

Molecular modeling and aggregation tendencies of asphaltenes heptol subfractions

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Asphaltenes are defined by their behavior in the presence of solvents. They correspond to fractions that are dissolved in aromatic solvents while remaining insoluble in aliphatic compounds. Generally, they are a collection of a great variety of molecules consisting of polyaromatic units with varying amounts of naphthenic rings and aliphatic chains, a few heteroatoms (such as, S, N, O), and traces of vanadium and nickel. Carbon/hydrogen ratios of asphaltene range between 1.0 and 1.2, with a heteroatom content of a few percent [1]. The study of asphaltene colloidal properties has been motivated by their propensity to aggregate, flocculate, precipitate, and adsorb onto interfaces. Consequently, it is important to understand the physical and chemical properties of these entities to ensure efficient use and processing of hydrocarbon resources. Significant progress has been made towards understanding asphaltene during the past decades [1]. However, understanding of asphaltene aggregation is limited.

Our approach to asphaltene studies is based on a combination of molecular modeling and structural features obtained from NMR and elemental analysis data, which takes into consideration the asphaltene's propensity for aggregation [2]. Thus molecular modeling has an important role in the investigation of aggregation processes and in identification of the interactions that are involved. Our most recent work was focussed on the determination of the solubility profiles of asphaltene from Brazilian vacuum residues in mixtures of heptane and toluene, or the so-called "heptol" mixtures. The results show that asphaltene are efficiently fractionated by heptol solutions and led to a distribution of constituents with varying degrees of aromatic content.

In the present work, the formation of aggregates of these asphaltene sub-fractions A and B, which have similar elemental compositions, was studied by molecular modeling. Structures were generated from ¹H and ¹³C NMR, molecular weights obtained by LIAD/MS [3] and elemental analysis. Molecular modeling studies on the association of asphaltene was used as a basis for selecting structures that would have a tendency to associate more strongly from among those that reflect the analytical data.

Each asphaltene molecule was initially minimized by a consistent valence force field (CVFF), using the conjugate gradient method. Molecular Dynamics (MD)

were run on this molecule (300 ps) at 300 K, and selected structures were further minimized by the same method. This force field has been successfully used to describe the aggregation behavior of asphaltene [2]. Manual docking was used to probe the best spatial approach between two asphaltene structures. The dimer, which corresponds to the most stable combination of monomers, was optimized by MD; the five lowest-energy conformers were further minimized under the same conditions.

For all the models, the calculated energies are very consistent, mainly for pairs of asphaltene for which aggregation is most favoured. Table 1 illustrates the variation in the distance between the two monomers of the aggregate during the simulation time.

Table 1. Variation of the distance between aromatic ring systems for asphaltene heptol subfractions.

VR-A Dimers	Distance (Å)	VR-B Dimers	Distance (Å)
A-0%	3.50	B-0%	3.70
A-10%	3.67	B-5%	3.72
A-20%	3.97	B-10%	3.75
		B-15%	3.71

Distances between aromatic rings for the more stable dimers in VR-B asphaltene remained at a value around 3.7 Å. However it was observed that for the VR-A asphaltene sub-fractions, this distance undergoes a tenuous change. The shortest distance was found for the dimer formed by monomers A-10%. This sub-fraction, according to RMN analytical data, [4] was the one with a higher aromatic content and the largest number of aromatic rings. Possibly this fraction has a higher tendency towards aggregation, and may have a lower degree of steric interference. This is a very interesting result, because it reflects the relationship between molecular modelling and structural properties related to aggregation processes.

References

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