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Structural Characterization of Langmuir−Blodgett Films of Octadecyldimethylamine Oxide and Dioctadecyldimethylammonium Chloride. 2. Thickness Dependence of Thermal Behavior Investigated by Infrared Spectroscopy and Wetting Measurements

Diyas A. Myrzakozha,[†] Takeshi Hasegawa,[‡] Jujiro Nishijo,[‡] Toyoko Imae,[§] and Yukihiro Ozaki*[,†]

Department of Chemistry, School of Science, Kwansei-Gakuin University, Uegahara, Nishinomiya 662-8501, Japan, Kobe Pharmaceutical University, Higashinada-ku, Kobe 658-8558, Japan, and Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-8602, Japan

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Infrared (IR) reflection−absorption (RA) spectra have been measured for one- and five-monolayer Langmuir−Blodgett (LB) films of octadecyldimethylamine oxide (C_{18}DAO) and dioctadecyldimethylammonium chloride (2C_{18}DAC) on gold- and silver-evaporated glass slides over a temperature range of 25−110 °C. Dependences of the thermal behavior of the LB films of C_{18}DAO and 2C_{18}DAC upon the substrates and the number of layers have been discussed. The LB films of C_{18}DAO on the gold-evaporated glass slides are more thermally stable than those on the silver-evaporated glass slides. The interaction between the headgroup and the substrate may be stronger for the former than the latter, providing the films with the higher thermal stability. The one-monolayer LB film of C_{18}DAO on the gold-evaporated glass slide shows a clear order−disorder transition around 70 °C. In contrast, the corresponding five-monolayer LB film gives a sharp transition at about 45 °C and a rather broad one around 80 °C. It seems that the accumulation of the upper layers yields independent transitions for the first layer and the rest of the layers and lowers the thermal stability of the first layer. The thermal behavior of the LB films of 2C_{18}DAC and C_{18}DAO is clearly different. For example, the 2C_{18}DAC films show partial recovery after the annealing from 110 °C, but the C_{18}DAO films undergo irreversible temperature-dependent changes. Probably, the difference in the thermal behavior results from the different nature of the substrate−headgroup interaction between them.

Introduction

In the previous and preceding papers,[1,2] we reported the molecular orientation and structure in one- and multilayer Langmuir−Blodgett (LB) films of octadecyldimethylamine oxide (C_{18}DAO) and dioctadecyldimethylammonium chloride (2C_{18}DAC) on gold- and silver-evaporated glass slides. It was found that the structures of the LB films show clear dependences upon the number of monolayers and substrates.[1,2] The most important finding in the preceding paper was that the orientation and order of alkyl chains in the first layers are changed largely upon the deposition of the second layers. The interaction between the headgroups and substrates is modified by the longitudinal interaction between the first and second monolayers.

This paper discusses thermal behavior of the one- and five-monolayer LB films of C_{18}DAO and 2C_{18}DAC on the gold- and silver-evaporated glass slides. Thermal stability and order−disorder transitions of LB films have been investigated by several research groups by use of infrared (IR), Raman, and ultraviolet−visible (UV−vis) spectroscopies.[3−18] It has been generally recognized that the interaction between a headgroup and a substrate and the longitudinal interaction between monolayers are two important factors which control the thermal stability of LB films. Since the LB films of C_{18}DAO and 2C_{18}DAC possess specific headgroup−substrate interactions and interlayer interactions, the investigation of their thermal behavior should be very interesting. In the present study,

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* To whom correspondence should be addressed. Fax: +81-798-51-0914. E-mail: ozaki@kwansei.ac.jp.

[†] Kwansei-Gakuin University.

[‡] Kobe Pharmaceutical University.

[§] Nagoya University.

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particular attention has been paid to the exploration of dependences of the thermal behavior on the number of monolayers and the substrates. The difference in the thermal behavior between the LB films of the two kinds of amphiphiles having quite unique headgroups has also been noted.

Experimental Section

The procedure for the preparation of one- and five-monolayer LB films of C_{18}DAO and 2C_{18}DAC was described in detail in the preceding paper;[2] the first and the rest of the monolayers were prepared by the vertical and horizontal lifting techniques, respectively, on gold- and silver-evaporated glass slides. They were dried for a few hours in a desiccator prior to the IR measurements.

The instruments employed for the IR and contact angle measurements were the same as those described in the preceding paper.[2] A copper block device which had a ceramic heater within was used together with an Omron E5T programmable thermocontroller to investigate temperature-dependent IR spectral changes of the LB films on the gold- and silver-evaporated glass slides. The temperature stability, provided by the thermocontroller, was better than ±0.2 °C. The temperature-dependent IR measurements were carried out by the stepwise temperature raising to each given temperature of one sample. The IR spectra were measured for the LB films in a thermal equilibrium state.

Results

Infrared Spectra of One-Monolayer LB Films of C_{18}DAO and 2C_{18}DAC. The temperature dependence of an IR RA spectrum of the one-monolayer LB film of C_{18}DAO on a gold-evaporated glass slide is presented in Figure 1A. Band frequencies and assignments for the spectrum at room temperature were reported earlier.[1,2] Bands at 2914 and 2847 cm^{-1} are assigned to the CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chains of C_{18}DAO, respectively.[1] The frequencies of the CH_2 stretching bands are sensitive to the conformation of the hydrocarbon chain.[19,20] When the chain is highly ordered (trans-zigzag conformation), the bands appear at 2918 and 2848 cm^{-1}, respectively, and their upward shifts are indicative of the increase in the conformational disorder; i.e., the number of gauche conformers in the chain increases. The observation in Figure 1A suggests that the alkyl chain is highly ordered in the film of C_{18}DAO on the gold-evaporated glass slide.[1] The appearance of a band due to Fermi resonance at 2933 cm^{-1} supports this conclusion.

Of note in Figure 1A is that a new band appears at 2927 cm^{-1} and the CH_2 symmetric stretching band becomes broad around 50 °C. Concomitant with the spectral changes in the 3000−2800 cm^{-1} region, the band progression in the 1400−1100 cm^{-1} region disappears around 50 °C. Above 90 °C, the two CH_2 stretching bands become singlet again, appearing at 2927 and 2856 cm^{-1}. These temperature-dependent spectral variations show that the hydrocarbon chain of C_{18}DAO undergoes an order−disorder transition in the temperature range 60−80 °C. The top trace in Figure 1A shows an IR RA spectrum of the LB film annealed from 110 °C. It suggests that the molecular orientation and structure do not recover after annealing.

Figure 1B plots the frequencies of the two CH_2 stretching bands versus temperature. It is very clear from Figure 1B that the one-monolayer film of C_{18}DAO on the gold-evaporated glass slide has the order−disorder transition between 60 and 80 °C.

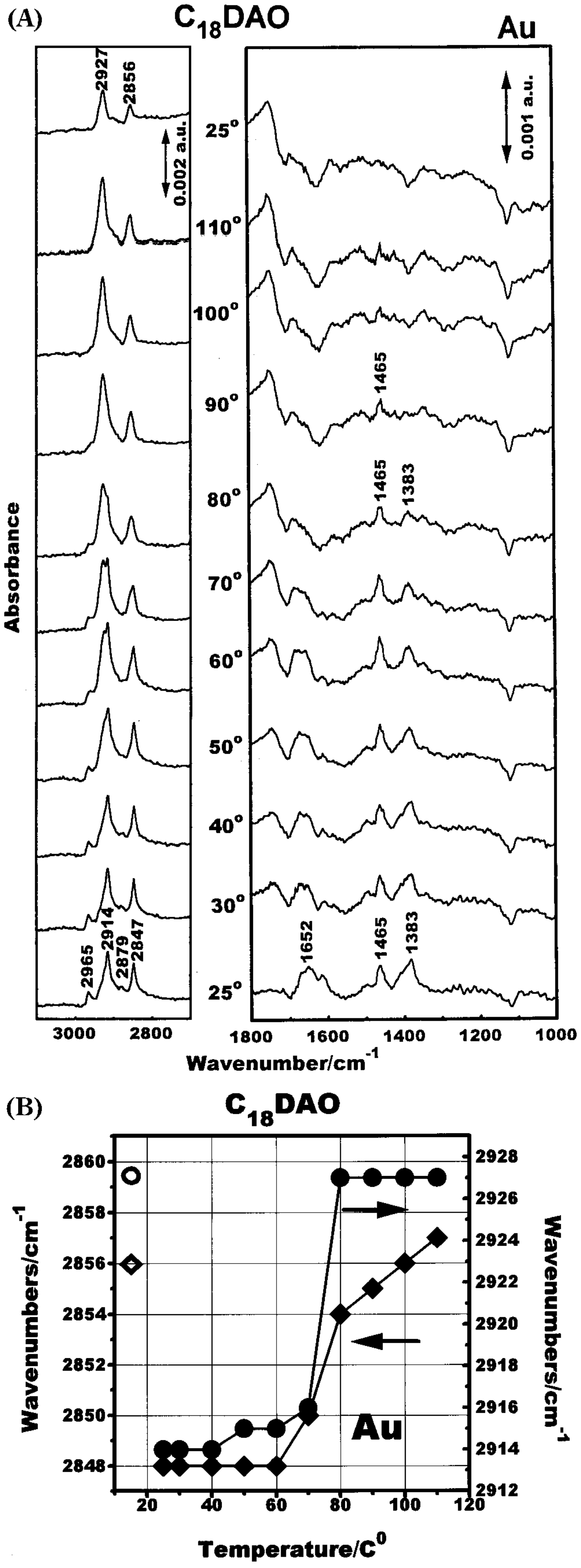

Figure 1. (A) Temperature-dependent changes in an IR RA spectrum of one-monolayer LB film of C_{18}DAO on a gold-evaporated glass slide. (B) Temperature dependences of the frequencies of the CH_2 stretching bands for the spectra shown in (A). Throughout this paper the frequencies for the annealing films are presented by open circles (○) and squares (◇).

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Figure 2A shows temperature-dependent changes in an IR RA spectrum of the one-monolayer LB film of $2C_{18}$-DAC on a gold-evaporated glass slide. At room temperature, the two CH_2 stretching bands appear at 2924 and 2855 cm^{-1}, indicating that the alkyl chains contain some gauche conformers, as previously reported.[1]

Figure 2B illustrates temperature dependences of the frequencies of the two CH_2 stretching bands for the one-monolayer LB film of $2C_{18}$DAC on the gold-evaporated glass slide. It can be seen from Figure 2B that the frequencies change rather gradually with temperature. The hydrocarbon chains become more disordered as the temperature is increased. The relative intensities of the two CH_2 stretching bands also increase gradually with temperature, indicating that the alkyl chains become more tilted.

The top trace in Figure 2A presents an IR RA spectrum measured at 25 °C of the LB film annealed from 110 °C. The spectrum in the 3000−2800 cm^{-1} region of the annealed film bears resemblance to that at 25 °C. Thus, it seems that the molecular orientation and structure of the one-monolayer LB film recover partly after the annealing.

Infrared Spectra of Five-Monolayer LB Films of C_{18}DAO and $2C_{18}$DAC on Gold-Evaporated Glass Slides. The temperature dependence of an IR RA spectrum of the five-monolayer LB film of C_{18}DAO on a gold-evaporated glass slide is presented in Figure 3A. Note that marked spectral changes take place between 40 and 50 °C and, surprisingly, again between 70 and 80 °C for most of the bands.

In Figure 3B, the frequencies of the two CH_2 stretching bands of the five-monolayer LB film of C_{18}DAO on the gold-evaporated glass slide are plotted against temperature. The plots clearly show that in contrast to the one-monolayer LB film of C_{18}DAO, the five-monolayer LB film has two phase transitions. The first transition near 45 °C is sharp, and the upward shifts by about 4 cm^{-1} of the two CH_2 stretching bands reveal that the alkyl chain becomes disordered partly. The intensity increases of these two bands may be brought about partly by the introduction of the conformational disorder. However, the intensity increases are so large that one cannot explain the increases only by the conformational disorder. Probably, the intensity increases are also induced by the tilt of the alkyl chain upon the transition. It is noted that the transition temperature of 45 °C is close to the phase transition temperature of 49 °C between the transparent solution and the turbid (or the birefringent) solution of C_{18}DAO in water.[21]

In Figure 4A are shown temperature-dependent spectra of a five-monolayer LB film of $2C_{18}$DAC on a gold-evaporated glass slide. It can be seen from Figure 4A that the most marked spectral changes occur between 30 and 40 °C, which is a rather low temperature. Figure 4B plots the frequencies of the two CH_2 stretching bands as a function of temperature. The observations in parts A and B of Figure 4 lead us to conclude that the alkyl tails become more disordered and tilted above 40 °C.

Another notable point in Figure 4A is that some bands in the 1700−1000 cm^{-1} region show temperature-dependent changes in parallel with the two CH_2 stretching bands; the intensities of bands in the 1650−1300 cm^{-1} region increase with the intensity increases in the 3000−2800 cm^{-1} region. After annealing from 110 °C, the spectrum recovers partly, showing a partially reversible process (see the top trace in Figure 4A).

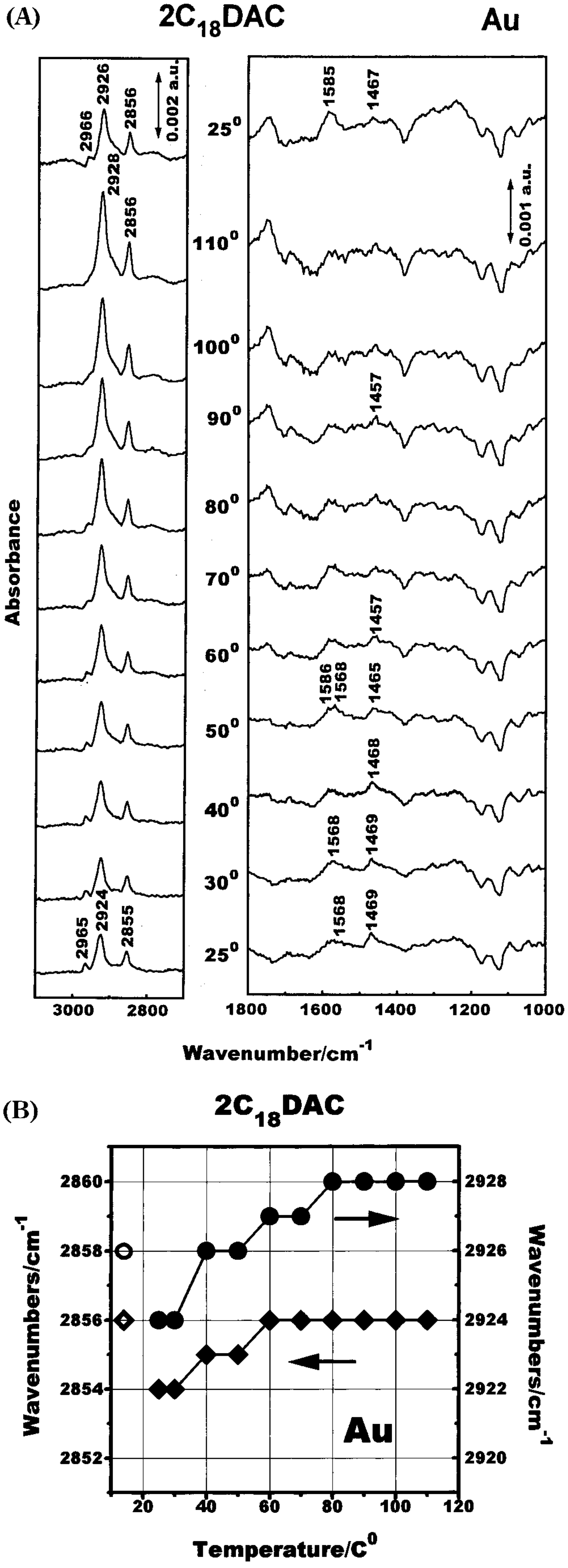

Figure 2. (A) Temperature-dependent changes in an IR RA spectrum of one-monolayer LB film of $2C_{18}$DAC on a gold-evaporated glass slide. (B) Temperature dependences of the frequencies of the CH_2 stretching bands for the spectra shown in (A).

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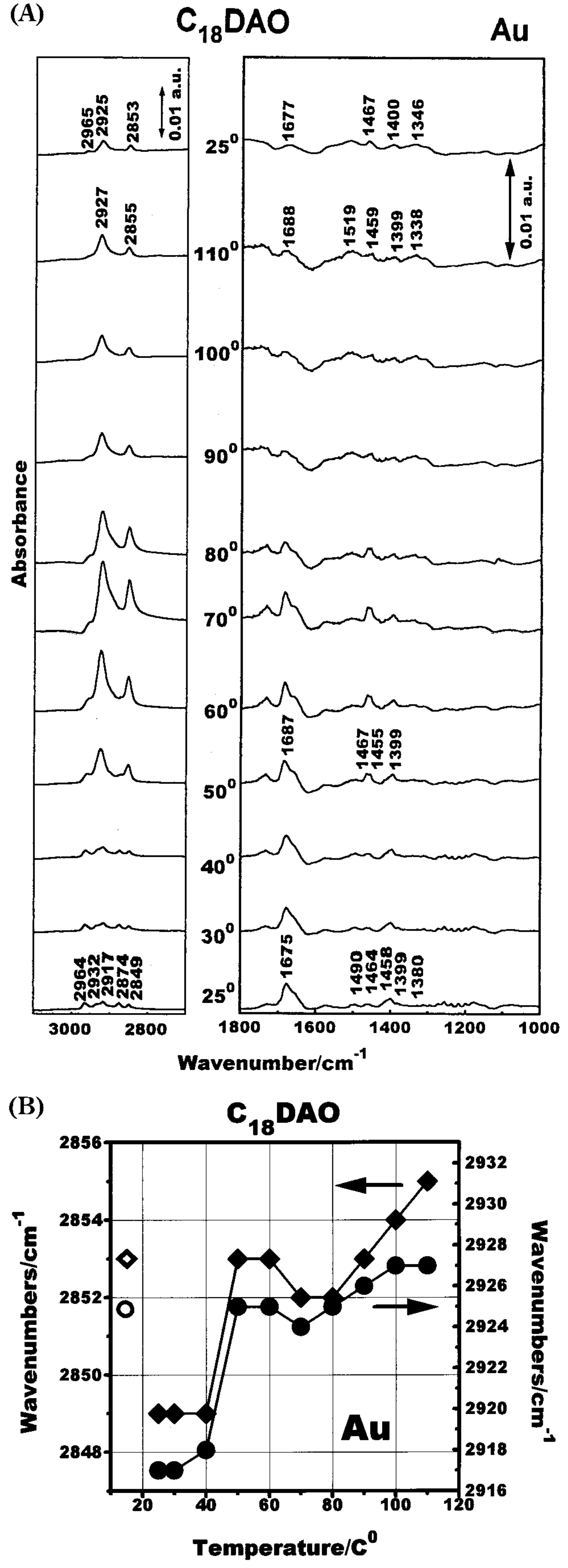

Figure 3. (A) Temperature-dependent changes in an IR RA spectrum of a five-monolayer LB film of $C_{18}DAO$ on a gold-evaporated glass slide. (B) Temperature dependences of the frequencies of the CH_2 stretching bands for the spectra shown in (A).

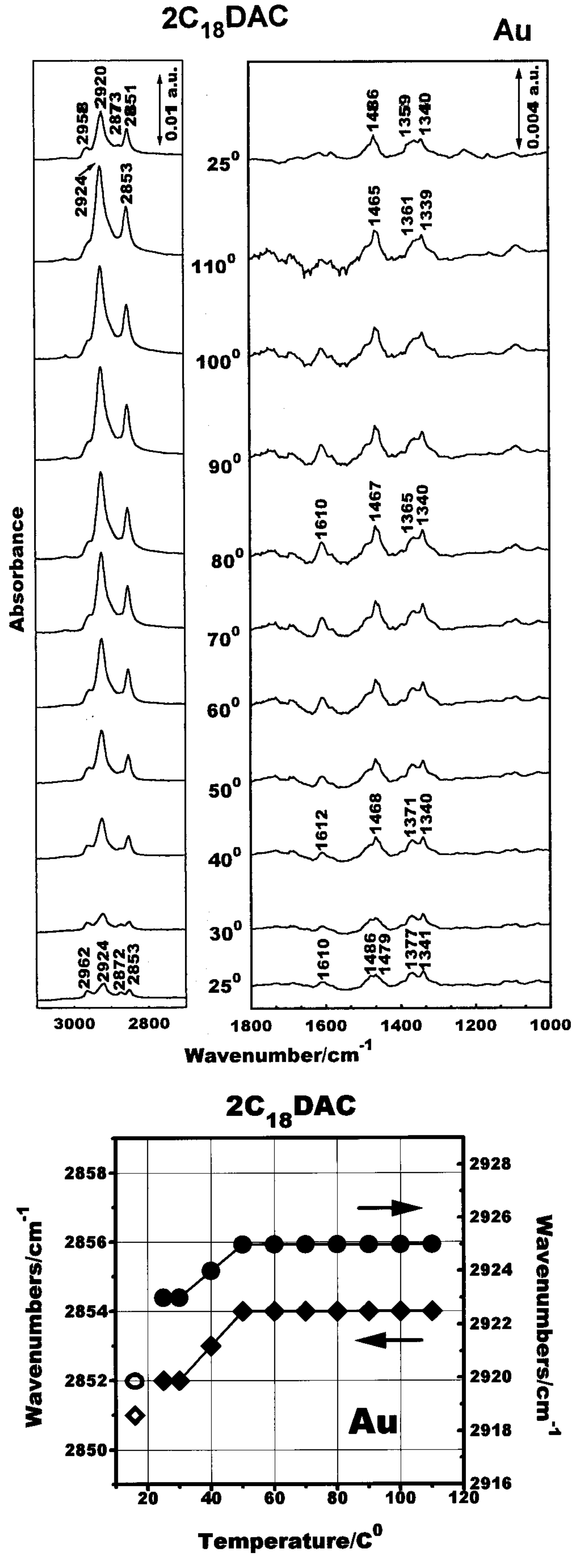

Figure 4. (A) Temperature-dependent changes in an IR RA spectrum of five-monolayer LB film of $2C_{18}DAC$ on a gold-evaporated glass slide. (B) Temperature dependences of the frequencies of the CH_2 stretching bands for the spectra shown in (A).

Infrared Spectra of Five-Monolayer LB Films of C_{18}DAO and $2C_{18}$DAC on Silver-Evaporated Glass Slides. In Figure 5A, IR RA spectra are shown for the five-monolayer LB film of C_{18}DAO on a silver-evaporated glass slide measured over a temperature range of 25−110 °C. An IR RA spectrum of the LB film annealed from 110 °C is also shown as the top trace in Figure 5A.

Figure 5B shows temperature-dependent frequency shifts of the CH_2 stretching bands for the LB film on the silver-evaporated glass slide. Comparison between Figures 3B and 5B elucidates that the LB films of C_{18}DAO on the silver- and gold-evaporated glass slides show significantly different thermal behavior. The LB film on the gold-evaporated glass slide undergoes the clear order−disorder transition but that on the silver-evaporated glass slide experiences only gradual temperature-dependent changes. The intensity decreases in the 3000−2800 cm^{-1} region at high temperatures are observed only for the film on the gold-evaporated glass slide.

Notable features in the 1800−1300 cm^{-1} region are characteristic for the LB films on the silver-evaporated glass slides. Similar features are observed also for one-monolayer LB films of C_{18}DAO and $2C_{18}$DAC on silver-evaporated glass slides. The LB films of C_{18}DAO always give much stronger features than those of $2C_{18}$DAC.

Figure 6A shows temperature-dependent spectral variations in an IR RA spectrum of the five-monolayer LB film of $2C_{18}$DAC on a sliver-evaporated glass slide. In Figure 6B are plotted the frequencies of the two CH_2 stretching bands as a function of temperature.

The temperature-dependent spectral variations of the five-monolayer film of $2C_{18}$DAC on the silver-evaporated glass slide are, in general, similar to those of the corresponding film on the gold-evaporated glass slide (parts A and B of Figure 4). However, the film on the silver-evaporated glass slide shows a specific background feature in the 1800−1400 cm^{-1} region. It is also noted that an IR spectrum of the annealed sample from 110 °C on the silver-evaporated glass slide shows clear differences from that of the annealed sample on the gold-evaporated glass slide; the frequencies of the two CH_2 stretching bands are slightly higher and the relative intensity of the band at 1613 cm^{-1} is stronger for the film on the silver-evaporated glass slide.

Parts A and B of Figure 7 plot the frequencies of the two CH_2 stretching bands versus temperature for the one-monolayer LB films of C_{18}DAO and $2C_{18}$DAC on the silver-evaporated glass slides. Of note is that the one-monolayer LB films on the silver-evaporated glass slides always show gradual spectral changes with temperature. In contrast, as shown in Figure 1B, the one-monolayer LB film of C_{18}DAO on the gold-evaporated glass slide shows the clear order−disorder transition.

Wetting Measurements for LB Films Annealed From 110 °C. We have reported a contact angle of water for one- and multilayer LB films of $2C_{18}$DAC and C_{18}DAO on gold- and silver-evaporated glass slides in the preceding paper.[2] We also measured the contact angle for the annealed one- and five-monolayer LB films of $2C_{18}$DAC and C_{18}DAO on both gold- and silver-evaporated glass slides. The annealed monolayer of $2C_{18}$DAC on the gold-evaporated glass slide gave the value of the contact angle, which is slightly higher than 101°. The annealed five-monolayer films of the same compound on the gold- and silver-evaporated glass slides showed angles of 103° and 101°, respectively. The contact angle was 100° for the annealed five-monolayer film of C_{18}DAO on the gold-evaporated glass slide. The rest gave the angle between 95° and 98°. The annealing causes a marked change in the contact for the five-monolayer film of C_{18}DAO on both gold- and silver-evaporated glass slides. This result

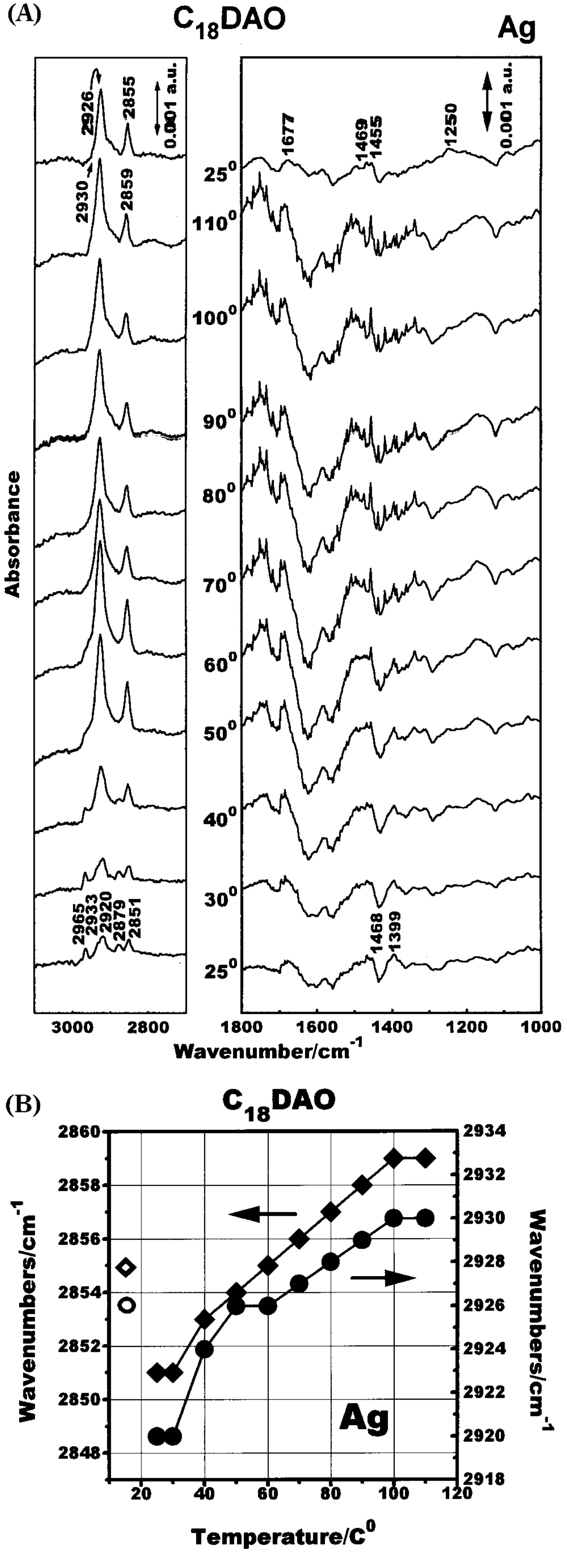

Figure 5. (A) Temperature-dependent changes in an IR RA spectrum of five-monolayer LB film of C_{18}DAO on a silver-evaporated glass slide. (B) Temperature dependences of the frequencies of the CH_2 stretching bands for the spectra shown in (A).

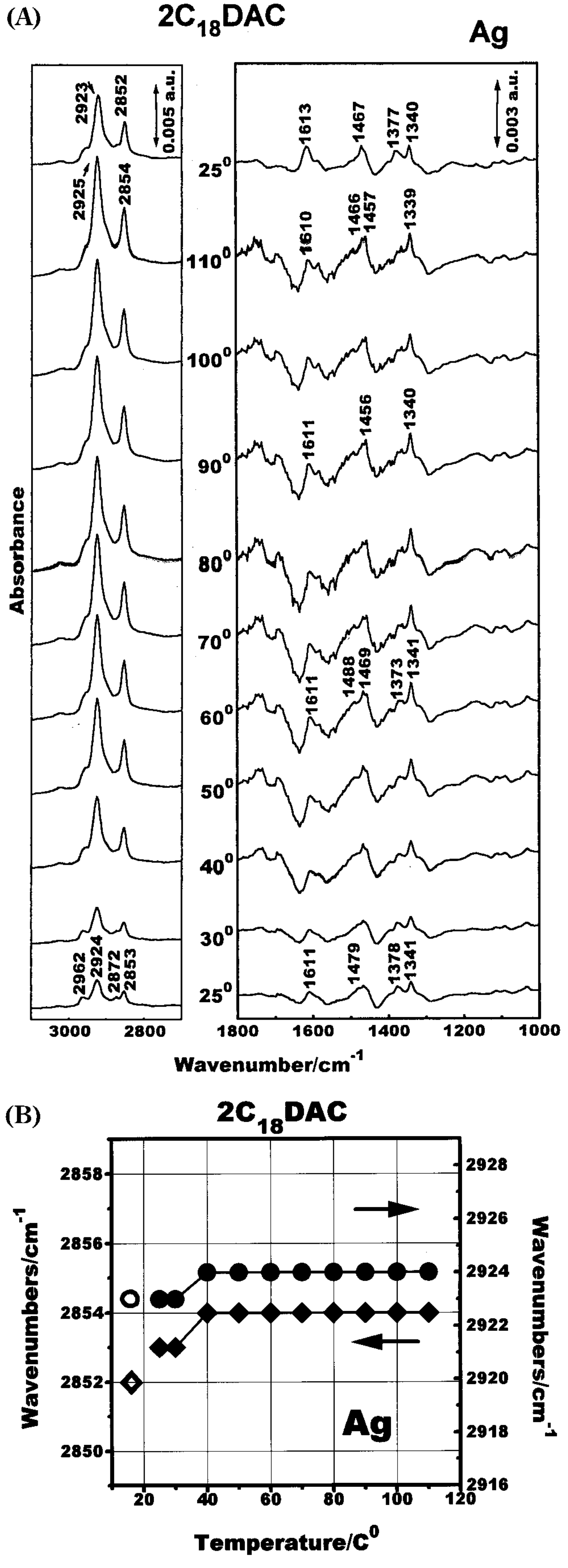

Figure 6. (A) Temperature-dependent changes in an IR RA spectrum of five-monolayer LB film of 2C$_{18}$DAC on a silver-evaporated glass slide. (B) Temperature dependences of the frequencies of the CH$_2$ stretching bands for the spectra shown in (A).

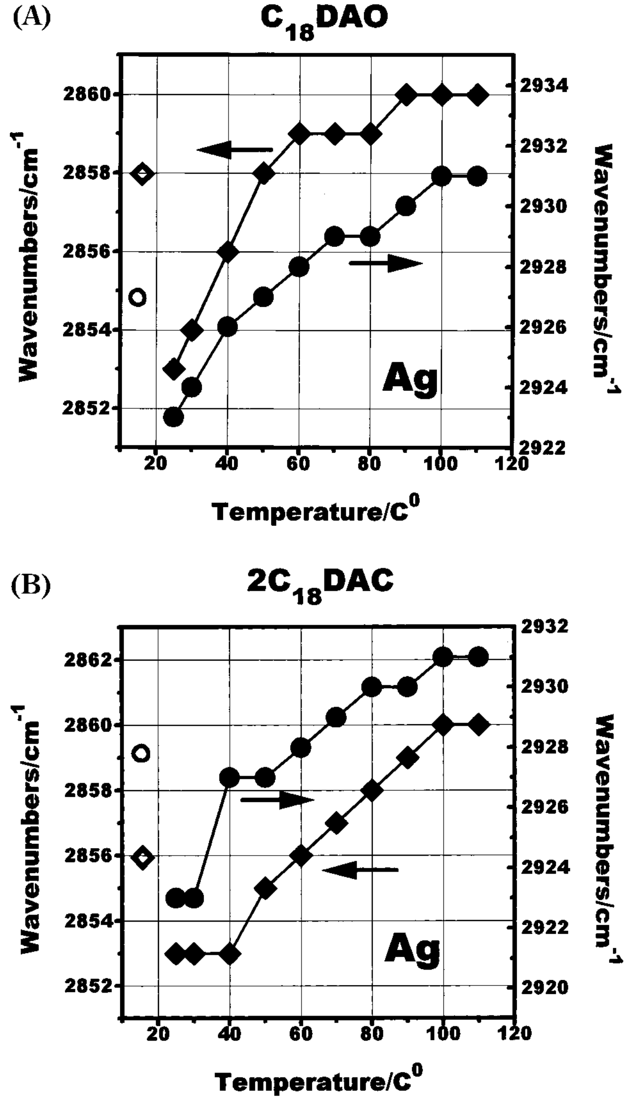

Figure 7. Temperature dependences of the frequencies of the CH$_2$ stretching bands for one-monolayer LB films of C$_{18}$DAO (A) and 2C$_{18}$DAC (B) on silver-evaporated glass slides.

suggests the occurrence of overturning of C$_{18}$DAO molecules in the films after the annealing.

Discussion

Comparison of the Thermal Behavior Between the One- and Five-Monolayer LB Films. As reported in the previous and preceding papers,[1,2] the structures of LB films of C$_{18}$DAO and 2C$_{18}$DAC show clear dependence on the number of monolayers. For example, the alkyl chain of the one-monolayer LB film of C$_{18}$DAO on the gold-evaporated glass slide is tilted, but that of the corresponding five-monolayer film is nearly perpendicular to the substrate (compare the bottom spectra in Figures 1A and 3A). Thus, comparison of the thermal behavior between the one- and five-monolayer LB films of C$_{18}$DAO and 2C$_{18}$DAC may be interesting.

Several research groups reported such comparison for LB films of stearic acid,[10] azobenzene-containing long-chain fatty acid,[13] and 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ).[15] In the case of the LB films of stearic acid, the one-monolayer film has a higher melting temperature than the three-monolayer film.[10] The reverse result for the thermal stability was obtained for the LB films of octadecyl-TCNQ.[15]

The one-monolayer LB film of azobenzene-containing long-chain fatty acid does not show a distinct phase transition while its multilayer LB films show a clear transition.[13] These differences in the thermal behavior between the one- and multilayer LB films may result from the difference in the effects of substrate−headgroup interaction and from the existence and absence of the longitudinal interactions between monolayers. The substrate−headgroup interaction and the longitudinal interactions are very much specific for each LB film so that it seems rather difficult to extract general conclusions for the differences in the thermal behaviors between one- and multilayer films.

In the present study, the LB films of C_{18}DAO on the gold-evaporated glass slides show clear dependence of the order−disorder transition on the number of monolayers. The one-monolayer LB film shows a distinct order−disorder transition near 70 °C while the five-monolayer film gives transitions stepwise near 45 and 70 °C. The first transition temperature is much higher for the one-monolayer film than for the five-monolayer film. Probably, the strong interaction of the large dipole moment of the headgroup (N→O) with the negative charge in the surface of the gold-evaporated glass slide increases the thermal stability of the one-layer film. In the case of the five-monolayer film, the interaction becomes weak upon the deposition of the upper layers, lowering the thermal stability of the first layer.

Comparison of the Thermal Behavior Between the Gold- and Silver-Evaporated Glass Slides. To our best knowledge, this is the first time that the temperature-dependent IR spectral changes have ever been compared for the same compound on the gold- and silver-evaporated glass slides. The structure of the LB films of C_{18}DAO and $2C_{18}$DAC show the substrate dependences so that the comparison of the thermal behavior between the gold- and silver-evaporated glass slides should be very important. The LB films of $2C_{18}$DAC show the similar temperature-dependent changes between the gold- and silver-evaporated glass slides. In contrast, the LB films of C_{18}DAO on the gold substrates are significantly more stable than those on the silver substrates (compare Figure 1B with Figure 7A and Figure 3B with Figure 5B). These results suggest that the interaction between the headgroup and gold surface is more effective than the interaction between it and the silver surface in stabilizing the films.

The LB films on the silver-evaporated glass slides show two other characteristic features. One is the variations in the baseline in the 1800−1300 cm^{-1} region (see Figures 5A and 6A). The variations were observed also for the one-monolayer LB films of C_{18}DAO and $2C_{18}$DAC on the silver-evaporated glass slides. Of particular note is that the baseline change is always much stronger for the C_{18}DAO films whose headgroup adsorbs water.[21,22] Thus, the baseline change may be ascribed to water.

Another characteristics for the LB films on the silver-evaporated glass slides is that the two CH_2 stretching bands show the larger upward frequency shift compared with those for the gold-evaporated glass slides. For example, the two CH_2 stretching bands appear at 2930 and 2859 cm^{-1} in the spectrum of the five-monolayer LB film of C_{18}DAO on the silver-evaporated glass slide at 110 °C, while they are seen at 2927 and 2855 cm^{-1} in the corresponding spectrum of C_{18}DAO on the gold-evaporated glass slide. Thus, in general, the hydrocarbon chains become less ordered at higher temperatures in the LB films on the silver-evaporated glass slides than in those on the gold-evaporated glass slides.

The significant differences in the thermal behavior of the LB films of C_{18}DAO between the gold- and silver-evaporated glass slides may come from the difference in the strength of the interaction between the large dipole moment of the headgroup (N→O) and the charge on the metal surface, as described above.

Comparison of the Thermal Behavior Between C_{18}DAO and $2C_{18}$DAC. We already discussed the difference in the thermal behavior between the LB films of C_{18}DAO and $2C_{18}$DAC. For example, the films of C_{18}DAO on the gold-evaporated glass slides show the distinct order−disorder transitions, whereas those of $2C_{18}$DAC do not give clear phase transitions irrespective of the substrates. Another notable difference in the thermal behavior between the LB films of C_{18}DAO and $2C_{18}$DAC is the annealing effect. The spectra of the annealed LB films of $2C_{18}$DAC always show some recovery. In contrast, those of the annealed samples of C_{18}DAO do not show recovery, indicating that the temperature-dependent structural changes occur irreversibly in the LB films of C_{18}DAO.

The reasons for the differences in the thermal behaviors between the LB films of C_{18}DAO and $2C_{18}$DAC may come from the following differences in the properties of the two compounds. One is that the former has one tail while the latter has two tails. Another is that the headgroup of C_{18}DAO is greatly hydrated but that of $2C_{18}$DAC 22 is not so hydrated.

Conclusions

The present study has provided new insight into the thermal behaviors and thermal stability of the LB films of two kinds of amphiphiles with the unique headgroups. The thermal behaviors have shown the dependences on the number of monolayers and the substances. The following three observations are particularly notable for the present study.

(i) The one-monolayer LB film of C_{18}DAO on the gold-evaporated glass slide undergoes a sharp phase transition near 70 °C while the corresponding five-monolayer film shows two stepwise transitions near 45 and 70 °C. The accumulation of the upper layers lowers the thermal stability.

(ii) The LB films of C_{18}DAO on the gold-evaporated glass slides are more thermally stable than those on the silver-evaporated glass slides.

(iii) The LB films of $2C_{18}$DAC show partly reversible temperature-dependent structural variations, but those of C_{18}DAO show irreversible structural changes.

The above three results and all other observations in the present study may be explained by the specific interaction between the gold or silver surface and the headgroups. The strong interaction between the N−O group with the large dipole moment and the negative charge on the gold surface stabilizes the one-monolayer LB film of C_{18}DAO on the gold-evaporated glass slide up to 60 °C which is higher by about 10 °C than the phase transition temperature of the bulk material. The strong interaction is weakened significantly by the deposition of the upper layers or by the exchange of the substrate from the gold-evaporated glass slide to the silver-evaporated glass slide.

We have carried out quantitative analysis of temperature-dependent changes in the molecular orientation in LB films of C_{18}DAO and $2C_{18}$DAC based upon a newly proposed analytical theory. The results will be reported elsewhere.[23]

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