Molecular Simulation of Surfactants in Span Series at the Decane/water Interface

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This paper aims to determine the electric field intensity in the emulsion dehydration from the microscopic perspective. For this purpose, molecular dynamics (MD) simulation and density functional theory (DFT) were adopted to model the surface feature, hydrophilic groups, and hydrophobic groups of three types of Span surfactants, namely, Span 20, Span 60, and Span 80. Considering the stability of the microemulsion and application of electric fields, the structural changes and the nature of the surfactants were discussed in details under the external electric field. The results show that the simulated interfacial tension agrees well with the experimental data, an evidence to the rationality and reliability of the simulation system; the surfactant hydrophilic groups could form medium-strong hydrogen bonds with water; the deformation of surfactant space structure enhanced the role of hydrogen bonding under the electric field, thus reducing the emulsion stability. The research findings shed new light on the molecular simulation of Span surfactants.

1. Introduction

Microemulsion systems have attracted a growing interest in the years following the global oil crisis of the 1970s. These systems can greatly enhance the effect of tertiary oil recovery methods, thanks to their ability to dissolve oil and water simultaneously and attain very low interfacial tension. Many microemulsion systems are applied with Span surfactants, which often serve as emulsifiers, dispersants, rust inhibitors, additives and fracturing agents in the oil industry. The structure and properties of Span surfactants have been a research focus around the world (Sanatkaran et al., 2014; Santini et al., 2007).

Recently, computer simulations like molecular dynamics (MD) have been extensively employed to investigate the properties of microemulsion systems containing surfactants. For instance, Kunieda et al. (2010) reported that the self-accumulation of aromatics at the oil-water interface is driven by the low tension of aromatics-water interface compared to that of other combinations, and attributed the low tension to the weak hydrogen bonding between the aromatic rings and the water protons. Xu et al. (2013) demonstrated that the addition of oxygen, benzene ring and oxyethyl group can enhance the polarity of surfactant, which, in turn, enhances the interactions between the head groups of surfactants and water molecules. Yan Hong et al. (2010) performed an MD simulation on the structural and dynamic properties of anionic surfactant at the n-alkane (i.e. nonane, decane and undecane)-water interface, revealing the existence of a well-defined interface between the n-alkane and water phases in the equilibrated model systems.

Because of the complex geological conditions, the aqueous solution of surfactants is injected in large amount during oil extraction, leading to a high-water content in crude oil. The dehydration of crude oil has been a major bottleneck in oil production and processing. Jong Ha et al. (Ha J.W et al., 1999) examined the multiphase water droplets in the emulsion under inform electric field. Based on the results of deformation and fracture tests, Eow J.S et al., (2002), Eow J.S et al., (2003) studied the electric field intensity of water droplets, the effect of oil-water interface coalescence on water droplets under high field intensity. Chen Qingguo (Chen

et al., 2015; Chen et al., 2015; Chen et al., 2014;) tested crude oil emulsion under AC and DC electric field dehydrations, and established a dehydration theory model.

Through the above analysis, this paper aims to determine the electric field intensity in the emulsion dehydration from the microscopic perspective. To this end, MD simulation was adopted to model the surface feature, hydrophilic groups, and hydrophobic groups of three types of Span surfactants, namely, Span 20, Span 60, and Span 80. Considering the stability of the microemulsion and application of electric fields, the structural changes and the nature of the surfactants were discussed in details under the external electric field. The research findings shed new light on the molecular simulation of Span surfactants.

2. Computational Methods

2.1 Experiment

The surfactant span20, span60, span80 (AP grade, >98% purity) was purchased from Shanghai, China The interfacial tension was measured by a Texas-500A spinning-drop interfacial tensiometer (Taylor et al., 2011) (measuring range: $10^{-5} \sim 10^{2} mN \cdot m^{-1}$).

2.2 Quantum chemistry calculations

The geometric structure of the Span 80 surfactant was optimized at the B3LYP/6-311+G(d,p) (Dkhissi A et al., 2000; Bailin Zhang et al., 2002)level using the Gaussian 09 package(Frisch et al., 2009). The optimized structure is illustrated in Figure 1. The molecular structure and water system were analysed frequency on the same level. The results show no negative vibration frequency, i.e. the optimized structure is stable with no imaginary frequency.
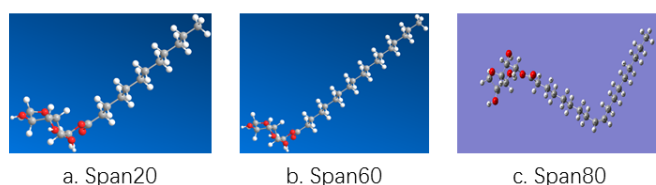

a. Span20   b. Span60   c. Span80

Figure 1: Chemical structure of the span series surfactants

2.3 Molecular dynamics simulation

The previous studies on MD simulation were all performed on Groningen Machine for Chemical Simulations (GROMACS) (Hess et al., 2008). For example, Reference (Berendsen et al., 1981) simulates water molecules with single-point charge model, and Reference (Oostenbrink et al., 2004) models Span 80 and decane by GROMACS 96 force field. Most of the existing modelling force fields for molecular system can be interpreted as a simple four-component image of intra- and inter-molecular forces within the system. The changes in specific internal coordinates can be described by various terms, including bond lengths, angles, bond rotation or atom movement.

For the surfactant monolayers at water-decane interfaces, the molecular simulation software Packmol (Martínez et al., 2003) was adopted to build a system with surfactants and 2,100 water molecules. The surfactants were distributed at both sides of the equilibrated water cell with their head groups near the water layer. After the equilibrium was established within 2ns, the ensemble was filled with 230 decane molecules at each side of the surface, forming the water-surfactant-decane model system. To simulate the properties of surfactant at water-decane interface, the steepest descent (200 steps) was performed for energy minimization, followed by data collection via 1,000ps isothermal–isobaric (NPT) ensemble position-restrained MD and 1,000ps canonical ensemble (NVT). In all cases, the time step for simulation was 0.002ps, and the trajectory data were collected every 20ps for structure and dynamics analysis.

3. Results and discussion

3.1 Interface morphology and behavior

Three substances (Span 20, Span 60 and Span 80) were selected in this study, each of which was simulated at eight different concentrations. Through the simulation, the morphology of each substance was

characterized at the oil-water interface. For convenience, Span 80 was taken as an example for analysis and contrasted with similar substances.

As shown in Figure 2, a stable interfacial film was formed through simulation, consisting of the water phase, oil phase (decane) and surfactant. The ternary system exhibited a good interfacial morphology. Owing to the amphiphilic properties of the surfactant, the hydrophilic groups extended into the water phase and hydrophobic groups extended into the oil phase. A limited number of surfactant molecules were distributed at the interface when surfactant molecules were few and sparse. With the increase in surfactant concentration and number, the surfactant molecules became increasingly aligned in the shape of a tadpole perpendicular to the interface. In this case, each molecule occupied a smaller area than before.
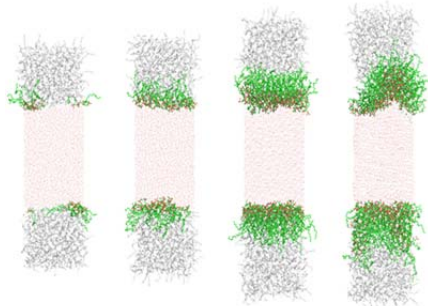

Figure 2: Sample snapshots with different numbers of surfactants

The interfacial tension refers to the difference between the vertical and the tangential liquid surface pressures (Nijmeijer et al., 1988)in the MD simulation:

$$\gamma(t) = \frac{1}{2}\int_0^{L_z}\left\{p_{zz}(z,t) - \frac{p_{xx}(z,t) + p_{yy}(z,t)}{2}\right\}dz$$
$$= \frac{L_z}{2}\left\{p_{zz}(t) - \frac{p_{xx}(t) + p_{yy}(t)}{2}\right\}$$

The minimum interfacial tensions of Span 20, Span 60 and Span 80 were measured as 42.67, 34.23, and 30.78 mN·m^{-1}, respectively. The interfacial tension gradually declined with the increase in the hydrophobic alkyl groups in the side chain of the surfactant.

Then, Span 60 and Span 80 were compared with the same number of carbon atoms in their hydrophobic chains. The comparison reveals that the emulsion is prone to bending deformation of oil-water interface in Span 80, due to the presence of double bond in the side chain. Therefore, the increase in branching widened the surface coverage by the molecules, causing further decrease in interfacial tension.
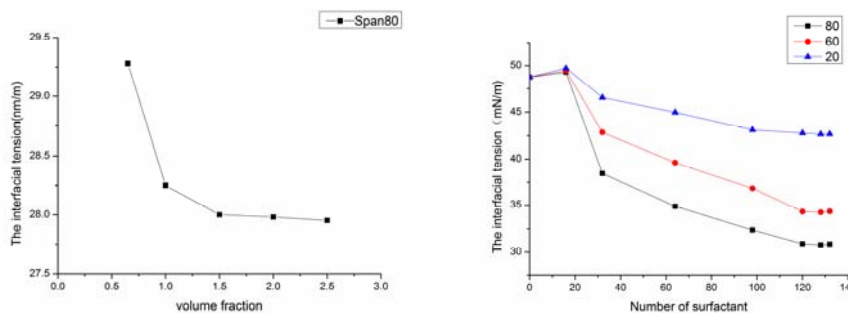

Figure 3: The experiment and the simulation of interfacial tension

In the process of obtaining the minimum interfacial tension, it is observed that the interfacial tension was not always negatively correlated with surfactant concentration. Figure 3 shows the variation in interfacial tension with the increase in Span 80 concentration. It can be seen that, as the surfactant became increasingly dense, the interfacial tension firstly increased, then decreased and finally stabilized. This is because the surfactant has a certain active concentration range: the interfacial tension will not be reduced obviously at a low surfactant concentration, and pronounced decline can only be witnessed in a certain range of concentration. When there were 122 surfactant molecules, the minimum interfacial tension acquired by the system was 30.78 mN·m^{-1}, while the measured value was 27.95 mN·m^{-1}.

3.2 Hydrophilic group

In the Span surfactants of this research, there are six hydrophilic groups containing polyols of the same structure. This subsection mainly discusses the structure of Span 80. The hydrophilic groups can interact with water and form hydrogen bonds. These bonds directly bear on the structure of surfactant. Currently, the density functional theory (DFT) and MD simulation are two widely accepted research methods for hydrogen bonding system. Here, the formation of hydrogen bonds by the hydrophilic groups of surfactants were investigated from two aspects. The surfactant was optimized by B3LYP/6-311+G(d,p) method in the DFT, while the water molecules were placed at six positions. In this way, the surfactants and water molecules constituted a stable structure. Then, zero correction was performed on the difference between the total energy and the energy of a single molecule.

The calculation results demonstrate that the polar head of surfactant and the water molecules could form medium-strong hydrogen bonds (length: 1.8~1.9Å; angle: 146~147°). When each position had a water molecule, i.e. a surfactant molecule was surrounded by six water molecules, the water molecules became interconnected, leading to formation of new hydrogen bonds at the polar head of surfactants. These hydrogen bonds are longer than those produced by the other method below. Moreover, the water molecules could also form hydrogen bonds if they were dense enough. The mean bond length was 2.89Å. Hence, the hydrogen bonds formed between polar head and water molecule were longer than the those formed between water molecules. In other words, the hydrogen bonds formed between water molecules were relatively weak.

The energy D is the sum of the total energy of hydrate and the total energy of the molecule. The calculated results on D indicate that hydrogen bonds could be formed in contact with water at different positions. When placed on the 2nd, 8th, and 30th positions to form a stable system, the water molecules had little positive impact on the formation of hydrogen bonds. When placed on the 29th, 42nd, and 43rd positions, the water molecules greatly boosted the formation of hydrogen bonds, because the surfactant head combined effectively with the hydroxyl groups. Relevant theoretical studies were conducted in the MD simulation to validate these observations.

Table 1: The energy of D calculation results

point	E	$\triangle E$
Span80	-1392.7971	0
2nd	-1469.2703	-26.3311
8th	-1469.2708	-26.3316
29th	-1470.2736	-27.3344
30th	-1469.2648	-27.3256
42nd	-1470.2667	-26.3275
43rd	-1470.2678	-27.3286
6 water molecules	-1851.6471	-157.998

Next, the radial distribution function was introduced to this research. This function can provide information about the groups in the molecular structure at the molecular level, and measure the probability of appearance of another particle or group within the specified radius. Focusing on hydrogen or oxygen from different groups in water, the interactions between hydrogen bond and hydrophilic group could be obtained for comprehensive analysis.

Therefore, the author extracted a set of radial distribution functions at different positions for water oxygen. The functions show no obvious wave peak at 2nd, 8th or 30th positions, indicating that the interactions between these groups and water were insignificant. However, the peaks of 0.27, 0.27 and 0.24 appeared respectively at the 29th, 42nd and 43rd positions, a signal of the hydrogen bonding between these groups and water.

To verify our conclusion, the number of hydrogen bonds in the GROMACS was extracted from the group. Then, the presence of hydrogen bonds between the surfactant and water molecules was evaluated in the GROMACS using the default cutoff radius of 0.35nm and the default cutoff angle of 30° between the acceptor-donor hydrogen atoms. The results show that the number of hydrogen bonds was 4, 3, 76, 3, 35 and 36 at the 2nd, 8th, 29th, 30th, 42nd and 43rd positions. Obviously, there were fewer hydrogen bonds at the 2nd, 8th and 30th positions, and more at 29th, 42nd and 43rd positions. The surfactant head groups were composed of the hydrogen bonds formed between the hydroxyl groups and water. Thus, the head base extended into the water phase, and tail chains into the oil phase. As a result, the surfactant was located between the oil-water interface.

3.3 Electric fields

Despite its wide application in demulsification, the electric field can boost the coalescence of emulsion beads and destroy the stable structure of emulsifier. Here, stable Span 80 microemulsion was formed under a uniform electric field. However, the surfactant structure could change with the addition of an electric field. It is the migration of water molecules that ensures the stabilization of the structure. The GROMACS uniform electric field was applied with a modified .mdp file: a sine wave was added along the Z-axis direction to the uniform electric field. Five cases were simulated with the electric field intensity of 0, 5, 10, 15, and 20V·nm-1, respectively

According to the simulated image, the structure of surfactant molecules was stretched under the external electric field, the degree of bending was reduced, the emulsion was kept stable by the electrical stability of the surfactant and the non-ionic surfactant remained stable in the space. Therefore, the surfactant became less stable under the external electric field. Nonetheless, Span 80 exhibited low structural variation under the electric field. A possible reason lies in its non-ionic feature due to the influence of electric field on the water.

Figure 4 shows the results of radial distribution functions on water hydrogen and oxygen. It can be seen that, with the growth in electric field intensity, the peak first increased and then declined and the valley continued to decrease, indicating that the electric field improves the degree of order of water molecules and enhances the hydrogen bonding effect.

Note that the results of radial distribution function fluctuated in the small peak between 0.3 and 0.6nm with the increase in electric field intensity. This could be attributed to the changing orientation of the molecules under the electric field. Specifically, the electric field induces the rotation of the water molecules, such that these molecules move away from the original positions to the small peak of the radial distribution function.

According to the results of radial distribution function, the external electric field intensified the movement of single water molecule and enhanced its role of hydrogen bonding. Hydrogen bonding interactions between the surfactant head groups and water molecules were weakened, resulting in a poorer stability. When the electric field intensity reached a certain degree, lots of water molecules were rearranged under the external electric field. The resulting change of the orientation of water molecules destroyed the balance between surfactant and water molecules. On the macroscale, these trends were displayed as demulsification.
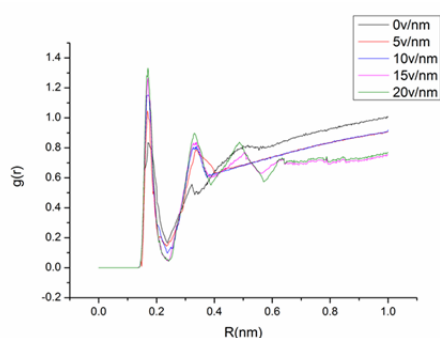

Figure 4: The radial distribution function in external electric field

4. Conclusions

This paper simulates Span surfactants by quantum chemistry and molecular dynamics, and compares the simulated results with experimental data. The main conclusions are as follows:

First, the simulated interfacial tension agrees well with the experimental data, an evidence to the rationality and reliability of the simulation system. The interfacial tension values of Span 20, Span 60 and Span 80 decreased with the increase in the carbon number of long alkyl chains. However, with the increase in the surfactant concentration, the interfacial tension firstly increased, then decreased, and finally stabilized.

Second, the surfactant hydrophilic groups could form medium-strong hydrogen bonds with water. In particular, the hydrophilic groups at the 29th, 42nd and 43rd could form lots of hydrogen bonds, which is the key factor of polar head effect.

Third, the deformation of surfactant space structure enhanced the role of hydrogen bonding under the electric field, thus reducing the emulsion stability. With the increase in electric field intensity, the spatial orientation of water molecules was changed, and a large number of water molecules was rearranged, leading to a demulsification effect.

Acknowledgments

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