Adsorption of asphaltene on rock surfaces from Molecular Dynamics simulation and Atomic Force Microscopy experiments

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The adsorption of molecular asphaltene from crude oil on rock surfaces is widely believed to cause wettability alteration and to affect the recovery of hydrocarbons in an adverse way. One typical example is the case of carbonate reservoirs, which often have intermediate or mixed wet properties. However, there is very little direct evidence for this process at the molecular scale. Here, we present preliminary results of a fundamental study to determine the free energy of adsorption of asphaltene on model surfaces using a combination of Molecular Dynamics (MD) computer simulations and Atomic Force Microscopy (AFM) experiments.

We have used MD simulations to calculate the Potential of Mean Force of model asphaltene molecules on a calcite surface. A snapshot of a typical MD simulation is shown in Figure 1.

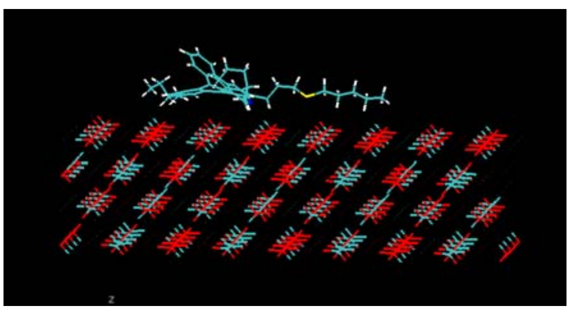

Figure 1: MD simulation snapshot of the calcite surface and an adsorbed asphaltene molecule

The model asphaltene molecules were obtained using our Quantitative Molecular Representation (QMR) software, which gives realistic 3D asphaltene structures based on experimental data [1]. As a model surface, we used calcite, representative of a carbonate rock. We constrain the distance between the center of mass of the asphaltene molecule and the calcite surface. By allowing conformational changes in the asphaltene molecule, we calculate the potential of mean force. This provides us with detailed information of the force and free energy of adsorption as a function of distance between the asphaltene molecule and calcite surface.

In a complementary set of AFM experiments at Imperial College, we have determined the force – separation dependence for a similar set of asphaltene – surface systems. We have measured the interactions between an asphaltene coated glass sphere and a calcite surface, immersed in water at various values of the pH.

In Figure 2 we present the data for pH=6. We observe that, on separation, there is an attraction between the two surfaces, which is likely to be a combination of van der Waals forces and attractive electrical double layer interactions. The explanation is that asphaltenes are likely to be negatively charged and the calcite positively charged at this pH. The absence of a long ranged attraction on approach of the surfaces suggests the presence of short ranged steric interactions, either due to surface roughness of the minerals or on the asphaltene surface. We observe that the experimental results are in good agreement with the simulations.

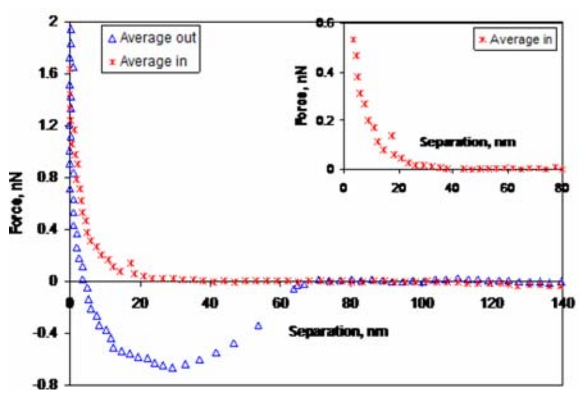

Figure 2: AFM measurement of force vs. Separation for interaction between an asphaltene coated sphere and a calcite surface in water (pH 6.0).

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).