Understanding the Interfacial Behaviors and Molecular Interaction Mechanisms of Asphaltenes Using Experimental and Theoretical Methods

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Asphaltenes adsorbed on oil/water/solid interfaces can significantly influence the interfacial properties, which play important roles in different oil production processes. Herein, the interfacial behaviors and molecular interaction mechanisms of asphaltenes in complex solvent conditions have been investigated using quantitative force measurements and molecular dynamic (MD) simulations. Moreover, Drop probe atomic force microscopy (AFM) was applied to quantify the interaction forces between emulsion drops in the absence/presence of asphaltenes under different conditions. This work provides useful insights into the fundamental understanding of the interfacial behaviors and molecular interaction mechanisms of asphaltenes at nanoscale in oil production.

Interfacial Behaviors of Asphaltenes

Fig. 1 clearly shows the adsorption of asphaltenes to the oil/water interface consists of three stages, which are illustrated by Fig. 2. Regime I is a diffusion-controlled process, during which asphaltenes diffuse to the oil/water interface spontaneously. The initial IFT reduction rate scales linearly with the square root of time. Regime II is a transition stage when the steric hindrance of adsorbed asphaltenes starts to impede adsorption, lowering the IFT reduction rate. Regime III is a long-term adsorption process, during which the IFT slowly decreases due to the continuous adsorption of asphaltenes to the sublayer of the interface and reconfiguration of adsorbed asphaltenes or asphaltene aggregates.

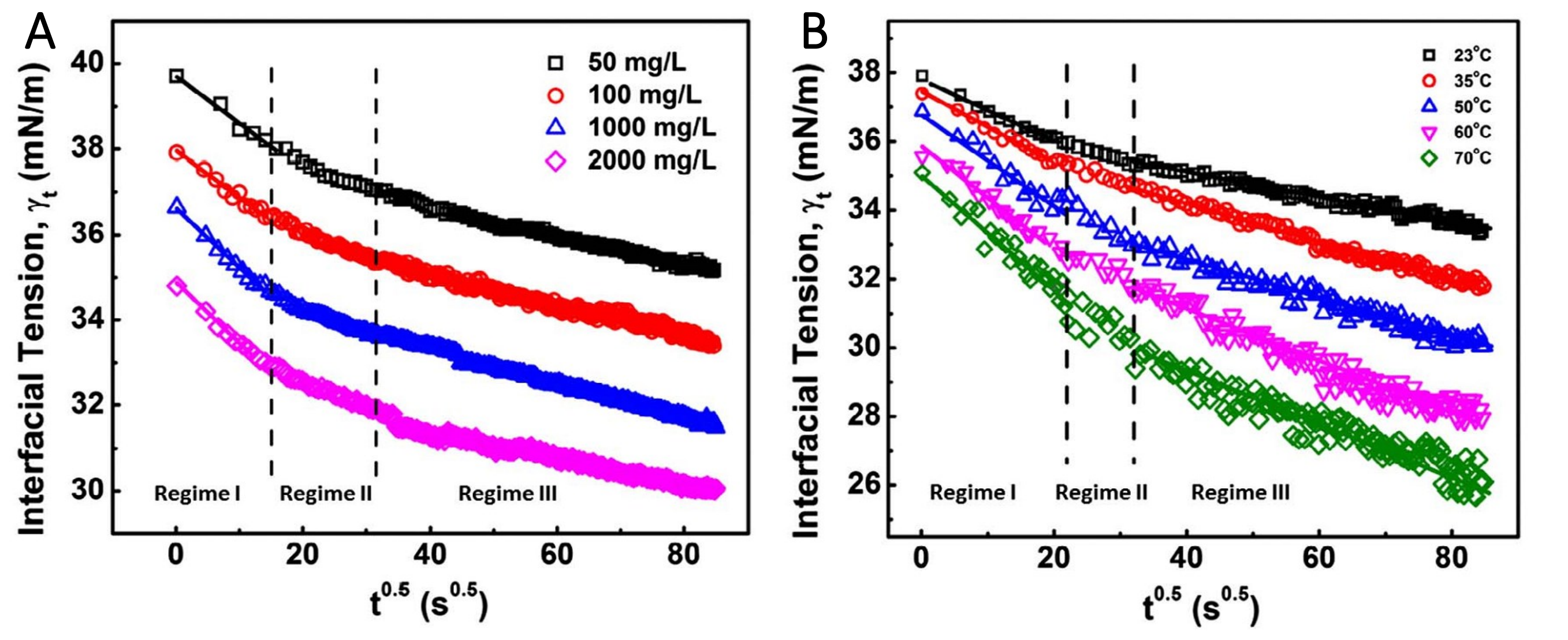


Figure 1. Dynamic toluene/water IFT vs. $t^{0.5}$: (A) for 50, 100, 1000 and 2000 mg/L asphaltene solutions in toluene at 23 ℃, and (B) for 100 mg/L asphaltene solution at different temperatures (23–70 ℃).

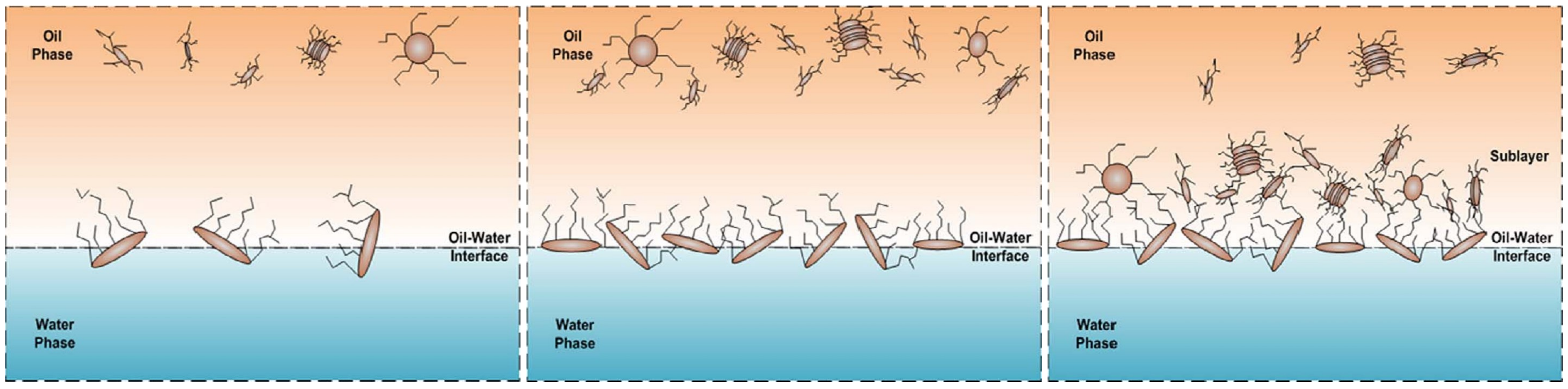
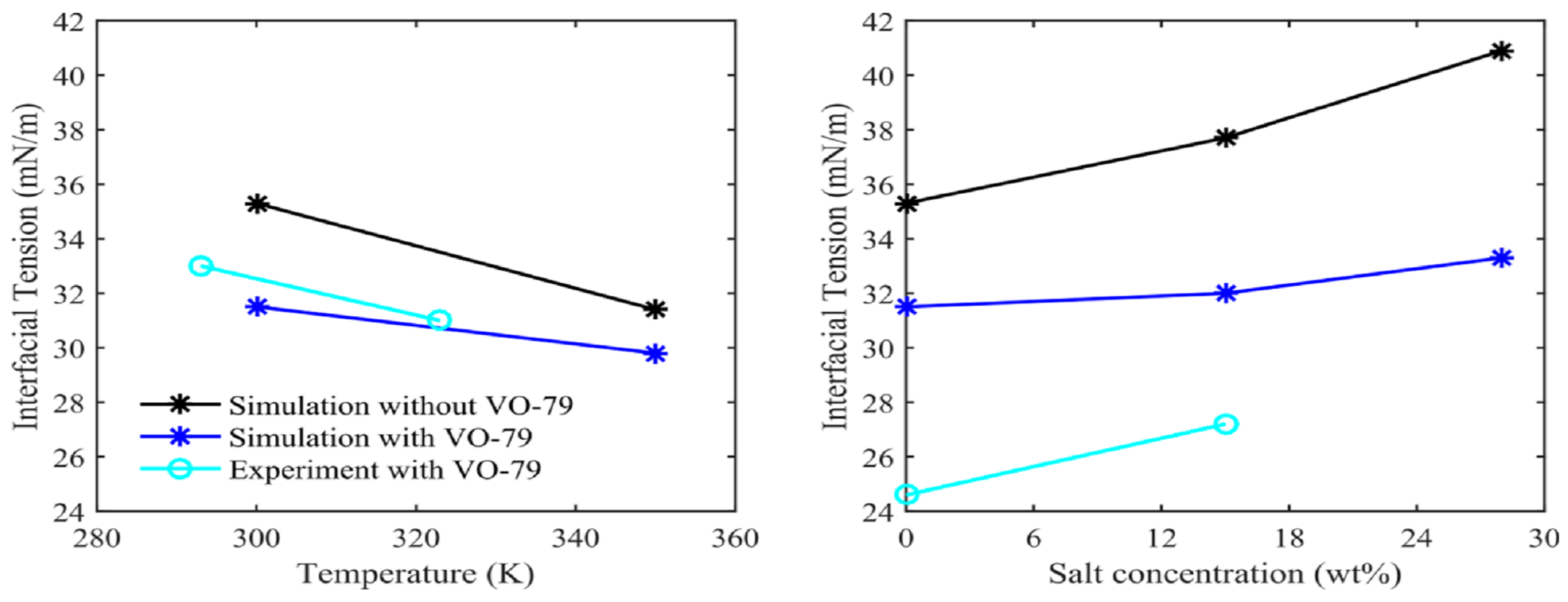


Figure 2. (A) Regime I that is controlled by the diffusion of asphaltenes to the oil/water interface, (B) Regime II where steric hindrance starts to slow down the adsorption, and (C) Regime III where the continuous adsorption of asphaltenes to the sublayer of the interface and reconfiguration of adsorbed asphaltenes or asphaltene aggregates occur.



For moderate ranges of temperature, the IFT of toluene/water interface was found to decrease with increasing asphaltene concentration and temperature as shown in Fig. 1, which was also validated by MD simulations (Fig. 3A). Elevating temperature decreases the number of hydrogen bonds formed among water molecules and the energy required to create a unit area of free water, thereby leading to a decreased IFT.

MD simulations also demonstrated that the addition of monovalent salts (NaCl) into aqueous phase increased the IFT (Fig. 3B). This is due to the hydration of ions, which results in a negative surface excess of ions at the interface and increases the free energy needed to create a unit area of free water surface.

Figure 3. IFT of toluene/water interface with Violanthrone-79 (VO-79) as model asphaltene, plotted as a function of (A) temperature and (B) salt concentration, obtained from MD simulations.

Molecular Interaction Mechanisms of Asphaltenes

For oil-in-water emulsion (Fig.4), the adsorbed asphaltenes resulted in more negative surface potential of the oil/water interface and induced steric repulsion between the two drops, whilst addition of divalent ions was found to disrupt this effect and induce coalescence of oil drops.

For water-in-oil emulsion (Fig. 5), low concentrations of asphaltenes induced interfacial adhesion during the separation of water drops, but the adhesion measured significantly decreased at relatively high asphaltene concentration. The addition of poor solvent (e.g., heptane) could strengthen the interfacial adhesion at relatively low asphaltene concentration but weaken the adhesion at relatively high asphaltene concentration.

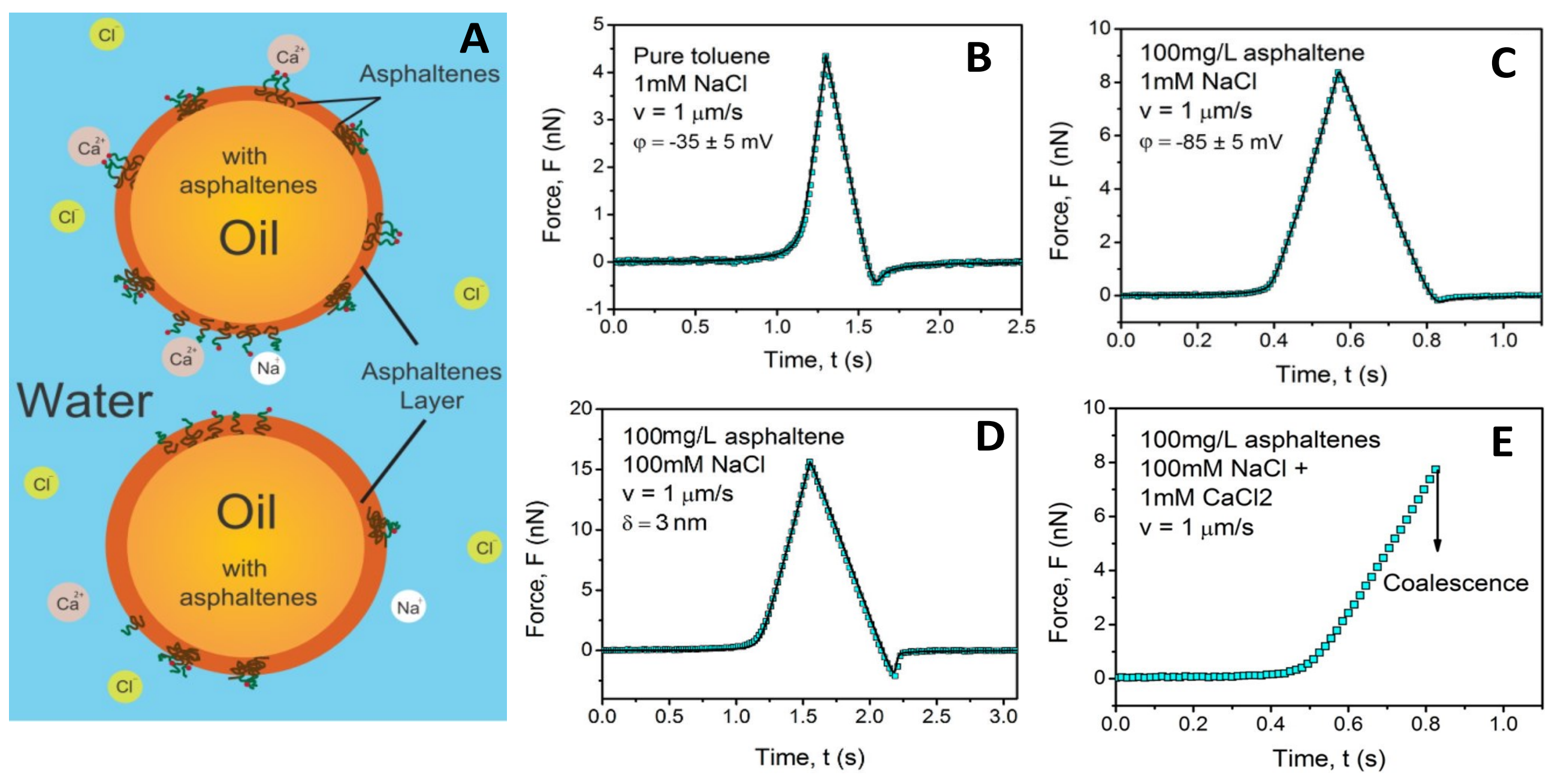


Figure 4. (A) Schematic of the interactions between oil-in-water emulsion drops with interfacial asphaltene molecules. The interaction force between two toluene drops with 0 mg/L (B and D) and 100 mg/L (C and E) asphaltenes in 1 mM NaCl (B and C) and 100 mM NaCl (D and E). The open symbols are experimental results obtained from AFM measurements at v = 1 μm/s, and the solid curves are theoretical calculations.

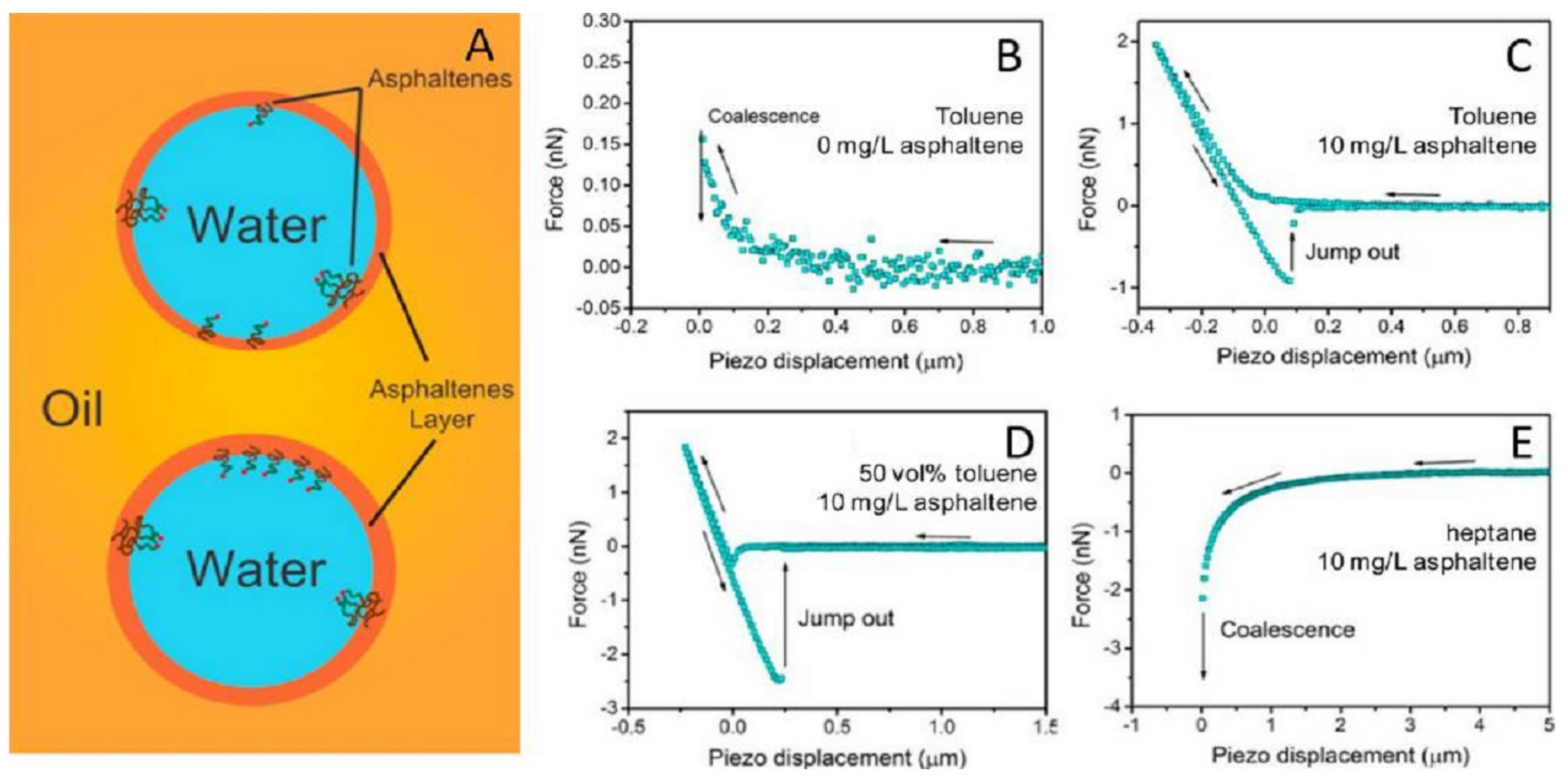
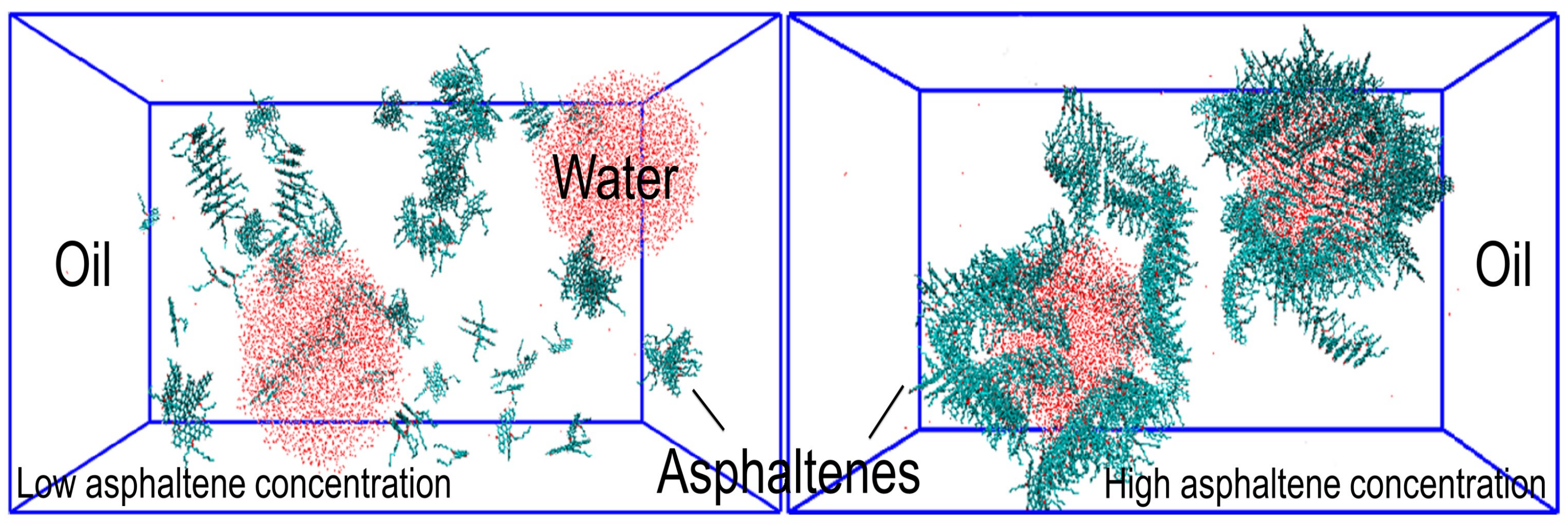


Figure 5. (A) Schematic of the interactions between water-in-oil emulsion drops with interfacial asphaltene molecules. AFM measured forces between two water drops in toluene after aging in asphaltene solution with concentrations of (B) 0 mg/L and (C) 10 mg/L at v =1 μm/s. AFM measured forces between two water drops in (D) 50 vol % toluene and (E) heptane after aging in 10 mg/L asphaltene solution at v =1 μm/s.



Corresponding MD simulations in Fig. 6 demonstrated that asphaltenes molecules could prevent the coalescence of water droplets.

At low concentrations, asphaltenes preferred to stay in the bulk toluene phase, and the unadsorbed free-floating molecules could create barriers for water droplets to collide and coalesce. With increasing concentration, a protective layer was formed by asphaltenes on the water droplets, and these adsorbed molecules could drag the coated water droplets to diffuse in the bulk toluene, thus bringing additional obstacles to coalescence.

Figure 6. Representative configurations in the final stage in (A) low and (B) high asphaltene concentration within oil (toluene) medium from MD simulations.

FES PROJECT OVERVIEW

1. The interfacial behaviors of asphaltenes demonstrated the three-staged adsorption process (i.e., Regime I: diffusion-controlled process, Regime II: transition stage, Regime III: long-term adsorption process), and the IFT decreased with increasing temperature and asphaltene concentration and decreasing salinity.
2. The molecular interaction mechanisms of asphaltenes showed the significant influence of asphaltene concentration, aqueous condition (e.g., salinity, pH and salt type), solvent type (e.g., ratio of toluene to heptane) and aging time on the interaction forces and molecular configurations of emulsion drops.

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