Friction and Adsorption Properties of Oleic Acid-Based Gemini Amphiphile at Silica/Ester Oil Interfaces

Kenichi Sakai¹*, Ryo Ishimado¹, Yuichiro Takamatsu², Masaaki Akamatsu¹, and Hideki Sakai¹

¹ Department of Pure and Applied Chemistry, Faculty of Science and Technology, and Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, JAPAN
² Miyoshi Oil & Fat Co., Ltd., 4-66-1 Horikiri, Katsushika, Tokyo 124-8510, JAPAN

Abstract: We characterized the friction and adsorption properties of an oleic acid-based gemini amphiphile having two carboxylic acid headgroups. We employed silica as a solid material, and diethyl sebacate and bis (2-ethylhexyl) sebacate as polar ester oils. Oleic acid and stearic acid were used as comparative amphiphilic materials. These amphiphiles were soluble in the ester oils, and the solubility of the gemini amphiphile was lower than that of the other two amphiphiles. Quartz crystal microbalance with dissipation monitoring measurements suggested that the gemini amphiphile had greater adsorption capability than the two comparative amphiphiles. The greater adsorption density of the gemini amphiphile resulted in the formation of a rigid interfacial film, as suggested by the normal force curves obtained by atomic force microscopy (AFM). We assessed the friction property of these systems using a ball-on-plate-type friction analyzer and by friction-mode AFM (friction force curve). These measurements confirmed that the gemini amphiphile had a smaller kinetic friction coefficient than that of the other two amphiphiles. These results suggest the potential of the gemini amphiphile as a friction modifier in polar oils.

Key words: gemini amphiphiles, friction, adsorption, silica, ester oil

1 Introduction

Gemini or dimeric surfactants are dimers of monomeric surfactants. One of the key properties of gemini surfactants in aqueous solutions is that their critical micelle concentrations are remarkably lower than those of the corresponding monomeric surfactants. This enables us to reduce the consumption of surfactants in chemical products, and hence, gemini surfactants are classified as environmental materials. One of the potential issues of gemini surfactants in industry is their high market price due to their complicated synthesis and purification procedures. To solve this problem, we developed a wide variety of oleic acid-based surfactants as cost-effective gemini amphiphiles and have studied their interfacial properties.

Herein we assessed the friction property of an oleic acid-based gemini amphiphile bearing two carboxylic acid headgroups and discussed the friction modification mechanism at a molecular level based on the adsorption data. Two ester oils were employed as solvents in this study: diethyl sebacate (DES) and bis (2-ethylhexyl) sebacate (DOS). Ester oils have attracted much attention recently in the mechanical industry owing to their excellent friction property as well as environment-friendly nature. We have already reported the adsorption characteristics of an oleic acid-based surfactant bearing a quaternary ammonium headgroup at a silica/aqueous solution interface. However, we have not yet characterized the friction and adsorption properties of such oleic acid-based gemini amphiphiles in non-aqueous media despite their importance in academia and industry.

The friction properties of surfactants in aqueous media have been extensively studied in the past. The most relevant study to our present system was reported by Boschkova et al. They studied the adsorption and friction properties of a series of cationic gemini surfactants with different spacer chain lengths and demonstrated good correlation between the adsorption amount and the friction coefficient: the cationic gemini surfactant having a shorter...
spacer chain resulted in a larger adsorption amount and a smaller friction coefficient. Later, the friction properties were discussed in terms of collapse or deformation of the surfactant adsorption layer under sliding conditions\(^\text{6}\). More recently, Li \textit{et al.}\(^\text{11}\) reported the superlubricity of an adsorption system of a cationic surfactant at a silica/aqueous solution interface, where a hydration layer formed on the admicelles plays an important role in the superlubricity. We will revisit these earlier findings in the Discussion section for interpreting our results.

2 Experimental

2.1 Materials

The oleic acid-based gemini amphiphile having two carboxylic acid headgroups (CC-9,9-EsH10) was synthesized in our laboratory according to the procedure mentioned in reference 12. The chemical structure of this amphiphilic molecule is shown in Fig. 1. The two carboxylic acid headgroups are covalently bound to the cis double bond of oleic acid via a spacer unit (\(-\text{CH}_2\text{CH}_2\text{COO}-\)), and stereochemically, they are oriented anti to each other. This implies that the sample is a mixture of their enantiomers (9R, 10R and 9S, 10S).

Oleic acid (Extra Olein 99, NOF) and stearic acid (Tokyo Chemical Industry, TCI) were used without further purification. The purities were more than 99\% and 98\%, respectively, as per the information provided by the suppliers. These amphiphilic materials have been frequently and historically used in many industrial applications as a friction modifier. From the aspect of their chemical structures, these materials have a carboxylic acid headgroup, similar to the gemini amphiphile (CC-9,9-EsH10). Furthermore, the number of carbon atoms in oleic acid and stearic acid is exactly half of that in CC-9,9-EsH10. Based on these considerations, we selected oleic acid and stearic acid as comparative amphiphilic materials.

DES and DOS were purchased from TCI. The purities of these ester oils were more than 98\%, as per the information provided by the supplier.

Flat silica plates were prepared from silicon wafers (Nilaco) via chemical oxidation in a mixture of H\(_2\)O/NH\(_3\)/H\(_2\)O\(_2\) in 5:1:1 ratio (by volume). The detailed procedure was reported in reference 6.

2.2 Instrumentation

Kinetic friction coefficients were measured using a ball-on-plate-type friction analyzer (Triboster TSf-503, Kyowa Interface Science). We employed a steel ball (JIS G 20) with 3 mm diameter for these measurements. The chemically oxidized silicon wafer was immersed in each sample solution, and friction measurements were performed after equilibration for 10 min in the solution. The measurement conditions were as follows: load = 0.49 N, sliding velocity = 0.1 mm/s, sliding distance = 5 mm, and sliding number = 5.

From the aspect of nanotribology, kinetic friction coefficients were measured using a Hitachi AFM5000II atomic force microscope. The chemically oxidized silicon wafer was assembled in the AFM instrument and a sample solution was injected into the AFM fluid cell at a given concentration. After equilibration for ca. 10 min, friction force measurements were performed using I-shaped silicon cantilevers (Hitachi SI-AF01, nominal spring constant = 0.2 N/m, nominal torsion spring constant = 81.3 N/m). The sliding velocity was set as 1 Hz \(\mu\)m, and nominal spring constant = 0.2 N/m. Normal force curve measurements were performed using the same AFM instrument and cantilevers.

Quartz crystal microbalance with dissipation monitoring (QCM-D) measurements were carried out using a Biolyn Scientific Q-Sense Explorer. The substrate used in this study was a silica-coated sensor (QX 303). Before each experiment, the silica sensor was cleaned according to the cleaning protocols mentioned in reference 13. In the first step, DES or DOS was injected into the QCM-D chamber and the system was equilibrated at a constant flow rate of 0.1 cm\(^3\)/min. In the second step, sample solutions dissolved in each of the ester oils were injected into the chamber under the constant flow rate, and the system was again equilibrated.

Unless otherwise stated, all measurements were performed at 25\°C or at room temperature.

3 Results

3.1 Friction behavior

Figure 2 shows the kinetic friction coefficient in DES, measured by the ball-on-plate-type friction analyzer, as a function of concentration of each amphiphilic material. The kinetic friction coefficients shown in this figure are an average of 5 sliding measurements. At a given concentration, the kinetic friction coefficient estimated for the CC-9,9-EsH10 system was significantly smaller than those of the other two systems. This indicates that the gemini am-
Friction and Adsorption of Gemini Amphiphile

Friction and Adsorption of Gemini Amphiphile

J. Oleo Sci. 68, (6) 567-572 (2019)

phiphile can modify the friction in DES on the oxidized silicon wafer surface effectively. It was somewhat surprising that the addition of oleic acid and stearic acid exerted a weak effect on the friction property in DES. Nevertheless, these two amphiphilic materials are generally used as friction modifiers in many industries. We discuss this point later based on their adsorption data.

We also studied the friction behavior from the aspect of nanotribology. Figure 3a shows the friction force data as a function of apparent normal load applied by the AFM cantilevers. As a typical example, the friction force data obtained at an amphiphile concentration of 0.1 wt% in DES are shown here. For all the systems, the friction force increased linearly with increasing apparent load. The slope value corresponds to the kinetic friction coefficient. As can be seen in this figure, the slope value (i.e., kinetic friction coefficient) of the CC-9,9-EsH10 system is slightly smaller than those of the other three systems. The kinetic friction coefficients evaluated in DES are summarized in Fig. 3b as a function of each amphiphile concentration. The results are in good agreement with the friction behavior assessed by the ball-on-plate-type friction analyzer. It is noted that the positive friction forces measured at an apparent load of 0 nN arise from the adhesion forces originating from the interaction between the cantilever and sample surfaces.

We also studied the friction behavior in DOS using the ball-on-plate-type friction analyzer and by friction-mode AFM. The kinetic friction coefficients assessed by these two techniques are given in the Supporting Information, Figs. S1 and S2. The trend was very similar to that observed in DES, which indicates that the gemini amphiphile can modify the friction property more effectively than the comparative amphiphilic materials in the ester oils do.

3.2 Adsorption characteristics

To discuss the effectiveness of the gemini amphiphile as a friction modifier, we characterized the adsorption of the three amphiphiles at the silica/ester oil interfaces. Figure 4a shows the change in frequency observed for the three amphiphiles in DES as a function of each amphiphile concentration. The decreased frequency primarily results from the increased mass on the silica sensor surface. As can be seen in this figure, the increased amphiphile concentration resulted in a negative increase in frequency, suggesting increased adsorption mass at the silica/DES interface. Importantly, the frequency change was observed to be negatively larger for the gemini amphiphile than for the two comparative materials at a given concentration. This indicates the
The force-distance data obtained by AFM force curve measurements provide further insight regarding the adsorption behavior. Figure 5 shows the normal force-distance data measured in DES with and without the additives (0.1 wt%). A weak attractive interaction was observed in the absence of the additives. It seems likely that this attractive interaction arises from the van der Waals interaction. Oscillating forces are sometimes observed when the solvent molecules form solvation layers on a solid surface. However, such oscillating forces were not detected here within the resolution of our experiments. The attractive interaction changed into a repulsive interaction in the presence of the additives because of their adsorption. Importantly, the magnitude of repulsive interaction was found to be larger for the gemini amphiphile than for oleic acid and stearic acid. It is reasonably accepted that the higher adsorption density of the gemini amphiphile results in increased lateral cohesive interaction between the adsorbed molecules, thus inducing greater repulsive interaction.
Friction and Adsorption of Gemini Amphiphile

Interaction against the normal pressure from the cantilever. It is also important to note that the normal loads applied by the cantilever in the friction measurements were in the constant compliance region in the force curves. This implies that friction occurred in the constant compliance region, where the cantilevers compress the adsorption layer of the amphiphiles. The continuous increase in the observed forces with decreasing apparent separation further suggests that the adsorbed molecules remain between the cantilever and silica surfaces in the constant compliance region. We suggest that these molecules contribute to the modification of the friction property.

4 Discussion

Based on the friction and adsorption results, we suggest the friction modification mechanism of the gemini amphiphile. The key parameter determining the friction property is the adsorption mass of the amphiphiles at the silica/ester oil interfaces, as suggested previously in the aqueous surfactant systems. The larger adsorption mass of the gemini amphiphile results in the formation of a rigid interfacial film, yielding greater stiffness against the normal load. This is the primary reason for the greater friction property of the gemini amphiphile than that of the other two amphiphiles. In the friction measurements, the normal pressure induces partial or full collapse of the adsorption layer. However, the amphiphile molecules remain between the two facing solid surfaces under this situation. The larger adsorption mass of the gemini amphiphile will provide a greater possibility that the amphiphile molecules remain on the silica surface under the sliding conditions, and hence, a greater friction property is achieved for the gemini amphiphile system. It was surprising that negligible effect of oleic acid and stearic acid on the friction properties was observed in Figs. 2 and 3 especially at low concentrations. This is rationalized by their low adsorption capabilities at the silica/ester oil interfaces.

The amphiphilic molecules remaining on the silica surface possibly play the following two roles: (i) a mediator inhibiting the direct contact of the two facing solid surfaces, and (ii) a viscosity modifier. The local concentration of amphiphilic molecules remaining within the confined space should be higher than that in the bulk solution, which will lead to an increased viscosity within the confined space, and hence, improvement in friction property.

One may suggest a possibility that the adsorption of the amphiphiles onto the steel ball (friction analyzer) and the AFM silicon cantilever affects the friction property. Unfortunately, we cannot evaluate the impact at present. The similarity of the observed kinetic friction coefficient trend (Figs. 2 and 3) might suggest a limited effect of the material type (steel ball vs. silicon cantilever) as well as different curvatures (mm vs. nm). For better understanding, the adsorption property on a steel surface and/or the friction property need to be assessed using a ball-on-plate analyzer equipped with a silicon ball.

5 Conclusions

In this work, we characterized the friction and adsorption properties of an oleic acid-based gemini amphiphile at the silica/ester oil interfaces, and compared the results with those of oleic acid and stearic acid. The adsorption mass of the gemini amphiphile was suggested to be significantly larger than those of the other two amphiphiles. The greater adsorption density of the gemini amphiphile resulted in the formation of a rigid film, as suggested by the normal force curve measurements. The adsorption layer is compressed and collapsed because of the normal load applied during the friction measurements; however, the adsorbed molecules remain between the two facing solid surfaces and reduce the kinetic friction coefficient. This effect is more significant for the gemini amphiphile than for the other two amphiphiles due to its greater adsorption density. This paper suggests the potentiality of the gemini amphiphile as a friction modifier in polar oils.

Acknowledgements

This work was supported by JSPS KAKENHI Grant-in-Aid for Scientific Research (C) 16K05669. We also thank Kyowa Interface Science Co., Ltd. for accessing the ball-on-plate type friction analyzer.
Supporting Information

This material is available free of charge via the Internet at http://dx.doi.org/jos.68.10.5650/jos.ess19015

REFERENCES

1) Zana, R.; Xia, J. Gemini Surfactants, Synthesis, Interfacial and Solution-Phase Behavior, and Applications (Zana, R.; Xia, J. eds.). Marcel Dekker, New York. Chapter 1 (2003).
2) Zana, R. Structure-Performance Relationships in Surfactants (Esumi, K.; Ueno, M. eds.). 2nd ed. Marcel Dekker, New York. Chapter 7 (2003).
3) Zana, R.; Alami, E. Novel Surfactants: Preparation, Applications, and Biodegradability (Holmberg, K. ed.). Marcel Dekker, New York. Chapter 12 (2003).
4) Sakai, K.; Sakai, H.; Abe, M. Recent advances in gemini surfactants: oleic acid-based gemini surfactants and polymerizable gemini surfactants. J. Oleo Sci. 60, 159-163 (2011).
5) Sugahara, T.; Sakai, K.; Sakai, H. Structure-performance relationship of oleic acid-based gemini surfactants. Acc. Mater. Surf. Res. 3, 179-189 (2018).
6) Sakai, K.; Saito, Y.; Uka, A.; Matsuda, W.; Takamatsu, Y.; Kitiyanan, B.; Endo, T.; Sakai, H.; Abe, M. Quaternary ammonium-type gemini surfactants synthesized from oleic acid: aqueous solution properties and adsorption characteristics. J. Oleo Sci. 62, 489-498 (2013).
7) Boschikova, K.; Feiler, A.; Kronberg, B.; Stålåkren, J.J.R. Adsorption and frictional properties of gemini surfactants at solid surfaces. Langmuir 18, 7930-7935 (2002).
8) Vakarelski, I.U.; Brown, S.C.; Ravinovich, Y.I.; Moudgil, B.M. Lateral force microscopy investigation of surfactant-mediated lubrication from aqueous solution. Langmuir 20, 1724-1731 (2004).
9) Theander, K.; Pugh, R.J.; Rutland, M.W. Friction force measurements relevant to de-inking by means of atomic force microscope. J. Colloid Interface Sci. 291, 361-368 (2005).
10) Zhang, J.; Meng, Y. Stick-slip friction of stainless steel in sodium dodecyl sulfate aqueous solution in the boundary lubrication regime. Tribol. Lett. 56, 543-552 (2014).
11) Li, J.; Zhang, C.; Cheng, P.; Chen, X.; Wang, W.; Luo, J. AFM studies on liquid superlubricity between silica surfaces achieved with surfactant micelles. Langmuir 32, 5593-5599 (2016).
12) Sakai, K.; Unemoto, N.; Matsuda, W.; Takamatsu, Y.; Matsumoto, M.; Sakai, H.; Abe, M. Oleic acid-based gemini surfactants with carboxylic acid headgroups. J. Oleo Sci. 60, 411-417 (2011).
13) Sakai, K.; Smith, E.G.; Webber, G.B.; Schatz, C.; Wanless, E.J.; Bütün, V.; Armes, S.P.; Biggs, S. pH-responsive diblock copolymer micelles at the silica/aqueous solution interface: Adsorption kinetics and equilibrium studies. J. Phys. Chem. B 110, 14744-14753 (2006).
14) Sauerbrey, G. Verwendung von schwingquarzen zur wägung dünner schichten und zur mikrowägung. Z. Phys. 155, 206-222 (1959).
15) Israelachvili, J.N. Intermolecular and Surface Forces. 3rd edn. Elsevier, Burlington. Chapter 15 (2011).