

Molecular dynamics simulations of asphaltènes and their A1 et A2 subfractions in the presence of solvents and silica nanoparticle

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Abstract:

The objective of this work is to study by molecular dynamics simulation the behavior of asphaltene subfractions A1 and A2 in solution, in the presence of a silica nanoparticle. The sub-fractions of asphaltenes A1 and A2 are obtained experimentally from a treatment of asphaltene solutions with p-nitrophenol in cumene. The work is divided into two parts. The first part deals with the behavior of the subfractions in solution in toluene and determined the computational conditions and selected the best models representing these subfractions. Then, a series of models was proposed and their behavior in heptane, THF and chloroform was characterized. In addition, the solubility parameters of each model were calculated and compared to literature values. The GROMACS 2019.3 calculation software was used. The radial distribution function (RDF) of the systems was calculated and the number, size, dipole moment and shape of the aggregates were analyzed along molecular dynamics simulations. The second part of the work deals with the interaction of asphaltene models with silica nanoparticle models. The objective of this part is to identify if one of the A1 or A2 subfractions will be preferentially adsorbed on the surface of the nanoparticle and under which conditions. Two models of nanoparticles, one spherical and the other assimilated to a periodic 2D surface, have been considered. The immersion enthalpy of these nanoparticles was calculated to check if the calculation conditions and the force field used for silica were adequate. To study the interaction between an asphaltene molecule or aggregate and a silica nanoparticle, the periodic 2D surface model was considered. The free energy profile was calculated using an Umbrella Sampling method to efficiently sample a reaction coordinate.

The molecular structure of the models associated with the A1 subfraction (insoluble in toluene) favors the stacking of the models, which also have the ability to interact by forming hydrogen bonds. Molecules containing oxygen atoms, in the form of phenolic and carboxylic groups, tend to form large aggregates and are poorly soluble in toluene. Mixtures between A1 and A2 type models show that the presence of A2 type models tends to reduce the size of the aggregates, leading to more soluble aggregates. Hydrogen bonding is a key factor in the stability of aggregates in solution. The asymmetric charge distribution with increasing aggregate size leads to a decrease in the dipole moment of the aggregate. The calculation of the solubility parameter for asphaltene models in general are reasonable at the values already reported for the A1 and A2 subfractions. The stiffness of a model affects the number of ways it can interact with a surface. The more rigid the model, the smaller the fluctuations in interactions, whereas the more flexible a molecule is, the larger the fluctuations will be and it will then be more difficult to identify overriding factors (due to the larger number of conformations). The different solvents have the effect of modifying the energy barriers associated with the adsorption of a model on the silica surface. The adsorption of aggregates depends on their size. The larger the aggregate, the greater the number of intermolecular interactions, resulting in a more attractive interaction energy at the surface.