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擬似微小重力環境下におけるオストワルド熟成に対する界面活性剤添加効果

Effects of Surfactants on Ostwald Ripening under Quasi-Microgravity

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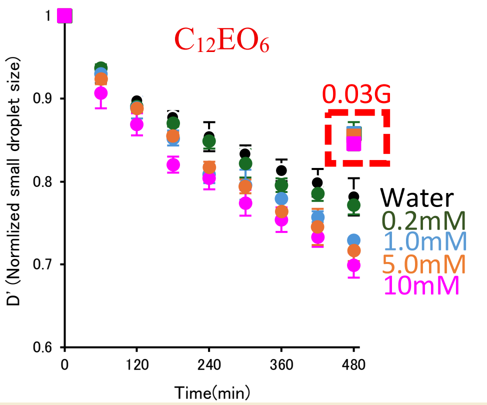
Abstract: An emulsion is a non-equilibrium colloidal system in which one liquid is dispersed in another immiscible liquid. These systems are destabilized through complex, interrelated processes such as creaming, coagulation, coalescence, and Ostwald ripening. To understand the essence of emulsion stability, therefore, each contribution of their processes should be separately evaluated, which is our challenge and main target. To achieve this, we have utilized a 3D clinostat to create a quasi-microgravity environment (0.03G), effectively inhibiting creaming and allowing for more accurate observation of emulsion decay. Two-droplet systems (water droplets in oil) with different surfactants was used to accurately evaluate Ostwald ripening, showing that Ostwald ripening was significantly suppressed under 0.03G, even when surfactants were present. In contrast, under terrestrial gravity (1G), ripening was clearly promoted by increasing surfactant concentrations, regardless of interfacial tension and micelle present. These results contradicted with the previous results using the nanoemulsions as well as Lifshitz–Slyozov–Wagner (LSW) theory that the ripening rate proportionally related with the interfacial tension. Our findings evidented the effects of microgravity on Ostwald ripening; (1) LSW thory was not applicable at least in microgravity, and (2) the surfactant molecules present in the solution were inactive in microgravity. These findings not only reveal gravity-dependent dynamics in emulsion destabilization but also provide new insight into the molecular transport mechanisms driven by surfactants.



Keywords: Emulsion, Ostwald ripening, Quasi-microgravity, Surfactant, 3D clinostat

1. Introduction

An Emulsion is a non-equilibrium colloidal dispersion system in which one of two or more incompatible liquids is dispersed in particulate form. These systems undergo four simultaneous decay processes: creaming, coagulation, coalescence, and Ostwald ripening, which ultimately lead to a two-phase separation. These decay processes do not proceed independently but occur jointly while influencing each other. Therefore, it is difficult to accurately evaluate each individual decay process.

We focused on a quasi-microgravity environment. It was expected that the time-averaged quasi-microgravity environment (0.03G) created by a 3D clinostat would suppress creaming caused by the density difference between water and oil, thereby enabling accurate evaluation of other collapse processes. Our previous studies showed 0.03G inhibited creaming as well as increase in the droplet size of the emulsions1).

We dropped two water droplets of different sizes into oil, as shown in Figure 1, and observed Ostwald ripening in an environment where coagulation and coalescence did not occur. Surprisingly, it was found that Ostwald ripening was suppressed at 0.03G compared to 1G under normal gravity. This cannot be explained by the general Lifshiz-Slezov-Wagner (LSW) theory (Eq. 1).

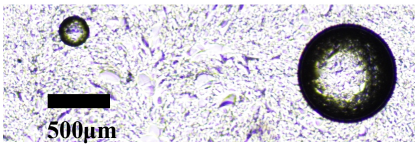


Figure 1. Micrograph of two water droplets in the oil

$$\omega = \frac{dr^3}{dt} = \frac{8D_C C_\infty \gamma M}{9\rho^2 RT} \quad (1)$$

Here, r is the particle radius, D_C is the diffusion coefficient of the dispersed phase, C_∞ is the solubility at zero curvature (flat surface), γ is the interfacial tension, M is the molar volume of the dispersed phase, ρ is density, R is the gas constant, and T is absolute temperature.

According to the Lifshitz–Slyozov–Wagner (LSW) theory, the addition of surfactants lowers interfacial tension and thereby suppresses Ostwald ripening. However, several studies have reported that surfactants can instead promote ripening, in contradiction to LSW predictions[2–4]. This enhancement is thought to arise from micelles acting as molecular carriers that facilitate mass transfer between droplets. In this study, we investigated the effect of surfactant addition on Ostwald ripening under both normal gravity (1G) and quasi-microgravity (0.03G), and clarified the underlying mechanism responsible for ripening suppression observed under microgravity.

2. Experiments

2.1. Equipment

Zeromo CL-5000C (Kitagawa Iron Works) was utilized as 3Dclinostat to create time-averaged microgravity. The rotational twin bodies equipped in the 3D clinostat individually turn around in all directions, providing quasi-microgravity environment (nominal value 0.03G) artificially on ground. The rotational rate of the external body was fixed at 10 rpm and the internal body rotates at a half rate of the external body. Using IJK-200S, droplets of μm size were adjusted for dedicated cells (width 3 mm, depth 1 mm). The cells were mounted on a 3D clinostat, and the droplet size was evaluated after 8 hours at 0.03 G.

2.2. Materials

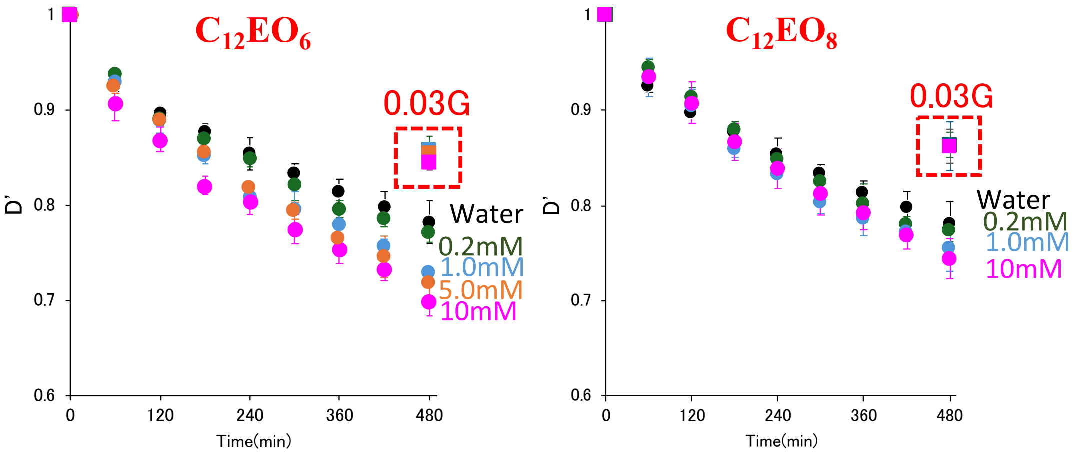
A silicone oil (SH200C Fluid 500CST, Dow) and Dodecane (FUJIFILM Wako Pure Chemicals CO.) were used as an oil phase, and ultrapure water (specific resistance >18MΩ-cm) were used as an aqueous phase. hexaoxyethylene dodecyl ether ($C_{12}EO_6$, >99%, Nikko Chemicals), octaoxyethylene dodecyl ether ($C_{12}EO_8$, >99%, Nikko Chemicals) and Sodium dodecyl sulfate (SDS,>99%, Sigma Aldrich Japan) were used as a surfactant.

2.3. Sample preparation

Using the IJK-200S, two drops of water (large: 476.92 ± 2.19 μm, small: 130.25 ± 2.99 μm) were dropped onto a dedicated cell and filled with a silicone oil/dodecane = 1/3 (wt%) solution. A cover glass was placed over the solution, and all gas was completely removed. In addition, fluorine coating (HR-FX033E, AGC Seimi Chemical) was applied to prevent wetting of the droplets.

3. Result and Discussion

The temporal evolution of the normalized relative radius of the smaller droplet, D', in a two-droplet system is shown in Fig. 2. Panels (a) and (b) represent the time-dependent changes in systems containing the nonionic surfactants $C_{12}EO_6$ and $C_{12}EO_8$, respectively. Additionally, Fig. 3 presents the interfacial tension between dodecane and surfactant aqueous solutions, along with the corresponding Ostwald ripening rates evaluated from the values of D'^3 at 480 minutes.



(a) (b)

Figure 2. Time evolution of normalized droplet size (D') over 480 minutes with different surfactants: (a) With $C_{12}EO_6$; (b) With $C_{12}EO_8$.● : Water, ● : 0.2mM, ● : 1.0mM, ● : 5.0mM, ● : 10mM.

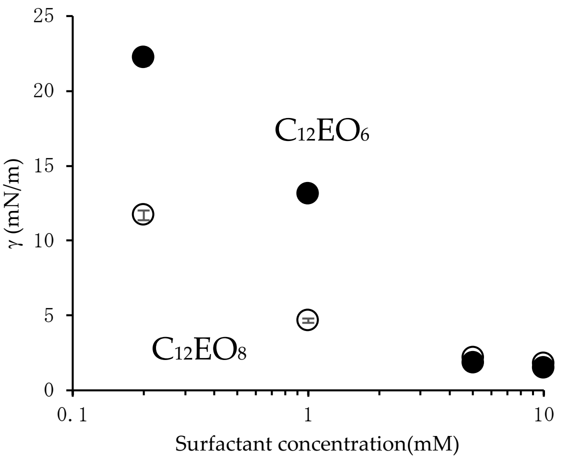


Figure 3. Interfacial tension (γ) curve of surfactant ($C_{12}EO_6$ or $C_{12}EO_8$) aq. / Dodecane as a function of the surfactant concentration. ● : $C_{12}EO_6$, ○ : $C_{12}EO_8$.

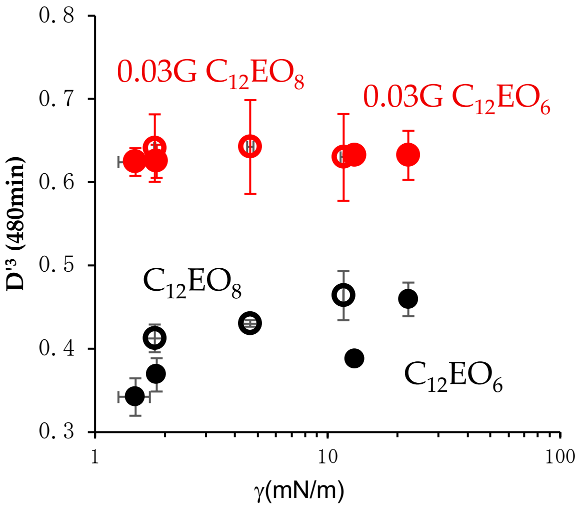


Figure 4. Relationship between interfacial tension (γ) and droplet volume (D'^3) after 480 min.
● : 1G $C_{12}EO_6$, ○ : 1G $C_{12}EO_8$, ● : 0.03G $C_{12}EO_6$, ○ : 0.03G $C_{12}EO_8$

In all systems with surfactants, the smaller droplets progressively shrank over time, indicating the progression of Ostwald ripening. For both $C_{12}EO_6$ and $C_{12}EO_8$, increasing the surfactant concentration resulted in an accelerated ripening rate. However, as shown in Fig. ○, the interfacial tension decreased with increasing surfactant concentration and became nearly constant beyond 5 mM, corresponding to the critical micelle concentration (CMC). This observation contradicts the prediction by the Lifshitz–Slyozov–Wagner (LSW) theory（Eq. 1）, which states that a reduction in interfacial tension should lead to a suppression of Ostwald ripening. Contrary to this theoretical expectation, our results showed a clear promotion of ripening with increasing surfactant concentration. The promotion of Ostwald ripening observed under 1 G conditions is likely attributed to the presence of monomeric surfactant molecules dissolved in the continuous phase. These monomeric surfactants, located between droplets, are presumed to act as molecular carriers that facilitate the diffusion of water molecules, thereby accelerating the ripening process. Indeed, numerous studies have reported that micelles in the continuous phase can contribute to the enhancement of Ostwald ripening. However, our results demonstrate that ripening was promoted even at surfactant concentrations below the critical micelle concentration (CMC), indicating that not only micelles but also monomeric surfactant molecules serve as effective carriers for mass transport between droplets. The observed enhancement of Ostwald ripening with increasing surfactant concentration can therefore be ascribed to the increased number of monomeric surfactant molecules in the continuous phase.

Notably, under 0.03 G, the Ostwald ripening rate was significantly suppressed, even in the presence of surfactants, reaching levels comparable to those observed in systems containing only water. In other words, surfactants that acted as promoters of ripening under 1 G conditions failed to exert such effects under microgravity, resulting instead in suppressed ripening. This striking result strongly suggests that the promoting role of surfactants in Ostwald ripening is critically dependent on the presence of a gravitational field, and provides compelling evidence that gravity plays an essential role in the underlying mechanism of ripening.

4. Conclusion

Our results indicate that Ostwald ripening at 0.03G exhibits different behavior than at 1G. At 0.03G, Ostwald ripening was suppressed to a certain extent across a wide range of surfactant concentrations, indicating that the promotion of Ostwald ripening by surfactant addition at 1G is not only due to the influence of reverse micelles, but also due to the surfactant present as a monomer acting as a carrier between droplets. However, to prove this, it is necessary to use unnecessary surfactants in the continuous phase to clarify the influence of the carrier.

Mathematical Components

$$\omega = \frac{dr^3}{dt} = \frac{8D_c C_\infty \gamma M}{9\rho^2 RT} \tag{1}$$

Nomenclature

r	diameter (nm)
t	time (min)
D_c	Diffusion coefficient of dispersed face (m^2/s)
γ	Particle surface tension or surface energy (mN/m)
C_∞	Solubility of dispersed phase relative to continuous phase on a flat surface (g/L)
M	Molar volume of the dispersed face (L/mol)
ρ	Density of dispersed face (g/cm^3)
R	Gas constant (J/mol・K)
T	Temperature (K)

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