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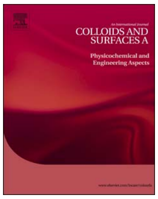

Investigation of oil-in-water emulsion stability with relevant interfacial characteristics simulated by dissipative particle dynamics

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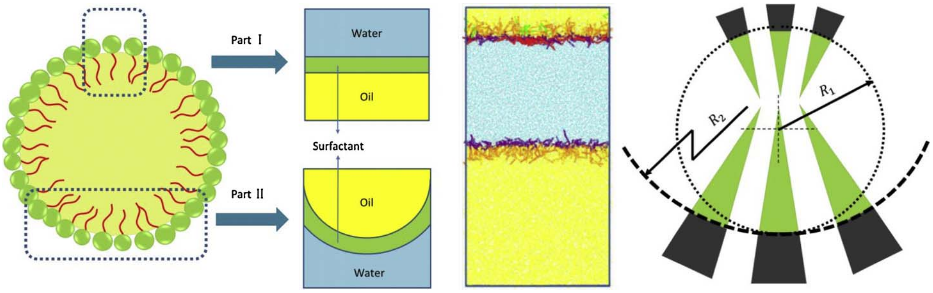
GRAPHICAL ABSTRACT



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ABSTRACT

Oil-in-water (O/W) emulsions were prepared by using non-ionic surfactants, Tween 80 and Span 20, and the stability of the emulsions was investigated under conditions of varied HLB, emulsifier concentration, stirring time and stirring intensity. It was found that the HLB of emulsifier has a significant effect on the emulsion stability. Moreover, the structures and properties of the interfacial film formed by emulsifier molecules with different HLB were characterized by dissipative particle dynamics (DPD) simulations. The results show that the interfacial film thickness increases with the HLB values changing from 9 to 15, while the most stable emulsion appears when HLB is 13 with the minimum interfacial tension. Neither too small nor too large oil droplet size, determined by molecular volume of emulsifier as well as the volume ratio of hydrophilic head and hydrophobic tail, could improve the emulsion stability when the preparation technology is the same. Therefore, the influence of HLB on the emulsion stability is essentially affected by the comprehensive result of interfacial film thickness, interfacial tension and molecular structure of emulsifier. This study could contribute to the development of controlling and preparation of emulsions with suitable stability from the point of view of emulsifier.

1. Introduction

Emulsions have found numerous applications in energy source, foods, metal processing, cosmetics, etc. The stability that is closely related to the performance and working life of the emulsion has been studied as an important topic in previous researches [1–4]. In summary, the factors that affect the emulsion stability can be divided into two aspects: emulsion components and preparation technology. Experiment has been the main method to investigate the emulsion stability to obtain the optimum formula and process conditions, but it takes plenty of time to search for the optimal decision because of the widely differences of chemical components and technological parameters. Therefore, it is necessary to take a deep insight into the mechanism of action of these factors, in order to efficiently prepare emulsion with suitable stability.

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For the oil-in-water (O/W) emulsion, its instability is a result of flocculation and/or coalescence of the oil droplets dispersed in water, leading to the creaming phenomena. In this regard, the interfacial film surrounded on the oil droplet can be considered as a cutting-in point that affects the emulsion stability. Opawale et al. [5]. found that the interfacial film strength and the emulsion stability followed the same trends. Huang et al. [6]. investigated the emulsification properties of fourteen hydrocolloid gums and produced the most stable emulsion. Al-Sabagh [7]. studied the relevance between hydrophile-lipophile balance (HLB) of surfactant and emulsion stability, and obtained the suitable range of HLB for different emulsions.

From the above, the interfacial film formed by surfactant molecules is of great importance in controlling the emulsion stability, and the information of the interfacial properties can be interpreted by viscosity, elasticity and density distribution of the interfacial film [8–10]. At this point, molecular dynamics (MD) simulation has been a widely used method to investigate the interfacial behaviours at microscopic molecular level with the development of computer technology [11–22]. However, it shows laborious and needs much computing resource especially for the simulation with macromolecular surfactant and/or large scale. To make up the deficiency, mesoscopic simulation could be developed in the studies of interfacial properties by using a more efficient computing method [23–25], and it demonstrates vast potential for future development. At this point, the mesoscale simulation would be an effective and convenient method to take a deep research into the microstructure and relevant properties of the interfacial film of emulsion system.

In this paper, the effects of process variables on emulsion stability were investigated experimentally. Based on the experimental result, the structures and properties of the interfacial film at the oil-surfactant-water interface were analysed using dissipative particle dynamics (DPD) simulations. Moreover, the relationship among the molecular structure of emulsifier, the droplet size and the emulsion stability was discussed. The research purpose of this work is to investigate the mechanism of emulsion stability, and lay the foundation for preparing emulsions with suitable stability efficiently.

2. Experimental

2.1. Materials and methods

Commercial non-ionic surfactants Tween 80 and Span 20 were selected as the emulsifiers, and the HLB values can be controlled by using mixtures of the two surfactants as follows:

$$\mathrm{HLB} = \frac{\mathrm{HLB_T} \times w_T + \mathrm{HLB_S} \times w_S}{w_T + w_S} \tag{1}$$

where w_T and w_S are the mass fractions of Tween 80 and Span 20 respectively, and $\mathrm{HLB_T}$, $\mathrm{HLB_S}$ are the values of HLB for them. Here, $\mathrm{HLB_T}$ is 15 and $\mathrm{HLB_S}$ is 8.6 [26–27].

The O/W emulsions were prepared by adding the mineral oil containing the surfactants blended at 70 °C to the deionized water with magnetic stirring. The emulsifier concentration was controlled well above the critical micellar concentration (CMC), and the mass ratio for oil and water was kept to 1:9. The stability of emulsion can be characterized by the creaming index (CI) which is changing with time:

$$\mathrm{CI} = \frac{h_s}{h_e} \times 100\% \tag{2}$$

where h_s is the height of the serum layer and h_e is the total height of the emulsion. Emulsions were observed for creaming at 10-min intervals during the first two hours and at 6-h intervals for the following five days.

The droplet size distribution was measured by dynamic light scattering technique using Mastersizer 2000, immediately after the preparation of emulsions. Note that the ultrasonic emulsification should be avoided in the process of measurement, in order to obtain the real particle size resulting from mechanical rabbling.

2.2. Computational methods

Dissipative particle dynamics is a simulation method to study the hydrodynamics behaviour of complex fluids over long length and time scales [28–30]. This method is based on molecular dynamics of a set of soft beads, which interact with other beads via soft potentials. The total force F_i on a single bead i is made up of a conservative term F_{ij}^C, a dissipative term F_{ij}^D and a random term F_{ij}^R.

$$F_i = \sum_{i \neq j} F_{ij}^C + \sum_{i \neq j} F_{ij}^D + \sum_{i \neq j} F_{ij}^R \tag{3}$$

The conservative force F_{ij}^C is a soft-repulsive interaction, which reflects the pair potential of two beads acting along the line of their centers.

$$F_{ij}^C = \begin{cases} a_{ij}(1-r_{ij}/r_c)\hat{r}_{ij}\ (r_{ij} < r_c) \\ 0\ (r_{ij} \gg r_c) \end{cases} \tag{4}$$

where a_{ij} is the repulsion parameter between beads i and j, and $\vec{r_{ij}} = \vec{r_i} - \vec{r_j}$, $r_{ij} = |\vec{r_{ij}}|$, $\hat{r}_{ij} = \vec{r_{ij}}/r_{ij}$. r_c is the cut-off radius.

The dissipative force F_{ij}^D and random force F_{ij}^R can be determined by the following equations:

$$F_{ij}^D = -\gamma w^D(r_{ij})(\hat{r}_{ij} \bullet \vec{v_{ij}})\hat{r}_{ij} \tag{5}$$

$$F_{ij}^R = \sigma w^R(r_{ij})\theta_{ij}\Delta t^{-1/2}\hat{r} \tag{6}$$

here γ is the dissipative parameter, σ is the noise amplitude, θ_{ij} is a random number between 0 and 1, and $w^D(r_{ij})$ and $w^R(r_{ij})$ are the weighting functions which become zero when $r \geq r_c$.

In this work, we assumed the representative structure for Tween 80 with the numbers of ethoxylate units, x, y, z and w in each of the four head groups equal to 5 based on the experimental evidence [31] and dodecane was considered as the oil phase component. The detailed mesoscopic models in the simulation system have been illustrated in Fig. 1.

As for the coefficient a_{ij}, there are several methods to evaluate the values, as mentioned in Ref. [23]. Based on the relationship between a_{ij} and Flory-Huggins interactions parameter χ [28] the interaction parameter can be calculated by using $a_{ij} = a_{ii} + 3.497\chi_{ij}$ or $a_{ij} = a_{ii} + 1.451\chi_{ij}$ for $\rho = 3$ or $\rho = 5$ respectively. And the χ_{ij} can be obtained by $\chi_{ij} = E_{ij}^{mix}/RT$, where E_{ij}^{mix} is the mean pair interaction energy which can be estimated by Monte Carlo method. If the heat of mixing obeys the Hildebrand-Scatchard regular solution theory, the χ_{ij} can also been determined from the Hildebrand solubility parameters by $\chi_{ij} = V_{ij}(\delta_i(T) - \delta_j(T))^2/RT$. Here V_{ij} is the partial molar volume which can be replaced by the average molar volume of the two involved beads, and $\delta_i(T)$ and $\delta_j(T)$ are the solubility parameters of components i and j respectively. But the solubility should be changed when this calculation method is applied to polar systems according to the Hansen solubility parameter theory [32]. In this case, Lindvig et al. [33]. have established relevant model to estimate the Flory-Huggins parameter χ_{ij} by using solubility parameter.

The self-repulsive interaction parameters a_{ii} and a_{jj} can be determined based on the isothermal compressibility, and $a_{ii} = 25$ is obtained for water. A basic assumption that i–i molecules have the same value of interaction parameter with j–j molecules has been made for binary mixture in most researches. However, it is not safe to make the assumption that $a_{ii} = a_{jj} = 25$, owing to the differences of mesoscopic scale of different component beads [34]. Therefore, the isothermal compressibility should be applied to calculate the self-repulsive interaction parameters of individual pure components. And then, the interaction parameters between different beads (a_{ij}) can be derived based on the energy values calculated by the atomistic molecular dynamics

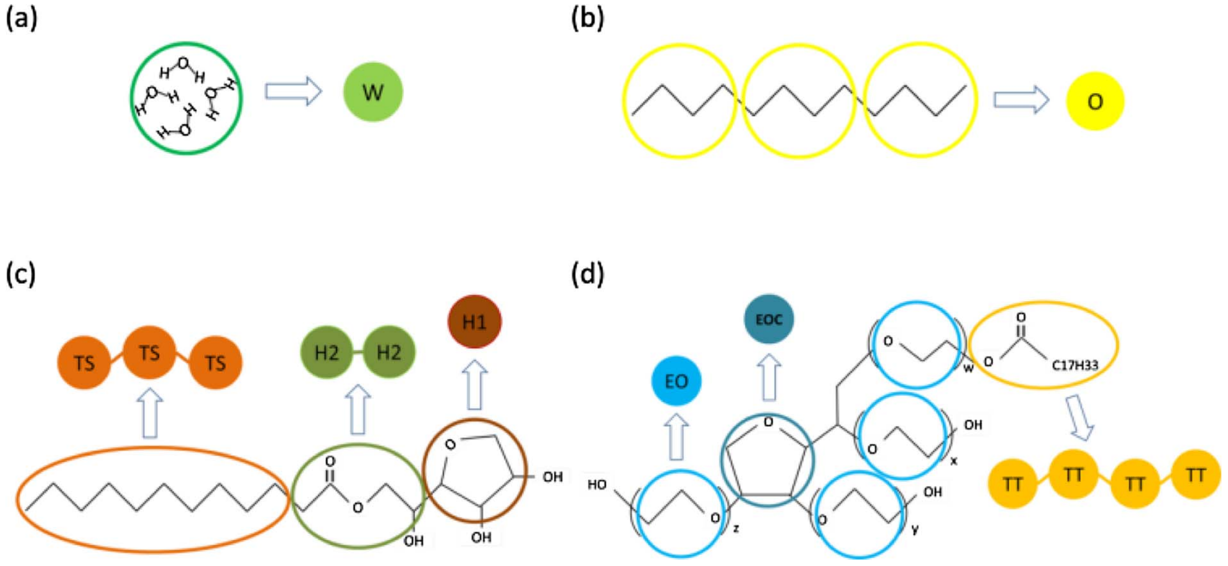

Fig. 1. The detailed mesoscopic models in the simulation system. Bead W: water; bead O: oil; beads H1 and H2: hydrophilic head of Span 20; bead TS: hydrophobic tail of Span 20; beads EO and EOC: hydrophilic head of Tween 80; bead TT: hydrophobic tail of Tween 80.

Table 1
Interaction repulsion parameters a_{ij} in simulation system[a] (unit: $k_B T/r_c$).

	W	O	EO	EOC	H1	H2	TT	TS
W	25	96	26	32	31	28	79	82
O	96	75	48	58	56	52	26	23
EO	26	48	29	24	28	26	53	50
EOC	32	58	24	33	31	34	57	55
H1	31	56	28	31	32	36	60	58
H2	28	52	26	34	36	29	55	57
TT	79	26	53	57	60	55	35	29
TS	82	23	50	55	58	57	29	33

[a] Abbreviations present the coarse-grained models illustrated in Fig. 1.

simulations. In this work, the interaction repulsion parameters used for the beads in the simulated system were presented in Table 1, which were calculated by P. Posocco et al. [35] And the other parameters in the dissipative and random forces were set to $\gamma = 4.5$ and $\sigma = 3$. The box size was $40 \times 20 \times 20\,{r_c}^3$ $(L_x \times L_y \times L_z)$ and periodic boundary conditions were applied in three directions. The 200,000 DPD steps with a time step of 0.05 were adopted in this research in order to obtain the balanceable results.

3. Results and discussion

3.1. Storage stability

The effects of surfactant properties and preparation technology on the stability of O/W emulsions were conducted by recording and calculating the creaming index, as well as observing the change of state of the emulsions. Specifically, the variables studied in this work included HLB value, emulsifier concentration (% wt), stirring time and stirring intensity. The detailed results are shown in Fig. 2.

It can be seen that the creaming phenomena mainly appears in the beginning 20 h after preparation, and keeps almost constant after 40 h. As shown in Fig. 2(a), the emulsion at HLB = 13 is the most stable when HLB values changes from 9 to 15. The influence of emulsifier concentration on the stability is presented in Fig. 2(b). It is interesting that there is a decline of CI for the emulsion with the emulsifier concentration below 1.6% during the first hour, and then it increases to a stable state after 40 h. This is because the emulsion with low emulsifier concentration is not stable due to agglomeration of the oil droplets, taking some water up to the creamed layer, and then the water goes down leading to the improvement of CI as time goes on. The optimal emulsifier concentration for the emulsion system is 1.6% because the emulsion destabilization occurs as a result of rapid coalescence at high surfactant concentrations. Compared with the result of different HLB values, there is no larger difference for the change of state of the emulsions with different emulsifier concentrations, because that the emulsifier dosage well above CMC is sufficient to prepare the O/W emulsions.

As shown in Fig. 2(c) and (d), the increases of stirring time and intensity are helpful to improve the emulsion stability. In order to compare the influence degrees of different factors on the stability of emulsions, the ranges of variation of CI are gathered in Fig. 3. It can be observed that the HLB value of emulsifier has the paramount impact on the emulsion stability. As said in Ref. [1] that the most important task in preparation of stable emulsions is the selection of suitable surfactant. It cannot be denied that the preparation technology of emulsion may play an important role in the stability of emulsion, as reported in Ref. [36]. So the results and discussion are based on the experiment conditions in this work.

As noted above, the HLB value of emulsifier plays the dominant role in the emulsion stability, indicating that the emulsion stability is closely linked with the interfacial film formed by surfactant molecules. Therefore, it is necessary to pay more attention to the properties of the interfacial film between the dispersed phase and the continuous phase in the emulsions.

3.2. Oil-surfacta materials and methods

It is safe to assume that the oil droplets dispersed in O/W emulsions are globate. In order to analyse the interfacial and structural properties comprehensively, the investigation of the interfacial film can be resolved into two parts for different scales: flat interface and curve interface, as illustrated in Fig. 4.

3.2.1. Structure and property of the flat interfacial film

Generally, the surfactant molecules adsorbed on the oil-water interface can reduce the interfacial tension and are benefit for the formation of emulsion with the help of external force. In partI, the amount of beads of oil and water is set equal to keep the oil-water interface perpendicular to the x axis. Fig. 5 presents the structures of oil-surfactant-water systems with different HLB values. It can be seen that the emulsifier beads accumulate at the interface with the hydrophilic

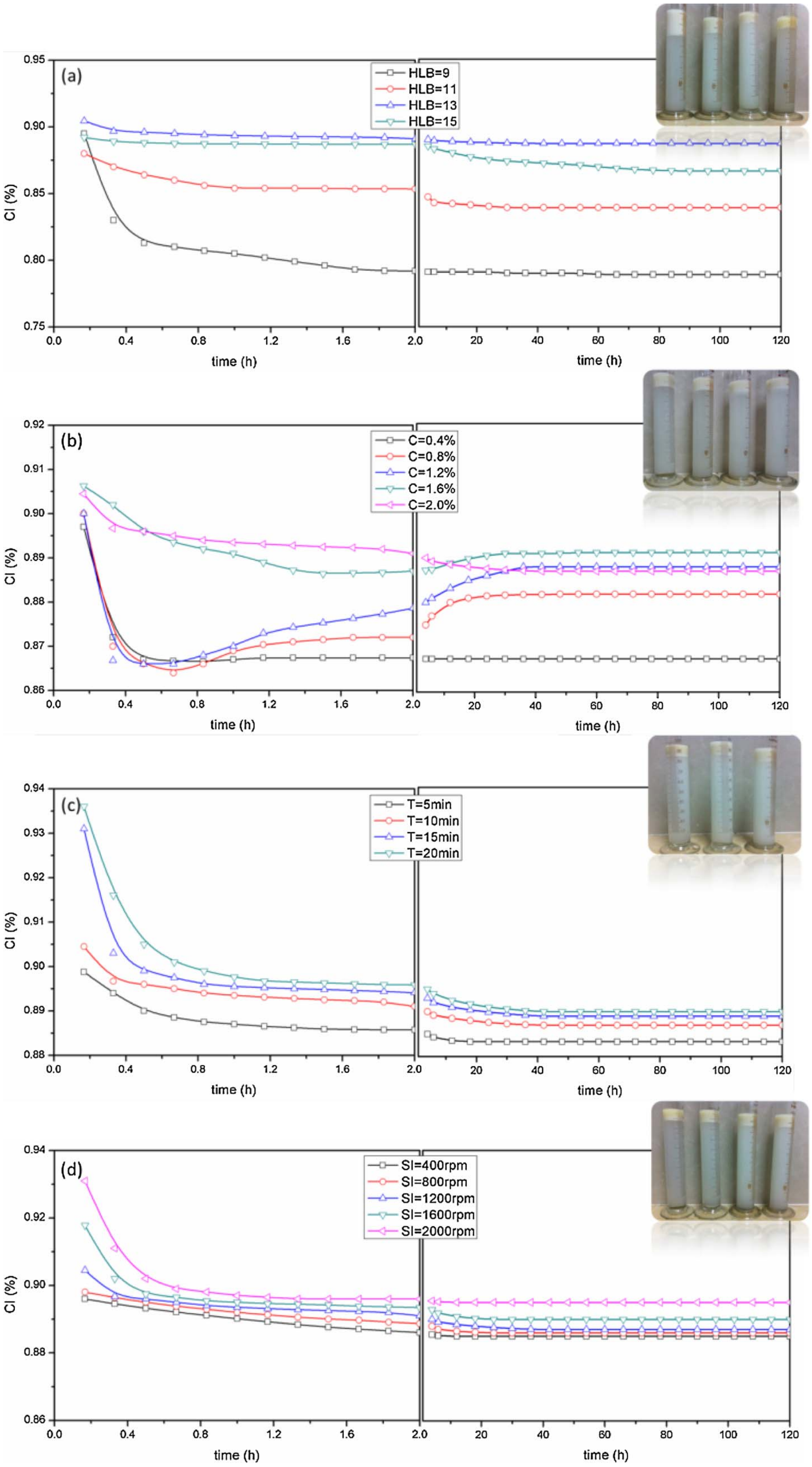

Fig. 2. Stability of O/W emulsions at different conditions: (a) HLB value (b) C: emulsifier concentration (c) T: stirring time (d) SI: stirring speed. The data is shared for the conditions of HLB = 13, C = 2%, T = 10 min and SI = 1200 rpm.

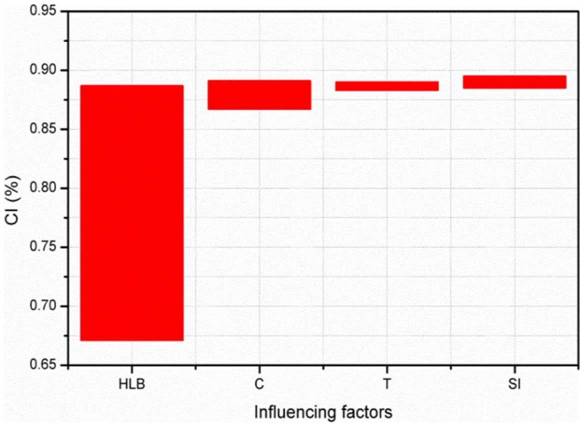

Fig. 3. Ranges of variation of CI under various factors.

groups and the lipophilic groups (including Tween 80 and Span 20) penetrating into the water phase and oil phase respectively. The density distributions of water beads, oil beads, hydrophilic head and hydrophobic tail of emulsifier beads along x axis are calculated and shown in Fig. 6 and the interfacial film thickness can be obtained based on the "10–90" criterion (Fig. 7).

It can be seen that the thickness of interfacial film increases with the increase of HLB. This is a result of the increased proportion of Tween 80 which has a large molecular volume of the hydrophilic head, indicating that the hydrophilicity of the surfactant is improved due to the increase of number of hydrophilic group.

However, the most stable O/W emulsion appears in the condition of HLB = 13, when the thickness of the interfacial film is not the maximum. The increase of interfacial film thickness, in one sense, indicates the increase of the film strength resulted from Van der Waals' force and coulombic force [37], but it does not take the dominant role in the emulsion stability. In this regard, the interfacial tension might have a significant influence on the stability of emulsions. Fig. 8 presents the interfacial tension with different HLB. Fortunately, the interfacial tension is the lowest when HLB is 13, and it does not always decrease with the increase of film thickness. To some extent, the blend of surfactant could reduce the interfacial tension better.

3.2.2. Curve of the oil-surfactant-water interface

In Section 3.2.1, the thickness and tension of the flat interface with different HLB values have been discussed without considering the interface curve. For the oil droplets in the O/W emulsion systems, the interfacial film formed by surfactant molecules is curving in a larger scale. Now, we focus on the relationship between the interface curvature and the surfactant molecules as well as the emulsion stability.

Firstly, the particle size distributions of the oil droplets in the emulsions prepared with different HLB values for emulsifier were measured by laser particle size analyzer, and the results are presented in Fig. 9. It can be obviously seen that the average particle size of oil droplet increases with the increased HLB values, with the size distribution getting narrow at the same time. This is because the Tween 80 molecules arranged at the oil-water interface have larger volume and cross-sectional area than those of Span 20 molecules, making the curvature radius of oil droplet bigger. It can be expressed vividly by schematic diagram, as shown in Fig. 10. Based on the Stokes formula (Eq. (7)), the oil droplet with lager size would be easier to move and come-up in the O/W emulsion systems, resulting in the instability of emulsion (when HLB value is 15).

$$v = \frac{2gr^2(\rho_s - \rho)}{9\eta} \tag{7}$$

where r is the radius of oil droplet, ρ is the water density for O/W emulsion, ρ_s is the density of oil droplet and η is the viscosity of the continuous phase. Although the emulsions with smaller droplets might be stable, the larger interfacial tension will also result in the instability as presented in Figs. 2(a) and 8.

Additionally, spontaneous curvature of the oil-surfactant-water interface might occur due to the relative volume of the hydrophilic head and the hydrophobic tail for the surfactant [38] as illustrated in Fig. 11. And the volume ratios for Tween 80 and Span 20 molecules were calculated respectively based on the bead number used in DPD simulations. It is found that Tween 80 has a larger volume ratio ($V_{head}/V_{tail} = 5.25$) than that of Span 20 ($V_{head}/V_{tail} = 1$), indicating the surfactant Tween 80 is more suitable to prepare the oil-in-water emulsions in which the emulsifier molecules could bend effectively to produce the oil droplet. On the contrary, water- in-oil emulsion would be easier to prepare when the emulsifier molecule has a volume ratio of $V_{head}/V_{tail} < 1$. Here, the relationship between volume ratio and HLB value can be deduced based on the molecule information of the surfactant (Eq. (8)), and the calculated result of volume ratio is 2.86 when HLB is 13. Moreover, the level of difficulty resulted from the molecular structure of emulsifier in preparing emulsions is also related to the

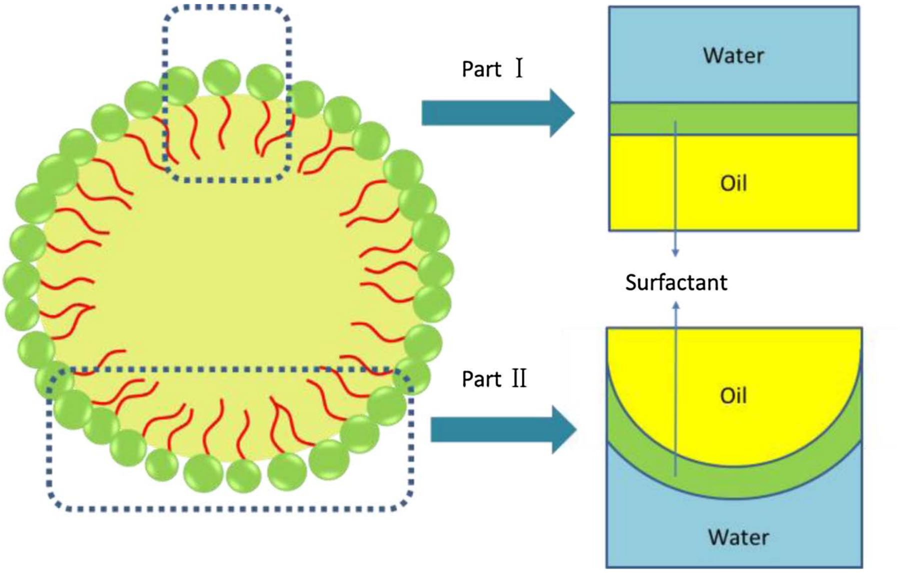

Fig. 4. Research process of the interfacial film, partI: flat interface; part II: curve interface.

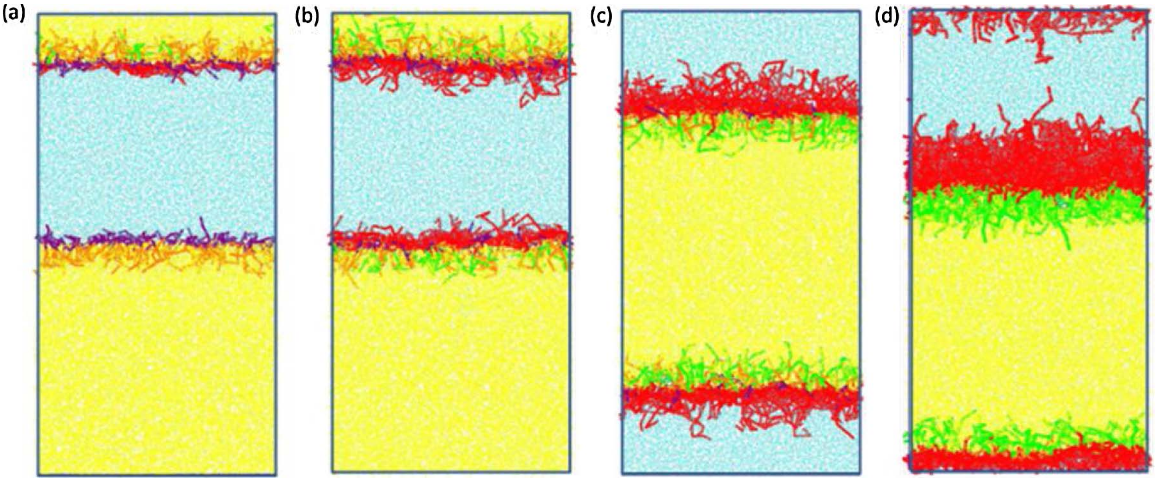

Fig. 5. Snapshots of the simulation of oil-surfactant-water system at different HLB values: (a) HLB = 9, (b) HLB = 11, (c) HLB = 13, (d) HLB = 15. Color legend: water, blue; oil, yellow; head group of Span 20, purple; tail group of Span 20, orange; head group of Tween 80, red; tail group of Tween 80, green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

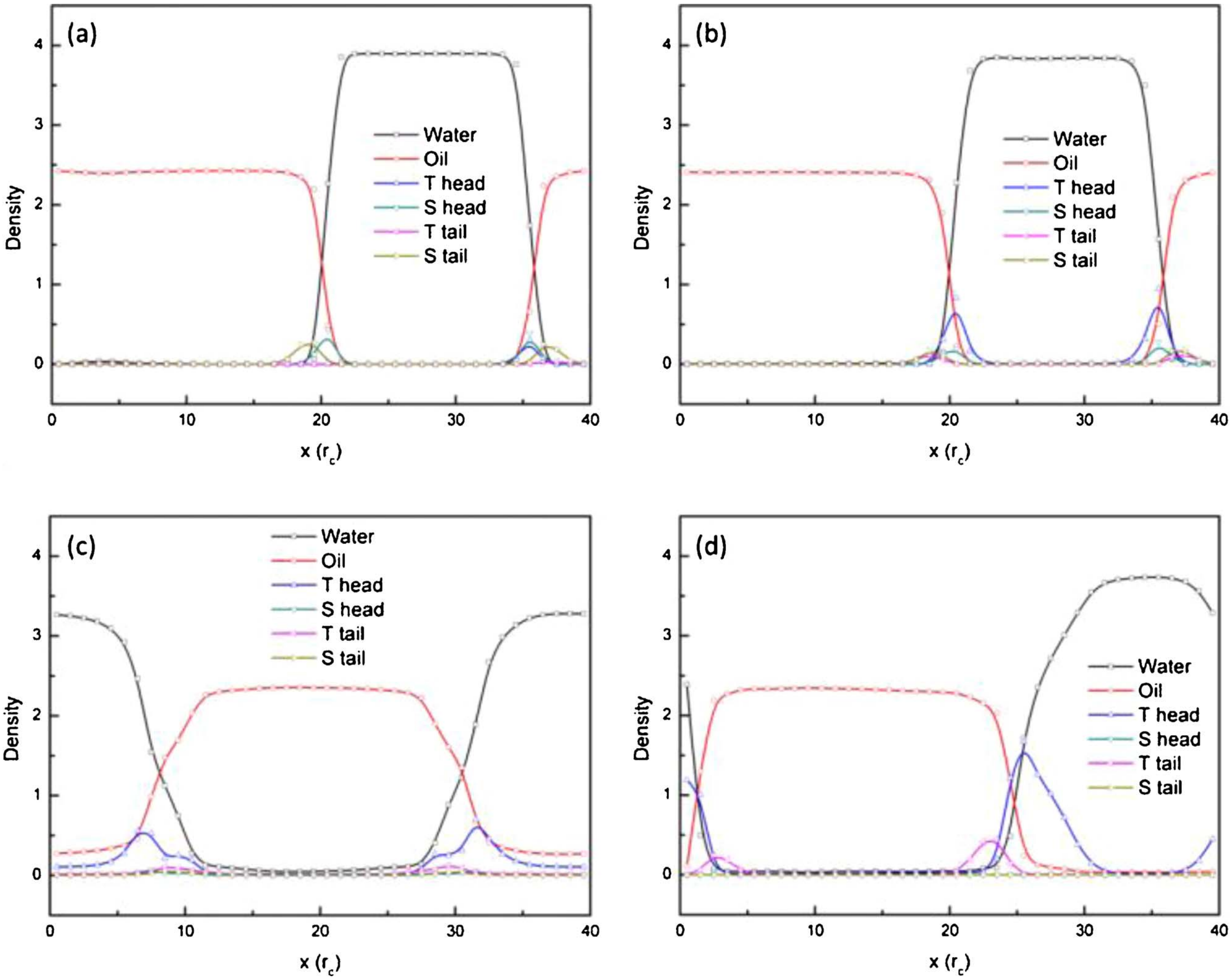

Fig. 6. Density profiles for beads of water, oil, hydrophilic head and hydrophobic tail of emulsifier beads. (a) HLB = 9, (b) HLB = 11, (c) HLB = 13, (d) HLB = 15. The density of Tween (T) head consists of EO and EOC beads, and the density of Span (S) head consists of H1 and H2 beads.

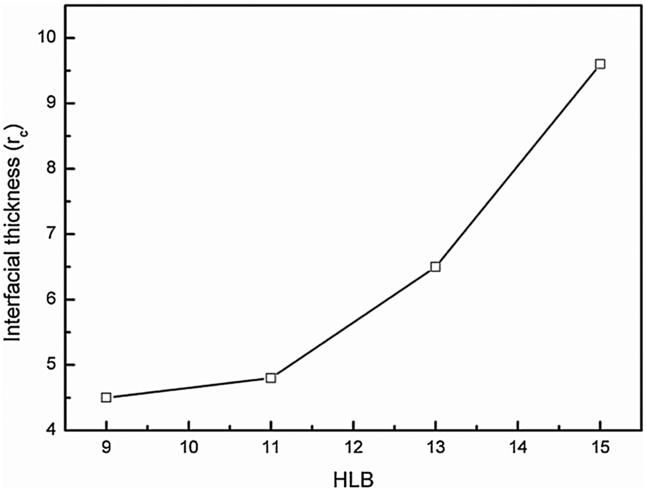

Fig. 7. Interfacial film thicknesses under conditions of different HLB values.

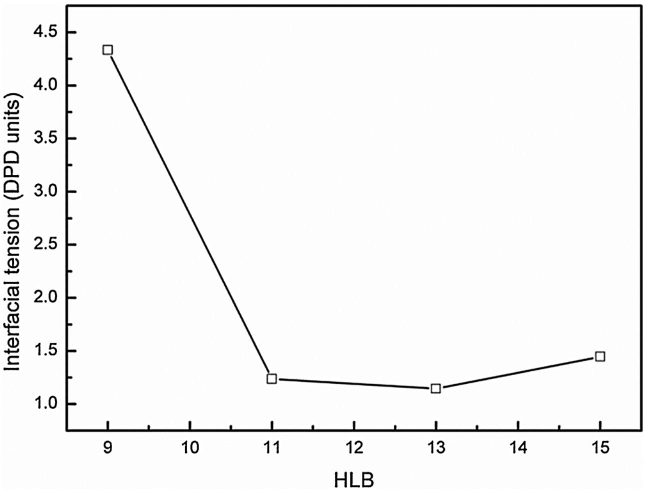

Fig. 8. Interfacial tensions under conditions of different HLB values.

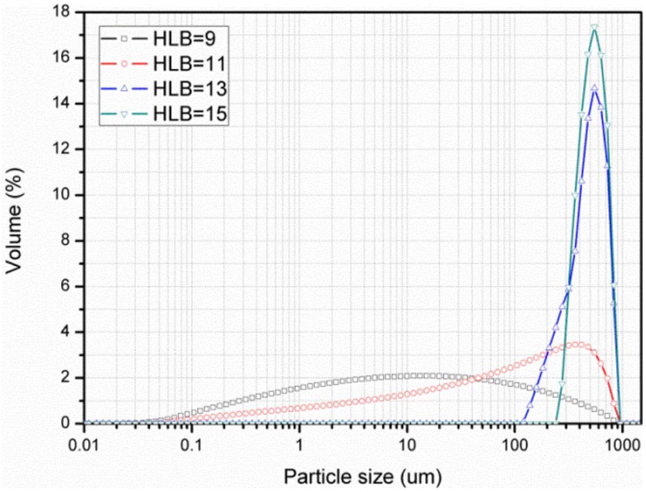

Fig. 9. Distributions of particle size with different HLB values.

emulsion stability. In other words, the emulsion will be more stable if the emulsifiers have suitable volume ratio of hydrophilic head and hydrophobic tail are used in the preparation process.

$$\frac{V_{head}}{V_{tail}} = \frac{9.64\,\mathrm{HLB}-10.23}{135.97-7.36\,\mathrm{HLB}} \tag{8}$$

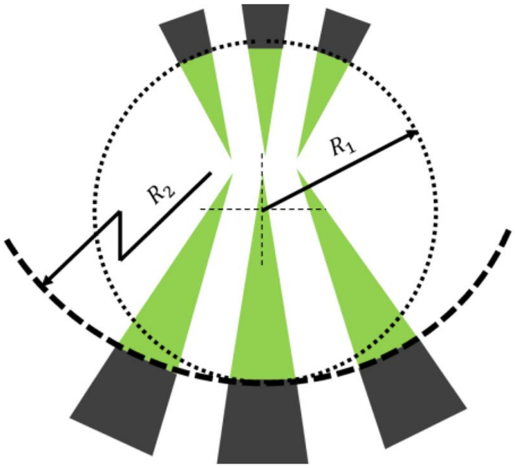

Fig. 10. Diagram of the relationship between particle size and volume size of surfactant.

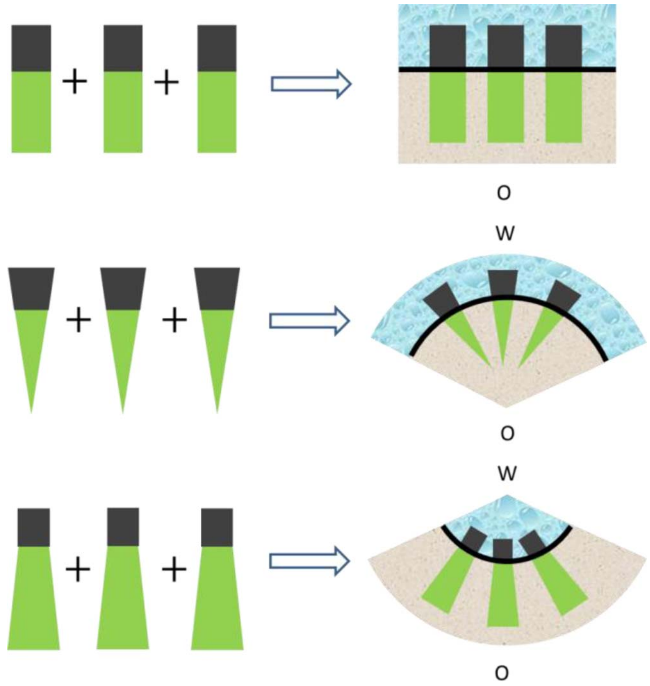

Fig. 11. The relationship between interface curvature and shape of surfactant molecule.

4. Conclusions

The stability of O/W emulsion emulsified by mixtures of Tween 80 and Span 20 has been investigated by experiment under different HLB values, emulsifier concentration, stirring time and stirring intensity. The optimal conditions for emulsifier in preparing the stable emulsion are: HLB, 13; emulsifier concentration, 1.6%. The increases of stirring time and intensity are helpful to increase the stability of emulsions. Among all these factors, HLB value has the paramount effect on the emulsion stability. In order to understand the mechanism of stability affected by emulsifiers with different HLB values, DPD simulations have been used to investigate the interfacial and structural properties at the oil-surfactant-water interface. The detailed results are summarized as follows:

(1) The thickness of interfacial film formed by emulsifier molecules increases with the increase of HLB values, while the emulsion stability does not follow the same trend with the thickness.

(2) Suitable blend of surfactants can decrease the interfacial tension and improve the emulsion stability as well.
(3) Although the interfacial film can be strengthened by improving the film thickness, the interfacial tension does not always decrease with the increased film thickness.
(4) The interfacial curvature is mainly determined by the volume ratio of the hydrophilic head and the hydrophobic tail as well as the molecular volume of the emulsifier.
(5) Neither too small nor too large droplet size could improve the emulsion stability, which is an integrated result of interfacial film thickness, interfacial tension and molecular structure of emulsifier.

Acknowledgments

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