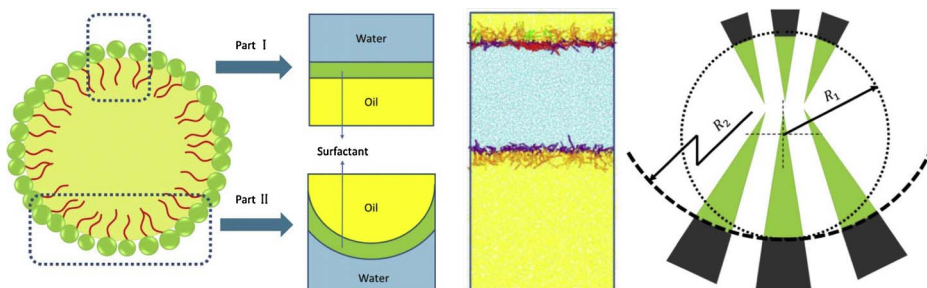# Investigation of oil-in-water emulsion stability with relevant interfacial characteristics simulated by dissipative particle dynamics

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G R A P H I C A L   A B S T R A C T



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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:

$$\text{HLB} = \frac{\text{HLB}_T \times w_T + \text{HLB}_S \times w_S}{w_T + w_S} \tag{1}$$

where $w_T$ and $w_S$ are the mass fractions of Tween 80 and Span 20 respectively, and $\text{HLB}_T$, $\text{HLB}_S$ are the values of HLB for them. Here, $\text{HLB}_T$ is 15 and $\text{HLB}_S$ 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:

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

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:

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

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

here $\gamma$ is the dissipative parameter, $\sigma$ is the noise amplitude, $\theta_{ij}$ 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 $\chi$ [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 $\chi_{ij}$ 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 $\chi_{ij}$ 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 $\chi_{ij}$ 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