Structural Characterization of Langmuir–Blodgett Films of Octadecyldimethylamine Oxide and Dioctadecyldimethylammonium Chloride. 1. Reorientation of Molecular Assemblies during the Accumulation of Upper Layers Studied by Infrared Spectroscopy

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One- and multilayer Langmuir–Blodgett (LB) films of octadecyldimethylamine oxide (C18DAO) and dioctadecyldimethylammonium chloride (2C18DAC) were prepared on gold- and silver-evaporated glass slides. The first and the rest of the layers were deposited by vertical dipping and horizontal lifting methods, respectively. Infrared (IR) reflection–absorption (RA) spectra were measured for the LB films to investigate the dependence of molecular orientation and structure on the number of layers and the substrates. X-ray diffraction and wetting properties were also measured for some of the films. For both C18DAO and 2C18DAC, there are remarkable changes in the 3000–2800 and 1700–1200 cm⁻¹ regions between spectra of the one-monolayer LB films and those of the two-monolayer LB films irrespective of the substrates. In the spectra of the LB films of C18DAO on gold-evaporated glass slides, bands due to CH₂ stretching modes show a downward shift by 5–7 cm⁻¹ and their intensities become much weaker upon the deposition of the second layer on the first layer, suggesting that the hydrocarbon chain becomes ordered and perpendicular to the substrate surface. In general, the rearrangement of the molecular assemblies takes place during the accumulation of the upper layers in the multilayer LB films of C18DAO and 2C18DAC on the gold-evaporated glass slides.

Introduction

One of the authors, Imae,¹,² has been investigating Langmuir (L) and Langmuir–Blodgett (LB) films of octadecyldimethylamine oxide (C18DAO) and dioctadecyldimethylammonium chloride (2C18DAC) (Figure 1) by use of atomic force microscopy (AFM) and surface pressure area isotherm measurements. The importance of the L and LB films of C18DAO and 2C18DAC stems from two major reasons. One is that they form unique molecular assemblies with various structures because the two amphiphiles have specific headgroups.¹,³–⁶ These headgroups are small compared with those of ordinary amphiphiles; C18DAO has an N−O group with a large dipole moment while that of 2C18DAC possesses positive charge. The second reason is that C18DAO and 2C18DAC offer good reaction matrices to explore structural effects of molecular assemblies constructed by the amphiphilic compounds upon the photocyclodimerization of cinnamic acid.²,⁷–⁹

Figure 1. Chemical structures of octadecyldimethylamine oxide (C18DAO) and dioctadecyldimethylammonium chloride (2C18DAC).

Despite the great interest in the LB films of the two kinds of amphiphilic compounds, there was no systematic and comprehensive study of their structural characterization. Thus, we have undertaken a series of structural studies of the LB films by use of infrared (IR) spectroscopy, X-ray diffraction, atomic force microscopy (AFM), and contact angle measurements.¹⁰–¹²

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In our previous paper, the first report of our series of papers concerned with the structural studies of the LB films of C18DAO and 2C18DAC, we reported an IR study of the molecular orientation and structure in one-monomolecular LB films of C18DAO and 2C18DAC. Dependence of the structure of the LB films on substrates, aging, and the pH of water subphase was discussed. The important conclusions reached in the last study were the following: (i) The one-monomolecular LB film of 2C18DAC on a gold-evaporated glass slide has ordered hydrocarbon chains, while that of C18DAO has an alkyl tail with some gauche conformers. (ii) The molecular orientation and structure in the LB films of both compounds depend significantly upon substrates. (iii) The hydrocarbon chain of C18DAO in the LB film on the gold-evaporated glass slide becomes more ordered over the time course, while those of 2C18DAC in the film become less ordered. (iv) The LB films of C18DAO and 2C18DAC prepared from the aged L films have less ordered hydrocarbon chains. (v) The molecular orientation and structure in the films of both amphiphilic compounds show strong dependence on the pH of the water subphase.

The present report consists of the two papers. This paper describes the dependence of the molecular orientation and structure in the multilayer LB films of C18DAO and 2C18DAC on the number of layers and substrates. The following paper reports thermal behavior of the LB films. Besides these two papers, we shall report quantitative analysis of the molecular orientation in the LB films of C18DAO and 2C18DAC prepared by the vertical dipping method. In this way, we may be able to delineate structural characteristics of the structurally heterogeneous LB films.

**Experimental Section**

C18DAO and 2C18DAC employed in the present study were the same as those previously described. Distilled and deionized water, whose resistance was greater than 18.2 MΩ, was prepared by use of an Advantec Ultrapure Water Apparatus GR-S-200 and CPW-101.

The LB films were fabricated by use of a Kyowa Kaimen Kagaku model HBM-AP Langmuir trough with a Wilhelmy balance. A 1.0 × 10⁻³ M chloroform (spectroscopic grade) solution of C18DAO or 2C18DAC was spread onto the aqueous subphase maintained at 20 ± 0.5 °C by a water circulator. After vaporization of the solvent (30 min), the monolayer was compressed at a constant rate of 20 cm² min⁻¹ up to the surface pressure of 35 mN m⁻². After being allowed to equilibrate for 0.5–30 h at the above surface pressure, the condensed films were transferred onto gold- and silver-evaporated glass slides by raising the surface pressure above the isotherm. The transfer ratio was found to be nearly unity throughout the experiments. The gold- and silver-evaporated glass plates were prepared by Shinyo Co. (Osaka, Japan) as follows: after chromium of 150 nm thickness had been evaporated onto each glass plate, a gold or silver film having a thickness of 300 nm was evaporated onto it. From the cross-section profile of atomic force microscopy (AFM) images of the gold-evaporated glass slides, their average height of protrusion on the surface was estimated to be about 2 nm. The gold- and silver-evaporated glass slides were cleaned first by rinsing them in deionized water, chloroform, and ethyl alcohol. Then, they were subjected to ultrasonic cleaning in chloroform, water, and acetone, followed by ultraviolet–ozone cleaning for at least 5 min.

IR spectra were measured at a 4 cm⁻¹ resolution with a Nicolet Magna 550 spectrometer equipped with a nitrogen cooled mercury–cadmium–telluride (MCT) detector. A minimum of 1000 scans were co-added. IR RA spectra of LB films were measured with a reflection attachment (Specra-Tech Inc.) together with a JOL IR-OPT02 wire grid polarizer. The incident angle of p-polarized light was set at 80°. X-ray diffraction patterns were obtained by a Rigaku CN2125, D2 powder diffractometer with the use of Cu Kα radiation.

Static contact angles of LB films deposited on the gold- and silver-evaporated glass slides were measured with a Ricoh digital camera DC-3Z, which enabled us to take microscopic pictures of water drops with high resolution. The obtained photos were treated with iXelPhoto DLU-3W software for Windows 95. At least two drops were used for the readings of the contact angles, and the readings were reproducible within ±1° for a given sample.

**Results and Discussion**

**X-ray Diffraction.** For a five-monolayer LB film of C18DAO on a gold-evaporated glass slide, we observed two peaks at 2θ = 3.1° and 6.3° in the small-angle X-ray diffraction pattern taken at 25 °C. The peaks are assigned to the first- and second-order diffraction from the layer structure, respectively. The layer spacing d of the film was found to be 2.8 nm. This value is consistent with the calculated length of C18DAO (≈2.8 nm). We were unable to observe a significant diffraction peak for five-monomonolayer LB films of 2C18DAC on both gold- and silver-evaporated glass slides and that of C18DAO on a silver-evaporated glass slide.

**Wetting Properties.** The contact angle of the water drop was measured for LB films of C18DAO and 2C18DAC on gold- and silver-evaporated glass slides, and the results are plotted as a function of the number of layers in Figures 2 and 3, respectively. The contact angle of the one-monomolecular LB films of C18DAO and 2C18DAC on both gold- and silver-evaporated glass slides is between 101 and 112°. These data suggest that the one-monomolecular LB films are hydrophilic and hydrophobic, respectively. The contact angle of the LB films of 2C18DAC remains in the 101–104° region irrespective of the number of monolayers, suggesting that the hydrocarbon chains in the top layers are always exposed to the air. In contrast, the contact angle of the LB films of C18DAO decreases largely upon the deposition of the second layer for both the gold- and silver-evaporated glass slides. Thus, it is likely that the headgroup is exposed to the air in the multilayer LB films of C18DAO.

Wetting properties may depend on not only surface hydrophilicity but also surface roughness. Therefore, there is also a possibility that the decrease in the contact angle of the LB films of C18DAO results from improvement of surface flatness by accumulation. However, in the present case the effects of the improvement of surface flatness may be small. While the LB films of C18DAO on the gold- and silver-evaporated glass slides show very similar...
wetting properties, they give quite different X-ray diffraction pattern. Probably, there is a significant difference in the surface flatness between the LB films of C18DAO on the gold- and silver evaporated glass slide.

Infrared Spectroscopy. IR RA spectra of one-, two-, three-, four- and five-monolayer LB films of C18DAO on gold-evaporated glass slides are shown in Figure 4a–e, respectively. Of particular note is that the appearance of the spectra of the multilayer films is totally different from that of the spectrum of the one-monolayer film. Bands at 2924 and 2854 cm\(^{-1}\) due to the CH\(_2\) antisymmetric and symmetric stretching modes are intense in the spectrum of the one-monolayer LB film, but the corresponding bands (2917 and 2849 cm\(^{-1}\)) are relatively weak in the spectra of the multilayer LB films. In contrast, bands at 2965 and 2877 cm\(^{-1}\) assigned to the CH\(_3\) asymmetric and symmetric stretching modes, respectively, are relatively strong in the spectra of the multilayer LB films, while they are relatively weak in the spectrum of the one-monolayer film.

In our previous paper, we already reported the IR RA spectrum of the one-monolayer LB film of C18DAO on the gold-evaporated glass slide.\(^\text{16}\) It was concluded based upon the band frequencies of the two CH\(_2\) stretching bands and the relative intensities of the CH\(_3\) and CH\(_2\) stretching bands that the alkyl chains are disordered and tilted with respect to the surface normal in the one-monolayer film. The spectrum changes dramatically upon the deposition of the second layer (see parts a and b of Figure 4. The multilayer LB films of C18DAO show four spectral characteristics: (i) low frequencies of the two CH\(_2\) stretching bands and the appearance of a Fermi resonance band at 2932 cm\(^{-1}\); (ii) weak intensities of the two CH\(_2\) stretching bands; (iii) the appearance of band progression in the 1380–1100 cm\(^{-1}\) region; (iv) an intense band at 1675 cm\(^{-1}\).

Characteristics (i) and (iii) lead us to conclude that the alkyl chains are highly ordered in the multilayer LB films of C18DAO on the gold-evaporated glass slides.\(^\text{13,14}\) It is clear from characteristic (ii) that the alkyl chains are nearly perpendicular to the substrate surface.\(^\text{15–17}\) The

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**Figure 2.** Dependence of a contact angle on the number of layers for LB films of C18DAO: (●) gold-evaporated glass slides; (●) silver-evaporated glass slides.

**Figure 3.** Dependence of a contact angle on the number of layers for LB films of 2C18DAC: (●) gold-evaporated glass slides; (●) silver-evaporated glass slides.

**Figure 4.** IR RA spectra of one- (a), two- (b), three- (c), four- (d), and five- (e) monolayer LB films of C18DAO on gold-evaporated glass slides.
molecular orientation and structure in the first layer of the multilayer LB films are improved largely upon the deposition of the upper layers.

In the one-monolayer LB film of C18DAO, the interaction between the N–O group and the gold substrate plays a very important role in determining the orientation and order of the alkyl tail.\(^{10}\) For the multilayer system, it is most likely that the hydrophobic interaction of the hydrocarbon chains between the first and second layers restructures the molecular assemblies of C18DAO. Based upon the results of the IR RA spectra in Figure 4, together with those of the X-ray diffraction and wetting properties, we propose a model structure shown in Figure 8 for the LB films of C18DAO on the gold-evaporated glass slides.

The band at 1675 cm\(^{-1}\) is assigned to the antisymmetric CH\(_3\)-N-CH\(_3\) stretching mode.\(^{10}\) The direction of its transition moment is that connecting the two methyl groups. Therefore, according to the surface selection rule of RA spectroscopy,\(^{15,17}\) the strong intensity of the 1675 cm\(^{-1}\) band means that the direction connecting the two methyl groups is nearly perpendicular to the substrate surface.

The band due to the antisymmetric CH\(_3\)-N-CH\(_3\) stretching mode is identified at 1622 cm\(^{-1}\) in the spectrum of the one-monolayer LB film. The observed shift of the antisymmetric stretching band from 1622 to 1675 cm\(^{-1}\) suggests that the nature of the interaction between the N–O group and the gold-evaporated glass slide changes upon the deposition of the upper layers.

substrate. Probably, the LB films of C_{18}DAO on the silver-evaporated glass slides have the structure shown in Figure 8.

Figure 6a–e depicts IR RA spectra of one-, two-, three-, four-, and five-monolayer LB films of 2C_{18}DAC on gold-evaporated glass slides, respectively. We previously reported the spectrum of the one-monolayer film.\textsuperscript{10} It was concluded in our previous paper that the hydrocarbon chains are ordered except for one or two gauche forms in one of the two tails near the headgroup in the one-monolayer LB film of 2C_{18}DAC on the gold-evaporated glass slide and that the chains are tilted with respect to the surface normal.\textsuperscript{10}

As in the case of the LB films of C_{18}DAO, there are marked spectral changes between the spectrum of one-monolayer LB film and that of two-monolayer LB film. The restructuring of the molecular assemblies takes place also in the multilayer LB films of 2C_{18}DAC. In the spectra of the multilayer LB films, the relative intensities of the two CH\textsubscript{2} stretching bands become weaker while those of the two CH\textsubscript{3} stretching bands become stronger. These observations indicate that the two hydrocarbon chains become more perpendicular in the multilayer LB films. The frequencies of the two CH\textsubscript{2} stretching bands change little from the spectrum of the one-monolayer LB film to that of the four-monolayer LB film, but they show a slight upward shift in the spectrum of the five-monolayer LB film. It seems that the accumulation of many layers makes the chains disordered.

Another notable point in Figure 6 is that the relative intensities of bands in the 1700–1200 cm\textsuperscript{-1} region change largely upon going from the three-monolayer film to the four-monolayer film. A band at 1228 cm\textsuperscript{-1} has significant intensity in the spectra of the two- and three-monolayer LB films, while in those of the four- and five-monolayer films a feature at 1612 cm\textsuperscript{-1} is noted. The band at 1612 cm\textsuperscript{-1} may be due to the CH\textsubscript{3}–N\textsuperscript{0}–CH\textsubscript{3} antisymmetric stretching mode.

As in the case of the CH\textsubscript{3}–N–CH\textsubscript{3} stretching band of C_{18}DAO, the strong appearance of the CH\textsubscript{3}–N\textsuperscript{0}–CH\textsubscript{3} antisymmetric stretching band means that the direction connecting the two CH\textsubscript{3} groups is nearly perpendicular to the substrate surface. The band at 1228 cm\textsuperscript{-1} may be assigned to the N\textsuperscript{0}–C(\text{CH\textsubscript{2}}) stretching mode because the CH\textsubscript{3} and CH\textsubscript{2} groups do not give vibrational modes in the 1250–1200 cm\textsuperscript{-1} region except for the band progression...
of the CH$_2$ wagging mode. Accordingly, the large spectral variations in the 1700–1200 cm$^{-1}$ region between the spectrum of the three-monolayer film and that of the four-monolayer film imply that the orientation of the headgroup changes largely during the accumulation of the monolayers.

On the basis of the following two reasons, we infer the structure with the two tail groups in opposite directions for the LB films of 2C$_{18}$DAC on the gold-evaporated glass slides (Figure 8). One reason comes from the observation of the wetting properties which suggest that the hydrocarbon chains in the top layers are always exposed to the air. Another reason is concerned with the observation that the IR RA spectra of the LB films of 2C$_{18}$DAC on the gold-evaporated glass slides change markedly in the whole region upon going from the one-monolayer film to the two-monolayer film.

In Figure 7a–e, IR RA spectra of one-, two-, three-, four-, and five-monolayer LB films of 2C$_{18}$DAC on silver-evaporated glass slides are shown. The spectra of the multilayer LB films on the silver-evaporated glass slides are similar to those of the corresponding films on the gold-evaporated glass slides. Therefore, the structures of the multilayer LB films of 2C$_{18}$DAC are similar between the gold- and silver-evaporated glass slides (Figure 8). However, small but significant changes are observed for the frequencies of the two CH$_2$ stretching bands and the relative intensity of the two bands at 1611 and 1233 cm$^{-1}$. It seems likely that the hydrocarbon chains are less ordered in the films on the silver-evaporated glass slides than in those on the gold-evaporated glass slides because the frequencies of the two CH$_2$ stretching bands are significantly higher in the spectra of the films on the silver-evaporated glass slides. In addition, the marked change in the orientation of the headgroup takes place earlier in the silver-evaporated glass slides than in the gold-evaporated glass slides.

The spectrum of the one-monolayer LB film of 2C$_{18}$DAC on the silver-evaporated glass slide is significantly different from that of the one-monolayer film on the gold-evaporated glass slide in terms of both the frequencies and intensities of the two CH$_2$ stretching bands. It seems likely that the alkyl chains are less ordered in the film on the silver-evaporated glass slide. Distribution of the negative charge on the metal surface may be different between the gold- and silver-evaporated glass slides so that the nature of the substrate–headgroup interaction is significantly different between the two kinds of metal substrates.

**Conclusions**

The present study has provided new insight into structural characterization of the multilayer LB films of the two kinds of amphiphiles with the unique headgroups. The most important finding in this study is that the molecular orientation and structure in the first monolayers of multilayer LB films of 2C$_{18}$DAC and C$_{18}$DAO are significantly different from those in their one-monolayer LB films. In other words, the process of the reconstruction of the first layer during the accumulation of the upper layers has been observed clearly. In our previous study, it was found that the structural features of the one-monolayer LB films are controlled largely by the specific interaction between the headgroups and substrates. The effects of the headgroup–substrate interaction may be weakened by longitudinal interaction between the monolayers in the multilayer LB films.

To analyze quantitatively the molecular orientation in these structurally heterogeneous LB films, we have applied a new theoretical analytical method for the molecular orientation to their RA spectra. The results will be reported elsewhere.\footnote{LA9810152}