Supporting Information

Evaluation of Asphaltene Adsorption Free Energy at the Oil-Water Interface: Role of Heteroatoms

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In this supporting information, we show simulation results that are not included in the main manuscript. Figure S1 shows the simulation procedure. Figure S2 shows time evolution of the z-coordinate of asphaltene molecules (As01–As06). Figure S3 shows density profiles for As01-s – As06-s interfacial systems. The simulation condition was the same as that for Figure 4 in the main manuscript. The asphaltene adsorption behaviors for As01-s – As06-s systems are also similar to those for As01 – As06 systems. These results mean that interfacial affinities of the As01-s, As02-s, As04-s and As05-s are higher than that of As03-s and As06-s. Figure S4 shows radial distribution functions (RDFs) between the heteroatom or carbon (As03-s) and hydrogen or oxygen of the water molecules for As01-s – As06-s interfacial systems for the window at or near the minimum point of the PMF curve. It is similar to Figure 6 in the main manuscript. The structure of RDF between the heteroatom and oxygen of the water molecules for As02-s system is more evident than that for As02 system because the steric effect was removed. Figure S5 shows comparison of the density profiles along the z-direction for the window at or near the minimum points of the As03 and As03-s PMF curves. Figure S6 shows angle dependent radial distribution functions between hydrogen or oxygen of the water molecules and the heteroaromatic ring of the asphaltene molecule for As01 – As06 interfacial systems for the window at or near the minimum points of the PMF curves. It is similar to Figure 13 in the main manuscript; however, the structures are less evident than those for As01 – As06 interfacial systems because of the steric effect (i.e. less water molecules available for weak hydrogen bonding). Nevertheless, a stronger weak hydrogen bonding is observed for As02 than the others in the same set.
Figure S1. Schematic of simulation procedure.
Figure S2. Z-coordinate of asphaltene molecule COM (center of mass) as a function of time in the simulation box: (a) As01, (b) As02, (c) As03, (d) As04, (e) As05, and (f) As06. Red dotted line shows the reference of the oil–water interface. In Figure S2 (b), As02 remained at the oil-water interface around 10 nm. In this work, we employed periodic boundary condition and As02 could move from an edge of simulation box to another.
Figure S3. Density profiles of (a) As01-s, (b) As02-s, (c) As03-s, (d) As04-s, (e) As05-s, and (f) As06-s systems.
Figure S4. Radial distribution functions (RDFs) between the heteroatom or carbon (As03-s) and hydrogen or oxygen of the water molecules. Dotted lines show the cumulative number of hydrogen and oxygen of water: (a) As01-s, (b) As02-s, (c) As03-s, (d) As04-s, (e) As05-s, and (f) As06-s.
**Figure S5.** Comparison of density profiles of As03 and As03-s systems. For the As03-s system, dotted lines are used.
**Figure S6.** Angle dependent radial distribution functions between hydrogen or oxygen of the water molecules and the heteroaromatic ring of the asphaltene molecule: (a) As01, (b) As02, (c) As03, (d) As04, (e) As05, and (f) As06.