

Molecular Organization of Photoreactive Unsaturated Carboxylates on Langmuir–Blodgett Film

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The surface pressure–area (π – A) isotherms of dioctadecyldimethylammonium chloride ($2C_{18}DAC$) and dioctadecyldimethylammonium cinnamate ($2C_{18}DA \cdot Cin$) were measured, and their time dependence was examined. The surfaces of Langmuir–Blodgett films of $2C_{18}DAC$ and $2C_{18}DA \cdot Cin$ were observed by atomic force microscopy. The effect and location of cinnamate anions against molecular organization on Langmuir monolayers of $2C_{18}DA$ are discussed. After preparation, cinnamate ions bind on the hydrophilic surface of the $2C_{18}DA$ monolayer, by forming ion pairs with $2C_{18}DA$ cations and by directing aromatic groups toward the interior of the aqueous subphase. When the Langmuir film is maintained for long periods at a constant surface pressure, cinnamate ions are intercalated into the monolayer, as aromatic groups penetrate into the hydrophobic interior of the monolayer.

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INTRODUCTION

Amphiphiles form different kinds of molecular assemblies, depending on conditions, when they are dissolved in solvents. The molecular assemblies can be utilized as matrices of specific chemical reactions such as photodimerization (1–8). Aromatic unsaturated carboxylates such as cinnamate photoreact in the solutions of amphiphiles, producing four kinds of isomeric dimers (9–12). Formation of *anti*-head-to-head (*anti*-HH) and *syn*-HH isomers was dominant in micellar solutions and in reversed micellar solutions, respectively (13–15).

The reaction efficiency and stereochemical selectivity of photodimerization are related to the adsorption and organization of cinnamate monomers on molecular assemblies as reaction matrices. Cinnamate monomers bind electrostatically with cationic amphiphiles and/or are intercalated in molecular assemblies. There are three possibilities for pairing of cinnamates around the surface of the molecular assem-

bly (13, 14). *Anti*-HH and *syn*-HH isomers should be formed by pairing between cinnamate ions bound on the same side of the water-assembly interface.

The formation of *anti*-HH isomers proceeds more on vesicular bilayers than on micelles (14, 16–19). This suggests that cinnamates are arranged in lamellar bilayers of vesicles at a site suitable for photodimerization. A similar bilayer arrangement of amphiphiles is formed on Langmuir–Blodgett (LB) films. When monolayers arranged on aqueous subphase by the Langmuir method are accumulated on solid substrate, lamellar structures with repeating units are constructed. Although a structure similar to vesicular bilayers can possibly be used as a reaction matrix, there are no reports of photodimerization on LB films and on other thin films.

In this work, Langmuir and LB films of double-tailed cationic amphiphiles, dioctadecyldimethylammonium chloride ($2C_{18}DAC$) and dioctadecyldimethylammonium cinnamate ($2C_{18}DA \cdot Cin$), were investigated. The surface pressure–area (π – A) isotherms were measured at different subphase temperatures, and their time dependence was examined in comparison with a Langmuir monolayer of $2C_{18}DAC$ exposed to sodium cinnamate in subphase. LB films of $2C_{18}DAC$ and $2C_{18}DA \cdot Cin$ were observed by atomic force microscopy (AFM). The effect and location of cinnamate ions on $2C_{18}DAC$ monolayer were compared with those on vesicular bilayers.

EXPERIMENTAL SECTION

$2C_{18}DAC$ was purchased from Tokyo Kasei Co., Ltd. $2C_{18}DA \cdot Cin$ was kindly donated by Professor Takagi. Other materials were commercial products. $2C_{18}DAC$ and $2C_{18}DA \cdot Cin$ were dissolved in chloroform at a concentration of 1–2 mg cm⁻³. An aqueous solution of sodium cinnamate at 10 mM was prepared by dissolving equimolar cinnamic acid and NaOH in water.

Surface pressure measurements and LB film preparation were carried out on a LB film deposition apparatus (Nippon Laser & Electronics Laboratory). Chloroform solutions of $2C_{18}DAC$ and $2C_{18}DA \cdot Cin$ were spread on aqueous subphase in a 5 × 35 cm² trough at temperatures of 10°, 25°, and 40°.

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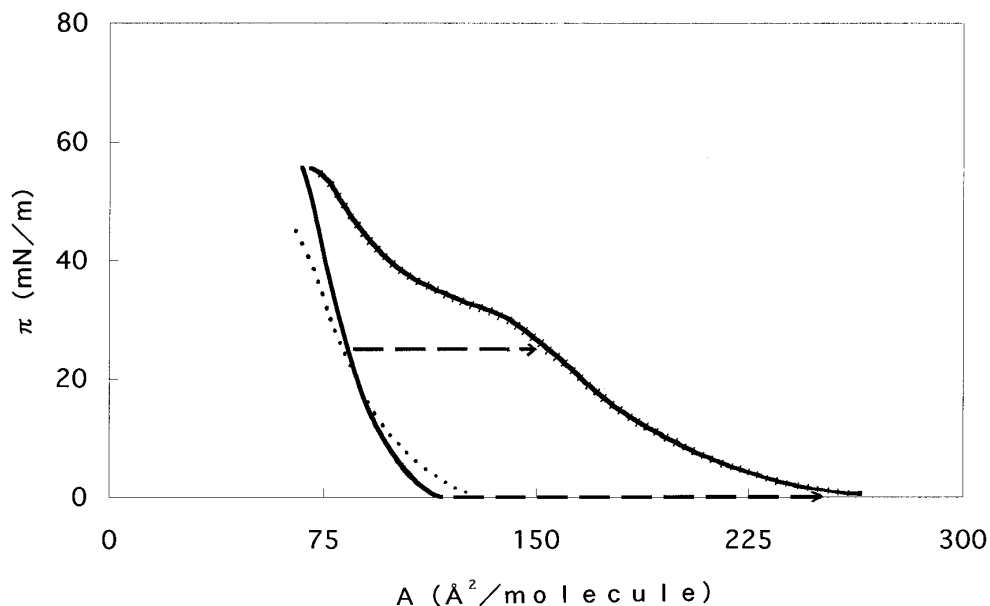


FIG. 1. The π - A isotherms of $2C_{18}DAC$ and $2C_{18}DA \cdot Cin$ monolayers on aqueous subphase at $25^{\circ}C$. \cdots , $2C_{18}DAC$; — , $2C_{18}DA \cdot Cin$ (after preparation); —|—|—| , $2C_{18}DA \cdot Cin$ (after aged for 30 h). Arrows indicate the path of rearrangement process.

and $35^{\circ}C$. After allowing 30 min for evaporation of the solvent, the surface was compressed at a constant rate of 10 mm min^{-1} . The Langmuir film was transferred onto freshly cleaved mica substrate by the upstroke and downstroke mode of the vertical dipping method at a surface pressure of 10 or 25 mN m^{-1} . Then monolayer and Y-type three-layer accumulate films were prepared. LB films were dried *in vacuo* for more than 3 h.

AFM observations were performed at room temperature on a Nanoscope III AFM (Digital Instruments, Inc.) in air by employing the tapping mode. A crystalline silicon tip on a cantilever with frequency of 280–410 Hz was used. Surface topography of LB films were evaluated by section analysis.

RESULTS

Surface pressures π of $2C_{18}DAC$ and $2C_{18}DA \cdot Cin$ monolayers are plotted as a function of surface area A per molecule in Fig. 1. It can be inferred from the expanded π - A isotherm curve that $2C_{18}DAC$ monolayers exist only in a liquid state. The apparent area occupied per amphiphilic molecule in the monolayer was calculated to be larger than that of regular double-chain amphiphiles. Figure 2 shows the temperature dependence of the π - A curve of $2C_{18}DAC$ monolayer. Although the π - A isotherm shifted into the direction for shrinking Langmuir film with decreasing temperature, the film in solid state was not formed even at $10^{\circ}C$.

When Langmuir film was prepared just after evaporation of solvent, the π - A curve of $2C_{18}DA \cdot Cin$ was similar to that of $2C_{18}DAC$, as seen in Fig. 1. The collapse pressures of $2C_{18}DAC$ and $2C_{18}DA \cdot Cin$ monolayers were 46 and 55

mN m^{-1} , respectively. Since cinnamate ions adsorb more strongly on the hydrophilic surface of $2C_{18}DA$ monolayer than chloride ions, the $2C_{18}DA \cdot Cin$ monolayer is stabilized even at high pressure as a result of lower electrostatic repulsion.

The surface area of $2C_{18}DA \cdot Cin$ monolayer increased with time, when the monolayer was maintained at a constant surface pressure. The increase was ended after 30 h. No time dependence of the π - A curve was observed for the $2C_{18}DAC$ monolayer, indicating no molecular rearrangement of the monolayer. The π - A curve of $2C_{18}DA \cdot Cin$ monolayer, which was compressed after rearrangement, is included in Fig. 1. The rearranged films, which ended at surface pressures of zero and 25 mN m^{-1} , orbited the same

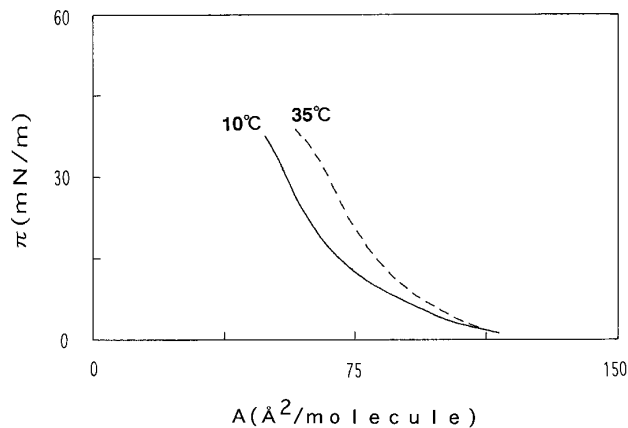


FIG. 2. The π - A isotherms of $2C_{18}DAC$ monolayers on aqueous subphase at 10 and $35^{\circ}C$.

curve. The surface area approximately doubled in comparison with that in the isotherm prior to rearrangement.

After $2C_{18}DAC$ monolayer was prepared, sodium cinnamate was added into the aqueous subphase in trough and the time dependence of the π - A curve was examined for a constant surface area. The surface pressure increased with time, as excess sodium cinnamate was added. The π - A curve after 30 h was similar to that of $2C_{18}DA \cdot Cin$ after rearrangement.

Monolayer LB films of $2C_{18}DAC$ on mica were observed by AFM, the photographs of which are shown in Fig. 3. The monolayer film prepared at a surface pressure of 10 mN m^{-1} displayed the rough surface with 4–8 Å height difference, which is low not to be compared with a molecular length of $2C_{18}DAC$. This suggests that the alkyl chains of molecules are not extended but randomly folded. An AFM photograph of film prepared at 25 mN m^{-1} exhibits the flat surface of 8 Å maximum height difference from rough parts. The height difference in flat surface consisting of extended alkyl chains was only 2–3 Å, although regular two-dimensional organization of molecules was not observed.

Figure 4 shows AFM photographs of monolayer and three-layer LB films of $2C_{18}DA \cdot Cin$ prepared at 25 mN m^{-1} after rearrangement. The monolayer had a rough surface with 10–17 Å and partly 30 Å height differences. The latter difference coincides with the length of the extended molecule. Although the monolayer surface was rougher than that of $2C_{18}DAC$, it was smoother than the surface of the three-layer film. The maximum roughness of the three-layer surface was 58 Å.

DISCUSSION

Cationic $2C_{18}DAC$ molecules arrange themselves in a wider separation on an aqueous subphase because of electrostatic repulsion between charged hydrophilic head groups. As a result, the π - A isotherm displays a curve of expanded film, and the monolayer is destroyed at lower pressure. The strong electrostatic repulsion between ionic $2C_{18}DAC$ results in the rough surface of the LB film. The roughness was larger than the LB film of arachidic acid and the annealed film of octadecyldimethylamine oxide (20), as apparent from the π - A curve and AFM photographs. The alkyl chains of $2C_{18}DAC$ molecules are folded at lower surface pressures and extended normal to the mica surface at higher pressures, as illustrated in Fig. 5. The 4–8 Å height difference observed by AFM is the difference between the extended and folded alkyl chains. The molecules extended at high surface pressure form a flat surface with a disordered two-dimensional arrangement of molecules.

Evans *et al.* (21, 22) have published the AFM photograph of $2C_{18}DA$ monolayer which was prepared by adsorbing molecules in organic solvent on mica. On such a monolayer, molecules arranged themselves in a regularly ordered struc-

ture. The occupied surface area of 51 \AA^2 per molecule obtained is smaller than that from the π - A curve in the present work. This means that the adsorbed molecules are arranged more compactly than in a Langmuir film. Since, in the adsorption process, cationic head groups of amphiphile bind electrostatically with the negatively charged mica surface, amphiphiles arrange themselves in the same order as mica anionic charges. In this situation, the electrostatic repulsion between head groups such as in the Langmuir film on an aqueous subphase has no effect.

Evans *et al.* (21) also investigated the temperature dependence of molecular arrangement in $2C_{18}DA$ monolayers at 25° – 50°C . While molecules arrange themselves regularly at 25°C , this arrangement becomes disorderly at 50°C . This indicates that the liquid crystal–gel transition temperature is between 25° and 50°C . Molecules in the Langmuir film maintained liquid state even at 10°C , demonstrating that the disordered arrangement of $2C_{18}DAC$ in Langmuir film does not result from the melting of alkyl chains but from the electrostatic repulsion between head groups, as discussed already.

It is assumed from the similarity of the π - A curves that, after preparation, $2C_{18}DA \cdot Cin$ molecules in Langmuir monolayer are arranged as the $2C_{18}DAC$ molecules are in Langmuir film. The schematic representation of the molecular arrangement is illustrated on the left side of Fig. 6. Here cinnamate anions are not intercalated into the monolayer of amphiphiles but bind on the hydrophilic surface of the monolayer, by forming ion pairs with $2C_{18}DA$ cations and by directing aromatic groups toward the interior of aqueous subphase. This kind of ion pair structure reflects the structure in chloroform where cinnamate ions make ion pairs with $2C_{18}DA$ ions. In this situation, we failed to prepare LB film on mica, because the hydrophobic aromatic part of a cinnamate ion comes in contact with mica substrate.

When the Langmuir film is compressed, the same arrangement is conserved even at high pressure. However, if the film is maintained at a constant surface pressure for long periods, cinnamate ions are intercalated into monolayers and arranged such as in the two lower right hand models of Fig. 6. The occupied surface area approximately doubles, as the π - A curve indicates. The rearrangement of cinnamate ions proceeds as a result of the relieving of energy disadvantage in the initial arrangement of $2C_{18}DA \cdot Cin$. The intercalation of cinnamate ions in monolayers was proved in a separate experiment, where excess sodium cinnamates were added in aqueous subphase in a trough after the $2C_{18}DAC$ monolayer was prepared. The π - A curve after rearrangement was similar to that of $2C_{18}DA \cdot Cin$ after rearrangement. Cinnamate ions bind electrostatically with $2C_{18}DA$ ions and then penetrate into the interior of monolayer, as illustrated in Fig. 6.

Figure 7 represents the molecular arrangement in LB films of $2C_{18}DA \cdot Cin$ after rearrangement. After cinnamate ions were intercalated into the monolayer, surface roughness in-

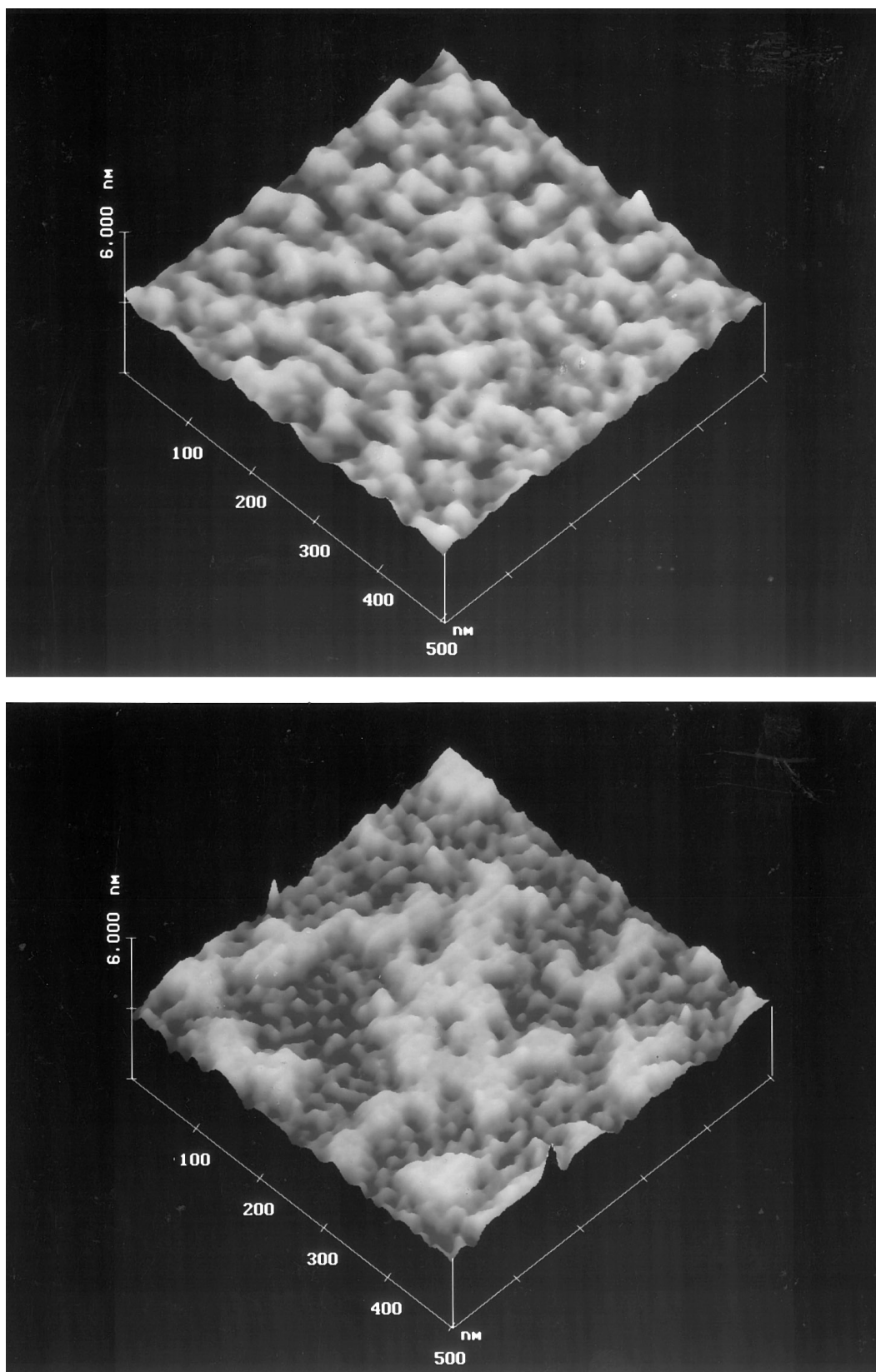


FIG. 3. AFM photographs of monolayer LB films of $2C_{18}DAC$ transferred on mica at surface pressures of 10 (upper) and 25 (lower) $mN m^{-1}$ at $25^{\circ}C$.

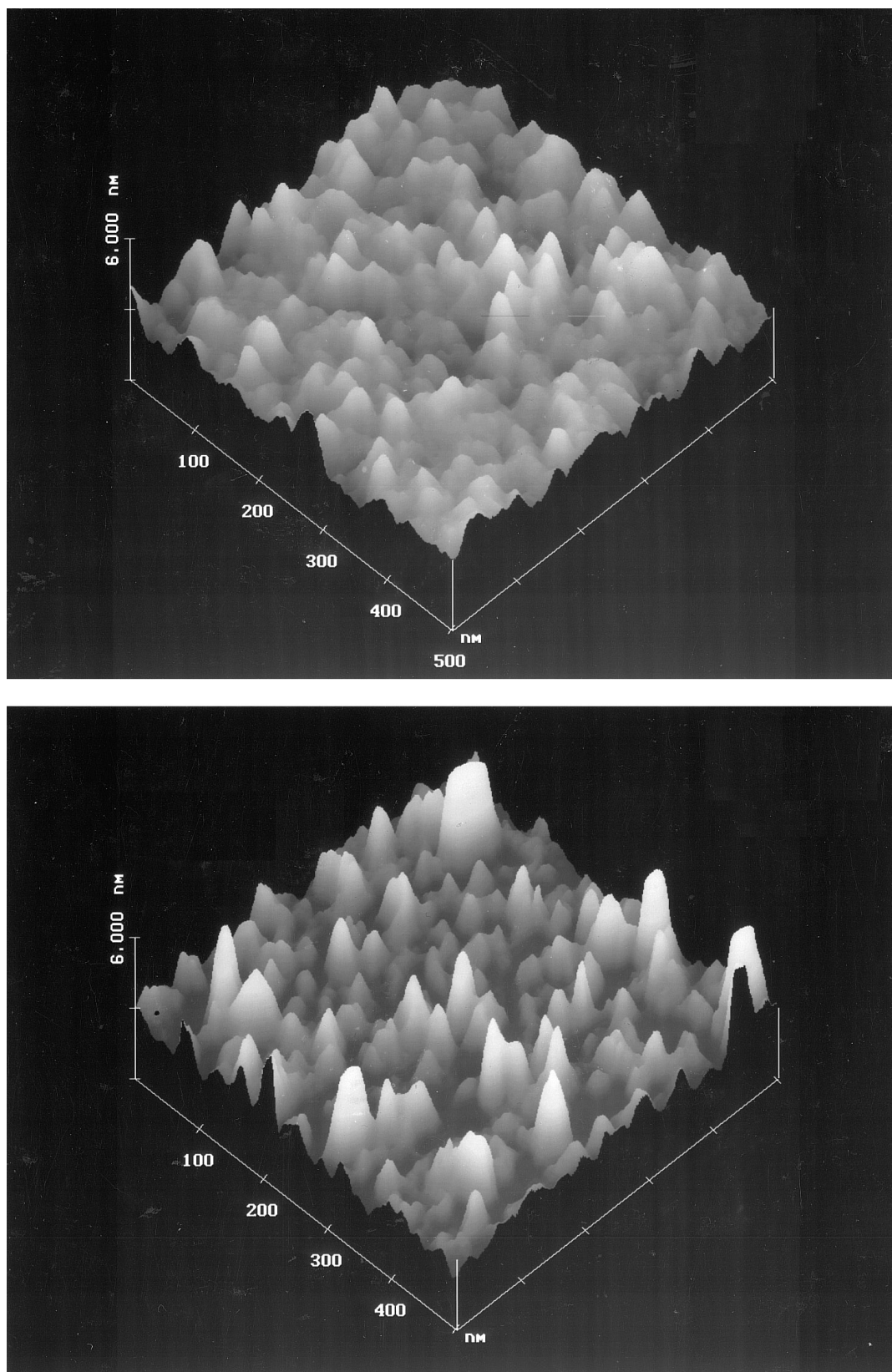


FIG. 4. AFM photographs of monolayer (upper) and three-layer (lower) LB films of $2C_{18}DA \cdot Cin$ transferred on mica at a surface pressure of 25 mN m^{-1} at 25°C .

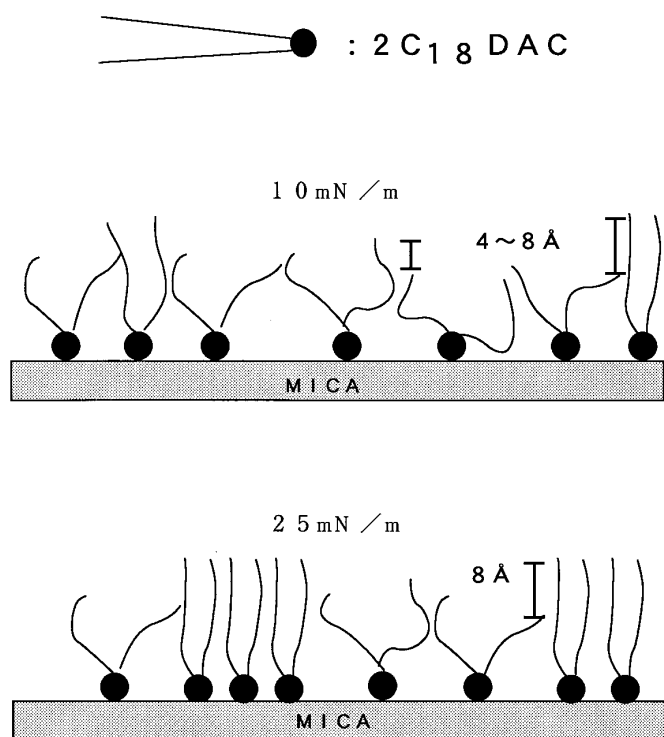


FIG. 5. Schematic representation of molecular arrangement in monolayer LB films of $2C_{18}DAC$ transferred on mica at surface pressures of 10 and 25 $mN\ m^{-1}$ at 25°C.

creases, since extended and folded $2C_{18}DA$ molecules coexist with cinnamate. While 30 Å height in monolayer corresponds to molecular length with extended alkyl chain, molecular length with folded alkyl chain is 13–20 Å. The height difference 58 Å of three-layer LB film indicates the forma-

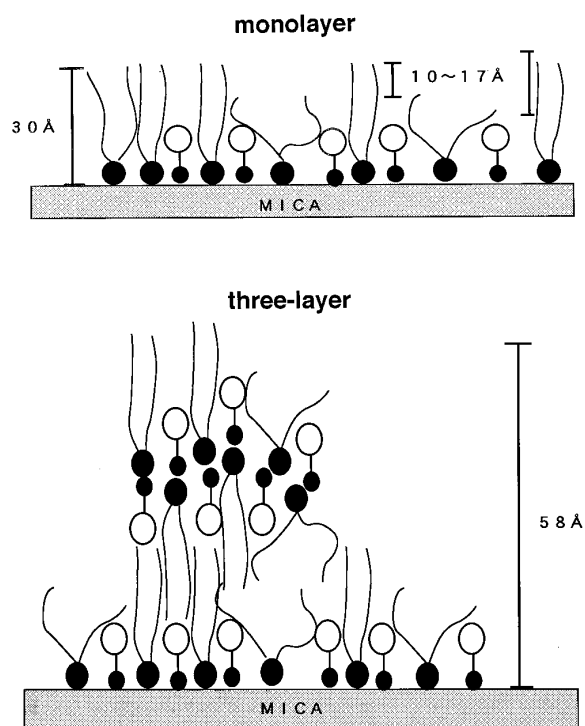


FIG. 7. Schematic representation of molecular arrangement in monolayer and three-layer LB films of $2C_{18}DA \cdot Cin$ after rearrangement transferred on mica at a surface pressure of 25 $mN\ m^{-1}$ at 25°C.

tion of layers with an average monolayer height of 19 Å. This suggests an interpenetrated arrangement of amphiphiles, as illustrated in Fig. 7, since the height 19 Å is shorter than the length of extended molecules.

Formation of the *anti*-HH dimer occurred predominantly among four possible isomers in the photodimerization of

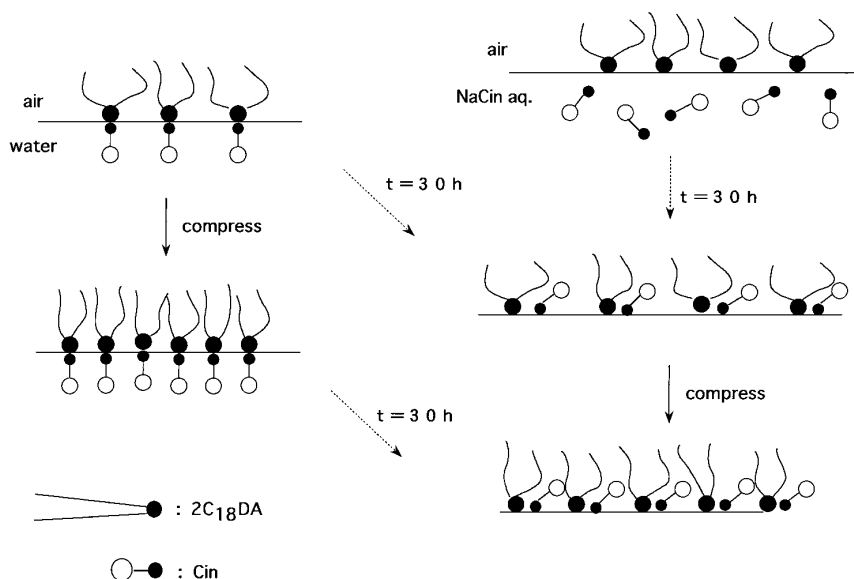


FIG. 6. Schematic representation of time dependence of molecular arrangement in monolayer of $2C_{18}DA \cdot Cin$ on an aqueous subphase at 25°C.

cinnamic acid on $2C_{18}DAC$ vesicles in water (14). The *anti*-HH dimer is constructed from the parallel arrangement of two cinnamic acid molecules. Such an arrangement is possible when cinnamic acid molecules bind on vesicle surfaces or penetrate into vesicles (13, 14). The latter model was confirmed for alkyldimethylamine oxide vesicles (17). In the present work, the intercalation of cinnamate into $2C_{18}DA$ Langmuir monolayer was clarified, supporting the parallel arrangement of two cinnamate molecules similar to that in $2C_{18}DA$ vesicles.

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