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Aggregation of Asphaltenes Using a Top-down Molecular Modeling Hierarchical Approach

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Abstract: Asphaltenes are a class of high-density molecules obtained from crude oil. The implications of asphaltene stability within the oil matrix production affect the whole oil supply chain production. This reduces the oil recovery because of mobility changes in the reservoir [1]. So far, the experimental and theoretical investigations no have addressed discussions at electronic level regarding a nanoaggregation mechanism influenced by resin molecules. We studied the molecular models already established in the literature for specific types molecules of asphaltene (**A**) with large aromatic island and resin (**R**) riches in heteroatoms [2,3]. From a hierarchical approach, we employed molecular mechanics simulations performed by the LAMMPS software [4] to calculate the potential energy surface to obtain the best conformations for the possible dimers **A-A**, **A-R** and **R-R**, as well as the relevant combinations of trimers **A-R-A**, **A-A-R** and **A-A-A.** After this, the energetically most favorable possibilities of aggregation conformations were further relaxed by the Density-Functional Theory calculations with corrections of dispersion forces implemented in the Quantum ESPRESSO package [5]. Our results show the aggregation mechanism is related to the rearrangement of the charge toward the stability of the $\pi - \pi$ stacking during the **A** + **R** interaction taking as reference the aggregates of **A**. The growth of the nanoaggregates was followed up by the changes toward to the degeneracy of the electronic states, dipole moment and radius of gyration. It is expected that **R** itself might be inner destabilizers on the aggregation process naturally present in oil. From industrial point of view, the knowledge of the aggregation mechanism may allow the design of new surfactants or compounds with specific functional groups to control the formation and destabilization of the asphaltene nanoaggregates.

Key-words: Asphaltenes, nanoaggregates, aggregation mechanism, molecular mechanics, DFT.
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