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# Adsorption of Rod-Shaped Surface-Active Particles at Liquid-Liquid Interfaces

**Yoshimune NONOMURA[1*], Shigeyuki KOMURA[2] and Kaoru TSUJII[3]**

[1] *Kao Corporation*
*(Bunka, Sumida-ku, Tokyo, JAPAN)*
[2] *Tokyo Metropolitan University*
*(Minami-Osawa, Hachioji-shi, Tokyo, JAPAN)*
[3] *Hokkaido University*
*(Kita-ku, Sapporo, JAPAN)*

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**Abstract**: The adsorption of a rod-shaped (rectangular parallelpiped) surface-active particle at a liquid-liquid interface has been theoretically studied. The adsorption energy, which is the free energy of the interface adsorbing the particle, is governed by the interfacial tensions between the particle and the liquids and the particle shape. The aspect ratio of the rod-shaped particle determines its adsorbing direction at the interface. The rod-shaped particle having aspect ratio larger than unity adsorbs in parallel direction with the liquid-liquid interface, while the plate-shaped one having the aspect ratio less than unity does perpendicularly. These theoretical results are important to understand the effects of the particle shape on the behavior of the surface-active particles in the self-assembled structures.

**Key words**: surface activity, adsorption energy, rod-shaped particle

## 1 Introduction

Surface-active particles have recently attracted much attention in the field of colloid and surface science, particularly in emulsion science (1, 2). The particles act like surfactant molecules if certain wettability conditions are satisfied. In such case, the particles are adsorbed at liquid-liquid interfaces and exhibit surface activity. Hydrophobic silica, iron oxide, clay mineral, carbon black and polymer latex are some examples of the particles. The particles form self-assembled structures and act as emulsifiers in the preparation of emulsions (3-5).

Thermodynamics is powerful discipline to understand the behavior of the surface-active agents (6). Interfacial tension, a free energy per unit area or a force per unit length, is one of the factors for the geometry and physical properties of the interfaces. Therefore, the mechanism for the adsorption of the surface-active particles has been proposed based on the adsorption energy argument (7). In the argument, the adsorption energy is the free energy of the interface with the surface-active particle. When a spherical particle is adsorbed at a planar liquid-liquid interface, the energy depends on the various interfacial tensions between the particle surface and the two liquids. The particle is adsorbed at the interface when the interfacial tensions among the three phases are balanced according to the Young's equation.

For traditional surfactant molecules, effects of the molecular shape on the interfacial properties have been extensively studied by the models of Israelachvili or Helfrich (8, 9). However, there is few precedent literature as to the shape of the surface-active particle. In our previous studies, we showed that the shape of the parti-

*Correspondence to: Yoshimune NONOMURA, Kao Corporation, 2-1-3, Bunka Sumida-ku 131-8501, Tokyo
E-mail: nonomura.yoshimune@kao.co.jp

cle actually affects their self-assembled structures (3-5). Rossmy also reported that the morphology of solid-stabilized emulsion depends on the geometry of the particles (10). These observations imply that the self-assembled structures of the surface-active particles are governed not only by the wettabilities but also the shape of the particle.

In the present work, we have calculated the adsorption energy of rod-shaped surface-active particles as illustrated in **Fig. 1**. Several situations of adsorption seem possible due to their strong anisotropic shape, and the adsorption energy is important to understand the stability of each condition. The direction of the particle at the liquid-liquid interface is estimated by the calculated adsorption energy. It is the first theoretical report to discuss the influence of the anisotropic shape on the behavior of the surface-active particle.

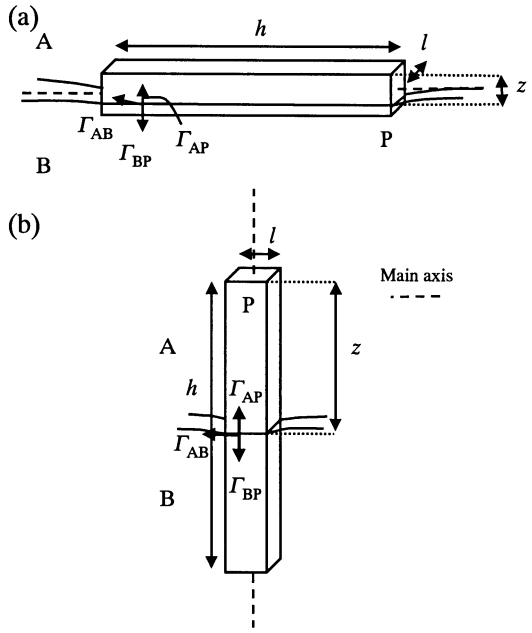


**Fig. 1** Schematic Illustrations of a Rod-Shaped Surface-Active Particle P Adsorbing (a) Parallel or (b) Perpendicular to the Interface of Liquid A and B. The interfacial tensions of $\Gamma_{AP}$, $\Gamma_{BP}$ and $\Gamma_{AB}$ are balanced at the contact line. In the illustrations, $l$ is the length of one side of the square, $h$ is the height of the particle, and $z$ is the immersion depth into liquid A.

## 2 Results and Discussion

We now make discussions for the adsorption of a rod-shaped surface-active particle at a liquid-liquid interface. In the model, $l$ is the length of one side of the square, $h$ is the height of the rectangular parallelepiped particle, and $\Gamma_{ij}$ is the interfacial tension between the phases i and j. Let $F_1$ [$F_2$] be the adsorption energy per particle when the rod-shaped particle P adsorbs at the interface between liquids A and B, and the main axis of the particle is parallel [perpendicular] to the interface (**Fig. 1**). Then, the energies are represented by $F_1 = F_2 = 2l(2h+l)\Gamma_{AP}$ or $F_1 = F_2 = 2l(2h+l)\Gamma_{BP}$ when the whole particle is immersed either in liquid A or B. When the particle is adsorbed at the interface between the liquids A and B, the adsorption energy changes with the formation of the new interfaces between the particle P and the two liquids and the disappearance of the interface between liquids A and B. The adsorption energies $F_1$ and $F_2$ are given by eqs (1) and (2), respectively:

$$F_1 = lh(\Gamma_{AP}+3\Gamma_{BP}-\Gamma_{AB})+2l^2\Gamma_{BP}+2(l+h)(\Gamma_{AP}-\Gamma_{BP})z \quad (1)$$

$$F_2 = l^2(\Gamma_{AP}+\Gamma_{BP}-\Gamma_{AB})+4lh\Gamma_{BP}+4l(\Gamma_{AP}-\Gamma_{BP})z \quad (2)$$

where $z$ is the depth of immersion into the liquid A. These equations are complicated, because they contain many interfacial or geometrical parameters. Then, we plot the dimensionless $F_1/(l^2\Gamma_{AB})$ against $z/l$ when $\Gamma_{AP}/\Gamma_{AB}=0.2$, $\Gamma_{BP}/\Gamma_{AB}=0.6$, and $h/l=10$ in **Fig. 2**(a). It is remarkable that the adsorption energy changes discontinuously at $z=0$ and $l$, that is, when the plane surface of the particle comes into contact with the liquid-liquid interface. The energy gap at $z=0$ is $\Delta F_1^0 = lh(-\Gamma_{AP}+\Gamma_{BP}+\Gamma_{AB})$, while that at $z=l$ is $\Delta F_1^l = lh(\Gamma_{AP}+\Gamma_{BP}-\Gamma_{AB})$. The adsorption energy changes linearly with $z$ due to the contact of the side surface with liquid A, and attains a minimum at $z=l$. The corresponding minimum energy is given by

$$F_1^{\min} = lh(3\Gamma_{AP}+\Gamma_{BP}-\Gamma_{AB})+2l^2\Gamma_{AP} \quad (3)$$

On the other hand, we plot dimensionless $F_2/(l^2\Gamma_{AB})$ against $z/l$ in **Fig. 2**(b) with the same parameter numbers. In such a case, the adsorption energy is minimized at $z=h$. The energy gap at $z=0$ is $\Delta F_2^0 = l^2(-\Gamma_{AS}+\Gamma_{BS}+\Gamma_{AB})$, while that at $z=h$ is $F_2^h = l^2(\Gamma_{AS}-\Gamma_{BS}+\Gamma_{AB})$. The corresponding minimum energy is given by

$$F_2^{\min} = l^2(\Gamma_{AP}+\Gamma_{BP}-\Gamma_{AB})+4lh\Gamma_{AP} \quad (4)$$

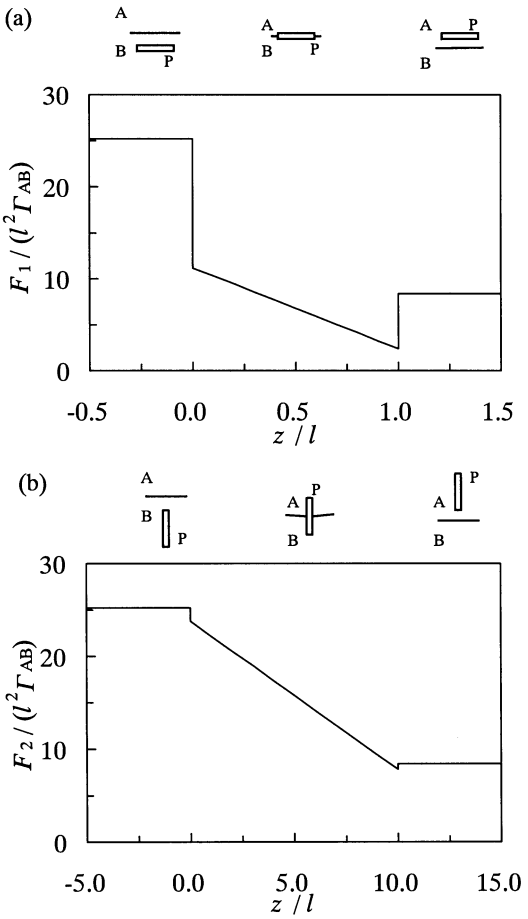


**Fig. 2** The Dimensionless Adsorption Energies against Immersion Depth $z/l$ when the Particle Adsorbs (a) Parallel $[F_1/(l^2\Gamma_{AB})]$ or (b) Perpendicular $[F_2/(l^2\Gamma_{AB})]$ to the Interface. The parameters are as follows; $\Gamma_{AP}/\Gamma_{AB}=0.2$, $\Gamma_{BP}/\Gamma_{AB}=0.6$, and $h/l=10$.

The minimum energies $F_1^{min}$ and $F_2^{min}$ and the energy gaps $\Delta F_1$ and $\Delta F_2$ are useful parameters to determine if the particle adsorbs at the liquid-liquid interface. When these parameters are positive, the particle adsorbs at the liquid-liquid interface spontaneously. These parameters indicate the stability of the interface adsorbing the particle, because they are the energies required to move the particle from the interface to the liquids. The larger the energy gap is, the more difficult it is to move the particle from the interface. If the energy gap is large enough, the adsorption is substantially irreversible.

The calculated adsorption energy indicates that the adsorbing condition depends on the anisotropy reflected by the aspect ratio $h/l$. The energy show the most stable adsorbed condition for the particle. In **Fig. 3**, we plot $F_1^{min}/(l^2\Gamma_{AB})$ and $F_2^{min}/(l^2\Gamma_{AB})$ against the aspect ratio $h/l$. Both energies of $F_1^{min}$ and $F_2^{min}$ increase with $h/l$ and coincides when $h/l=1$. The minimum energy $F_1^{min}$ is smaller than $F_2^{min}$ when the aspect ratio is smaller than unity, and vice versa when the aspect ratio is more than unity. Thus, the rod-shaped particle adsorbs in parallel direction to the liquid-liquid interface, while the plate-shaped one does in perpendicular direction. In our previous study, we actually observed solid-stabilized emulsions in which plate-shaped surface-active powders adsorbed perpendicularly at the liquid-liquid interface (4).

## 3 Conclusions

In the present study, we study the physical properties of the interface adsorbing the rod-shaped surface-active particle based on the adsorption energy argument. The energy profiles indicate that the particle adsorbs in parallel direction to the liquid-liquid interface, while the plate-shaped one does in perpendicular direction. The conversion of the adsorbing direction is a unique behavior of the surface-active particle. Our investigations will contribute to controlling the behavior of the surface-active particles and their applications.

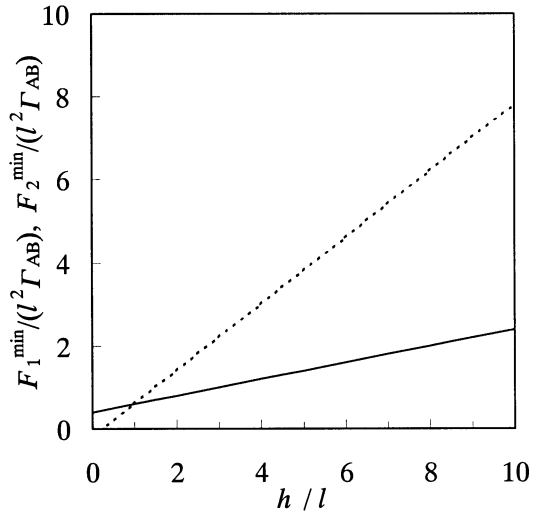


**Fig. 3** The Dimensionless Minimum Adsorption Energies $F_1^{min}/(l^2\Gamma_{AB})$ (——) and $F_2^{min}/(l_2\Gamma_{AB})$ (·····) against the Aspect Ratio $h/l$. The parameters are as follows; $\Gamma_{AP}/\Gamma_{AB}=0.2$, $\Gamma_{BP}/\Gamma_{AB}=0.6$, and $h/l=10$.

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