Molecular Dynamics simulations of asphaltene aggregation in supercritical carbon dioxide with and without aggregation inhibitors

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It is well known that asphaltene has a strong tendency to aggregate in the presence of supercritical carbon dioxide. Here we present Molecular Dynamics (MD) simulations of the phase behaviour of asphaltene in supercritical carbon dioxide (sc-CO_2) with and without aggregation inhibitors. The model asphaltene molecules were obtained using our Quantitative Molecular Representation (QMR) software, which gives realistic 3D asphaltene structures based on experimental data [1]. Our specific asphaltene molecules were taken from a recent paper, where we studied the aggregation of asphaltene in both toluene and heptane [2].

First we present simulations of bulk sc-CO_2 at a range of temperatures and pressures and observed that the force-field used correctly reproduces the experimental system density. Simulations of asphaltenes were conducted in a fashion similar to those presented in ref [2] for simulations in toluene and heptanes: six asphaltene molecules in a bath of solvent at a concentration of 7 wt%. Simulations were conducted at a range of different temperatures and pressures in both sc-CO_2 and a 50 wt% mixture of sc-CO_2 with an organic additive. Asphaltenes in sc-CO_2 showed a strong propensity for aggregation, with all six molecules forming a strongly bound aggregate at all temperatures and pressures. Simulations in 50 wt% additive : sc-CO_2 show a considerable decrease in the aggregation compared with pure CO_2. The temperature and pressure dependence of asphaltene aggregation in the mixture was complex, showing minimum aggregation (for the limited range of conditions studied) at 150 bar and 350K. The simulation results are confirmed by filtration experiments.

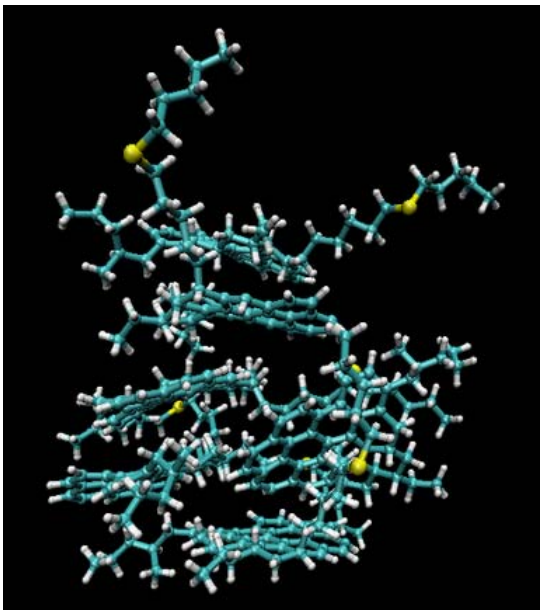

Figure 1: Snapshot of MD simulation of asphaltene aggregation in CO_2 without inhibitor at 350K and 150 bar. CO_2 molecules have been removed for clarity.

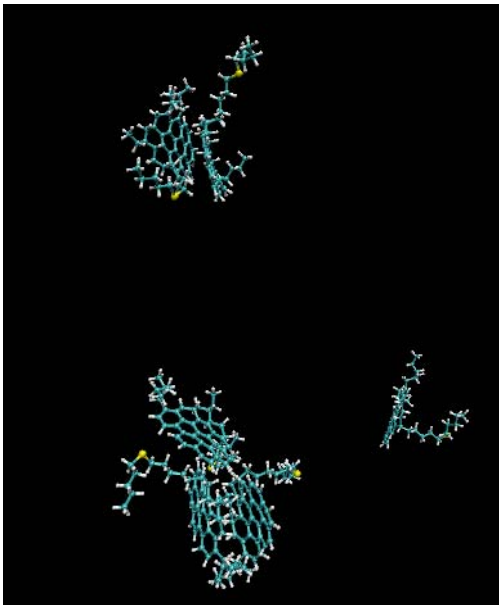

Figure 2: Snap-shot of MD simulation of 7wt% asphaltene in 50 wt% mixture of additive and carbon dioxide (350K and 150bar). This shows that the 6 molecule aggregate has split up in smaller units.

References

[1] E.S. Boek, D.S. Yakovlev, T.Headen, "Quantitative Molecular Representation of asphaltenes and Molecular Dynamics simulation of their aggregation", *Energy & Fuels* 23, 1209-1219 (2009).
[2] Headen, T. F.; Boek, E. S.; Skipper, N. T.; Energy and Fuels, 2009, 23, 1220 - 1229