18e A Molecular Dynamics Study of the Coalescence Mechanism of Nanometer-Sized Water Clusters with Adsorbed Naphthenic Acids

Zhiying Li, Liyan Zhao, Sherwin Newhook, and Phillip Choi

Stabilization of residue water in oil by naphthenic acids and their salts is a significant problem in oil production. Understanding how naphthenic acids stabilize such water/oil interfaces has thus received extensive attention experimentally. Here, we employed molecular dynamics simulation to study its molecular origin. Two models were adopted in our simulation, wherein naphthenic acid coverage of water/n-heptane interfaces, spherical and flat, respectively, were hypothesized. It was found that the coalescence of two water clusters was entirely due to the diffusional motion of the components involved which required the initial departure of the acid molecules from the interface to form a water bridge. The coalescence of two water clusters fully covered by naphthenic acid molecules was a low-probability event even at evaluated temperatures. In addition, the results from the flat interface models suggested that the emulsion stability was weakly dependent on the molecular weight of the naphthenic acids utilized. Order parameter calculations reveal liquid-crystal-like ordering of naphthenic acids at the water/n-heptane interface. All these observations are consistent with the corresponding experimental results. Interestingly, our work offers additional insights about the role of naphthenic acids in stabilizing the emulsions: The coalescence is hindered by naphthenic acids (low mobility) when water clusters are in close proximity, whereas the process is facilitated by the departure of the acid (high mobility) when water clusters are far apart from each other.