The Influence of Asphaltene-Resin Molecular Interactions on the Colloidal Stability of Crude Oil

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Abstract

In the colloidal hypothesis of vacuum residua and asphalt, micelles are assumed to have an asphaltenic core with the greatest weight and aromaticity and an outer shell composed of lighter and less aromatic molecules. The true nature of the micelles, and the asphaltenic core in particular, has always been a debatable issue among asphalt researchers. One of the frequently asked questions is whether asphaltenes exist as stacked layers within the micelles or as single molecular units stabilized by resin molecules. In this paper, we investigate the correlation between the number of asphaltene sheets and the final stability of the system in a medium of asphaltene and resin components. Our evaluation is based on rigorous quantum mechanical calculations using a DFT-D approach. Our quantitative findings corroborate the view that the colloidal behavior of crude oil is better described by asphaltene-asphaltene associations. Moreover, our calculations show that if both asphaltene and resin are present, resin–asphaltene interactions are preferred over asphaltene–asphaltene interactions only if the number of resin molecules per micelle is greater than the number of asphaltene molecules per micelle.

Keywords: colloidal state, asphaltene micelles, petroleum resin, density functional theory (DFT)

73 1. Introduction

74 The bitumen refining process uses a distillation column or fractionation tower to separate lighter
 75 petrochemical fractions from the non-boiling components, which are known as an atmospheric residue. The
 76 atmospheric residue, a dark and viscous adhesive material, is then introduced to a vacuum distillation unit to
 77 be prepared for the solvent de-asphalting process. *Asphaltenes* and *maltenes* are two main fractions of the
 78 extracted asphalt. Asphaltene is the wax-free material that precipitates in light paraffinic solvents, while
 79 resins along with saturates and aromatics constitute the maltene phase of asphalt.^{[1],[2]} Although
 80 characterization of asphaltene and resin has been a controversial topic among the research community, there
 81 seems to be a commonly accepted view that these components, as the heaviest, most polar, and most
 82 aromatic components of crude oil, contain polycyclic aromatic sheets with a variety of functional groups,
 83 some traces of transition metal elements, and alkyl chains on the edges.

84 The matter of asphaltene precipitation and its technical consequences in refinery processing is a
 85 serious concern in the petroleum industry. Self-association of the asphaltene sheets is considered as the first
 86 step in the formation of precipitated asphaltene particles. The nature of the stacks formed (number,
 87 orientation angle, and interlayer spacing between asphaltene monomers) has been frequently investigated in
 88 asphaltene studies. Based on high-resolution transmission electron microscopy (HRTEM) and fluorescence
 89 depolarization techniques, the size of asphaltene stacks is estimated to be about $1\text{nm (width)} \times$
 90 1nm (height) , mainly comprised of two or three individual asphaltene molecules.^{[3],[4],[5],[6],[7]} However, new
 91 findings of laboratory centrifugation of a live crude oil indicate that the size of asphaltenes in crude oil is
 92 $\sim 2\text{nm}$, and their aggregation number (in nano-aggregates) is between 3-8.^[8]

93 The micellar model is one of the multiple models proposed to describe asphaltene behavior in crude
 94 oil. Despite its limitations,^{[9],[10],[11]} this model has been generally accepted^{[12],[13],[14],[15],[16],[17]} and is the most
 95 widely used viewpoint in descriptions of the nature of vacuum residua (VR) and bitumen. The idea of
 96 colloidal suspension of asphaltenes in bitumen/crude oil goes back to experiments by Nellensteyn^[18] in 1924
 97 that were further developed by Pfeiffer and Saal in later years.^{[19],[20]} Since then, outstanding contributions
 98 have been made to demonstrating the colloidal structure of vacuum residua and the role of petroleum resins
 99 in the micellar model.^{[13],[14],[21],[22],[23],[24],[25],[26],[27]} These micelles are molecular aggregates of heavy

asphaltene molecules that are peptized by light resin molecules, dispersing in a surrounding medium of lighter resins, aromatics, and saturates.^[28] Resin molecules are well known for their stabilizing effect on asphaltene molecules and suspending them in a medium. It should be noted that the micellar model of asphaltene, in its traditional definition of one micelle, has been recently criticized by some research groups^{[29],[30],[31]} who believe that resin molecules do not act as “surfactants” and strongly question the stabilizing or peptizing effect of resins on asphaltene aggregates, though they accept the general hypothesis of colloidal dispersion of asphaltene in crude oil/bitumen/organic solvents. In the current study, irrespective of the role of resin molecules, the term of “micelle” is used for a nano-aggregate structure composed of an asphaltenic core surrounded by lighter resins, other aromatic hydrocarbons, and saturates.

There seems to be some evidence that asphaltenes may not form large aggregates in crude oil, rather they exist at a much smaller scale (even a molecular scale) associated with resins in a colloidal structure of crude oil.^{[14],[32],[33],[34]} This view is further strengthened by the fact that asphaltenes with low aggregation number are well dispersed at very low concentrations.^{[35],[36],[37]} Proponents of this view argue on the grounds that asphaltene aggregates are formed only when the phase separation is occurring and asphaltene flocculation/precipitation is starting.

Against this view, other groups of the asphalt community (with a dominant majority) believe that the micellar behavior of crude oil is better described by “aggregates”.^{[21],[38],[7]} Indeed, they theorize that the asphaltene-asphaltene association builds graphite-like stacks constituting the center of micelles, at which the shape, size, and number of aggregation are functions of the solvent, the temperature, and other environmental constraints.^[29] Advocates of this view point out the asphaltene stacks exist not only in solid phase, but also before reaching the critical micelle concentration (CMC) limit that is considered as the onset of precipitation/flocculation.^[38]

Jefferson Creek^[39] describes the nature of studies carried out in this fieldwork; at one end of the spectrum are experimental studies that are involved in compositional analysis of the live single-phase reservoir samples, and at the opposite extreme are computational modeling studies that focus on the isolated molecules in a matrix even quite different from the original crude oil. Nevertheless, all of what we know about asphaltene micellization and its peripheral issues are apparently coming from experimental studies,

and this approach has shaped our understanding of the issue. Indeed, the contribution of theoretical studies on the complex behavior of the systems like asphaltene under extreme conditions of temperature and pressure is insignificant, and is mostly restricted to classical molecular mechanics/dynamics (MM/MD).^{[12],[40],[41],[42],}

In the realm of quantum studies, factors like the specific nature of interactions, the complexity, and the massiveness of asphaltene aggregates/micelles have turned the subject of petroleum micelles into a challenge from a computing resource perspective. Additionally, the diversity of interpretations and the lack of consensus on experimental results (structural information, in particular) make asphaltene modeling even more challenging. Accordingly, this challenge and some doubts about the true nature of asphaltene micelles were the main motivation for the present work. In this work, we investigate the interplay between asphaltene and resin molecules in the formation of petroleum micelles. We also try to find a solution for the frequently posed question of whether individual petroleum micelles are stacked aggregates of asphaltene-asphaltene units or single entities of asphaltene (monomers) that are environed, peptized, and consequently stabilized by resin components. This evaluation is based on [quantum mechanical calculations through a DFT-D](#) approach, and our emphasis is on refining energy parameters to establish a correlation between the number of asphaltene sheets and final stability of the system in a medium of asphaltene-resin components.

143

144 **2. Methodology**

The geometry of all structures was optimized through a DFT approach implemented in Gaussian 09. [All geometry optimizations were performed at 298 K with default convergence criteria for residual forces and energy variations \(displacements\), without imposing any constraints or extra keyword options.](#) To accurately describe π -stacking interactions, as well as to emphasize the importance of dispersion energy as a key factor in stabilizing the stacked dimers, dispersion-corrected DFT functional, B97-D^[43], associated with basis sets 6-31G* and 6-311+G**, was selected as the level of DF calculations to optimize the structures. Recently, B97-D has been widely used to describe macro structures like asphaltene sheets and DNA-base pairs.^{[44] , [45] , [46],[47],[48]} Counterpoise (CP) correction^{[49],[50]} was performed to limit basis set superposition error (BSSE) while studying intermolecular interactions.

Binding energy (E_{bind}), indicative of the thermodynamic stability of the system, is evaluated by subtracting the total energy of the complex, $E_{complex}$, from the sum of its constituent parts, $E_{fragment}$, when they are in their lowest energy structure:

$$E_{bind} = E_{complex} - (\sum E_{fragment}) \quad (1)$$

Binding energy, indeed, reflects the net energy change through adsorption. However, in most cases the adsorption process is associated with the structural deformation of interacting fragments (mostly adsorbate). The energy required for this deformation is almost supplied from the molecular binding of the adsorbate over the substrate as an energy gain process. In such situations, the actual value for stabilizing interactions is mostly compensated by structural deformation of the fragments. So, for the systems at which interacting constituents undergo major restructuring over interaction, the binding energy, E_{bind} , cannot be an appropriate descriptor for the characterization of interactions. On this basis, the interaction energy, E_{int} , considering both binding and deformation energies, could be a reliable signifier for the strength of interactions in systems with substantial reconstruction.^{[51],[52],[53]} This term is calculated by the following equation:

$$E_{int} = E_{bind} - (\sum \Delta E_{fragment}) \quad (2)$$

where $\Delta E_{fragment}$ (sometimes shown with $\Delta E_{deformation}$ or $\Delta E_{distorsion}$) refers to the amount of energy required for the geometric distortion and electronic excitation of the fragments from their equilibrium ground state to the corresponding geometric and electronic structure in a complex.

Models of asphaltene and resin monomers

The morphology of asphaltene aggregates is a direct consequence of the asphaltene molecular structure and the particular orientation of asphaltene monomers through aggregation processing. Therefore, to present a clear picture of intermolecular interactions in asphaltene aggregation, our choice of asphaltene model is of prime importance. Although the structure of asphaltene is not unique, there are two commonly proposed molecular architectures for asphaltenes that are consistent with the results of experiments: archipelago,^{[54],[55],[56]} containing two or more separate polyaromatic hydrocarbons (PAHs) connected to each other through aliphatic side chains; and island,^{[57],[31]} containing a single unified PAH with 4-10 fused aromatic rings, with a centroid of the distribution around 7^{[58],[59]}. This study used the island structure, based

on the latest Yen–Mullins-modified model^{[60],[31]} proposed by Greenfield,^[61] including one pyrrolic nitrogen (a nitrogen atom embedded in a pyrrole ring, located in the aromatic part)^[62] as shown in Figure 1-a. Greenfield's modification was based on a rearrangement of some aliphatic chains of the Yen-Mullins model to reduce the pentane effect^[63] and its corresponding high internal energy. The pentane effect arises from bonding conflicts between atoms separated by six bonds that attempt to locate in a limited space for just six atoms, like a benzene or cyclohexane. The designation as the pentane effect comes from the five carbon and two hydrogen atoms involved in this conflict. Hydrogen atoms at the two ends of this seven-atom configuration overlap in a position suited for one atom, to form a cyclic conformer. A significant feature of asphaltene-pyrrole in this model is the non-planarity of the aromatic core, due to the pentane effect and the geometrical strain of neighboring rings.^{[61],[64],[65]}

While asphaltenes consist of more than 48% aromatic carbons (in some cases even more than ~85%)^[66], the content of aromatic carbon in petroleum resin is significantly lower^[67], which might be indicative of the less advanced aromatization in resins. In the current study, we used 6-methyl-dibenzothiophene as the resin molecule, based on the resin structure proposed by Murgich et al.[68] (Figure 1-b).

3. Results and discussion

In following sections, monomers of asphaltene and resin, and subsequently dimers of asphaltene are optimized and surveyed. The optimized structures are then used to build the starting structures in the next optimizations.

3.1 Monomers of Asphaltene and Resin

The first challenge for any type of theoretical study is the high molecular weight and large size of the asphaltene molecule, with the consequent computational cost. The first and most logical approach to this difficulty would be to simplify the structure. In the case of the asphaltene molecule, the extensive size of the aromatic region is responsible for the significant non-covalent interactions between asphaltene sheets and the formation of asphaltene aggregates. A reduced asphaltene without any aliphatic side chains retains its large size π -region and geometrical effect over self-association. Accordingly, to reduce the computational

cost and enhance the number of samples (different arrangements), we deal with the reduced form of the asphaltene in some parts of the present calculations. However, side chains are still important, for the simple reason that petroleum asphaltene is composed of more than 48% aromatic carbons and the remaining is aliphatic carbons, as indicated by ^{13}C NMR studies.^[69] So we compare the results arising from two structures, with and without aliphatic side chains, to give credence to the results obtained with the reduced structures.

Our calculation starts with refining the energetic and geometrical structure of the complete and reduced forms of an asphaltene-pyrrole monomer and a resin molecule. Optimization is carried out with B97-D functional and basis sets 6-31G* and 6-311+G**, mentioned in the preceding section. Frequency calculation is carried out for each optimized molecule at the HF/6-31G* level to ensure being in a real minimum. The results of this optimization will be used in later sections.

Figure 1 also shows the charge distribution over the reduced form of asphaltene and a resin molecule, visualized through an electrostatic potential surface (ESP) map. The main priority of ESP visualization is to find the reactive sites of the molecules to design an effective interaction between two unit sheets of asphaltene or between asphaltene and resin. This map has been generated at the B97-D/6-31G* level, with isosurfaces of 0.01 electrons au^{-3} through the Gauss View package.^[70] Sites with the lowest electrostatic potential energy value are in red, and sites with the highest are in blue, indicating the relative abundance and absence of electrons in these regions (negative and positive charge), respectively. This map vividly shows a positively charged region around peripheral hydrogens and a negatively charged region in the centers of reduced asphaltene, resin, pyrrolic nitrogen, and the sulfur of a thiophene group. We analyze this type of charge distribution in the formation of asphaltene-asphaltene and asphaltene-resin complexes in the following sections.

229

230 **Figure 1.** Optimized structures of (a-1) asphaltene-pyrrole molecule based on modified Yen–Mullins model,^[61] (a-2)
 231 reduced asphaltene-pyrrole molecule (excluding aliphatic chains), (b-1) 6-methyl-dibenzothiophene, the resin molecule
 232 proposed by Murgich et al.^[68], and (a-3, b-2) electrostatic potential surface (ESP) for the reduced asphaltene and resin,
 233 respectively, generated at the B97-D/6-31G* level, scaled between -0.6 (red) to 37.7 (blue) kcal/mol. Red and blue
 234 colors signify the regions with charge accumulation and depletion, respectively.

235

236 3.2 Asphaltene Dimers

237 After preparation of an asphaltene monomer, modeling of an asphaltene dimer is the second step to
 238 simulate the process in which self-association of asphaltene molecules and their interactions with resin
 239 molecules occurs. To do so, the diversity of the probable structures is one of the limitations. This diversity
 240 arises from the different arrangements of the asphaltene sheets with respect to each other. The presence of
 241 heteroatoms in asphaltene sheets and also in peripheral chains causes a wider intermolecular orientation
 242 distribution even for the simulation of a dimer, the simplest form of asphaltene aggregate. There are four
 243 most commonly proposed arrangements for an asphaltene dimer: parallel or face-to-face (π - π interaction);

parallel-displaced or offset (σ - σ interactions); T-shape or face-to-edge (π - σ interactions); and T-shape or edge-to-edge (σ - σ interactions).^{[71],[72],[73]}

Among the various conformations examined here, Table 1 shows optimized structures concerning three preferential orientations: parallel, offset, and diagonal. Because of a negligible difference between corresponding structures at two basis set levels (6-31G* and 6-311+G**), just one series of structures is shown in this table. The energy information and the optimum distance between two asphaltene sheets have also been reported in this table. Binding distances reported in this table are the vertical distance (d_{ver}) between two approximate centers of asphaltene sheets, and the optimum distance between two mass centers of asphaltene sheets (d).

Table 1. Three lowest energy structures of asphaltene-pyrrole dimer, and corresponding relative energy (ΔE_{tot}) of different conformations with respect to the lowest energy structure, binding energy (E_{bind}), binding distance between two asphaltene mass centers (d), and vertical binding distance between two approximate centers of asphaltene sheets (d_{ver}). Energies are counterpoise corrected and reported in kcal/mol.

	Diagonal	Parallel	Offset
B97-D/6-31G*			
ΔE_{tot}	0.0	+4.0	+5.7
E_{bind}	-32.3	-28.0	-27.1
d, d_{ver}	4.239, ~3.5	3.926, ~3.4	4.949, ~3.6
B97-D/6-311+G**			
ΔE_{tot}	0.0	+3.6	+5.7
E_{bind}	-34.7	-30.7	-29.4
d, d_{ver}	4.209, ~3.5	3.883, ~3.4	4.942, ~3.4

In Table 1, relative energy (ΔE_{tot}) is defined with respect to the total energy of the lowest energy structure (diagonal), and binding energy (E_{bind}) is related to the thermodynamic stability of the system. Due to the stiffness and rigidity of the polyaromatic rings of individual asphaltene molecules, they do not notably deform over dimerization, and their corresponding deformation energy is small. As an example, the

deformation energy of a diagonal structure is 1.4 kcal/mol (not tabled). Therefore, based on Equation 2, the binding energy and interaction energy are somewhat the same, and binding energy could be also considered as a representative of the strength of interaction between two asphaltene sheets. Based on the values reported in Table 1, the range of energy is from -29.4 to -34.7 kcal/mol at the B97-D/6-311+G^{**} level, and with a very small difference (about 2 kcal/mol) from -27.1 to -32.3 kcal/mol at the B97-D/6-31G^{*} level.

The energy values reported here seem to be remarkably lower than -55 kcal/mol, the value reported by Pacheco-Sánchez et al.[73] for one asphaltene dimer in a vacuum using COMPASS Force Field,^{[74], [75]} derived using classical Molecular Mechanics (MM) for a parallel arrangement with binding distance of 4 and 5 Å. In another study^[76] based on MM and semiempirical calculations, the interaction energy was reported to be -45 kcal/mol for two asphaltene dimers, each containing a hydroxyl group. A small percentage of the difference between DFT results and MM results could be attributed to the removal of aliphatic side chains in our calculations, and a portion of the difference may be caused by the inadequacy of the level of calculations based on COMPASS Force Field parameters.

To examine this possibility, we added the side branches of real asphaltene to the reduced asphaltene dimer in its most stable conformer (the diagonal dimer), and compared the results, as shown in Table 2. Due to the high computational cost of the Gaussian package to (structurally) optimize the branched asphaltene dimer, we resorted to other software with higher computational speed. Geometric optimization of the branched asphaltene was carried out by a DFT-based DMol³ module^{[77],[78]} embedded in Accelrys Materials Studio using Perdew-Burke-Ernzerhof (PBE) functional^[79] with Grimme's dispersion correction scheme^[44] and a double numerical plus polarization (DNP) basis set (comparable to a Gaussian 6-31G^{**} basis set). DMol³ benefits from numerical basis functions that reduce the practical computational time compared to Gaussian-based methods. The energy of this optimized structure was calculated via B97-D/6-31G^{*} in the Gaussian package. Binding energy values (-36.7 vs. -32.3kcal/mol) for two asphaltene dimers, with and without aliphatic side chains, reinforce the aforementioned explanation that MM-based results are associated with some overestimation on the binding energy value.

Table 2. Comparing asphaltene dimers in the presence and absence of aliphatic side chains. Binding energies (E_{bind}) are counterpoise corrected and reported in kcal/mol. Binding distances between two asphaltene centers (d) and vertical distances (d_{ver}) are in Å.

E_{bind}	-32.3		-36.7
d, d_{ver}	4.239, ~3.5		5.454, ~3.6

On the other hand, the bond distance calculated between the centers of mass of asphaltene sheets was found to be around 4-5 Å, and the vertical distance to be 3.5Å, which are in good agreement with X-ray diffraction and small angle scattering results reported by Yen et al.,^{[2], [80]} who reported the interlayer distance between two asphaltene sheets to be 3.55-3.70 Å. In addition, our result is comparable with those from Molecular Dynamics (MD) simulations that reported an interlayer distance of 3.5-4 Å.^{[73], [81]}

The stability of the systems is another notable point in Table 1. As shown in this table, the most stable structure is the diagonal structure, in which two nitrogen atoms are at the maximum distance from each other (located in opposite corners of a rhombus frame), with energy of -34.7 kcal/mol at the B97-D/6-311+G^{**} level, although the binding distance between two monomers is not the lowest of the three proposed structures. Comparison of the other two structures (parallel and offset) shows that these two structures are not very different energetically; with a small energy difference, the parallel dimer is more stable than the offset dimer. At the B97-D/6-311+G^{**} level, the energy difference between the two structures is not more than 1.3 kcal/mol.

Based on the ESP map in Figure 1, the negative charge (red color) accumulation in the center of the asphaltene molecule increases the contribution of electrostatic repulsion between two asphaltene sheets, due to the π -electron cloud, which, in turn, should reduce the stability of parallel structures, while our results confirm that parallel conformers are the most stable structures (note that the diagonal structure is a parallel structure in nature). Indeed, stacking interaction is favorably affected by a nitrogen heteroatom attached to

the aromatic core of asphaltene. The positive role of a nitrogen atom in stabilizing some particular asphaltene dimers is attributed to the Hunter-Sanders^{[71], [82]} rule and the electron-withdrawing nature of this atom, which can pull the negative charge of the ring π -electrons and provide a favorable π stacking interaction. Thus, the polarization of π -electron density due to the presence of electron-withdrawing groups on aromatic rings as well as the induced electrostatic forces (London dispersion) are attraction forces that favor stacking the asphaltene planes.

In addition, the greater stability of a diagonal arrangement, which is a typical parallel structure with the maximum distance between two nitrogen atoms, compared to a parallel structure at which nitrogen atoms are very close and in front of each other, make us believe that at greater distances, the electrostatic interaction of the two nitrogen atoms with distinct partial charges is reduced, and the positive role of nitrogen becomes pronounced.

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T-shaped conformers

Another notable point in Table 1 is the absence of the T-shape as one of the expected structures for an asphaltene dimer. A tilted T-shape with the minimum electron repulsion between two fragments is the most favorable conformer for simple π -stacking structures like a benzene dimer,^{[83],[84],[85],[45]} whereas theoretical studies on PAHs show that parallel or nearly parallel stacking structures are preferred over T-oriented structures.^{[86], [28]} This could be attributed to the steric repulsion between aliphatic side chains of two molecules in T-shape structures.^[87]

In the case of our study, at the B97-D level, irrespective of the temperature range applied (not tabled) and even in the absence of aliphatic chains, no T-conformation was observed for asphaltene, and all different initial T-shape structures rearranged to the offset π -stacked geometries. To be confident of accurate identification of the geometric preference, all starting T-shaped structures were reexamined under the M06-2X functional, which also benefited from the improved dispersion correction. Except for one case (a lower energy structure with intermolecular orientation angle $\sim 30^\circ$), almost all starting T-conformers rearranged into parallel-displaced, indicative of the priority of π - π stacking over π - σ interactions in the perpendicular position.

342

343 **3.3 Micellar structure of asphaltene: pros and cons**

344 Referring to a “micelle” (“a surfactant micelle” in its traditional definition) as an asphaltene nano-
 345 aggregate in crude oil, bitumen, or organic solvents has encountered opposition in the last few
 346 years.^{[29],[31],[30]} However, the colloidal hypothesis of asphaltenes is still one of the most generally accepted
 347 and commonly used viewpoints about the state of asphaltene in crude oil (or in bitumen).^{[12],[13],[14],[15],[16], [17]}

348 In the colloidal model, components with the greatest molecular weight and highest aromaticity (like
 349 asphaltene) are located in the center of micelles, and lighter components with less aromatic nature (such as
 350 aromatics and saturates) constitute outer shells. Resin molecules are supposed to be onto the surfaces or into
 351 the interiors (gap spaces) of asphaltene molecules.^{[13],[19],[88]} In the surfactant micellar model, the highly
 352 dispersive character of resin-asphaltene micelles is attributed to the surfactant-like property of resins, which
 353 contain polar functional groups such as carbonyl, aldehyde, amine, etc. On this basis, the stability of
 354 asphaltene aggregates in hydrocarbon solutions is guaranteed by resin molecules. Figure 2 shows the
 355 arrangement of SARA (the acronym of saturates, aromatics, resins, and asphaltene) fractions in one
 356 hypothetical micelle.

362 **Figure 2.** Colloidal suspension of one hypothetical micelle of asphaltene in a dispersing medium of lighter resins,
 363 aromatics and saturates

365 Although opponents of the surfactant model believe that resins are not surfactants and that colloidal
 366 suspensions of asphaltene are still formed in solvent models even in the absence of resin molecules, they do
 367 not reject some degree of interaction between asphaltene and resin.^[31] Accordingly, steric repulsion between

asphaltene molecules is a factor that increases the maintenance of the asphaltene particles at a distance sufficient to inhibit coalescence. In the opposition group, Mullins^[31] has a more positive look at the issue. He accepts the colloidal view of asphaltene aggregates and that there is some degree of interaction between asphaltene and resin, but he (along with some other researchers^{[29],[89],[30]}) rejects the surfactant-like or peptizing role of resin molecules in the stability of asphaltene colloidal suspensions.

There seems to be a general consensus on the colloidal suspension of asphaltenes, even if they are different from the “micelle” in its traditional definition. As stated in the introduction section, in this study, the term “micelle” is used for a molecular aggregate depicted in Figure 2, which is a cluster composed of an asphaltenic core surrounded by other fractions like lighter resins, aromatics, and saturates, irrespective of the role of resin molecules and whether they act as surfactants.

A question often posed about the nature and composition of each individual micelle is whether asphaltenes exist as stacked layers within the micelle or as single molecular units surrounded by resin molecules. Simply stated, are there suspended particles of asphaltene-asphaltene aggregates surrounded by resins, or are there single layers of asphaltene (i.e., non-stacked layers) peptized and consequently stabilized by resins? In the third part of this study (which is the main purpose of the present work), we try to find a solution for the posed question and to investigate the probable structure of the asphaltenic core, to answer whether one or more than one asphaltene exist per micelle in vacuum residue and asphalt. This evaluation is based on refining the energy parameters to establish a correlation between the number of asphaltene sheets and the final stability of the system in a medium of asphaltene and resin components. To do so, we set up interacting models for all required pairs of asphaltene and resins: asphaltene-resin (**A-R**) and asphaltene-asphaltene-resin (**A-A-R**).

389

3.3.1 Interaction of resin and asphaltene

The structural similarity between a resin molecule and asphaltene (resins are smaller, with lower molecular weight) leads us to investigate π - π stacked (face-to-face) conformations as the most efficient interacting geometries between the two components asphaltene and resin, as we found for asphaltene-asphaltene. In another DFT study, Alvarez-Ramirez et al.^[90] reported face-to-face orientation as the preferred

395 configuration for resin and asphaltene molecules. In the current study, the proposed structure, 6-methyl-
 396 dibenzothiophene, by Murgich et al.,^[68] was considered and optimized as the resin molecular structure.

397 Based on molecular mechanical calculations,^[28] the formation of molecular aggregates of asphaltene
 398 and resin in a colloidal medium is due to the suitable fitting between aromatic planes of two fragments (as
 399 the action of a lock and key) and the lowest steric repulsion between the peripheral chains. We took into
 400 account this point while designing the initial structures of asphaltene-resin complexes to be optimized. The
 401 most stable structures of each component (resin and asphaltene) were used to build the starting structures of
 402 resin-asphaltene complexes. Full geometric optimization, without imposing any constraints, was performed
 403 to find the lowest energy structures. Calculations were performed at the B97-D/6-31G* level.

404 To construct our interacting model of asphaltene-resin, the number of resin molecules required to
 405 interact with an asphaltene target is of particular importance. Resin molecules are smaller and lower in
 406 molecular weight compared to asphaltene molecules, so the asphaltene micelles are expected to be
 407 surrounded by more than one resin molecule.^{[91], [92]} Indeed, the quantitative ratio of resin to asphaltene (not
 408 all the resin molecules participate in the formation of micelles) characterizes the colloidal stability of VR, or
 409 the onset of destabilization of the system and precipitation or phase separation. In addition to asphaltene(s)
 410 and a fraction of resin molecules, the intra-micelle space is occupied by other fractions like aromatics and
 411 saturates. The size of the asphaltene core and the number of aromatic fused rings, which are indicative of the
 412 active sites, determine the number of resin molecules surrounding the asphaltenic core. With these
 413 considerations, three or four resin molecules may fulfill the requirements of our model, as shown in Table 3.

414 Table 3 displays energy information for the interaction between a single asphaltene (branched and
 415 reduced forms) and resin molecules. As shown, increasing the number of resin molecules increases the
 416 thermodynamic stability of the system; when the number of resins is increased from one to three, binding
 417 energy is increased about three times (from -17.0 to -47.2 kcal/mol). This correlation between
 418 thermodynamic stability of the complex and the number of resin molecules is strongly supported by the
 419 experimental evidence: the greater the number of resins, the higher the colloidal stability. As stated above,
 420 the colloidal stability of the vacuum residue relies on the ratio of resin to asphaltene.

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Table 3. Interaction between a single asphaltene (reduced and branched forms) and resin molecules. Binding energies are counterpoise corrected and reported in kcal/mol. Asphaltene and resin are denoted by **A** and **R**, respectively.

<p>A-R(monomer) $E_{\text{bind}} = -17.0$</p>	<p>A-R(monomer) $E_{\text{bind}} = -19.4$</p>
<p>A-R(dimer) $E_{\text{bind}} = -27.5$</p>	<p>A-R(dimer) $E_{\text{bind}} = -35.5$</p>
<p>A-R(dimer) $E_{\text{bind}} = -32.4$</p>	<p>A-R(dimer) $E_{\text{bind}} = -38.12$</p>
<p>A-R(trimer) $E_{\text{bind}} = -47.2$</p>	<p>A-R(trimer) $E_{\text{bind}} = -56.1$</p>

Comparison between the energy values of an asphaltene dimer in Table 1 and the reduced structures of asphaltene-resin in Table 3 clearly shows that if both asphaltene and resin are present, resin-asphaltene

interactions are preferred over asphaltene–asphaltene, *only if* the number of resin molecules is greater than the number of asphaltene molecules. Accordingly, while the binding energy for an asphaltene dimer (in the most stable conformer) is 32.3 kcal/mol, the binding energy of an asphaltene-resin trimer, **A-R(trimer)**, reaches 47.2 kcal/mol.

Our results in this part with asphaltene - asphaltene micelles and asphaltene – resin micelles also provide a reasonable answer about the homogeneous or heterogeneous nature of the micelles we encounter.^{[14],[33],[93]} Stronger interactions in asphaltene-resin complexes (in high ratios of resin to asphaltene) reinforces the postulation that micelles are heterogeneous in nature if the number of resin molecules is greater than the number of asphaltene molecules.

Reduced structures of asphaltene-pyrrole might be blamed for the absence of aliphatic chains and exaggerated behaviors of stacking, which could affect its willingness towards other molecules like resins, and question the validity of our results. To add credence to the use of reduced structures of asphaltene-pyrrole, and to verify that these structures can simulate the behavior of branched structures, we also calculated interaction energies for asphaltene-resin monomers in the presence and absence of peripheral groups of asphaltene. The results are also shown in Table 3. A simple comparison indicates that the reduced structures of asphaltene generate more than 84% of the total interaction energy arising from branched structures. The atoms responsible for this contribution are aromatic carbons located in the center of an asphaltene monomer, highlighting the importance of the ring-ring interactions between resin and asphaltene.

Nevertheless, the role of aliphatic side chains in stabilizing the complex is undeniable, in particular for large systems. As an example, in an asphaltene-resin (trimer), **A-R(trimer)**, the contribution of the side chains to stability of the system is 8.9 kcal/mol. This is in line with Takanohashi et al.'s results, which emphasize the stabilizing effects of aliphatic side chains.^[94]

Furthermore, we should point out the two different arrangements proposed for an asphaltene-resin (dimer), **A-R (dimer)**. As shown in Table 3, the structure in which two resin molecules are arranged in symmetrical positions (above and below asphaltene) is energetically more favorable than the scenario in which both resins are on the same side of the asphaltene surface: -32.4 versus -27.5 kcal/mol for the reduced forms, and -38.12 versus -35.5 for the branched structure. This can be attributed to the extent of π - π overlap

between the fused aromatic rings of asphaltene and the aromatic region of resin molecules; this overlap is significantly higher when two resin molecules are arranged on opposite sides of the asphaltene molecule compared to having both resins on the same side. This observation further indicates the importance of ring-ring interactions between resin and asphaltene molecules.

To pursue our primary objective in this study, we increased the dimension of the asphaltenic core to two asphaltene molecules per micelle and investigated the influence of resin molecules on the stability of the new structures. The results are shown in Table 4. In this table, all structures have been optimized at the B97-D/6-31G* level. Based on the asphaltene-resin (dimer) results in Table 3, only the arrangement that led to the most stable structure (two resins located on opposite sides of the asphaltene surface), was examined and is reported in Table 4.

Table 4. Interaction between an asphaltene dimer and resin molecules. Binding energies are counterpoise corrected and in kcal/mol. Asphaltene and resin are denoted by **A** and **R**, respectively.

A(dimer)-R(monomer)	A(dimer)-R(dimer)	A(dimer)-R(trimer)
$E_{\text{bind}}=-19.0$	$E_{\text{bind}}=-37.8$	$E_{\text{bind}}=-60.0$

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We are now in a position to take a look at the results in Table 3 (as a micellar model with monolayer asphaltenic core) and Table 4 (as a micellar model with double layer asphaltenic core), which provide valuable points of comparison. Energy values reported in the tables clearly show that resin molecules stabilize asphaltene dimers better than asphaltene monomers.

For example, in structures enriched with resin (including three resin molecules), binding energy increases from -47.2 to -60.0 kcal/mol (a 27% increase), indicative of more stability of the structure with the

double-layer asphaltene compared to that of the single-layer asphaltene. The same trend is observed for other structures. Our results give more credence to the idea that micellar behavior of crude oil is better described by stacked layers of asphaltene-asphaltene environed by resin molecules, rather than non-stacked single layers of asphaltene.

As the last part of our study, we decided to investigate the interaction between two asphaltene unit sheets in the presence and absence of resin molecules. To do so, different fragmentation has been carried out. To get an easier understanding of the interactions, we have shown the interacting components as separate elliptical planes in Table 5.

Table 5. Interaction between two asphaltene sheets in the absence and presence of resin molecules;. To get more convenient understanding, interacting components are shown by separate elliptical planes. d is the distance between two asphaltene centers. Counterpoise corrected energies are binding energy (E_{bind}), deformation energy of fragments (E_{def}), and interaction energy between two asphaltene planes (E_{int}). Energies and distances are in kcal/mol and Å, respectively.

A + A	R-A + A	R-A + A-R	R-R-A + A-R
$d=4.239$	$d=3.746$	$d=3.737$	$d=3.709$
$E_{\text{bind}}=-32.3$	$E_{\text{bind}}=-37.6$	$E_{\text{bind}}=-34.5$	$E_{\text{bind}}=-34.4$
$E_{\text{def}}=+1.44$	$E_{\text{def}}=+3.2$	$E_{\text{def}}=+3.4$	$E_{\text{def}}=+5.1$
$E_{\text{int}}=-33.7$	$E_{\text{int}}=-40.8$	$E_{\text{int}}=-37.9$	$E_{\text{int}}=-39.5$

In Table 5, the first notable point is the significant reduction of binding distance (d) between two asphaltene centers from adding resin molecules: addition of the first resin to an asphaltene dimer reduces the binding distance from 4.239 to 3.746 Å. This reduction of distance is associated with an increase in interaction energy from -33.7 to -40.8 kcal/mol. The presence of the resin component and the positive

evolution of the system towards the enhancement of interaction between the planes corroborate the experimental findings that the dispersive character of asphaltene micelles is increased in the presence of resin. In contrast to binding distance, no regular trend is observed in correlation between the number of resin molecules and reported energies. This might be due to the fact that except for the bare asphaltene dimer, which is in its lowest energy state (examined in section 3.2), the others may not be in their lowest energy structures, though they have been completely optimized.

4. Conclusion

The interplay between asphaltene and resin molecules in the formation of micelles and consequently the identification of the micellar structure of asphaltenes have been a matter of some speculation and intense debate in recent years. One of the issues discussed is that formation of coherently small asphaltene micelles in high ratios of resin/asphaltene might indicate that these suspended particles are individual entities of asphaltene (monomers) that are environed by resin components, and not necessarily stacked aggregates of asphaltene-asphaltene units.

Given a substantial body of experimental and somewhat MD reports on the physics of asphaltene micelles, we examined this subject from a different perspective using rigorous quantum mechanical calculations. As the building blocks of our study, we used one of the Yen–Mullins-modified structures^{[60],[31]} proposed by Greenfield^[61] as the asphaltene molecule, and 6-methyl-dibenzothiophene, proposed by Murgich et al.,^[68] as the resin molecule. While our initial comparison was conducted on a reduced form of asphaltene (without aliphatic side chains), we further examined the full structures (including side chains) to determine the relative effect of aliphatic side chains on colloidal stability. Based on our quantitative findings, the reduced forms of asphaltene reproduce more than 84% of the total interaction energy arising from the branched structures. This further indicates the importance of the Van der Waals and π - π interactions associated with the aromatic core of the two components.

To find a correlation between the number of asphaltene sheets and the final stability of the system after their interaction with resin molecules, we set up interacting models for all required pairs of asphaltene and resins: asphaltene-resin (**A-R**) and asphaltene-asphaltene-resin (**A-A-R**). The calculated energy values

521 clearly show that resin molecules stabilize asphaltene dimers better than asphaltene monomers. Simply
522 stated, the micellar behavior of crude oil is better described by asphaltene-asphaltene associations.

523 In support of the role of resins, the binding distance between the center of mass of two asphaltene
524 sheets is notably reduced in the presence of resin molecules. The addition of the first resin molecule to an
525 asphaltene dimer reduces the binding distance from 4.239 to 3.746 Å; this value is further reduced to 3.709
526 Å when the number of resins in the complex is increased to three. This adds more credence to the postulation
527 that resin molecules increase the effective interaction between asphaltene sheets.

528 Moreover, our calculations show that if both asphaltene and resin are present, resin–asphaltene
529 interactions are preferred over asphaltene–asphaltene interactions, *only if* the number of resin molecules is
530 more than the number of asphaltene molecules. This is in line with experimental evidence indicating that the
531 colloidal stability of petroleum residua relies on the ratio of resin to asphaltene: thermodynamic stability of
532 VR is achieved only when the relative concentration of resin is higher than that of asphaltenes.

533

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TOC Graphic

Micellar structure of asphaltene in a dispersing medium of lighter resins, aromatics, and saturates