

Mechanism Analysis of Heavy Oil Viscosity Reduction by Ultrasound and Viscosity Reducers Based on Molecular Dynamics Simulation

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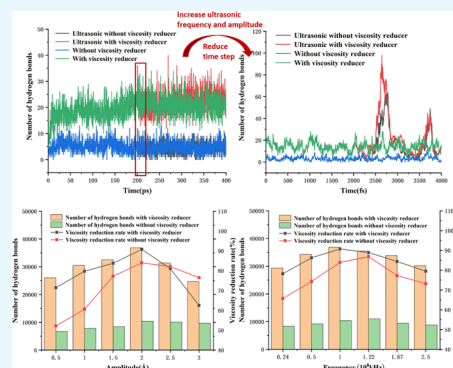
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ABSTRACT: Ultrasound and viscosity reducers are commonly used methods to reduce the viscosity of heavy oil. In order to compare the viscosity reduction effects of ultrasound and viscosity reducers and study their mechanism of interaction on heavy oil, molecular dynamics simulation was carried out in this paper. First, a molecular model of heavy oil composed of asphaltene, resin, aromatic hydrocarbon, and saturated hydrocarbon was established in this work. Through molecular dynamics simulation, the different effects of ultrasound and viscosity reducers on the viscosity reduction rate, hydrogen bond number, hydrogen bond type, and occupation rate were obtained, and the viscosity reduction mechanism of ultrasound and viscosity reducers was analyzed. By calculating the viscosity reduction rate and the number of hydrogen bonds of five oil-soluble viscosity reducers with or without ultrasound, it was found that the types of hydrogen bonds affecting the viscosity reduction effect were different with or without ultrasound or viscosity reducer, and the type and content of viscosity reducer would affect the effect of ultrasonic viscosity reduction. The amplitude, frequency, and temperature of ultrasound were also the factors affecting the effect of viscosity reducers. The simulation results helped to explain the mechanism of jointly reducing the viscosity of heavy oil by ultrasound and viscosity reducers from the microscopic point of view and provided a theoretical basis for the industrial application of ultrasound and viscosity reducers to reduce the viscosity of heavy oil.



1. INTRODUCTION

With the continuous consumption of petroleum resources, the demand for crude oil has increased significantly. Heavy oil is considered to be one of the most important sources to meet the future energy demand. High density, high freezing point, high viscosity, and poor fluidity are the main problems in heavy oil exploitation and transportation.^{1–4} Ultrasound and viscosity reducers are commonly used methods of viscosity reduction at present.

Treatment by ultrasound is a green, high-efficiency, and low-cost technology, which can effectively reduce the requirements and costs of transportation equipment in oil production and transportation processes. At present, it is widely used to reduce the viscosity of heavy oil in oil fields.^{5,6} The cavitation, heating, and mechanical oscillation of ultrasonic treatment reduce the molecular weight of macromolecules by splitting the most susceptible chemical bonds, thereby decreasing the viscosity of oil.^{7–9} Some researchers have carried out experiments on the effect of ultrasound on oil viscosity. Mousavi et al.¹⁰ used a series of steady shear flow and oscillation tests to investigate the rheological changes of several crude oil samples exposed to ultrasonic waves for different time intervals. Hamidi et al.¹¹ studied the effect of ultrasonic waves on viscosity changes of paraffin, synthetic oil, and kerosene in a smooth capillary tube. Razavifar and Qajar¹²

investigated the influence of ultrasonic waves on the viscosity and thermal behavior of a crude oil with high asphaltene content at different irradiation times and powers/frequencies. At present, there are also some microscopic studies on ultrasonic viscosity reduction. Taheri-Shakib et al.¹³ found that both microwaves and ultrasonic waves could lead to the cracking of large chain molecules and produce light components, which would reduce the viscosity of heavy oil. Mullakaev et al.¹⁴ found that the ultrasonic treatment of low-paraffinic oils with a high tar and asphaltene content leads to a substantial decrease in viscosity and the pour point, while ultrasonic treatment was not effective for crude oil with high n-alkane content. Liu et al.¹⁵ used elemental analysis, four-component analysis, and gas chromatography analysis to analyze the micro-mechanism of the oil chemical structure change and water samples under ultrasonic wave.

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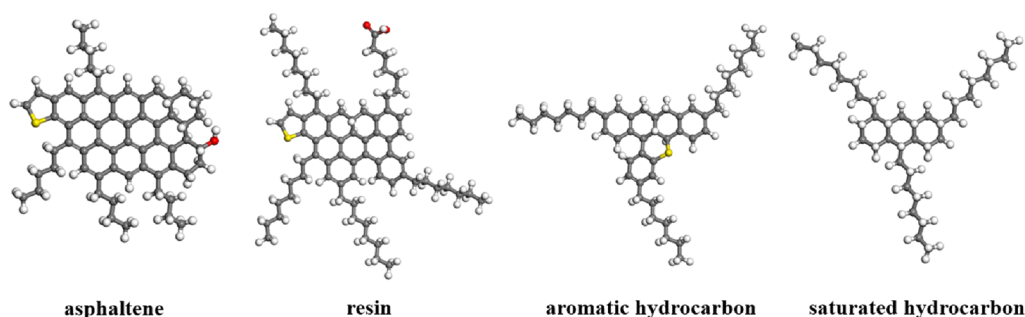


Figure 1. Average molecular model.

Oil-soluble viscosity reducers mainly reduce viscosity through a molecular similarity dissolution mechanism, intermolecular hydrogen bonding, and solvation. Viscosity reducer molecules are dispersed and penetrated into the resin and asphaltene sheet-like molecules by means of hydrogen bonds, disassembling the aggregates formed by overlapping planes and forming a new poorly ordered and more dispersed structure, thus playing the role of viscosity reduction.^{16,17} Viscosity reducers have been widely used in reservoir exploitation and oil recovery improvement.^{18,19} Guo et al.²⁰ used the orthogonal method to synthesize an oil-soluble polybasic copolymer viscosity reducer for heavy oil. Two new monomers, acrylic acid phenethyl alcohol ester and benzyl acrylate, were synthesized by Zhu et al.,²¹ and six copolymers were synthesized by free radical copolymerization with styrene, octadecyl acrylate, and *N*-methoxyphenyl maleimide. Xu et al.²² synthesized magnetic graphene oxide (MgO) and assisted microwave to reduce the viscosity of heavy oil. Xiang et al.²³ analyzed the mechanism of oil-soluble viscosity reducers, investigated the viscosity reduction effect of monomers, and synthesized a variety of oil-soluble copolymers as viscosity reducers. Xu et al.²⁴ reviewed various methods to improve oil recovery, such as water flooding, gas flooding, chemical flooding, and emerging oil production technologies. The experimental results confirm that viscosity reducers have a great influence on the reduction of the viscosity of heavy oil. In order to study the feasibility of the synthesis of viscosity reducers and their effect on heavy oil on the molecular scale, molecular dynamics simulation was applied to the microscopic study of viscosity reducers. Cui et al.²⁵ used the Materials Studio simulation software to verify the molecular dynamics feasibility of the synthesis of viscosity reducers using styrene, octadecyl acrylate, and maleic anhydride as raw materials. Mao et al.²⁶ synthesized a series of oil-soluble quaternary polymers and established a heavy-component model and a copolymer model to simulate the interaction process. Sun²⁷ established molecular models of binary viscosity-reducing polymers and quaternary viscosity-reducing polymers and studied the effect of viscosity-reducing agents on heavy oil systems through molecular dynamics simulations.

Both ultrasound and viscosity reducers are effective methods for viscosity reduction. However, there are few studies on the combined effects of the two methods. In this study, molecular dynamics simulation was used to study the mechanism of the combined action of ultrasound and oil-soluble viscosity reducers on heavy oil. The influence of ultrasound and viscosity reducers on the hydrogen bond of heavy oil was studied by calculating the changes of hydrogen bonds with or without ultrasound and viscosity reducers, so as to explore the reasons why ultrasound and viscosity reducers

reduced the viscosity of heavy oil. By simulating the viscosity reduction of different kinds of viscosity reducers and ultrasound under different conditions, the interaction between ultrasound and viscosity reducers for heavy oil viscosity reduction was obtained.

2. MOLECULAR DYNAMICS SIMULATION

2.1. Molecular Models. Ren et al.²⁸ inferred the average molecular structure of heavy oil through experiments, which is composed of asphaltenes ($C_{61}H_{64}SO$), resins ($C_{72}H_{94}SO_2$), aromatic hydrocarbons ($C_{46}H_{64}S$), and saturated hydrocarbons ($C_{38}H_{72}$), as shown in Figure 1. The contents of its group components are asphaltene 20%, resin 30.3%, aromatic hydrocarbon 30.8%, and saturated hydrocarbon 18.8%.

The molecular model was established by the commercial molecular simulation software Materials Studio. Various component models were constructed under the 3D atomic document module. The molecular model was established by the Amorphous Cell Tools module. The force field was selected as Compass force field under Construction, and the boundary condition was set as Periodic Cell. After 10,000 steps of molecular energy minimization at 298 K, a $40 \text{ \AA} \times 40 \text{ \AA} \times 40 \text{ \AA}$ mixed system was established, as shown in Figure 2. The total number of atoms constituting the system was 3451, including 13 different atomic types of the four elements C, H, O and S, and the total number of 25 chemical bonds was 3610.

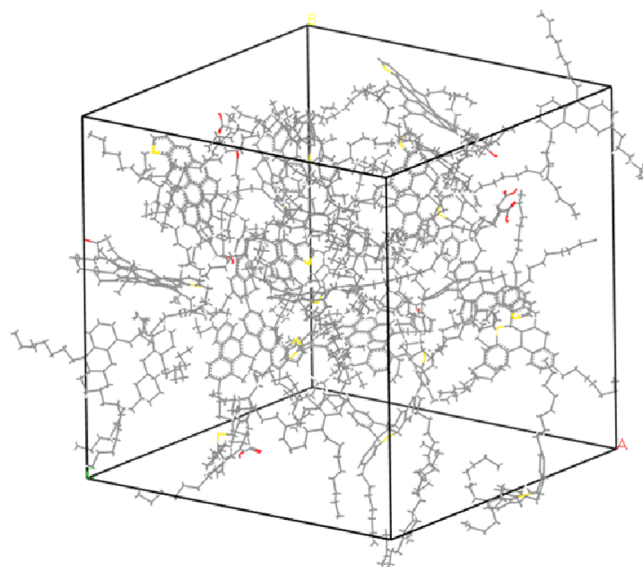


Figure 2. Molecular model of heavy oil.

Due to the different contents and spatial structures of asphaltenes and resins in different heavy oils, different viscosity reducer polymers are suitable for different heavy oils. In this study, five oil-soluble viscosity reducer polymers that are widely used at present were used. The amount ratio of reactive monomers is shown in Table 1. The mixed system of heavy oil molecules and viscosity reducer molecules is established as shown in Figure 3.

Table 1. Monomer Ratio of Viscosity Reducer Polymers

system name	viscosity reducer polymer monomers	ratio of monomers
R1	octadecyl acrylate:maleic acid	5:1
R2	octadecyl acrylate:styrene:maleic anhydride	5:1:1
R3	octadecyl acrylate:styrene:maleic anhydride:acrylamide	25:5:5:3
R4	octadecyl acrylate:styrene:acrylic acid	8:2:1
R5	octadecyl acrylate:styrene:vinyl acetate	5:1:3

2.2. Simulation Parameters. Molecular dynamics simulations were performed with the open-source software Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).²⁹ The parameters of molecular dynamics calculation were set as NPT ensemble, simulated temperature of 313 K, simulated pressure of 0.1 MPa, and cutoff distance 16 Å. The main simulated force field used was the CVFF force field. Periodic boundary conditions were used in X, Y, and Z directions, and the long-range coulombic interactions were calculated by the particle–particle particle-mesh (PPPM) method with an accuracy value of 10^{-6} . The energy of the system was minimized. The time step was 1 fs, the molecular dynamics calculation of 400 ps was performed, and the calculation results were output every 200 steps. The molecular configurations were visualized by Visual Molecular Dynamics (VMD).³⁰

When there was ultrasound in the system, the simulation process was divided into two stages. First, a relaxation of 200 ps was carried out to make the system tend to balance. Then, an ultrasonic vibration of 200 ps was applied to the system along the X direction. The loading speed and displacement are shown in eqs 1 and 2.

$$x = A \sin \frac{2\pi}{T} t \quad (1)$$

$$v = \frac{2\pi A}{T} \cos \frac{2\pi}{T} t \quad (2)$$

where x is the loading displacement, v is the loading speed, A is the applied ultrasonic amplitude, T is the applied ultrasonic vibration period, and t is the loading time.

3. RESULTS AND DISCUSSION

3.1. Effects of Ultrasound and Viscosity Reducers on Hydrogen Bond. Heavy oil macromolecules with branched planar fused rings and heteroatoms make it easy for molecules to produce strong non-covalent bonds and aggregate with each other. Among these non-covalent bonds, the hydrogen bond has the strongest binding ability. Heavy oil macromolecules increase the viscosity of heavy oil through the interaction of hydrogen bonds.³¹ Viscosity reducer molecules penetrate between asphaltene and resin flake molecules and combine with heavy oil macromolecules through strong electronegativity to form new hydrogen bonds, which prevent the aggregation of asphaltene, resin, and other macromolecules and make them disperse evenly and reduce the viscosity of the system. Element X has strong electronegativity, and the hydrogen atom connected to it will form a weak interaction with atom A in another molecule, and atom A also has strong electronegativity. This weak interaction is the hydrogen bond, which can be expressed as $X-H \cdots A$. X–H is the donor and A is the acceptor, as shown in Figure 4, where D is the hydrogen bond length and θ is the hydrogen bond angle.^{32,33}

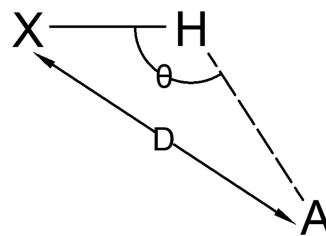


Figure 4. Schematic diagram of the hydrogen bond.

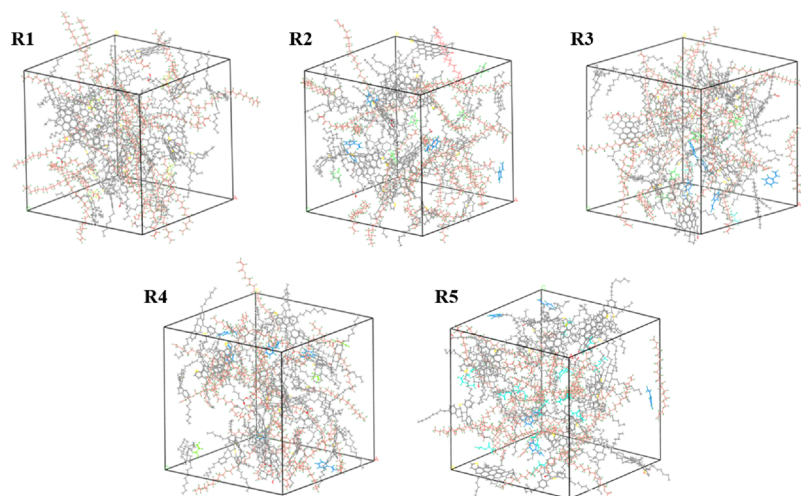


Figure 3. The mixed system of heavy oil molecules and viscosity reducer molecules.

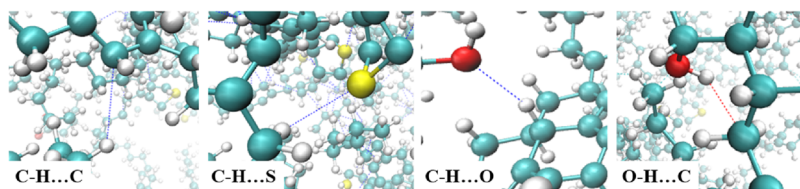


Figure 5. Hydrogen bond between heavy oil and viscosity reducer molecules.

When the viscosity reducer molecules are octadecyl acrylate and maleic acid, four kinds of hydrogen bonds, C–H...C, C–H...S, C–H...O, and O–H...C, can be observed between heavy oil molecules as well as between heavy oil molecules and viscosity reducer molecules in VMD, as shown in Figure 5.

In order to more obviously observe and analyze the specific changes of hydrogen bonds between viscosity reducers and heavy oil molecules at the moment of ultrasonic application, the time step and output time were reduced at the moment of ultrasonic application, and the frequency and amplitude of the ultrasound were increased. The variation of the number of hydrogen bonds with time, the total number of hydrogen bonds, and the occupancy of different types of hydrogen bonds with or without ultrasound and viscosity reducer were calculated, as shown in Figures 6–8. Since all four kinds of hydrogen bonds are weak hydrogen bonds, according to the classical hydrogen bond range,³⁴ the hydrogen bond cutoff length $X\cdots A$ is set between 3 and 4 Å and the cutoff angle is set between 110 and 180°.

When viscosity reducer molecules were added to the heavy oil system, the number of hydrogen bonds was more than that without the viscosity reducer, because hydrogen bonds would be formed between the viscosity reducer molecules and heavy oil macromolecules. In the presence of ultrasound, the number of hydrogen bonds changed in a sinusoidal pattern, as shown in Figure 6. The strength of the hydrogen bond is between the covalent bond and the van der Waals force, and the effect of ultrasound can break the hydrogen bond. However, the activation energy required for the formation and destruction of hydrogen bonds is small, and the spatial conditions for forming hydrogen bonds are relatively flexible. Hydrogen bonds are constantly broken and formed under the condition of intermolecular and intramolecular motion. Ultrasound can break heavy oil macromolecules into small molecules, and new hydrogen bonds will be formed between small molecules, and the number of newly formed hydrogen bonds is more than that destroyed by ultrasound. Therefore, the number of hydrogen bonds will be greatly increased with the effect of ultrasound.

With the increase in cutoff length, the effect of ultrasound on the number of hydrogen bonds increased. When the cutoff length was too large, there were more long hydrogen bonds. At this time, hydrogen bonds, especially those between viscosity reducer molecules and heavy oil molecules, were more likely to be broken by ultrasound. With the increase in the cutoff angle, the effect of ultrasound on the number of hydrogen bonds decreased. The number of hydrogen bonds with a large bond angle was less and increased less under the action of ultrasound.

When the cutoff length was small, the total number of hydrogen bonds was the highest under the combined action of ultrasound and viscosity reducer, followed by only the action of the viscosity reducer and only the action of ultrasound

(Figure 7a). With the increase in cutoff length, the total number of hydrogen bonds increased, and the number of longer hydrogen bonds increased. The longer the hydrogen bond, the weaker it was. With the increase in weak hydrogen bonds, the influence of ultrasound on hydrogen bonds gradually decreased, so the number of hydrogen bonds in the absence of ultrasound was gradually more than that in the presence of ultrasound. As the cutoff angle increased, the total number of hydrogen bonds decreased (Figure 7b). The total number of hydrogen bonds was the largest when ultrasound and viscosity reducer worked together, followed by when only the viscosity reducer worked and only ultrasound worked, and the number of hydrogen bonds was the least when there was no viscosity reducer and ultrasound.

The hydrogen bond lifetime is related to the occupancy of hydrogen bonds: the greater the occupancy of hydrogen bonds, the longer the lifetime of hydrogen bonds. At different cutoff lengths and cutoff angles, the trend of the total occupancy curve of hydrogen bonds (Figure 8a,b) was consistent with the change in the total number of hydrogen bonds (Figure 7). With the increase in cutoff length, the occupancy of hydrogen bonds increased, and the average life of hydrogen bonds increased. With the increase in the cutoff angle, the occupancy of hydrogen bonds decreased, and the average life of hydrogen bonds shortened.

When the cutoff length was small, C–H...S had the largest occupancy with the combined action of ultrasound and viscosity reducer. With the increase in the cut-off length, the occupancy of C–H...S without ultrasound was greater, but the difference was not significant with or without the viscosity reducer (Figure 8c). This showed that ultrasound was conducive to the formation of C–H...S with a short bond length between heavy oil molecules and viscosity reducer molecules and would break some C–H...S with a long bond length. When the cutoff angle was large, C–H...S had the largest occupancy with the combined action of ultrasound and viscosity reducer. With the decrease in cutoff length, the occupancy was the largest when there was no ultrasound and viscosity reducer, and the occupancy was the smallest when ultrasound and viscosity reducer worked together (Figure 8d). Ultrasound was conducive to the formation of C–H...S with a large bond angle between heavy oil molecules and viscosity reducer molecules, while C–H...S with a small bond angle mostly appeared between heavy oil macromolecules and was easy to be destroyed by ultrasound.

Under different cutoff lengths and angles, the occupancy of C–H...C was the largest when ultrasound and viscosity reducer worked together. In the absence of ultrasound and viscosity reducer, C–H...C had the smallest occupancy; that is, under the action of ultrasonic and viscosity reducer, various lengths and angles of C–H...C were easier to form (Figure 8e). When the cutoff length was small, the occupancy with only ultrasound was larger than that with only the viscosity reducer. Compared with the viscosity reducer, ultrasound had

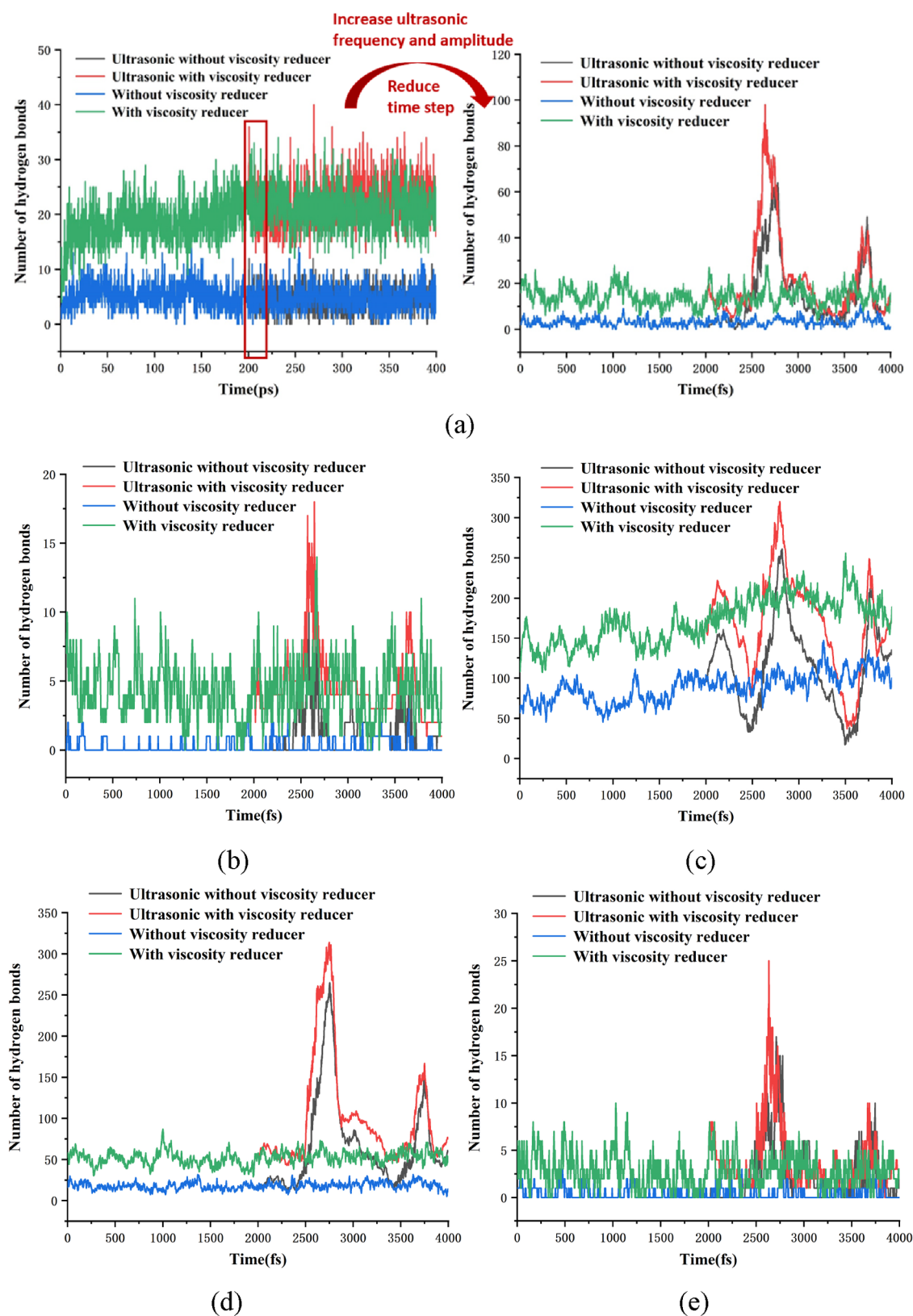


Figure 6. Variation of the number of hydrogen bonds with time at different cutoff lengths and angles ((a) cutoff length = 3.5, cutoff angle = 140° ; (b) cutoff length = 3, cutoff angle = 140° ; (c) cutoff length = 4, cutoff angle = 140° ; (d) cutoff length = 3.5, cutoff angle = 120° ; (e) cutoff length = 3.5, cutoff angle = 160°).

a greater impact on C–H...C with a small bond length. When the bond length was large, on the contrary, with the increase in the cutoff length, the occupancy increased gradually with

only the viscosity reducer. The viscosity reducer had a greater impact on C–H...C with a large bond length. For C–H...C

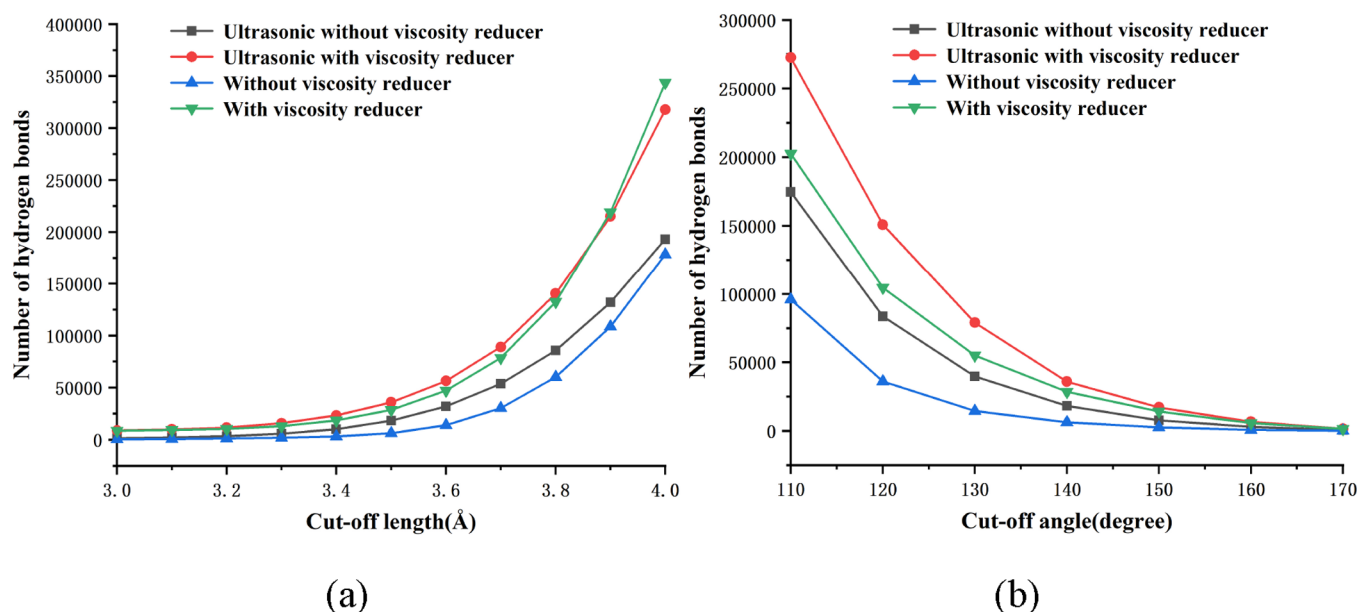


Figure 7. The total number of hydrogen bonds ((a) different cutoff lengths, (b) different cutoff angles).

with different bond angles, the effect of ultrasound was greater than that of the viscosity reducer (Figure 8f).

For C–H···O and O–H···C, the viscosity reducer was the main factor affecting their occupancy. C–H···O and O–H···C with different bond lengths and bond angles had the largest occupancy when only the viscosity reducer was used, followed by the combined effect of ultrasound and viscosity reducer, and the occupancy was very small without the effect of the viscosity reducer (Figure 8g,h). Ultrasound had little effect on the formation of C–H···O and O–H···C, while the addition of the viscosity reducer would form a large number of C–H···O and O–H···C between heavy oil molecules and viscosity reducer molecules.

3.2. Effects of Ultrasound and Viscosity Reducer on Viscosity. When adding octadecyl acrylate molecules and maleic acid molecules as a viscosity reducer to the heavy oil molecular system, the results of 400 ps were simulated by the molecular dynamics software LAMMPS. According to calculations, when ultrasound and viscosity reducer worked together, the viscosity was 0.084 mPa·s, and the viscosity reduction effect was the best; when only the viscosity reducer molecules acted, the viscosity was 0.125 mPa·s; when only ultrasound was applied, the viscosity was 0.146 mPa·s; and when there was no other action conditions, the viscosity was 0.908 mPa·s. In order to more obviously observe and analyze the specific changes of total energy and temperature at the moment of ultrasonic application, the time step and output time were reduced at the moment of ultrasonic application, and the frequency and amplitude of ultrasound were increased. The temperature, total energy, potential energy, pressure, total bond length, and total bond energy of the system are shown in Figure 9.

With the effect of ultrasound, the temperature, total energy, and potential energy of the system increased at the moment of applying ultrasound and then fluctuated in a sinusoidal-like trajectory. After adding the viscosity reducer, the growth range decreased (Figure 9a–c). It could be seen from Figure 6 that when ultrasound was acted, the molecular chain of heavy oil macromolecules was broken by ultrasound, and new hydrogen

bonds would be formed between the small molecules, and the number of hydrogen bonds would increase greatly. After adding the viscosity reducer, the viscosity reducer would break up the aggregated macromolecular groups and form hydrogen bonds with the small molecules interrupted by ultrasound, and the number of hydrogen bonds would be greater. At this time, a large number of hydrogen bonds made the movement between molecules less violent. Therefore, when ultrasound and viscosity reducer acted at the same time, the increase range of temperature and energy decreased, as shown in Figure 9.

The initial total bond length of heavy oil with the viscosity reducer was more than that without the viscosity reducer (Figure 9e); the total bond length in this work was the distance between atoms after bond breaking. Since the number of hydrogen bonds increased after adding the viscosity reducer, the movement between atoms was limited by hydrogen bonds, so the increase in total bond length was less than that without the viscosity reducer. The chemical bonds of heavy oil macromolecules were broken by ultrasound, the broken bond absorbed energy, and the bond energy of the system increased. However, in the presence of the viscosity reducer, more hydrogen bonds would be formed between the viscosity reducer and the small molecules formed under the action of ultrasound. The energy would be released during bonding, and the total bond energy was less than that under the action of ultrasound only (Figure 9f).

When there was no ultrasonic action, the temperature of heavy oil with the viscosity reducer would suddenly increase at a certain time and then recover rapidly (Figure 9(a)), and the trend of total energy change was to increase first and then decrease gradually. When there was no viscosity reducer, the total energy would gradually recover to basically the same as the initial energy after a period of time, while the viscosity reducer will cause a sudden increase in the process of total energy balance, and the total energy after balance was greater than the initial energy (Figure 9b). When there was no ultrasonic effect, the total bond length was almost unchanged,

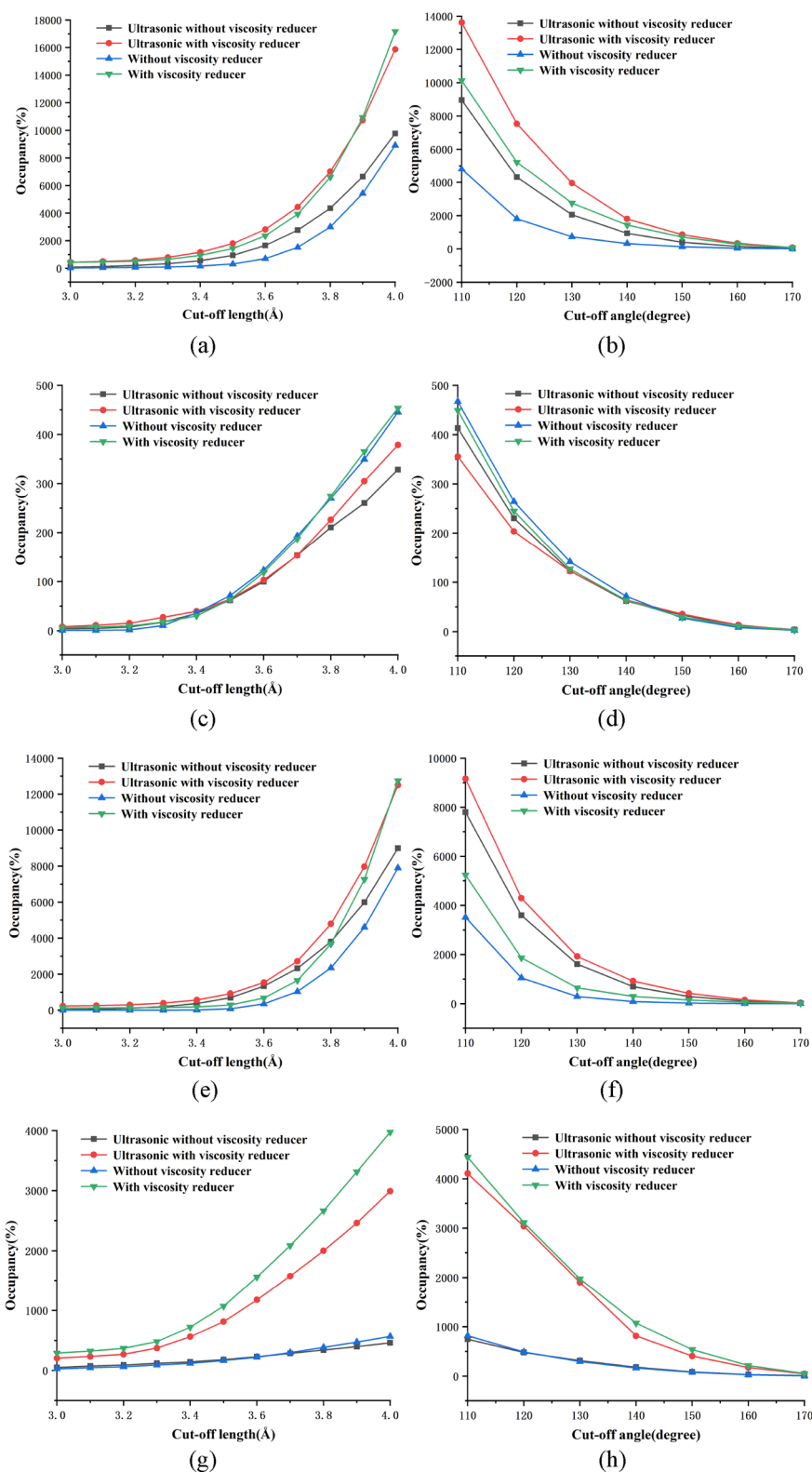


Figure 8. Occupancy of different types of hydrogen bonds ((a) total occupancy of different cutoff lengths, (b) total occupancy of different cutoff angles, (c) occupancy of different cutoff lengths of C–H...S, (d) occupancy of different cutoff angles of C–H...S, (e) occupancy of different cutoff lengths of C–H...C, (f) occupancy of different cutoff angles of C–H...C, (g) occupancy of different cutoff lengths of C–H...O and O–H...C, and (h) occupancy of different cutoff angles of C–H...O and O–H...C).

while the total bond energy had an upward trend (Figure 9e,f).

According to the calculation results in Figures 6–9, the more significant the viscosity reduction effect is, the higher the

total number of hydrogen bonds, the greater the occupancy of hydrogen bonds, and the longer the average lifetime. The total number of hydrogen bonds with the combined action of ultrasound and viscosity reducer was the highest, followed by

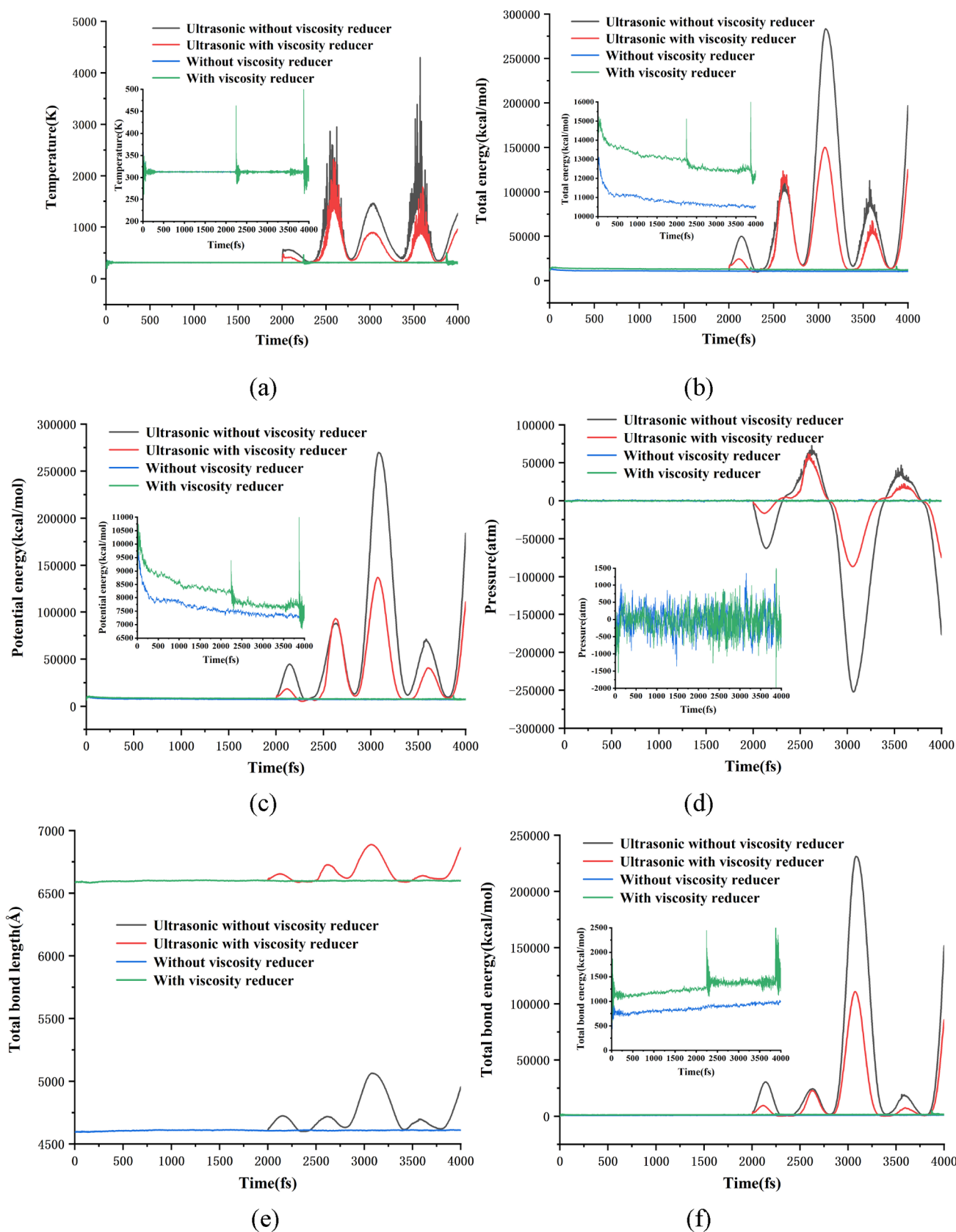


Figure 9. State change of the system with or without ultrasound and viscosity reducer ((a) temperature, (b) total energy, (c) potential energy, (d) pressure, (e) total bond length, and (f) total bond energy).

only the effect of the viscosity reducer, then only the effect of ultrasound, and finally for no other effect. Ultrasound broke

heavy oil macromolecules into small molecules, and the viscosity reducer penetrated between heavy oil molecules. A

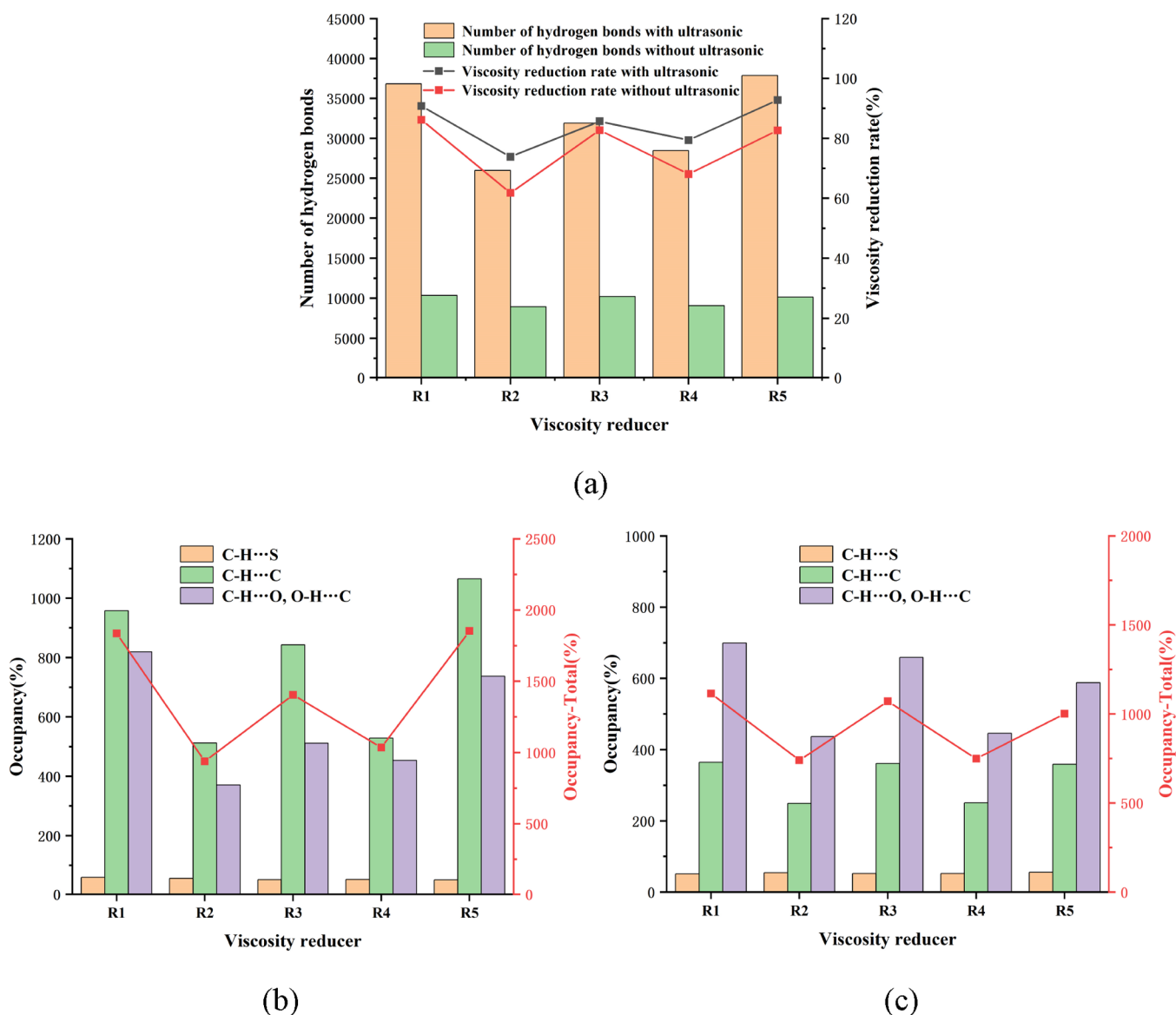


Figure 10. The number of hydrogen bonds and viscosity reduction rate (a), the occupancy of different types of hydrogen bonds of different types of viscosity reducers with ultrasound (b) or without ultrasound (c).

large number of hydrogen bonds would be formed between small molecules and viscosity reducer molecules. The heavy components in the system were transformed into light components under the action of ultrasound, and the aggregation was prevented by the viscosity reducer molecules, so the viscosity reduction effect was the most significant with the combined action of ultrasound and viscosity reducer.

3.3. Effects of Ultrasound and Viscosity Reducer on Each Other. Figure 10a shows the comparison of the number of hydrogen bonds and viscosity reduction rate with and without ultrasound when five kinds of viscosity reducers are added to heavy oil, respectively. The number of hydrogen bonds in the system was consistent with the viscosity reduction rate. The higher the number of hydrogen bonds, the more significant the viscosity reduction effect. Ultrasound has different effects on different viscosity reducers. When there was no ultrasonic effect, R1 had the best viscosity reduction effect and R2 had the worst viscosity reduction effect. When the ultrasound was present, R5 had the best viscosity reduction effect and R2 had the worst viscosity

reduction effect. Moreover, compared with the viscosity reduction rate with or without ultrasound, ultrasound had the least effect on R3 and had a greater effect on R2, R4, and R5.

For heavy oil added with five kinds of viscosity reducers, respectively, when there was no ultrasonic effect, C-H...O and O-H...C had the largest occupancy, among which the occupancy of R1 was the largest and R1 had the best viscosity reduction effect (Figure 10b). Therefore, C-H...O and O-H...C, which formed between heavy oil molecules and viscosity reducer molecules, were the main reasons affecting the viscosity reduction effect at this time. After applying ultrasound, the occupancy of C-H...C increased greatly and became the hydrogen bond with the largest occupancy (Figure 10c). For R5, C-H...C accounted for the largest occupancy, and the viscosity reduction effect was the best under ultrasound effect. At this time, C-H...C, C-H...O, and O-H...C were the reasons that jointly affect the viscosity reduction effect. The occupancy of C-H...S was relatively small, and there was little change with or without ultrasound.

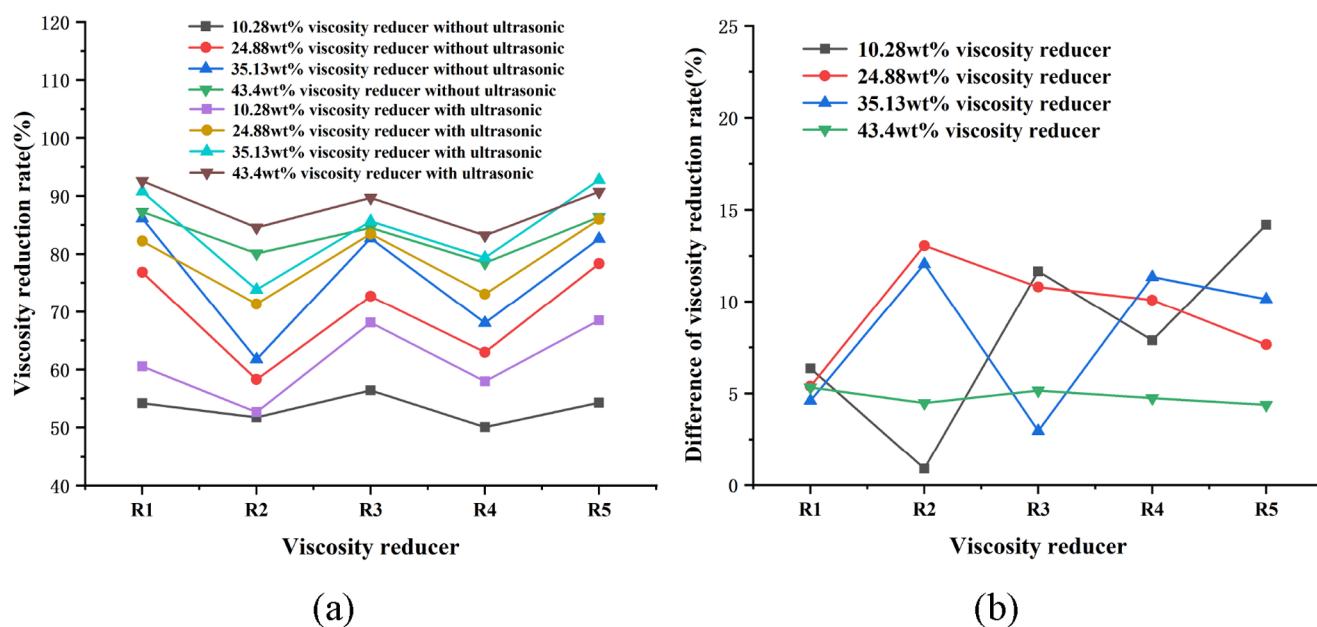


Figure 11. The viscosity reduction rate (a) and the difference in viscosity reduction rate (b) of different types and contents of viscosity reducers with or without ultrasound.

Different contents of the viscosity reducer have different effects on viscosity reduction (Figure 11a). Figure 11b shows the difference in viscosity reduction rates of five viscosity reducers added with or without ultrasound. Since the number of viscosity reducer molecules is small in the heavy oil, the contents of the five viscosity reducers are not exactly the same, and the average content is taken as shown in Table 2. Under

Table 2. Average Content of the Viscosity Reducer

name	10.28 wt %	24.88 wt %	35.13 wt %	43.4 wt %
R1	9.35	23.62	34.02	41.92
R2	9.76	24.51	35.11	43.1
R3	10.11	24.75	35.64	43.64
R4	11.67	25.44	33.85	43.16
R5	10.53	26.1	37.05	45.17

four different viscosity reducer contents in Figure 11b, the effect of ultrasound on R1 was the least. When the average content of the viscosity reducer was 10.28 wt %, ultrasound had the greatest effect on R5. When the average contents of the viscosity reducer were 24.88 and 35.13 wt %, ultrasound had the greatest effect on R2. When the average content of the viscosity reducer was 43.4 wt %, ultrasound had little effect on the five viscosity reducers.

When octadecyl acrylate molecules and maleic acid molecules are added to the heavy oil molecular system as a viscosity reducer, Figure 12 shows the comparison of the number of hydrogen bonds and viscosity reduction rate of ultrasound under different amplitudes, frequencies, and temperatures. As above, the higher the number of hydrogen bonds, the more significant the viscosity reduction effect. Since the square of ultrasonic amplitude is proportional to the sound intensity, the amplitude can be used to characterize the magnitude of the sound intensity. With or without the viscosity reducer, the viscosity reduction rate first increased and then decreased with the increase in amplitude. When the amplitude was 2 Å, the joint viscosity reduction effect of the

viscosity reducer and ultrasound was the best (Figure 12a). When the amplitude increased to a certain extent, the cavitation of ultrasound was suppressed by the sound intensity and tended to be saturated. At this time, with the further increase in sound intensity, the viscosity reduction effect became worse. When the viscosity reduction and ultrasound worked together, the viscosity reduction rate increased first and then decreased with the increase in frequency. When the frequency was 10^8 kHz, the viscosity reduction effect of the viscosity reducer and ultrasound was the best (Figure 12b). The increase in frequency would shorten the period, which was not conducive to the occurrence of ultrasonic cavitation and the viscosity reduction rate would be reduced. The relative viscosity reduction rate of the viscosity reducer and ultrasound increased first and then decreased with the increase in frequency. The viscosity reduction effect was the best at 313 K (Figure 12c). With the increase in temperature, the molecular motion intensified. At this time, ultrasound was not the main reason for the viscosity reduction of heavy oil, and the relative viscosity reduction rate decreased. The combined action of viscosity reducer and ultrasound had a better viscosity reduction effect at low temperature.

Under different ultrasonic amplitudes, frequencies, and temperatures, when there was no viscosity reducer, the occupancy of C–H...C was the largest, which was the main reason affecting the viscosity reduction effect (Figure 13). After adding the viscosity reducer, the occupancy of C–H...O and O–H...C increased greatly and the occupancy of C–H...C increased slightly, indicating that a large number of C–H...O and O–H...C were formed between viscosity reducer molecules and heavy oil molecules. At this time, C–H...C, C–H...O, and O–H...C were the reasons that jointly affect the viscosity reduction effect. The occupancy of C–H...S was relatively small, and there was little change with or without the viscosity reducer.

Through molecular dynamics simulation, the different effects of ultrasound and viscosity reducer on viscosity reduction rate, hydrogen bond number, hydrogen bond

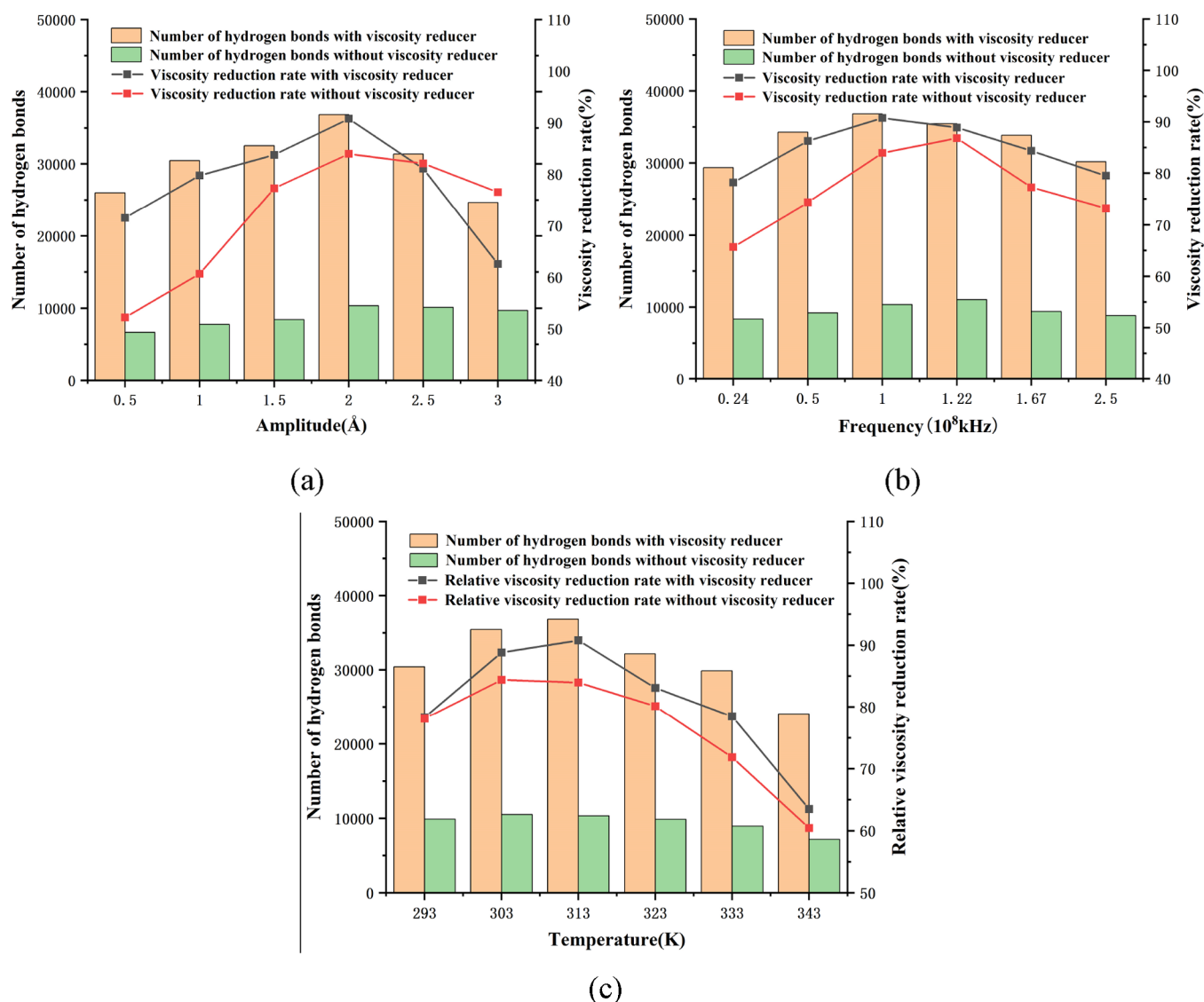


Figure 12. Comparison of the number of hydrogen bonds and viscosity reduction rate of ultrasound in different amplitudes (a), frequencies (b), and temperatures (c), with or without the viscosity reducer.

type, and occupation rate were obtained, and the viscosity reduction mechanism of ultrasound and viscosity reducer was analyzed. By calculating the viscosity reduction rate and the number of hydrogen bonds of five oil-soluble viscosity reducers with or without ultrasound, it was found that the types of hydrogen bonds affecting the viscosity reduction effect were different with or without ultrasound or viscosity reducer, and the type and content of the viscosity reducer would affect the effect of ultrasonic viscosity reduction. The amplitude, frequency, and temperature of ultrasound were also the factors affecting the effect of the viscosity reducer.

4. CONCLUSIONS

In this work, the molecular dynamics simulation method was used to study the mechanism of the combined action between ultrasound and viscosity reducer on heavy oil, focusing on the changes of hydrogen bonds under ultrasound. Based on the results of the study, the following conclusions can be drawn:

(1) Molecular dynamics simulation results showed that the number of hydrogen bonds increased greatly under the action of ultrasound. With the increase in cutoff length, the total

number of hydrogen bonds increased, and the effect of ultrasound on the number of hydrogen bonds increased. With the increase in cutoff angle, the total number of hydrogen bonds decreased and the effect of ultrasound on the number of hydrogen bonds decreased.

(2) When octadecyl acrylate and maleic acid were added into heavy oil as a viscosity reducer, the combined action of ultrasound and viscosity reducer had the greatest viscosity reduction rate, followed by only the effect of the viscosity reducer, then only the effect of ultrasound, and finally for no other effect. The better the viscosity reduction effect, the higher the total number of hydrogen bonds, the greater the occupancy of hydrogen bonds, and the longer the average lifetime.

(3) When five kinds of viscosity reducers were added to heavy oil, the number of hydrogen bonds was consistent with the viscosity reduction rate. The higher the number of hydrogen bonds, the more significant the viscosity reduction effect. The type and content of the viscosity reducer would affect the effect of ultrasonic viscosity reduction. The

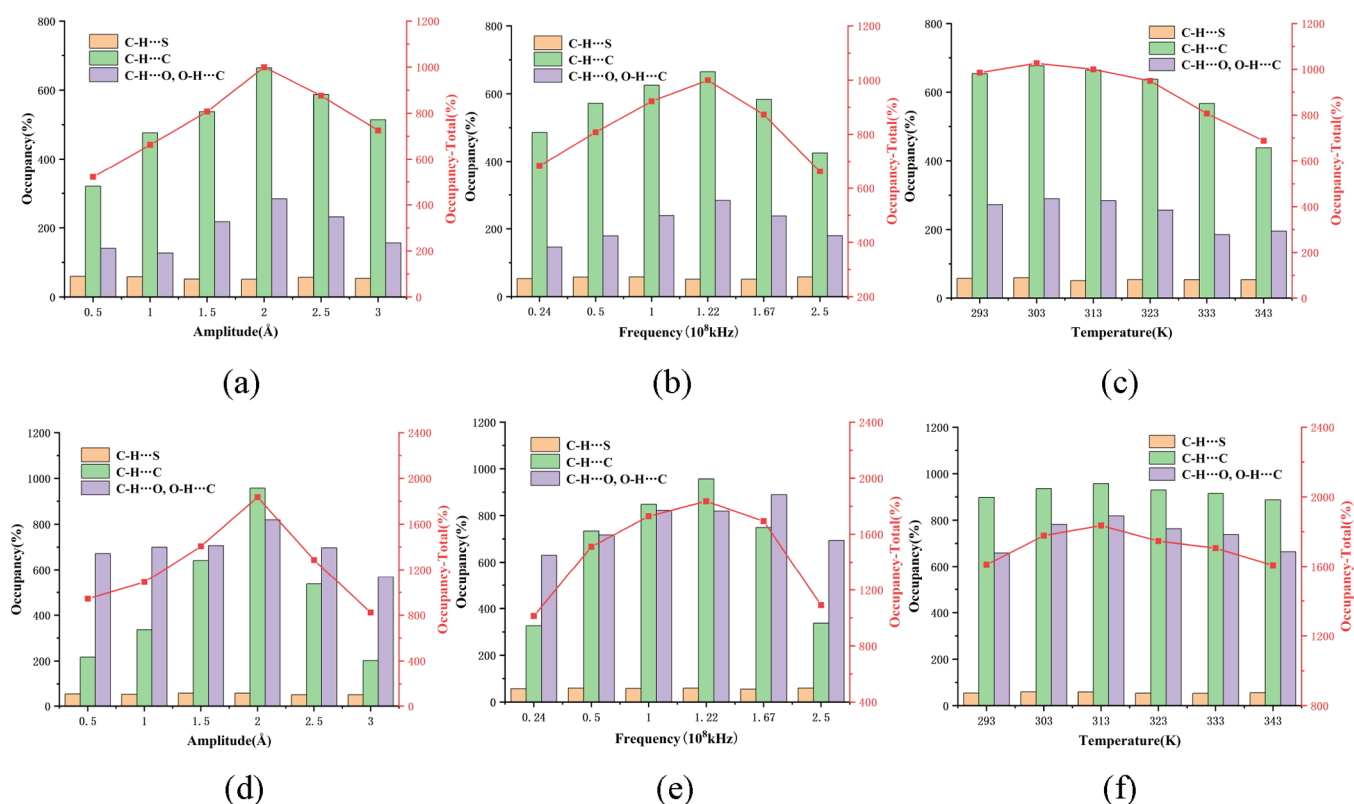


Figure 13. The occupancy of different types of hydrogen bonds of ultrasound in different amplitudes (a), frequencies (b), and temperatures (c) without the viscosity reducer and ultrasound in different amplitudes (d), frequencies (e), and temperatures (f) with the viscosity reducer.

ultrasonic amplitude, frequency, and temperature were the factors that affect the effect of the viscosity reducer.

The structure of heavy oil is complex and diverse. In the follow-up work, different types and configurations of molecules can be used to make the molecular model of heavy oil closer to the composition of actual heavy oil. At the same time, more types of viscosity reducers and composite viscosity-reducing methods can be further considered to better combine with engineering applications.

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Notes

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