Adsorption of Disk-Shaped Janus Beads at Liquid−Liquid Interfaces

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Surface-active powders have recently attracted much attention in the field of colloid and surface science, particularly in emulsion science.[1] When certain wettability conditions are satisfied, solid particles exhibit surface activity.[1−4] Hydrophobic silica, iron oxide, clay mineral, carbon black, and polymer latex are some examples of the particles. The adsorbed surface-active powders align at liquid−liquid interfaces and form self-assembled structures.[2,3] The so-called "Janus beads" (J-beads) having two surface regions of different wettability are unique particles which can be compared with ordinary surfactant molecules.[5] As a result of their amphiphilic nature, the J-beads exhibit stronger surface activity than the homogeneous surface-active powders. It was shown that spherical J-beads are anchored along the boundary line of two surface regions.

A mechanism for the adsorption of homogeneous surface-active powders has been described by Levine et al. based on the adsorption energy argument.[6] When a spherical particle is adsorbed at a planar liquid−liquid interface, the adsorption energy is governed by the various interfacial tensions between the particle and the liquids as well as the particle radius. The particle is adsorbed at the interface when the interfacial tensions among the three phases are balanced according to the Young's equation. For the J-beads, on the other hand, Clint and Binks obtained the corresponding adsorption energy to see the effect of the particle amphiphilicity.[7] They showed that the amphiphilic J-beads have a typically larger adsorption energy (hence, stronger adsorption) than the homogeneous particles.

For traditional surfactant molecules, effects of the molecular shape on the interfacial properties have been extensively studied by using the models proposed by Israelachvili or Helfrich.[8,9] However, there is little precedent literature as to the shape of the surface-active

particle. In our previous experimental studies, we showed that the shape of the particles indeed affects their self-assembled structures.[2,3] Rossmy also reported that the morphology of the emulsions stabilized by J-beads depends on the geometrical property of the beads.[10] Recently, Brown et al. have shown that amphiphilic curved disks distort an air−water interface, giving rise to anisotoropic forces between the disks.[11] These observations imply that the self-assembled structures of the surface-active particles are governed not only by the wettabilities but also by the shapes of the particle.

In the present work, we obtain the adsorption energy of the disk-shaped J-beads as illustrated in Figure 1a. In contrast to the spherical J-beads, the adsorption energy changes discontinuously for the disk-shaped J-beads. We also show the effect of the adsorption on the geometry of the liquid−liquid interface.

We discuss the adsorption of a disk-shaped J-bead at a liquid−liquid interface. As shown in Figure 1a, a disk-shaped J-bead consists of part P_1 with thickness l_1 and part P_2 with thickness l_2. Let F be the adsorption energy per bead when it is adsorbed at the interface between the liquid A and the liquid B (see Figure 1b). When the whole bead is immersed either in liquid A or in liquid B, F is given by eq 1 or 2:

$$F = \pi R_p{}^2(\Gamma_{AP_1} + \Gamma_{AP_2}) + 2\pi R_p(l_1\Gamma_{AP_1} + l_2\Gamma_{AP_2})$$
$$\text{in liquid A} \quad (1)$$

$$F = \pi R_p{}^2(\Gamma_{BP_1} + \Gamma_{BP_2}) + 2\pi R_p(l_1\Gamma_{BP_1} + l_2\Gamma_{BP_2})$$
$$\text{in liquid B} \quad (2)$$

where Γ_{ij} is the interfacial tension between phases i and j and R_p is the radius of the disk-shaped particle. When the bead is adsorbed at the interface between the liquid A and the liquie B, F is now given by eqs 3 and 4:

$$F = \pi R_p{}^2(\Gamma_{AP_1} + \Gamma_{BP_2} - \Gamma_{AB}) + 2\pi R_p(l_1\Gamma_{BP_1} +$$
$$l_2\Gamma_{BP_2}) + 2\pi R_p(\Gamma_{AP_1} - \Gamma_{BP_1})z \quad \text{for } 0 \leq z \leq l_1 \quad (3)$$

$$F = \pi R_p{}^2(\Gamma_{AP_1} + \Gamma_{BP_2} - \Gamma_{AB}) + 2\pi R_p\{l_1\Gamma_{AP_1} - l_1\Gamma_{AP_2} +$$
$$(l_1 + l_2)\Gamma_{BP_2}\} + 2\pi R_p(\Gamma_{AP_2} - \Gamma_{BP_2})z$$
$$\text{for } l_1 \leq z \leq l_1 + l_2 \quad (4)$$

where z is the depth of immersion into the liquid A. In Figure 2 we plot $F/(\pi R_p{}^2\Gamma_{AB})$ as a function of z/R_p when $\Gamma_{AP_1}/\Gamma_{AB} = 0.25$, $\Gamma_{BP_1}/\Gamma_{AB} = 1$, $\Gamma_{AP_2}/\Gamma_{AB} = 0.9$, $\Gamma_{BP_2}/\Gamma_{AB} = 0.3$, and $l_1/R_p = l_2/R_p = 0.1$. It is remarkable that the adsorption energy changes discontinuously at $z = 0$ and $l_1 + l_2$, that is, when the plane surface of the bead contacts with the liquid−liquid interface. The energy gap at $z = 0$ is $\Delta F_1 = \pi R_p{}^2(-\Gamma_{AP_1} + \Gamma_{BP_1} + \Gamma_{AB})$, while that at $z = l_1 + l_2$ is $\Delta F_2 = \pi R_p{}^2(\Gamma_{AP_2} - \Gamma_{BP_2} + \Gamma_{AB})$. The adsorption energy changes linearly with z as a result of the contact of the side surface

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

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

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

(4) Nonomura, Y.; Komura, S.; Tsujii, K. *J. Oleo Sci.*, in press.

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

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

(7) Clint, J. H.; Binks, B. P. *Langmuir* **2002**, *18*, 1270.

(8) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1992; Chapter 17.

(9) Safran, S. A. *Statistical Thermodynamics of Surfaces, Interfaces, and Membrane*; Addison-Wesley: New York, 1994; Chapter 6.

(10) Rossmy, D. *Prog. Colloid Polym. Sci.* **1998**, *111*, 17.

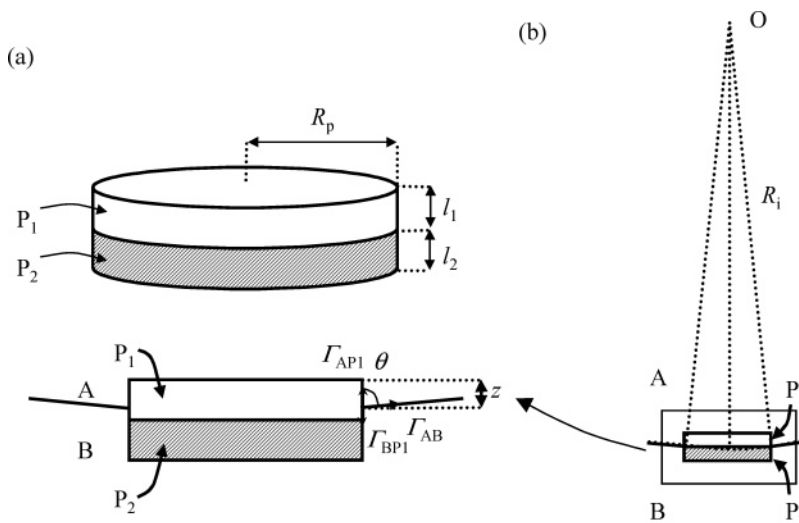(11) Brown, A. B. D.; Smith, C. G.; Rennie, A. R. *Phys. Rev. E* **2000**, *62*, 951.

Figure 1. Schematic illustrations of (a) a disk-shaped J-bead and (b) an interface adsorbing the bead. The bead consisting of the P_1 part and P_2 part is adsorbed at the interface between liquid A and liquid B. In the illustrations, R_p is a radius of the disk-shaped bead, l_1 and l_2 are the thicknesses of the P_1 and P_2 parts, and θ is a contact angle. The interfacial tensions of Γ_{AP_1}, Γ_{BP_2}, and Γ_{AB} are balanced at the contact line.

with liquid A and attains a minimum at $z = l_1$. The corresponding minimum energy is given by

$$F_{\min} = \pi R_p^{\,2}(\Gamma_{AP_1} + \Gamma_{BP_2} - \Gamma_{AB}) + 2\pi R_p(l_1\Gamma_{AP_1} + l_2\Gamma_{BP_2}) \quad (5)$$

It is characteristic of disk-shaped J-beads that they are anchored at the liquid−liquid interface along the boundary line of two surface regions. Similar to the present case, the position of the liquid−liquid interface does not change with the wettabilities between the bead and the liquids for spherical J-beads.[5]

Suppose that we can control the depth of immersion z in Figure 1, and then the contact angle θ of the contact line would depend on z. If the side surface of the particle is completely smooth and homogeneous, θ should be determined by the Young's equation. As discussed above, the adsorption energy is minimized when the contact line is attached to the boundary line between P_1 and P_2. In this case, however, θ can take any value which satisfies $\theta_1 < \theta < \theta_2$, where θ_1 and θ_2 are the contact angles between P_1/A/B phases and between P_2/A/B phases, respectively (Figure 3).[12,13] Namely, θ_1 and θ_2 are related to the interfacial tensions Γ_{ij} by the Young's equation:

$$\cos\theta_1 = \frac{-\Gamma_{AP_1} + \Gamma_{BP_1}}{\Gamma_{AB}} \quad \text{and} \quad \cos\theta_2 = \frac{\Gamma_{AP_2} + \Gamma_{BP_2}}{\Gamma_{AB}} \quad (6)$$

From a simple geometrical consideration, the curvature $1/R_i$ of the liquid−liquid interface is given by eq 7 when $\Gamma_{AP_1} < \Gamma_{BP_1}$ and $\Gamma_{AP_2} > \Gamma_{BP_2}$,

$$\frac{-\Gamma_{AP_2} + \Gamma_{BP_2}}{\Gamma_{AB}}\frac{1}{R_p} \leq \frac{1}{R_i} \leq \frac{-\Gamma_{AP_1} + \Gamma_{BP_1}}{\Gamma_{AB}}\frac{1}{R_p} \quad (7)$$

because the relation $\cos\theta \approx R_p/R_i$ holds. The curvature changes from a positive value to negative one at the boundary line. It indicates that the outer phase of the emulsion could be inverted. However, the actual situation
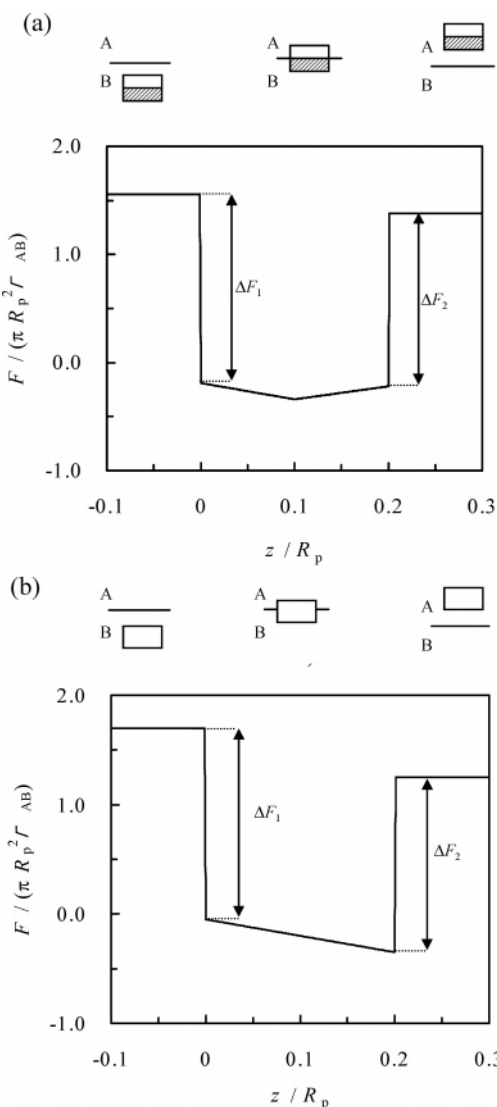
(12) Kralchevsky, P. A.; Nagayama, K. *Particles at Fluid Inrterfaces and Membranes*; Elsevier: Amsterdam, 2001; Chapter 2, 6.

(13) de Gennes, P.-G.; Brochard-Wyart, F.; Quere, D. *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*; Springer-Verlag: New York, 2003; Chapter 3, 9.
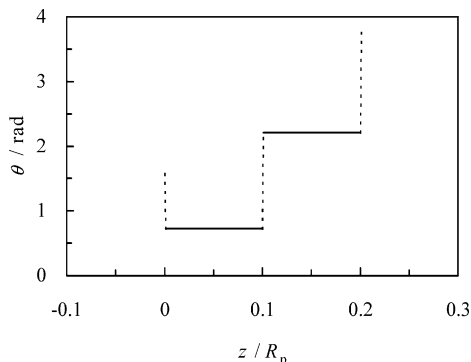

Figure 2. Dimensionless adsorption free energy $F/(\pi R_p^{\,2}\Gamma_{AB})$ against immersion depth z/R_p for (a) a disk-shaped J-bead and (b) a homogeneous surface-active powder at constant radius of the disk-shaped powder R_p and interfacial tensions Γ_{ij}. The parameters are as follows: $\Gamma_{AP_1}/\Gamma_{AB} = 0.25$, $\Gamma_{BP_1}/\Gamma_{AB} = 1$, $\Gamma_{AP_2}/\Gamma_{AB} = 0.9$, $\Gamma_{BP_2}/\Gamma_{AB} = 0.3$, and $l_1/R_p = l_2/R_p = 0.1$ ($l_1/R_p = 0.2$ and $l_2/R_p = 0$ for a homogeneous surface-active powder).

Figure 3. Contact angle θ against immersion depth z for a disk-shaped J-bead. The contact angle θ is calculated when the bead moves from phase B to phase A.

is more complicated than the prediction. The curved surface of the emulsion droplet leads to a pressure difference across the interface. If the particle is attached at the droplet surface, the pressure difference pushes it outward. The curvature of the interface may be determined from the condition that the surface tension force counterbalances the Laplace pressure force acting on the particle.

A contact angle hysteresis is expected for a disk-shaped J-bead. We consider how θ varies as the bead is moved from the phase B to the phase A through the liquid–liquid interface. The contact angle θ is a constant value θ_1 when $z = 0 \leq z \leq l_1$, while it is θ_2 when $l_1 \leq z \leq l_1 + l_2$. In the process, three discontinuous changes are observed at $z = 0, l_1$, and $l_1 + l_2$. On these special positions, θ changes discontinuously as a result of the pinning effect at the boundary line between the P_1 and the P_2 parts and at the edge of the particle. This unique behavior is characteristic of the disk-shaped surface-active particles and is not observed for spherical beads.

A homogeneous particle consisting of the P_1 part only is the special case of the J-bead. In such a case, the adsorption energy is minimized at $z = l_1$ as shown in Figure 2b. This occurs when the plane surface of the particle contacts with the liquid–liquid interface. The adsorption of such a homogeneous particle affects the shape of the liquid–liquid interface similar to the disk-shaped J-bead. The discontinuous change of θ is also expected when $z = 0, l_1$.

In general, the adsorption of the spherical or the disk-shaped surface-active particles at liquid–liquid interfaces is much stronger than that of ordinary surfactant mol-

ecules. The adsorption energy for the surface-active particle of $1-10$ μm size is approximately 10^8-10^9 k_BT, while that for the ordinary surfactant molecule is $1-10$ k_BT. For example, F_{min} is 4×10^8 k_BT when $\Gamma_{AB} = 36$ mN m^{-1}, $\Gamma_{AP_1} = 6$ mN m^{-1}, $\Gamma_{BP_2} = 32$ mN m^{-1}, $R_p = 10$ μm, $l_1 = l_2 = 1$ μm, and the temperature $= 298$ K. An extremely large gain in the adsorption energy results in an irreversible adsorption of the particle at the liquid–liquid interface.[1] Detachment of the disk-shaped particle from the interface is almost impossible because of the large energy gap either at $z = 0$ or at $z = l_1 + l_2$ in Figure 2a.

The irreversible adsorption of the powder leads to the stabilization of emulsions, because the coalescence of emulsion droplets depends on the surface area covered with the particles. These predictions are confirmed by our experimental investigations where we showed that solid-stabilized emulsions are stable for more than 2 weeks.[2,3] Arditty et al. reported that the growth of solid-stabilized droplets is rather slow because their coalescence is supressed by the adsorbed powders.[14] The stability of the emulsion is a great advantage in the production of industrial materials.

The geometrical change of the liquid–liquid interface caused by the adsorption of the disk-shaped J-bead is an important result of the present study. As shown in eq 7, the range of R_i is determined by the interfacial tensions between the liquid and the solid phases. The hysteresis of the contact angle is one of the important properties of the disk-shaped particles. For ordinary surfactants, the molecular structure rules the curvature of the interface.[8,9] However, the curvature of the interface adsorbing the disk-shaped particles is not uniquely determined. Therefore, the common sense for the surfactants does not apply to the surface-active particles.

In summary, the adsorption energy of the surface-active disk-shaped J-beads at the liquid–liquid interfaces has been obtained. The estimated adsorption energy is remarkably larger than that of the ordinary surfactant molecules. We also predict the geometrical change of the liquid–liquid interfaces as a result of the adsorption of the beads and the contact angle hysteresis. Some predictions in this work have not yet been proved by the experiments. Further experimental and theoretical studies are necessary to understand the behavior of the surface-active powders.

(14) Arditty, S.; Whitby, C. P.; Binks, B. P.; Schmitt, V.; Leal-Calderon, F. *Eur. Phys. J. E* **2003**, *11*, 273.