Applying the Langmuir-Blodgett Technique to a Well Defined Model Detergent System

Кеіко Gotoн¹

Kyoto University of Education, Fushimi-ku, Kyoto 612-8522, Japan

NORIKO NAKAZAWA

Lion Corporation, Analytical Research Center, Sumida-ku, Tokyo, 130-8644, Japan

MIEKO TAGAWA

Kanazawa Institute of Technology, Nonoichi, Ishikawa 921-8501, Japan

ABSTRACT

The Langmuir-Blodgett technique is used to obtain a well defined model detergent system. Spreading monolayers of arachidic acid as a model organic contaminant are transferred onto glass plates untreated and treated with two silane coupling agents, γ -aminopropyltriethoxysilane (APTES) and methyltriethoxysilane (MTES). Brewster angle microscopic images show that the LB films of arachidic acid are uniformly deposited on the substrate. Glass plates with the LB films are ultrasonically washed in various aqueous solutions, and the detergency is evaluated from the change in FTIR spectra of the substrate due to washing. The efficiency of detergency decreases as a result of the silanization of glass, especially for the APTES treated glass. The wettability and the surface charge of the substrate play important roles in the detergency, suggesting that the LB films of arachidic acid are removed directly from the substrate. Removal of LB films from the APTES-treated glass increases with increasing surfactant or ethanol concentration, and the removal rate strongly depends on temperature. As a removal technique without washing liquids, exposure of the substrates with LB films to 172 nm ultraviolet light is also attempted.

In commercial cleaning of wearing apparel and detergent processes of many industrial products, organic solvents are used as washing media. Recently, chlorofluorocarbons were phased out because of their potential to cause harm to the stratospheric ozone layer [11]. In addition, the manufacture of chlorinated hydrocarbons was discontinued and disposal strictly controlled. As a result, interest in water has been increasing. Water is an excellent washing medium with no toxicity and no environmental impacts, but contaminants soluble in organic solvents are difficult to remove in water. Further experimental studies are necessary to develop removal techniques for oily contaminants in water as well as soil removal techniques without washing media. Well defined model systems for studies on detachment processes are highly desirable.

In this study, we attempt to construct a model system by applying the Langmuir-Blodgett (LB) method [7], a structure and thickness. An analysis of skin surface lipids that collect on textiles or penetrate underwear while it is being worn indicates that there is a large amount (30%) of free fatty acids in skin lipids [2]. Long-chain fatty acids, which have a hydrophilic head group and a hydrophobic tail, are known as monolayer-forming materials on water. Therefore, we have used arachidic acid as a model oily contaminant and transferred onto substrates the spreading monolayers of arachidic acid on water. Glass plates are a model substrate because of geometric simplicity. We treat the plates with two silane coupling agents to change the wettability of the surfaces. The LB multilayers of arachidic acid on the plates are ultrasonically washed in aqueous solutions. We investigate the effects of the surface properties of the plates, sodium dodecyl sulfate and ethanol concentrations, and the temperature of the solutions on the removal of the LB films. We also attempt to remove the LB films of arachidic acid with UV irradiation in air.

technique of preparing a thin film with well controlled

¹e-mail: keiko@kyokyo-u.ac.jp, fax: +81-75-645-1734, phone: +81-75-644-8318.

Experimental

MATERIALS

Arachidic acid $(CH_3(CH_2)_{18}COOH)$, Wako Chemical Co., Ltd.) was the model organic contaminant. As the substrate, glass plates $(5 \times 5 \times 30 \text{ mm}^3)$ were soaked in a dichromate sulfuric acid solution, rinsed with running water, and boiled in doubly distilled water. The plates were treated with two silane coupling agents, γ -aminopropyltriethoxysilane (APTES) and methyltriethoxysilane (MTES): plates were immersed in silane coupling agent solutions, heated in an oven at 100°C, and rinsed with medium [4]. Silane coupling agents were provided by Shinnetsu Kagaku Kougyou Co., Ltd., Japan, and used as received.

Table I lists the advancing and receding contact angles of water on the untreated and silanized glass plates, measured by the Wilhelmy method [5]. The wettability of the substrate decreased as a result of the silanization.

TABLE I. Advancing and receding contact angles of water, θ_a and θ_r , on untreated and silanized substrates.

Substrates	θ_a , degree ^a	θ_r , degree
Untreated glass	30.6	14.0
APTES-treated glass -	76.4	29.4
MTES-treated glass	85.3	53.3

^a Taken from reference 5.

The surfactant was sodium dodecyl sulfate (SDS, Wako Chemical Co., Ltd.). From the surface tension measurements, the critical micell concentration (cmc) in the presence of 1×10^{-3} mol/dm³ sodium chloride and 1×10^{-3} mol/dm³ sodium hydroxide was determined to be 8×10^{-3} mol/dm³ at 25°C. The pH was adjusted with sodium hydroxide. Ethanol, sodium hydroxide, and sodium chloride were extrapure grade reagents used without further purification. The water was deionized, doubly distilled using a borosilicate glass apparatus from alkaline potassium permanganate, and purified (resistivity of 18 MΩcm) by an Easy Pure RF apparatus (Barnstead, Germany).

SURFACE PRESSURE MEASUREMENTS AND FILM DEPOSITION

Measurements of the surface pressure of the arachidic acid monolayers as a function of the surface area and the film deposition of the acid onto the glass plates involved a computer-controlled LB film deposition apparatus (FW-2, Lauda, Germany). The apparatus was equipped with a poly(tetrafluoroethylene) trough 200 mm wide, 600 mm long, and 10 mm deep, with a floating barrier to measure the surface pressure. The trough was filled with water as a subphase, and the temperature of the subphase was controlled within 20 ± 0.1 °C.

The arachidic acid was spread as a 0.2 g/dm³ benzene solution onto the subphase using a 1 mL syringe. Small drops of solution were dispersed at the air-water interface as the syringe passed over the subphase. Typical quantities of the solution were 0.7 mL. After allowing 15 minutes for benzene evaporation, the monolayer was compressed continuously with a barrier speed of 10 mm/min to a surface pressure of 30 mN/m, which was maintained throughout the entire deposition. The monolayer was transferred onto the substrate by the vertical dipping method. Dipping velocity was 5 mm/min, and the dipping cycles were repeated ten times. The compressed area of the water surface at each immersion-withdrawal cycle was automatically calculated and displayed on a monitor.

In our previous study [6], we observed that the contact angles of water on silica glass with the LB films of arachidic acid gradually increased and became constant with ageing time after LB deposition. We believe the increase in the angles was caused by molecular rearrangement in the LB films. Therefore, in this study, the glass plates were aged for 24 hours in a desiccator with silica gel after LB deposition prior to the removal experiments.

A BAM-1 Brewster angle microscope (Nanofilm Technologie) was used for the images of the arachidic acid monolayers on water and the LB films on the substrates. A rotatable polarizer was positioned between the reflected beam and a CCD camera. Polarization of the incident laser beam (He-Ne) was set to p-polarization, and the angle of incidence was adjusted to the Brewster angle to get the lowest reflection from the pure water surface.

REMOVAL EXPERIMENTS

The LB films of arachidic acid were washed in aqueous solutions containing 1×10^{-3} mol/dm³ sodium chloride by ultrasonic waves. Sodium hydroxide, SDS, and/or ethanol were added to the solution.

Removal of the LB films by exposure to 172 nm UV light was attempted with a Xe_2 eximer vacuum UV apparatus (UER20-172, Ushio, Japan). The intensity of the UV eximer light at the upper window of the lamp house was determined to be 15.8 mW/cm² with a UV monitor (UIT-150 and VUV-S172, Ushio, Japan). The substrate with the LB films of arachidic acid was exposed to UV light in air 1 mm away from the window. The removal efficiency of the LB films was evaluated from FTIR reflectance spectra of the substrate before and after the removal experiment.

FTIR SPECTROSCOPY

Infrared reflectance spectra of the glass plates were recorded on a Nicolet Magna 550 Fourier transform infrared spectrophotometer equipped with an MCT detector in absorbency units in the range 400-4000 cm⁻¹. A focus transfer accessory was used for p-polarized beams obtained through a AgBr wire-grid polarizer, the angle of incidence was 70°, and the background was Au mirror. For each spectrum, 126 scans were accumulated at 4 cm⁻¹ resolution.

Results and Discussion

ARACHIDIC ACID MONOLAYER

A typical surface pressure-area isotherm of the arachidic acid monolayers on water is shown in Figure 1. In the horizontal region of a surface area larger than 24 $Å^2$ molecule⁻¹, arachidic acid molecules are considered to lie flat on the water surface. At a surface area of 24 $Å^2$ molecule⁻¹, there is a transition to a steeply sloping linear region where the molecules are expected to be compressed, and an abruptly increased slope follows. This is clearly due to a phase change and represents a transition to an ordered solid-like arrangement of the two-dimensional array of molecules [1, 3, 9]. The decrease in the surface pressure at smaller surface areas suggests that the phenomenon of collapse occurs.



FIGURE 1. Surface pressure-area isotherm for arachidic acid monolayer on water surface at 20°C.

The phase behavior of the arachidic acid monolayer observed with BAM is shown in Figure 2. After being spread, the monolayer has circular holes (a in Figure 2).



FIGURE 2. Brewster angle microscopic images of arachidic acid monolayer on water: (a) before compression, (b) surface pressure 15 mN/m and surface area 22 Å²/molecule, (c) surface pressure 30 mN/m and surface area 20 Å²/molecule, (d) after collapse.

After compression of the monolayer, there is a growth of the liquid-like domains (b in Figure 2). At a surface pressure of 30 mN/m (c in Figure 2), the monolayer becomes completely homogeneous, indicating the formation of the solid-condensed film. Further compression causes a collapse of the monolayer (d in Figure 2). From these experimental findings, it is clear that the solidcondensed monolayer at a surface pressure of 30 mN/m is transferred onto the substrate using our system.

LB FILMS OF ARACHIDIC ACID

The BAM images of the arachidic acid film deposited on the substrate are given in Figure 3. Image a in Figure 3 shows the substrate with the LB films of arachidic acid, which are uniformly distributed on the substrate. When a drop of the arachidic acid benzene solution used for spreading the acid onto the subphase is placed on the substrate and the benzene evaporates, there is a patchy deposition of arachidic acid (b in Figure 3). There is little deposition of arachidic acid onto the substrate after dipping the substrate into the arachidic acid benzene solution (c in Figure 3). Therefore, the LB technique is adequate for depositing arachidic acid as a model contaminant.

Typical FTIR spectra of the substrate before and after LB film deposition are illustrated in Figures 4 a and b. Spectra for the untreated and the two silanized glass plates are confirmed as identical. After LB deposition, the bands are observed at wavelengths of 2916 and 2848



FIGURE 4. FTIR spectra of the APTES-treated glass: (a) before LB deposition, (b) after LB deposition, (c) after washing LB films in aqueous solution containing 1×10^{-3} mol/dm³ sodium chloride, 1×10^{-3} mol/dm³ sodium hydroxide, and 1×10^{-2} mol/dm³ sp at 25°C.

 cm^{-1} and assigned to asymmetric and symmetric stretching of CH₂ groups, respectively [8].

The heights in the 2916 and 2848 cm⁻¹ peaks of the FTIR spectra of the untreated and silanized glass plates after LB deposition are plotted in Figure 5 as a function of dipping cycles of deposition. In all cases, the relations are linear, which indicates that the monolayers of arachidic acid are transferred onto the substrate at each immersion-withdrawal cycle. Because the surface area of the subphase is compressed at each immersion-withdrawal cycle, we expect the LB multilayer to have a Y-type structure. In Figure 5, the slope of each curve is different, *i.e.*, untreated glass < MTES-treated glass < APTES-treated glass. For LB deposition, adhesion of the first monolayer to the underlying solid is particularly critical because it dominates the adhesion of the monolayers in the immersion-withdrawal cycles that follow. Therefore, the slope of each curve in Figure 5 corresponds to the ratio of the arachidic acid monolayer transferred onto the substrate to the monolayer on water at the first dipping cycle and hence depends on the adhesion interaction between the substrate and the monolayer.

FIGURE 3. Brewster angle microscopic images of arachidic acid deposited on APTES-treated glass plate: (a) transferring monolayers of arachidic acid, (b) placing a drop of arachidic acid solution, (d) dipping into arachidic acid solution.



FIGURE 5. Height of 2916 cm⁻¹ (\bigcirc , \triangle , \square) and 2848 cm⁻¹ (\bigcirc , \blacktriangle , \blacksquare) peaks as a function of dipping cycles in LB deposition onto untreated glass (\bigcirc , \bigcirc), APTES-treated glass (\triangle , \bigstar), and MTES-treated glass (\square , \blacksquare).

REMOVING LB FILMS

Figures 4 b and c clearly show that the peak intensities at wavelengths of 2916 and 2848 cm⁻¹ decrease after washing. We have evaluated the removal efficiency of LB films from the peak heights before and after washing, because peak intensity is considered to be proportional to the amount of arachidic acid deposited from the linear relations in Figure 5.

We have investigated the removal of LB films of arachidic acid from untreated and silanized glass substrates in the absence of SDS and ethanol. The results are shown in Figure 6. For all substrates, removal efficiency increases with time and shows saturation at 20-30 minutes. Figure 6 demonstrates that removal efficiency decreases as a result of silanization of the substrate. The order of magnitude of efficiency among the three substrates does not contradict the order of the deposited amount of LB films in Figure 5 (untreated glass < MTEStreated glass < APTES-treated glass). Silanization of the silica substrate results in decreased detergency. This indicates that detergency is dominated by the adhesive



FIGURE 6. Changes in removal efficiency of LB films of arachidic acid from untreated glass (O), APTES-treated glass (Δ), and MTES-treated glass (\Box) with time in an aqueous solution containing $\tilde{1} \times 10^{-3}$ mol/dm³ sodium chloride at 25°C.

interaction between the LB films and the substrates, which depends on the surface properties of the substrates such as wettability and surface charge. Thus, the model system we propose here is adequate for investigating detergency. The difference in detergency between the MTES-treated and the APTES-treated substrates is probably associated with the surface charge: MTES-treated and APTES-treated glasses are negatively and positively charged in the aqueous solutions, respectively [4].

Figure 7 shows the removal efficiency at 30 minutes, R_{30} , for the APTES-treated glass as a function of SDS concentration in the presence of sodium hydroxide (pH 11). As expected, R_{30} increases with increasing SDS concentration and attains 70% at 1×10^{-2} mol/dm³ above cmc. We have also investigated the effect of SDS concentration on LB film removal in the absence of sodium hydroxide (pH 6). Adding SDS is less effective for removal compared with pH 11, although we have eliminated these results.

Figure 8 illustrates the temperature dependence of LB film removal from APTES-treated glass in the presence of sodium hydroxide and SDS. Removal of LB films is promoted at high temperatures and the removal efficiency attains 100% at 80°C. The melting point of arachidic acid is 76.1–76.3°C [10], which may somewhat decrease in the presence of SDS. Therefore, the decreased fluidity of arachidic acid with increasing temperature can be attributed to the considerably increased detergency.

The effect of ethanol concentration on R_{30} for APTEStreated glass is presented in Figure 9. Detergency largely



FIGURE 7. Removal efficiency of LB films of arachidic acid from APTES-treated glass at 30 minutes, R_{30} , as a function of sDs concentration in aqueous solutions containing 1×10^{-3} mol/dm³ sodium chloride and 1×10^{-3} mol/dm³ sodium hydroxide at 25°C.



FIGURE 8. Changes in removal efficiency of LB films of arachidic acid from APTES-treated glass with time in an aqueous solution containing 1×10^{-3} mol/dm³ sodium chloride, 1×10^{-3} mol/dm³ sodium hydroxide, and 5×10^{-3} mol/dm³ sDS at 10°C (\bigcirc), 25°C (\triangle), 40°C (\square), 60°C (\diamondsuit), and 80°C (\bigtriangledown).

increases with added ethanol, and the LB films are completely removed at an ethanol concentration of 50 vol%.

In order to remove arachidic acid without washing liquids the APTES-treated substfate with the LB films is exposed in air to eximer UV light. The effect of UV irradiation time on removal is shown in Figure 10. Removal efficiency increases with irradiation time, and the LB films are perfectly removed by a UV irradiation of 5



FIGURE 9. Removal efficiency of LB films of arachidic acid from APTES-treated glass at 30 minutes, R_{30} , as a function of ethanol concentration in aqueous solutions containing 1×10^{-3} mol/dm³ sodium chloride at 25°C.



FIGURE 10. Effect of UV irradiation time on removal efficiency of LB films of arachidic acid from APTES-treated glass.

minutes. It is commonly accepted that a UV eximer laser causes photodissociation and ablation of organic polymers [12]. The LB films of arachidic acid are probably removed by the eximer UV irradiation on the basis of a similar mechanism. In this case, evaporation of the chemical species produced by dissociation may pollute the air. Since UV irradiation of oily contaminants generally increases their solubility in water, ultrasonic washing in aqueous solutions following UV irradiation before ablation will be effective for removing contaminants. We will discuss the validity of UV exposure before ultrasonic washing in aqueous solutions in the future.

Conclusions

We have proposed a model detergent system constructed by transferring monolayers of arachidic acid onto untreated and two silanized glass substrates. The LB films are ultrasonically washed in aqueous solutions, and the detergency is evaluated from FTIR spectra of the substrate before and after washing. Silanization of the glass plate decreases the removal efficiency of the LB films, indicating that detergency depends on the surface properties of the substrates, such as wettability and surface charge, and that LB films are removed directly from the substrates. LB film removal from the APTES-treated glass plate increases with increasing concentrations of sDs and ethanol. The temperature dependence of detergency is remarkable, and LB films are completely removed at 80°C in the presence of sodium hydroxide and SDS. Exposure to 172 nm UV light in air is effective for removing LB films. These results confirm the effectiveness of our proposed detergent system.

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Effects of Ferrous Mordanting on Bleaching of Camel Hair

Ariyajavin Khishigsuren, Masaru Nakajima, and Masaoki Takahashi

Faculty of Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

ABSTRACT

The ferrous mordanting process used for bleaching pigmented fibers has been improved. The serious problems of discoloring and excessive damaging of bleached fibers associated with the deposition of iron during the mordant bleaching process are resolved. All mordanting parameters are critical for successful bleaching of pigmented fibers. When used at a specific temperature and a specific time during mordanting, a reagent (reductive agent or acid) capable of stabilizing the mordant bath (during treatment) produces the most complete reaction of melanin with the iron, while not allowing the iron to be deposited on the keratin. Thus, in the subsequent bleaching process, maximum whiteness is achieved with less damage in terms of the mordanting. Sodium bisulfite can be used as an auxiliary, *i.e.*, at the initial 4.0 pH of the bath, and acetic acid and citric acid can also be applied during mordanting without causing discoloration and excessive damage. The optimum conditions for mordanting are 20°C and 15 minutes when sodium bisulfite is used, and 60°C and 15 minutes with a stabilizer of acetic acid or citric acid. The improved process is, in all respects, superior to conventional processes, with no need for aftertreatment with a reducing agent.

In nature, specialty animal fibers such as cashmere and camel hair are usually found in various shades of brown or grey, due to the natural pigment, melanin. For white or pastel color requirements, these fibers should be bleached. Dark fibers in wool often give rise to annoying and expensive problems for manufacturers at all stages of wool processing. Manual removal of these fibers is an extremely labor- and cost-intensive, eye-straining job. A more convenient and economical alternative is a wet treatment, which is much more productive and in many cases also cheaper. Human hair cut for wigs needs to be chemically and physically modified to improve its appearance and to increase the value of the end use through successive cosmetic finishing processes, including bleaching.

Bleaching is common with all of these fibers, the aim of which is to selectively decolorize the natural pigments with minimal damage to the keratin matrix of the fiber. The method used for this purpose involves a treatment with ferrous salts (mordanting) followed