

# Langmuir–Blodgett Films of Surface-Active Azodye. Investigation by Atomic Force Microscopy

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Langmuir–Blodgett (LB) films of surface-active azodye, YOPE, were prepared at different surface pressures and observed by atomic force microscopy. The surface structure was compared with that of LB films of the arachidic acid/YOPE hybrid. The two-dimensional phase separation was observed in hybrid LB films. The molecular arrangement of YOPE on Langmuir films was inferred from the AFM observation of LB films and the surface pressure–area ( $\pi$ -A) isotherms. At lower surface pressures, the dye chromophores of YOPE molecules were lying along the air–water interface. The arithmetic additivity of  $\pi$ -A isotherms was substantiated for hybrids.

## Introduction

Planar dyes, such as azobenzene derivatives, aggregate reversibly in water by intermolecular stacking interactions between conjugated  $\pi$ -electrons.<sup>1–3</sup> The dye aggregates display physicochemical properties different from those of individual molecules. It is interesting that the higher ordering of aggregates induces an anisotropic system with a valuable function, in connection with the development of the photochromic liquid crystal display device. The structure of aggregates and their ordering can be controlled by changing the chemical structure of the dye, that is, by including long alkyl chains in the molecules. Dyes with surface-activity are expected to form the more ordered systems, since they have an aggregation ability due to the hydrophobic interaction between alkyl chains and the hydrophilic interaction between polar head groups in addition to the dye-stacking interaction. Kunitake et al.<sup>4,5</sup> have reported the formation of bilayer assemblies by chromophore-containing amphiphiles in water.

As well as the three-dimensional organization in solution, the two-dimensional organization of the dye is of interest to the basic and applied sciences of energy transfer and photochemical reaction. The organization of dye-containing amphiphilic molecules has been investigated at the air–water interface.<sup>6–8</sup> Moreover, the two-dimensionally organized structure, orientation, and anisotropy of Langmuir (L) and LB films have been examined by surface spectroscopies such as UV–vis absorption, FT-IR, and resonance Raman scattering.<sup>9–14</sup> However, the

morphological information of the two-dimensional organization was not obtained from the spectroscopy.

An azobenzene-containing amphiphile, *p*-tert-octylphenol yellow amine poly(ethylene oxide) (YOPE), forms the primary micelles, which have an aggregation number less than 15, above a critical concentration (0.01–0.035 mM) in dilute, aqueous methanol solutions at neutral pH.<sup>15–17</sup> The aggregates arise from the stacking interaction between dye molecules. At high concentrations above 0.03–0.36 mM, the secondary micelles originated from the hydrophobic interaction characteristic to micelles of common amphiphiles are formed, followed by the lyotropic liquid crystal formation in more concentrated solutions. Although the two-dimensional organization of YOPE at the interface is expected owing to the high aggregation ability in solutions, such organization has never been reported for YOPE.

In this work, two-dimensional thin films with high organization of surface-active azodye, YOPE, are constructed on a mica substrate by the LB method. The LB films are observed by atomic force microscopy (AFM) in order to examine the morphological surface structure of the films and the mechanism of molecular aggregation. The hybrid LB films of arachidic acid and YOPE, which may be used as photoresponse films, are also constructed and observed by AFM. The miscibility of YOPE in an arachidic acid monolayer is discussed on the basis of a morphological investigation. Heesemann<sup>7</sup> has investigated the mixed films of surface-active azodye and common amphiphiles. They concluded the complete miscibility of the components. The results in the present work are compared with those by Heesemann.

## Experimental Section

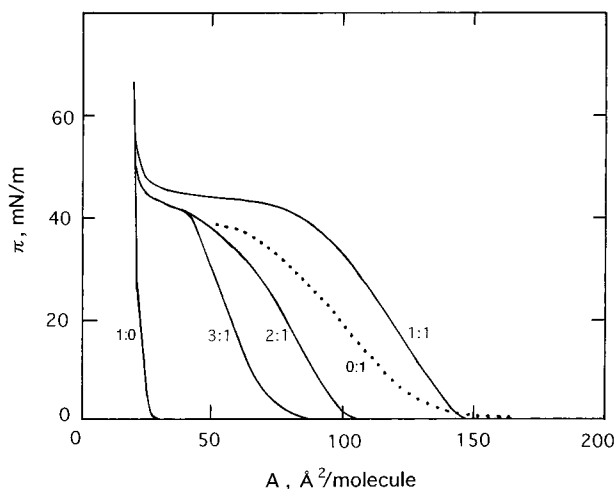
The YOPE sample was the same as that previously used.<sup>15–17</sup> Arachidic acid (purity >99%) and chloroform (purity >99%) were purchased from Wako Pure Chemical Industries, Ltd., Osaka. Water was redistilled from alkaline  $\text{KMnO}_4$ .

The measurement of surface pressure–area ( $\pi$ -A) isotherm curves and the preparation of LB films were carried out on a LB

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**Figure 1.**  $\pi$ - $A$  isotherms of arachidic acid, YOPE, and their hybrids at 25 °C. Numerical values in the figure represent the mixing ratio [arachidic acid]/[YOPE]. The  $x$ -axis in the  $\pi$ - $A$  isotherms of hybrids is normalized to the number of arachidic acid molecules used in the mixtures.

film deposition apparatus (Nippon Laser & Electronics Lab, Nagoya). Chloroform solutions of amphiphiles and their hybrids were prepared at a concentration of 1.0 mg cm<sup>-3</sup> and were spread on a water subphase at 25 °C. After the solvent was evaporated, surface pressures were measured under continuous compression at a constant rate of 10 mm min<sup>-1</sup>. Molecules on the air-water interface at various surface pressures were transferred at a rate of 3.0 mm min<sup>-1</sup> onto a freshly cleaved mica substrate by the upstroke mode of the vertical dipping method. Then the amphiphilic molecules had their hydrophilic head groups directed toward the mica substrate. The transfer ratio was larger than 95%. LB films were dried in vacuo for more than 3 h.

Atomic force microscopic observation was performed at room temperature on a Nanoscope III AFM (Digital Instruments, Inc.) using the tapping mode. A crystalline silicon tip on a cantilever with a frequency of 280–410 Hz was used. Vertical distances of images were evaluated from the section analysis.

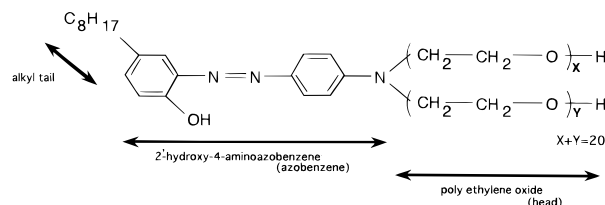
## Results

**$\pi$ - $A$  Isotherm.** The  $\pi$ - $A$  isotherm of YOPE is given in Figure 1. The surface pressures increased at surface areas below 150 Å<sup>2</sup> molecule<sup>-1</sup> and displayed a plateau below 70 Å<sup>2</sup> molecule<sup>-1</sup>. The occupied area per molecule obtained from the  $\pi$ - $A$  isotherm was 129 Å<sup>2</sup> molecule<sup>-1</sup>. This value is very large in comparison with that of arachidic acid (22 Å<sup>2</sup> molecule<sup>-1</sup>), as seen in Figure 1. The surface pressures of arachidic acid increased sharply below 27 Å<sup>2</sup> molecule<sup>-1</sup>.

Figure 1 includes  $\pi$ - $A$  isotherm curves of hybrids of YOPE and arachidic acid. The surface pressures of the hybrids increased gradually, reached a plateau, and then increased again for lower molecular areas before collapsing. The LB films of hybrids collapsed at a surface pressure of 65 mN m<sup>-1</sup>, as did the film of arachidic acid, while the collapse of the YOPE film occurred at less than 40 mN m<sup>-1</sup>. The plateau surface pressures of hybrids were close to that of YOPE only. The increase of surface pressure below the plateau occurred at higher surface areas for hybrids with higher YOPE content, although the steep increase of surface pressure above the plateau was consistent with that of arachidic acid, independent of the coexistence of YOPE.

**Atomic Force Microscopy.** Figure 2 shows AFM photographs of YOPE LB films prepared at surface pressures of 5 and 25 mN m<sup>-1</sup>. The surface at 5 mN m<sup>-1</sup> was almost smooth, although there were slight bumps. On the other hand, at 25 mN m<sup>-1</sup>, the number of bumps

**Chart 1**



increased and the height difference from the smooth surface increased up to 70 Å.

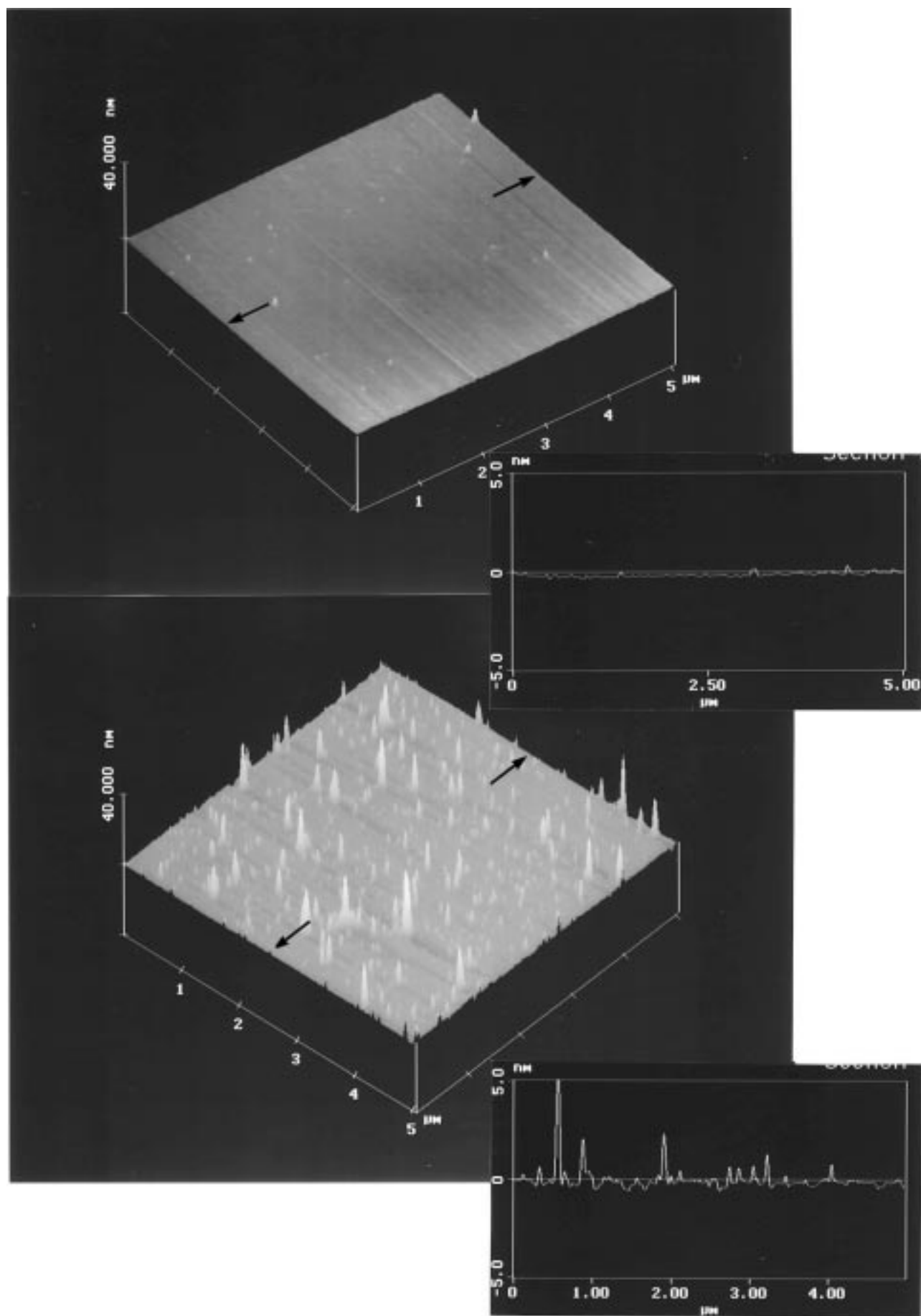
AFM photographs of LB films of an arachidic acid/YOPE (3:1) hybrid prepared at surface pressures of 10 and 30 mN m<sup>-1</sup> are shown in Figure 3. At the lower surface pressure 10 mN m<sup>-1</sup>, there were circular domains with smooth surfaces, different from AFM images of homogeneous YOPE films. The continuous phase surrounding the domains was rather like the surface of the homogeneous YOPE film. It was observed from the section analysis of AFM photographs that the continuous phase was 10 Å lower than the flat surface of circular domains.

When the surface pressure was increased, circular domains maintained their smooth surface and constant sizes (less than 2 μm in diameter). On the other hand, the continuous phase reduced its area and increased its roughness. It should be noticed that AFM images of homogeneous YOPE films also showed the increased roughness with compressing areas. The rough surfaces at 30 mN m<sup>-1</sup> consisted of bumps with various height differences, 80 Å being the maximum. Such bumps occurred preferentially from the edges of circular domains during the compression of hybrid films, as seen in Figure 3. The AFM textures in Figures 2 and 3 were homogeneous in the wide scale. The number of circular domains decreased on the LB film of the 1:1 hybrid. Moreover, the surfaces of such domains were rather rough, indicating imperfect molecular packing.

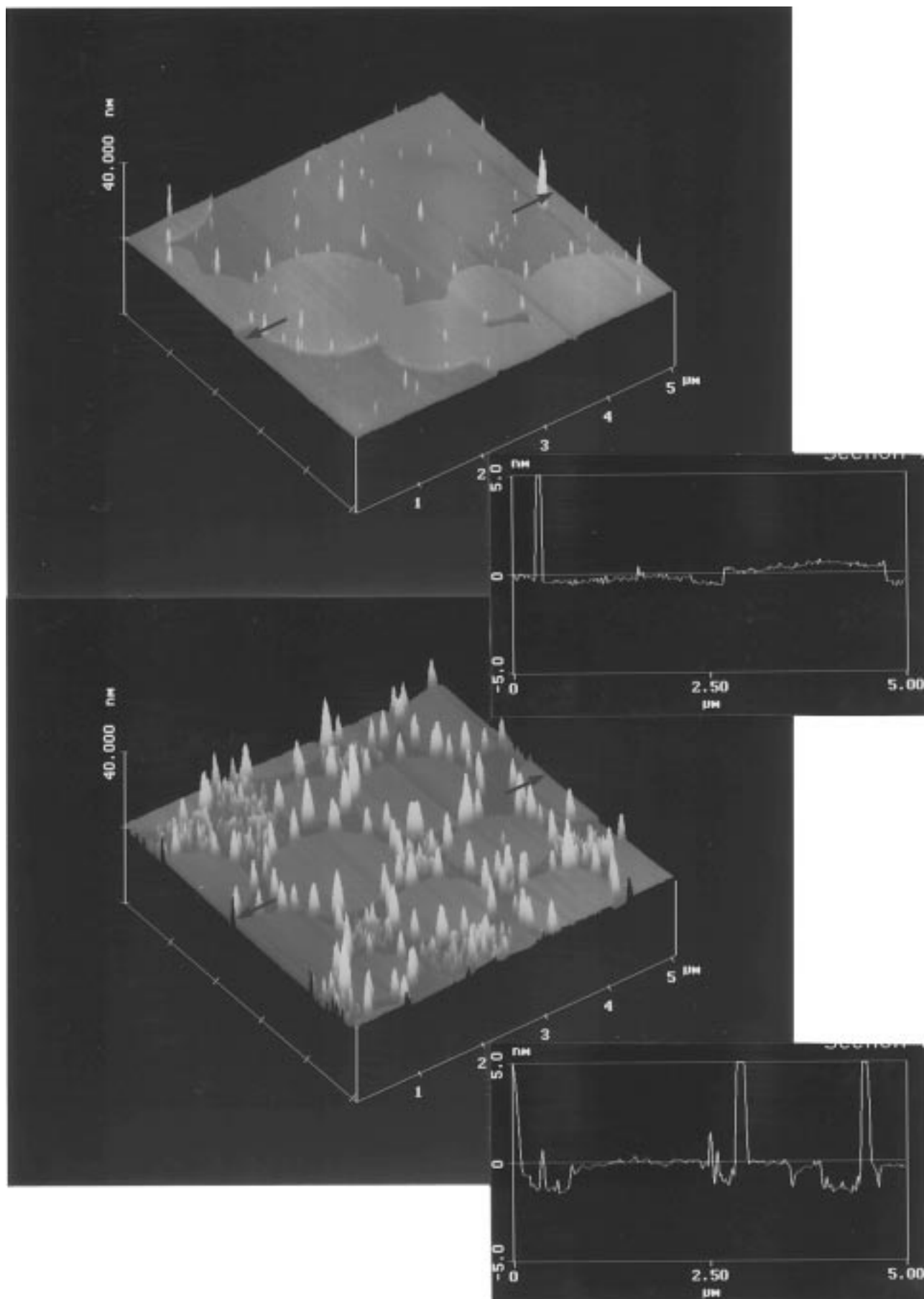
## Discussion

The YOPE molecule consists of a hydrophobic alkyl tail, a hydrophilic poly(ethylene oxide) head, and a rigid 2'-hydroxy-4-aminoazobenzene intermediate, as illustrated in Chart 1. The lengths of the extended alkyl tail and *trans*-azobenzene are 12 and 13 Å, respectively, and poly(ethylene oxide) has an 8–20 Å length depending on the folding conformation. The occupied area of 129 Å<sup>2</sup> molecule<sup>-1</sup> per YOPE molecule was evaluated from the  $\pi$ - $A$  isotherm. This area is satisfied only if YOPE molecules on the air-water interface assume an arrangement contacting the head and intermediate groups with water, as schematically represented in Figure 4. The occupied area of about 150 Å<sup>2</sup> molecule<sup>-1</sup> calculated for this arrangement is consistent with the one evaluated from the  $\pi$ - $A$  isotherm. This arrangement is possible, because YOPE has a hydrophilic OH residue in the 2' position of the azobenzene, although azobenzene itself is hydrophobic. The arrangement of YOPE in the monolayer is completely different from that of arachidic acid, a typical fatty acid with long saturated alkyl chains.<sup>18</sup> Arachidic acids are oriented with the molecular axis perpendicular to the water subphase.

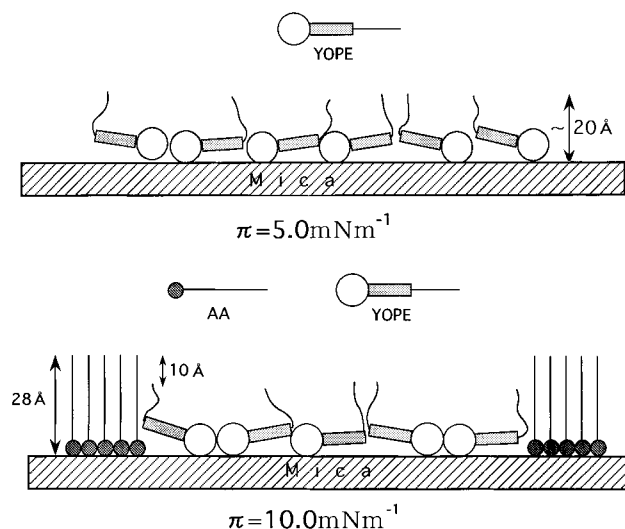
A two-step increase of surface pressure with compressing molecular area was observed at both sides of inflection in the  $\pi$ - $A$  isotherms of hybrids of YOPE and arachidic acid. The occupied areas of the YOPE molecule were arithmetically evaluated from the  $\pi$ - $A$  isotherms, as-



**Figure 2.** AFM photographs of LB films of YOPE prepared at surface pressures of 5 (upper) and 25 (lower) mN m<sup>-1</sup>. The section analyses which were taken between arrows are also included.



**Figure 3.** AFM photographs of LB films of the [arachidic acid]/[YOPE] (3:1) hybrid prepared at surface pressures of 10 (upper) and 30 (lower)  $\text{mN m}^{-2}$ . The section analyses which were taken between arrows are also included.



**Figure 4.** Schematic representation of molecular arrangement in Langmuir films of YOPE at the surface pressure of  $5 \text{ mN m}^{-1}$  (upper) and of the [arachidic acid]/[YOPE] (3:1) hybrid at the surface pressure  $10 \text{ mN m}^{-1}$ .

**Table 1.** Occupied Area of YOPE Molecule (in  $\text{\AA}^2 \text{ Molecule}^{-1}$ )

[arachidic acid]/[YOPE]	occupied area
0:1	129
1:1	118
2:1	137
3:1	147

suming the additivity of the occupied area in hybrids. The consistency with observation for homogeneous YOPE was good, as seen in Table 1. Therefore, it can be inferred that the arithmetic additivity of  $\pi$ - $A$  isotherms of YOPE and arachidic acid was substantiated for those of hybrids.

The AFM texture in Figure 3 suggests that the hybrid displays phase separation in the two-dimensional arrangement. The morphology of the continuous phase and its surface pressure dependence are very similar to those of homogeneous YOPE LB films, as seen in Figures 2 and 3. The bumps increased in number and height at high surface pressure. Similar bumps (or grains) were observed by AFM on a LB film of 4-octyl-4'-(5-carboxypentamethyleneoxy)azobenzene.<sup>19</sup> The isolated domains in hybrid LB films increase in number per unit area with increasing arachidic acid content. Moreover, it is known that arachidic acid forms L films with a two-dimensionally ordered structure.<sup>18</sup> Therefore, in the phase separation, the isolated phase is arachidic acid-rich and the continuous phase is YOPE-rich. Circular domains are energetically preferable, because the contact line of different phases in two-dimensional phase separation is minimized. Similar circular domains were observed for a hybrid of partly fluorinated carboxylic ether acid with arachidic acid<sup>20</sup> and a hybrid of perfluorotetradecanoic acid with arachidic acid or perfluorooctadecanoic acid.<sup>21</sup>

Since the molecular length of arachidic acid is  $28 \text{ \AA}$ ,<sup>18</sup> the height of the YOPE-rich phase from the mica substrate on a hybrid LB film prepared at low surface pressure is only  $18 \text{ \AA}$ , as the height difference  $10 \text{ \AA}$  between the circular domain and the continuous phase was observed.

The corresponding height ( $\sim 20 \text{ \AA}$ ) was obtained for a homogeneous YOPE LB film at  $5 \text{ mN m}^{-1}$ . Molecules were removed by repeated scratching at the contact mode to measure the height relative to the substrate.<sup>18</sup>

Since the height of  $18$ – $20 \text{ \AA}$  is lower than the YOPE molecular length ( $30$ – $35 \text{ \AA}$ ), extended YOPE molecules cannot be arranged normal to the substrate. Then YOPE molecules in the YOPE-rich phase of the hybrid L film must be lying along the air–water interface in the same mode as that in the homogeneous YOPE L film, which was already inferred from the  $\pi$ - $A$  isotherm. This means that YOPE and arachidic acid in each segregated phase of the hybrid maintain a two-dimensional molecular arrangement as well as in each homogeneous L film, as illustrated in Figure 4. This is also supported by the arithmetic additivity of  $\pi$ - $A$  isotherms, which was discussed above.

At the higher surface pressure, the roughness by bumps was observed on the surfaces of the homogeneous YOPE LB film and the YOPE-rich region in the hybrid LB film, although the arachidic acid-rich region is always the same. The bumps were heterogeneous in height and width, and some of them were higher than the surface of the arachidic acid-rich region. Therefore, those may be the small collapsed regions of piled-up YOPE, while arachidic acids in hybrid LB films maintain their solid-state arrangement even at different surface pressures.

The  $\pi$ - $A$  isotherms of surface-active azodyes have been investigated by some workers.<sup>6–9,14</sup> It was reported that the phase transition from liquid crystal (fluid) to gel (two-dimensional crystalline) occurred when the surface areas were compressed on spread monolayers of long-chain fatty acids containing hydrophobic azobenzene.<sup>9,14</sup> However, the 'lying' structure of the surface-active azodye was not observed in their reports, because surface pressures increased only at surface areas less than  $60 \text{ \AA}^2 \text{ molecule}^{-1}$ . On the other hand, for some molecules containing dye chromophore, the  $\pi$ - $A$  isotherms with a liquid-expanded state, a phase-transition region, and a condensed state have been reported.<sup>6,7</sup> In the liquid-expanded state at  $\sim 100 \text{ \AA}^2 \text{ molecule}^{-1}$ , the chromophores were lying flatly on the water subphase. It must be noted that the organization of the monolayer on the air–water interface was immensely influenced by small changes in the molecular structure. The azodye chromophores of YOPE in the present work are lying on the air–water interface and on the mica surface, at least, at the lower surface pressure, since the azodye in YOPE includes a hydrophilic OH group.

Heesemann<sup>7</sup> has reported that three components of stearic acid, stearylamine, and 12-(4'-nitro-4-dimethylaminoazobenzene-3'-carbonyloxy)stearic acid were completely miscible in the monolayer film. Azodyes are suggested to be loosely packed, due to their unfavorable geometry, in the L films. Then it is expected that the highly ordered monolayers of surface-active dyes are obtained, when the other molecules occupy the vacancy in L films of azodye, as was the case in Heesemann's system. However, the situation was different in our system. YOPE molecules were segregated from arachidic acids.

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