Aggregation of sub-fractions of A1 and A2 asphaltenes in different solvents from the perspective of molecular dynamics simulation

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Résumé

The behavior of model molecules of asphaltene subfractions A1 and A2 dissolved in heptane, toluene and THF was studied using molecular dynamic simulations methods. These structures are based on previously studied models in toluene and here two new models were added: a highly aromatic, island-type molecule and another one with archipelago type architecture. Here we studied aggregate formation in toluene, THF and heptane solvents. For the molecular dynamics calculations, two different initial systems were constructed, after inserting 80 asphaltene molecules at a concentration of 7 wt.% of solvent in a cub**ic** box. One system consisted of molecules initially dispersed in solvents and the other where the 80 molecules were placed in vacuum and within the box to form a single cluster. Their behavior was studied in a 60-ns molecular dynamics simulation and the aggregates formed during the simulation were analyzed. Ten different molecules were studied and we characterize if they behave as expected for asphaltenes, and their subfractions A1 and A2. The results in heptane were consistent with the very low solubility of asphaltenes in heptane and with its solubility in toluene. Comparison with toluene values afforded reasonable THF solubilities for these molecular models. Tendency of models for aggregation correlate well with aromaticity. Histograms of the calculated aggregate size shows bimodal distributions with profiles similar to the time-frequency profiles usually found in GPC for asphaltene samples in THF. Corresponding simulations were calculated in THF starting from either dispersed or clustered initial stages. When a large cluster is placed in THF this large cluster is subsequently broken down into smaller size aggregates. This could lead to the mixture of high, medium and low molecular weight bands, usually found in the asphaltene samples when measured in THF.

*Intervenant