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擬似微小重力下でのエマルション安定性

Emulsion Stability under Quasi-microgravity

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Abstract: Emulsion 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 colloidal dispersion systems, they reach equilibrium viavarious elementary disruption processes such as coalescence and creaming (sedimentation), but the influence of gravity must be taken into consideration to understand individual contribution of these processes. Microgravity would be a promissing and frontier field to investigate the essential phenomena during the emulsion decay, that is, allowing more accurate evaluation of the emulsion dynamics. We have attempted to apply the quasi-microgavity codition (0.03 G) generated by a 3D clinostat to study the liquid-liquid dispersion system (emulsion) for long time. Our results clearly demonstrated that microgravity markedly impacted on not only the apparent emulsion stability but the elementary process. Ostwald ripening, one of the emulsion disruption processes, is caused by the difference in “solubility” between the dispersed droplets with different curvatures, and therefore Ostwald rippening has been thought to be an inevitable phenomenon regarding the emulsion stability. However, the quasi-microgravity condition significantly suppressed the growth of emulsion droplets, which could be due to the delay of Ostwald ripening rate. Furthermore, a added surfactant was able to suppress the Ostwald ripening rate in microgravity, which is the very opposite effect of 1G. Utilizing this microgravity phenomenon, we had investigated variouos emulsions stabilized by surfactants with different HLB numbers. Likely the previous results, microgravity stabilized all emulsions compared to 1 G, while growth of the emulsion droplets was observed depending on the composition in the emulsion. Assuming that suppression of Ostwald ripening at 0.03G was operative in any systems, it was considered that coalescence could take place and the interfacial properties would be significant even in microgravity. The droplet size and stability were correlated with the interfacial tension, but the interfacial elasticity, which was considered as a critical parameter in coalescence, did not significantly affect the emulsion stability (coalescence) in the present system. Our presentation will show further results in different systems comsisting of various surfactants and oils.

Keywords: Emulsion, HLB number, Solubility, Ostwald Ripening

1. Introduction

1.1. Emulsion and Its Stability

A liquid-liquid dispersion in a non-equilibrium state, called "emulsion", is one of essential dosage forms for industry, and the stability control is an important subject from the point of view of quality assurance. Emulsions can be stabilized by various methods such as mechanical input and interfacial control. A surfactant is used as a stabilizer for colloidal dispersions and chemically alters the interfacial property by adsorbed to the boundary plane between two immiscible substances. The surfactant is able to reduce the excess free energy at the water/oil interface when adsorbs there. This property of the surfactant is very important to produce a fine emulsion in terms of thermodynamics. On handling emulsions especially in the industrial fields, the characteristic of a surfactant is often expressed by the HLB (hydrophilic-Lipophilic Balance) number. The HLB number is an index of the affinity of a surfactant toward a solvent; for example, a high HLB number indicates that the surfactant is more attracted to water (water-soluble). It is well-known as a practical example of the HLB number that the type and appropriate amount of surfactant can be estimated to emulsify a kind of oil-in-water (O/W) solution. As discussed from Bancroft's rule, oil-soluble surfactants preferably form W/O emulsions, and water-soluble ones does O/W emulsons. In other words, any emulsion becomes unstable unless a surfactant with an appropriate HLB number is used.

Although a change in the free energy on forming emulsions can be calculated, the rate of emulsion break-down and the aspect changing with time may be unpredictable. Therefore, it would be significant to focus on and understand a kinetic stability of an emulsion. Droplets dispersed in emulsions always move around due to the thermal- and gravitational-effects, and repeatedly collide each other. Factors involved in the kinetic emulsion stability can be attributed to a kinetic state of a dispersed droplet and interactions operative between the droplets, suggesting that emulsions can be stabilized by controlling their interface and bulk properties. Emulsion disruption can occur via various elementary steps. These steps are known to be creaming, coagulation, coalescence, and Ostwald ripening, and may not independently take place but some or all of them simultaneously progress with time. Although the emulsion stability should be improved if either process can be inhibited or delayed, any systematic mechanisms such as interrelation between these processes have not been established yet. Difficulties of individually evaluating these processes would prevent comprehensive answers to stabilize emulsions.

1.2. Ostwald Ripening

Ostwald ripening is an observed phenomenon in solid or liquid solutions that describes the change of an inhomogeneous structure over time, i.e., small crystals dissolve, and redeposit onto larger crystals, and it can be also observed in liquid-liquid systems, for example, in an oil-in-water emulsion In this case, Ostwald ripening causes the diffusion of monomers (i.e. individual molecules or atoms) from smaller droplets to larger droplets due to greater solubility of the single monomer molecules in the larger monomer droplets. The solubility (S(r)) of a dispersed droplet with a radius (r) is expressed by the following equation:

$$S(r) = S(\infty) \cdot exp\left(\frac{2\gamma V_m}{rRT}\right) \qquad (1)$$

where $S(\infty)$ is solubility of the droplet with the infinite radius (flat plane, curvature = 0), γ is interfacial tension, V_m is molar volume of a solute, R is gas constant, and T is absolute temperature. The rate of this diffusion process is linked to the solubility of the monomer in the continuous (water) phase of the emulsion. This can lead to the destabilization of emulsions.

1.3. Objects of Study

As mentioned above, it would be difficult to study the four processes involving in the emulsion decay separately in ground experiments. Since 2014, therefore, our research team has been working in collaboration with the European group to study emulsion dynamics under microgravity. In Japan, we have utilized a 3D clinostat for the microgravity experiments, which was the first challenge to evaluate a fluid system. Our previous experiments using various emulsions have revealed that besides the suppression of creaming due to the difference in specific gravity as predicted by Stokes' theory, an unexpected suppression of droplet growth takes place in microgravity. Furthermore, two water droplets in an oil medium, where no coagulation and coalescence happens, demonstrated that Ostwald ripening rate depended on gravity which could not be interpreted by the LSW theory. In the present study, we have systematically investigated various factors relating the emulsion stability such as the HLB number of surfactant and oil species, and the effects of interfacial properties and solubility on the emulsion stability in microgravity will be discussed in terms of Ostwald ripening and coalescence.

2. Experiments

2.1. Equipment

Zeromo CL-5000C (Kitagawa Iron Works) was used to create time-averaged microgravity. The rotational twin bodies equipped in the 3D clinostat individually turn around in all directions, and the rotational rate of the external body was fixed at 10 rpm and the internal body rotated at a half rate of the external body. The emulsion droplets were evaluated by the optical microscope (ECLIPSE Si, Nikon). The interfacial tension and dilational rheology were evaluated by the pendant drop method (DMs-301, Kyowa Interface Science) and dilational rheometer (Teclis Tracker), respectively.

2.2. Materials

Dodecane (C12, FUJIFILM Wako Pure Chemicals), tributyrin (TB, FUJIFILM Wako Pure Chemicals), and medium-chain fatty acid oil (MCT, Nikkol Chemicals) were used as an oil phase, and ultrapure water (specific resistance >18MΩ•cm) were used as an aqueous phase. Polyoxyethylene sorbitan monostearate (HLB 13.7, FUJIFILM Wako Pure Chemicals) and sorbitan monostearate (HLB 5.8, FUJIFILM Wako Pure Chemicals) were used as a surfactant.

2.3. Sample preparation

The surfactant (surfactants), water, and oil were weighed at a given composition in a glass vessel and simply emulsified by a mixer. The emulsified solution was filled in another glass vessel without air.

3. Results and Discussion

The HLB number has been widely used in industry as an indicator of the surfactant properties. When a surfactant emulsifies an oil and water, its HLB number not only determine the type of emulsions but also influence on the stability of the emulsion. The appropriate HLB number of the surfactant should be tuned considering the properties of the emulsified oil which are commonly expressed as "required HLB number (rHLB)". As seen in PIC and PIT methods which are representative emulsification methods, very fine emulsions are formed when the surfactant passes through a phase state of higher interfacial activity in the emulsification process. In other words, the phase behaviour in the surfactant system can be roughly predicted from the HLB and rHLB numbers. Nevertheless, unstable emulsions are often encountered even though the surfactant is properly selected according to the HLB theory for emulsification. Thus, the HLB theory should be important for emulsification, while it has not been well understood how the HLB numbers contribute to the stability of emulsion after emulsification. In this study, therefore, we have investigated the stability of O/W emulsions in surfactants/oil/water systems with different HLB and rHLB numbers, particularly utilizing the microgravity condition. Our previous results demonstrated that quasi-microgravity remarkably suppressed creaming as well as Ostwald ripening, so it can be expected that the microgravity experiments would reveal the significance of the surfactant HLB number.

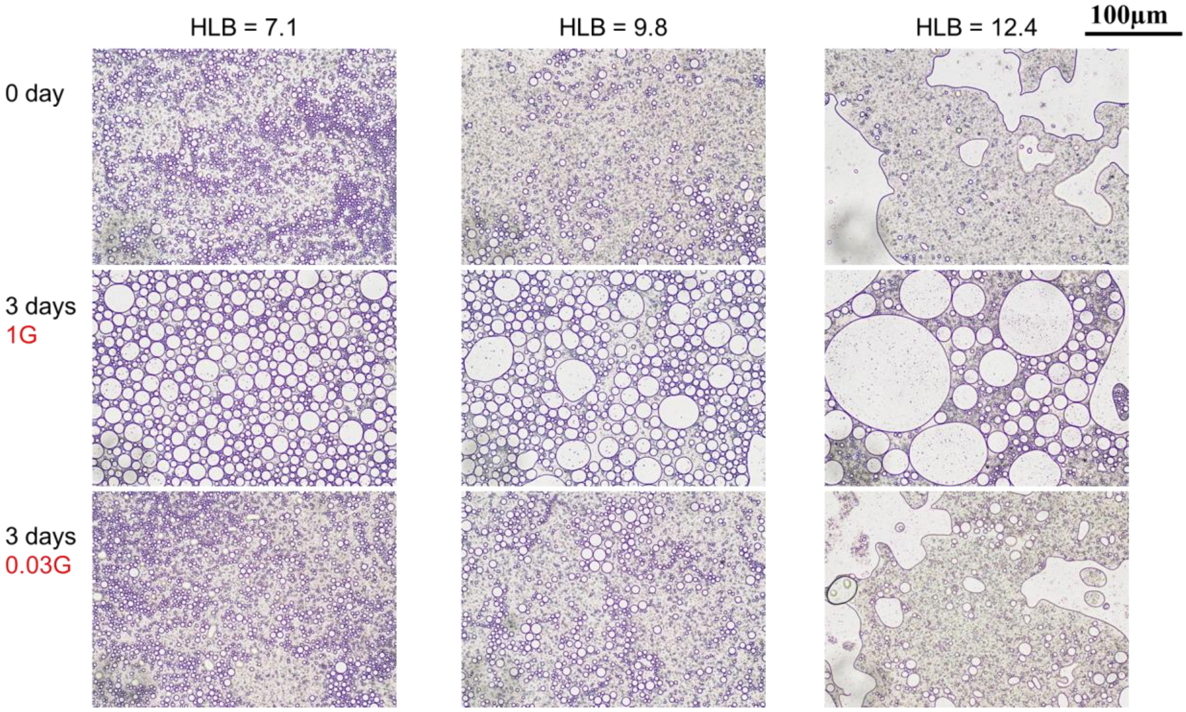

Figure 1. Micrographs of the O/W emulsions at different HLB numbers in 1G (middle) and 0.03G (bottom) 3 days after preparation. The composition of surfactant/oil/water is 4/40/56 in weight.

The O/W emulsions were prepared in the surfactant mixture/MCT/water (4/40/56 in weight) system (Figure 1). The HLB number was changed by the mixing ratio of two surfactants. The appearances and droplet sizes of these emulsions with different HLB numbers were different just after emulsification; the higher the HLB number was, the larger the droplet size became. In particular, the sample at HLB =12.4 was macroscopically separated into two phases within 1 hour. This HLB number dependency would be attributed to the rHLB of MCT (~5), and the lower HLB number of the surfactants was suitable for production of the finer emulsion. On the other hand, the droplet growth with time was observed even for the emulsion with the lower HLB number close to rHLB in terrestrial gravity (1G), while the droplet size remained constant or the growth rate of droplet was delayed in micro-gravity (0.03G). Comparing to the emulsions at lower HLB number (<10), the droplet growth was observed at HLB =12.4. Assuming that suppression of Ostwald ripening at 0.03G was operative in any systems, it was considered that coalescence could take place and the interfacial properties would be significant even in microgravity.

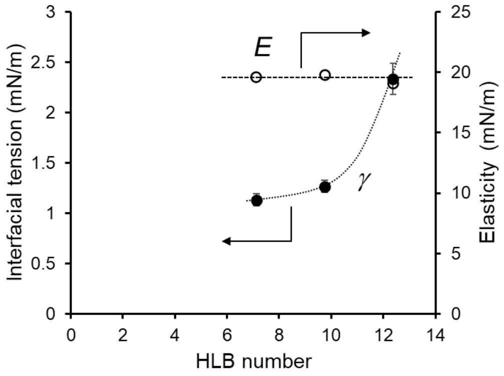

Figure 2. Change in the interfacial tension (γ) and dilational elasticity (E) with the HLB number.

Figure 2 showed the plots of interfacial tensiton (γ) and dilational elasticity (E) as a function of the surfactant HLB number. γ increased with the HLB number, being consistent with the emulsion droplet size just after preparation (0 days, Figure 1). On the other hand, E was almost independent on the HLB number. This was very curious result because it was known that E strongly correlated with coalescence, while the present results were not the case. Although it has not been definitively concluded from these results yet, we can expect that there could be several factors impacted on the coalescence between the oil droplets: (1)

Marangoni effect over the interface of the emulsion droplet, and (2) collision frequency of the emulsion droplets. The second hypothesis would not be plausible because the more hydrophilic interface (higher HLB) arises the higher repulsive force of inter-droplet, resulting in lowering the collision frequency. On the other hand, fluctuation of the surfactant molecules over the oil-water interface occurs when the emulsion droplets come close to each other. If the surfactant molecules can quickly compensate the increase in the interfacial free energy, coalescence is unlikely to occur. Although this has not been fully verified to date, we will investigate the relationship between the Marangoni effect at the interface and coalescence in the future.

4. Conclusions

We had investigated the stability of the various O/W emulsions in terms of different HLB numbers and oils. Our results in quasi-microgravity suggested that coalescence may play a significant role in the stability of the emulsion where surfactant and oil are not optimized. In addition, the interfacial elasticity, which was considered as a critical parameter in coalescence, did not significantly affect the emulsion stability (coalescence) in the present system. Coalescence is a very difficult phenomenon to evaluate even in terrestrial gravity, but our current predictions will be verified by accumulating further data in the future.

Conflicts of Interest

The authors declare no conflict of interest.

Nomenclature

Nomenclature is an optional section where the many variables and symbols are defined. Nomenclature should be provided as the Table with transparent border lines.

r	Radius of droplet (nm)
γ	Interfacial tension (mN/m)
V_m	Molar volume of dispersed phase (L/mol)
R	Gas constant (J/(mol・K))
T	Absolute Temperature (K)