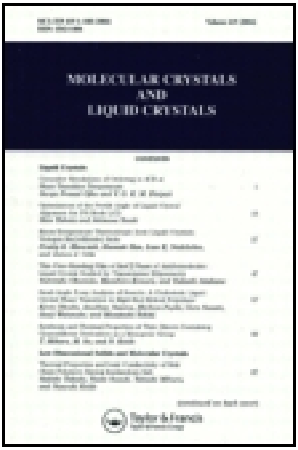

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Structure of the Langmuir-Blodgett Films of Arachidic Acid Mixed with Amphiphilic Ammonium Ions and an Amphiphilic Amine

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Structure of the Langmuir-Blodgett Films of Arachidic Acid Mixed with Amphiphilic Ammonium Ions and an Amphiphilic Amine

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In the Langmuir-Blodgett (LB) films of arachidic acid (AA) with amphiphilic ammonium ions or an amphiphilic amine, components were mixed at the molecular level and formed salt. The alkyl chains of the two components took almost the same tilt angle. The fraction of the second component in the mixed LB films was smaller than that in the spreading solution when the fraction of the second component was larger than 0.5.

Keywords LB films; salt formation; molecular orientation; IR; XPS

INTRODUCTION

The Langmuir-Blodgett (LB) technique has been used to fabricate molecular films having supramolecular structures with multiple components [1]. Phase separation often observed in the mixed LB films [2,3] is a major problem in this respect. To solve this problem, salt formation may be used to mix the components at the molecular level. In this case, the molecular orientation and mixing ratio in the LB films are important parameters to define the structures of the LB films.

In this study, we will report on the structures of LB films of AA (or dAA: deuterated arachidic acid) with 1-docosyltrimethylammonium bromide (DAB), 1-docosylpyridinium bromide (DPB) or stearylamine (SA). Preliminary results have been reported in the literature [4].

EXPERIMENTAL

All the monolayer measurements were done on a Lauda film balance at 290 K. AA was mixed with DAB, DPB or SA in chloroform and spread on pure water. Infrared transmission and reflection-absorption spectra of the LB films were measured using a Perkin-Elmer Spectrum 2000. XPS spectra were recorded on a Perkin-Elmer PHI5600ci ESCA system.

RESULTS AND DISCUSSION

AA/DAB System

Figure 1 shows the π-A isotherms of AA/DAB system. It is evident that the Raoult's law or the additivity rule does not hold in this case, indicating that the two components are mixed at the molecular level.

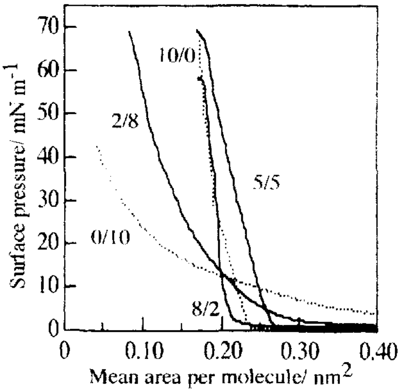

FIGURE 1 Surface pressure-area isotherms of AA/DAB mixed monolayers at the air-water interface at 290 K. Mixing ratio of AA to DAB is shown.

IR transmission and reflection-absorption spectra of the dAA/DAB LB films were measured to investigate the dissociation of dAA and the packing of each component [5]. First, the IR spectra in the region of C=O stretching of dAA/DAB LB films were examined. At the mixing ratio of 8/2, a band assigned to the C=O stretching vibration of COOH was seen at around 1720 cm^{-1}, whereas this band was missing at the mixing ratio of 5/5 and 2/8. On the other hand, two bands assigned to the C=O antisymmetric stretching (ca. 1570 cm^{-1}) and symmetric stretching (ca. 1390 cm^{-1}) vibration of COO$^-$ were recognized except when the mixing ratio was 8/2. This shows that dAA is deprotonated when the fraction of dAA is equal to or less than 0.5. This suggests that the deprotonated dAA forms salt with DAB and is mixed at the molecular level due to electrostatic interaction. Second, we studied the IR spectra in the region of CD_2 bending vibration of dAA/DAB LB films. This vibration mode is a doublet when the alkyl chains crystallize with the orthorhombic subcell packing as in dAA single-component LB films [6,7]. However, this band was a singlet for all the mixing ratios, which indicates that the packing of dAA is modified by DAB. Possible modification mechanisms are (1) a significant number of the dAA molecules in the orthorhombic subcell are replaced by the DAB molecules and (2) replacement of dAA by DAB is accompanied by the change in the packing mode.

Figure 2 shows the tilt angles of alkyl chains of dAA and DAB in the mixed LB films obtained using the calculations in the literature [8,9]. It is evident that both the components have virtually the same tilt angle and oriented almost vertically except for the mixing ratio of 1/1. One of the possible reasons of the large tilt angles at the mixing ratio of 1/1 is that the alkyl chains may crystallize with the monoclinic subcell packing.

The fraction of DAB in the LB films were estimated using the results of the IR and XPS measurements. For the former case, the intensity of antisymmetic stretching band of CD_2 of dAA and that of CH_2 of DAB in the IR spectra were compared considering the difference in the molar absorptivity of these bands. Figure 3 shows the fraction of DAB of the dAA/DAB LB films plotted against that in the spreading solution. The fraction of DAB in the LB film is smaller than that in the spreading solution when the fraction of DAB in the spreading solution is larger than 0.5, whereas the composition of the LB film is similar to that in the spreading solution with the fraction of DAB equal to or less than 0.5. In other words, when the number of DAB is smaller than that of dAA in the spreading solution, the composition does not change during the transfer, whereas some of the DAB molecules are not readily transferred onto solid substrates when the number of DAB is larger than that of dAA. This suggests that some of the DAB molecules which do not form salt with the dAA molecules are not deposited on solid substrates probably due to the solubility of DAB or to the scarcity of intermolecular interaction with the surrounding molecules.

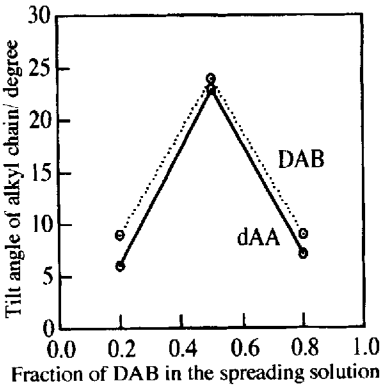

FIGURE 2 Tilt angle of the alkyl chain of dAA and DAB as a function of the fraction of DAB in the spreading solution.

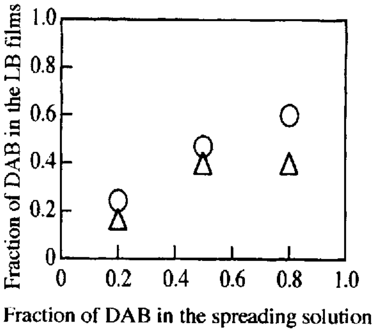

FIGURE 3 Fraction of DAB in the LB films obtained from IR (circles) and XPS (triangles) measurements as a function of the fraction of DAB in the spreading solution.

AA/DPB and AA/SA systems

The structures of the AA/DPB and AA/SA LB films were similar to those of AA/DAB LB films: (1) Raoult's law did not apply to the π-A isotherms, (2) dAA was deprotonated in the LB films when the fraction of dAA was equal to or less than 0.5, (3) the orthorhombic subcell packing of dAA was not maintained in the LB films, and (4) the fraction of DPB or SA in the LB film was smaller than that in the spreading solution when the fraction of dAA was smaller than 0.5. However, a significant difference was observed in the molecular orientation. Figure 4 shows the tilt angle of the alkyl chain of the dAA/DPB LB films. It is clear that the tilt angle of the alkyl chain is almost the same for both the components and that the alkyl chains are oriented almost vertically in the LB films for all the mixing ratios. These features were also observed in the dAA/SA LB films. Considering all the results including those of AA/DAB system, it is suggested that the alkyl chain of the second component takes the orientation similar to that of AA and that, for most of the mixed LB films with salt formation, the alkyl chains tend to be oriented almost perpendicularly with respect to the film surface.

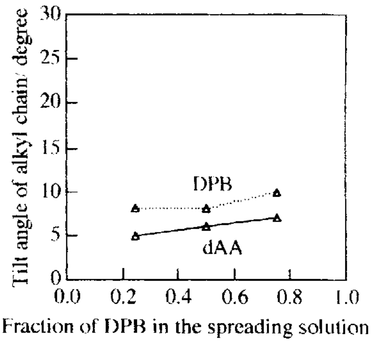

FIGURE 4 Tilt angle of the alkyl chain of dAA and DPB as a function of the fraction of DPB in the spreading solution.

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