

Theoretical insight into the effect of polar organic molecules on heptane-water interfacial properties using molecular dynamic simulation

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ABSTRACT

Hydrocarbon-water interface plays an important role in many cases and industries. However, the effect of polar oil molecules on hydrocarbon-water interfacial properties is still unclear. In this work, 9 molecular scale heptane-water interface models containing different polar oil molecules were established by molecular dynamic simulation to study the effect of polar oil molecules on hydrocarbon-water interface properties. Interfacial tension (IFT), molecular configuration, molecular orientation and interaction energy between oil and water were calculated to quantitatively characterize the heptane-water interfacial properties containing different oil components. The IFT results show that IFT decreases as the molecular polarity increases. The molecular configuration results indicate that the stronger polar oil molecules tend to adsorb to the interface while the weaker polar oil molecules tend to stay in the oil bulk space. The molecular orientation shows that the polar oil molecules possess more orderly regularity at the interface while nonpolar oil molecules can only randomly adsorb at the interface. Specifically speaking, chain polar oil molecules tend to be perpendicular to the interface while the ring structure polar oil molecules tend to be parallel to the interface. The ring oil molecules containing branched functional groups should also tend to be perpendicular to the interface under the influence of the branches. The heptane-water interaction energy results indicate that the interaction energy increases as the molecular polarity increases. Furthermore, the electrostatic energy predominates over van der Waals energy when the oil contains polar oil molecules while van der Waals energy predominates over electrostatic energy when the oil contains nonpolar oil molecules. The conclusions in this work should provide some fundamental understanding of interfacial information and some industries involving hydrocarbon-water interface.

1. Introduction

With the development of the world economy, there has been a stable growing market demand for crude oil (Al-Fattah; Yakasai et al., 2021). To meet the expanding crude oil demands, economy and high efficiency oil recovery technologies and methods have been one of the most popular subjects of scholarly investigation (Li et al., 2021a; Zhang Ning et al., 2020; Wang et al., 2022). Water flooding is the most widely used oil recovery technology across the world (Farhadi et al., 2021; Li et al., 2021b). Many recovery problems, for example the low water flooding recovery and high water cut, however, negatively affect the production efficiency of the water flooding reservoirs (Zahra et al., 2021; Peng et al., 2019; Li et al., 2022). Oil-water interface properties play an important role on water flooding efficiency in the water flooding reservoirs (Mahmud and Mahmud, 2020; Huang, 2020). Uncovering the

mechanisms of oil-water interfacial properties provides guarantee for stable and efficient oil production in the water flooding reservoirs (Ayirala et al., 2018; Perles et al., 2018). Currently, it is believed that the polar oil components show obvious influence on oil-water interface and thousands of publications have been reported to share various and meaningful studies revealing the effect of oil components on oil-water interfaces in water flooding reservoirs (Hamed et al., 2021; Simon et al., 2016). The main conclusion by the researchers is that the polar oil components are surface-active and stabilize oil-water film to improve displacement efficiency of water flooding (Jungin and Tayfun, 2020; Mokhtari and Ayatollahi, 2019).

Therefore, it is essential for revealing oil-water interface mechanisms to clearly portray the behaviors of polar oil components at oil-water interface (Ganeeva et al., 2020; Ashoorian et al., 2021; Han et al., 2021). Aromatic oil compounds and organic acids are the representative

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surface-active crude oil components and influence the oil-water interface (Yuan et al., 2019; Cagna et al., 2018). Griselda and coworkers conducted visco-elasticity measurements on brine-water interfaces. They concluded that increasing asphaltene concentration increased interfacial visco-elasticity while higher acid concentration decreased interfacial visco-elasticity for a given brine (Griselda et al., 2016). Gao and coworkers reported that naphthenate acids in crude oil can decrease the interfacial tension and destabilize the oil-water emulsion (Gao et al., 2010). Marcia carried out some water-flooding experiments on several different crude oil samples with different resin and asphaltene concentrations by high and low salinity water injection. Their results indicated that oil samples with low concentration of resin and asphaltene are less responsive to low-salinity water injection while oil samples with high concentration of resin and asphaltene show significantly additional OOIP by low salinity water flooding salinity. It showed that resin and asphaltene play an important role during low salinity water flooding (Marcia et al., 2016). Sun reported that asphaltenes and surfactants formed cross-linked aggregates on the oil-water interface (Sun et al., 2021a). All the studies and conclusions are informative and useful. However, the current studies provide limited information about the effect of oil component on oil-water interface and oil recovery. The polar oil components adsorption performance at the oil-water interface is still unclear. It may be difficult to discover the mechanism behind the oil-water interface with different oil component, since the crude oil contains thousands of components (Sayed et al., 2019). Furthermore, the physical chemistry performances during water flooding process are extremely complex because of the various heterogeneity, high pressure and temperature and oil-water interaction (Liu et al., 2019; Ni, Miao, Lv, Lin). Various and complex geological and geochemical factors make the study on oil-water interface properties difficult tasks.

It is significantly necessary to study the basic effect of the oil components on oil-water interfacial properties. Molecular dynamic simulation provides an alternative tool to imitate the microscope behaviors of oil-water interface and has been reported as an effective study instrument in many publications. Molecular dynamic simulation is efficient and reliable (Chen et al., 2021; Sun et al., 2021b). Li and coworkers conducted several molecular dynamics simulations to study the effect of heteroatoms in the oil molecules on oil-brine interface at reservoir temperature and pressure. They established different oil-water interface systems containing different oil compositions and salinity in brine. They concluded that different oil components show different effect on oil-water interface. The oil molecules containing O atom can significantly decline the oil-water interface tension but the oil molecules containing N or S atom only slightly reduce the interface tension. Salinity should also influence the orientation of the polar oil molecules

should be influenced by oil composition, which follows the order of toluene > heptol > heptene (Hasan Badizad et al., 2020a).

Many researchers have made significant progress on revealing the performance and mechanism of the oil-water interfacial properties, however, the effect of polar oil molecules on oil-water interface is still unclear. In fact, a real reservoir is a complex research object. The crude oil includes thousands of components. The salts in formation water and reservoir gases should play an important role on the oil-water interface. All the factors bring difficulties to study the oil-water interface. In many cases and industries, one may be more concerned with the hydrocarbon-water interface though a real reservoir is complex. Therefore, this work focuses on the effect of polar oil component on heptane-water interface properties. We established 9 heptane-water interfacial models to reveal the performance and mechanism by MD simulation. Every interfacial model consists of heptane phase and water phase and every heptane phase contains different polar oil molecules representing the polar components in crude oil. We found that the polarity of the oil molecules can significantly influence the heptane-water interface and exhibited quantitative evidence.

2. Simulation details and method

2.1. Force field

The most important parameter for the molecular dynamic simulation is the force field. Selecting a proper force field is the guarantee for successful simulation. According to the literatures, the COMPASS (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies), an ab initio force field that can accurately simulate thermodynamic properties of a single molecule or condensed matter over a wide range and predict the structure, conformation, vibration frequency, has been used in hundreds of material simulations and successfully reflected the quality of the parameters. Sun and coworkers later extended the primary COMPASS force field and reported the COMPASS II force field (Sun Zhaoet al., 2016). The extended COMPASS II force field can imitate some new fundamental particles including aromatic molecules, hydrocarbon, organic acid, carbanion, nitrate ion, and many basic organic and inorganic particles. In this work, the basic particles in all the molecular models are water molecules and basic organic molecules. Therefore, the COMPASS II force field is applicable to simulate the oil-water interface.

The fundamental mathematic method of the COMPASS II force field can be expressed as follow:

$$E_{total} = E_b + E_a + E_t + E_{i-a} + E_{b-b} + E_{b-a} + E_{a-a} + E_{b-t} + E_{a-t} + E_{a-t-a} + E_{van\ der\ waals} + E_{electrostatic\ energy} \quad (1)$$

at the oil-water interface (Li et al., 2019). Yohei et al. built oil-water interface molecular models to study the interfacial behavior of asphaltene molecules by molecular dynamic simulation. They found that the asphaltenes molecules prefer to disperse in the oil phase when the organic solvent is pure toluene whereas they tend to adsorb to the oil-water interface when the organic solvent is pure heptane. When the asphaltenes adsorb to the oil-water interface, they can form a steady film to reduce IFT (Yohei et al., 2013). Siddhesh and coworkers carried out molecular dynamic simulation to study behaviors and properties of dicarboxylic acids at oil-water interface. They concluded that the hydrocarbon tail of monocarboxylic acids tends to insert into the oil-water interface (Kamat et al., 2019). Mohammad conducted a series of molecular dynamic simulation to study the effect of oil components on oil-water electrical property. They concluded that interfacial charge

In the formula, the E_b , E_a , E_t , E_{i-a} are behalf of bond, angle, torsion and inversion (out of plane) angle, on behalf of intramolecular interaction. E_{b-b} , E_{b-a} , E_{a-a} , E_{b-t} , E_{a-t} , E_{a-t-a} are bond-bond energy, bond-angle energy, angle-angle energy, bond-torsion energy, angle-torsion energy and angle-torsion-angle energy respectively. E_{vdw} and E_{elec} are van der Waals energy and electrostatic energy respectively, on behalf of intermolecular interaction. In this work, we need to introduce the intermolecular interaction: $E_{van\ der\ waals}$ and $E_{electrostatic\ energy}$.

$$E_{van\ der\ waals} = \sum \varepsilon_{ij} \left[\left(\frac{r_{ij}^0}{rij} \right)^9 \times 2 - \left(\frac{r_{ij}^0}{rij} \right)^6 \times 3 \right] \quad (2)$$

Table 1

Kinds and numbers of the basic molecules in the models.

Case	Numbers and kinds of oil molecules		Water	Total
	Nonpolar molecules	polar molecules		
1	heptane	140	–	1140
2		100	toluene	1140
3		100	thiophene	1140
4		100	ethyl mercaptan	1140
5		100	phenol	1140
6		100	cyclohexane acid	1140
7		100	pyridine	1140
8		100	benzoic acid	1140
9		100	Heptanoic acid	1140

$$E_{\text{electrostatic energy}} = \sum \frac{q_i \times q_j}{\epsilon_0 r_{ij}} \times \frac{1}{4\pi} \quad (3)$$

2.2. Simulation programs

In this work, we presented 9 different heptane-water interface programs to simulate effect of different polar oil components on heptane-water interface. The numbers and kinds of oil molecules and water molecules in each model are shown in Table 1. The interface models consist of heptane phase and water phase. The heptane phase contains nonpolar organic solvent and polar components. In case 1–9, the nonpolar organic solvent is heptane. The polar oil components are no polar components (control case), toluene, thiophene, ethyl mercaptan, phenol, cyclohexane acid, pyridine, benzoic acid, and heptanoic acid, respectively, as shown in Fig. 1.

All the oil molecules are representative and common components in the crude oil. Heptane and heptanoic acid have similar carbon chain structure and heptanoic acid holds one carboxyl group, which are suitable for reveal the effect of O atom and carboxyl group on the oil-water interface. Pyridine and thiophene are both characterized by benzene ring without branched chain structure. Their difference is that pyridine holds N atom and thiophene holds S atom. These two components should provide evidence of the effect of aromatic molecules on oil-water interface and comparing the different role of N atom and S atom. Benzoic acid and cyclohexane acid are both hex-atomic ring organic acid, which can reveal the special characteristic of benzene ring. Benzoic acid, phenol and toluene are 3 different aromatic compounds with different functional groups, which can be used to analyze the influence of aromatic compounds with different functional groups on oil-water interface. Ethyl mercaptan is a common S-containing oil component, which can reveal the effect of aldehydes on oil-water interface. The water phase contains only water molecules.

2.3. Heptane-water interface molecular models

According to the simulation programs shown in Table 1, it is necessary to build 9 heptane-water interface molecular models containing different polar oil components (See Fig. S1 in the Supporting Information). Each model consists of 2 parts: heptane phase and water phase, as shown in Fig. 2. For the heptane phase, 100 heptane molecules were put into a box as the nonpolar solvent and 40 polar oil molecules were added into the solvent. The density of the oil phase is 0.75 g/cm³ and the volume of the oil box is 3.5 × 3.5 × 2.4 nm³, as shown in Fig. 2 (a). The water phase contains 1000 water molecules with a density of 1 g/cm³ and a volume of 3.5 × 3.5 × 2.4 nm³, as shown in Fig. 2 (b). We combined the heptane box and water box to build the heptane-water interface model, as shown in Fig. 2 (c). All the models are periodic boundary conditions.

2.4. Simulation details and validation

2.4.1. Details

The objective of this work is to reveal the effect of polar oil components on heptane-water interface. Therefore, we need to get the most stable molecular configuration of the oil-water interface model. Before molecular dynamic simulation, geometry optimization was conducted by steepest descent method for all the 9 models to give an optimal initial configuration. After the geometry optimization, all the molecular dynamic simulations were carried out under NPT ensemble for 5ns with a time step of 1 fs. The simulation temperature and pressure were set as 298 K and 0.0001 GPa. We applied the Ewald method to address the electrostatic interaction and atom-based cutoff method with a cutoff distance of 15.5 Å to describe the van der Waals force. All the simulations were carried out under periodic boundary conditions. During the simulation process, interfacial tension, molecular configuration, relative concentration, molecular orientation and interaction energy were monitored to provide quantitative evidences for performance analysis. The calculation method and details are described in the Supporting Information.

2.4.2. Validation

In order to guarantee the accuracy of the parameters and methods used in this work, three tentative simulations were carried out by the molecular dynamic simulation method before the major work as accuracy inspection. We simulated the interfacial tension of the hexane-water interfacial model, heptane-water interfacial model and decane-water interfacial model. The simulation results were compared to the experimental results (room temperature and pressure) in several literatures (Rajalakshmi Seetharaman et al., 2021) as shown in Table 2.

It is obviously that the simulation coincides with the experimental result. The experimental hexane-water IFT is 50.38 mN/m and the

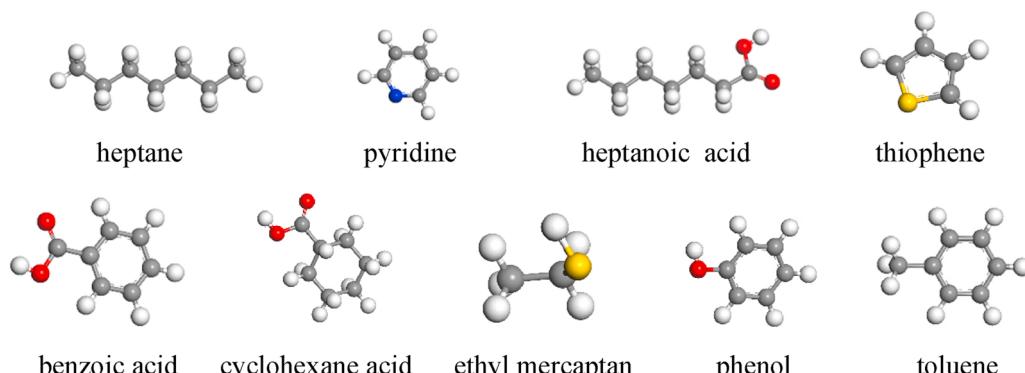


Fig. 1. The oil molecules in the oil-water interface models. (Color label: red-O atom; blue-N atom; yellow-S atom; gray-C atom; white-H atom). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

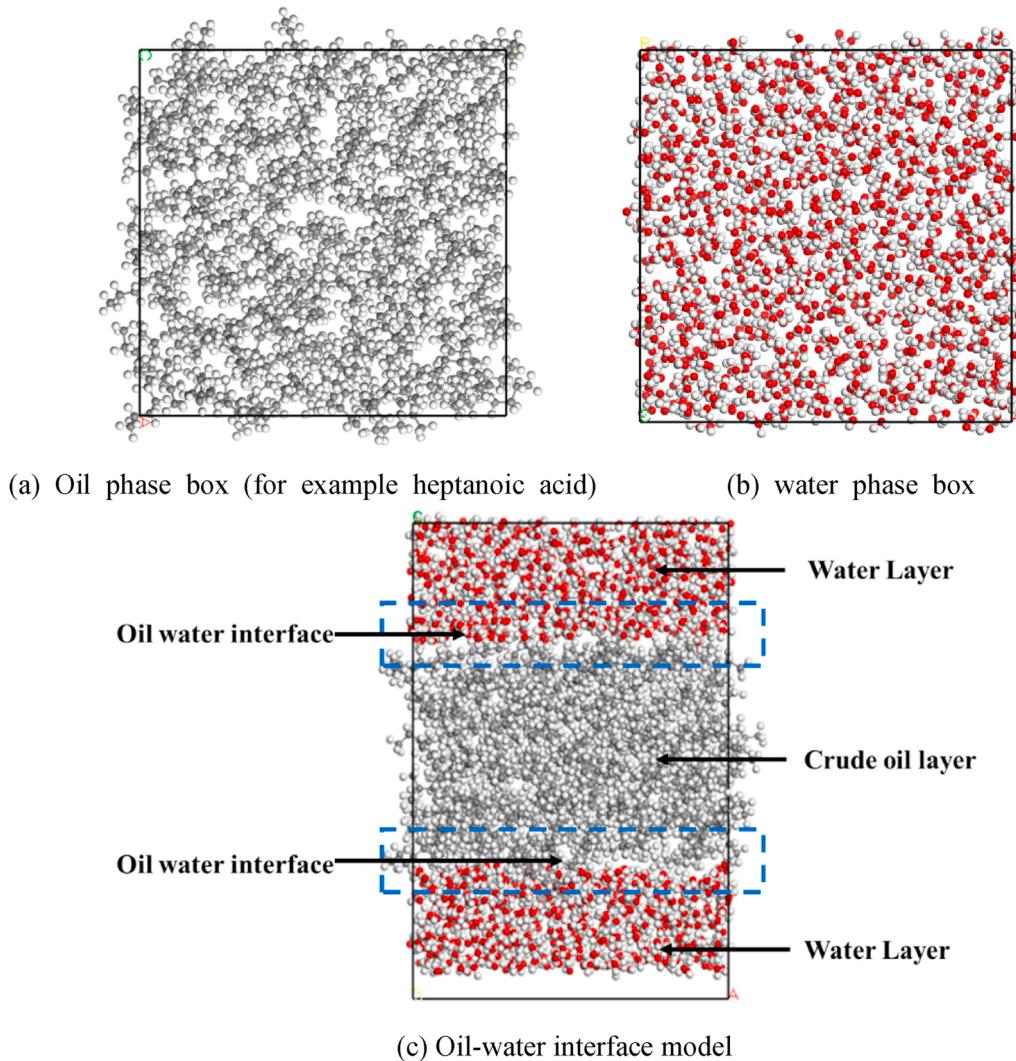


Fig. 2. The oil-water interface models.

Table 2
Comparison between the results of simulation and experiment.

Model	Interfacial tension (mN/m)		
	Simulation	Experiment (RajalakshmiSeetharaman et al., 2021)	Error
hexane-water	50.66	50.38	0.5%
heptane-water	50.33	50.17	0.3%
decane-water	51.05	51.10	-0.1%

simulative hexane-water IFT is 50.66 mN/m. The error is only 0.5%. The experimental heptane-water IFT is 50.17 mN/m and the simulative heptane-water IFT is 50.33 mN/m. The error is only 0.3%. The experimental decane-water IFT is 51.10 mN/m and the simulative decane-water IFT is 51.05 mN/m. The error is only -0.1%. The errors of the 3 models are at most 1%. Therefore, we could believe that the simulation method and details in this work should be reliable.

3. Results and analysis

3.1. Molecular polarity

In order to quantificationally discuss the effect of polar oil molecules on oil-water interface, it is necessary to quantify the polar intensity of all the oil molecules in this work. By definition, a molecule where the centers do not coincide is called a polar molecule. Dipole moment is a useful parameter to quantificationally describe the polar intensity of the oil molecules. In this section, we calculated the dipole moments of all the molecules to quantificationally rank the polar oil molecules, as shown in Fig. 3. The dipole moments calculation formula is:

$$\mu = q \times d \quad (4)$$

In this formula, q is the quantity of the charge center (unit: coulomb, C). d is the distance between the centers (unit: meter, m). μ is the dipole moment (unit: C·m). Customarily, one electron charge is $e = 1.6022 \times 10^{-19}$ C and the order of magnitude of the charge q of the bond dipole moment is 10^{-10} esu, where esu is a symbol of electrostatic unit, $1\text{esu} = 3.335 \times 10^{-10}$ C. The order of magnitude of the length of the dipole moment is 10^{-8} cm. The order of magnitude of multiplying the two parameters is 10^{-18} esu·cm. Therefore, the common dipole moment unit is Debye, which is shortened to D, $1D = 10^{-18}$ esu·cm.

It is obviously that the dipole moments vary with the structures and

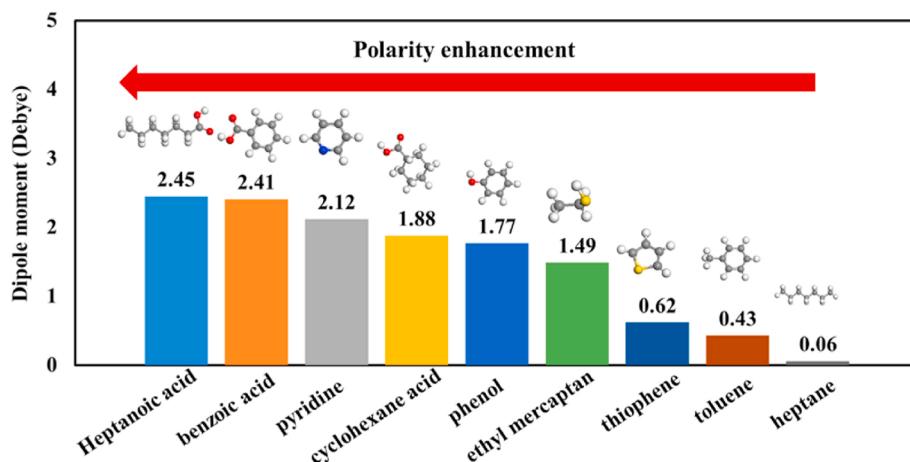


Fig. 3. Dipole moment of the polar oil molecules.

atoms of the oil molecules. The strongest polar oil molecule is the chain-structure heptanoic acid molecule, whose dipole moment is 2.45 Debye. Not far behind are the benzoic acid molecule, pyridine molecule and cyclohexane acid molecule, with dipole moment of 2.41 Debye, 2.12 Debye and 1.88 Debye, respectively. What the 3 oil molecules have in common is a strong polar cyclic structure. Their difference is benzoic acid molecule and pyridine molecule containing benzene ring structure while cyclohexane acid molecule is ring saturated organic acid. The dipole moment of phenol molecule is 1.77 Debye, which represents the alcohols in the crude oil. The less polar oil molecules are the ethyl mercaptan molecule, thiophene molecule, and toluene molecule, whose dipole moments are 1.49 Debye, 0.62 Debye and 0.43 Debye, respectively. These 3 molecules represent common and weak polar aromatic components in the crude oil. The weakest polar oil molecule in this work is the heptane molecule (0.06 Debye), representing the nonpolar alkane components in crude oil.

3.2. Relative concentration and molecular configuration

Fig. 4 Show the equilibrium molecular configuration and relative concentration of the 9 interfacial models. **Fig. 4.** (a)–(i) are heptane-water interface, toluene-water interface, thiophene-water interface, ethyl mercaptan-water interface, phenol-water interface, cyclohexane-water interface, pyridine-water interface, benzoic acid-water interface, heptanoic acid-water interface, respectively.

It should be observed that the oil polarity influences the equilibrium molecular configuration and relative concentration of the interfaces. For the heptane-water interface model (control case) shown in **Fig. 4.** (a), the heptane molecules (oil phase) aggregated at the center of the model and the water molecules (water phase) distributed at the sides. Because the heptane molecule is the weakest polar oil molecule in this work, all the heptane molecules uniformly distributed in the box. The relative concentration profile only amounted to fluctuations around a state of equilibrium. For the toluene molecules, thiophene molecules and ethyl mercaptan molecules, the equilibrium molecular configuration and relative concentration were a little different because of these three kinds of oil molecules possessing some polarity, as shown in **Fig. 4.** (b)–(d). The molecular configurations show that the moderate polar toluene molecules, thiophene molecules and ethyl mercaptan molecules tend to adsorb to the oil-water interface to some extent. The relative concentration profiles exist significant peaks at the oil-water interface position. This indicates that the polar oil molecules can adsorb to the oil-water interface and the equilibrium adsorption configurations are heterogeneous. However, this adsorption is incomplete. The molecular configurations show obvious dissociative toluene molecules, thiophene molecules and ethyl mercaptan molecules. The relative concentration

profiles of the three oil molecules are non-vanishing at the oil phase position. For the strong polar phenol molecules, cyclohexane molecules, benzoic acid molecules, pyridine molecules and heptanoic acid molecules, the absorption capacity is maximum. The molecular configurations show that all the strong polar oil molecules can adsorb to the oil-water interface and there exists no strong polar oil molecules dissociating in the oil phase. The relative concentration profiles of the 5 oil molecules show significant peaks at the oil-water position and return to zero at the oil phase position. It could be concluded that the oil molecular polarity plays an important role in the adsorption configuration at the oil-water interface. The strong polar oil molecules tend to adsorb to the oil-water interface and weak polar oil molecules tend to dissociate in the oil phase.

3.3. Interfacial tension

Fig. 5 exhibits the interfacial tension (IFT) results of the 9 interfacial models in this work. The calculation method was described in the Supporting Information. It is obviously that the oil molecular polarity affects the oil-water interfacial tension significantly. The IFT of heptane-water interface is 50.15 mN/m. The IFT of toluene-water interface is 48.32 mN/m. The IFT of thiophene-water interface is 45.17 mN/m. The IFT of ethyl mercaptan-water interface is 42.84 mN/m. The IFT of phenol-water interface is 36.14 mN/m. The IFT of cyclohexane acid-water interface is 29.73 mN/m. The IFT of pyridine-water interface is 25.95 mN/m. The IFT of benzoic acid-water interface is 19.48 mN/m. The IFT of heptanoic acid-water interface is 16.65 mN/m. It should be noted that the IFT decreases as the oil molecular polarity enhances. The strong polar oil molecules should contribute to reduce the IFT.

In order to further quantitatively describe the influence of oil molecular polarity on the IFT, the IFT-dipole moment profile was exhibited in **Fig. 6**. The IFT-dipole moment profile shows that the IFT decreases from 50.15 mN/m to 16.65 mN/m as the oil molecular dipole moment increases from 0.06 Debye to 2.45 Debye. This provides quantitative evidence of the ability of polar oil molecules to reduce the oil-water interface.

3.4. Molecular orientation at the oil-water interface

Fig. 7 shows the equilibrium polar oil molecular orientation at the interface. The orientation parameter, S_z , was selected and calculated to quantitatively describe the molecular orientation of the polar molecules at the oil-water interface. The calculation method was described in the Supporting Information. The value range of S_z is (-1, 1). If the S_z is close to -1, it could be evidence for the polar oil molecule tend to be parallel to the oil-water interface preferentially. On the contrary, if the S_z is close

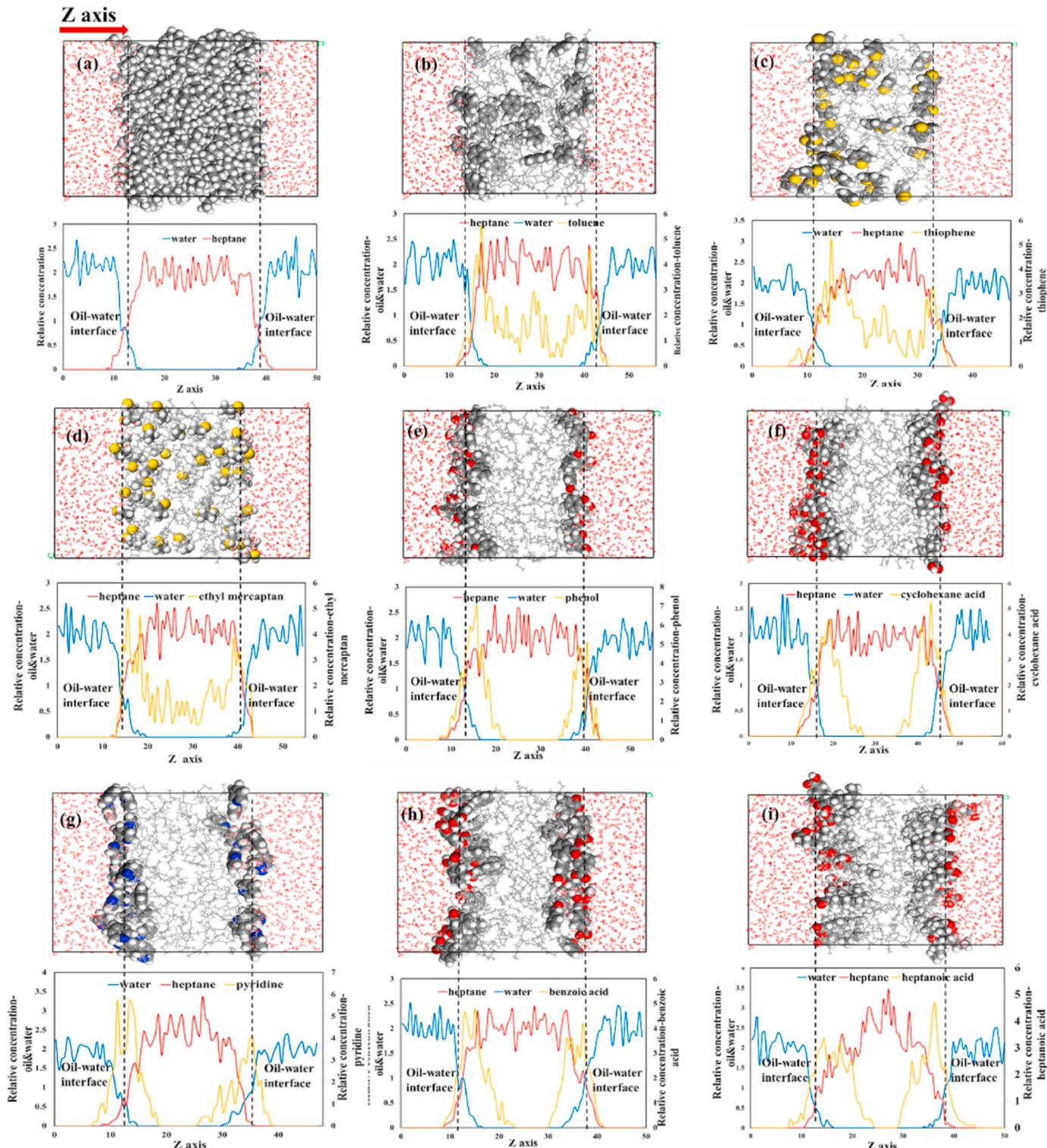


Fig. 4. The molecular configuration and relative concentration of the 9 oil-water interfaces at the dynamic equilibrium state. (The water and heptane molecules were simplified as line model and the polar oil molecules were characterized for observation.)

to 1, it could be evidence for the polar oil molecule tend to be perpendicular to the oil-water interface preferentially. If the S_z is close to 0, which means that the polar oil molecules randomly distribute at the oil-water interface. Neither perpendicular nor parallel. It should be observed that both the molecular polarity and structure can influence the polar oil molecular orientation at the oil-water interface.

For the weak polar heptane molecules and toluene molecules, the

values of S_z are close to 0.1, which means that these two weak polar oil molecules could only adsorb to the oil-water interface with random orientation. For the thiophene molecules, the S_z holds values of -0.14 and -0.15, which means that thiophene molecules adsorb to the oil-water interface more orderly. The values are close to -1, which means that the thiophene molecules tend to be parallel to the oil-water interface preferentially. For the ethyl mercaptan molecules, the S_z holds

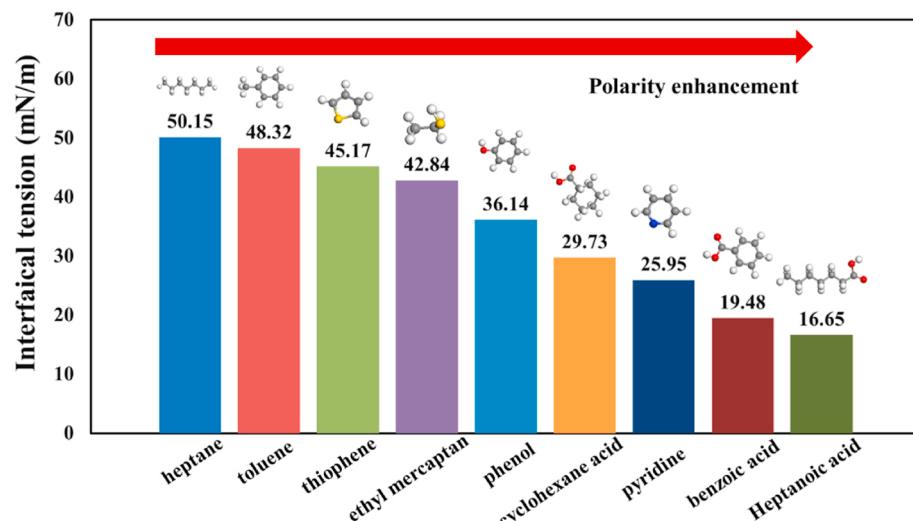


Fig. 5. The interfacial tension of the 9 oil-water interfacial models at the molecular equilibrium state.

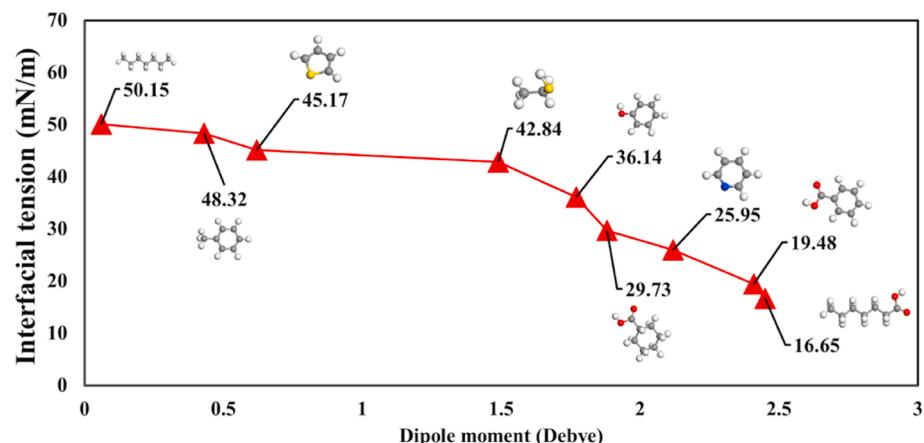


Fig. 6. The relationship between IFT and dipole moment of the 9 oil-water interfacial models at the molecular equilibrium state.

values of 0.17 and 0.18 and the values are close to 1, which means that ethyl mercaptan molecules orderly adsorb to the oil-water interface and should be perpendicular to the oil-water interface preferentially. For the phenol molecules, the values S_z are 0.29 and 0.30 and for cyclohexane molecules, the S_z values are 0.38 and 0.34, respectively. The values indicate that these two polar oil molecules could also adsorb to the oil-water in an organized way and be perpendicular to the oil-water interface preferentially. The S_z values of pyridine molecules are -0.22 and -0.25, close to -1. It means that the pyridine molecules are tend to be parallel to the oil-water interface. The S_z values of benzoic acid molecules (0.48 and 0.45) and heptanoic acid molecules (0.48 and 0.47) are highest and closest to 1 among all the polar oil molecules, which means that the two molecules could most orderly absorb to the oil-water interface and be perpendicular to the oil-water interface preferentially. Not only polarity, but also molecular structure should also influence the molecular orientation at the oil-water interface. The heptanoic acid molecules and ethyl mercaptan molecules are chain organic molecules containing polar functional groups. The chain structures force the heptanoic acid molecules and ethyl mercaptan molecules to be perpendicular to the oil-water interface. On the contrary, the pyridine molecules and thiophene molecules are ring organic molecular without branched groups. The ring molecular structure could force the pyridine molecules and thiophene molecules to be parallel to the oil-water interface preferentially. Furthermore, the phenol molecules, cyclohexane molecules and benzoic acid molecules are ring organic

molecules containing branched functional groups. Under the influence of branched functional groups, the ring molecules could not keep parallel to the oil-water interface while be forced to be perpendicular to the oil-water interface by the branched functional groups.

3.5. Interaction energy

Table 3 shows the results of interaction energy between the oil and water of the 9 interfaces in this work. The intermolecular interaction energy between oil and water molecules was assumed as the interaction energy, which included the van der Waals energy (E_{vdw}) and electrostatic energy (E_{elec}), as described in the chapter 2.1. The calculation method is:

$$E_{intermolecule} = E_{vdw} + E_{elec} \quad (4)$$

$$E_{interaction} = E_{total} - (E_{oil} + E_{water}) \quad (5)$$

The negative sign of the interaction energy values means that the oil and water attract each other. And the absolute values of the interaction energy values indicate the strength of the attraction. The percentage is the proportion of E_{elec} and E_{vdw} in the E_{int} .

Fig. 8 Shows the effect of polar oil molecules on the oil-water interaction energy of the 9 models. It should be noted that the oil molecular polarity significantly influences the oil-water interaction. The interaction monotonically increases with the molecular polarity. The interaction energy increases from -173.60 kcal/mol (for heptane) to

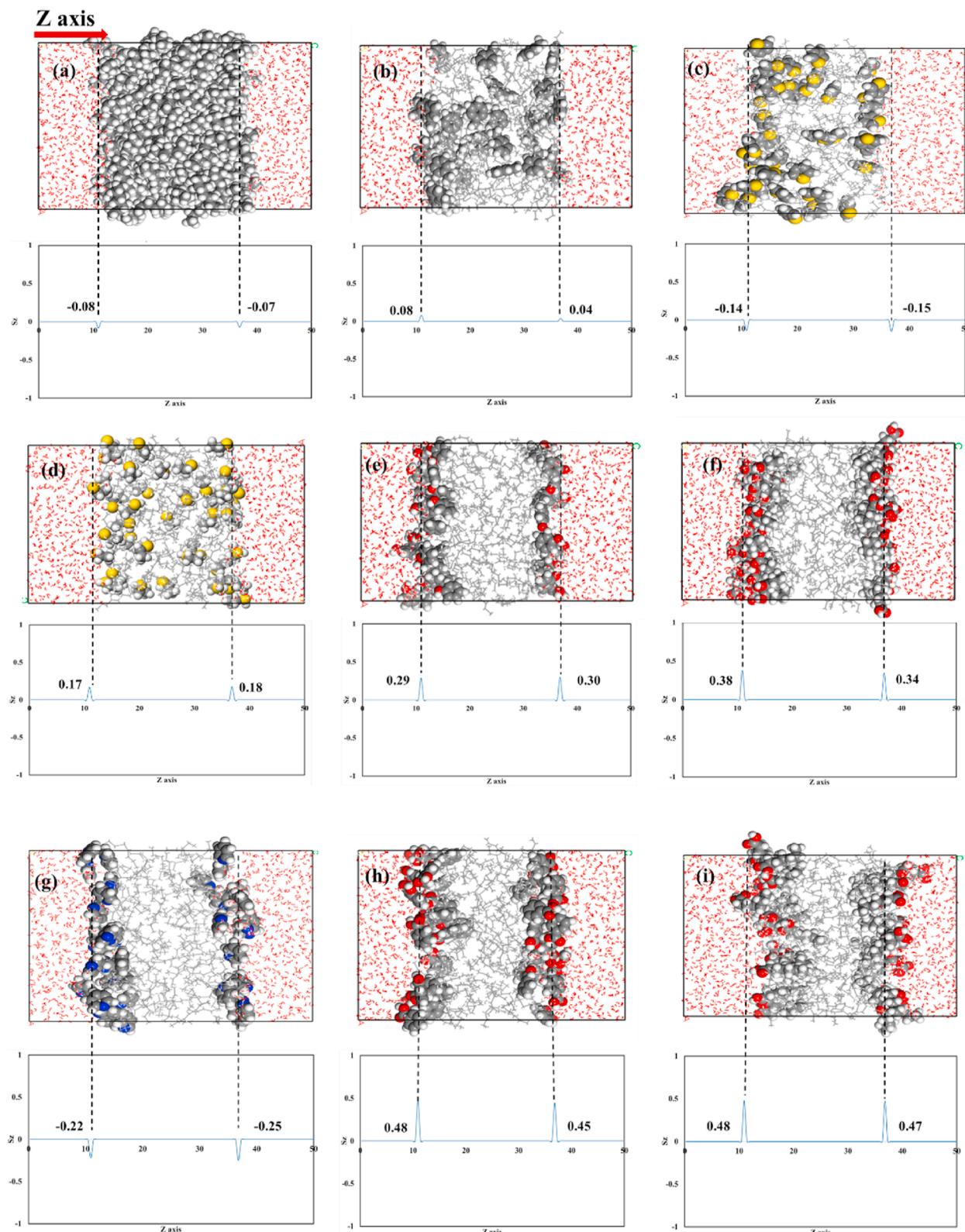


Fig. 7. The polar oil molecular orientation of the 9 oil-water interfacial models at the molecular equilibrium state. (Fig. 7. (a)–(i) are heptane-water interface, toluene-water interface, thiophene-water interface, ethyl mercaptan-water interface, phenol-water interface, cyclohexane-water interface, pyridine-water interface, benzoic acid-water interface, heptanoic acid-water interface, respectively.).

Table 3

The interaction energy between the oil and water of the 9 oil-water interfacial models.

case	Polar oil molecule	Interaction energy (kcal/mol)			Percentage %	
		E _{int}	E _{elec}	E _{vdw}	E _{elec}	E _{vdw}
1	Heptane	-173.60	-0.02	-173.58	0.01%	99.99%
2	Toluene	-226.40	-64.29	-162.11	28.40%	71.60%
3	Thiophene	-228.26	-73.80	-154.46	32.33%	67.67%
4	Ethyl mercaptan	-275.74	-154.36	-121.38	55.98%	44.02%
5	Phenol	-414.74	-335.55	-79.19	80.91%	19.09%
6	Cyclohexane acid	-552.05	-498.30	-53.75	90.26%	9.74%
7	Pyridine	-621.49	-592.47	-29.02	95.33%	4.67%
8	Benzoic acid	-701.51	-692.09	-9.42	98.66%	1.34%
9	Heptanoic acid	-714.63	-709.35	-5.28	99.26%	0.74%

-714.63 kcal/mol (for heptanoic acid) as the molecular polarity increases. Similarly, the electrostatic energy increases from -0.02 kcal/mol (for heptane) to -709.35 kcal/mol (for heptanoic acid) as the molecular polarity increases. On the contrary, the van der waals energy decreases from -173.58 kcal/mol (for heptane) to -5.28 kcal/mol (for heptanoic acid) as the molecular polarity increases. It could be concluded that the molecular polarity can enhance the interaction between oil and water. Increasing the molecular polarity should increase the intermolecular interaction strength and electrostatic interaction but decrease the van der waals interaction. Table 3 also indicates the percentages of E_{elec} and E_{vdw} in the E_{int} of the 9 oil-water interfacial models. The percentage of E_{elec} in the E_{int} increases while the percentage of E_{vdw} in the E_{int} decreases as the molecular polarity increases. For weak polar heptane molecules, toluene molecules and thiophene molecules, the percentage of E_{vdw} is higher than that of E_{elec}. For the other strong polar oil molecules, the percentage of E_{elec} is higher than that of E_{vdw}. This indicates that the van der waals interaction plays a leading role in the oil-water interaction for weak polar oil-water interface, while electrostatic interaction plays a leading role in the oil-water interaction for strong polar oil-water interface.

4. Discussions

The effect and adsorption behaviors of polar oil molecules on the heptane-water interface were studied by molecular dynamic simulation. IFT, molecular configuration, interaction energy and orientation parameters were monitored to quantificationally characterize the

adsorption behaviors and effect of the polar oil molecules at the heptane-water interface. The results reveal that the polar oil molecules should tend to adsorb to the interface while the nonpolar should dissociate in the heptane phase. The adsorption configurations of the polar oil molecules vary with the polar molecular structures. The ring polar oil molecules tend to be parallel to the interface while the chain oil molecules tend to be perpendicular to the interface. The IFT decreases as the molecular polarity increases while the interaction energy increases as the molecular polarity increases. Furthermore, the van der Waals interaction energy should take over the interaction energy when there exists no polar oil molecule. But the electrostatic interaction energy should take over the interaction energy when there exist polar oil molecules adsorbing to the interface. All the results indicate that polar oil molecules can influence the interface and different oil molecules behave differently at the interface. These findings should relate to some published literatures and provide a possible explanation for some experimental phenomenon, to some extent. Many publications focus on the effect of organic molecules on the hydrocarbon-water interface using experimental methods. For example, the frequency vibrational spectroscopy (SFVS) technology is well established in order to determine the orientation of molecules at oil/water interfaces. Scientists carried out a series of SFVS experiments to study molecular scale interfacial information and structure information. They found that the interfacial water molecules were more organized and formed a hydrogen-bonding network different from bulk (Shen and Ostroverkhov, 2006). The interaction among interfacial molecules and bulk molecules are significantly weaker and it is the weak interaction drive the water molecules into organic phase (Moore and Richmond, 2008). Also, Stiopkin combined an experimental and theoretical study of the air-water interface by surface-selective heterodyne-detected vibrational sum frequency spectroscopy. It was found that the water molecular hydrogen bond could pass through the interface and be weaker than the bulk water molecular H-bond (Stiopkin et al., 2011). Robel B et al. reported that the hydrophobic aromatic molecules hindered the oil molecules adsorbing to the interface while the carboxylic functional group enhanced the adsorption of oil molecules to the interface (Robel, 2014). The organics-water interface is influenced by not only molecules, but also ions. Mohammad reported that ions could adsorb to the oil-water interface though the oil molecules are charge-neutral. Moreover, the interfacial ions adsorption behaviors are influenced by hydrocarbon molecules, for example toluene and heptane (Hasan Badizad et al., 2020b). Alotaibi used advanced Sum Frequency Generation (SFG) spectroscopy to describe the effect of ions molecular adsorption at the oil-brine interface.

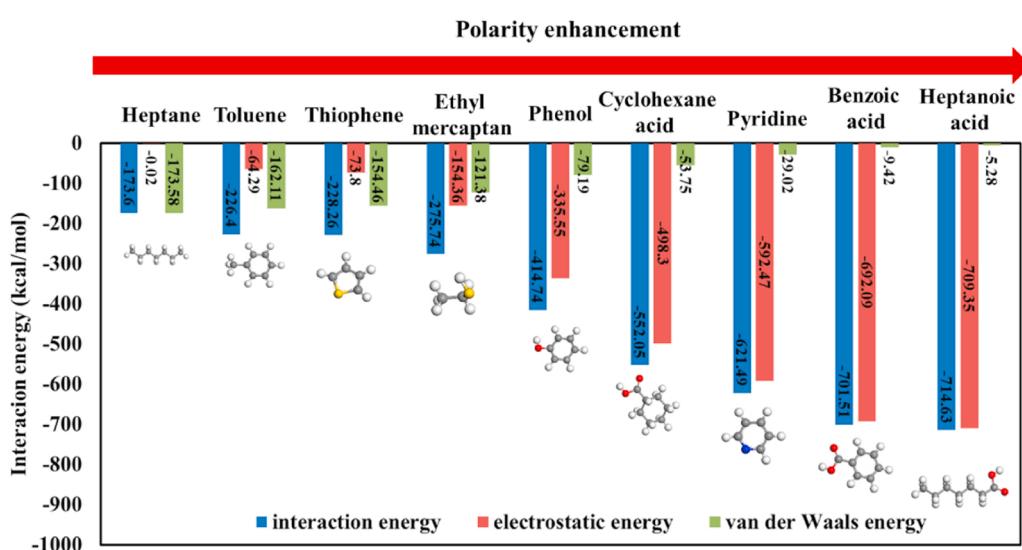


Fig. 8. The effect of polar oil molecules on the interaction energy between oil and water of the 9 oil-water interfacial models.

Their results indicated that the DI water-oil interfacial H-bond was significantly strong and the interfacial H-bond strength enhanced as the salinity decreased. At low salinity, mixing various ions in water should enhance the water-oil interaction more effectively than individual ions (Mohammed, 2019).

5. Conclusion

In this work, the effect of oil molecular polarity on the heptane-water interface was studied by molecular dynamic simulation. 9 interfacial models containing different polar oil components were built at molecular scale. The strong polar oil molecules and weak polar oil molecules behave differently at the oil-water interface. The strong polar oil molecules tend to adsorb to the oil-water interface and reduce the oil-water interfacial tension while the weak polar oil molecules tend to dissociate in the oil phase and increases the oil-water interfacial tension. The interaction energy increases as the molecular polarity increases. Specifically speaking, the van der waals energy decreases while the electrostatic energy increases as the molecular polarity increases. For the weak polar oil-water interface, the van der waals interaction plays a leading role in the oil-water interaction while for the strong polar oil-water interface, the electrostatic interaction plays a leading role in the oil-water interaction. Both oil molecular polarity and structure influence the molecular orientation at oil-water interface. The adsorption configuration of the strong polar oil molecules is more organized than that of the weak polar oil molecules. Chain polar heptanoic acid molecules and ethyl mercaptan molecules tend to be perpendicular to the oil-water interface preferentially. Ring polar pyridine molecules and thiophene molecules tend to be parallel to the oil-water interface preferentially. The benzoic acid molecules and cyclohexane molecules are ring organic molecules containing branched functional groups, resulting in perpendicular to the oil-water interface preferentially. The weakest polar toluene molecules and heptane molecules tend to randomly adsorb to the oil-water interface. The findings and conclusions in this work should provide basic information about the effect of molecular polarity on the heptane-water interface, which should also serve for researches of related industries.

CRediT author statement

Songqi Li: Conceptualization, Methodology, Investigation, Writing-Original Draft; Visualization. Yuetian Liu: Resources, Writing – Review & Editing; Supervision; Project administration; Funding acquisition. Liang Xue: Writing – Review & Editing; Data Curation; Supervision; Project administration. Dongdong Zhu: Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2022.110259>.

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