Research Article

Effect of Polar Molecule Aggregation on the Stability of Crude Oil/Water Interface: A Molecular Simulation Study

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To ensure the efficient operation of crude oil dehydration and sewage treatment technology in oilfield surface production system, the effect mechanism of polar components represented by asphaltene and resin on the formation and stability of oil-water emulsion needs to be revealed at nanoscale. In this paper, the molecular dynamics simulation method was used to construct the crude oil/polar component/water system models with different molar ratios of asphaltene to resin by adjusting the number of asphaltene and resin molecules, so as to reveal the molecular arrangement and aggregation process and film forming characteristics of asphaltene, resin, and their mixture at the oil-water interface. The simulated results showed that the aggregation process of asphaltene molecules under the influence of hydrogen bonds can be divided into three stages. The addition of resin molecules enhanced the connection between molecules of all polar components at the interface. The π−π stacking and T-shaped stacking structures were found in all aggregations, and the higher the molar ratio of asphaltene molecules, the higher the proportion of π−π stacking structure. With the increase of the molar ratio of asphaltene to resin increases from 0:1 to 1:0, the interfacial film thickness and interface formation energy increase from 2.366 nm and -143.89 kJ/mol to 3.796 nm and -304.09 kJ/mol, respectively, which indicated that asphaltene molecules play a more significant role in promoting the formation of interfacial film and maintaining its structural stability than resin molecules. The investigations in this study provide theoretical support for demulsification of the crude oil emulsion.

1. Introduction

Although the adjustment and optimization of the global energy structure have decreased the rate of traditional fossil energy demand growth, the oil demand of major developing countries is still increasing, which makes oil recovery enhancement an important direction of oil field development and construction [1]. The chemical flooding technology represented by alkali/surfactant/polymer (ASP) flooding has been applied in Daqing oilfield as an efficient enhanced oil recovery method [2–4], while the chemical agent components such as surfactant and polymer will affect the stability of crude oil emulsion, which will bring challenges to the efficient oil-water separation of oilfield gathering and transportation system [2, 4–9]. However, to research the emulsion stability of chemical flooding produced liquid, it is necessary to master the emulsion mechanism of the crude oil emulsion. As important natural components in crude oil, asphaltene and resin are the two types of substances with the largest molecular weight and polarity. Meanwhile, they have strong interfacial activity, so they are generally regarded as natural surface active substances [8–11]. The promoting effect of polar molecules such as asphaltene and resin on the formation and stabilization of oil-water emulsion has been confirmed in many experiments. Goual et al. used a transmission electron microscope to characterize the oil-water interface film at nanoscale and found that the thin film consisted of vertically accumulated wormlike clusters of asphaltene, and one side of
the film was rough and hydrophobic, while the other side was smooth and hydrophilic [12]. Rocha et al. extracted different types of asphaltenes to prepare emulsions and tested their stability. The results showed that only a small part of asphaltenes could play the role of emulsion stability. These asphaltenes are generally rich in heteroatomic functional groups and have large molecular weight, which are easy to aggregate and form aggregates. In addition, the aggregation structure containing these functional groups also has stronger adsorption capacity on the interface [13]. Some researchers believe that asphaltenes do not have amphiphilic structures similar to surfactants. The stabilizing effect of asphaltenes on emulsions is that they aggregate in layers within the oil film to form a network structure, which changes the rheological properties of the film and thus affects the coalescence of emulsion droplets [14]. Although there is no unified understanding of the effect mechanism of polar components such as asphaltene and resin on emulsion stability, it has become a consensus that this effect is generated by their aggregation at the interface.

Compared with experimental analysis methods, molecular dynamics (MD) simulation has unique advantages in microstructure characterization; so in recent years, it has become a trend to explore the aggregation structure of asphaltene and resin molecules from the microscale by molecular simulation [15]. Many studies have shown that the interaction between polar molecules is mainly through the $\pi - \pi$ stacking of aromatic rings. The increase of aromatic ring number will enhance the interaction energy between molecules, and the $\pi - \pi$ stacking is not limited to two molecules. When multiple molecules interact, the aggregation force between them will also increase greatly [16–21]. The hydrogen/carbon (H/C) ratio of asphaltenes also plays an inevitable role in the asphaltene aggregation behavior. A lower H/C ratio resulted in increasing asphaltene aggregation tendency [22]. In addition, when the molecules contain N, O, S, and other heteroatoms, hydrogen bonds will be formed, which can be divided into two types: one is between polar molecules, and the other is between polar molecules and water molecules [23–26]. Due to the hydrogen bond being a kind of weak intermolecular interaction, the single bond energy is not significant but the increase in the number of hydrogen bonds in polar component aggregation will greatly enhance the intermolecular force [16, 21]. Furthermore, the formation of hydrogen bonds between polar component molecules and water molecules is the main reason that aggregates can be adsorbed to the oil-water interface, and the polar component molecules will form supramolecular structure under the synergistic effect of hydrogen bonds and $\pi - \pi$ stacking. Thanks to the encapsulation of water droplets by this supramolecular structure, the coalescence of water droplets is prevented to a great extent, and the stability of crude oil emulsion is enhanced [27, 28].

Whether based on experimental analysis or molecular simulation methods, the current research mainly focuses on the aggregation structure of asphaltenes and the analysis of intermolecular interaction. However, there is still a lack of research on resins, especially the lack of considering the effect of the change of molecular ratio of asphaltene to resin on the aggregation structure, and the arrangement, aggregation behavior, and film forming evolution process of them and their self-assembly structure at the oil-water interface are not yet described in detail. In this paper, the molecular dynamics models of different crude oil/polar components/water interface systems were established by adjusting the molecular ratio of asphaltene to resin. Visual analysis, molecular density distribution, radial distribution function, and interface formation energy were used to describe the alignment, aggregation, and film forming process of asphaltene, resin molecules, and their self-assembly structures at the crude oil water interface, and the effect of molar ratio of asphaltene to resin on film thickness and structural strength was revealed. The investigations in this study can provide theoretical support for demulsification of crude oil emulsion.

2. MD Simulation

2.1. Force Field Model. The force field model for describing the arrangement, aggregation behavior, and film formation of asphaltene and resin molecules at the oil-water interface was given. Numerous works in the literature calibrated the capability of this force fields to model complex systems containing a wide range of materials [29–32]. The total potential energy consists of the bond term and nonbond term. The bond term contains bond stretching energy, bond angle bending energy, dihedral angle torsion energy, out-of-plane vibration energy, and the cross-coupling energy includes combinations of two or three internal coordinates, respectively. The nonbond term includes van der Waals interaction and Coulomb interaction, in which van der Waals interaction adopts Lennard Jones 9-6 potential function.

For the potential energy of bond term,

$$E = \sum_b \left[ k_2 (b - b_0)^2 + k_3 (b - b_0)^3 + k_4 (b - b_0)^4 \right]$$

$$+ \sum_{\theta} \left[ k_2 (\theta - \theta_0)^2 + k_3 (\theta - \theta_0)^3 + k_4 (\theta - \theta_0)^4 \right]$$

$$+ \sum_{\phi} \left[ k_1 (1 - \cos \phi) + k_2 (1 - \cos 2\phi) + k_3 (1 - \cos 3\phi) \right]$$

$$+ \sum_{b'} \sum_{b} k(b - b_0) (b' - b_0')$$

$$+ \sum_{b} k(b - b_0) (\theta - \theta_0)$$

$$+ \sum_{b} \sum_{\phi} (b - b_0) [k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$$

$$+ \sum_{\theta} \sum_{\phi} (\theta - \theta_0) [k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$$

$$+ \sum_{\theta} \sum_{\theta'} k(\theta - \theta_0) (\theta' - \theta'_0)$$

$$+ \sum_{\theta} \sum_{\phi} \sum_{\phi'} k(\theta - \theta_0) (\theta' - \theta'_0) \cos \phi.$$  (1)
For the potential energy of nonbond term,

\[ E_{\text{nb}} = \sum_{i,j} \varepsilon_{ij} \left( \frac{r_{ij}}{r_{ij0}} \right)^{9} - 3 \left( \frac{r_{ij}}{r_{ij0}} \right)^{6} + \sum_{i,j} q_i q_j \frac{1}{r_{ij}}, \tag{2} \]

where \( k \) is the elastic constant, \( b \) is the bond length, \( \theta \) is the bond angle, \( \phi \) is dihedral angle, \( \chi \) is the vibration angle from the plane, \( \varepsilon \) is the potential well depth, \( q_i \) and \( q_j \) are the charges of the ion \( i \) and the ion \( j \) in the molecule, and \( r_{ij} \) is the equilibrium distance between the ion \( i \) and the ion \( j \).

2.2. Molecular Models. Crude oil is a mixture containing a variety of hydrocarbon components. In addition to liquid hydrocarbons such as alkanes, naphthenes, and aromatic hydrocarbons, it also contains heavy components such as asphaltenes and resins. In order to fit the actual situation and break through the limitation that the crude oil model in the previous molecular dynamics simulations only contains a single component, eight types of hydrocarbons including hexane, heptane, octane, cyclohexane, cyclohexane, benzene, toluene, octane, cyclohexane, cyclohexane, benzene, and toluene were selected as the components of the basic crude oil model [33]. For asphaltene molecules, the models were established based on the three types of asphaltene molecules extracted by Takanohashi et al. [34]. For the resin molecules, the models were established by referring to the six types of resin molecules involved in Castellano’s study [35]. All the molecular models adopted in this study are shown in Figure 1.

2.3. Construction of the Simulation Models. According to the component composition of each phase, the lattices representing the layer of crude oil, water, and polar molecules in the simulation system were constructed, respectively. The number of eight types of hydrocarbon molecules in the oil layer is shown in Table 1. There were 3000 water molecules that have been put into the water layer, and the middle layer
was filled with a total number of 24 asphaltene and resin molecules in different proportions. All the lattices size were \( X \times Y \times Z \), and then, the three lattices were combined to form the crude oil/polar component/water simulation system. In order to avoid the interference of molecular overlap between different layers on the accuracy of simulation, two vacuum layers with the thickness of 0.5 nm were added between each layer in the assembly process.

The constructed crude oil/polar component/water simulation system can be divided into three types: pure asphaltene system, pure resin system, and asphaltene resin mixture system. In order to investigate the effect of the ratio of asphaltene to resin on the self-assembly structure characteristics of the two components and the thickness and structural strength of the viscoelastic interfacial film formed by them, five mixture systems with molecular molar ratio of asphaltene to resin of 4:1, 2:1, 1:1, 1:2, and 1:4 were established by adjusting the number of asphaltene and resin molecules. Taking the mole ratio of 1:1 as an example, the completed model is shown in Figure 2.

### Table 1: Composition of oil layer and the number of molecules of each component.

<table>
<thead>
<tr>
<th>Category</th>
<th>Hexane</th>
<th>Heptane</th>
<th>Octane</th>
<th>Nonane</th>
<th>Cyclohexane</th>
<th>Cycloheptane</th>
<th>Benzene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
<td>72</td>
<td>66</td>
<td>78</td>
<td>90</td>
<td>48</td>
<td>78</td>
<td>30</td>
<td>78</td>
</tr>
</tbody>
</table>

![Water lattice, Polar molecules lattice, Crude oil lattice](image)

**Figure 2**: Molecular dynamics model of the crude oil/polar component/water simulation system.

2.4. Governing Parameters. Periodic boundary condition was used in each direction of the simulation systems. The long-range Coulomb electrostatic interaction among particles adopted the Ewald algorithm, and the atom-based algorithm was used to calculate the van der Waals interaction, with a cutoff radius of 15.5 Å. The temperature was set at 298 K during the dynamic relaxation process, and the atmospheric pressure (0.1 MPa) was selected as the simulation pressure. The simulation step length was 1 fs, and the trajectories were collected at 1 ps intervals. The detailed simulation steps are shown in Figure 3.

### 3. Results and Discussion

3.1. Model Validation. Before simulating the crude oil/polar component/water systems in which the eight types of hydrocarbons in Table 1 are mixed as the crude oil phase, they were, respectively, filled into eight lattices, and the molecular dynamics simulations were performed at the temperature of 298 K and the pressure 0.1 MPa by using the simulation steps in Figure 3. Then, the densities of eight types of hydrocarbons were statistically calculated and compared with the simulation results of Kunieda’s study [36], as shown in Figure 4. For the relative error \( \delta \) between this paper’s data and Kunieda’s simulation results were calculated based on the equation

\[
\delta = \frac{\rho_{\text{this paper}} - \rho_{\text{Kunieda results}}}{\rho_{\text{Kunieda results}}} 
\]

which can be seen in Table 2.

From Figure 4 and Table 2, the simulated results of density of the eight types of hydrocarbons are basically in agreement with Kunieda’s study, and the relative error is less than 5%, which shows that the results simulated by the established MD method are reliable. So, it can be used to study the aggregation behavior of asphaltene and resin molecules at the oil-water interface and the micromechanism of film formation.

3.2. Aggregation Behavior of Polar Molecules at Oil-Water Interface

3.2.1. Asphaltene Molecules. The instantaneous snapshots in the dynamic relaxation process of crude oil/asphaltene/water
simulation system are shown in Figure 5. In the initial state, asphaltene molecules are evenly distributed, and then, the order of asphaltene molecules becomes disordered and two aggregates are formed gradually; one aggregate on the surface of the crude oil phase, and the other is close to the water phase. Starting at 800 ps, the two aggregations attract each other and approach slowly until 1200 ps; they fuse into a larger aggregation at the oil-water interface, and then, the aggregation gradually becomes thinner by the compression of the crude oil phase and water phase. Moreover, it is worth noting that, as asphaltene itself is one of the polar components of crude oil, part of asphaltene molecules near the side of crude oil phase dissolves in the crude oil phase during the relaxation process, but the degree is not significant.

As shown in Figure 6, due to the heteroatoms of S, O, and N in the molecule, O–H···S and O–H···N type hydrogen bonds are formed between asphaltene and water molecules, and O–H···O, O–H···S, O–H···N, and N–H···S type hydrogen bonds.
Figure 5: Snapshots of crude oil/polar component/water simulation system in different stages. (a) 0 ps. (b) 400 ps. (c) 800 ps. (d) 1200 ps. (e) 1800 ps. (f) 2400 ps.

Figure 6: Snapshots of hydrogen bond formation of asphaltene molecules. (a) O–H···S type hydrogen bond between asphaltene and water molecules. (b) O–H···N type hydrogen bond between asphaltene and water molecules. (c) O–H···O type hydrogen bond between asphaltene molecules. (d) O–H···S type hydrogen bond between asphaltene molecules. (e) O–H···N type hydrogen bond between asphaltene molecules. (f) N–H···S type hydrogen bond between asphaltene molecules.
bonds are formed between asphaltene molecules. As one of the intermolecular forces, the formation of hydrogen bonds between asphaltene molecules and water molecules is the main reason for the aggregation of asphaltene molecules at the oil-water interface [37, 38]. Therefore, the aggregation process of asphaltene molecules can be described as three stages: (i) The asphaltene molecules near the water phase form hydrogen bonds with water molecules and aggregate on the surface of the water phase, while the asphaltene molecules far away from the water phase are slightly dissolved in the crude oil phase. (ii) More asphaltene molecules are attracted due to hydrogen bonds formed between themselves and gradually forming two small aggregations on the surface of the crude oil phase and water phase. (iii) Under the promotion of the crude oil phase and water phase diffusion, the two aggregations fuse into a larger ellipsoidal aggregation, which is continuously compressed until it is “tiled” at the oil-water interface, that is, in the form of dense asphaltene films arranged at the oil-water interface.

3.2.2. Resin Molecules. The instantaneous snapshots in the dynamic relaxation process of crude oil/resin/water simulation system are shown in Figure 7. Different from the pure asphaltene system, although there are still three obvious aggregation regions of resin molecules in the early relaxation stage, due to the better solubility and dispersion of resin molecules, the addition of resin molecules enhances the connection between all polar molecules at the interface, so that each region is connected with resin molecules rather than completely isolated [39]. Moreover, when the relaxation time reached 500 ps, the resin molecules aggregate on the surface of the water phase gradually began to separate and completely separate at 1500 ps. The whole resin molecular aggregation is almost completely dissolved in the crude oil phase. Finally, as the crude oil phase and water phase gradually approach, the resin molecules are closely arranged at the oil-water interface, and the interfacial film is formed.

As shown in Figure 8, since the heteroatoms in the resin molecules selected in this paper only contain S atoms and are not connected with other H atoms in the molecule, which leads to no S-H bond in the molecule. Therefore, the resin molecules cannot form hydrogen bonds between each other and can only form a single type of O-H·- S hydrogen bond with water molecules, which is also the reason why the resin molecules near the water phase aggregate on the surface of the water phase. However, as one of the weak intermolecular interactions, the hydrogen bond formed between resin molecules and water molecules is obviously not sufficient to maintain the stability of the structure. Therefore, with the diffusion of crude oil phase, resin molecules gradually separate away from the surface of water.

Figure 7: Snapshots of crude oil/resin/water simulation system in different stages. (a) 0 ps. (b) 100 ps. (c) 300 ps. (d) 500 ps. (e) 1500 ps. (f) 2400 ps.

Figure 8: Snapshot of hydrogen bond formation between resin and water molecules.
phase and dissolve in crude oil phase. In addition, the solubility is significantly higher than that of asphaltene molecules.

3.2.3. Asphaltene and Resin Molecules. Since the dynamic relaxation processes of the five systems are generally similar, only the typical instantaneous snapshots of the relaxation processes of each system were extracted and analyzed, as shown in Figure 9. It can be found that asphaltene and resin molecules in the mixture system are still aggregated on the surface of the crude oil phase and water phase and then gradually converge on the oil-water interface with the diffusion of the crude oil phase and water phase.

When the molar ratio of asphaltene to resin is relatively high (4 : 1 and 2 : 1), as shown in Figures 9(a) and 9(b), the polar component molecules in the simulation system appear obviously concentrated regions in the dynamic relaxation process, showing a bipartite structure that half of them are aggregated on the surface of crude oil phase and the other half is aggregated on the surface of water phase. However, this clear regional aggregation structure gradually becomes blurred when the molar ratio of asphaltene to resin decreased to 1 : 1, 1 : 2, and 1 : 4, as shown in Figures 9(c)–9(e). Specifically, all polar molecules are connected except for the initial state, and the lower the molar ratio of asphaltene to resin, the more obvious this phenomenon. It can also be found that, similar to the pure resin system, all polar molecules are linked throughout the dynamic relaxation process, and there would be no two disconnected aggregation structures similar to the pure asphaltene system.

In summary, although the resin molecules are scattered around the asphaltene molecules, which strengthen the molecular connection of all polar components at the interface, this dispersion effect of resin on asphaltene also hinders the aggregation of asphaltene molecules to some extent.

3.3. Aggregation Characteristics Analysis

3.3.1. Stacking Structure. The stacking structures of asphaltene and resin molecules in the aggregations are shown in Figure 10. It indicates that there are both $\pi - \pi$ stacking structure and T-shaped stacking structure in the aggregations. In the process of decomposing the aggregation of each system, it can be found that the number of $\pi - \pi$ stacking structures is the most dominant and the number of molecules forming $\pi - \pi$ stacking is not fixed, which may be composed of two or more polar molecules, while the number of T-shaped stacking structures is relatively less and all of them are dimer structures formed by the combination of two molecules. Moreover, with the increase of the molar ratio of asphaltene to resin, the number of T-shaped stacking structures decreases.

3.3.2. Interaction Strength. Radial distribution function (RDF) is often used as a characterization method to describe the distribution probability of particles or groups. When the particles or groups are regularly arranged or gathered within a certain distance, the corresponding function curve will appear a peak point. Therefore, RDF can provide local information of the structure at the molecular level and reflect the strength of the interaction between molecules to a certain extent [40–43]. The RDF of asphaltene and resin molecules in each system is shown in Figure 11. It can be found that all the RDF curves have only one peak point, indicating that polar molecules in each system are generally concentrated in an aggregation. However, through detailed observation, it can be found that the functional curves of pure asphaltene with molar ratios of 4 : 1, 2 : 1, and 1 : 2 have "tiny concave" at the peak point, showing two independent small peaks. It indicates that the degree of polar molecule accumulation is not uniform in the whole aggregations of these systems, and some molecules can form a dense accumulation.

![Figure 9: Snapshots of crude oil/asphaltene-resin/water simulation system in different stages. (a) 4 : 1. (b) 2 : 1. (c) 1 : 1. (d) 1 : 2. (e) 1 : 4.](attachment:image.png)
The density distribution curves of the asphaltene and resin molecules are shown in Figure 12 (asphaltene is represented by Asp and resin is represented by Res). These curves show that the system is divided into two phases and an interface layer between the two phases, and the polar component molecules are distributed as a monolayer at the interface. The area formed by the intersection of the polar component curve and crude oil phase curve is significantly larger than that formed by the polar component curve and water phase curve, which indicates that the polar molecules dissolved with the crude oil phase. In addition, with the decrease of the mole ratio of asphaltene to resin, the peak value of the density distribution curve of the polar components gradually decreases, revealing that the increase of the mole ratio of resin molecules would decrease the density of the interfacial structure formed by the polar components.

Based on the density distribution curves of the above systems, defining the distance between two positions where the density varies from 10 to 90% of the density of the crude oil phase and the water phase as the crude oil-polar component interface thickness ($t_{oil}$) and the water-polar component interface thickness ($t_{water}$), respectively. Considering the complexity of oil/polar component/water interface system, the “90-90” interfacial thickness criterion is proposed to calculate the thickness of oil-water interfacial film ($t_{total}$), which is the distance between two positions where the densities of the crude oil and water are 90% of their own bulk densities [44]. The results of the interfacial thickness analysis are summarized in Table 3.

It can be seen from Table 3 that as the molar ratio of asphaltene to resin increases from 0:1 (pure asphaltene system) to 1:0 (pure resin system), $t_{oil}$ and $t_{water}$ increase from 2.116 nm and 0.662 nm to 2.084 nm and 1.161 nm, respectively, and $t_{total}$ increases from 2.366 nm to 3.796 nm. Moreover, $t_{oil}$ is significantly larger than $t_{water}$, showing a quantitative relationship of about three times. The analysis suggests that the thickness difference between the two is mainly due to the dissolution of the polar component as one of the crude oil components in the crude oil phase, making the interface become relatively blurred, which is also consistent with the conclusion obtained in the previous section.

3.4.2. Interface Film Structural Strength. In order to compare the structural strength of the interfacial film formed by various systems, the interface formation energy (IFE) of each system is calculated. The interface formation energy can be used to analyze the stability of interfacial film [45, 46]. In the crude oil/polar component/water interface system involved in this study, the equation of IFE is given as

$$ IFE = \frac{E_{total} - (nE_{pol} + E_{oil-water})}{n}, $$

where $E_{total}$ is the total energy of the system when the interface reaches equilibrium, kJ/mol; $E_{pol}$ is the energy of a single polar component molecule, kJ/mol; $E_{oil-water}$ is the energy of the oil-water interface system without polar molecules, kJ/mol; and $n$ is the number of polar component molecules.

Since asphaltene and resin molecules are regarded as natural surface active substances in crude oil, and the...
addition of surface active substances in oil-water system will inevitably decrease the total energy of the interface, so the interface formation energy is a negative value, and the larger the absolute value is, the more stable it is, and the more conducive it is to the formation of the interface [47].

Figure 12: Density distribution of simulation systems with different molar ratios. (a) Pure asphaltene. (b) 4 : 1. (c) 2 : 1. (d) 1 : 1. (e) 1 : 2. (f) 1 : 4. (g) Pure resin.
It can be seen from Table 4 that the addition of asphaltene and resin molecules will significantly decrease the energy of the system and promote the system to reach a stable state. As the molar ratio of asphaltene to resin increases from 0:1 to 1:0, the interface formation energy increases from -143.89 kJ/mol to -304.09 kJ/mol, which indicates that the interfacial strength of different asphaltene/asphaltene/water systems enhances with the increase of the molar ratio of asphaltene molecules. It also reveals that asphaltene molecules play a more important role in promoting interfacial film formation and maintaining structural stability than resin molecules.

4. Conclusions

The simulated results showed that the aggregation process of asphaltene molecules under the influence of hydrogen bonds can be divided into three stages of "aggregation–attraction–fusion". While the addition of resin molecules enhanced the connection between molecules of all polar components at the interface due to their good solubility and dispersion, which made the isolated aggregation structure disappear in the first stage. The aggregations of pure asphaltene, pure resin, and asphaltene-resin mixture all show two types of structures: π–π stacking and T-shaped stacking. The higher the molar ratio of asphaltene to resin is, the higher the proportion of π–π stacking structure is, and the interaction strength between asphaltene molecules is higher than that of resin molecules. As the molar ratio of asphaltene to resin increases from 0:1 to 1:0, the interfacial film thickness and interface formation energy increase from 2.366 nm and -143.89 kJ/mol to 3.796 nm and -304.09 kJ/mol, respectively, which indicates that asphaltene molecules play a more significant role in promoting the formation of interfacial film and maintaining its structural stability than resin molecules.

Data Availability

All data and models generated or used during the study appear in the submitted article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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