

Surface-Active Particles with Microstructured Surfaces

Yoshimune Nonomura,^{*,†} Shigeyuki Komura,[‡] and Kaoru Tsujii[§]

Tokyo Research Laboratories, Kao Corporation, 2-1-3 Bunka, Sumida-ku, Tokyo 131-8501, Japan, Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji-shi, Tokyo 192-0397, Japan, Nanotechnology Research Center, Research Institute for Electronic Science, Hokkaido University, N21, W10 Kita-ku, Sapporo 001-0021, Japan

Received July 6, 2005. In Final Form: August 23, 2005

Interfaces adsorbing solid particles have recently attracted great attentions in the field of materials science, because they are useful as templates of well-ordered particle arrays or of microstructured hollow spheres. The solid particles are adsorbed at the interfaces and form self-assembled structures when the particles have suitable wettability to both fluids. Here, we show theoretically how the microstructure on the particle surface affects their adsorption properties. The physical properties of the interface adsorbing a particle will be described with consideration for surface area magnification due to the microstructure. The microstructure on the surface changes drastically the wettability and the equilibrium position of the adsorbed particle and prevents the particle from adsorption at the interface. The range of the interfacial tensions at which the particle is adsorbed becomes narrower with the increase of the magnification. On the other hand, the particle which is partially covered with the microstructured surface is adsorbed firmly at the interface in an oriented state. We should consider not only the interfacial tensions but also the surface structure to control the adsorption behavior of the particle.

Introduction

The surface-active adsorbed particles align at fluid–fluid interfaces^{1,2} and stabilize emulsions and foams.^{3,4} These emulsions and foams have been applied to food or cosmetic products, because they are stable due to the adsorption of the particles on the interfaces.^{5,6} In recent years, some scientists have focused on the emulsions as a template of functional composite materials. A hollow sphere and a ribosome-like nanocapsule were obtained through the emulsion state.^{7,8}

The mechanism for the adsorption of the surface-active particle has been discussed based on the interfacial energy argument.⁹ The equilibrium position of the adsorbed particle can be quantitatively predicted from the interfacial energy. When spherical particles are adsorbed at a planar interface, the energy depends on the three kinds of interfacial tensions, i.e., between the particle surface and the two fluids. The particle is adsorbed at the interface when the interfacial tensions among the three phases are balanced according to Young's equation. The effect of the particle shape on the adsorption state was also described elsewhere.^{10,11}

The interfacial properties of the particles with the microstructured surface are interesting due to their great potential as industrial materials, such as electronic materials, medical materials, and supported catalysts.¹² Complicated rough structures which exist on the solid surfaces change their wettability drastically.¹³ Wenzel, Cassie, and Baxter supposed the theoretical models which describe the effect of the roughness on the wettability.^{14,15} For example, Tsujii et al. showed that fractal surfaces of a wax, alkylketene dimer, is super water-repellent.^{16–19} Then, the microstructure must affect the behavior of the surface-active particle.

In the present work, we have calculated the interfacial energy of the fluid–fluid interface adsorbing spherical particles with a microstructured surface as illustrated in Figure 1a. We study the effect of the microstructured rough surface on the interfacial energy. The surface area of the spherical particle is r times larger than that of a spherical particle having a smooth surface. The quantity of r is designated as the surface area magnification factor. We can obtain r by measuring specific surface area or by analyzing the surface geometry based on the concept of fractal.¹⁷ The interfacial energy can be calculated taking the increase of the particle surface area into account. We can also predict the behaviors of the spherical particles partially covered with microstructured surface. In general, partial modification of the surface causes the particles to be adsorbed with a fixed orientation at the fluid–fluid

* To whom correspondence should be addressed. E-mail: nonomura.yoshimune@kao.co.jp. Tel: 81-3-5630-9419. Fax: 81-3-5630-9339.

† Kao Corporation.

‡ Tokyo Metropolitan University.

§ Hokkaido University.

(1) Binks, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21.

(2) Kralchevsky, P. A.; Nagayama, K. *Particles at Fluid Interfaces and Membranes*; Elsevier: Amsterdam, 2001.

(3) Nonomura, Y.; Sugawara, T.; Kashimoto, A.; Fukuda, K.; Hotta, H.; Tsujii, K. *Langmuir* **2002**, *18*, 10163.

(4) Nonomura, Y.; Fukuda, K.; Komura, S.; Tsujii, K. *Langmuir* **2003**, *19*, 10152.

(5) Dickinson, E. *An Introduction to Food Colloids*; Oxford University Press: Oxford, 1992.

(6) Kubo, S.; Hirano, I.; Yamada, J. *IFSCC VIIIth International Congress* **1974**, A8.

(7) Velev, O. D.; Furusawa, K.; Nagayama, K. *Langmuir* **1996**, *12*, 2374.

(8) Dinsmore, A. D.; Hsu, M. F.; Nikolaidis, M. D.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006.

(9) Levine, S.; Bowen, B. D.; Paetridge, S. K. *Colloids Surf.* **1989**, *38*, 325.

(10) Nonomura, Y.; Komura, S.; Tsujii, K. *Langmuir* **2004**, *20*, 11821.

(11) Nonomura, Y.; Komura, S.; Tsujii, K. *J. Oleo Sci.* **2004**, *53*, 607.

(12) Yu, S.; Colfen, H. *J. Mater. Chem.* **2004**, *14*, 2124.

(13) Johnson, R. E.; Dettre, R. H. *Contact angle, Wettability and Adhesion*; Wiley: New York, 1964; p 112.

(14) Wenzel, R. N. *Ind. Eng. Chem.* **1949**, *28*, 988.

(15) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.

(16) Onda, T.; Shibuishi, S.; Satoh, N.; Tsujii, K. *Langmuir* **1996**, *12*, 2125.

(17) Shibuishi, S.; Onda, T.; Satoh, N.; Tsujii, K. *J. Phys. Chem.* **1996**, *100*, 19512.

(18) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuishi, S. *Angew. Chem., Int. Ed.* **1997**, *36*, 1011.

(19) Shibuishi, S.; Yamamoto, T.; Onda, T.; Tsujii, K. *J. Colloid Interface Sci.* **1998**, *208*, 287.

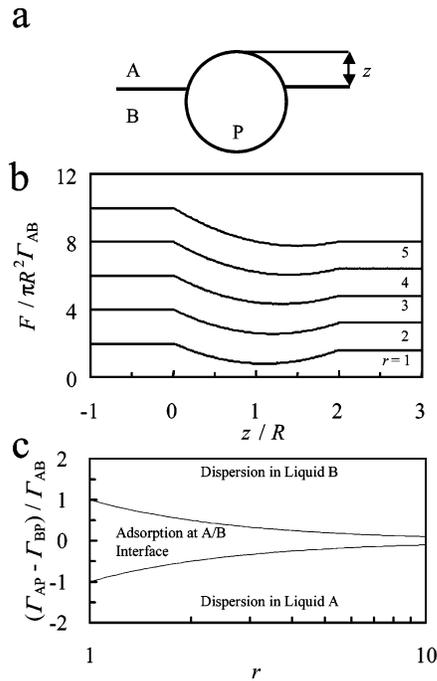


Figure 1. Effect of microstructured surface on the adsorbing state of the particle. (a) Schematic illustration of an interface adsorbing a particle P. The particle P is adsorbed at the interface between fluid A and B. z is an immersion depth of the particle. (b) The dimensionless interfacial energy $F/(\pi R^2 \Gamma_{AB})$ against immersion depth z/R . The parameters are as follows, $\Gamma_{AP}/\Gamma_{AB} = 0.4$, $\Gamma_{BP}/\Gamma_{AB} = 0.5$. The surface area magnification factor r is the ratio of the surface area of the particle P to that of the particle of smooth surface whose diameter is R . (c) The adsorption-dispersion state diagram of the particle as functions of $(\Gamma_{AP} - \Gamma_{BP})/\Gamma_{AB}$ and r .

interface.²⁰ Some methods for the partial modification have been proposed recently.^{21,22} We demonstrate here that the partial modification of the surface is one of the most effective methods to control the surface activity of the particles.

Results and Discussion

We now discuss the adsorption of particle P at the fluid–fluid interface as shown in Figure 1a. Let F be the interfacial energy per particle when it is adsorbed at the interface between fluid A and B. Then F is given by $F = 4\pi r R^2 \Gamma_{AP}$ or $F = 4\pi r R^2 \Gamma_{BP}$ when the whole particle is immersed either in the fluid A or B, respectively. Here R is the radius of the particle, and Γ_{ij} is the interfacial tension between the phases i and j . When the particle is adsorbed at the interface between the fluid A and B as shown in Figure 1a, F is given by eq 1

$$F = 4\pi r R^2 \Gamma_{BP} - 2\pi R \{ \Gamma_{AB} - r(\Gamma_{AP} - \Gamma_{BP}) \} z + \pi \Gamma_{AB} z^2 \quad (1)$$

where z is the immersion depth into the fluid A. In this interfacial energy, we have taken into account both the contact of the particle surface with the fluid A and the elimination of the interface between the fluid A and B. The above energy F attains a minimum at z_{\min}

$$z_{\min} = \left\{ \frac{\Gamma_{AB} - r(\Gamma_{AP} - \Gamma_{BP})}{\Gamma_{AB}} \right\} R \quad (2)$$

Then the corresponding minimized energy is given by

$$F_{\min} = 4\pi r R^2 \Gamma_{BP} - \pi R^2 \frac{\{ \Gamma_{AB} - r(\Gamma_{AP} - \Gamma_{BP}) \}^2}{\Gamma_{AB}} \quad (3)$$

where the first term is the energy when the particle is immersed in the fluid B, and the second term is the energy change due to the adsorption of the particle at the fluid–fluid interface.

The surface area magnification factor r highly changes the adsorbing state of the particle. Figure 1b shows the profile of F in the range of $1 \leq r \leq 5$ when $\Gamma_{AP}/\Gamma_{AB} = 0.4$ and $\Gamma_{BP}/\Gamma_{AB} = 0.5$. Both z_{\min} and F_{\min} become larger with increasing the factor r . The equilibrium position of the particle at the fluid–fluid interface is determined not only by the interfacial tension of the particle surface but also the surface area of the microstructured particle. This can be understood by noting that the interfacial energy F consists of two parts. The first one is the surface energy between the particle P and the liquids. The second one is the energy change due to the elimination of the interface between fluids A and B. The effective increment of the particle surface area influences the first factor directly, although it does not affect the second one. Therefore, the equilibrium position shifts to the fluid A side when the particle has a relatively higher affinity to the fluid A.

The particle cannot be anchored at the fluid–fluid interface and is dispersed in the fluid phases when its surface area becomes large. Thus, wettability of the particle determines if the particle exhibits the surface activity or not. The particle is adsorbed at the interface when the equilibrium position satisfies $0 \leq z_{\min} \leq 2R$ and, hence, eq 4

$$-r^{-1} \leq \frac{\Gamma_{AP} - \Gamma_{BP}}{\Gamma_{AB}} \leq r^{-1} \quad (4)$$

The above condition is drawn in Figure 1c which indicates that the particle adsorbs at the fluid–fluid interface when the values of r and Γ_{ij} are suitable. The particle is dispersed in the fluid A [B] if $(\Gamma_{AP} - \Gamma_{BP})/\Gamma_{AB}$ is smaller than r^{-1} [larger than r^{-1}]. The range of the interfacial tensions at which the particle is adsorbed becomes narrower with the increase of r . The allowed range for adsorption is

$$-1 \leq \frac{\Gamma_{AP} - \Gamma_{BP}}{\Gamma_{AB}} \leq 1$$

when $r = 1$, whereas it is

$$-0.2 \leq \frac{\Gamma_{AP} - \Gamma_{BP}}{\Gamma_{AB}} \leq 0.2$$

when $r = 5$. We should consider not only the interfacial tensions but also the surface structure to control the adsorption behavior of the particle.

Let us consider next a spherical particle partially covered with the microstructured surface as shown in Figure 2a,b. We assume here that (i) the hemisphere P_m is covered by microstructured surface, whereas the other hemisphere P_s is a smooth one, and (ii) the surface area of the P_m region is r times larger than that of P_s . The interfacial energy F decreases drastically when the particle in fluid B approaches to the interface from the P_m side

(20) Casagrande, C.; Fabre, P.; Raphael, E.; Veyssie, M. *Europhys. Lett.* **1989**, *9*, 251.

(21) Fujimoto, K.; Nakahama, K.; Shidara, M.; Kawaguchi, H. *Langmuir* **1999**, *15*, 4630.

(22) Hugonnot, E.; Carles, A.; Delville, M. H.; Panizza, P.; Delville, J. P. *Langmuir* **2003**, *19*, 226.

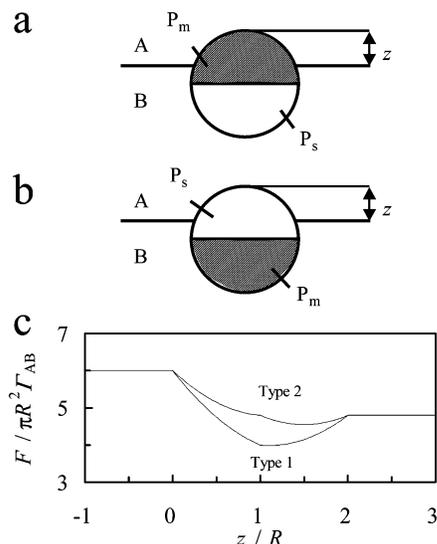


Figure 2. Adsorption of partially microstructured particle. (a) The particle consisting of the hemisphere of P_m and P_s part approaches from the P_m side (type 1). (b) The particle of above approaches from the P_s side (type 2). (c) The dimensionless interfacial energy $F/(\pi R^2 \Gamma_{AB})$ against immersion depth z/R . The parameters are as follows, $\Gamma_{AP}/\Gamma_{AB} = 0.4$, $\Gamma_{BP}/\Gamma_{AB} = 0.5$, $r = 5$.

(Figure 2a,c type 1). In this case, the energy F decreases with the particle adsorption and the cusp is located at the boundary between the P_m and the P_s part, i.e., $z = R$. On the other hand, when the particle contacts with the interface from the P_s side, the energy change is smaller than the previous case (Figure 2b,c type 2). The cusp appears also at $z = R$. These results indicate that the partial modification of the surface increases the surface activity and fixes the particle direction at the fluid–fluid interface, even if the bulk material is completely the same.

The present theory can be applied only with the particle having fine microstructures. The assumption, that the

interfacial energy is seen as multiplied by the factor r , does not work when the roughness is above a critical value r_c .²³ If $r > r_c$, the contact surface of the particle with the fluid consists of the solid surface and the fluid which exist in the ditch on the particle surface. The quantity r_c is found to be $(\phi_s - 1)/\cos \theta + \phi_s$ which is close to $-1/\cos \theta$.^{24,25} Here, θ and ϕ_s are the Young contact angle at the three phase contact line and the actual ratio of the solid–fluid interface on the surface. For example, the quantity of r_c is 10 when $\Gamma_{AP} = 16 \text{ mN m}^{-1}$, $\Gamma_{BP} = 20 \text{ mN m}^{-1}$ and $\Gamma_{AB} = 40 \text{ mN m}^{-1}$.

Conclusions

In this paper, we have shown that the surface activity of the solid particle can be controlled by the microstructure on the particle surface. The strength of the adsorption and the direction of the particle at the fluid–fluid interface are governed by the interfacial tensions and the microstructure of the particle surface. We can inscribe the microstructure on the particle surface. For example, one of the present authors (K.T.) has succeeded in preparing microstructured particles by the spray dry method.²⁶ Some predictions in this work have not yet been proven by the experiments. Further experimental and theoretical studies are necessary to understand the behavior of the surface-active particles.

Acknowledgment. The authors thank Drs. T. Onda, N. Sato, S. Shibuichi, Y. Murase, and H. Mayama for their kind and useful discussions.

LA051816M

(23) de Gennes, P.-G.; Brochard-Wyart, F.; Quere, D. *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*; Springer-Verlag: New York, 2003; Chapter 9.

(24) Bico, J.; Thiele, U.; Quere, D. *Colloids Surf. A* **2002**, *206*, 41.

(25) Patankar, N. *Langmuir* **2003**, *19*, 1249.

(26) Mayama, H.; Tsujii, K. Creation of a Fractal Body, *11th International Conference on Organized Molecular Films*, O55, June 26–30, Sapporo, Japan 2005.