Drying of Water Droplets Stabilized by Surfactant Molecules or Solid Particles Immersed in a Non-Volatile Oil Layer

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Introduction

Liquid droplets disperse stably in another immiscible liquid when the liquid-liquid interface is sufficiently stabilized. Surfactant molecules are widely used to form emulsions, but solid particles are also known as a stabilizer. Dispersed liquid droplets are wrapped by solid particles, which severely prevents coalescence of droplets. Particle-stabilized emulsions, sometimes called Pickering emulsions, have been extensively studied and several applications, such as cosmetics[1,2] and drug carriers,[3] are proposed. One of the important features of particle-stabilized emulsions is that particles that adsorb at the liquid-liquid interface form solid shells. They buckle during drying and droplets severely deform, in contrast to the isotropic shrinkage of drying liquid droplets stabilized by surfactant molecules. Deformation of liquid droplets could affect drying kinetics of individual dispersed droplets, but detailed relation is not studied sufficiently. This is one of the motivations in this work.

We also focus on the effect of thickness of the continuous phase in which the dispersed liquid droplets are immersed. When we use emulsion-based cosmetics or paints, we coat them and drying spontaneously occurs. In this situation, dispersed liquid droplets are generally in a thin liquid layer of the continuous phase. Since drying droplets are immersed, it is reasonable to consider that they do not directly contact to air. Thus direct vaporization of drying liquid droplets is not the main path for

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drying and different kinetics is necessary to understand the drying kinetics. In this sense, we consider that study of drying kinetics of immersed liquid droplets is necessary.

In this work, we studied drying of water droplets stabilized by solid particles. We also examined drying of water droplets stabilized by surfactant molecules for comparison. Drying kinetics of water droplets is discussed.

Experimental

Materials: We used pure water as dispersed phase. Dimethylpolysiloxane (KF-96L-5cs, Shin-Etsu Chemical Co., Ltd, Tokyo, Japan) was used as the involatile oil phase. As surfactant molecules, we used PEG-9 polydimethylsiloxyethyl dimethicone (KF-6028, Shin-Etsu Chemical Co., Ltd) with a hydrophile–lipophile balance (HLB) of 4.0. We also used four types of hydrophobic particles, SiO_2 nanoparticles (AEROSIL R 972, Nippon Aerosil Co., Ltd, Tokyo, Japan) with a diameter of 16 nm, SiO_2 submicrometer particles (QSG-100, Shin-Etsu Chemical Co., Ltd) with a diameter of 110 nm, silicone microparticles (KMP-590, Shin-Etsu Chemical Co., Ltd) with a diameter of 2 μm, and plate-like mica particles (SA-Maika M-302, Miyoshi Kasei, Inc., Tokyo, Japan). Three types of particles except for the mica particles were spherical. The size of mica particles is on the order of tens of micrometers. All materials were used as received.

Sample preparation: In preparation of emulsions, we used a vortex mixer (VORTEX Genius 3, IKA Works, Inc., Staufen, Germany) or a stirred mixer (Pencil mixer DX type, AS ONE Co., Osaka, Japan). In some cases, we further used a rotor–stator homogenizer (T25 digital ULTRA-TURRAX, IKA Works, Inc.). The weight fraction of water to the oil was 1:1. The weight fractions of the stabilizers were different owing to the difference in the ability to stabilize the water-oil interface. We set 0.4 wt% for the nanoparticles, 6 wt% for the submicrometer particles, 14 wt% for the silicone microparticles, 6 wt% for the mica particles, and 0.2 wt% for the molecular surfactant. More detailed preparation procedures are in ref. 4.

Observation of drying water droplets

An optical microscope (AZ100, Nikon, Tokyo, Japan) was used to observe drying droplets. Images were recorded at a constant interval by a digital camera (D5300, Nikon). The creamed sample was put on a glass plate. We diluted the drying sample by adding the silicone oil to decrease the number density of water droplets for clear observation. Drying was conducted in a chamber, in which temperature was kept 33-35 ℃. Humidity controlled air was introduced into the chamber so that the relative humidity in the chamber was 36-38%. The thickness of oil layer for observation was about 110 μm.

Results and Discussion

Fig.1 shows images of drying droplets stabilized by the molecular surfactant (Fig. 1a) or solid particles (Fig. 1b). Isotropic shrinkage was observed for surfactant-stabilized droplets. Conversely, droplets buckled and deformed in the samples stabilized by solid particles. We first analyzed drying kinetic of surfactant-stabilized water droplets. Fig. 2a shows time lapses of diameter of drying droplets. We shifted the drying time so that the total drying time of each droplet was 14.5 min, which was the drying time of the droplet with a diameter of 110 μm. All data was collapsed on a single master curve. This clearly shows that the initial diameter of droplet is not an important issue in drying kinetics.

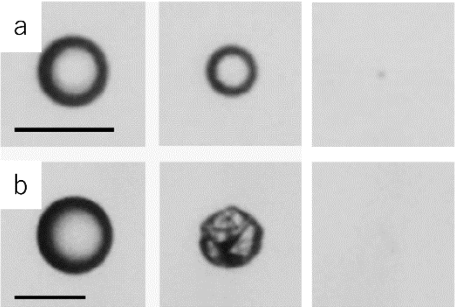

Fig. 1 Optical microscope images of water droplets stabilized by (a) the molecular surfactant and (b) SiO_2 nanoparticles. Drying proceeded from left to right. The scales bars are 100 μm

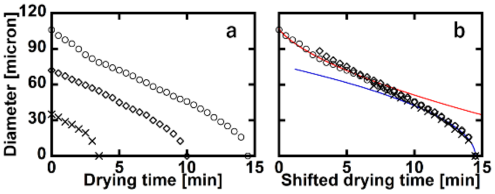

Fig. 2 (a) Time lapses of diameter of drying droplets and (b) shows the same data but drying time was shifted so that the total drying time of each droplet is 14.5 min, which corresponds to the drying time of the droplet with a dimeter of 110 μm. The red and blue lines in (b) represent simulated results using “vertical diffusion” (red) and “radial diffusion” (blue), respectively.

Drying of water droplets immersed in an involatile oil consists of four steps, (i) dissolution of water molecules into the oil phase, (ii) diffusion of dissolved water molecules to the oil-air interface, (iii) vaporization of dissolved water molecules and (iv) transport of water vapor from the interface to gas. [5,6] We examined drying of water droplets in a thicker oil layer with a thickness of 450 μm and found that drying rate clearly decreased. This strongly suggests that the diffusion of dissolved water molecules in the oil layer would be rate-determining step.

On the basis of this results, we proposed two diffusion models.[4] The first one is that the oil-air interface is very close to the oil-water interface of a droplet. In this situation, transport of dissolved water molecules is approximately described as vertical diffusion to the oil-air interface (Fig. 3 left). This approximation is applicable to droplets, the size of which is comparable to the thickness of the oil layer. The other case is that droplets are small and the oil-air interface is far away from the droplets (Fig. 3 right). Radial diffusion is considered in this case. Mathematical models for these two cases agree well with the master curve in Fig. 2b. This suggests that diffusion of water molecules is a key factor that determines drying rate of water droplets immersed in oil layer.

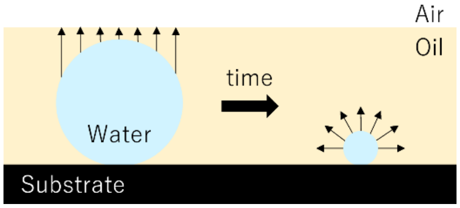

Fig. 3 Schematic illustration of two diffusion models.

For particle-stabilized droplets, we are not able to measure time lapses of the total volume of drying droplets, since droplets buckled in these samples. Thus we measured the total drying time of individual droplets t_0 and used them as the representative values for drying rate. Fig. 4 shows all data of t_0 from the droplets stabilized by spherical particles. We did not find any clear difference between droplets stabilized by spherical solid particles or surfactant, suggesting that drying kinetics is not affected by the particulate shells or its deformation during drying. This is probably because the diffusion of dissolved water molecules is the rate-limiting step in this system. Droplets stabilized by plate-like mica particles shows a scatted data of t_0. Some droplets showed slower drying, while some others showed faster drying compared to the other samples. Because of the plate-like shape of particles, packing structure on the oil-water interface is different from those of spherical particles and it would lead to different drying kinetics.

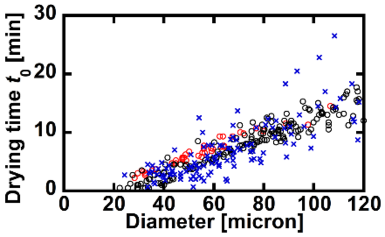

Fig. 4 Dependence of the total drying time t_0 on the initial diameter of droplets. Droplets stabilized by surfactant molecules (red circles), SiO_2 nanoparticles (black circles) and mica particles (blue crosses) were summarized.

Conclusions

Drying of water droplets immersed in involatile oil layer was examined. For spherical solid particles, formation of the particulate shells as the oil-water interface or its deformation did not affect drying kinetics compared to those of droplets stabilized by surfactant molecules. Conversely, we found variation in drying time in droplets stabilized with plate-like mica particles, suggesting that shape of particles would be a key issue to control drying droplets stabilized by solid particles.

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