Structures of Silica Particles Localized at the Interface of Liquid Droplet

エマルション界面におけるシリカ微粒子の局在化構造

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1. Introduction

Pickering emulsion consisting of liquid droplets stabilized by solid microparticles has gained much attention in the field of cosmetics, inks and drug delivery system. In order to ensure that the microparticles are localized at the interface of liquid droplet, the ultrasonic spectroscopy technique with scattering function analysis is considered to be an effective method since megahertz ultrasound is suitable to evaluate the micron-sized emulsion, and more recently the effective shell properties can be determined by a core-shell model.[1, 2]

In this paper, two model systems were considered to study the effects of particle localization at the interface of droplet on the ultrasonic properties; i.e., Case 1: the silica particles and the droplets are independently dispersed in liquid (**Fig. 1a**), and Case 2: the silica particles are effectively localized at the interface of the droplets (**Fig. 1b**). Note that the properties of the shell part in the core-shell model should be given by the average parameters consisting of solid particles and liquid components. Therefore, the composition of silica particle in the shell part was evaluated by taking account of the particle coverage at the droplet interface.
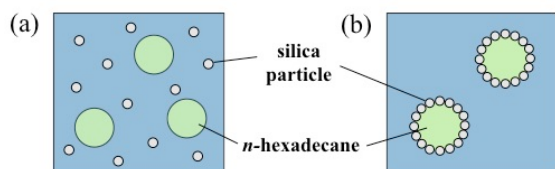

Fig. 1 (a) silica particles are dispersed in water phase (case 1), (b) ideal Pickering emulsion (case 2).

2. Materials

Monodisperse hydrophilic silica particles (Seahoster KE-P10) were purchased from Nippon Shokubai Co. (Japan). Scanning electron microscopy (SEM) images of the silica particles are shown in **Fig. 2**. The average particle diameter was $d_p = 116$ nm, and the density was $\rho_p = 1.9$ g/cm^3.

n-hexadecane (Wako pure Chemical Co., Japan) was employed as an oil phase.
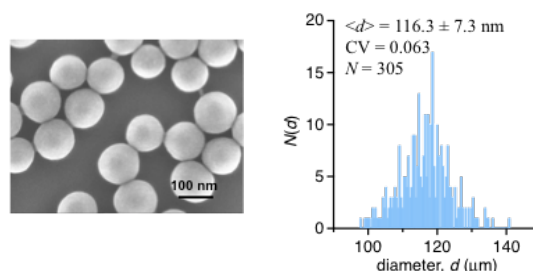

Fig. 2　SEM image (left) and size distribution of silica particles (right).

Case 1: Silica particles are dispersed in water phase.

In order to stabilize the oil droplets without silica particles, 0.2 wt% SDS (Sodium Dodecyl Sulfate) was added to the water phase. Such an O/W emulsion was prepared using SPG (Shirasu Porous Glass) membranes to obtain monodisperse emulsion (**Fig. 3a**). Then, the silica particles were dispersed in 0.2 wt% SDS solutions, and the silica-particle suspension and the emulsion were mixed together to obtain the sample as shown in Fig.1a.

Case 2: Silica particles are localized at the droplet interface.

Adsorption of solid particles at the oil-water interface requires the partial wetting of the solid surface to the water and oil phases. Hydrophobically modified silica particles were prepared by condensation of DMDES (dimethyldiethoxysilane) and hydrophilic silica particles with hydrochloric acid in ethanol solution. In order to reduce the strong repulsion between the charged particles at the water / oil interface, the silica particles were dispersed in 1 M NaCl aqueous solution under sonication. Then, O/W Pickering emulsion was prepared using a homogenizer (7000 rpm, 10 min.) with the 0.5 wt% hydrophobically modified silica particles as a stabilizer (**Fig. 4a**). The sample was purified by removing the remaining silica particles by precipitation.

3. Measurements and Rsults

The sample was placed between two water-immersion transducers to carry out ultrasonic measurements in water at 25°C. Longitudinal wave transducers with the nominal center frequencies of 20 and 30 MHz were used to investigate the frequency dependence of the attenuation coefficient α and the phase velocity c of the sample in the range of 10 - 35 MHz.

The results of the case 1 sample are shown in **Fig. 3b**. The two dotted lines respectively represent the theoretical curves reproduced by silica particles in water and O/W emulsion stabilized by SDS. On the other hand, the solid line corresponds to the sum of the two dotted lines. The experimental results agreed with the solid line, indicating that the silica particles and the droplets were dispersed independently in liquid. The results were supported by the acoustic scattering model.
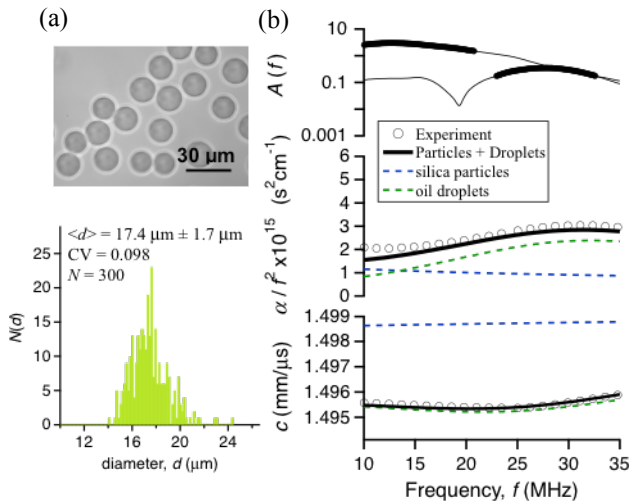

Fig. 3 (a) Size distribution of emulsion stabilized with SDS, (b) The frequency dependence of α and c of Case 1.

Subsequently, the ultrasonic spectra of Pickering emulsion (case 2) were studied by US as shown in **Fig. 4b**. From the first look, the result was quite different from the case 1. While the similar calculation to the case 1 was performed, the experimental data could not be reproduced by the sum of silica suspension and O/W emulsion. Therefore, the scattering theory based on the core-shell model is examined. In this model, the silica particles localized at the droplet interface are considered as a shell where the particle diameter is employed as the shell thickness. It should be noted that the shell part consists of silica particle and liquid components. Provided that the particle structure satisfies closest packing on the liquid interface, the volume fraction in the shell part is approximately 60%. In addition, there are many

reports showing that Pickering emulsion stably exists for long period even at very low surface coverage.[3] Therefore, the average acoustic properties of shell part were calculated as a function of the composition of water, hexadecane and silica particles. As the result, when the volume fraction of the silica particles was 22% (which corresponds to surface coverage of 38%), the theoretical curve satisfactory reproduced the experimental data.
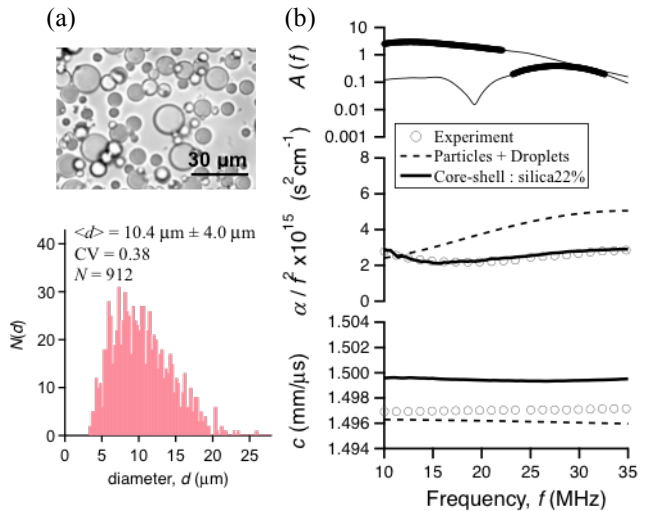

Fig. 4 (a) Size distribution of Pickering emulsion, (b) The frequency dependence of α and c of Case 2.

4. Conclusion

We proposed a new method to evaluate particle localization at the interface of micron-sized emulsion by the ultrasonic spectroscopy technique. When the particles were localized at the droplet interface, the result was reproduced by the scattering theory of the modified core-shell model. The shell properties were calculated as a function of the volume fraction of the solid particles and liquid.

References

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