An Analysis on Multi-Step-Growth of Oil Droplets Dispersed in Water

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Abstract: Multi-step-growth of oil droplets dispersed in water was theoretically studied in terms of mean free path. If $r_0, r_1, r_2, \dots$ are the radii of oil droplets for each step, they were found to be in a geometrical series with the common ratio of $(V_t / 3V_o)^{1/3}$. Here, V_o is the volume of oil dispersed in water, and V_t the total volume of the oil-in-water emulsion. The theory developed was applied to the three-step-growth of benzene droplets, and the experimental results were explained well throughout the whole steps.

Key words: oil-in-water emulsion, benzene droplet, multi-step-growth, mean free path, geometrical series

1 Introduction

Flocculation, coagulation and coalescence processes of droplets (1-6) are theoretically described by the Derjaguin-Landau-Verwey-Overbeek theory (1,7). The form of the energy barrier between two droplets is calculated from the van der Waals attraction and the electrical repulsion. There are a lot of computer simulations of the droplet growth in liquid medium (8,9).

We have recently observed multi-step-growth of surfactant-free oil droplets dispersed in water by a dynamic light scattering method (10-12) and a single-droplet detection method (13). **Figure 1** shows the three-step-growth of benzene droplets measured at $\sim 25^\circ\text{C}$ as a function of elapsed time, where r_0, r_1 and r_2 are the radii of benzene droplets for primary, secondary and tertiary steps, respectively (10,11). The experimental data shown in **Fig. 1** were obtained under the following conditions: The volume 1.56×10^{-2} ml of benzene was

ultrasonically dispersed in water. The total volume of benzene-in-water emulsion was 25.0 ml. The dynamic light scattering method was used to measure the droplet radii. We can see from **Fig. 1** that $r_0 = 20.0$ nm in the primary step, $r_1 = 150$ nm in the secondary step, and $r_2 \approx 1660$ nm in the tertiary step at $\sim 25^\circ\text{C}$. Benzene droplets grew up faster at higher temperature. Fourth, fifth and further steps were not observed for benzene droplets because of buoyancy of micrometer size droplets. On the basis of this experimental result, we have proposed a flocculation/coagulation model for the multi-step-growth of oil droplets as shown in **Fig. 2** (10). The model was supported by a direct observation of flocks and droplets with such sizes with a freeze-fracture electron microscope (11).

In this paper, we will make an attempt to explain the multi-step-growth in terms of mean free path, a fundamental concept of particle motion, and coagulation process. A simplified model system should be introduced

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Fig. 1 Three-Step-Growth of Benzene Droplets Dispersed in Water, Measured at $\sim 25^\circ\text{C}$ by a Dynamic Light Scattering Method as a Function of Elapsed Time (10, 11). The volume of benzene dispersed in water was 1.56×10^{-2} ml, and the total volume of benzene-in-water emulsion was 25.0 ml. Symbols r_0 , r_1 and r_2 represent the radii of benzene droplets for the primary, secondary and tertiary steps, respectively. The mean values of r_0 , r_1 and r_2 are shown by the circles, $r_0 = 20.0$ nm, $r_1 = 150$ nm and $r_2 \approx 1660$ nm. The vertical bars show the widths of droplet radius distributions.

so as to evaluate the essential features that the oil droplets themselves own. In this regard, surfactant-free oil droplets are one of the most adequate systems for scrutiny, because the emulsion is free of surfactants which would introduce irresolvable complexities in understanding the dynamic behaviors.

2 Theory

Oil droplets dispersed in water undergo the Brownian motion. If an oil droplet with radius r_0 collides with another droplet with the same radius, its mean free path, l , is given by (14)

$$l = \frac{1}{4\sqrt{2}\pi n r_0^2}, \quad (\text{eq. 1})$$

where n is the number of oil droplets in unit volume. Let V_o be the volume of oil dispersed in water and V_t the total volume of the oil-in-water emulsion, then the factor n in eq. 1 is represented as

$$n = \frac{V_o}{(4/3)\pi r_0^3 V_t}. \quad (\text{eq. 2})$$

As seen later, the ratio V_o / V_t plays the important role in the multi-step-growth of oil droplets.

Consider a spherical shell with the radius l and the thickness $2r_0$ as shown in **Fig. 3**, where l is the mean free path and r_0 the radius of primary droplet. The shell volume, V , is given by,

$$V = 8\pi r_0 l^2, \quad (\text{eq. 3})$$

Fig. 2 Schematic Illustration of Droplet Growth Modeled by Results of Dynamic Light Scattering Measurements (Flocculation/Coagulation Model) (10). Primary droplets with radius of r_0 aggregate and then merge into a secondary droplet with radius of r_1 . Similarly, secondary droplets with radius of r_1 aggregate and then merge into a tertiary droplet with radius of r_2 .

Fig. 3 Model of Forming a Secondary Droplet. Here, l is the mean free path, r_0 the radius of primary droplet, and the shell volume $V=8\pi r_0 l^2$. All primary droplets in the shell move towards the origin O to form a secondary droplet.

provided that $l \gg r_0$. All primary droplets in the shell move towards the origin O to form a secondary droplet. The radius of the secondary droplet, r_1 , is obtained from the condition of volume conservation, $(4/3)\pi r_1^3 = (4/3)\pi r_0^3 nV$, as $r_1 = r_0(nV)^{1/3}$. This equation is simplified by considering eqs. 1-3;

$$r_1 = r_0 \left(\frac{V_t}{3V_o} \right)^{1/3} \quad (\text{eq. 4})$$

A tertiary droplet with the radius r_2 is considered to be made from secondary droplets in the same manner as described above. Since $r_2 = r_1(V_t / 3V_o)^{1/3}$, it follows that

$$r_2 = r_0 \left(\frac{V_t}{3V_o} \right)^{2/3} \quad (\text{eq. 5})$$

After all, the radii of oil droplets are:

r_0 in the primary step,

$$r_1 = r_0 \left(\frac{V_t}{3V_o} \right)^{1/3} \text{ in the secondary step,}$$

$$r_2 = r_0 \left(\frac{V_t}{3V_o} \right)^{2/3} \text{ in the tertiary step,}$$

$$r_{n-1} = r_0 \left(\frac{V_t}{3V_o} \right)^{(n-1)/3} \text{ in the } n\text{th step.}$$

It is clear that they are in a geometrical series with the common ratio of $(V_t / 3V_o)^{1/3}$.

3 Comparison with Experimental Results and Discussion

Three-step-growth of benzene droplets experimentally observed is examined by applying the theory above. **Figure 4** shows the radii r_0 , r_1 and r_2 as a function of the step number. Using the least squares method, we have obtained $r_0 = 20.7$ nm under the experimental conditions of $V_o = 1.56 \times 10^{-2}$ ml and $V_t = 25.0$ ml. This leads to the conclusion that $r_1 = 168$ nm and $r_2 = 1363$ nm. These theoretical values agree well with

Fig. 4 Radii r_0 (Primary), r_1 (Secondary) and r_2 (Tertiary) of Benzene Droplets as a Function of the Step Number. The circles and vertical bars show the experimental results following **Fig. 1** (10, 11). The crosses show the calculated results, $r_0 = 20.7$ nm, $r_1 = 168$ nm and $r_2 = 1363$ nm under the experimental conditions of $V_o = 1.56 \times 10^{-2}$ ml and $V_t = 25.0$ ml. The broken line is the guide for the eye.

the experimental values as seen from **Fig. 4**.

The following facts were confirmed through the study of the three-step-growth of benzene droplets: Primary, secondary and tertiary droplets are formed one after another. Secondary droplets are made from primary droplets, and tertiary droplets from secondary droplets. Primary and tertiary droplets do not interact with each other. Fourth, fifth and further steps are not observed for benzene droplets because of buoyancy of micrometer size droplets as stated in the introduction. The three-step-growth of benzene droplets is explained well by the theory developed in this paper. The flocculation/coagulation model for the multi-step-growth, which is described in **Fig. 2**, is reasonable. The mean free path is generally applied to molecules in gas medium (14). The present study suggests that the mean free path can be applied to the surfactant-free emulsion system.

4 Conclusion

The mean free path plays the essential role in understanding the multi-step-growth of oil droplets dispersed in water. The radii of oil droplets for each step are in a geometrical series with the common ratio of $(V_t / 3V_o)^{1/3}$; in fact, r_0 in the primary step, $r_1 = r_0(V_t / 3V_o)^{1/3}$ in the secondary step, and $r_2 = r_0(V_t / 3V_o)^{2/3}$ in the tertiary step,..... Here, V_o is the volume of oil dispersed in water, and V_t the total volume of the oil-in-water emulsion. The theory developed explains well the three-step-growth of benzene droplets. The mean free path can be applied not only to molecules in gas medium but to oil droplets in aqueous medium.

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