Adsorption Behavior of Methyl Orange on the Monolayer and Langmuir–Blodgett Films of Octadecylamine

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The monolayer properties of octadecylamine (ODA) on both distilled water and aqueous Methyl Orange (MO) solution were studied from the measurements of surface pressure–area (π–A) isotherms. From the π–A isotherms at various pHs, hydroxide ions, and MO anions in the subphase were confirmed to interact competitively with the ODA monolayer. Furthermore, Langmuir–Blodgett (LB) film of ODA was fabricated from the surface of an alkaline subphase, and the adsorption characteristics of the ODA LB film were investigated by using MO as an adsorbate. As a result, the ODA LB film exhibited specific adsorbability for the MO anion, similar to that of the LB film of long-chain quaternary alkylammonium salt, but the adsorption rate of the MO on the ODA LB film was slower than that on the LB film of long-chain quaternary alkylammonium salt. In addition, adsorbability of the ODA LB film showed pH dependence.

The cationic amphiphilic substances such as long-chain alkylamines and alkylammonium salts are attracting interest for their specific properties, exemplified by a potent bactericidal activity and specific adsorption behavior. The molecular organized films of cationic materials are, therefore, expected to afford some particular functions.

Several studies concerning cationic properties of the monolayers at the air/water interface have been reported. For examples, Petrov et al. reported that the monolayer of octadecylamine strongly interacted with inorganic divalent anions analogous to that of fatty acid with the divalent cations, and the dry and irreversible deposition of the monolayer was successfully achieved from the aqueous solution containing divalent anions.[1)] Sukhorukov et al. have recently investigated the preparation and the structural characterization of the LB films deposited from the monolayers of the complexes between aliphatic amines and nucleic acids.[2)]

As to the preparation of LB films, LB films which preserve the cationic property by nature would be required for their applications. However, the fabrication of LB films of long-chain quaternary alkylammonium salts would be difficult because of the liquid-expanded property of the monolayers on distilled water. Some attempts were, therefore, made by incorporating some additives in the subphase. Shimomura et al. have described that the polyion complex technique is one of the most effective methods for the preparation of LB films of alkylammonium salts.[3)] In this technique, as pointed out by Berndt et al., the surface charge of these LB films was neutralized by the addition of polyanions.[4)] In contrast, we have reported the preparation of cationic LB films of long-chain quaternary alkylammonium salts without any additives in the subphase; we elucidated that these LB films preserved the cationic property from the measurement of adsorbability of dye molecules.[5—7)]

On the other hand, LB films of long-chain alkylamines could be prepared by weakening the charge repulsion among the polar head groups. Hazell et al. reported the fabrication of bilayer LB films of octadecylamine by using a higher pH subphase.[8)] In this case, these LB films are expected to possess cationic property.

In this paper, we examined the monolayer property of ODA at the air/water interface from π–A isotherm measurements. In a similar manner as for the long-chain alkylammonium salts, film-forming property and adsorbability of the ODA LB films were also evaluated by spectroscopic methods.

Experimental

The cationic film material of octadecylamine (ODA) used throughout the experiments was supplied from Aldrich Chemical Company, Inc. Dye material of Methyl Orange (MO) used as an adsorbate was purchased from Wako Pure Chemical Industries, Ltd. These substances were used without further purification. These structural formula are shown below:

$CH_3(CH_2)_{17}$–NH_2 (ODA)
$(CH_3)_2N$–C_6H_4–N=N–C_6H_4–$SO_3^-Na^+$ (MO)

All other chemicals used in this study were analytical or spectroscopic grade.

The measurements of surface pressure–area (π–A) isotherms and the deposition of monolayers on solid substrates were performed with a Langmuir-type film balance (Kyowa Interface Science, model HBM AP-type). The monolayers of ODA were spread from a chloroform solution (1.0×10^{-3} mol dm^{-3}) on the surface of triply distilled water and aqueous 1.0×10^{-4} mol dm^{-3} MO solution. The subphase temperature was maintained at 20 °C, and the subphase pH was adjusted for the pH dependence experiments by adding hydrochloric acid or sodium hydroxide. Regardless of the incorporation of acid or base, the subphase containing no MO was referred to as "distilled water" in order to distinguish it from that containing MO. Using the conventional vertical dipping (LB) method, the multilayer depositions of the ODA monolayer were carried out under the conditions of an alkaline subphase (pH = 10.1—10.5) and at the constant surface pressure of 45 mN m^{-1}. The dipping speed was kept at 7 mm min^{-1}. Gold-coated brass and calcium fluoride plates were used for Fourier transform infrared (FTIR) spectroscopy, and the quartz and glass plates were employed for UV-visible spectroscopy. The surfaces of the former two plates were rendered hydrophobic by coating a few layers of cadmium stearate LB film and the latter two plates were cleaned by soaking in a cleaning solution of chromic acid mixture.

Adsorption of MO was performed by immersing the ODA LB film into the aqueous MO solution of 1.0×10^{-4} mol dm^{-3} for a given period of time. These LB films were denoted as "MO-adsorbed ODA LB film" for convenience's sake in this study.

The transfer of the monolayer on the solid substrate was confirmed by using a FTIR spectrometer (JASCO, FT/IR-8900) equipped with MCT detector. The adsorbability of MO molecules on the LB film was evaluated by a UV-vis-near-IR scanning spectrophotometer (Shimadzu, UV-3100PC).

Results and Discussion

1. ODA Monolayer on Distilled Water and Aqueous MO Solution. Figure 1 shows the effect of pH on the π–A isotherms measured with the ODA monolayer spread on distilled water and an aqueous MO solution at 20 °C. As can be seen in this figure, ODA at the acidic pH (curve a) formed an expanded monolayer due to protonation of the amino group and dissolved into the subphase at higher surface pressure. In contrast, the ODA monolayer exhibited the more condensed state at higher pH. In particular, the monolayers above pH of 10.1 (curve c, d) showed the typical condensed behavior, and they were stable enough to withstand the high surface pressure of 55 mN m^{-1}. For these monolayers, the limiting area per molecule was estimated to be 0.22 nm^2 molec^{-1}. Since this value is close to the cross section area of the hydrocarbon chain (0.21 nm^2), the hydrocarbon chains are supposed to be almost packed closely in the monolayer. The results obtained above are approximately compatible with the π–A isotherms of docosylamine studied by Bardosova et al.[9]

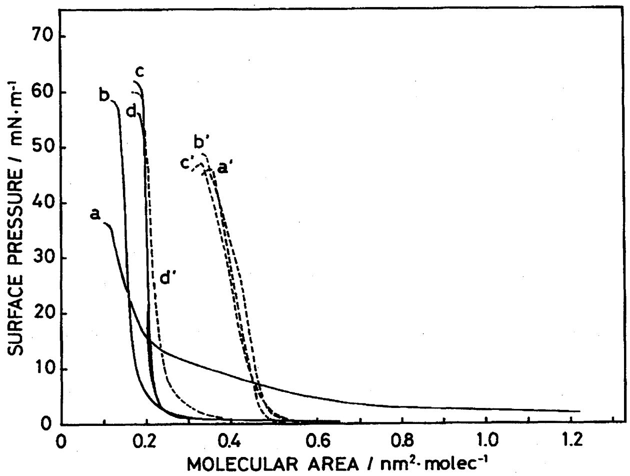

Fig. 1. π–A isotherms of the ODA monolayers on the distilled water (solid lines) and aqueous MO solution (dotted lines) at 20 °C. pH: a, 3.0; b, 5.7; c, 10.1; d, 11.7; a′, 3.0; b′, 5.5; c′, 10.3; d′, 11.7.

On the other hand, the π–A isotherms of the ODA monolayer on an aqueous MO solution showed a fairly expanded state in the pH range of 3.0—10.3 (curve a′, b′, c′), and the shapes of these isotherms resembled each other. However, the monolayer on the aqueous MO solution at pH = 11.7 (curve d′) exhibited more condensed behavior, indicating an isotherm similar to that on the distilled water at pH = 11.7. Such behavior can be understood from the following reasons. Adsorption of MO onto the ODA monolayer is considered to consist of two processes. The primary process is the protonation of ODA, and the secondary process is the complex formation of ODA cation (ammonium ion) and MO anion. For the monolayers of long-chain alkylamines on the distilled water, pK_a of 10.1 ($-NH_3^+ + H_2O \rightarrow -NH_2 + H_3O^+$) has been reported;[10] hence, the protonation of the amines in the monolayer is practically forbidden above pH of 10.1. However, owing to ionic interaction, the equilibrium constant of the secondary process is anticipated to be quite large; thereby, adsorption of MO would be accelerated. As a result, MO adsorption on the ODA monolayer takes place at pH = 10.3 (curve c′) even at the fairly dilute concentration of MO, while MO adsorption is limited at pH = 11.7 (curve d′) due to the decrease in the degree of ionization of the amino group prior to the interaction with the MO molecule.

2. Adsorbability of MO Molecules onto the ODA LB Film. The LB deposition was subsequently attempted for the monolayers on distilled water and on aqueous MO solutions at various pHs. Only the monolayer on the distilled water at higher pH (corresponding to the curve c in Fig. 1) was successfully deposited on the solid substrate in the multilayer form. Under these conditions, the transfer ratio was nearly unity, and the monolayer transfer with water-repellency was observed.

In order to confirm the regular transfer of the ODA monolayer on the solid substrate, we measured FTIR-transmission spectra for two to eight layers of the ODA LB film. It was observed that the bands due to CH_2 symmetric and antisymmetric stretching vibration mode appeared at 2851 and 2918 cm^{-1}, respectively (as shown in Fig. 2), and these absorbances increased linearly with increasing number of layers. Accordingly, the wavenumbers of these bands suggest that the ODA molecules have ordered trans-zigzag hydrocarbon chains, and such a linear relationship indicates that the ODA monolayer is regularly and uniformly transferred onto the substrate. In order to examine the orientation of molecules, we also applied FTIR-reflection absorption (RA) spectroscopy to the ODA LB films. Figure 2 shows the RA spectrum of eight-layer ODA LB film together with the transmission spectrum. In the RA spectrum, the electric field vector of the incident light is polarized perpendicular to the film surface. The transition moments perpendicular to the film surface are thereby sensitive in the RA spectrum, while

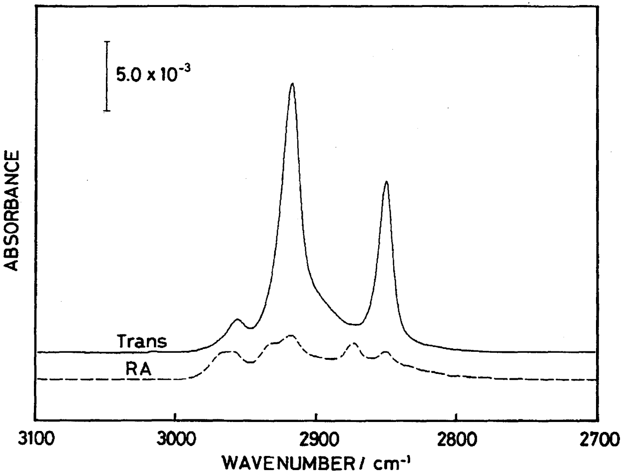

Fig. 2. FTIR-transmission and RA spectra of the eight-layer ODA LB film in the wavenumber range of 2700—3100 cm^{-1}.

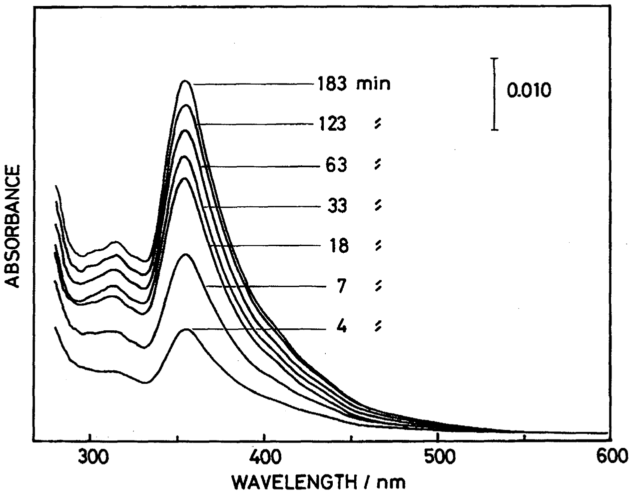

Fig. 3. Time dependence of UV-visible spectra for MO molecules adsorbed on the nine-layer LB film.

those parallel to the film surface are selectively observed in the transmission spectrum. Taking into account the selection rule described above, the result that the intensities of CH_2 symmetric and antisymmetric stretching vibration bands in the RA spectrum were weaker than those of corresponding bands in the transmission spectrum (intensity ratio of transmission and RA spectra, I_{trans}/I_{RA} is approximately 5.1 on the average) indicates qualitatively that the long axis along the hydrocarbon chains are oriented almost perpendicular to the film surface. This orientation angle from the surface normal is considered to be smaller than that of cadmium stearate LB film (the value was reported to be about 7° in early works[11,12]) because the corresponding ratios of I_{trans}/I_{RA} for the cadmium stearate LB film were obtained to be 3.4—3.6 in our measurements.

Next, adsorbability of the ODA LB films was evaluated by using the MO molecule as an adsorbate. The ODA LB film was immersed into an aqueous MO solution so that the adsorption of the MO molecules occurred on the LB film. Figure 3 shows the UV-visible spectra of the nine-layer MO-adsorbed ODA LB films measured at various immersing times. The maximum absorption of MO at around 355 nm is attributed to the π–π^* transition moment of MO chromophore. As shown in this figure, the intensity of the peak increased with increasing immersing time, but reached an apparent saturation after two hours. Since the absorption intensity corresponds to the adsorbed amount of MO molecules, this indicates that the adsorbed amount of MO gradually increased with increasing immersing time, but the adsorption rate of MO on the ODA LB film is slower than that on the LB films of long-chain alkylammonium salts, as observed in our previous studies.[6,7] This would be explained by the following reason. In the adsorption process, water molecules are considered to penetrate into the inner layers of the LB film in preference to the MO molecules. The mobility of the layer structures, thereby, increases so as to be favorable for the MO adsorption. Compared with the LB films of long-chain alkylammonium salts, the ODA LB film has the less hydrophilic property of the polar head group (amino group) and the more closely packed hydrocarbon chains. Such structures of the ODA LB film are inferior for the water penetration, and therefore the adsorption rate of MO is supposed to become slower.

The adsorption isotherm was measured for the five-layer ODA LB film at 20 °C. The immersing time of two hours was employed for the complete MO-adsorption. As shown in the result of Fig. 4, the ODA LB film showed high adsorbability for the MO molecules even at the quite dilute concentration of MO (1.0×10^{-5} mol dm^{-3}), and the saturated adsorption of MO was obtained at the concentration of 1.0×10^{-4} mol dm^{-3}. Such an adsorption behavior may be caused by the ionic interaction between amino groups of ODA and sulfonato groups of MO, similar to the LB films of long-chain alkylammonium salts.[6,7] Simultaneously, we studied the layer-dependence of the MO adsorption at the constant concentration of MO (1.0×10^{-4} mol dm^{-3}), and found that adsorbed amount of MO was proportional to the number of layers for the first seven layers. It is therefore

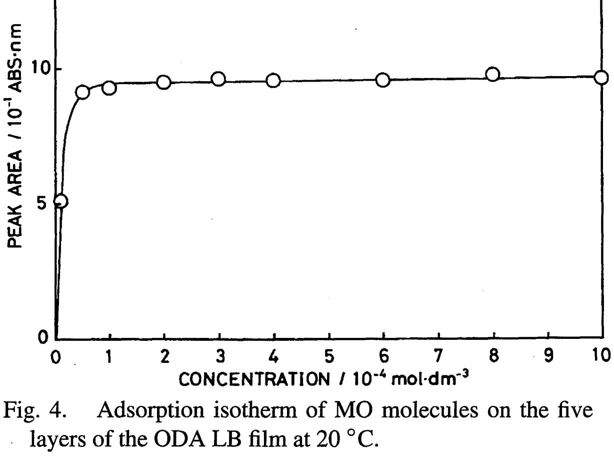

Fig. 4. Adsorption isotherm of MO molecules on the five layers of the ODA LB film at 20 °C.

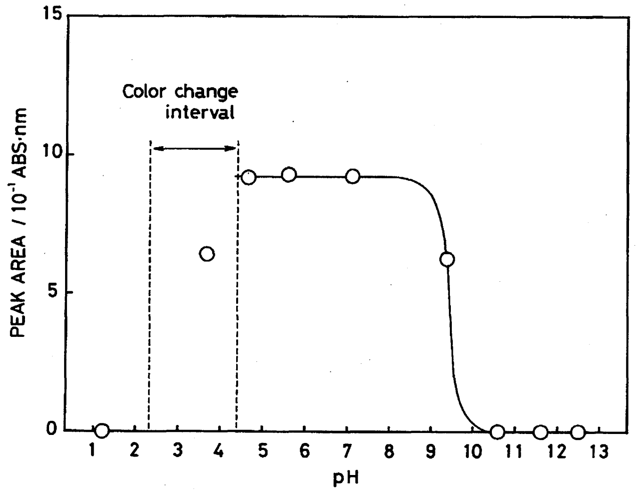

Fig. 5. pH dependence on the adsorbability of the five-layer ODA LB film.

clear that adsorption of MO quantitatively proceeds with the deposited amount of ODA.

The adsorbability of the ODA LB film also showed pH dependence. Figure 5 shows the results obtained by the ODA LB films with the MO adsorption at various values of pH. It was observed that the pH value suitable for the MO adsorption was limited to the range of about 4.5—8.5. The abrupt drop in adsorbability at around pH = 9.5 is considered to occur because of the decrease in the ammonium ion in the ODA LB film. This behavior corresponds to the change of the π–A isotherm from the curves c′ to d′ in Fig. 1. However, this critical pH value is smaller than that for the monolayer on the aqueous MO solutions (pH range of 10.3—11.7). This is probably due to the difference in the molecular environment between the LB film and the monolayer on the subphase. In addition, little adsorption of MO was admitted at the acidic pH region in Fig. 5. This is attributable to the ionization of the amino groups in both MO and ODA molecules. That is to say, the protonation of MO occurring at the pH below the color change interval (the value of pK_a is 3.5) especially hinders the adsorption of MO. Further, the enhancement of the hydrophilic property of ODA would result in the breakage of the layer structure of the ODA LB film at the same time.

In conclusion, the property of the ODA monolayer at the air/water interface was considerably affected by the addition of MO and the pH change in the subphase. The ODA monolayer could be regularly deposited in the multilayer form by using alkaline subphase (above pH = 10.1). Owing to ionic interaction, the ODA LB film exhibited high adsorbability for the MO molecules. The adsorption behavior of MO on the ODA LB film was similar to that on the LB films of long-chain alkylammonium salts but the adsorption rate was found to be slower. The adsorbability of the ODA LB film showed pH dependence.

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