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Order–Disorder Transition in a Dioctadecyldimethylammonium Chloride LB Film Studied by FT-IR ATR Spectroscopy

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An order–disorder process in Langmuir–Blodgett (LB) films of dioctadecyldimethylammonium chloride (DODAC) has been studied by FT-IR ATR spectroscopy. This order–disorder process gradually occurred over a wide temperature range, and the transition was shifted to a higher temperature with the number of monolayers. In DODAC LB films immersed in water a similar thermotropic phase behavior was observed, except for the transition temperature. However, this behavior completely differed from that of cast film.

Cationic quaternary ammonium amphiphiles with a double-chain, such as dioctadecyldimethylammonium chloride (DODAC) in an aqueous environment, have been known to form a bilayer structure analogous to biological membranes.[1—3] These cationic amphiphiles have also been used as softening agents for clothes, rinse, etc. Previous papers have described the thermotropic phase behavior of a DODAC–water system investigated by differential scanning calorimetry (DSC) and FT-IR techniques; also, the presence of coagel, gel and liquid crystalline phases and the states of DODAC and of water molecules in each phase were clarified in detail.[4—8] However, the thermal behavior in a thin film of DODAC has not yet been revealed. This behavior is very important for understanding the peculiar properties of a low-dimensional solid, its thermal stability, and factors governing the performance of softening agents. Although the thermal behavior of an ultrathin organic film, especially well-organized Langmuir–Blodgett (LB) films, has been studied using infrared reflection-absorption spectroscopy, optical reflection measurements, etc., these attempts were only applied to a few compounds, such as stearic acid an its metal salts,[9—17] and those with functional groups.[18—22]

The present paper describes the thermotropic phase behavior in DODAC LB films investigated by measuring the temperature dependence of the FT-IR ATR spectra. Further, in DODAC LB films immersed in water the phase transition behavior were also examined, and then compared with the result of aqueous solutions reported in previous papers.[7,8]

Experimental

DODAC (TCl, GR grade) was recrystallized three times from an acetone solution. Deionized water was doubly distilled. D_2O (99.9%) was purchased from Kanto Chemical Co., Inc. and used without further purification.

DODAC monolayers were spread on the water surface from a 1.0×10^{-3} M chloroform solution ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$). The spread monolayers were compressed at a constant rate of $10\ \mathrm{cm^2\,min^{-1}}$ up to $35\ \mathrm{mN\,m^{-1}}$ at 15 °C ($0.40\ \mathrm{nm^2}$/molecule), and then transferred on an ATR plate (Ge) cleaned by ultrasonication in acetone and chloroform. The surface pressure was measured with a Wilhelmy balance (Kyowa Kaimenkagaku Co., Ltd). The first monolayer and the subsequent monolayers of the DODAC were transferred by the standard LB (vertical dipping) method and by the horizontal lifting method, respectively. The transfer ratios were in the range 0.90—1.05 in this experiment.

Cast film of DODAC was prepared by dropping a chloroform solution on an ATR plate and by evaporating the solvent under a N_2 atmosphere at room temperature. The film thickness was about 0.2 μm.

A Harrick multiple internal-reflection attachment was used for ATR measurements; the angle of incidence was 45°. The ATR plates were placed in a mount with a water jacket thermostated by a refrigerated bath circulator (Fig. 1). The sample was subjected to FT-IR measurements during the heating process. After the temperature of the bath circulator reached each set point, 10 min was wasted to assure the thermal equilibrium of the sample. The temperature was monitored by a copper–constantan thermocouple inserted between an ATR plate and an O-ring. All infrared spectra were recorded on a Nicolet Model 510M FT-IR spectrophotometer equipped with a triglycine sulfate (TGS) detector. The resolution was $4\ \mathrm{cm^{-1}}$ and interferograms were accumulated 500 times. The accuracy of the peak positions was ca. $0.1\ \mathrm{cm^{-1}}$, since the data points were interpolated by a zero-filling technique.

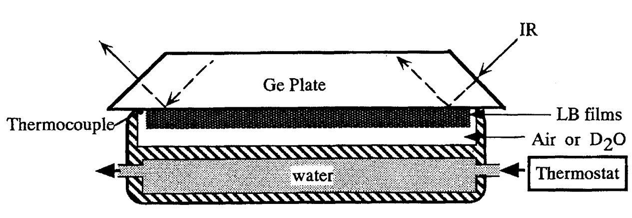

Fig. 1. Schematic illustration of the experimental and sample arrangement used in this work.

Results and Discussion

Order–Disorder Transition of a DODAC LB Film. Figure 2 shows the ATR spectra of an 11-monolayer LB film of DODAC on Ge in the CH_2 stretching and CH_2 scissoring vibration regions at various temperatures. The strong bands at around 2920 and 2850 cm^{-1}, assigned to the antisymmetric and symmetric CH_2 stretching modes,[7,8] gradually shifted to a higher wavenumber with increasing temperature. On the other hand, the peak of the single band of the CH_2 scissoring modes shifted to a lower wavenumber. This CH_2 scissoring band, which is known to be very sensitive to the intermolecular force, provides information concerning the state of packing of the methylene chain; i.e., the CH_2 scissoring band at 1473 and 1468 cm^{-1} corresponds to the methylene chains in the triclinic packing and in the hexagonal packing, respectively, and at ca. 1467 cm^{-1} is typical of methylene chains in the fused state.[7,8]

The temperature dependence of the wavenumber of the antisymmetric CH_2 stretching $\nu_a(CH_2)$ and the scissoring $\delta(CH_2)$ modes is shown in Fig. 3. The wavenumber of $\nu_a(CH_2)$ showed a gradual increase with increasing temperature; the increment was greater above 40 °C. On the other hand, the value of $\delta(CH_2)$ was constant at 1468.3 cm^{-1} in the temperature range from 25 to 40 °C. Here, to consider the state of packing of the methylene chain in the DODAC LB film, we divided the profiles of $\nu_a(CH_2)$ and $\delta(CH_2)$ into three parts, that is, region I below 25 °C, region II between 25 and 40 °C, and region III above 40 °C, although the bound-

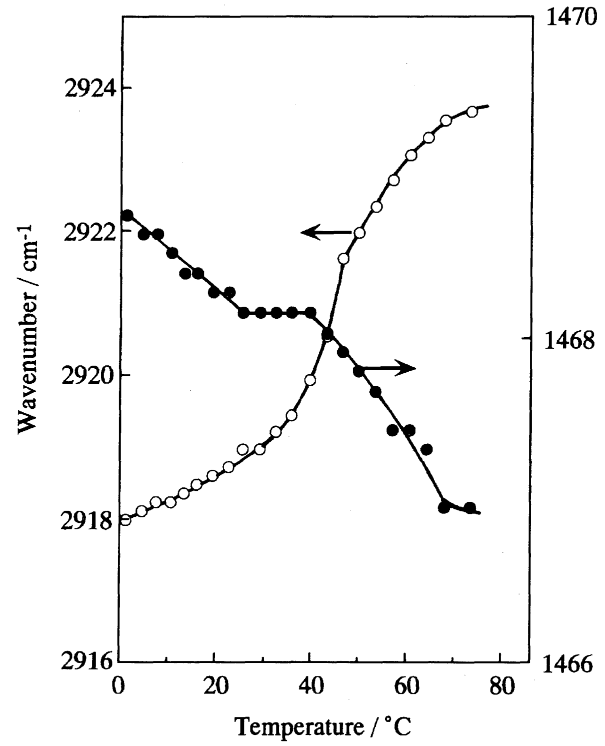

Fig. 3. Temperature dependence of the wavenumbers of antisymmetric CH_2 stretching (○) and CH_2 scissoring (●) bands of 11-monolayer LB film of DODAC.

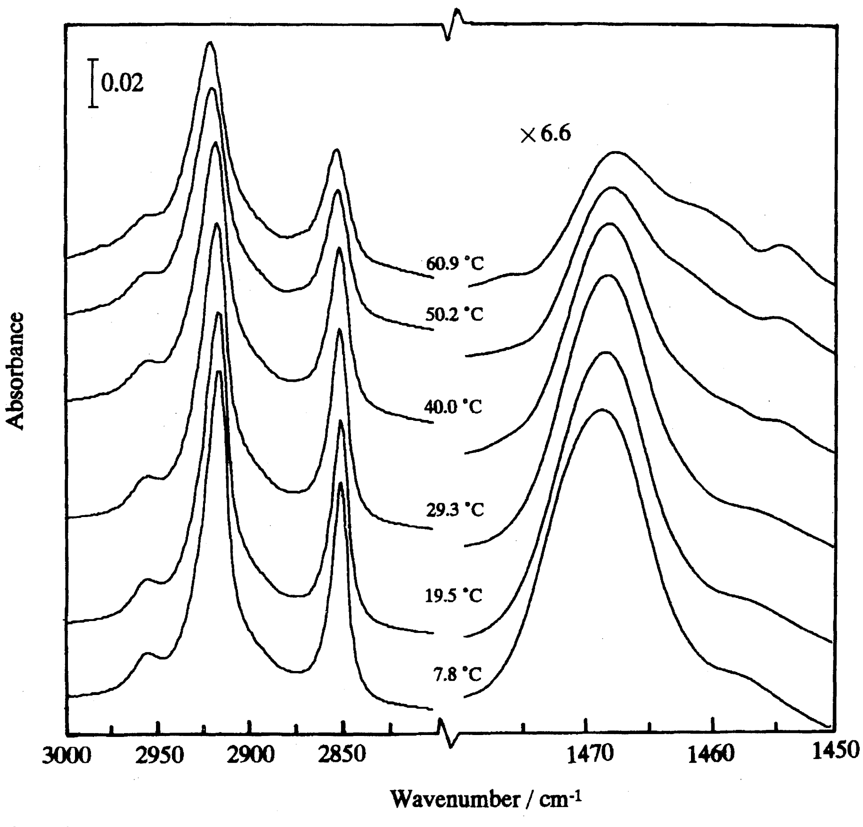

Fig. 2. Infrared ATR spectra of 11-monolayer LB film of DODAC as a function of temperature.

aries between the regions are somewhat obscure. The states of DODAC in each region are discussed below.

Since the values of $\delta(CH_2)$ observed in region I were about in the middle between the values obtained in the triclinic packing and in the hexagonal packing, it can be estimated that the LB film of DODAC in region I has a domain structure consisting of triclinic and hexagonal packing regions. In addition, the wavenumber decrease of this band with increasing temperature may be due to a decrease in the proportion of the domain of the triclinic packing.

In region II, the constant value of $\delta(CH_2)$ at 1468.3 cm^{-1} indicates that the methylene chains are packed in a hexagonal lattice.[7,8] Thus, in region II the LB film could be regarded as being homogeneous. On the other hand, the wavenumber of ca. 2918 cm^{-1} for $\nu_a(CH_2)$ in regions I and II, which provides a sensitive monitor of the degree of conformational disorder in the methylene chains, is characteristic of the *trans*-methylene chains.[7,8]

In region III the increase in the wavenumber of $\nu_a(CH_2)$ with increasing temperature suggests that the conformational disorder of the methylene chains gradually proceeds over a wide temperature range. Further, above 68 °C the almost constant wavenumber at 2924 cm^{-1}, which is a characteristic of melting of the methylene chain, indicates that the DODAC molecules are in fused state, just as in a liquid crystalline state. Thus, the temperature range from 40 to 68 °C may be defined as the boundary between ordered (hexagonal) and disordered phases.

Based on the above consideration, the resultant phase transition behavior of DODAC in 11-monolayer LB films is depicted schematically in Fig. 4. As already mentioned, in region I hydrocarbon chains with triclinic and hexagonal packings coexist, whereas in region II only the latter packing is present. Here, in the former packing the methylene *trans*-zigzag planes are packed in parallel with each other, and in the latter packing the rotational motion of the methylene *trans*-zigzag planes takes place as a whole around its axis.[7,8] In region III the flexibility and *gauche* conformation of the methylene chains and activity of the rotational motion gradually increase along with the temperature. It should be noted that this order–disorder transition temperature in region III was broad, and further, was lower than that of the chain melting (about 100 °C) in bulk DODAC, determined by DSC measurements.[4—6] The reason for the lowering temperature of the order–disorder transition in the DODAC LB film was not clarified in this work, but may come from: 1) the difference in the molecular packing between in the LB film and in the bulk,[7,8] 2) a low-dimensional effect,[16,17] and 3) the influence of trace amounts of water.[4—6]

Effect of the Number of Monolayers. Figures 5 and 6 show the temperature dependence of the wavenumber of $\nu_a(CH_2)$ and $\delta(CH_2)$ in the 1-, 3-, and 11-monolayer LB films of DODAC. The wavenumbers of $\nu_a(CH_2)$ at high temperatures for each LB film system reached 2924 cm^{-1} due to chain melting. From Figs. 5 and 6, it was found that the order–disorder transition temperature of DODAC in LB films decreases along with decreasing the number of

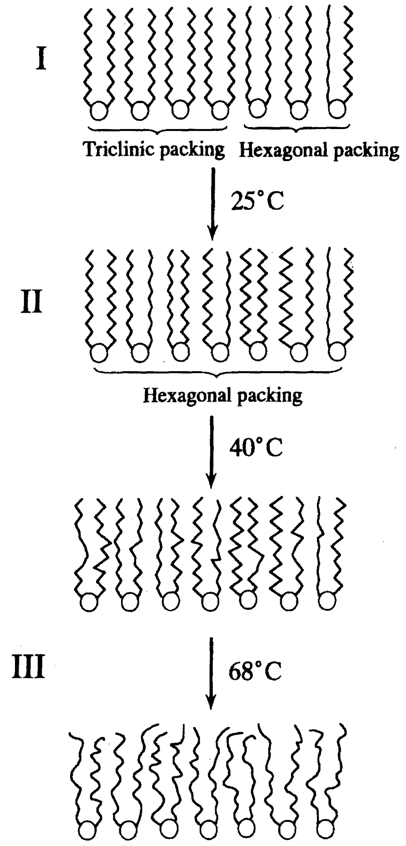

Fig. 4. Schematic illustration of the phase transition behavior of 11-monolayer LB film of DODAC.

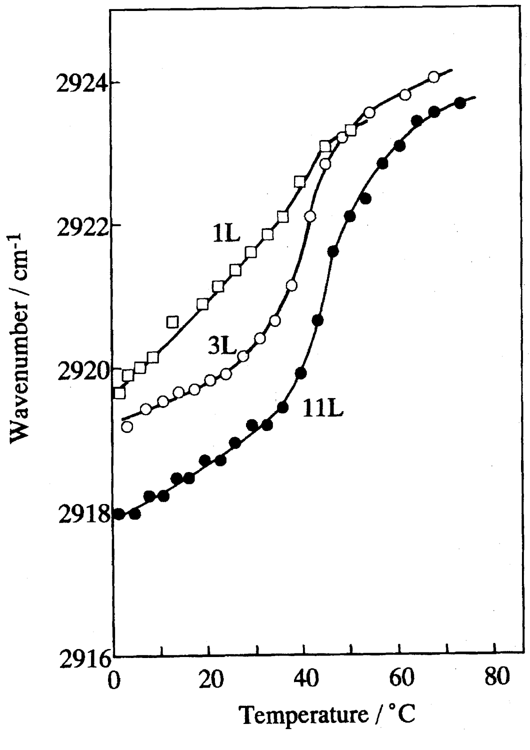

Fig. 5. Temperature dependence of the wavenumbers of antisymmetric CH_2 stretching of 1-,3-, and 11-monolayer LB film of DODAC.

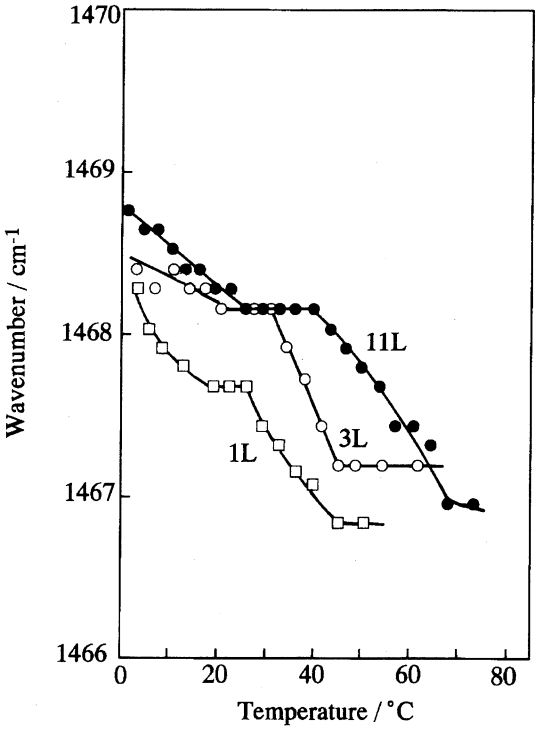

Fig. 6. Temperature dependence of the wavenumber of CH_2 scissoring band of 1-,3-, and 11-monolayer LB film of DODAC.

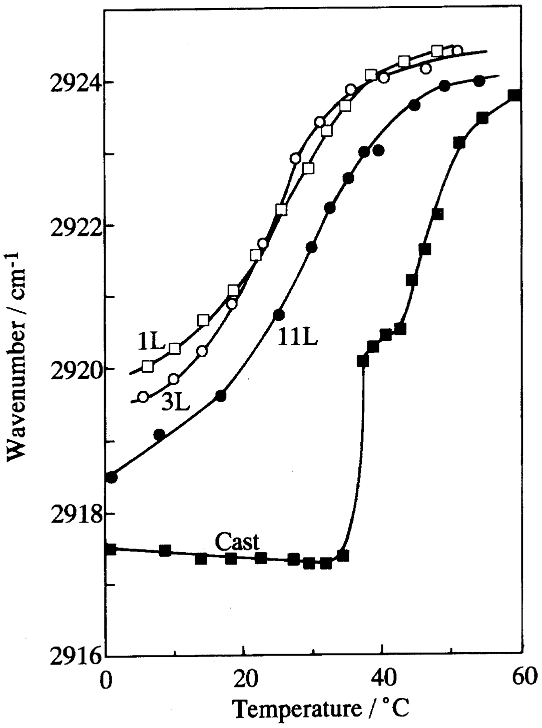

Fig. 7. Temperature dependence of the wavenumbers of antisymmetric CH_2 stretching of 1-,3-, 11-monolayer LB film and cast film of DODAC immersed in D_2O.

monolayer, as in the LB film of stearic acid.[16] Further, since the profiles of $\delta(CH_2)$ have similar shapes regardless of the number of monolayers, the phase transition behavior of 1- and 3-monolayer LB films is the same as that of 11-monolayer LB films (Fig. 4).

Laxhuber et al.[10] have examined the thermostability of monolayers of magnesium and cadmium arachidates in LB films by measuring the thermodeposition spectra, and have revealed that the increased thermostability with the number of monolayers can be explained as being due to the existence of stronger interactions between different monolayers and/or van der Waals forces extending over long distances. Thus, the observation of a transition temperature decrease along with decreasing the number of monolayers in the DODAC system could also be understood from these effects.

On the other hand, the 1-monolayer system provided a more broaden profile of $\nu_a(CH_2)$, and shows a lower value of $\delta(CH_2)$ at 1467.7 cm^{-1} in region II. This may be related to the fact that the first monolayer of an LB film directly interacts with the Ge substrate, and is completely free from a hydrophobic interaction between the interlayers. Similar gradual changes with temperature in a 1-monolayer LB film have been reported in a stearic acid system.[16,17]

Order–Disorder Transition of DODAC LB Film in Water. In order to examine the phase transition behavior of a DODAC LB film in a wet system, the FT-IR ATR spectra of DODAC LB films immersed in D_2O were measured at various temperatures. Figure 7 shows the temperature dependence of the wavenumbers of $\nu_a(CH_2)$ of DODAC in the LB films and the cast film.[23] In the cast film, stepwise changes in the wavenumber were observed at 36 and 42 °C, coinciding with the temperatures of the phase transitions between the coagel–gel and gel–liquid crystalline states in the DODAC–water system.[4—8] Further, the values of $\nu_a(CH_2)$ in each region were in good agreement with those in the coagel, gel and liquid crystalline states, respectively.[7,8] Thus, the cast film of DODAC in water is found to exhibit coagel–gel and gel–liquid crystalline phase transitions, just as does an aqueous solution of DODAC.

On the contrary, in LB films the wavenumbers of $\nu_a(CH_2)$ gradually increased with temperature, and the profiles shifted to higher temperatures with the number of monolayers. Since these profiles are very similar to the corresponding profiles without water, except for the transition temperature, the order–disorder phase transition of DODAC LB films in water may gradually occur, as illustrated in Fig. 4. Therefore, it can be concluded that the presence of water affects only the transition temperature in the DODAC LB film systems, and not the behavior of the phase transitions, themselves.

In the LB film DODAC molecules must be densely packed as a high degree of structural order and the hydrocarbon chains are oriented mostly along the surface normal,[24] whereas in the cast film DODAC molecules are in a lower packing order and in a random orientation. This suggests that the penetration of water molecules into the interlayers and the intralayers in the DODAC LB films is more depressed than in cast film. Thus, one of the possible reasons for the remarkable distinction between the phase transition behavior of LB films and in the cast film is the differences in the interaction between DODAC and water molecules.

Conclusion

Changes in the states of the hydrocarbon chains of DODAC in the LB films and in the cast film with temperature were examined using infrared ATR spectroscopy to reveal the thermal order–disorder phase transition behavior. In LB films a phase transition gradually occurs regardless of the presence of water and the number of monolayers, which govern only the phase transition temperatures. This phase transition behavior is found to differ from that in a cast film immersed in water, which shows the phase transitions of a coagel–gel and a gel–liquid crystal.

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23) The peak positions of $\delta(CH_2)$ band could not be determined due to overlapping the bands of H_2O and HOD vapors.

24) The surface area of DODAC at transferring to the substrate was close to the cross section of two hydrocarbon chains, indicating that the orientation of the hydrocarbon chain axis of DODAC is almost perpendicular to the water surface. From the transfer ratio of DODAC in this experiment, it can be deduced the perpendicular orientation of the hydrocarbon chains in the LB films of DODAC.