An Infrared Study of Molecular Orientation and Structure in One-Layer Langmuir−Blodgett Films of Octadecyldimethylamine Oxide and Dioctadecyldimethylammonium Chloride: Dependence of the Structures of the Langmuir−Blodgett Films on Substrates, Aging, and pH of Water Subphase

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Molecular orientation and structure in one-layer Langmuir−Blodgett (LB) films of octadecyldimethylamine oxide ($C_{18}DAO$) and dioctadecyldimethylammonium chloride ($2C_{18}DAC$) were investigated by use of infrared (IR) transmission, reflection−absorption (RA), and attenuated total reflectance (ATR) spectroscopy. The IR measurements suggest that the alkyl chains of the one-layer LB film of $2C_{18}DAC$ on a gold-evaporated glass slide are highly ordered, whereas those of the $C_{18}DAO$ LB film have some gauche conformers. The molecular orientation and structure in both LB films show significant substrate dependence. Probably, the headgroup−substrate interaction controls them. Aging effects on the LB and Langmuir (L) films on an air−substrate interface were studied for the two kinds of amphiphiles. The alkyl chains of $C_{18}DAO$ in the LB film on the gold-evaporated glass slide become more ordered with time whereas the reverse trend is observed for those of $2C_{18}DAC$ in the film. The effects on the L films were investigated by measuring IR spectra of the LB films prepared from the L films at various stages. The alkyl chains are less ordered in the LB films of $C_{18}DAO$ and $2C_{18}DAC$ prepared from the aged L films. It is also noted that the molecular orientation and structure in the films of both compounds show strong pH dependence, presumably because of the strong interaction between the headgroups and substrates.

Introduction

In recent years Langmuir−Blodgett (LB) films have been a matter of keen interest because of their fundamental importance in surface science as well as their potential applications in optoelectronics.[1−3] Because the elucidation of the relationship between the structure and function of the films is essential for both basic studies and applications, structural characterization has been made for LB films of various compounds from simple fatty acids to complicated organic dyes by use of IR,[4−6] UV−vis, and Raman spectroscopies[4,5] and atomic force microscopy (AFM).[7] Structural changes in the films induced by aging,[8] doping,[9,10] and variations in pH and temperature[11−21] have also been explored extensively. In the line with this, herein

we present an IR study of structure and aging behavior of one-layer LB films of octadecyldimethylamine oxide ($C_{18}DAO$) and dioctadecyldimethylammonium chloride ($2C_{18}DAC$), shown in Figure 1.

The two compounds, $C_{18}DAO$ and $2C_{18}DAC$, were selected because one of the authors (T.I.) has been investigating effects of organic additives or counterions on the LB films and other supramolecular assembly structures constructed by $C_{18}DAO$ and $2C_{18}DAC$.[18−21] The structures and morphology of the LB films of $C_{18}DAO$ and $2C_{18}DAC$ were investigated in some detail by use of AFM and surface force measurements. However, there has been

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† Kwansei-Gakuin University.
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(1) Roberts, G. *Langmuir−Blodgett Films*; Plenum Press: New York, 1990.
(2) Ulman, A. *An Introduction to Ultrathin Organic Films, From Langmuir−Blodgett to Self-Assembly*; Academic Press: New York, 1991.
(3) Adamson, A. W. *Physical Chemistry of Surfaces*; 5th ed.; Wiley-Interscience: New York, 1990.
(4) Takenaka, T.; Umemura, J. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1991; Vol. 19, 215.
(5) Swalen, J. D. *Annu. Rev. Mater. Sci.* **1991**, *21*, 373.
(6) Urban, M. W. *Attenuated Total Reflectance Spectroscopy of Polymers; Theory and Practice*, and refs therein; American Chemical Society: Washington, DC, 1996.
(7) Schwartz, D. K. *Surf. Sci. Rep.* **1997**, *27*, 241.
(8) Mori, O.; Imae, T. *Langmuir* **1995**, *11*, 4779.

(9) Wang, Y.; Nichogi, K.; Iriyama, K.; Ozaki, Y. *J. Phys. Chem.* **1996**, *100*, 17232.
(10) Wang, Y.; Nichogi, K.; Iriyama, K.; Ozaki, Y. *J. Phys. Chem.* **1996**, *100*, 17238.
(11) Naselli, C.; Rabolt, J. F.; Swalen, J. D. *J. Chem. Phys.* **1985**, *82*, 2136.
(12) Naselli, C.; Swalen, J. D.; Rabolt, J. F. *J. Chem. Phys.* **1989**, *90*, 3855.
(13) Kawai, T.; Umemura, J.; Takenaka, T.; Kodama, M.; Seki, S. *J. Colloid Interface Sci.* **1985**, *103*, 56.
(14) Kimura, F.; Umemura, J.; Takenaka, T. *Langmuir* **1986**, *2*, 96.
(15) Katayama, N.; Enomoto, S.; Sato, T.; Ozaki, Y.; Kuramoto, N. *J. Phys. Chem.* **1993**, *97*, 6880.
(16) Terashita, S.; Nakatsu, K.; Ozaki, Y.; Takagi, S. *J. Phys. Chem.* **1995**, *99*, 3618.
(17) Wang, Y.; Nichogi, K.; Iriyama, K.; Ozaki, Y. *J. Phys. Chem.* **1996**, *100*, 374.
(18) Imae, T.; Sasaki, M.; Ikeda, S. *J. Colloid Interface Sci.* **1989**, *131*, 601.
(19) Imae, T.; Trend, B. *J. Colloid Interface Sci.* **1991**, *145*, 207.
(20) Imae, T.; Iwamoto, T. *J. Colloid Interface Sci.* **1992**, *152*, 289.
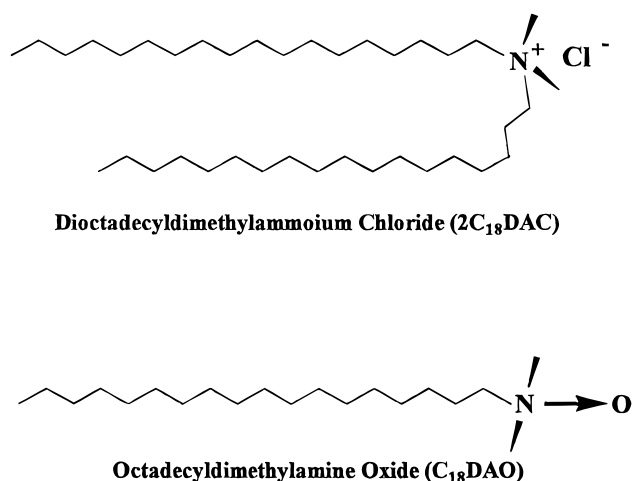(21) Hashimoto, K.; Imae, T. *Langmuir,* **1991**, *7*, 1734.

Figure 1. Structures of 2C$_{18}$DAC and C$_{18}$DAO.

no IR study of them, and molecular orientation and thermal behavior of the LB films of these two compounds have never been well-elucidated. The purpose of the present study was to investigate the molecular orientation and structure in the LB films of C$_{18}$DAO and 2C$_{18}$DAC by means of IR spectroscopy, and to explore their dependence upon substrate, aging, and pH of aqueous subphase.

The most important point of the present study is the interaction between the headgroups and substrates in the first monolayers. Several papers reported significant effects of substrates on distribution/orientation of molecules near the substrate interface.[6] However, the substrate dependence reported in this paper is particularly interesting because both C$_{18}$DAO and 2C$_{18}$DAC have unique headgroups that interact strongly with the substrates. The headgroup of C$_{18}$DAO, amine oxide, has a large dipole moment due to three electron-donating alkyl groups and one strong electron-withdrawing oxygen atom around the nitrogen atom. This large dipole moment brings about strong hydration around the headgroup of C$_{18}$DAO.[8] In contrast, the positively charged headgroup of 2C$_{18}$DAC is neutralized by a counteranion, Cl$^-$. The number of the alkyl chain is also different between C$_{18}$DAO and 2C$_{18}$DAC; one for C$_{18}$DAO and two for 2C$_{18}$DAC. Therefore, the nature of the interaction may be quite different between the LB films of C$_{18}$DAO and 2C$_{18}$DAC.

It was expected that the interaction between the headgroups and the substrates would change not only with the substrates but also with the pH. IR transmission, reflection−absorption (RA), and attenuated total reflection (ATR) spectroscopy have proved to be powerful in investigating the interaction. The different chemical structures of C$_{18}$DAO and 2C$_{18}$DAC also induce different aging at the LB films and Langmuir (L) films on the air−substrate interface. We investigated the aging effect on the L films by measuring IR spectra of LB films of two kinds of amphiphiles prepared from the L films at various stages of aging.

Experimental Section

C$_{18}$DAO and 2C$_{18}$DAC employed in the present study were the same as those previously described.[22−25] The LB films were fabricated by use of a Kyowa Kaimen Kagaku model HBM-AP

(22) Imae, T.; Tsubota, T.; Okamura, H.; Mori, O.; Takagi, K.; Itoh, M.; Sawaki, Y. *Langmuir,* **1995**, *99*, 6046.
(23) Imae, T.;.Takahashi, Y.; Muramatsu, H. *J. Am. Chem. Soc.* **1992**, *114*, 3414.
(24) Okamura, H.; Imae, T.; Takagi, K.; Sawaki, Y.; Furusaka, M. *J. Colloid Interface Sci.* **1996**, *180*, 98.

Langmuir trough with a Wilhelmy balance. A 1.0×10^{-3} M chloroform (spectroscopic grade) solution of C$_{18}$DAO or 2C$_{18}$DAC was spread onto the aqueous subphase. After evaporation of the solvent (30 min), the monolayer was compressed at a constant rate of 20 cm^2 min^{-1} up to the surface pressure of 35 mNm^{-1}. After the films were allowed to equilibrate for 0.5−30 h range at the above surface pressure, the condensed films were transferred onto gold-evaporated glass slides, CaF$_2$ windows, and germanium ATR crystals (Pier Optics Co.) by raising the immersed substrates at a rate of 0.5 cm min^{-1}.

The gold-evaporated glass plates were prepared by Shinyo Co. (Osaka, Japan) as follows: a 150 nm thick chromium film was first deposited by evaporation onto the glass slides, followed by a 300 nm thick gold film. From the cross-section profile of AFM images of the gold-evaporated glass slides, their average height of protrusion on the surface was estimated to be about 2 nm.

The germanium ATR crystals have 45° end faces and 52×20 mm horizontal sampling surfaces. The number of internal reflections in the crystal were 26. The ATR plates were cleaned by rinsing them in deionized water, chloroform, and ethyl alcohol, followed by ultraviolet-ozone cleaning of both sides of the plates for at least 5 min. The crystals were then rinsed again and sterilized in ozone for at least 3 min. The gold-evaporated glass slides and CaF$_2$ plates were cleaned by a similar procedure, with additional ultrasonic cleaning in chloroform, water, and acetone.

The temperature of the subphase water was kept at 20.0 ± 0.5 °C by a water circulator. Distilled and deionized water (Advantec Ultrapure Water Apparatus GRS-200 and CPW-101), the resistivity of which was greater than 18.2 MΩ cm, was used for the aqueous subphase. The pH of the water subphase was kept at 3.0 or 5.8. The transfer ratio was found to be higher than 0.95 throughout the present experiments.

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. To record IR reflection−absorption (RA) spectra of LB monolayers on the gold-evaporated glass slides, a reflection attachment (Spectra-Tech Inc.) was used at the incident angle of 80°, together with a JEOL IR−OPT02 wire grid polarizer. The IR spectra of C$_{18}$DAO and 2C$_{18}$DAC in crystal states were measured with a JEOL JIR-6500 FTIR spectrometer equipped with an MCT detector and micro IR attachment (JEOL IR-MAU 110).

FT-Raman spectra were measured with a JEOL JRS−FT 6500N FT-Raman spectrometer equipped with an InGaAs detector. An excitation wavelength at 1064 nm was provided by a continuous wave Nd:YAG laser (Spectron SL 301 1355), and the laser power at the sample position was 500 mW. The Raman data were collected at a spectral resolution of 4 cm^{-1} and a few hundred scans were accumulated.

Results and Discussion

Band Assignments of IR Spectra of C$_{18}$DAO and 2C$_{18}$DAC in Solid States. Before RA, transmission, and ATR spectra of one-layer LB films of C$_{18}$DAO and 2C$_{18}$-DAC can be interpreted, IR bands of these compounds in solid states must be assigned. To do that, transmission IR spectra of C$_{18}$DAO and 2C$_{18}$DAC were recorded in KBr matrixes. Figure 2(a) and (b) show these spectra, respectively. Bands due to the CH$_2$ antisymmetric and symmetric stretching modes of the alkyl chains are identified at 2917 and 2850 cm^{-1}, respectively. It is well-known that the frequencies of CH$_2$ antisymmetric and symmetric stretching bands are very sensitive to the degree of conformational order of a hydrocarbon chain.[26−28] When the chain is highly ordered (trans-zigzag conformation), the bands appear

(25) Imae, T.; Kakitani, M.; Kato, M.; Furusaka, M. *J. Phys. Chem.* **1996**, *100*, 20051.
(26) Sapper, H.; Cameron, D. G.; Mantsch, H. H. *Can. J. Chem.* **1981**, *59*, 2543.
(27) Cameron, D. G.; Martin, A.; Moffat, D. G.; Mantsch, H. H. *Biochemistry,* **1985**, *24*, 4355.
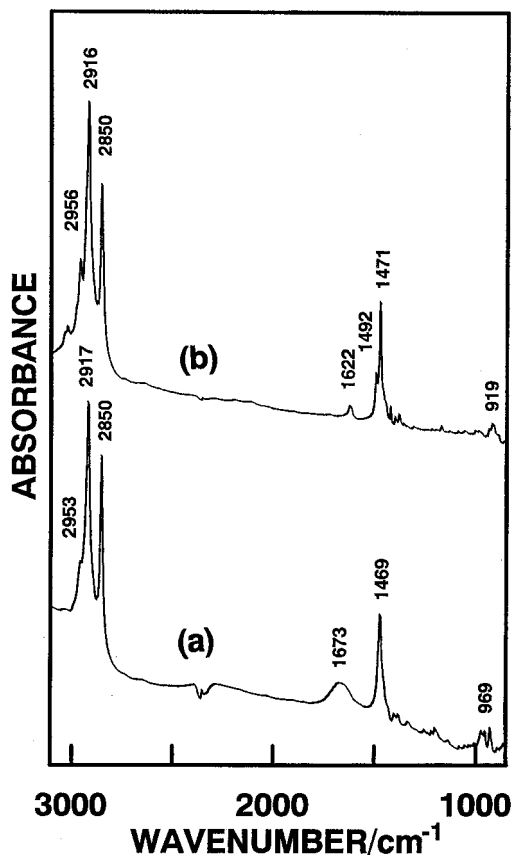(28) Tian, Y. *J. Phys. Chem.* **1991**, *95*, 9985.

Figure 2. IR transmission spectra of $C_{18}DAO$ (a) and $2C_{18}DAC$ (b) dispersed in KBr matrixes.

Table 1. Band Assignments for Infrared Spectra of $C_{18}DAO$ and $2C_{18}DAC$ in Solid States

$C_{18}DAO$, cm^{-1}	$2C_{18}DAC$, cm^{-1}	band assignments[a]
2953	2956	CH_3 asym str
2917	2916	CH_2 antisym str
2875	2877	CH_3 sym str
2850	2850	CH_2 sym str
1673		CH_3-N-CH_3 antisym str
	1622	$CH_3-N^+-CH_3$ antisym str
1469	1492, 1471	CH_2 scissoring
1383		CH_3 sym def
1300−1100		CH_2 wagging + twisting
990−960		N→O str
	919	NC_3 asym str

[a] Abbreviations: asym: asymmetric, sym: symmetric, antisym: antisymmetric, str: stretching, def: deformation.
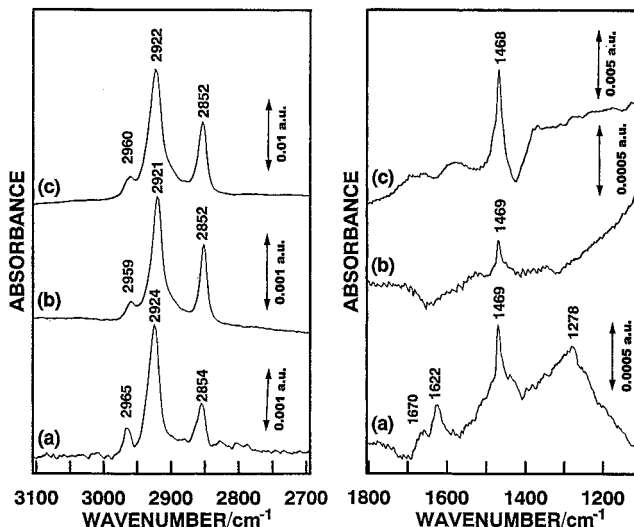

Figure 3. (a) An IR RA spectrum of one-layer LB film of $C_{18}DAO$ on a gold-evaporated glass slide. (b) An IR transmission spectrum of a one-layer LB film of $C_{18}DAO$ on a CaF$_2$ plate. (c) An IR/ATR spectrum of a one-layer LB film of $C_{18}DAO$ on a Ge prism.

near 2918 and 2848 cm^{-1}, respectively, whereas if the conformational disorder is included in the chain, the bands appear at higher frequencies, i.e., 2927 and 2856 cm^{-1} depending upon the content of gauche conformers. Therefore, the observations in Figure 2 suggest that the hydrocarbon chains of $C_{18}DAO$ and $2C_{18}DAC$ in the KBr disk are nearly ordered. In the 1700−900 cm^{-1} region a band due to the scissoring mode of CH_2 groups appears at 1469 cm^{-1} in the spectrum of $C_{18}DAO$, but splits into two bands at 1492 and 1471 cm^{-1} in the spectrum $2C_{18}DAC$. It was reported that the upward shift of the scissoring band results from the interaction of the CH_2 group with N^+ of ammonium chloride, which causes a change in the charge distribution on the carbon atoms.[29,30]

As recently indicated by Wong et.al.,[31] the band assignments of headgroup vibrational modes of the alkylammonium salts were neglected in most of the previous studies.[32] In the present study we compare the IR spectra of $C_{18}DAO$ and $2C_{18}DAC$ with the corresponding Raman spectra (not shown) to investigate the assignments. An IR band at 1673 cm^{-1} in the spectrum of $C_{18}DAO$ and that at 1622 cm^{-1} in the spectrum of $2C_{18}DAC$ (Figure 2) may be due to vibrational modes of the headgroups because it is very unlikely that the alkyl chains give a band near 1650 cm^{-1} and because these two bands show pH dependence, as will be described later. We assign these bands to antisymmetric CH_3-N-CH_3 stretching modes of the headgroups. Probably, the CH_3-N-CH_3 bonds

have double bond character because of effects of the two methyl groups.

According to a reference book,[33] tertiary amine oxides show a N−O stretching band in the 970−950 cm^{-1} region of the IR spectra. Thus, IR bands in the 990−960 cm^{-1} region of $C_{18}DAO$ and Raman bands in the same region may be assigned to the N→O stretching mode. Two or three bands appear in this region of both IR and Raman spectra, suggesting that some N→O groups are involved in the formation of dimers. The band assignments of the IR spectra of $C_{18}DAO$ and $2C_{18}DAC$ are summarized in Table 1.

IR Spectra of One-Layer LB Films of $2C_{18}DAC$ and $C_{18}DAO$. Figures 3 and 4 show IR RA, transmission, and ATR spectra of one-layer LB films of $C_{18}DAO$ and $2C_{18}DAC$ on gold-evaporated glass slides (a), CaF$_2$ plates (b), and Ge prisms (c), respectively. In Figures 3 and 4, note that the IR spectra of the one-layer LB films change with the substrates in terms of both frequencies and intensities. To the best of our knowledge, it is rather rare that one can observe such marked spectral differences between the substrates. These observations suggest that the interaction between the headgroups and the substrates is significantly strong. One of the reasons why the structure of the LB films of $C_{18}DAO$ shows the substrate

(29) Baker, A. W.; Lord, R. C. *J. Chem. Phys.* **1955**, *23*, 1636.

(30) Duncan, J. L.; McKean, D. C. *J. Mol. Spectrosc.* **1968**, *27*, 117.

(31) Wong, T. C.; Wong, N. B.; Tanner, P. A. *J. Colloid Interface Sci.* **1997**, *186*, 325.

(32) Rathman, J. F.; Scheung, D. R. In *Fourier Transform Infrared Spectroscopy in Colloid and Interface Science*; Scheung, D. R., Ed.; American Chemical Society: Washington, DC, 1990; p. 123.

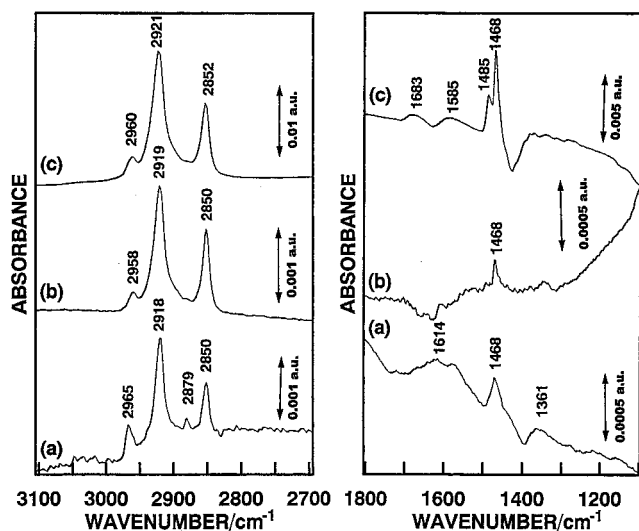(33) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1975.

Figure 4. (a) An IR RA spectrum of one-layer LB film of $2C_{18}DAC$ on a gold-evaporated glass slide. (b) An IR transmission spectrum of a one-layer LB film of $2C_{18}DAC$ on a CaF_2 plate. (c) An IR/ATR spectrum of a one-layer LB film of $2C_{18}DAC$ on a Ge prism.

dependence is that the N→O group of $C_{18}DAO$ has a large dipole moment and thus is largely hydrated. Probably, these characteristic properties of the headgroup produce a different interaction with the different substrates. For the LB films of $2C_{18}DAC$, it seems that the positive charge of its headgroup plays an important role in the interaction with the substrates.

The CH_2 antisymmetric and symmetric stretching bands of $C_{18}DAO$ appear at 2924 and 2854 cm^{-1}, respectively, in the spectrum of the one-layer LB film on the gold-evaporated glass substrate (Figure 3(a)), whereas they are identified at 2921 and 2852 cm^{-1}, respectively, in those of the one-layer films on the CaF_2 (Figure 3(b)) and Ge prism (Figure 3(c)). Therefore, it seems that the alkyl chains of $C_{18}DAO$ are disordered in the LB film on the gold-evaporated glass slide, but they become more ordered in the films on the CaF_2 plate and Ge crystal.

In the 1800−1100 cm^{-1} region, bands at 1670 and 1622 cm^{-1} appearing in the RA spectrum may be ascribed to the antisymmetric CH_3−N−CH_3 stretching modes. The corresponding band is located at 1673 cm^{-1} in the spectrum of $C_{18}DAO$ in the KBr pellet (Figure 2(b)). The appearance of the band at 1622 cm^{-1} suggests that the CH_3−N−CH_3 groups interact strongly with the gold-evaporated glass substrate. A band at 1278 cm^{-1} may be due to a CH_3 symmetric bending mode of the headgroup of $C_{18}DAO$.

In contrast to the LB film of $C_{18}DAO$ on the gold-evaporated glass slide, the one-layer LB film of $2C_{18}DAC$ on the gold-evaporated glass slide shows the CH_2 antisymmetric and symmetric stretching bands at 2918 and 2850 cm^{-1}, respectively (Figure 4(a)). Therefore, it seems that the alkyl chains are ordered in the film of $2C_{18}DAC$. The same conclusion can be reached for the LB film of $2C_{18}DAC$ on the CaF_2 plate because the two CH_2 stretching bands are observed at 2919 and 2850 cm^{-1} (Figure 4(b)). According to an X-ray analysis of crystalline dioctade-cyldimethylammonium bromide ($2C_{18}DAB$),[34] one of its two hydrocarbon chains is bent at almost right angle in the third carbon atom, but after the third carbon atom both chains have a trans-zigzag conformation with their molecular planes parallel to each other. It has also been

stated that molecules with a large headgroup and two hydrocarbon chains adopt this sort of very simple and compact folding pattern.[34] Probably, $2C_{18}DAC$ in the LB films on the gold-evaporated glass slide and CaF_2 plate has very similar conformation to that of $2C_{18}DAB$ described above (Figure 1). In the LB films it seems that the strong interaction of the positively charged headgroup with the substrate supports the ordered structure of the alkyl chains.

In the 1650−1570 cm^{-1} region, one can observe a broad band, which shows pH dependence as will be described later. This band may be due to the antisymmetric CH_3−N^+−CH_3 antisymmetric stretching mode. The band appears as two distinct and separate peaks at 1683 and 1585 cm^{-1} in the ATR spectrum (Figure 4(c)). The CH_2 scissoring band is observed as a singlet near 1468 cm^{-1} in the RA and transmission spectra of the $2C_{18}DAC$ LB films, but it splits into two at 1485 and 1468 cm^{-1} in the ATR spectrum. According to Cameron et. al.,[27,35] if the band appears as a singlet, it means that the hydrocarbon chains exhibit so-called "rotator" phase with relatively small interaction in the hexagonal subcell packing. The remarkable rise in the frequency for the split band may result from the interaction of the CH_2 groups with N^+, which causes the change in the charge distribution on the α carbon atoms of $2C_{18}DAC$, as described above.

According to the surface selection rule in RA spectros-copy,[36−38] vibrational modes with their transition moments perpendicular to the surface are enhanced in an RA spectrum. The intensities of the two CH_2 stretching bands are not weak in the RA spectrum of the film of $2C_{18}DAC$, indicating that the hydrocarbon chains are tilted with respect to the surface normal. The hydrocarbon chains may be randomly orientated in the film of $C_{18}DAO$ because a number of gauche conformers are involved in the chains.

A comparison between Figures 3 and 4 indicates that the molecular orientation and structure in the one-layer LB films of $C_{18}DAO$ and $2C_{18}DAC$ are largely different from each other. The two compounds have different headgroups, and thus the nature of the interaction between the headgroups and the substrates may be quite specific. The number of the alkyl tails is also different; one for $C_{18}DAO$ and two for $2C_{18}DAC$. There is little doubt that the interaction between the first layer and the metal surface controls the molecular orientation and structure in the LB films.

Aging Effect on Langmuir Films of $C_{18}DAO$ and $2C_{18}DAC$. One of the authors (T.I.) et al.[8,39] found that Langmuir films of both $C_{18}DAO$ and $2C_{18}DAC$ showed interesting aging phenomena; in the trough the area per molecule of the films compressed until the surface pressure of 35 mNm^{-1} started to decrease approximately 30 min after the compression (the surface pressure was kept at 35 mN m^{-1}). The decrease in the surface area was dramatic; for example, 47% after 30 h for the $2C_{18}DAC$ film and more than 75% after the same period for $C_{18}DAO$. To investigate the aging effect spectroscopically, we transferred the films onto gold-evaporated substrates at the different stages of aging and measured their RA spectra.

(34) Okuyama, K.; Soboi, Y.; Iijima, N.; Hirabayashi, K.; Kunitake, T.; Kajiyama, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1485.
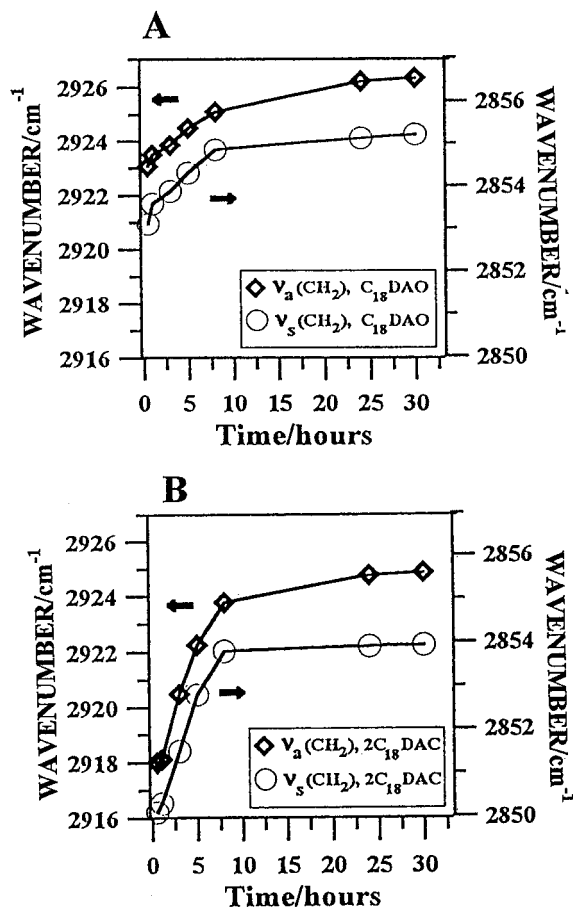
(35) Cameron, D. G.; Umemura, J.; Wong, P. T. T.; Mantsch, H. H. *Colloid Surf.* **1982**, *4*, 131.

(36) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310.

(37) Chollet, P.-A.; Messier, J.; Rosilo, C. *J. Chem. Phys.* **1976**, *64*, 1042.

(38) Chollet, P.-A. *Thin Solid Films* **1978**, *52*, 343.

(39) Kakitani, M.; Imae, T.; Furusaka, M. *J. Phys. Chem.* **1995**, *99*, 16018.

Figure 5. Frequencies of the CH_2 antisymmetric and symmetric stretching bands of $C_{18}DAO$ (A) and $2C_{18}DAC$ (B) LB monolayers on the gold-evaporated glass slides prepared from L monolayers at various times.

Figure 6. (a) An IR RA spectrum of an aged one-layer LB film of $C_{18}DAO$ on a gold-evaporated glass slide. (b) An IR transmission spectrum of an aged one-layer LB film of $C_{18}DAO$ on a CaF_2 plate. (c) An IR/ATR spectrum of an aged one-layer LB film of $C_{18}DAO$ on a Ge prism. All of the spectra in this figure were measured after the films were kept in a desiccator for 24 h.

In Figure 5A and B, the frequencies of the CH_2 antisymmetric and symmetric stretching bands are plotted for the LB films of $C_{18}DAO$ and $2C_{18}DAC$, respectively, prepared by transferring the Langmuir films kept under the surface pressure of 35 mN m^{-1} for 30 min to 30 h. In both cases their frequencies shift upward with time, indicating that the hydrocarbon chains become disordered with aging.

One of the authors (T.I.) investigated the aging process of a $C_{18}DAO$ monolayer on water subphase by observing AFM images of LB films prepared from the aged L films.[8] The characteristic properties of the $C_{18}DAO$ monolayer on the water subphase result from the hydration on the amine oxide group. Reportedly, one $C_{18}DAO$ molecule is surrounded by eight water molecules in the initial stage of the monolayer preparation, allowing $C_{18}DAO$ molecule and hydrated water molecules to occupy a rather large surface area. It was considered that as time passes, the hydrated water molecules are pulled into bulk water, decreasing the occupied area per $C_{18}DAO$ molecule.[8] It is likely that $C_{18}DAO$ molecules are lying in the monolayer with disordered alkyl chains in the initial stage (because each molecule is enveloped by water molecules), but that they are rearranged with time, the tails becoming ordered tails. Thus, we expected that the freshly prepared $C_{18}DAO$ monolayer would give an LB film with less ordered alkyl chains while the aged one would provide the film with ordered chains. However, the results in Figure 5A suggest that the alkyl chains in the LB film prepared from the fresh L film of $C_{18}DAO$ are disordered and those in the films from the aged L films are even more disordered.
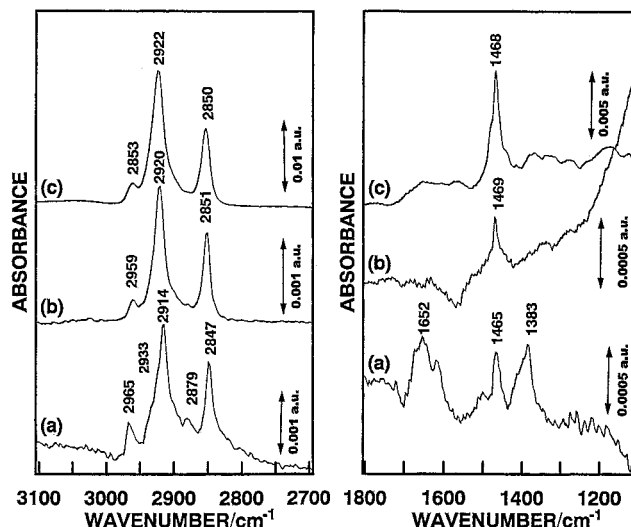
Probably, the conformation of the alkyl chains observed by IR spectra is not exactly the same as the conformation formed in the L films. We tried both 25 and 35 mN m^{-1} surface pressures. No significant difference was observed in the molecular conformation in the LB films, although there was a large difference between the L films at the surface pressures of 5 and 25 mN m^{-1}.[8]

Aging Effect on Langmuir−Blodgett Films of $C_{18}DAO$ and $2C_{18}DAC$. One-layer LB films of $C_{18}DAO$ and $2C_{18}DAC$ on the gold-evaporated glass slides, CaF_2 plates, and Ge prism were stored in a desiccator for 24 and 72 h, and then their IR spectra were measured to explore aging effects on the LB films. Dramatic changes were observed for both compounds between the fresh LB films and those stored in the desiccator for 24 and 72 h. Figure 6 (a), (b), and (c) show the IR spectra of the one-layer LB films of $C_{18}DAO$ on the gold-evaporated glass slide, CaF_2 plate, and Ge prism, respectively, stored in the desiccator for 24 h.

The striking feature in Figure 6 is the surprisingly low peak positions of the CH_2 antisymmetric and symmetric stretching bands of $C_{18}DAO$ in the aged LB monolayer on the gold-evaporated glass slide. The lower frequencies are characteristic of highly ordered, trans-zigzag conformations of methylene chains.[26−28] Note that even a band due to the Fermi resonance is seen at 2933 cm^{-1} as a shoulder of the CH_2 antisymmetric band. These observations lead us to conclude that the alkyl chains in the LB film of $C_{18}DAO$ in the gold-evaporated glass slide become highly ordered (trans-zigzag) with time. An appearance of CH_2 wagging progression in the 1300−1150 cm^{-1} region also supports this. A similar trend for the aging effect on the molecular conformation of the alkyl chains is observed for the CaF_2 and Ge plates, although the changes are smaller for them.

Another noteworthy age-dependent change is the appearance of a broad, strong band around 1652 cm^{-1} assignable to the CH_3-N-CH_3 antisymmetric stretching band in Figure 6(a). This indicates that the orientation of the headgroup changes with time. The change in the conformation of the alkyl chain might be linked with the reorientation of the headgroup.
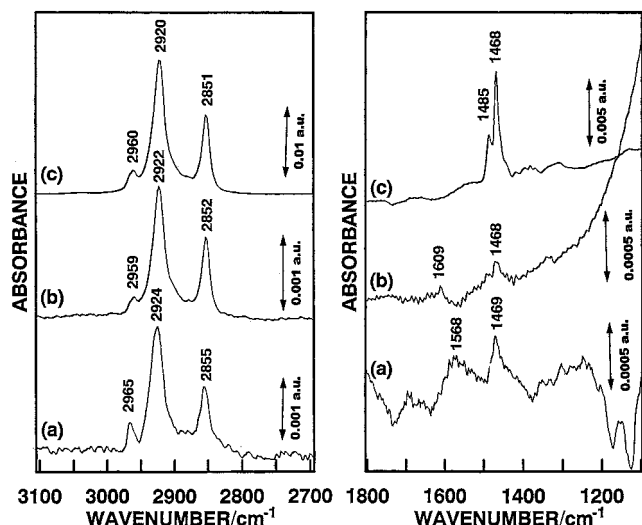
Figure 7. (a) An IR RA spectrum of an aged one-layer LB film of 2C$_{18}$DAC on a gold-evaporated glass slide. (b) An IR transmission spectrum of an aged one-layer LB film of 2C$_{18}$DAC on a CaF$_2$ plate. (c) An IR/ATR spectrum of an aged one-layer LB film of 2C$_{18}$DAC on a Ge prism. All of the spectra in this figure were measured after the films were kept in a desiccator for 24 h.

The age-dependent changes for the LB films of 2C$_{18}$DAC are quite different from those for the LB films of C$_{18}$DAO. In Figure 7(a), (b), and (c) are shown the IR spectra of the one-layer LB film of 2C$_{18}$DAC on gold-evaporated glass slide, CaF$_2$ plate, and Ge prism, respectively, stored in the desiccator for 24 h. In contrast to the two CH$_2$ stretching bands of the LB films of C$_{18}$DAO on the gold-evaporated glass slide and CaF$_2$ plate, those of the corresponding films of 2C$_{18}$DAC show an upward shift by 2−6 cm^{-1}. Thus, the hydrocarbon chains become less ordered as time passes in the LB films of 2C$_{18}$DAC.

The age-dependent changes are small for the LB films of both C$_{18}$DAO and 2C$_{18}$DAC on the Ge prisms. Accordingly, the aging effects also depend on the substrates.

Dependence of the Molecular Orientation and Structure in the LB Films on the pH of the Water Subphase. To investigate the headgroup−substrate interaction and the headgroup−headgroup interaction further, the effect of the pH of the water subphase on the molecular orientation and structure in one-layer LB films of C$_{18}$DAO and 2C$_{18}$DAC was examined by IR spectroscopy. Figures 8 and 9 present IR RA and transmission spectra of the LB films of C$_{18}$DAO and 2C$_{18}$DAC transferred from the water subphase at pH 3.0 onto gold-evaporated glass slides and CaF$_2$ plates, respectively. Comparison of the IR spectra of the LB films of C$_{18}$DAO transferred from the water subphase at pH 5.8 (Figure 3) with those transferred from the subphase at pH 3.0 (Figure 8) enables us to discuss the effect of pH on the above-mentioned interactions.

When we compare Figure 3(a) with Figure 8(a), we notice several major spectral changes. First, the intensities of the bands in the 1680−1620 cm^{-1} region assignable to the CH$_3$−N−CH$_3$ antisymmetric stretching modes vary upon going from pH 5.8 to 3.0. This may result from the molecular orientational change of the headgroup with decreasing pH. It is likely that the change in pH of the subphase water induces a change in the headgroup−substrate interaction, leading to the reorientation of the headgroup. The CH stretching band region undergoes a marked spectral variation with pH; the two CH$_2$ stretching bands show a downward shift by 2−4 cm^{-1} and the relative
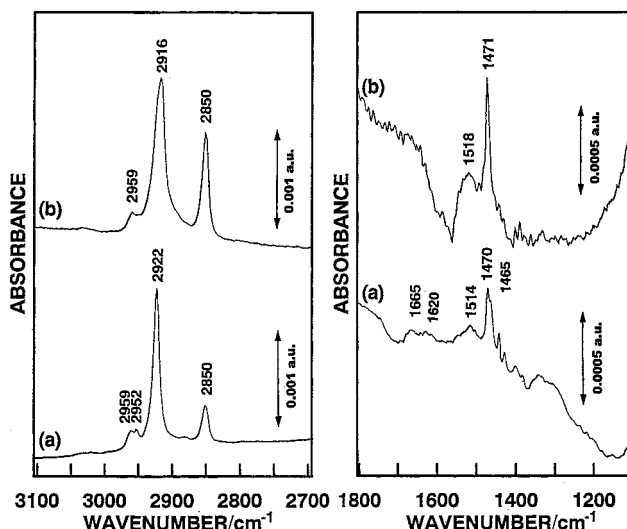

Figure 8. (a) An IR RA spectrum of a one-layer LB film of C$_{18}$DAO on a gold-evaporated glass slide prepared from the aqueous subphase at pH 3.0. (b) An IR transmission spectrum of a one-layer LB film of C$_{18}$DAO on a CaF$_2$ plate prepared from the aqueous subphase at pH 3.0.
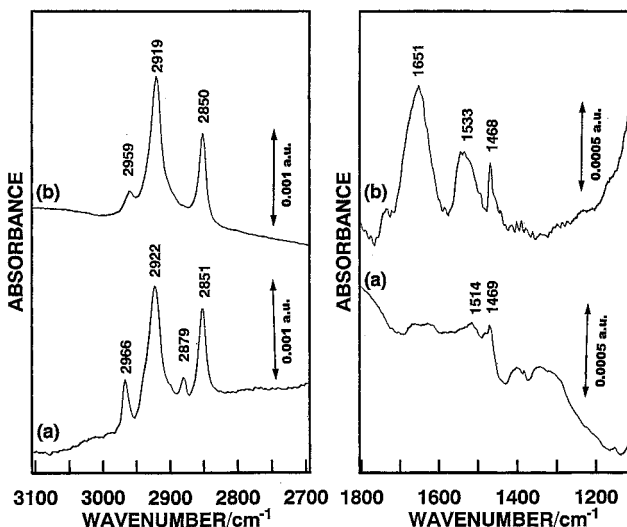

Figure 9. (a) An IR RA spectrum of a one-layer LB film of 2C$_{18}$DAC on a gold-evaporated glass slide prepared from the aqueous subphase at pH 3.0. (b) An IR transmission spectrum of a one-layer LB film of 2C$_{18}$DAC on a CaF$_2$ plate prepared from the aqueous subphase at pH 3.0.

intensity of the CH$_2$ symmetric band becomes very weak. The downward shifts suggest that the alkyl chains become more ordered with decreasing pH. In Figure 8(a) the CH$_2$ antisymmetric stretching band is much stronger than the CH$_2$ symmetric stretching band. The transition moments of the CH$_2$ antisymmetric and symmetric stretching modes are parallel and perpendicular to the plane of alkyl chain. Thus, the observed intensity pattern for the two CH$_2$ stretching bands indicates that the molecular plane is tilted somewhat from the surface normal, whereas the planes are considered to have an ordered packing. The band progression peaks in the 1465−1350 cm^{-1} region support the ordered packing. Therefore, it seems that the alkyl chains are crystallized with highly packed alkyl planes in the LB film of C$_{18}$DAO on the gold-evaporated glass slide prepared from the aqueous subphase at pH 3.0.

As in the case of the gold-evaporated glass plate, the decreased pH induces a downward shift for the two CH$_2$

stretching bands of the LB film on the CaF$_2$ plate. Thus, the hydrocarbon chains of C$_{18}$DAO become more ordered in the LB films on both the gold-evaporated glass slide and CaF$_2$ plate upon going from pH 5.8 to 3.0. The reverse trend is observed for the alkyl chains of 2C$_{18}$DAC in the LB film on the gold-evaporated glass slide; both the CH$_2$ antisymmetric and symmetric stretching bands shift upward with decreasing pH.

Another notable pH-dependent change for the LB films of 2C$_{18}$DAC is the intensity enhancement of the band at 1651 cm^{-1} in Figure 9(b). It seems likely that the molecular orientation of the headgroup changes considerably on lowering the pH.

We may be able to interpret the pH-dependent structural changes of C$_{18}$DAO and 2C$_{18}$DAC in the LB films as follows. C$_{18}$DAO has a hydrophilic N→O group. The repulsive interaction among the dipole moments of the N→O groups is strong in the LB films formed at a neutral pH, and thus, C$_{18}$DAO does not have highly ordered (trans-zigzag) structure. On the other hand, in the low pH region the repulsive interaction of the dipole moments of the N→O groups becomes weak, so that the alkyl tails of C$_{18}$DAO can take trans-zigzag conformation more easily. The additional positive charge from proton may be stabilized by the negative charge of the metal surface, resulting in the solid structure on the LB films.

In contrast to C$_{18}$DAO, 2C$_{18}$DAC does not have a strong dipole moment in the neutral pH. However, repulsive interaction may occur among the headgroups of 2C$_{18}$DAC molecules in the low pH because of the protonation. Therefore, the L films of 2C$_{18}$DAC become unstable because of charge repulsion, resulting in the less ordered structure of the alkyl tails.

Conclusion

This paper reported the IR study of the molecular orientation and structure in the one-layer LB films of two kinds of amphiphilic molecules with the unique headgroups, dimethylammonium chloride and dimethylamine oxide. Particular emphasis was put on the aging effects on the LB and L films of C$_{18}$DAO and 2C$_{18}$DAC and on the effect of pH of the aqueous subphase on the LB films. Even one-layer films gave high-quality IR spectra with a high signal-to-noise ratio, so that we could explore the molecular orientation and structure in the LB films and the interaction between the headgroups and the substrates in detail.

The conclusions reached from the present study are summarized as follows.

(1) The molecular orientation and structure of the one-layer LB films of both C$_{18}$DAO and 2C$_{18}$DAC show significant substrate dependence. The interaction between the headgroups and the substrates plays an important role in determining the molecular orientation and structure.

(2) The alkyl chains contain some gauche conformers in the LB film of C$_{18}$DAO on the gold-evaporated glass slide, whereas they assume nearly trans-zigzag conformation in that of 2C$_{18}$DAC on the gold-evaporated glass slide (see models for pH 5.8 in Figure 10).

(3) The molecular orientation and structure in the LB films of C$_{18}$DAO and 2C$_{18}$DAC change with pH of the subphase water. Probably, decreasing the pH induces the changes in the substrate−headgroup interaction, leading

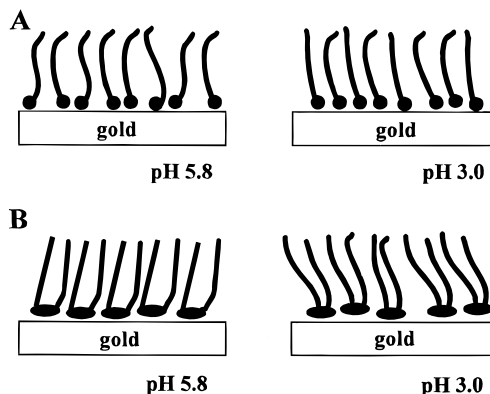**Figure 10.** Schematic models for the molecular assembly of C$_{18}$DAO (A) and 2C$_{18}$DAC (B) on gold-evaporated glass slides transferred from water subphase at pH 5.8 and 3.0.

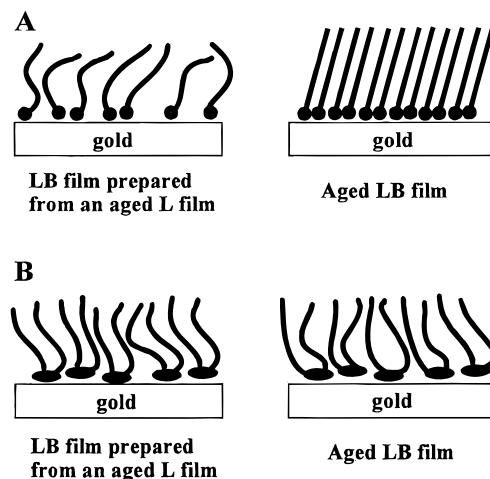**Figure 11.** Schematic models for the molecular assembly of LB films prepared from aged L films and of aged LB films of C$_{18}$DAO (A) and 2C$_{18}$DAC (B) on gold-evaporated glass slides.

to a reorientation of the alkyl chains. As shown in Figure 10, the alkyl chains become less ordered on decreasing pH in the LB film of 2C$_{18}$DAC on the gold-evaporated glass slide, whereas they become more ordered in the film of C$_{18}$DAO on the gold-evaporated glass slide.

(4) The aging effects on the structure of the L films were investigated by transferring the aged L films onto the gold-evaporated glass slides. The alkyl chains are less ordered in the LB films prepared from the aged L films (Figure 11).

(5) The LB films of C$_{18}$DAO and 2C$_{18}$DAC on the gold-evaporated glass slides show the reverse changes for aging effect (Figure 11). The alkyl chains become more ordered in the LB film of C$_{18}$DAO, whereas they become less ordered in that of 2C$_{18}$DAC (Figures 10 and 11).

In summary, the differences in the number of the alkyl chain and in the chemical structure of the headgroup cause a number of significant changes in the molecular orientation and structure of the one-layer LB films of C$_{18}$DAO and 2C$_{18}$DAC. Investigations on multilayer LB films of the two kinds of amphiphilic compounds by IR and AFM are now under way in our research groups.