

Molecular modelling and the asphaltenes aggregates in solution

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Asphaltenes have been assumed to form only solid nanoparticles when they are dissolved in crude oils, etc., [1]. The asphaltene molecules forming the core of the nanoparticles were also assumed to be stacked and ordered via their aromatic regions [2]. It is then reasonable to expect that solid asphaltenes should be formed only by such particles. Surprisingly, all solid asphaltenes studied were found to be amorphous with only a small number of crystalline nanoparticles present in them [3]. Then, either the precipitation process disorders most nanoparticles found in solution or only a small fraction of the asphaltenes actually form the aggregates that are the core of the proposed nanoparticles. Precipitation does not seem to provide a reasonable mechanism to disorder the asphaltene nanoparticles [4]. Then, only a few of them seem to exist while the rest the asphaltene molecules are free in solution. This is in agreement with the nano calorimetric result that showed that asphaltenes behave as aromatic dyes and not as typical surfactants in solution [5]. Most dye molecules in solution are free monomers although aggregates are present at any concentration [6]. The population of the dye n-mers decays exponentially with the number of components in the aggregates [6]. The chemical and conformational diversity of the asphaltene molecules adds further complications to aggregate formation so a study using archipelago type asphaltene models was performed to obtain information about their aggregation behaviour in solution. Molecular Mechanics calculation of the energy of dimers formed by all possible combinations of 4 asphaltene models from Athabasca [3] were carry out in toluene solutions. The calculations were performed in 14 different stacking/aggregation positions (a to n). In all cases, the aggregates were formed by maximizing the contacts between different parts of the molecules. In many cases, the stacking of the aromatic regions was important while in others, the interaction between saturated and aromatics ones generated also stable aggregates. Except a few that were repulsive, all aggregates were attractive although with large variations in the resulting energy (See Fig. 1). This shows that only in a few pairs the energy will be such that a long-lived aggregate is likely to be formed. In most other pairs, they will have a rather limited lifetime. For a few others, no dimer will be formed for the specific set of asphaltenes. It easily seen that the molecular diversity and conformational flexibility is reflected in a wide distribution of possible lifetimes for the aggregates. Recently, the X-ray/neutron low angle scattering data of asphaltenes in solution has been interpreted as resulting from dynamic concentration fluctuations within the solution

[7]. The above results agree with this new interpretation, as these fluctuations are just another way of describing the dynamic aggregation of asphaltenes that occurs within the solution if the description used with the dyes is valid for asphaltenes in solution.

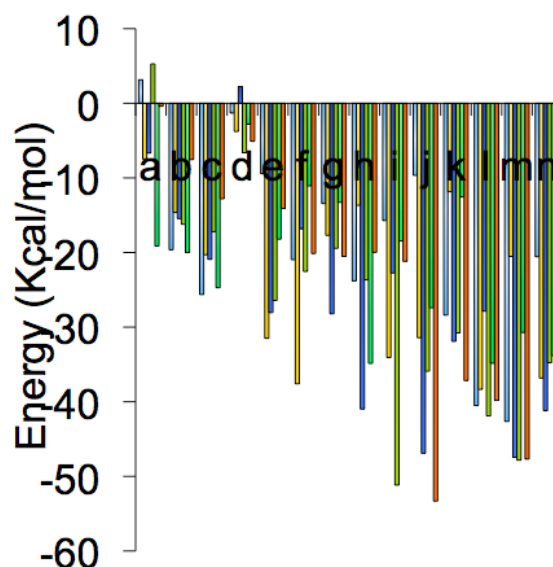


Fig. 1. Energy of four dimers formed with models of asphaltenes from Athabasca in each of the 14 different aggregation arrangements (a to n) used in the calculation.

References

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