The effects of temperature on surfactant solution: A molecules dynamics simulation

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Abstract—We use molecules dynamics simulation to investigate the effects of temperature on surfactant solution, both the microcosmic and macroscopic performance of the surfactant solution. Results show that the increase of temperature has bidirectional influence on the capability of the surfactant solution. From the microscopic point of view, the thermophoresis of the free water molecules has arisen in the forward of the temperature, which causes the hydrogen bonding between molecules fracture and reconnection. And the micelles keep close to and detached from each other for these. From a macro perspective, viscosity will decrease with temperature. But when the temperature is about 392.15K, the viscosity-temperature curve will have a peak value. Combining the micro results and macro results of the molecules dynamics simulation, we can clearly draw a conclusion that the effects of temperature on the surfactant solution never are monotonic.

1. Introduction
Since oilfield engineers of Mitchell Energy & Development Corporation first applied a polymer-free water-based fracturing fluid to the shale gas fracturing operation of Barnett and achieved good results in 1997 \(^{1-3}\), the viscoelastic surfactant based fracturing fluid (VES) has become one possible replacement of guar and polymer in the fracturing fluid systems for the advantages of gel to be broken easily, simple operation, no need for crosslinker and biocides \(^{4-9}\). The VES frequently consist of viscoelastic surfactants \(^{10-11}\). Therefore, the high temperature has a negative impact on the performance of the VES \(^{12}\), but the reservoirs are increasingly deep. Researchers have done much experimental work to synthetize various dilute cationic, cationic, zwitterionic, non-ionic and mixed surfactants or other auxiliary agents to improve the viscoelasticity of the solution at high temperature \(^{13-16}\), which shows us that the temperature surely play a great role in the measure of the performance of the surfactant solution. However, despite the large amount of experimental data on surfactant solution, the understanding of the link among forming microstructures, their macroscopic rheological properties and the external temperature is still lacking.

As the computers developing faster and faster, the molecules dynamics simulation has become an efficient tool for the investigation of the performance of surfactant solution \(^{17}\). As a mesoscale simulation algorithm, the dynamic mean field density functional method (MesoDyn) is proposed and has successfully been used to investigate the density distribution of various surfactant solutions \(^{18-22}\). MU et al. put this simulation method into studying the self-assembled morphologies of polyelectrolytes \(^{23}\). Elistratova et al. investigate the effect of the external temperature in aqueous solutions of the triblock copolymers \(^{24}\). However, they cannot link the self-assembled morphologies and the rheological properties of the surfactant solution to the external temperature. In this work, we apply the MesoDyn...
method to simulate the self-assembled morphologies of the surfactant solution in different external temperature, apply the shear flow method to simulate the rheological properties of the surfactant solution in different external temperature, and associate with each other.

In this paper, Section 2 describes two simulation methods, field density functional method and shear flow method, to simulate the self-assembled morphologies and calculate shear viscosity, respectively. The computational details of the simulation are given in Section 3. Section 4 first presents and discusses the results of the simulation, and then the performance of the surfactant solution can be achieved in different external temperature. In Section 5, we draw conclusions from this work.

2. Method

2.1. Theory

2.1.1. Theory in MesoDyn
The Mesodyn method is based on the dynamic mean field density functional method, which is a coarse-grained method for simulating the dynamics and equilibrium of complex fluids at long time and large space scales. And it is on account of the idea that the free energy $F$ of an inhomogeneous liquid is a function of the local density function $\rho$. From the free energy, all thermodynamic functions can be derived\[^{25-26}\].

The model used in the MesoDyn project consists of beads of various types D, O… with interactions described by harmonic oscillator potentials for the intramolecules interactions (Gaussian chain) and a mean field potential for all other interactions\[^{27}\]. Each bead is of a certain component type representing covalently bonded groups of atoms such as those given by one or a few structural units of a polymer chain. The dynamics of the system is described by a set of functional Langevin equations. They represent diffusion equations in the component densities, which take account of the noise in the system\[^{28}\].

2.1.2. Shear flow method
The shear flow methods are as similar as real experiments: the cause is an appropriate field or gradient, which is imposed on the system, then the ensemble average of the effect, the resulting flux, is measured and the ratio of flux and field gives the viscosity\[^{29}\]. In the shear flow simulations, we have to tackle two problems: for one thing, we must mechanically impose the temperature. To generate a fix shear flow, we have to use a moving periodic boundary condition, which is called Lees–Edwards boundary condition\[^{30}\]. For another, the temperature is enforced by constantly pumping energy into the system. Hence, we must get rid of the heat by applying an appropriate thermostat.

2.2. Module

2.2.1. MesoDyn module
In MesoDyn simulation, the surfactant molecules structures were simplified. A mass model was proposed for real-time elastic deformable modeling that each particle represented a particular group of molecules structure, and different particles were connected with each other. Considering the special molecules of the surfactants, five kinds of MesoDyn particles were defined. Groups of ‘$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$’, ‘$-\text{CH}_2\text{NHCO}-$’, ‘$-\text{CH}_2\text{CH}_2\text{NOH}-$’, ‘$-\text{CH}_2\text{OH}$’, and ‘$\text{H}_2\text{O}$’ were represented by letters D, S, O, T and W in sequence. These letters correspond to the colors deep blue, red, green, light blue, and purple, respectively. For example, simplified MesoDyn topology of the surfactant is D4S1O1T2 (see Fig.1).
2.2.2 Rheological properties simulation module
In molecules dynamics (MD) simulation, we put the surfactant and water molecules in a cube to simulate rheological properties of the surfactant solution. Fig 2 are the cubic structures of the surfactant in aqueous solution using molecule model. And we mark the distribution of surfactant molecules in the system by red symbols.

2.3 Simulation parameters

2.3.1 MesoDyn simulation parameters
In the simulation of the surfactant solution, interactions between the surfactant molecules and water were accurately determined by Flory–Huggins interaction parameters. Flory–Huggins interaction parameters coincide with the relationship as follows:

$$\chi_{ij} = \frac{V_{mol}(\delta_i - \delta_j)^2}{RT}$$  \hspace{1cm} (1)

where \(\chi_{ij}\) is Flory–Huggins parameter, \(\delta_i\) and \(\delta_j\) are solubility parameters, \(V_{mol}\) is the molar volume, \(R\) is the molar gas constant and \(T\) is the temperature. Repulsion parameters in the surfactant solution are listed in Table 1.

|     | D  | O  | S  | T  | W  |
|-----|----|----|----|----|----|
| D   | 0.0| 6.0| 3.5| 2.7| 18.8|
| O   | 7.8| 0.0| 0.5| 1.2| 2.2 |
| S   | 5.3| 0.1| 0.0| 0.1| 5.3 |
| T   | 2.2| 1.2| 0.5| 0.0| 7.8 |
| W   | 18.8| 2.7| 3.5| 6.0| 0.0 |

The dimensions of the simulation lattice are 32 × 32 × 32. The bond length is set to 1.1543 to ensure isotropy of all grid-restricted operators \([31]\), to ensure a stable numerical algorithm, as an approximation, all bead diffusion coefficients of types D, S, O, T and W were \(1.0 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1}\). The volumes of the beads were 0.05, 0.03, 0.03, 0.03 and 0.01 nm$^3$, respectively. The shear rate in simulation was 0.001
The simulation temperatures were from 262.15 K to 402.15K, and the time step was 50.0 ns. The noise-scaling parameter was 100, and the compressibility parameter was fixed at 10.0 \cite{32-33}.

### 2.3.2 Rheological properties simulation parameters

The dimensions of the simulation lattice are $67.92 \times 67.92 \times 67.92$. The forcefield is compass, to ensure a stable numerical algorithm for the fact that there are both molecules and ions. The simulation temperatures were from 262.15 K to 402.15K, and the time step was 50.0 ns. The noise-scaling parameter was 100, the pressure was 18MPa, the ensemble was NPT, and the Initial velocities were random.

### 3. Results and discussions

#### 3.1 The self-assembly of the surfactant in different temperature

We simulated the surfactant solution with 3% surfactant under different temperatures from 272.15K to 412.15K for 5,000 steps. The snapshots after 5,000 steps are given in Fig.3. We can observe that every surfactant molecule self-assembles into different micelles from 272.15K to 412.15K. These micelles are randomly distributed in the simulation box and entwined with each other, and they are worm-like, sphere-like and stick-like. When the temperatures are 272.15K and 282.15K, the outermost shell of the micelles are all O beads which are hydrophilic groups. However, the W beads occupy the outermost shell of the micelles after 292.15K (e.g. (c) (d) (e) (f) (g) (h) (i) (j) (k) (l) (m) (n) (o)). In addition, in Fig.3, there is an intriguing pattern that the beads are scattered as layers like the KFC chicken rolls or chocolate cream. Finally, it is obviously that the micelles have been changing from 272.15K to 412.15K.

![Fig.3 Snapshots of system with 3% surfactant fraction under temperature of 272.15K (a), 282.15K (b), 292.15K(c) and et al. after 5,000 simulation steps.](image)

#### 3.2 The models of the micelles

It is clearly that the beads distribute layer by layer like the coiling block in Fig.3, in a storyboard (see in Fig.4) for example. The W beads occupy the outermost shell of the micelles, near them are the hydrophilic groups, including O beads and T beads, and the intermediate group, S beads, link the hydrophilic groups and the hydrophobic groups, and the hydrophobic groups called D beads are enveloped in the innermost layer of the micelles.
Although the models of the micelles are shown as the coiling block like the KFC chicken rolls or chocolate cream because they consist of a great quantity of beads, they should be the layers like the cakes. We can see it in the Fig.5 that the upper and the lower layer should be the water molecules, and the interface layer should be the surfactant molecules.

And if we put the water and surfactant molecules into the system, we can observe the phenomenon shown in the Fig.6.

3.3. Thermophoresis of the free water molecules
Obviously, we can survey in Fig.3 that the ‘green robes’ of the micelles become the ‘purple robes’ suddenly when the temperature rise from 272.15K to 292.15K. But there is not the changing of the beads’ color, instead, it is the movement of the molecules (see in Fig.7), which is known as ‘Thermophoresis’.
Thermophoresis is the time-averaged movement caused by the Brownian motion of particles within a fluid subjected to a steady temperature gradient \cite{34}. The free water molecules impulses inside of the micelles, on the average, drive the free water particles toward the outside. Hence, the ‘green robe’ changes the ‘purple one’. In other words, the network structures of the micelles are destroyed in the process that the free water particles go toward the outside.

3.4. The hydrogen bonding between the surfactant and water

The aggregation of the surfactant molecules essentially dominated by the interactions between their polar groupheads in aqueous phase. The nitrogen-bearing and oxygen-bearing surfactant molecules may form Hydrogen bondings with water or theirselves. And HBs are one of the key mechanisms behind the formation of various supramolecular structures from small moieties \cite{35}. In this simulation, the HBs play a great role in the self-assembly of the micelles.

Firstly, at the low external temperature, the micelles are close together, which can be seen in the Fig.8. There is no doubt that the hydrogen bonding has played a great role in the process that a lot of molecules gather together, because the hydrogen bondings between the two surfactant molecules connect them together (see in Fig.9).

![Fig.8 the micelles at the low external temperature](image1)

![Fig.9 the hydrogen bonding between the two surfactant molecules](image2)

Secondly, resulting from the thermophoresis of the free water molecules, the hydrogen bonding between the two surfactant molecules has to break down, and the hydrogen bonding between the surfactant molecule and the water molecule (see in Fig.10) instead of it. Yet, the number of the water molecule is not larger. Thus, the hydrogen bonding between the two water molecules (see in Fig.11) cannot be built that there are coexistence of green and purple shell for micelles (see in Fig.12). All these clarify that the micelles give up entanglement for each other.

![Fig.10 the hydrogen bonding between the surfactant molecule and the water molecule](image3)

![Fig.11 the hydrogen bonding between the two water molecules](image4)
Thirdly, with an increasing number of free water molecules rushing out of network structure, the hydrogen bonding between the two water molecules gradually gets to be established. Even more, the hydrogen bonding links the surfactant molecules and the water molecules all together like the Fig.13. The distance between micelles is narrowed for it.

Finally, as the external temperature continues to rise, the structure of the micelles is going to suffer devastating damage, which is shown in Fig.14.

3.5. The rheological properties of the surfactant solution in different temperature
In order to acquire the rheological properties of the surfactant solution under macroscopic conditions, almost 10000 molecules and ions were aggregated to a box whose volume is $67.92 \times 67.92 \times 67.92 \text{ Å}^3$ (see in the Fig.15), which was used to calculate the rheological properties of the surfactant solution in different temperature. The shear viscosity of the system should be one of the foremost parameters to measure the rheological properties of the surfactant solution, which need to be attached great importance during the whole process of reservoir reconstruction.
Accordingly, we simulated and calculated the shear viscosities of the surfactant solution from 272.15K to 412.15K, and we recorded every 10K. Consequently, we got a set of data of the shear viscosities of the surfactant solution, and they will be shown in the Fig.16.

![Viscosity of systems as a function of temperature](image)

From the Fig.16, you can find that we divided the whole picture into three sections, called Section A, Section B and Section C. In Section A, the viscosities of the surfactant solution continue to reduce, but they increase abruptly in the Section B, and they go down too in Section C. Combining the phenomenon with the theory about the thermophoresis and hydrogen bonding in the previous article, it is not hard to find that the free water molecules get rid of the network structure of the surfactant molecules for the increasing temperature, which break off the hydrogen bonding between the surfactant molecules, and cut down the entanglement of micelles. So the viscosities in the Section A have been decreasing steadily.

In the Section B, the number of the free water molecules is larger and larger that the water molecules and the surfactant molecules would like to bond together to become the structure shown in Fig.13, which bringing about the micelles bound more tightly and the viscosities upper. However, the temperature continues to go up, which resulting to the structural collapse of all the molecules. Unfortunately, the viscosities must decline.

4. Conclusion
The effect of the temperature on the surfactant solution should be bidirectional in fact. In pace with increasing of the temperature from 272.15K to 412.15K in the simulation, the viscosities showed markedly changes. That is to say, the rheological properties of the surfactant solution ought not to be thought to change simply from wellhead to the target reservoir for the increasing of the formation temperature.

Thermophoresis of the free water molecules is the most directive expression of the rise in the temperature. The free water molecules extricate themselves from the network structure of the surfactant molecules, which destroys the structure between the surfactant molecules from different micelles, and isolates the micelles.

The changes of hydrogen bonding between different molecules are the most important reason that the shear viscosities go up and down. Hydrogen bonding plays an important role in drawing the micelles closer and far them away.

The micelles keep close and detach from each other is the simplest reason that the viscosities go up and down. When we improve micelles’ entanglement, it could increase the viscosity, vice versa.

With the exception of temperature, other factors such as the types and the values of sludge addition of counterion, molecule topological structure, the types and the value of sludge addition of surfactant, shear rate and so on also affect the rheology of surfactant solutions. We will put these influencing factors into our work for some time to come.
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