他物質衝突時の乳剤安定性に及ぼす初期粒子密度の影響

Influence of the Initial Particle Packing Density on the Final Stability of an Emulsion Upon Collision with Another Material.

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A monolayer of particles at an air/water interface was used to model a Pickering emulsion, in order to determine the effect of the size of the particles in a monolayer at an air/water interface and their packing density on the physico-chemical properties of a model Pickering emulsion (a monolayer), e.g., stiffness, adhesive ability, and change in particle packing, after a collision by a particle in the water phase. A Langmuir trough was used to obtain surface pressure-area per molecule isotherms of bare TiO_2 particulate monolayers at an air/water interface and the Monolayer Particle Interaction Apparatus (MPIA) to directly study the forces between the TiO_2 monolayers at an air/water interface and a micro-sized TiO_2 particle in the subphase. The effect of the packing density of the particles in the monolayer on its stability was observed by optical microscopy, while the forces were being measured by bringing the micro-sized TiO_2 particle in the subphase in and out of contact with the TiO_2 monolayer.

Langmuir monolayers of bare, hydrophilic TiO_2 particles were directly formed at the air/water interface by using a subphase with a pH below the isoelectric point of TiO_2 . The effects of the particle size on the physical properties of the monolayer were then investigated by using particles with a diameter of 75 nm, 300 nm, 3 μm and 10 μm . The packing density influence was determined by measuring the forces and by imaging the air/liquid interface in the presence of the monolayer at different surface pressures. We found that the particulate monolayer became more deformable and instable as the size of the particle decreased. Large particles (micro-sized) gave the least deformable monolayer, where monolayers of a high particle packing density gave stable monolayers even upon contact by a micro-sized particle.

研究目的

乳剤は食料・化粧品・薬剤等身の回りの多くの分野で利用されている。一般に乳剤の形成には両親媒性の界面活性剤が用いられるが、水-油界面へ吸着した粒子も同様の働きを示すことが知られており、Pickering乳剤と呼ばれる。粒子サイズ、種類、形、

パッキングが安定性に影響するが、前3者はほとんど経時変化しないと考えられる。一方、界面粒子のパッキングは、界面での粒子間相互作用やバルク相からの粒子衝突により時々刻々と変化する。パッキング密度が小さくなると、乳剤が不安定化することは容易に想像できる。

本研究では、 TiO_2 粒子膜をPickering乳剤のモデル

系として実験を行うことにより、界面粒子パッキング及び水相からの他粒子の衝突がPickering乳剤の安定性に与える影響を解明することを目指す。具体的には、ラングミュア・トラフ、フォース測定装置と光学・蛍光顕微鏡が一体化した装置(MPIA)を用いて、気-水界面の TiO_2 粒子膜と水相にある $10\mu\text{m}$ 程度の TiO_2 粒子間に働く相互作用力、及び水相から TiO_2 粒子が衝突する際に引き起こされる粒子膜の構造変化を評価する(図2)。 TiO_2 粒子サイズ・粒子密度を系統的に変化させて実験を行うことにより、初期粒子密度及び粒子の衝突強度が TiO_2 粒子膜の安定性に与える影響を明らかにし、安定なPickering乳剤形成に必要な最適粒子パッキング条件を見いだす。

研究成果の概要

1. Introduction

Emulsions are used in food, drinks, cosmetics, pharmaceutical and technological applications to produce high quality products at a cheaper price. A stable emulsion inhibits the coalition of oil droplets and the coagulation of phases in the materials. Oil in water emulsions can be stabilized by the adsorption of particles at the oil/water interface of the emulsion, giving a Pickering emulsion. The size, shape, chemical and mechanical properties, and packing density of the particles have been reported to determine the stability of the emulsion.

In this study, we determined how the size of the particles used in a Pickering emulsion and their packing density affects the stability of the emulsion,

after another material has collided with it. We achieved these studies by modelling the Pickering emulsion with a monolayer of particles at an air/water interface, see Fig. 1. The Monolayer Particle Interaction Apparatus (MPIA) was used to control the packing density of the particles at the air/water interface, and to measure the change in the physical properties of the monolayer upon contact with a large particle from bulk (probe), which models the colliding material. Information on the physical properties was obtained by measuring the force curves between the probe particle and the particles in the monolayer, by observing the movement of the particles in the monolayer with the overhead microscope.

2. Experimental

Stable monolayers of TiO_2 particles can be made at air/pH 2 water interfaces for particles diameters (D) ranging from 300 nm to $10\mu\text{m}$ [1]. We therefore used TiO_2 particles of different sizes ($D=75\text{ nm}$, 300 nm, $3\mu\text{m}$ and $10\mu\text{m}$) and made TiO_2 particulate monolayers at air/pH 2 water interfaces.

The forces between a large particle in the bulk water and the particulate monolayer at an air/water interface were measured by using the MPIA, see Fig. 2. A large TiO_2 particle ($D=3\mu\text{m}$) was used as the probe particle, which was glued onto an Atomic Force Microscope cantilever. The forces between the probe and the particulate monolayer were measured while moving the probe from the bulk pH 2 water to

Pickering emulsion

Nano/micro-particle monolayer at air/water interface

Fig.1

Fig.2

the monolayer. Information on the adhesion between particle and interface and the deformability (stiffness) of interface can also be obtained from the force curves. The adhesion is determined from magnitude of the adhesion in the retraction force curve, and is divided by the square radius of the approaching TiO_2 particle (F_{ad}/R^2) in order to compare the adhesion data from different systems. The stiffness (S_N) is determined from the slope of the force curve in the compliance region, and is calculated by dividing the slope of the force curve obtained for the particulate monolayer at the air/pH 2 water interface and a force curve obtained at a hard surface (mica) in water. $S_N=1$ means that the monolayer has the same stiffness of a mica surface, and $S_N<1$ means that the interface is deformable.

The surface pressure (Π)-area isotherms of the particulate monolayer were simultaneously measured using the Langmuir trough and Wilhelmy plate part of the MPIA. The optical images of the particulate monolayers were taken from above the monolayer, while the probe was moved from the bulk to the monolayer.

3. Results and discussion

3.1 Surface pressure-area isotherms of the particulate monolayers

Langmuir monolayers of bare, hydrophilic TiO_2 particles were directly formed at the air/water interface by using a subphase with a pH below the isoelectric point of TiO_2 [1]. Particles with $D=75$ nm,

300 nm, $3\mu\text{m}$ and $10\mu\text{m}$ formed stable monolayers at the air/pH 2 water interface, as seen by the surface pressure- area isotherms in Fig. 3. All the particle sizes showed loose and dense packing regimes. This result meant that we could use these particles to determine the effect of the particle size and particle packing on the physical properties of the monolayer.

Fig.3

Information about the stability of the particulate monolayers upon the collision of a particle from the bulk was obtained by using the MPIA. Here, the surface pressure versus area isotherms of the particulate monolayers, the force versus particle-monolayer separation distance curves, and the optical images of the monolayers were simultaneously measured. The effects of the size of the particles used in the monolayers on the physical properties of the monolayers were investigated by using particles with a diameter of 75 nm, 300 nm, $3\mu\text{m}$ and $10\mu\text{m}$. The packing density influence was determined by measuring the forces and by imaging the air/pH 2 water interface in the presence of the monolayer at different surface pressures.

3.2 Optical microscope images: effect of surface pressure on packing and aggregation

Optical microscope images showed that decreasing the area per particle increased the packing density of the particles, see Figs. 4A-B. The particles were seen to aggregate to form islands of particles at the air/water interface at low surface pressures ($\Pi=3$

mN/m, i.e., high area per particle) to also give areas of bare air/pH 2 water interfaces, see Fig. 4A. The effect of decreasing the area per particle, i.e., increasing the surface pressure ($\Pi=9$ mN/m), caused these particulate islands to be pushed together to form densely packed particulate monolayers, see Fig. 3B. No bare air/pH 2 water interfaces could be seen at high surface pressures.

Fig.4

Information on how the packing of the particles in the monolayer affects its stability can be obtained by comparing the optical images of the monolayers at the air/pH 2 water interface before and after several impacts of the probe particle from the bulk. The images of the particles in the monolayers with a loose packing density ($\Pi=3$ mN/m) showed a change in the shapes, sizes and positions of the islands formed by the particles at the air/pH 2 water interface, i.e., lateral movement of the particles, when a particle from the bulk was brought to the air/water interface, compare images Fig. 4A and Fig. 4C. However, no lateral movement in the particles in the monolayer was observed for the densely packed monolayers ($\Pi=9$ mN/m), compare images Fig. 4B and Fig. 4D. This result indicates that a densely packed monolayer is more robust than a loosely packed monolayer.

3.3 Force curves: ability of probe particle to enter particulate monolayer

The force curves were measured between the probe and the monolayer, as the probe was brought from the bulk to the monolayer. The approach force curves showed a repulsive force, commencing when the probe was in the vicinity of the monolayer. A linear repulsive force regime was observed, once the probe was in contact with the monolayer. Some of the force curves showed a discontinuity in the repulsive force region, indicated by the arrow in the force curves, see Fig. 5. This discontinuity indicates that the probe particle can break through and enter the particulate monolayer, indicating that the probe particle is attracted to the air/particle/water interface. The occurrence of the break-through increased with the size of the particles used to make the particulate monolayer. Particles with $D \geq 300$ nm showed a break-through for the low packing densities, i.e., loose packing (surface pressure of 3 mN/m). Only particles with $D \geq 3 \mu\text{m}$ showed a discontinuity for the high packing densities, i.e., dense packing (surface pressure of 9 mN/m).

Lateral forces act between two neighbouring particles at the air/pH 2 water interface. The five sources of lateral forces include ¹⁾ van der Waals attraction²⁾, dipole-dipole electric repulsion³⁾, capillary forces due to interfacial deformation by the weight of the particles⁴⁾, capillary forces due to interfacial deformation by contact-line undulation, and ⁵⁾ capillary forces due to interfacial deformation by electric stresses.

The weight induced lateral capillary force between two similar spherical particles can be estimated by calculating the capillary interaction energy and then by comparing that energy with the energy of the thermal motion, kT , where k and T are the Boltzmann constant and temperature. The lateral capillary interaction energy is given by

$$\Delta W = -\frac{\pi \gamma R^6}{18 \kappa^4} \left(2 - 4 \frac{\rho_{\text{TiO}_2}}{\rho_{\text{H}_2\text{O}}} + 3 \cos \theta - \cos^3 \theta \right)^2 K_0(L/\kappa) \quad (1)$$

where K_0 is a modified Bessel function of the second kind zeroth order and $\kappa = \sqrt{\gamma/\rho_{\text{H}_2\text{O}}g}$ is the capillary constant. The lateral capillary interaction energy

Fig.5

therefore increases as the size of the particle increases.

The interaction of the particles in the monolayer is thought to be caused by the repulsive electrostatic forces at larger separations, attractive van der Waals interaction at short separation distances, and inter-particle attractive capillary forces at shorter separations. At low packing densities (low surface pressures), small particles repel each other because of their electrostatic dipole. At high packing densities (high surface pressure), the particles are attracted, due to attractive van der Waals and capillary interactions. The larger particles experience a weight-induced capillary attraction in addition to the dipole repulsion at low surface pressures, causing them to aggregate. Once the particles are close enough, i.e., high surface pressures, the van der Waals attraction also becomes important.

In the case of monolayers with the small particles ($D \leq 300\text{nm}$), the probe particle can enter the monolayer at low surface pressures due to the lateral movement of the particles in the monolayer as a result of their electrostatic dipole, and the attractive van der Waals and capillary interactions between the probe and the monolayer particles. At high surface pressures, the attractions between the particles in the monolayer are too strong to allow the probe to

break and enter the monolayer. In the case of monolayers with larger particles ($D \geq 3\mu\text{m}$), the probe can enter the monolayer at low and high surface pressures, i.e., loose and dense packing regions, due to the stronger electrostatic repulsion between the particles in the monolayer as a result of their larger size, and the van der Waals and capillary force between the probe particle and the particles in the interface.

3.4 Adhesion and deformability of the monolayers

Information on the adhesion between particle and interface and the deformability of interface can also be obtained from the force curves. The adhesion (F_{ad}/R^2) and stiffness (S_N) values of the particulate monolayers are shown in Figs. 6A and B, respectively, as a function of the monolayer surface pressure.

A surface pressure increase caused the adhesion between the colliding probe particle and the particles in the monolayer at the air/pH 2 water interface to decrease, see Fig. 6A. A surface pressure increase decreased the stiffness for particles with $D \leq 3\mu\text{m}$, and increased the stiffness for particles with $D > 3\mu\text{m}$.

An increase in the packing density of the particles in the monolayer decreases the area of the bare air/pH 2 water interface, i.e., the non-particle covered area. The wetting of the probe particle will be

Fig.6

greatest in the case of a bare air/pH 2 water interface, and least in the case of a densely packed particulate monolayer with no bare air/pH 2 water areas. The probability that the probe particle will contact a non-particle covered area will decrease with a surface pressure increase (particle packing density increase), thereby causing the wetting to decrease, and the adhesion of the probe to the air/particle/pH 2 water interface to decrease.

The surface tension of the interface decreases with a surface pressure increase. Thus, the decrease in the stiffness of the particulate monolayers with a surface pressure increase can be explained by the surface tension change. Increasing the surface pressure also decreases the spacing between adjacent particles in the monolayer. Thus, the increase in stiffness with a surface pressure increase can be explained by the increased lateral adhesion between adjacent particles, due to van der Waals and capillary forces. As the capillary interaction increases with size of the particles, the difference in the behavior of the dependence of stiffness on surface pressure for the different particle sizes is thought to be due to the magnitude of the capillary force between the particles. We can conclude from our results that the capillary interactions are important for particles with $D > 3 \mu\text{m}$.

The effect of increasing the particle size on the adhesion and stiffness results can be obtained by comparing obtained at the dense packing densities

($\Pi = 9 \text{ mN/m}$), see Fig. 7. This is because loose and medium packing densities ($\Pi < 9 \text{ mN/m}$) showed air/pH 2 water interfaces that were bare or covered with moveable islands of TiO_2 particles. The forces curves measured in this region can therefore be thought to be the forces between the TiO_2 probe and the bare air/pH 2 water interface and the forces between the TiO_2 probe and the TiO_2 particulate islands at the air/pH 2 water interface. Thus, the effect of the size of the particles in the monolayer on the forces is not clear. Forces obtained in the densely packed regions (surface pressure $\geq 9 \text{ mN/m}$), however, are only the forces between the TiO_2 probe and the TiO_2 particulates at the air/pH 2 water interface, allowing the effect of the size of the particles in the monolayer on the forces to be clear. Here the adhesion is compared as F_{ad} and not F_{ad}/R^2 , so as to remove the size dependence from the adhesion values, enabling the size effect to be seen more clearly.

Fig. 7 shows that decreasing the particle size caused the adhesion to decrease and the stiffness to increase. This result is explained by the increased stiffness of the particulate monolayer with a particle size increase. The particle-particle lateral capillary interactions are thought to increase with a particle size increase, stabilizing the monolayer and making it stiffer.

A deformable monolayer acts as a soft material, and deforms to cover the colliding particle. In this case, the contact is not the point contact as is found

Fig.7

in the adhesion between two hard surfaces. It is instead a contact that should be considered in two dimensional terms. A non-deformable monolayer acts as a hard material. It therefore does not cover the colliding particle, but only gives a point of contact. Fig. 7 shows that the particulate monolayer acts as a soft material for small particles but acts as a hard material for larger particles. Further, in the case of the particles in the monolayer being smaller than the probe particle, a deformable monolayer can cover the probe particle more, causing the adhesion to increase, i.e. adhesion between a soft surface (monolayer) and a hard surface, see Fig. 8A. In the case if the particles in the monolayer being larger than the probe particle, the monolayer cannot cover the probe particle, i.e. adhesion between two hard surfaces. Thus, the adhesion will be due to a point contact in this case (regular adhesion force between two hard surfaces), see Fig. 8B.

The stiffness of the particulate monolayer can be controlled by the size of the particles used in the

monolayer, as the particle-particle lateral capillary interactions stabilize the monolayer and are thought to increase with a particle size increase. The stiffer monolayers appear to be able recover quicker than deformable monolayers, after the collision of a particle from the bulk.

4. Conclusions

A particulate monolayer becomes more deformable and instable as the size of the particles in the monolayer decreased. Large particles (micro-sized) gave the least deformable monolayer, where monolayers of a high particle packing density gave stable monolayers even upon contact by a micro-sized particle. The most stable particulate monolayers are therefore thought to be achieved by using micro-sized particles and high particle packing densities.

5. Outlook

The interactions between the particles in the monolayer and interactions between the incoming particle from the bulk and the particles in the monolayer appear to affect the behaviour of the monolayer at the air/liquid interface. Thus, the type of particle colliding with the particles in the particulate monolayer from the bulk is also expected to affect the properties of the monolayer. The effect of using different particles as the probe and as the monolayer particles (e.g., particles with different charges, surface chemical groups) on the physical

Fig.8

properties of the monolayer will be investigated.

6. References

- 1) McNamee, C.E., Yamamoto, S., Butt, H.-J., Higashitani, K. *Langmuir*, 2011, 27, 887-894.

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発表論文

Cathy E. McNamee, Michael Kappl, Hans-Jürgen Butt, "Influence of the size of the particle and packing density in a particulate monolayer on its physical properties at an air/water interface", In preparation.