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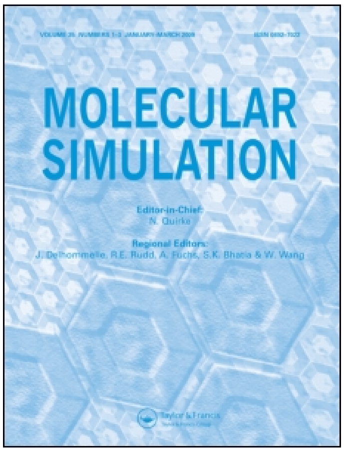

Molecular Simulation

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Molecular Simulation and the Aggregation of the Heavy Fractions in Crude Oils

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Molecular Simulation and the Aggregation of the Heavy Fractions in Crude Oils

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The use of Molecular Simulation in the study of aggregates of the molecules of the heavy fractions of crude oils is reviewed. Molecular Mechanics calculations of aggregates of asphaltenes having a single large aromatic region (continental type) and others having smaller aromatic regions connected by alkyl chains (archipelago type) are discussed in terms of the molecular recognition processes present in petroleum. Stacking of the aromatic regions was the most important process in the formation of aggregates of asphaltenes of the continental type with some unfavorable contributions from its saturated rings and alkyl side chains. The steric interference of these groups limits the growth of the aggregates to a small number of molecules. The asphaltenes of the archipelago type showed more complex aggregates because some molecules act as bridges and tangling between them may occur. The interaction of the asphaltene aggregates with resin molecules was analyzed and it was found that the high selectivity for some sites of the asphaltenes explains the specificity of the resins for its own crude oil.

Keywords: Molecular simulation; Asphaltenes; Resins; Molecular aggregates; Petroleum colloidal theory; Molecular recognition

INTRODUCTION

Crude oil is an essential commodity that is presently produced at a rate of approx. 78 millions barrels a day (12.8×10^9 l). Paradoxically, detailed information about its chemical composition is still scarce and only very few crudes have been studied in some detail [1]. Several estimates indicate that crude oils may contain around 500 000 different compounds while others even double that quantity [1]. In the last decade, molecular models of the heavy fractions of crude oils have become available [2–6]. These fractions are assumed to be part of a colloidal system formed by the heavier molecules of the crude oil (resins and asphaltenes) [1]. The molecular recognition processes that lead to the formation of aggregates of the components of the heavy fraction of crude oil will be reviewed. In particular, the use of Molecular Mechanics calculations in the study of the aggregation mechanisms occurring between asphaltenes and resins will be emphasized and its limitation discussed. Also the use of model molecules that represent averages over the different fractions and its implication on the calculations will be analyzed.

CHEMICAL COMPOSITION OF CRUDE OIL

The study of crude oil is even more complex because is a natural product that has been subjected to many chemical and physical modifications occurring over millions of years [7]. Many of these modifications are unknown at the present time and some may take even geological times to be completed. Crude oil has migrated from the original source rock through porous ones to the reservoir [1,7]. Along this tortuous path through many microscopic pores and channels, the crudes incorporate different elements such as S and V and also inorganic particles of quite different sizes and chemical composition [1,7]. For practical purposes crude oil is generally divided into four somewhat overlapping fractions [1]. They are, in terms of increasing molecular weights, saturated hydrocarbons, aromatics, resins and asphaltenes [1]. Some crude oils contain also additional heavy fractions called carbenes and carboids [1]. There are no molecular models for

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the last fractions so this work will be limited to the four most common ones.

EARLY COLLOIDAL THEORY OF PETROLEUM

It was assumed quite early in its study that crude oil was a colloidal system containing particles formed by its heavier fractions [1]. Nellensteyn [8] first developed this model in 1924 in order to explain the large differences found in the rheology of asphalts and bitumens. Sachanen [9] extended this theory to crude oils in 1927. At this stage, little or no molecular structural information was available for the asphaltenes and resins. In 1931, Marcusson [10] advanced the theory that polycyclic aromatic molecules formed the heavy fractions of crude oil. These asphaltene molecules were not pure hydrocarbons as assumed by Nellensteyn [8] but were found later to contain small amounts of S, O and N [11]. Simple chemical reasoning based in relative solubility led Hillman and Barnett in 1937 [12] to conclude that the asphaltenes had a chain structure formed by regions containing a limited number of saturated and aromatic rings connected by short alkyl chains. Sachanen in 1945 [11] modified this molecular model of asphaltenes by introducing more complex links between the polycyclic units such as $-CH_2-(CH_2)_n-CH_2-$, $-CH_2-S-CH_2-$, etc. and included S, N and O atoms in the some of the aromatic rings. Sachanen also concluded that the asphaltenes contained more aromatic and saturated rings than the resins [11]. In 1927, Sachanen also published the mechanism involved in the precipitation of asphaltenes when large quantities of light paraffinic hydrocarbons such as n-heptane were added to the crude oil [9]. Sachanen assumed that the asphaltene were lyophobic with respect to the paraffins and lyophilic with respect to aromatic hydrocarbons and resins. The asphaltenes adsorbed both types of compounds readily and thus are dispersed in the crude oil as a sol (a colloidal dispersion of a solid in a liquid). The aromatic hydrocarbons and resins act, in this case, as peptizing agents that are able to disperse the asphaltenes. When a large amount of light paraffin is added to the crude oil, some peptizing molecules leave the surface of the asphaltene particles for the solution. Then the asphaltene particles are not "protected" by the peptizing compounds and the precipitation process starts [11,13]. In 1940, Pfeiffer and Saal [14] showed simplified 2D drawings of the asphaltene and resin aggregates. No 3D details of the molecular aggregates were given in any of them as the molecules were drawn mostly as flat objects. In this classical work, (that has been many times erroneously cited as origin of the colloidal theory), the asphaltene molecules were represented as simple 2D planar aromatic hydrocarbons without any alkyl branches or saturated rings. These molecules were surrounded by lighter resin molecules and other aromatic hydrocarbons. The aggregates were depicted as a rather chaotic cluster of resin and aromatic molecules located around the asphaltene core. It was assumed then [14] that: (1) the core of these "aggregates" contained the more aromatic and heavier molecules of crude oil, and (2) the resins and related aromatic molecules were adsorbed at random on the surface and also some absorbed in the interior of the asphaltene particles. The aromaticity and molecular weight decreased continuously from the center to the surface of the "aggregate". Between 1945 and 1960, only few additional studies were performed on the asphaltene fractions. In 1961, Yen and coworkers [15] started to study solid asphaltenes by means of X-ray diffraction and other techniques. They found that some degree of short-range order existed in *solid* asphaltenes. That order was explained by assuming that the stacking of the aromatic regions in the asphaltene molecules was responsible for the diffraction patterns. Stacking was assumed then to be the typical molecular arrangement of the asphaltenes found in the core of the "aggregates" [13,15]. Therefore, the present colloidal model of petroleum is such that particles contained a core formed by stacks of rather large asphaltene molecules surrounded by an unspecified number of resins adsorbed around them. No specific details are given in this theory regarding the intermolecular interactions between the components or about the lifetimes of the aggregates, etc. Stacking was the main molecular recognition effect used in building the asphaltene aggregates and other types of intermolecular interactions were, generally, neglected [13,15] or not mentioned. It was much later that charge transfer and H bonding were invoked as responsible for the asphaltene and resin aggregation [1]. On the other hand, some authors favored the intermolecular interaction between the atomic electric charges [16] (polarity) while others attributed to the coupling of unpaired spins present in the asphaltene radicals [17] a determinant effect in their aggregation.

MODEL ASPHALTENE MOLECULES

The introduction of spectroscopic techniques opened new routes in the study of the molecular aggregates formed by the heavy fractions of crude oils. A lot of attention has been paid to the asphaltene fraction because part of it precipitates during production causing well and reservoir plugging and thus generating significant economic losses [1]. Unfortunately, very few works have been done instead on the resin fraction [1] even if the classical colloidal theory of the crudes gave them a crucial role in the stability of the asphaltenes in petroleum.

The great chemical complexity of the crudes led the researchers to try to separate the heavy fractions in order to apply different spectroscopic techniques to each of them. The crude oil fractions show considerable overlap [1] so the researchers either obtain average information about each of the heavy fractions as they are isolated or they may try to further separate them in order to obtain purer samples. Most if not all have chosen the first approach so the results collected for the asphaltene fraction that is obtained by simple precipitation and washing is assumed to be valid for all its components. The first problem of this latter approach is that the average molecular weight MW of the asphaltene fractions may not be the best representation of a rather complex multimodal distribution of molecules [18]. Moreover, the experimental determination of the average MW proved to be quite difficult because the marked tendency of the asphaltene components to aggregate even at very low dilution [1,18]. A representative average MW is still in debate because even the way in which the asphaltenes is washed after precipitation influences the resulting values [19]. Nevertheless, the availability of the spectroscopic data led many researchers to propose model molecules that are believed to be faithfully *average* representations of the whole asphaltene fraction [1]. These model molecules reproduced, with different degrees of accuracy, the spectroscopic results, the elemental analysis and average MW of the sample. Most of these molecular models were built directly by inspection of the spectroscopic data employing simple relationships while a few others where generated by specific computer programs [20]. Unfortunately, there are some rather large uncertainties involved in each of these model molecules so they have to be used with great care. The significant uncertainty in the value of the average MW of the asphaltene fraction is further complicated by the fact that two molecules with quite different 3D shapes may have the same MW. Clearly, they will have quite different molecular recognition process in the crude [2]. In an ultra complex fluid such as crude oil, the possibilities of finding such set of molecules are not entirely negligible thus further complicating the analysis. An additional problem in building the models is the difficulty in obtaining 3D structural information for the asphaltene molecules [1]. In most cases, one start with the 2D representation of the model build from the experimental data and by means of Molecular Mechanics searches for the conformation of minimum energy either in vacuum or in a representative solution.

To further complicate the matter, it should be mentioned that the relative localization of the heteroatoms in the asphaltene molecules cannot be determined unambiguously from the experiments [1]. Then, from a single set of experimental data, many different alternative models may be build even if just a few heteroatoms are present in the molecule. An important degree of arbitrariness is then *always* present in the models of the asphaltenes because it is impractical to consider all the different variations that can be built from the same data. Chemical "intuition" has been used extensively in the building of model asphaltenes [1]. Clearly, any molecular simulation using these types of asphaltene models must be done with great care [2]. In no way the quality of the conclusions obtained for well-known molecules or macromolecules can be approached using any of the model asphaltenes available today. These limitations should not be taken as a barrier that prevents doing any molecular simulation involving the heavy fractions of crude oils. Information of qualitative value can be always obtained from these model molecules if proper precautions are taken in the analysis of the results. Any attempt to perform detailed quantitative calculations is of questionable and rather dubious value because the starting model contains so many approximations. Molecular simulation of these model asphaltene and resins aggregates will not provide accurate quantitative predictions of the properties of the real aggregates. Instead, it will generate *qualitative* information that helps to understand many of their features.

The molecular organization of the components of the heavy fraction must follow the same laws that determine the interaction between a ligand and a receptor site or any other simple molecular aggregate [2,21]. The thermodynamic characteristics of all these aggregates must be the same and consequently one could learn from the modeling used in the study of the ligand-receptor interaction [21]. Molecular simulation

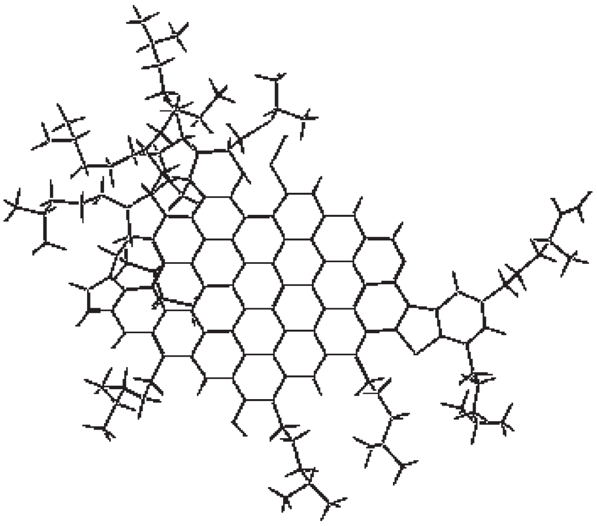

FIGURE 1 Top view of the model molecule for the asphaltene fraction of a 510°C vacuum residue from a Venezuelan Crude oil.

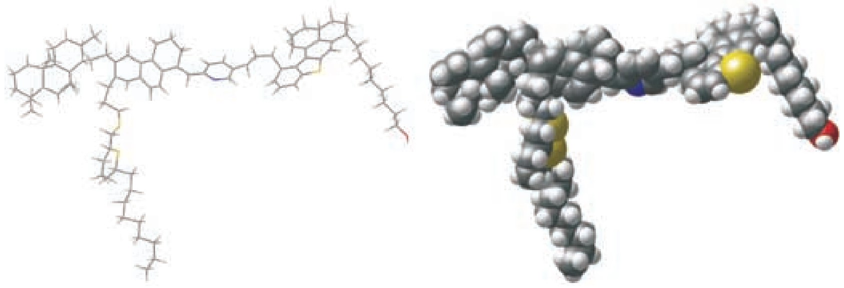

FIGURE 2 One of the model molecules of the asphaltene from the Athabasca sand oil minimized in a toluene solution.

techniques used in the study of the drug receptor interaction were first applied to investigate the asphaltene and resin aggregates in the mid 90 [2]. The first work was about the characteristics of the asphaltene aggregates present in a vacuum residue of the distillation of a Venezuelan crude [2]. The average model molecule used is shown in Fig. 1 and contains a central planar core formed by a large number of condensed aromatic rings plus saturated ones near the upper left edge.

Several heteroatoms (S, N and O) are present in this structure and are not shown for simplicity [2]. This molecular model of the asphaltenes contains only a large central aromatic region and will be called continental. Many models of asphaltenes from different crudes having similar features have been built using diverse theoretical and experimental approaches [2–6]. Only the number of aromatic rings present in the models has been reduced overtime [2–6] as lower MWs are assumed to be more representative.

Recently, selective Ru catalyzed oxidation of the aromatic rings present in asphaltenes has produced new information about the number of aromatic rings present, the extension and type of the alkyl side chains and of the bridging groups found in these molecules [22–25]. It was found that the asphaltenes from several sources from Canada, Venezuela, Indonesia and China have a similar distribution of alkyl side chains and also bridging chains between regions containing aromatic and/or saturated rings [22–25]. Other specific reactions showed the presence of several types of sulfides in some these bridging chains [25]. Model molecules derived from these experimental results [26] are shown in Figs. 2 and 3.

The asphaltene molecules containing bridging groups will be called of the archipelago type. The presence of the bridging chains in these models generates many molecular conformations that are not present in asphaltenes having only a central aromatic core. The differences will prove to be quite important in the formation and in the stability of the molecular aggregates of asphaltenes.

MODEL RESIN MOLECULES

Resin molecules are much easier to isolate and identify than asphaltenes [1] because they do not tend to form stable aggregates as the asphaltenes. Unfortunately, very few molecular structures of resins are known. In Fig. 4 are shown two of the aromatic resins used in the study of their interaction with the model asphaltene from a Venezuelan residue [2]. In Figs. 4 and 5 are shown two resins identified in the Athabasca sand oil [25].

In Fig. 6 are shown a simple and a complex resin found in the Athabasca sand oil [25].

It is easily seen from Figs. 4–6 that the 3D shapes vary considerably from the light resins to the more complex ones. The resin shown at the left side of Fig. 6 contains a relatively large planar aromatic region while the other on the left only shows an acidic –OH fragment and a more or less cylindrical 3D shape.

INTERMOLECULAR INTERACTIONS AND ASPHALTENE AGGREGATES

The forces between asphaltene and/or resin molecules as in any organic ones [21,27] may be divided into (a) the electrostatic forces existing between their net atomic charges, (b) the polarization forces that arise from the dipole moments induced by the electric fields of neighboring molecular charges and

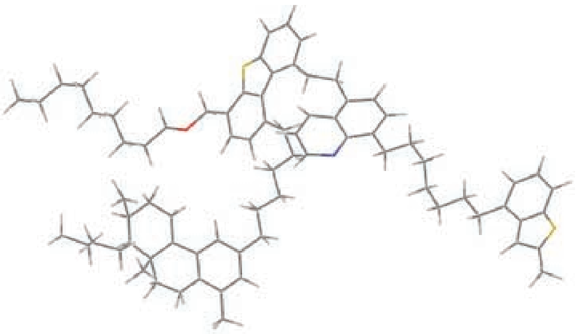

FIGURE 3 A second molecule of the asphaltene fraction obtained from the Athabasca sand oil also minimized in a toluene solution.

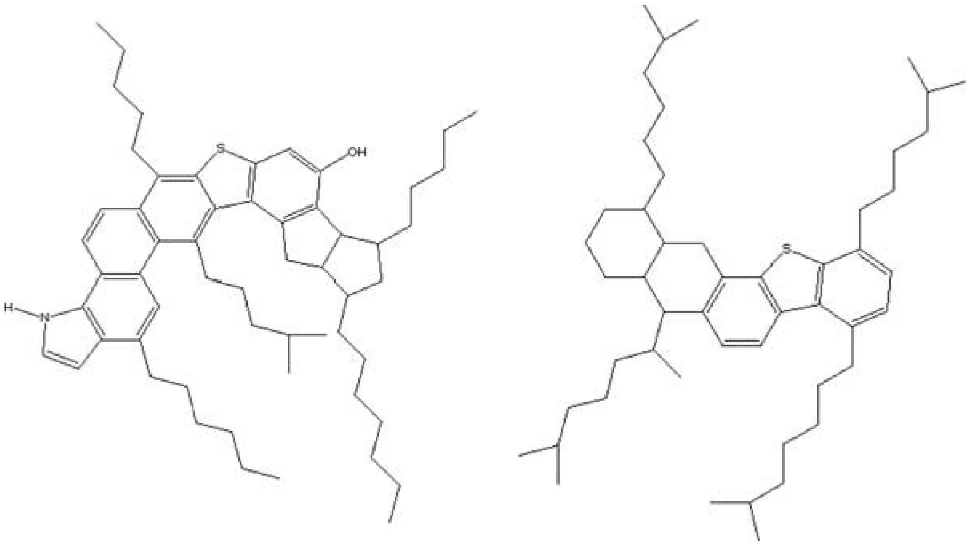

FIGURE 4 Wire frame drawing of two model resins [2].

permanent dipoles and (c) the forces that are quantum mechanical in origin such as the dispersion, exchange (repulsion), and charge transfer interactions. There is evidence that the van der Waals and the electrostatic interactions are the main factors in the molecular recognition in solutions of most organic compounds [21,27]. Unless strong donors and acceptor molecules are involved, the polarization and charge transfer effects play only a minor role in the molecular recognition process and in the stability of the aggregates [27]. Therefore, they will not be considered in this work.

METHODOLOGY

The energy minimization algorithm used in the Molecular Mechanics calculations is part of the InsightII and Discover programs [2]. The well-tested CFF91 interatomic force field [2] has been used to describe the intra- and intermolecular interactions. The conformation of minimal energy of the model asphaltene and resin molecules either isolated or forming aggregates was determined using a summation cutoff distance of 15 Å. Molecular Mechanics can only guarantee to find the local minimum of the energy surface that is nearest to the starting point [21]. At the start of a run, a minimization was first done in order to relax any initial strain left from the construction of the molecules or aggregates. A period of equilibrium of several thousand steps (each of 10^{-15} s) was then established in order to equipartition the potential and kinetic energies. In order to better explore the conformational space, dynamical runs were performed at 800–1200 K for 50 ps. At predetermined intervals, a snapshot of

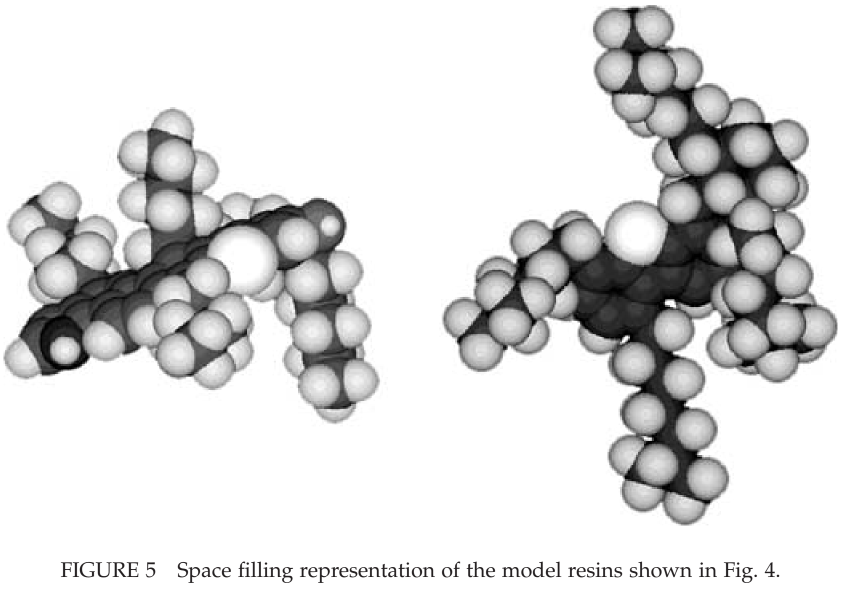

FIGURE 5 Space filling representation of the model resins shown in Fig. 4.

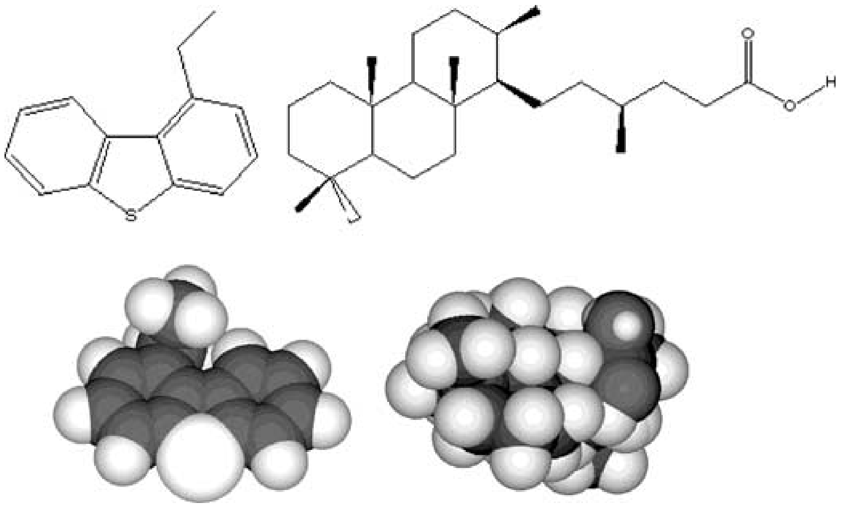

FIGURE 6 Simple (left) and complex (right) resin found in the Athabasca sand oil [2].

the system was taken. These high-temperature structures were annealed by subjecting the system to a dynamic run at 300 K for 50 ps [21]. A minimization process was then applied until the maximum derivative was less than 0.001 kcal/(mol Å). From the set of these conformations, the one with the lowest energy was chosen as the most stable. Several initial configurations were tried, including ones where the aromatic plane of the approaching molecule was perpendicular to that of the others. In all cases, the distance between molecules was chosen in such a way that unwanted short intermolecular contacts were prevented. In the trimers, the approaching molecule was placed near an already minimized dimer before the minimization process was started.

In order to determine the stable conformations in solution, boxes containing the asphaltenes, the resins and the molecules representing the rest of the crude were built with the Amorphous Cell program [2]. The average density was fixed at the corresponding measured value. Periodic boundary conditions were employed in these types of calculations so that an unbound liquid medium could be modeled around the asphaltenes. The cell multipole summation method was used in the calculation [2,21].

STRUCTURE OF THE MODEL AGGREGATES

The results obtained from the first Molecular Mechanics calculations showed that the most stable conformation for the different aggregates of the model of large asphaltenes of the continental type was stacking [2]. The presence of alkyl, cycloalkyl, and other bulky groups at the edges of the aromatic part of the model introduces additional contributions to the molecular recognition process [2]. These groups perturb the interaction between the aromatic rings if their spatial conformation is such that steric interferences are produced when the molecules approach each other. Nevertheless, the orientation and/or conformation of the molecules forming the aggregate may be modified in order to better accommodate approaching ones. In some cases the molecules have just to rotate a few degrees in order to diminish steric interference as seen in many discotic liquid crystals [28]. In other cases, a slight deformation of the molecular backbone is required in order to allow a more favorable stacking [2]. This deformation of the covalent bonds will produce an increase in the molecular energy that must be compensated by net gains in the intermolecular interactions. This effect was found in the model asphaltene aggregates of the continental type as some departures from planarity of the aromatic system were observed [2] in the minimized conformations as seen in Fig. 7.

The results reported for large numbers of crystal structures, host-guest and intercalation complexes indicate that the main feature in the molecular recognition between large aromatic molecules is the ring–ring (stacking) interaction [27,29]. It was found that model asphaltene with large aromatic planes always showed parallel (or nearly) parallel molecular stacking [2]. Calculation of the model asphaltene dimers with the aromatic planes located perpendicular to each other showed a much lower energy and, if allowed to evolve in time, always led to the more stable stacking of the aromatic planes [2]. In Fig. 7, one can see that the formation of a stable dimer has to go through some degree of deformation of the alkyl side chains of the molecules involved. In the minimization process, they are pushed away from the plane defined by the aromatic regions in order to maximize the contact between these regions.

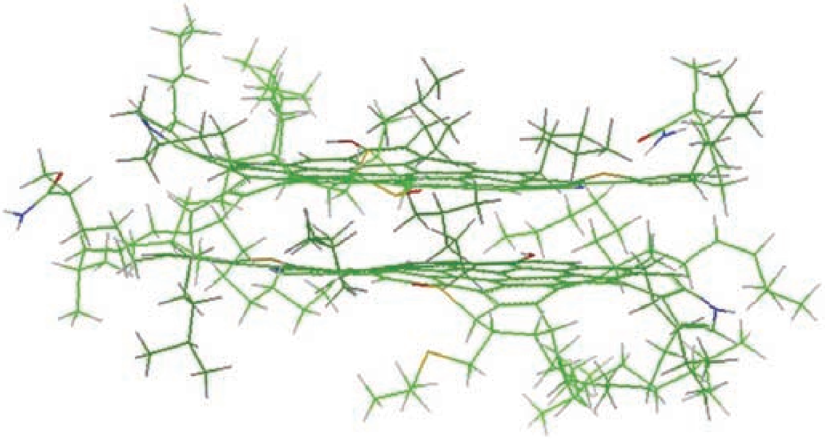

FIGURE 7 Side view of a dimer of a model asphaltene shown in Fig. 1.

If a trimer of this model asphaltene molecule is build and its energy minimized, one finds that the gain by the second stacking process is much less than that that of the dimer. The formation of a tetramer is even less favored because the steric interference grows quite rapidly with the number of components of the aggregate as seen in Fig. 8. The steric interference then seems to set a limit to the growth of the stable aggregates of asphaltenes of the continental type by means of stacking.

The formation of aggregates of asphaltenes of the archipelago type is more complex than in the case of the continental one. In the former molecules, the presence of bridging chains of great flexibility generates conformation that may even lead to the formation of "self" aggregates if the extend of the chain is long enough [30]. In these aggregates, the aromatic regions of just one molecule may form stacks if the chain is bended in such a way that these regions are allow to approach each other. The interaction between aromatic regions is the driving mechanism for the formation of aggregates in asphaltenes with large aromatic regions [2,27]. The interaction of large number of rings prevails and stacking will result as the most stable from of aggregation. In the case of asphaltene of the archipelago type, the aromaticity is noticeably lower and the aromatic regions will, on average, contain around five or six rings [18]. Then, other interactions may become important and compete with stacking. The existence of acid and basic groups in asphaltene and resins is well known [1,7] and, therefore, H bonds are likely to exist between these molecules. It is interesting to mention that the acid part of most crude oils is concentrated in its resin fraction while the basic one is found mostly in the asphaltenes [1]. Molecular Mechanics calculations showed that the formation of such intermolecular bond has an energy similar (within 1 kcal/mol) than that produced by the stacking of the aromatic parts of molecules such as that of Figs. 2 and 3. Therefore, in the asphaltenes of the archipelago type, H bonding provides an additional aggregation mechanism that is relatively much weaker in continental asphaltenes.

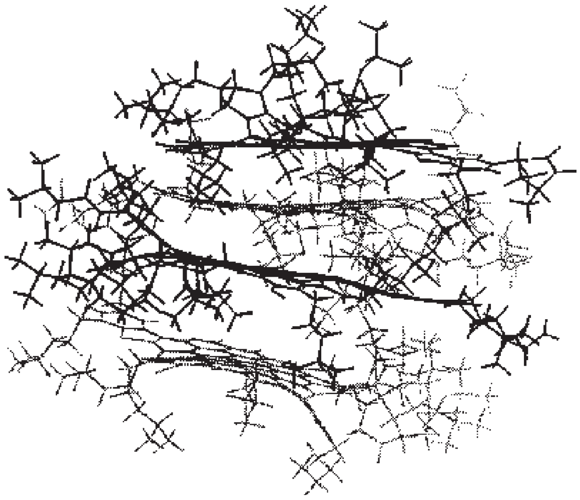

FIGURE 8 Side view of a tetramer formed by the model asphaltene of the continental type and minimized in vacuum.

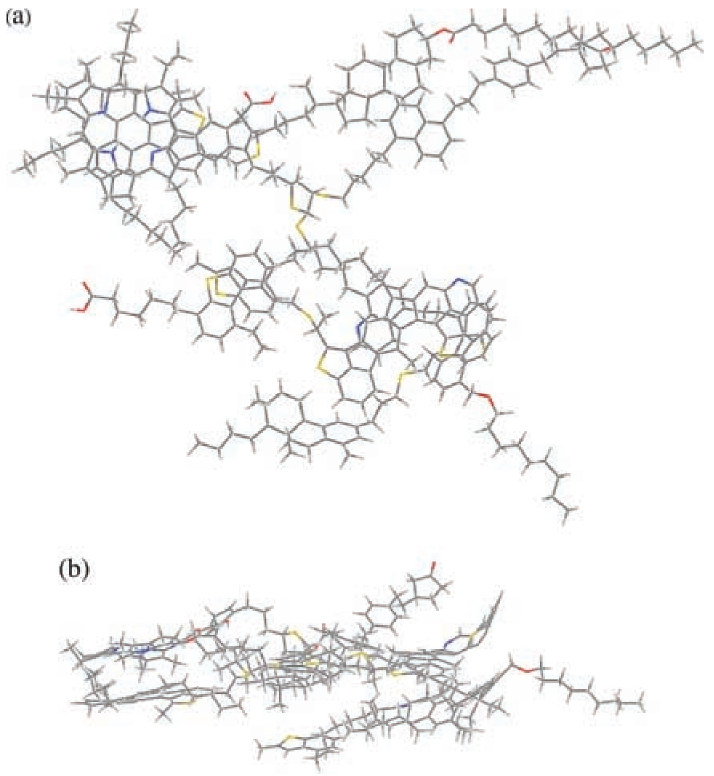

FIGURE 9 a) shows the overlapping between the aromatic regions from a direction perpendicular to them while in b) a side view of this aggregate is shown.

The existence of long bridging chains in some of the asphaltenes suggests also the existence of molecular tangling [31]. As in some polymers in solution, such type of molecule changes its conformation in such a way that they may become entangled with similar neighboring ones [31]. The tangling and untangling of these asphaltenes may be a slow process if some of the conformations required for its existence are difficult to achieve. This type of tangling process may explain the extraordinary long times (several weeks) that takes to dissolve aggregates of some fractions of asphaltenes from Athabasca [18].

In Fig. 9 are shown two views of an aggregate of four asphaltene molecules of the archipelago type in solution. They also form stacks involving most of their aromatic regions as the asphaltene of the continental type. The existence of bridges between aromatic regions of an asphaltene molecule induces the formation of inter aggregate links. One of these asphaltenes may have one of its aromatic regions in one aggregate and another in a neighboring one. Therefore, the asphaltenes of the archipelago type have other ways of forming aggregates that are not available for those having only a central aromatic core and short side chains.

A combination of limited stacking with lateral H bonding that produces lateral intermolecular bridging may explain the formation of more or less planar (carpet like) aggregates found in some asphaltenes in solution [32]. These results are difficult to explain if only asphaltenes with one large aromatic core were present in the sample because they will only tend to form stacks with weak lateral interaction [2]. It is then reasonable to assume that the main molecular recognition process in asphaltenes with large aromatic regions is stacking while in those of the archipelago type a more complex set of aggregates may be formed by bridging and H bonding.

MOLECULAR AGGREGATES OF RESINS AND ASPHALTENES

The classical colloidal theory of crude oils assumes that the resins peptize the asphaltene aggregates [8,9]. In order to be effective, the resins must form strongly bonded aggregates with the asphaltenes. If they do not form such aggregates, the resins will not protect the asphaltenes from neighboring ones and precipitation should occur. In Fig. 10, is shown a side view of the structure obtained for the tetramer formed by an aromatic resin and the model asphaltene molecule of Fig.1.

The resulting minimized structure shows how tight these aromatic resins fit into the asphaltene molecules upon minimization. The stacking resulting from the interaction between the aromatic planes

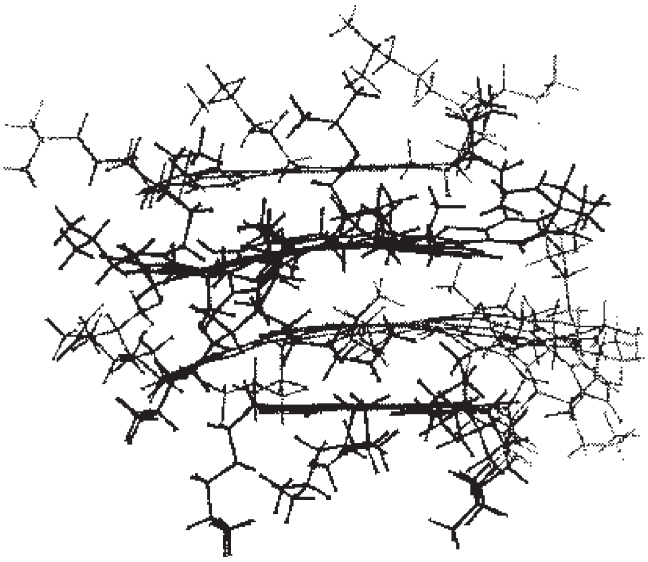

FIGURE 10 Side view of a central asphaltene dimer with two resins located above and below it.

is again the main factor in the formation of the aggregates as seen from Fig. 10.

It is interesting to notice that the external part of the aggregate contains mainly alkyl side branches. The resins then block the available aromatic sites while adding further alkyl branches to the aggregate. This large number of external alkyl branches makes the aggregate much more soluble in the rest of the crude oil formed by saturated and aromatic parts as implied by the colloidal theory. If other of types of resins with quite different 3D shapes is used in the formation of aggregates, the resulting interaction energy diminishes noticeably [33]. In cases where the area of contact between the resin and asphaltene molecules is small, the interaction energy is so low that no long lasting aggregate is formed because their energy is similar or smaller that the thermal energy. This effect is a clear indication that selectivity must be present in the interaction between resins and asphaltenes. An analysis of the energies involved [2] showed that the formation of tetramer of the type resin + asphaltene + asphaltene + resin is favored with respect to that of asphaltene + resin + resin + asphaltene for asphaltenes of the continental type. In the tetramer with the resin dimer in its core, the values of the interaction energy showed an important decrease with regard to that of the other. It has been shown that in a mixture, the organic molecules containing the largest area of favorable interatomic contacts (aromatic areas) will form aggregates between them rather than with other molecules [34]. This is simply because they will have more favorable contacts per molecule than the smaller ones. This result confirms the early colloidal model of crude oil [8,9] where the asphaltenes were assumed to be the core of the aggregates and the resins the outer layer.

The limiting trend found for the growth of the aggregates above may be erroneously interpreted as indicating that there will not flocculate and, correspondingly, no precipitation of the asphaltenes should occur. This is not the case because the shifts in composition produced, e.g. by the addition of light *n*-paraffins, detaches resins and other alkylbenzenes forming the external alkyl "layer" of the aggregates that face the lighter fraction of the crude [9]. The separation of the resins allows, in turn, the direct interaction between the molecules of neighboring aggregates that favors flocculation. It is interesting to point out that an increase in the concentration of the *n*-paraffins will also allow the side chains to attain more extended conformations thus decreasing their steric interference. It is known that in bad solvents the alkyl branches tend to coil while in good ones they have well-extended conformations [35]. This change in the conformation of the alkyl side branches will also favor further stacking of the asphaltenes and will consequently contribute to their precipitation.

The asphaltene and resin molecules have complex 3D shapes and the molecular recognition processes that lead to aggregate formation depend on the fit of the resins with the adsorption sites of the asphaltenes [1,33]. This selectivity explains the reason why the resins of one crude do not necessarily contribute to the solubility of the asphaltene of another one [2]. If the 3D shape of the resins does not match some of the adsorption sites of the asphaltene molecules, then the aggregate will not have a significant lifetime and, consequently, the resin will not contribute to its solubility [33].

H BONDING

The existence of atomic groups containing basic N and O atoms implies not only that most of the asphaltene and resin molecules will be polar but also that they may interact with molecules capable of H bonding such as acidic asphaltenes, resins and other components of crude oil. The reverse is also valid and the acidic asphaltene may interact with the basic components of the crude. The H bond is a strong interaction that contains contributions from all the intermolecular forces. It involves the interaction of an H atom, attached to a highly electronegative one (i.e. O, N), with an electronically rich atom of a neighboring molecule or molecular fragment [21]. This type of interaction between fragments/molecules with closed electronic shells is mostly determined by the *local* atomic charges of both of them (electrostatic interaction). Little or no charge transfer in the H bond is found although charge re-arrangements may occur, through polarization and induction effects. H bonding may contribute to the aggregate generation through its formation in different sites of the asphaltene molecules [27,36]. These sites must be free of steric hindrances in such a way that proper interatomic contact is possible between the approaching acidic molecule and the accepting groups. Moreover, the strength of H bonding is orientation dependent so the approach of the molecules involved should be at proper angles to generate a strong interaction [21,27]. Otherwise, the H bond will be weak and contribute little to the aggregation process. As the asphaltene molecules may contain several kinds of basic (or acid) sites [1], it is expected that H bonding will contribute to the aggregate formation if they are available for interaction. As in other compounds, the extension of the H bonding depends on the chemical composition of the asphaltene molecules and on their shapes. The great chemical complexity of the heavy fractions suggests that a wide distribution of H bonds is likely to exist in the molecular aggregates formed by the different asphaltenes and resins. The existence of H bonding does not mean that the other parts of the asphaltene and resins molecules are not important in the formation of the aggregates. Depending on the strength of the interactions present in there, in some of aggregates the interaction between the aromatic regions will be the governing factor while in others the H bonds will be dominant one [27,36]. A mixed aggregate may be also envisioned where both types of interactions have similar contributions.

We have to remember that molecular recognition is a dynamic process based on distinct chemical interactions and not only on the passive action of a lock and a key. If the molecules of asphaltene and resin have sufficient flexibility, a conformational reorganization or induced fit is possible and an aggregate formed even if small discrepancies exist between the host (lock) and the guest (key) molecules. We have, then, that the flexibility of parts of the participating molecules plays also an important role in the formation of all these aggregates.

CONCLUSIONS

Molecular Mechanical calculations of aggregates of a model asphaltene from a vacuum residue from Venezuela with a single and large aromatic region and resin molecules showed that the main driving interaction in the aggregate formation was the attraction between the aromatic planes. In this case, the molecular recognition was completed with the unfavorable contributions from its saturated rings and side chains. These fragments contributed to the formation of the aggregate through the combined effect of the steric repulsion and the van der Waals attraction. It was shown that the complex 3D shape arising from the presence of alkyl and cycloalkyls groups in asphaltenes limits the growth of the aggregates to a small number of molecules. The complex 3D shape of the continental model asphaltene allowed the readily formation of aggregates with resins that were able to fit into the aromatic regions without interferences from the alkyl groups and saturated rings. Molecular Mechanics have been also used to compute the most stable aggregates of model asphaltene molecules from the Athabasca oil sand. These model archipelago molecules have several smaller aromatic regions connected by different types of alkyl and sulfide bridges. It was found that this type of asphaltenes showed a more complex set of aggregates than the asphaltenes of the continental type. The interaction energies for solvent and resin molecules at different adsorption sites of the asphaltene molecules from Athabasca were also analyzed. The lowest energy of interaction was found to be for solvent toluene and *n*-octane and the highest for polar resins. Also, the results indicate that the selectivity of the resins for some sites of the asphaltene molecules provides an explanation of the specificity of them for its own crude oil and for all those containing asphaltenes with similar adsorption sites.

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