Molecular Organization of Photoreactive Unsaturated Carboxylates on Langmuir–Blodgett Film

Osamu Mori and Toyoko Imae

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

Received March 31, 1997; accepted November 4, 1997

The surface pressure–area (π–A) isotherms of dioctadecyldimethylammonium chloride (2C18DAC) and dioctadecyldimethylammonium cinnamate (2C18DA·Cin) were measured, and their time dependence was examined. The surfaces of Langmuir–Blodgett films of 2C18DAC and 2C18DA·Cin were observed by atomic force microscopy. The effect and location of cinnamate anions against molecular organization on Langmuir monolayers of 2C18DA are discussed. After preparation, cinnamate ions bind on the hydrophilic surface of the 2C18DA monolayer, by forming ion pairs with 2C18DA 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.

Key Words: photoreaction; unsaturated carboxylate; cinnamic acid; surface pressure-area isotherm; Langmuir–Blodgett film; dioctadecyldimethylammonium chloride; atomic force microscopy.

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 when 2C18DAC was purchased from Tokyo Kasei Co., Ltd. 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 (2C18DAC) and dioctadecyldimethylammonium cinnamate (2C18DA·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 2C18DAC exposed to sodium cinnamate in subphase. LB films of 2C18DAC and 2C18DA·Cin were observed by atomic force microscopy (AFM). The effect and location of cinnamate ions on 2C18DAC monolayer were compared with those on vesicular bilayers.

EXPERIMENTAL SECTION

2C18DAC was purchased from Tokyo Kasei Co., Ltd. 2C18DA·Cin was kindly donated by Professor Takagi. Other materials were commercial products. 2C18DAC and 2C18DA·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 2C18DAC and 2C18DA·Cin were spread on aqueous subphase in a 5 x 35 cm² trough at temperatures of 10°, 25°,
and 35°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 2C₁₈DAC and 2C₁₈DA·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 2C₁₈DAC 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 2C₁₈DAC 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°C.

When Langmuir film was prepared just after evaporation of solvent, the π–A curve of 2C₁₈DA·Cin was similar to that of 2C₁₈DAC, as seen in Fig. 1. The collapse pressures of 2C₁₈DAC and 2C₁₈DA·Cin monolayers were 46 and 55 mN m⁻¹, respectively. Since cinnamate ions adsorb more strongly on the hydrophilic surface of 2C₁₈DA monolayer than chloride ions, the 2C₁₈DA·Cin monolayer is stabilized even at high pressure as a result of lower electrostatic repulsion.

The surface area of 2C₁₈DA·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 2C₁₈DAC monolayer, indicating no molecular rearrangement of the monolayer. The π–A curve of 2C₁₈DA·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. 1](image1.png)  
**FIG. 1.** The π–A isotherms of 2C₁₈DAC and 2C₁₈DA·Cin monolayers on aqueous subphase at 25°C: · · · · , 2C₁₈DAC; ———, 2C₁₈DA·Cin (after preparation); ———, 2C₁₈DA·Cin (after aged for 30 h). Arrows indicate the path of rearrangement process.

![Fig. 2](image2.png)  
**FIG. 2.** The π–A isotherms of 2C₁₈DAC monolayers on aqueous subphase at 10 and 35°C.
After 2C₁₈DAC monolayer was prepared, sodium cinnamate was added into the aqueous subphase in trough and the time dependence of the $\pi - A$ curve was examined for a constant surface area. The surface pressure increased with time, as excess sodium cinnamate was added. The $\pi - A$ curve after 30 h was similar to that of 2C₁₈DA·Cin after rearrangement.

Monolayer LB films of 2C₁₈DAC 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 2C₁₈DAC. 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 2C₁₈DA·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 2C₁₈DAC, it was smoother than the surface of the three-layer film. The maximum roughness of the three-layer surface was 58 Å.

### DISCUSSION

Cationic 2C₁₈DAC molecules arrange themselves in a wider separation on an aqueous subphase because of electrostatic repulsion between charged hydrophilic head groups. As a result, the $\pi - A$ isotherm displays a curve of expanded film, and the monolayer is destroyed at lower pressure. The strong electrostatic repulsion between ionic 2C₁₈DAC 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 octadecyl(dimethylamine oxide (20), as apparent from the $\pi - A$ curve and AFM photographs. The alkyl chains of 2C₁₈DAC 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 2C₁₈DA monolayer which was prepared by adsorbing molecules in organic solvent on mica. On such a monolayer, molecules arranged themselves in a regularly ordered structure. The occupied surface area of 51 Å² per molecule obtained is smaller than that from the $\pi - A$ 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 2C₁₈DA 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 2C₁₈DAC 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 $\pi - A$ curves that, after preparation, 2C₁₈DA·Cin molecules in Langmuir monolayer are arranged as the 2C₁₈DAC 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 2C₁₈DA 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 2C₁₈DA 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 $\pi - A$ curve indicates. The rearrangement of cinnamate ions proceeds as a result of the relieving of energy disadvantage in the initial arrangement of 2C₁₈DA·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 2C₁₈DAC monolayer was prepared. The $\pi - A$ curve after rearrangement was similar to that of 2C₁₈DA·Cin after rearrangement. Cinnamate ions bind electrostatically with 2C₁₈DA ions and then penetrate into the interior of monolayer, as illustrated in Fig. 6.

Figure 7 represents the molecular arrangement in LB films of 2C₁₈DA·Cin after rearrangement. After cinnamate ions were intercalated into the monolayer, surface roughness in-
FIG. 3. AFM photographs of monolayer LB films of 2C₈DAC transferred on mica at surface pressures of 10 (upper) and 25 (lower) mN m⁻¹ at 25°C.
FIG. 4. AFM photographs of monolayer (upper) and three-layer (lower) LB films of 2C₆DA·Cin transferred on mica at a surface pressure of 25 mN m⁻¹ at 25°C.
creases, since extended and folded 2C₁₈DA 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 formation 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 

![Diagram of molecular arrangement](image)

**FIG. 5.** Schematic representation of molecular arrangement in monolayer LB films of 2C₁₈DAC transferred on mica at surface pressures of 10 and 25 mN m⁻¹ at 25°C.

![Diagram of molecular arrangement](image)

**FIG. 6.** Schematic representation of time dependence of molecular arrangement in monolayer of 2C₁₈DA·Cin on an aqueous subphase at 25°C.

![Diagram of molecular arrangement](image)

**FIG. 7.** Schematic representation of molecular arrangement in monolayer and three-layer LB films of 2C₁₈DA·Cin after rearrangement transferred on mica at a surface pressure of 25 mN m⁻¹ at 25°C.
cinnamic acid on 2C18DAC 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 2C18DA Langmuir monolayer was clarified, supporting the parallel arrangement of two cinnamate molecules similar to that in 2C18DA vesicles.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research (No. 08640736) by the Ministry of Education in Japan and by a grant from the Cosmetology Research Foundation. We are grateful to Professor K. Takagi in Nagoya University for his valuable discussion.

REFERENCES