MOLECULAR MECHANICS OF AGGREGATES OF ASPHALTENES AND RESINS OF THE ATHABASCA OIL

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ABSTRACT

An analysis of the effects of a almost continuous chemical distribution of asphaltenes and resins on the molecular recognition processes occurring in crude oil indicates that their aggregates will have a broad distribution both in chemical composition and in strength of the intermolecular interactions responsible for the aggregation. Then, crude oil can not be described just as a sol formed by solid asphaltene particles dispersed by resins or as a simple micellar system of asphaltene and resin molecules. The molecular aggregates may vary from solid particles formed by asphaltenes and resins to loosely bound micelles with quite short lifetimes. These different aggregates may coexist within the crude oil and many will exchange components with others. The entropic contributions to the changes in free energy upon aggregation is also discussed. Molecular mechanics calculations showed that a model asphaltene aggregate from Athabasca exhibit stronger interactions with its resins than with solvents such as toluene and n-octane. The resins showed a considerable selectivity for the different adsorption sites of the asphaltene aggregate. This selectivity was stronger than that found for the solvent molecules indicating that is enthalpically more favorable for them to form aggregates with the asphaltenes. The selectivity may also help to explain the specificity of some resins that are able to disperse only the asphaltenes of certain types of crudes while failing to do the same for others.

INTRODUCTION

It is generally accepted that crude oil is a complex colloidal system where part of the heavy fraction forms molecular aggregates of different sizes (Speight, 1991). The extraordinary chemical complexity of this fraction of crude oil (Tissot and Welte, 1978) implies the existence of molecules of many different shapes and sizes. The shape determines the contact area between molecules and this, in turn, is one of the elements that govern the type, number and lifetime of the molecular aggregates formed in crude oil. Therefore, it is necessary to analyze the influence of this complexity at molecular level on the aggregates. The determination of the molecular structure of components of crude oil is complicated by the formation of molecular aggregates. This makes the interpretation of the spectroscopic data in terms of the molecular structure a demanding task. The isolation of the different fractions is of great importance and the use of sophisticated methods of determining the molecular structure is mandatory to unravel the chemical components of the different fractions of crude oil.

Many of these methods were used in the study of the heavy fraction of oil obtained from the Athabasca sands. In particular, the acetone fraction of the asphaltenes was studied in great detail (Strausz et al., 1992). Beside the information about this particular asphaltene fraction, a systematic analysis of the resins present in the Athabasca bitumen was also available (Payzant et al., 1986). Then, not only the molecular components of a major fraction of the asphaltene but also that of several of their most abundant resins are known for this oil. In very few oils, this type of detailed structural information is available for the heavy fractions. Therefore, these experimental studies provide a unique opportunity of studying the formation of the molecular aggregates present in crude oil.

The stability of the micelles and molecular aggregates of asphaltenes and resins is quite significant because severe problems are linked to their separation from the oil (Speight, 1991). In order to obtain information about these aggregates, a comparison of the characteristics of solutions of surfactants with those of asphaltenes and a molecular mechanics study of the molecular recognition pattern acting on asphaltenes and resins from the Athabasca oil sands were undertaken.

THEORY

In contrast with simple molecular liquids, complex fluids contain molecular aggregates that may have a significant lifetime. Well-studied examples of these fluids are the aqueous solutions of pure organic surfactants. There, the molecular aggregates formed by the surfactants may have lifetimes of up to a second (Evans and Wennerström, 1999). Similar surfactant aggregates or micelles are found also in many non-polar

solvents, such as benzene, (Eicke, 1980) that are part of crude oil. The micelles are formed and dissolved continuously because they are in a dynamical equilibrium with the monomers present in the solution. The lifetime of these micelles depends on the type of surfactants present in the sample. If the complex fluid contains a colloidal dispersion of a solid, then, the lifetime of the aggregates may be considered to diverge (Russell et al., 1989). The dispersed solid particles may exchange some of their molecules with the liquid. The number involved in this exchange will depend on the solubility of the solid. Crude oil has been assumed to be a colloidal dispersion of a solid (asphaltenes) in oil that is solubilized by the resins (Syuniaev et al. 1997). In this model, asphaltenes are assumed to be practically insoluble in oil. Then, the exchange of asphaltene molecules with the liquid will be an unlikely event and it will be a very slow process. The molecules of the micelles formed with surfactants are exchanged with the surroundings within 10^{-6} to 10^{-3} s (Evans and Wennerström, 1999). There is no information about the exchange rate of asphaltene molecules between the micelles or solid particles and the crude oil or other solvents. Indirect evidence shows that the process is several order of magnitudes slower than in the micelles of surfactants in aqueous solution (Sheu, 1996).

When several types of surfactants are present in the solution, complex synergic and antagonistic effects are present (Evans and Wennerström, 1999). The distribution in molecular shapes and properties present in a mixture of surfactants allows the formation of a large variety of different types of aggregates (Vila-Romeu & Taddei, 1997). This variety is not present in a solution of a single type of surfactant. The heterogeneity within the aggregates found in a solution with only two different kinds of amphiphiles, shows that if micelles are present in crude oil, one should expect a very large variety of them. An analysis of the chemical components of crude oil shows that the molecular shapes there varies from a rather simple for the n-paraffins to complex one for resins and asphaltenes as seen in Figs. 1 and 2. In the liquid phase, the molecules are in continuous contact with their neighbors (Israelachvili, 1991) and are subjected to the thermal motion. If the intermolecular area of contact is large enough, then, the total interaction energy may be larger than the thermal one and a molecular aggregate that lasts in time may be formed. On the other hand, if the intermolecular contact area is small so that only a few atoms are in close contact, then, the aggregate will have a very short lifetime (Dunitz and Gavezzotti, 1999).

The small size of the measured asphaltene-resin aggregates, (30-50Å) (Sheu, 1996) and the size of the known asphaltene and resin molecules, shows that the number of them in each particle will be small (<5-10). In such a small system, it is difficult to determine if it forms a crystal because the surface effects are very important. In a system as chemically complex as the heavy fraction of crude oil, it is unlikely that the particles will contain just only one type of asphaltene. The packing requirements in molecular crystals are quite stringent (Kitaigorodsky, 1973) so, in order to accommodate different types of molecules in such a

small particle, it is, generally, more favorable to form a glassy or disordered rather than a crystalline phase.

At the time, there is not experimental data that determine unambiguously if the asphaltenes in crude oil are part of dispersed solid particles or form micelles similar to those found in solutions of surfactants. The near continuous distributions of the heavy molecules present in crude oil suggests that it should generate a distribution also in the types of their molecular aggregates. The aggregates formed by the most strongly interacting molecules may form solid particles (Dunitz and Gavezzotti, 1999). In general, asphaltenes that can have a large number of close interatomic contacts (big aromatic areas) will form this type of particles because they generate a large number of attractive contacts per molecule. The other aggregates formed with molecules that show smaller areas of contact will resemble more and more typical micelles of surfactants as the intermolecular interaction energy decreases. We have; then, that the nearly continuous distribution in chemical composition is reflected in the lifetime of the molecular aggregates formed by the resin and asphaltene molecules present in crude oil. It is likely that crude oil can not be described by a simple concept such as a solid dispersion or a traditional micellar system. These concepts were derived for simple systems such as the sols formed by polyehtylene spheres or for solutions with only one or two different surfactants. New concepts have to be developed for the description of such a chemically complex fluid as crude oil.

The main attractive intermolecular force between pure hydrocarbon molecules is that that of van der Waals (Stone, 1996).

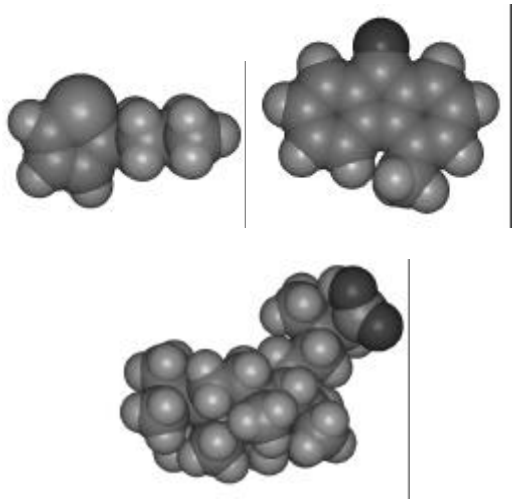

FIGURE 1 Molecular shapes of three resins from the Athabasca sand crude

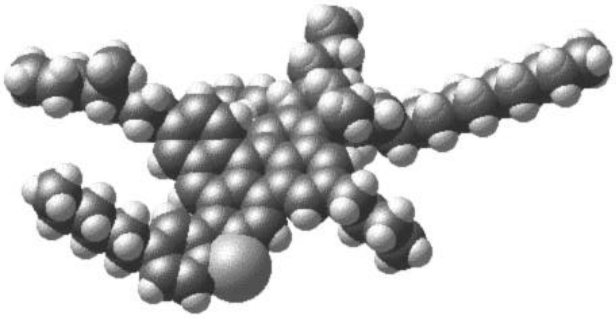

FIGURE 2. Molecular shapes of a model asphaltene molecule

It is a rather weak interatomic force, it is almost always non-directional and it acts between *all* types of atom. It is responsible for the existence of liquids and solids of pure hydrocarbons where the other intermolecular forces such as electrostatic and charge transfer are negligible or nonexistent. Crude oil is composed, in general, by more than 95% of C and H atoms (Speight, 1991), then, the van der Waals plus the repulsive forces are the main ones in determining its properties. Nevertheless, the presence of heteroatoms in asphaltenes and resins introduces contributions from the interactions of the different atomic charges (Murgich et al.1999). In particular, Hydrogen bonding may play an important role in the formation of the aggregates. This type of bonding is strongly directional and it is mainly determined by the electrostatic interaction between sites. The atoms involved in Hydrogen bonding must be available for close contact. Unless the donor or acceptor sites of the H bond are free from steric hindrances, they will not contribute to the aggregation process. This is also true for the interactions between aromatic planes of resins and asphaltenes where the area of contact between the planes must be large in order to be effective (Dunitz and Gavezzotti, 1999). Then, the 3D conformation of the asphaltenes and resins plays an important role in the molecular recognition process that generates their aggregates and determine their lifetime. Consequently, the conformation of the asphaltene and resin molecules can not be ignored in the analysis of the formation and stability of aggregates. Nevertheless, there are other factors linked to the entropy that also should be considered in the study of the formation of molecular aggregates of asphaltenes and resins. These factors are related to the loss and gain of degrees of freedom from both the molecules involved in aggregate and those of the solvent next to it. In order to determine the relative importance of the different factors involved in the aggregate formation, one has to consider the changes occurring in the free energy of system.

THERMODYNAMICS OF AGGREGATE FORMATION

The formation and stability of molecular aggregates such as the micelles or disperse solids present in crude oil will be determined by the changes in the total free energy, $\Delta G = \Delta H - T\Delta S$, of the system. In this case, ΔH is the change in enthalpy while ΔS is the change in entropy of the system upon aggregate formation. We have to analyze each of the different contributions to ΔG to gain insight on the aggregation process occurring between resins, asphaltene and the rest of the molecules of the crude. Unfortunately, the calculation of the entropic contributions is an open matter (Searle and Willams, 1991) so only estimates will be made here.

The binding of a molecule A with B has always an unfavorable entropic term arising from the reduction in the number of translational and rotational degrees of freedom system (Searle and Willams, 1991) (Vinter, 1996). This reduction was estimated to be 10-12 kcal/mol for molecules binding to large receptors. Nevertheless, the molecules in the aggregates are not rigidly attached so low frequencies vibrations are also present. These vibrations produce an entropic contribution that partially compensates the changes due to the reduction in the degrees of freedom (Willams et al. 1991). The reduction is connected with the intensity of the intermolecular interactions. A strong interaction implies a deeper potential well than in the case of a weaker one. Upon aggregation, the decrease in entropy is much larger in the deep well than in the shallow one. For bimolecular interactions, there is compensation between the enthalpic and entropic parts arising from these differences (Willams, et al. 1991). In the case of the formation of typical asphaltene-resin micelles, the interactions are, in general, weak and involve mainly the van der Waals, Coulomb and repulsive interactions (Murgich et al.1999a). One may then expect a rather shallow potential well upon adsorption with closely spaced levels capable of generating a sizable entropic contribution. This vibrational source will compensate part of the entropy loss brought about by the reduction of the degrees of freedom. It is expected that this contribution will be reduced by around 20-30% of the value corresponding to a rigid interaction.

The desolvation of the contact area between the molecules forming the aggregate also generates an additional source of compensation of the entropy loss resulting from the formation of the aggregate. Desolvation generates a gain in the translational and rotational degrees of freedom of the molecules of the solvent involved in the process. As in the case of drug-receptor interaction, the gain in entropy in this case is also smaller than expected because the solvent molecules are not rigidly attached to the aggregate and residual vibrations exists during solvation. This contribution is connected to the transference of a number of solvent molecules to the bulk phase with the accompanying increase in the translational and rotational entropy ΔG_{t+r} (Willams et al. 1991) of the system. It will depend on the number of solvent molecules that are desorbed in the aggregate formation and on the way that the solvent molecules interact with

themselves. Consequently, the gain in entropy is proportional to the area of direct contact between the molecules forming the aggregate. For our model asphaltenes and resins, the area of contact is relatively large (30 to 50Å^2). A considerable number of solvent molecules must be desorbed to allow the direct contact between the asphaltene aggregate and some of the resin molecules.

There is also an additional entropic contribution to ΔG arising from the restrictions of the internal molecular rotors of the generated by the aggregate formation ΔG_{rot}. The contribution per rotor was estimated to be 1.7 kcal/mol although smaller values have been used (1.0 kcal/mol) because these rotations are generally replaced by hindered ones rather than being totally frozen (Willams et al. 1991). The asphaltenes and resins contain only a few short paraffinic branches that may have their rotational freedom impaired upon adsorption. Nevertheless, it is not expected that these restrictions will be much larger than those found in the isolated molecules within the liquid oil. So, we may neglect these rotational contributions to ΔG in the present case.

The comparison of the molecules before and after aggregation shows that the process of micelle or solid particle formation generates changes in their conformations that produce an unfavorable enthalpic contribution to the free energy (Willams et al. 1991), ΔH_{conf}. This term represents the strain energy in the aggregate associated with the introduction of bond bending, rotation around bond and dihedral angles, etc., produced by the aggregation process.

Most of the terms mentioned above are unfavorable to aggregation so, in order that a lasting binding may exist, additional favorable factors must be present in the process. One of them is the sum of the changes in the energy of interaction between the charges present in the system $\Sigma\Delta G_i$. This contribution contains the differences in the Coulomb interaction between the molecules when they are free and separated in solution and when aggregated (Willams et al., 1991). Asphaltenes and resins contain heteroatoms such as N, O and S (Speight, 1991) that have some significant atomic charges. Even if the number of such atoms is rather small (< 6%), their contribution may be significant and can not be disregarded.

The second enthalpic term favorable towards aggregation arises from the changes resulting from the gain in van der Waals energy ΔG_{vdW} (Willams et al. 1991) produced by the substitution of a portion of the solvent molecules by the atoms of the other asphaltene or resin molecules. An additional favorable contribution arises from the changes in the van der Waals energy ΔG_{vdW} produced by the improved contact generated by the deformation of the molecules forming the aggregate. This term compensates the disfavorable enthalpic term arising from conformational changes produced by the aggregate formation.

In general, the binding of the asphaltene and resins in the micelles or solid particles will be favored if the resulting ΔG is such that (Willams et al. 1991):

$$\Delta G = \Delta G_{t+r} + \Delta G_{rot} + \Delta H_{conf} + \Sigma \Delta G_i + \Delta G_{vdW} < 0 \quad (1)$$

In the present case, we have that

$$\Delta G \approx \Delta G_{t+r} + \Delta H_{conf} + \Sigma \Delta G_i . + \Delta G_{vdW} < 0 \quad (1)$$

All the terms of this last equation are present in the aggregation process of asphaltenes and resins. In some cases, the enthalpic contribution ($\Delta H_{conf} + \Delta G_{vdW}$) may become dominant while, in others, the adsorption will be governed by the entropic (ΔG_{t+r}) or by the Coulombic one $\Sigma \Delta G_i$ while in others by a combination of the different contributions.

MOLECULAR MECHANICS

Molecular mechanics provides information about the most stable conformation of molecules and their aggregates. This method makes use of analytical functions to represent bond stretching, bending, and torsional as well as nonbonded (electrostatic interactions, dispersion attraction and exchange repulsion) energies of molecules (Leach, 1996). The procedure is such that an initial configuration is specified and the interatomic distances and bond angles are adjusted, using an iterative computational method, until the minimum energy configuration is obtained. The algorithm used in this work was part of the INSIGHTII and DISCOVER set of programs (Molecular Simulations, 1997). Molecular mechanics can only guarantee to locate the nearest local minimum of the energy surface to the starting point of the calculation (Leach, 1996). In order to obtain the most stable conformation for the molecules and aggregates, it is necessary to use procedures that include molecular dynamics. In this way, the system may surmount energy barriers that lead to more stable molecular or aggregate conformations (Leach, 1996). The CFF91 interatomic force field has been used in this work to describe the intra- and intermolecular interactions (Molecular Simulations, 1997). The conformation of minimal energy of the asphaltene and resin molecules and aggregates was determined using a summation cutoff distance of 14Å (Leach, 1996).

MOLECULAR AGGREGATE MODEL

A molecular aggregate, derived from the fragments identified from the Athabasca sand oil, (Murgich et al. 1999b) was used in this study. The aggregate that represents the asphaltene fraction is shown in Figure 3. The resulting adsorption sites were very similar or identical to those found in an earlier work (Murgich et al. 1999a) where a macromolecular model was used instead of an asphaltene aggregate.

The molecular mechanical calculation was performed for the complexes formed by the asphaltene aggregate with each of the nine

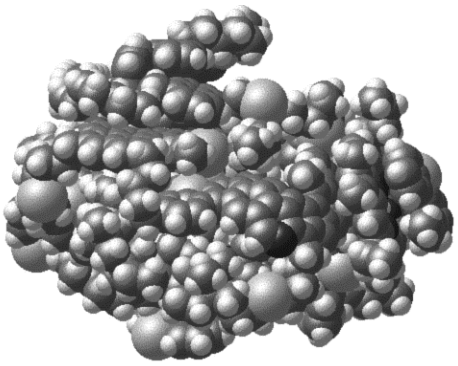

FIGURE 3 Model of the asphaltene molecular aggregate of Athabasca

different resins, toluene and n-octane, (Murgich et al. 1999a). The large size of the asphaltene aggregate made the calculation of the system in a cube full of solvent prohibitively expensive in terms of computer time so the calculations were done in vacuum. The resulting complex was minimized using the simulated annealing method (Leach, 1996). The energy of these complexes was analyzed by means of the Docking Module of the InsigthII program (Molecular Simulation, 1997). The results obtained for the different resins and for toluene and n-octane are shown in Figure 4. The enthalpy of interaction is directly the intermolecular energy as calculated by programs such as Discover (Leach, 1996). Fig. 4 shows a graph of the enthalpies of adsorption of nine resins plus toluene and n-octane at nine different adsorption sites that are available in the asphaltene aggregate (Fig. 3). These sites were chosen because they contain mostly aromatic parts that are known to strongly bind most of the resins (Murgich et al.1999a). These parts are flat and thus favoring the interaction between atoms of similar regions in other molecules. The saturated regions also attract the resins and the solvent but with lower intensity because the number of close interatomic contacts is smaller. The low enthalpy of adsorption in this case can not compete with the thermal energy and the aggregate will have only a very short lifetime. From Fig. 4, we see that both toluene and n-octane have a lower enthalpy of adsorption when compared with that found for resins. The resins have, in general, a larger

contact area with the asphaltene aggregate than toluene or n-octane. Consequently, the energy of interaction between the asphaltene and the resins will be higher than that for the asphaltene and the smaller molecules forming the solvent (Dunitz and Gavezzotti, 1999). The adsorption of the larger molecules on the asphaltene aggregate will be also favored by the increase in entropy produced by the desolvation of the contact area. The

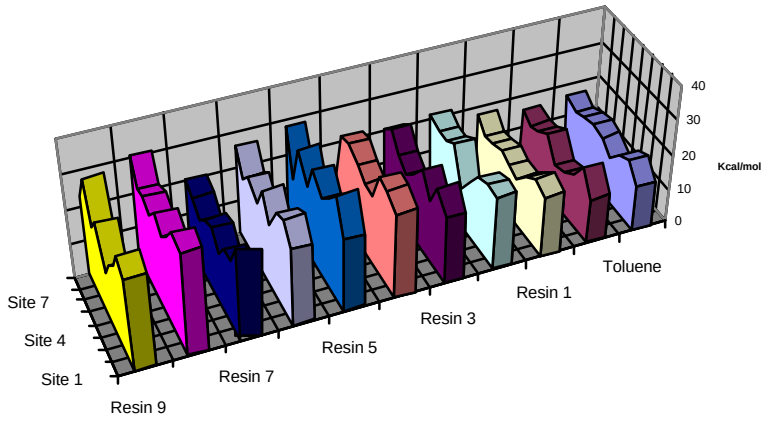

FIGURE 4 Enthalpy of interaction of nine resins of the Athabasca oil and of toluene and n-octane for nine different adsorption sites of the asphaltene aggregate.

number of solvent molecules that has to be displaced by the adsorption is larger for most of the resins than for toluene or n-octane thus further favoring their adsorption. Fig. 4 also shows that the solvent molecules and the resins display a noticeable selectivity for the adsorption sites of the asphaltene aggregate. The selectivity for the resins is higher than that found for the molecules forming the model solvent. This means that the resins will tend to substitute these molecules in most of the adsorption sites. Fig. 4 shows that the enthalpic contribution favors the formation of micelles/solid particles with the resin molecules rather than solvation with the other components of the crude oil.

AGGREGATE LIFETIMES

For pure surfactants, the aggregation number is centered on values that are determined by molecular parameters such as the polar head surface and the non-polar chain length. The aggregation number distribution is such that has peaks at the monomer concentration and around the most likely aggregation number (Israelachvili, 1991). For common surfactants in water solution, this number is around 30 to 120 molecules (Evans and Wennerström, 1999). In non-polar solvents, this number varies over even a much larger range (2 to 200) although lower values than in aqueous solutions are much more common (Eicke, 1980). Aggregates with much more or much less molecules than the more stable number are less likely to occur so that the lifetime of the micelles (10^{-3} - 1s) is many orders of magnitude larger than the typical molecular times (10^{-13} - 10^{-9} s). The long lifetimes are the result of the fact that the micelle has to go through aggregation numbers that have a very low probability of occurrence. So, it takes a long time and many fluctuations to reach such a state. This kinetic bottleneck is responsible for the observed lifetimes in micelles of surfactants such as sodium dodecylsulphate in water solution. In the case of the asphaltene aggregates, if they do form micelles, they must be in equilibrium with the corresponding monomers in solution. There is some evidence showing that asphaltene aggregates have a much longer lifetime than the surfactant ones (Sheu, 1996). This will mean that the kinetic bottleneck is much stronger in the asphaltene aggregates. The interaction between the relatively large and flat asphaltene and resin molecules is stronger than that found between typical surfactant molecules. In other words, the intermolecular potential well is much deeper in the case of asphaltene than in the surfactants. Therefore, only a few fluctuations will provide enough energy for the break up the aggregate.

Further experimental and theoretical work is needed in order to further clarify the type and nature of the molecular aggregates formed by resins and asphaltenes in different crude oils.

CONCLUSIONS

If the molecular shapes of the asphaltenes and resins are such that they have a large contact area, their aggregates will have a favorable enthalpic contribution to the changes in free energy ΔF. In particular, the extension and availability of the aromatic regions plays an important role in the stability of these aggregates. These regions offer a large number of close interatomic contacts per molecule than the others in typical asphaltene and resin molecules. Then, if other atomic groups do not block the aromatic regions, the molecules containing them will tend to form stacked aggregates with long lifetimes. The above considerations are based only in the enthalpic contribution to ΔF. In order to have a complete estimate of the stability of the asphaltene aggregates, the entropic contributions have to be considered. The gain or loss of molecular rotational and translatory degrees of freedom should be considered in the calculation of the entropic contribution. An analysis of the different

changes produced by the aggregation suggest that the most important contributions to the changes in entropy arises from the desolvation of the contact areas while the loss in translatory degrees of freedom are partially compensated by the gain in the vibrational entropy of the new low frequency modes. The existence of a nearly continuous chemical distribution of asphaltene and resin molecules in crude oil suggest that their aggregates will have a broad distribution both in chemical composition and in shapes similar to those found in the micelles of mixed surfactants. The small size of the asphaltene-resin aggregates (<30-40Å) and of the molecules forming them plus the chemical complexity suggests that these compounds may form disordered (amorphous) phases rather than crystalline ones. The very complex distribution of aggregates suggests that crude oil can not be described simply as a pure sol formed by solid asphaltene particles dispersed by resins or as a simple and uniform micellar system similar to those found in aqueous solutions of pure surfactants. The crude oil is an extremely complex system where the continuous distribution of molecules generates also a distribution in the types of aggregates present. These molecular aggregates may vary from solid asphaltene particles to loosely bound micelles of asphaltene and resins with short lifetimes and coexist within the crude oil. Molecular mechanics calculations showed that the asphaltene aggregate representing the heavy fraction of a crude oil from Athabasca exhibit stronger interactions with its resins than with solvents such as toluene and n-octane. It was found that the resins showed a considerable selectivity for the different adsorption sites of the asphaltenes. This selectivity was stronger than that found for the solvent molecules indicating that is enthalpically more favorable for them to form aggregates with the asphaltenes. The selectivity may also help to explain the specificity of some resins that are able to disperse only the asphaltenes of certain types of crudes while failing to do the same for others.

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