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3D クリノスタットを用いた非平衡コロイド分散系の研究

Study on non-equilibrated colloidal dispersion systems using 3D clinostat

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1. Introduction

A colloidal dispersion in a non-equilibrium state is one of essential dosage forms for industry, and the stability control is an important subject from the point of view of quality assurance. In such liquid/liquid colloidal dispersion systems, they reach equilibrium via various elementary disruption processes such as flocculation, coalescence, creaming (sedimentation) and so on, but the influence of gravity must be taken into consideration to understand individual contribution of these processes.

3D clinostat is a device that creates a time-averaged pseudo-microgravity environment (0.03G) on the ground and has been often utilized in the research fields of biology and botany. We have attempted to apply the 3D clinostat to evaluate the liquid-liquid dispersion system (emulsion) and found out that the 3D clinostat could be a promising tool to elucidate the real emulsion destabilizing process. Our previous studies showed that quasi-microgravity condition created by a 3D clinostat inhibited creaming as well as increase in the droplet size of the emulsions[1)]. It is expected from these results that the 3D clinostat can independently analyzes four elementary processes during emulsion disruption.

Figure 1. Picture of two water droplets in the silicone oil.

Recently, we have investigated the influence of the gravity on Ostwald ripening in the simple system where two aqueous drops with different size were present in the oil (Figure 1). According to the solubility difference between the small and large droplets (Kelvin's rule), the small droplet was shrinking with time. However, the shrinking rate at 0.03G was much slower than that at 1G, which could not be interpreted by the general Lifshiz-Slezov-Wagner (LSW) theory. Thus, our present study has attempted to elucidate the effect of gravity on Ostwald ripening phenomenon in various binary and ternary systems. Furthermore, we will also report on the resent status of the Emulsion Dynamics and Droplet Interfaces (EDDI) project jointly implemented with ESA and European research group.

2. Experiment

2.1. Equipment

Zeromo CL-5000C (Kitagawa Iron Works) was utilized as 3D clinostat 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. The time-lapse camera (TLC200Pro, Brinno) and the microscope (homemade, Figure 2) were loaded in the 3D clinostat for in-situ observation.

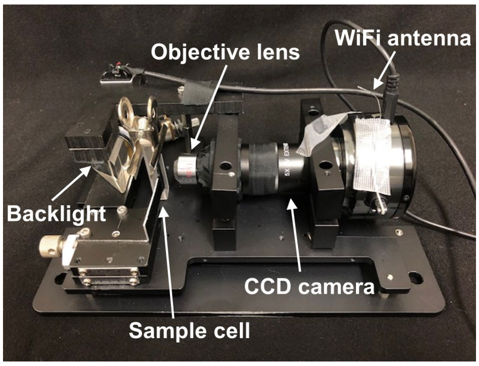

Figure 2. Microscope developed exclusively for 3D-clinostat.

2.2. Materials

A silicone oil (SH200C Fluid 500CS, Dow) and liquid paraffin (>90%, Nakalai Tesque) were used as an oil phase, and ultrapure water (specific resistance >18MΩ·m) were used as an aqueous phase. Sodium dodecyl sulfate (SDS, >99%, Fujifilm Wako Chemicals) and hexaoxyethylene dodecyl ether ($C_{12}EO_6$, >99%, Nikko Chemicals) were used as a surfactant.

2.3. Sample Preparation

Two water droplets were produced in an oil filled in a plastic cuvette using a micropipette. The volumes of droplets were 1 mL, 3 mL, or 7 mL, of which various combinations (small and large droplets) were evaluated. After the gas (bubble) was completely removed from the cuvette and the samples were sealed with a Teflon tape.

Emulsion samples were prepared in the water/silicone oil system using the homomixer (FILMIX 40-L, 10 m/s, 180 seconds, PRIMIX). The volume fraction of the dispersed water phase was fixed at 0.05 to avoid coagulation and the contact between droplets. After gas was completely removed from the cuvette and the emulsion samples were sealed with a Teflon tape.

3. Results and Discussion

3.1. Two Droplets System

The simplest system, two water droplets in the oil, were adapted to directly observe Ostwald ripening. The volume of the small droplet (D'^3, normalized by the volume of the large droplet) gradually decreased with time under both the terrestrial (1G) and quasi-microgravitational (0.03G) conditions, while the decrease rates (ω_{ost}) at 1G and 0.03G were different in both the silicone oil and liquid paraffin. ω_{ost} at 0.03G was much slower than that at 1G, suggesting thus that the gravity could enhance Ostwald ripening. Furthermore, it was found that the added surfactant accelerated ω_{ost} with increasing its concentration at 1G, while oppositely delayed it at 0.03G. This result at 0.03G was imcompatible with contribution of the interfacial tension in the LSW theory, and thus it could be expected that the surfactant would influence on the chemical potential of water droplets.

3.2. Multiple Droplets System (Emulsion)

The water-in-oil (W/O) emulsion in the water/silicone oil system was examined with a microscope camera. The emulsion prepared by the present mixing condition (shear rate = 10 m/s, applied time = 180 seconds) had high polydispersity ranging from a few to 50 μm (Figure 3), and noticeable coagulation was not observed during the measurement. The disperesed water droplets were gradually moving downwards at 1G desptite using the high viscous oil (kinetic viscosity = 500 mm^2/s), but macroscopically no phase separation occurred at 0.03G as with our previous results. The histograms in Figure 3 showed the size distribution of 100 droplets at t = 0 and 20 hours later. In 20 hours, it was noted that the numbers of the smaller droplets in 5 to 15 μm and the larger droplets in 30 to 40 μm relatively increased at 1G. This could be the result that the droplets in the intermediate sizes shrunk and the relatively larger droplets swelled via Ostwald ripening. On the other hand, the size distribution was almost unchanged at 0.03G, and it was suggested from these results that gravity would influence Ostwald ripening in the emulsion system as well.

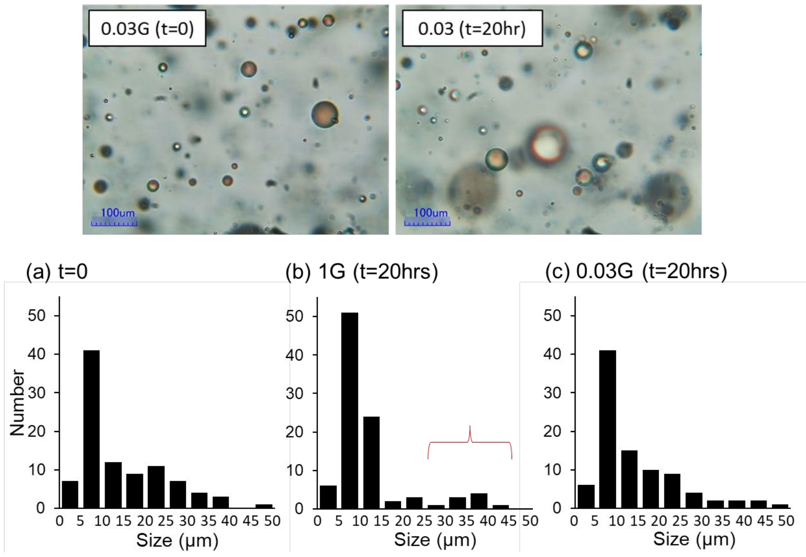

Figure 3. Microscope images of the emulsion (top, 0.03G) and size distribution of the emulsion droplets (bottom) in the water/silicone oil system. The droplet size was measured at t= 0 and 20 hours later. The histograms represented the number of droplets in each size range (total 100) at (a) t = 0, (b) t = 20 hrs., 1G, and (c) t = 20 hrs., 0.03G.

4. Conclusion

Our results demonstrated that an abnormal manner in Ostwald ripening phenomenon occurred in the wide range of droplet size under the quasi-microgravity condition. Although our results were not enough to explain this phenomenon and some doubts such as interfacial fluctuation and friction still remained unclear in the 3D-clinostat experiments, it was expected that gravity should be taken into account in the current theory, or a new theory for microgravity would be necessary. Hopefully, ISS experiments will support and prove our results in the future.

References

1) Y. Yamashita, et al., ISTS Paper, 2015-h-05 (2015); Y. Yamashita, et al., ISTS Paper, 2017-h-07 (2017)