

Supporting Information (SI)

Molecular Dynamics Simulation of Self-Aggregation of Asphaltenes at an Oil/Water Interface: Formation and Destruction of the Asphaltene Protective Film

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Validation of the molecular mode and force field used in this study

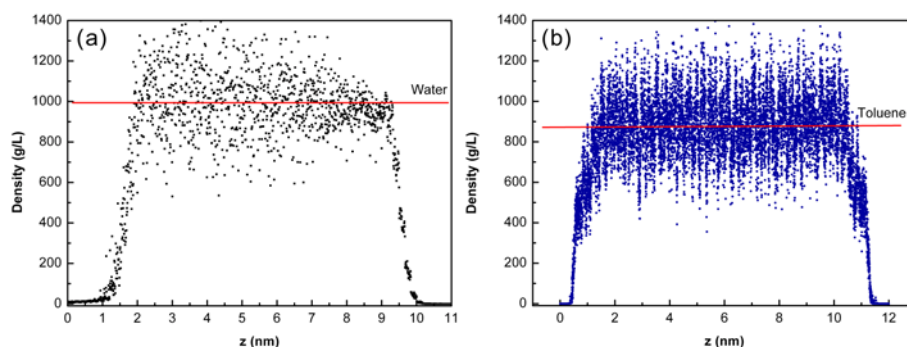


Figure S1. Density of the water (a) and toluene (b) in the simulations.

In order to validate the molecular mode and force field used in this work, simulations were performed to obtain the properties of the water and toluene

molecules including the density and diffusion coefficient, which were compared with the reported experimental data or previous calculated data.

About 8360 water molecules were put into a simulation box of 5.0×5.0×12nm and the water molecule was modeled by the extended simple point charge potential (SPC/E). Simulation was performed for sufficient time (4ns) at 300K. To compute the density distribution of the system, the simulation box was divided into 1000 slabs with equal thickness along with the z-direction. Similar procedure was conducted to compute the density of toluene. The results are shown in Figure S1. The average value of the density obtained from the bulk water and toluene are about 984.1g/L and 867.4g/L, which are close to the actual situations^{1, 2}.

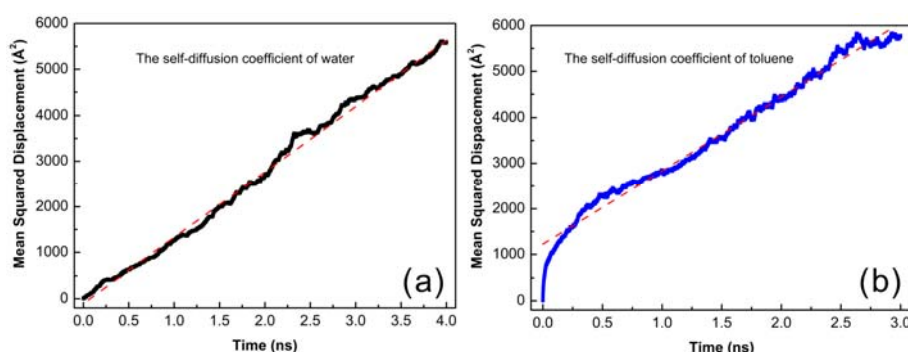


Figure S2. Mean squared displacements of water (a), toluene (b).

The mean squared displacements of the molecules were calculated and recorded during the simulation. According to the Einstein equation:

$$D = \frac{1}{2N_d} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle |\overline{r(t)} - \overline{r(0)}|^2 \right\rangle$$

Where N_d is the dimensionality ($N_d=3$) and $\overline{r(t)}$ is the position of given molecule at time t . The slope of mean-squared displacement (MSD) versus time is proportional to the diffusion coefficient of the molecule. As shown in Figure S2, the self-diffusion

coefficients of water and toluene are 2.42×10^{-9} and $2.49 \times 10^{-9} \text{ m}^2/\text{s}$, respectively, which are well agreement with the reported data^{3,4}. The asphaltene molecules tend to assemble and form nanoaggregates with a few molecules. The total energies of various asphaltene aggregates in vacuum are shown in Figure S3. It is observed that the total energies remain stable with increasing the simulation time after 0.1ns. The stabilization energy for the aggregates was calculated from the difference between the total energy of aggregates and the sum of energy of the monomers.

The stabilization energy is thereby calculated as: $E_{st} = E_{agg} - nE_{mon}$, where E_{agg} and E_{mon} are the total mechanical energy for an aggregate and a single molecule respectively, and n is the molecular number. The stabilization energy obtained according to this equation represents the energy releasing when several noninteracting molecules come together to form an aggregate⁵. The stabilization energies for various aggregates in vacuum/toluene are listed in Table 1. Taking coal asphaltene dimer in vaccum as an example, the monomer total energy is $5.41 \times 10^{-19} \text{ J}$, and the dimer total energy is $8.34 \times 10^{-19} \text{ J}$. Therefore, the stabilization energy of a dimer was calculated: $8.34 \times 10^{-19} \text{ J} - (2 \times 5.41 \times 10^{-19} \text{ J}) = -2.48 \times 10^{-19} \text{ J}$.

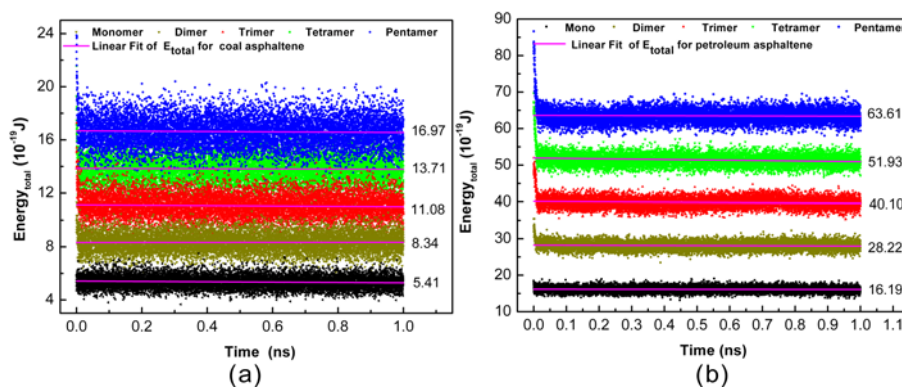


Figure S3. Total energies of aggregates for coal (a) and petroleum (b) asphaltenes in

vacuum.

The system energy and the force between molecules were monitored to indicate the equilibrium of the simulation system. In this work, the equilibrium state of the simulation system was determined by examining the system energies. It is believed that the system approach to its equilibrium state as the energies become convergence. The sum of the kinetic and potential energy of the system is regarded as the total mechanical energy. The energies of coal asphaltene aggregate at vacuum/water surface are shown in Figure S4. It is found that the total mechanical energy become stable and convergence after 0.5ns. Therefore, simulation time of 6ns for the system is enough. Similarly, the simulations of petroleum asphaltene aggregate at vacuum/water surface and coal asphaltene at toluene/water interface reach their equilibrium state within the given simulation time (Figure S5 and Figure S6).

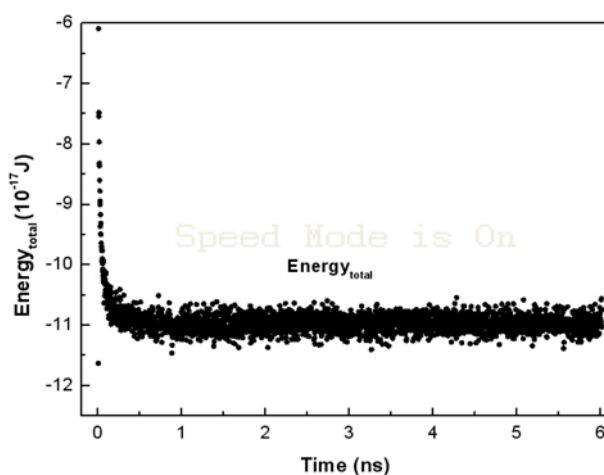


Figure S4. Function of the total energies of coal asphaltenes with simulation time at vacuum/water surface.

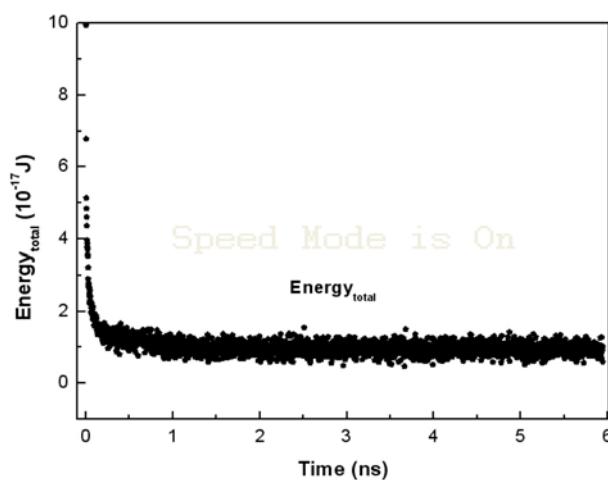


Figure S5. Function of the total energies of petroleum asphaltenes with simulation time at vacuum/water interface.

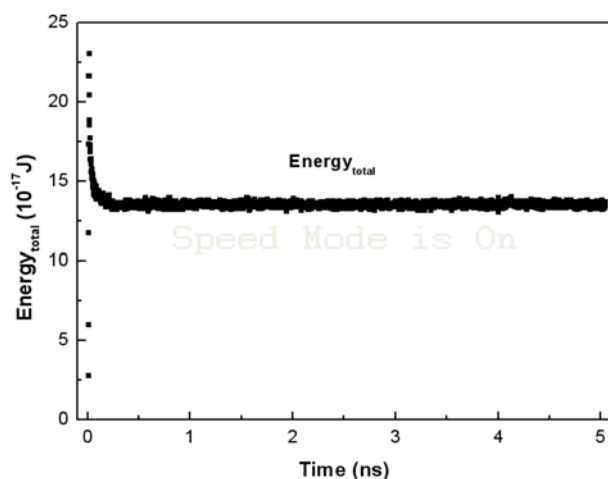


Figure S6. Function of the total energies of coal asphaltenes with simulation time at toluene/water interface.

The coalescences of two water drops in toluene with and without asphaltene were conducted in the MD simulations. Two water droplets ($R=3\text{nm}$, 3780 water molecules in each droplet) were put into the simulation box of $10.0\times 15.0\times 10\text{nm}$ and the box was full of toluene (about 7000 toluene molecules). Simulation was performed for 2ns at 300K. The results of the two situations are depicted in Figure S7. It was found that the two water droplets in toluene coalesced into a bigger one within

2ns (Figure S7a). As to the two water droplets wrapped by asphaltenes, they did not exhibit the trend to coalesce within 2ns (Figure S7b).

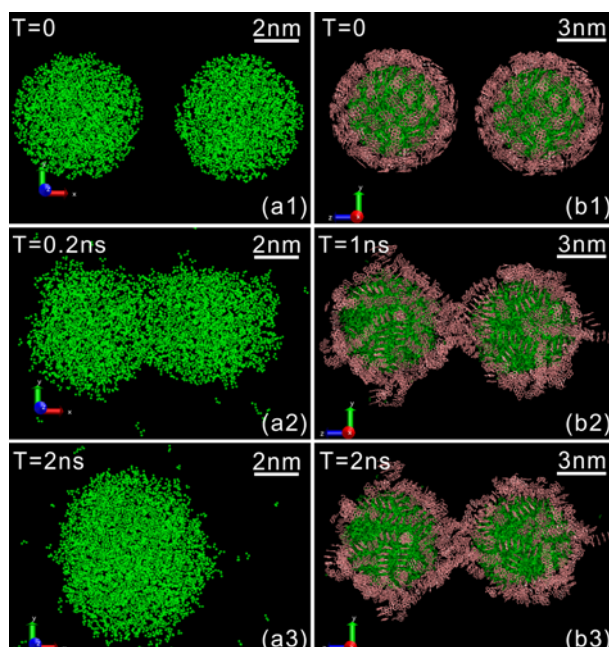


Figure S7. Sample snapshots of the coalescences of two water drops in toluene without (a) and with (b) asphaltenes. Water, asphaltenes are represented in green and pink, respectively. The toluene molecules are hidden.

To make the simulation findings more intuitive, the dynamic images of the simulations are provided:

S8a (corresponding to Figure 2a1-Dimer): Formation of the aggregate for coal asphaltene in vacuum.

S8b (corresponding to Figure 2a1-Pentamer): Formation of the pentamer aggregate for coal asphaltene in vacuum.

S9a (corresponding to Figure 2b1-Dimer): Formation of the dimer aggregate for petroleum asphaltene in vacuum.

S9b (corresponding to Figure 2b1-Dimer): Formation of the pentamer aggregate for petroleum asphaltene in vacuum.

S10a (corresponding to Figure 3a): The aggregation processes of coal asphaltene molecules at the vacuum/water interface.

S10b (corresponding to Figure 3b): The aggregation processes of petroleum asphaltene molecules at the vacuum/water surface.

S11 (corresponding to Figure 4a): The aggregation processes of coal asphaltene molecules at the water/toluene interface.

S12 (corresponding to Figure 9): The demulsification processes by EC: The EC molecules encroached on the asphaltenes film and gradually pull out the fence-like structure like peeling off an orange.

S13a (corresponding to Figure S7a): The two water droplets without asphaltenes coalesced in toluene.

S13b (corresponding to Figure S7b): The two water droplets with asphaltenes did not coalesce in toluene.

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