltene material adsorbed on the silica to give a stable dispersion. When *n*-pentane was added, the silica spheres flocculated because of the interaction of the adsorbed asphaltenes and sedimented at concentrations just below the onset of precipitation of the asphaltenes in solution. In this case, asphaltene-coated surfaces on 1 μm spheres gave flocculation at a slightly higher solubility parameter in the solution than the 2–20 nm asphaltene aggregates, which is entirely consistent with van der Waals forces on colloidal particles. These examples demonstrate that colloidal stability in nonpolar solvent mixtures and crude oils could be used to model asphaltene coagulation with changes in the liquid-phase solubility parameter. These examples also illustrate that these trends are observed in suspensions that contain little or no resin material.

■ IMPLICATIONS OF THE SUPRAMOLECULAR ASSEMBLY MODEL

The supramolecular assembly paradigm that we propose for asphaltene aggregates, as illustrated in Figure 3, is intended as a basis for new hypothesis testing, both experimentally and by computational methods. This physical model indicates new directions for investigating the formation of aggregates and their subsequent interactions in solution and with interfaces. Understanding the assembly of multiple molecular species into stable aggregates demands a different approach to studies using model compounds and computational methods. Clearly, the association of pairs of molecules in the absence of solvent is unlikely to give useful insight. Hysteresis or time dependence and path dependence are extremely likely with such compositionally complex aggregates, as observed in the restructuring of interfacial films of asphaltenes over time, the association of aggregates upon drying that disrupts subsequent dispersion in solvent (i.e., lower apparent solubility), and the release of guest compounds upon dissolution of an aggregate and reprecipitation. Finally, rather than treating asphaltenes as a class of material that has no clear analogue in the physical chemistry of defined mixtures, we suggest that studies of the interactions between asphaltenes and pure model compounds designed to elicit different types of supramolecular association should prove extremely fruitful.

The end result of this approach would be synthetic and computational models of asphaltene mixtures that faithfully mimic the behavior of the actual material.

■ EXPERIMENTAL METHODS

C_{12} -HBC was synthesized and generously provided by Professor Klaus Müllen of the Max Planck Institute for Polymer Research (Germany). C_{12} -HBC was dissolved in toluene at a concentration of 30 μM (46 mg/L) for experiments afterward.

A Zeiss Axioplan polarizing microscope equipped with LD ACHROLAN 40 \times /0.60 KORR and EPIPLAN NEOFLUAR 10 \times /0.30 POL objectives for normal and polarized light illuminations was used for the observations. A drop of C_{12} -HBC solution was taken and placed on a glass microscope slide. The drop was immediately covered with a slide cover. The sample was then observed under the microscope between crossed polarizers and normal light. A ZVS47E capturing system (Zeiss) was used to obtain photographs.

Dynamic light scattering (DLS) measurements in solution were performed on a Zetasizer Nano S (Malvern Instruments) (4 mW He–Ne 633 nm laser) with temperature control. The C_{12} -HBC solution was first heated to 50 °C to break the aggregation of C_{12} -HBC and then immediately filtered with 0.45 μm polytetrafluoroethylene (PTFE) membrane (Whatman) to remove dust and other dispersed particles. The filtered solution (1.5 mL) was transferred to a square quartz cuvette for DLS measurements. The measurements were performed in the range of temperatures between 25 and 42 °C. The temperature of the square cuvette was changed by intervals of 2–3 °C, and optical alignment was performed after each temperature change. Data were then collected after the stabilization of the cuvette temperature (10–15 min).

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