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Control of Chromophore Orientation in Langmuir-Blodgett Films: Molecular Mixing of Two Homologous Amphiphiles

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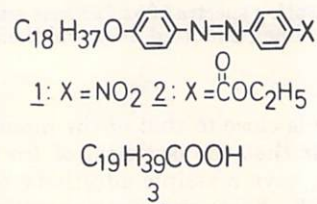
A novel technique to improve the orientational order of chromophores in Langmuir-Blodgett (LB) films utilizing molecular mixing of two homologous amphiphile was proposed. Two azobenzene-linked amphiphiles which possess the same chemical structure except for a hydrophilic head group formed a molecularly mixed monolayer at the air-water interface. The polar amphiphile with a nitro group as the head group oriented vertically through the molecular mixing with the nonpolar amphiphile. The orientation was preserved in an LB film consisting of the mixed monolayer.

We propose a novel technique to improve the orientational order of chromophores in Langmuir-Blodgett (LB) films utilizing the mixing capability of two amphiphiles which possess the same chemical structure except for hydrophilic head groups. A polar azobenzene-linked amphiphile formed the vertical chromophore orientation through molecular mixing with a homologous azobenzene-linked amphiphile with small polarity in the mixed monolayer. The orientation was preserved in an alternating LB film consisting of the mixed monolayer.

Several investigators have reported that specific aggregated structures, which can never appear in single-component LB films, could be realized in two-component LB films through the complete mixing of two amphiphiles with utterly different chemical structures.¹⁻³ The molecular origin of complete mixing of two components in the mixed monolayers has been ascribed to the sophisticated close packing of the component molecules. When one considers the control of orientation of polar molecules in LB films by the blending of a second component amphiphile, one anticipates that the simple close-packing principle may not operate on account of a molecular interaction, especially electric dipole-dipole repulsive interaction in this case. Then, we focused our attention not only on the geometrical packing but on the molecular interaction between component amphiphiles and found that the fabrication of the LB films with excellent orientational order by use of a variety of polar amphiphiles was possible, when we used an assisting second component which possessed small polarity but almost the same chemical constitution as the polar amphiphiles.

Two homologous azobenzene derivatives, 1 and 2, were employed.⁴ The polar amphiphile 1 possesses a strong electron-withdrawing nitro group as a hydrophilic head group. In its monolayer, polar molecules did not orient vertically to the monolayer plane, owing to strong repulsion between the polar molecules, even though it has a rodlike shape favorable for the formation of a card-pack structure called H-aggregation.⁵ The less polar amphiphile 2, which possesses the same chemical structure as 1 except for the hydrophilic head, gave a monolayer with a well-

defined H-aggregated structure. When the polar amphiphile was mixed into the monolayer of the less polar amphiphile, we expected that mixing of two components on the molecular level was attained, because the electric repulsion between the polar molecules was markedly decreased without losing the close-packing condition. Moreover, we expected that the orientation of the polar amphiphile may be forced to improve owing to the less polar component, which has a strong tendency of vertical orientation. In other words, the formation of a "mixed-crystal" structure with high orientational order would be realized.



Azobenzene derivative 1 was mixed with the homologous amphiphile 2 (molar ratio 1:2 = 1:1). For comparison, 1 was also mixed with a conventional fatty acid 3 (molar ratio 1:3 = 1:3). Surface pressure-area isotherms of the azobenzene amphiphiles were measured with a Wilhelmy-type film balance (Kyowa Kaimen Kagaku Co. HBM-AP) after the monolayers were spread on a sub-phase of pure water (18 MΩ, from a Millipore Milli-Q system) at 20 °C from the chloroform solutions. The absorption spectra at the air-water interface were measured by use of a multichannel detector (Tracor Norther TN-6133) after compression to a surface pressure of 15 mN m⁻¹.⁶ Light of a deuterium lamp was incident at a normal to the monolayers.

Figure 1 shows the surface pressure-area isotherms of the azobenzene amphiphiles. While a limiting area of monolayer 2, which was obtained by extrapolating the isotherms in a condensed region to a surface pressure of 0 mN m⁻¹, is 26 Å² molecule⁻¹, the polar amphiphile 1 has a very small limiting area (10 Å² molecule⁻¹). The results suggest that 1 formed not the two-dimensional monolayer but the three-dimensional crystal at the air-water interface as observed in a Langmuir film of a polar molecule, namely, a *p*-nitroaniline derivative.⁷ On the other hand, a limiting area of their mixed monolayer (28

(1) Kuhn, H. *Thin Solid Films* 1983, 99, 1.
(2) Buecher, H.; Kuhn, H. *Chem. Phys. Lett.* 1970, 6, 183.
(3) Xu, X.; Era, M.; Tsutsui, T.; Saito, S., to be published.
(4) 4-Nitro-4'-(octadecyloxy)azobenzene (1) and 4-(ethoxycarbonyl)-4'-(octadecyloxy)azobenzene (2) are prepared by the Williamson reaction. Anal. Calcd for C₃₀H₄₅N₃O₃ (1): C, 72.67; H, 9.17; N, 8.48. Anal. Calcd for C₃₃H₅₀N₂O₃ (2): C, 75.80; H, 9.66; N, 5.36. Found for 1: C, 72.50; H, 8.93; N, 8.41. Found for 2: C, 75.84; H, 9.68; N, 5.38.
(5) McRae, E.; Kasha, M. *Physical Processes in Radiation Biology*; Academic Press: New York, 1964; pp 23-45.

(6) Xu, X.; Era, M.; Tsutsui, T.; Saito, S. *Chem. Lett.* 1988, 773.
(7) Inoue, T.; Yase, K.; Okada, M.; Okada, S.; Matsuda, H.; Nakanishi, H.; Kato, M. *Jpn. J. Appl. Phys.* 1988, 27(9), 1635.

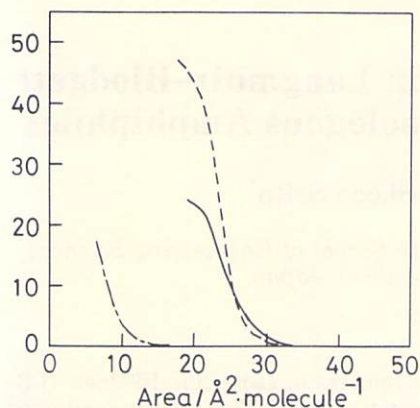


Figure 1. Surface pressure-area isotherms of azobenzene amphiphile 1 (dash-dotted line), 2 (broken line), and their mixture (solid line).

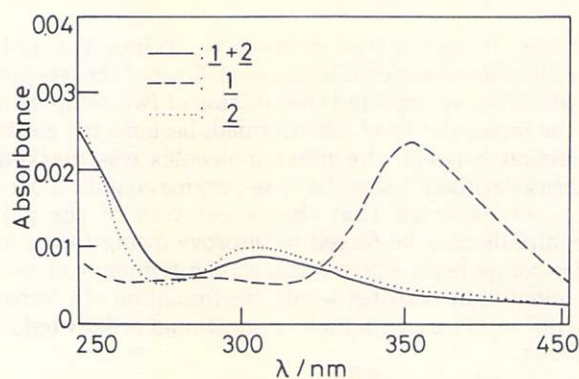


Figure 2. Absorption spectra of azobenzene amphiphile monolayers: 1 (broken line), 2 (dotted line), and their mixture (solid line).

$\text{\AA}^2 \text{ molecule}^{-1}$) is close to that of the monolayer 2. Further, it is clear that the isotherm of the mixed monolayer does not have a simple additivity relationship to those of 1 and 2. From the above-mentioned results, it should be assumed that the two-component molecules are miscible^{8,9} and that they formed a monolayer with an aggregation structure similar to that of the monolayer 2.

The absorption spectrum of the mixed monolayer (1 + 2) is depicted in Figure 2. The spectrum differs from that of the monolayer 1. While the absorption peak at 350 nm of the monolayer 1 disappeared in the spectrum, a new peak appeared at 305 nm, which is 65 nm shorter than that of 1 in hexane. Rather, the spectrum looks very similar to that of 2. Therefore, the spectra also demonstrate that complete solubilization of polar molecules 1 into 2 occurred and that both components take the same aggregation structure as that of monolayer 2. In other words, both amphiphiles oriented nearly normal to the film plane and formed the H-aggregation.

On the contrary, the mixed monolayer of 1 and 3 gave the same spectrum as the single monolayer 1. It is implied that the aggregation and orientation structures remained unchanged, when 1 was mixed with 3. They formed the mixture of domains composed of each single monolayer in the mixed monolayer.⁸ Figure 3 schematically shows the difference of complete mixing in the 1 + 2 system and incomplete mixing, domain formation, in the 1 + 3 system.

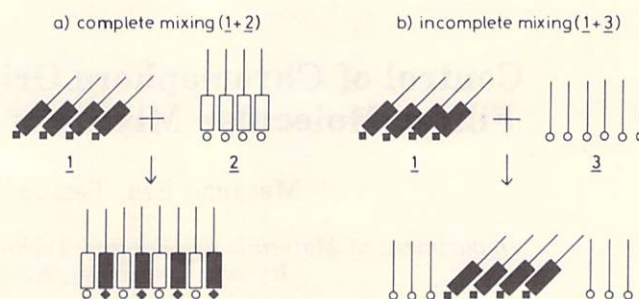


Figure 3. Schematic representation of the difference between complete mixing (1 + 2) and incomplete mixing (1 + 3).

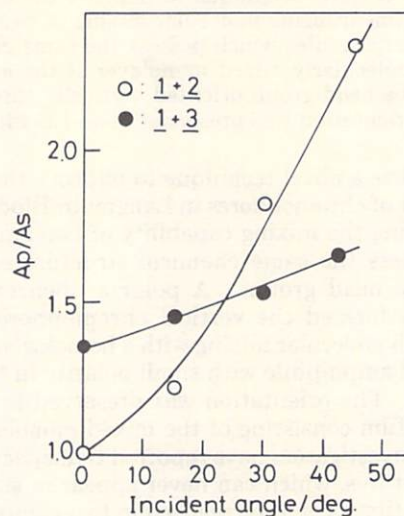


Figure 4. Incident angle dependences of the dichroic ratio A_p/A_s of the alternating multilayer films consisting of the mixed monolayers: 1 + 2, open circle; 1 + 3, solid circle.

We obtained the LB film of the mixed monolayer (1 + 2) when the mixed monolayer and a monolayer of cadmium arachidate were deposited alternately on quartz substrates. (Note: CdCl_2 aqueous solution (10^{-4} M) was used as subphase.) The spectrum of the alternating multilayer corresponded well with that obtained at the air-water interface. The aggregation structure at the air-water interface was preserved in the alternating multilayer film. Figure 4 is the incident angle dependence of the dichroic ratio A_p/A_s of the alternating multilayer film, where A_p and A_s are the absorbances of p- and s-polarized light, respectively. Large dependence in dichroic ratio on incident angle demonstrates large chromophore orientation normal to the film plane. On the other hand, the alternating multilayered film of a mixed monolayer of 1 + 3 shows a small incident angle dependence of the dichroic ratio. According to ref 10, an order parameter $(3 \cos^2 \theta - 1)/2$ of the multilayer film was calculated to be 0.74 from the dichroic ratio. This value is quantitative proof of predominantly vertical orientation of polar molecules in the 1 + 2 mixed multilayers.

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(8) Gaines, G. L., Jr.; Bellamy, W. D.; Tweet, A. G. *J. Chem. Phys.* 1964, 41, 538.

(9) Gaines, Jr. *J. Colloid Interface Sci.* 1966, 21, 315.

(10) Blinov, L. M.; Dubinin, N. V.; Romyantsev, V. G.; Yudin, S. G. *Opt. Spectrosc.* 1983, 55, 403.