

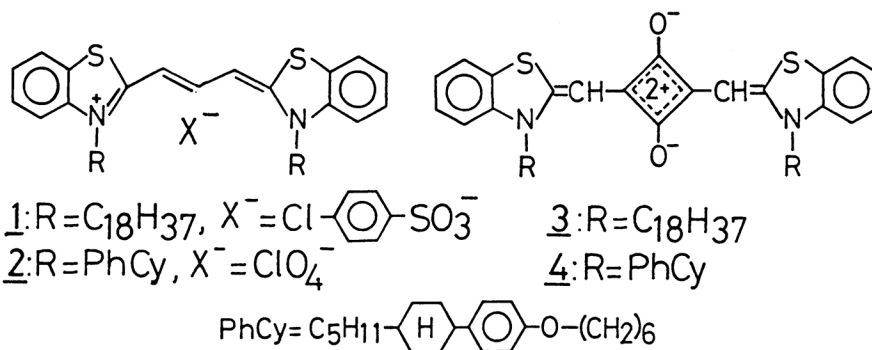
Effect of Hydrophobic Group on the Structure of Langmuir-Blodgett
Films of Amphiphilic Cyanine and Squarylium Dyes

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Phenylcyclohexyl group, a mesogenic unit, was introduced into the hydrophobic part of the amphiphilic cyanine and squarylium dyes. Surface pressure-area isotherms were explained in terms of the bulkiness and the stronger dispersion force of the mesogenic unit. In-plane anisotropy was observed for mixed LB films of the amphiphilic cyanine dye containing the mesogenic unit.

Langmuir-Blodgett (LB) technique has been applied for preparing organic thin films in which functional moieties are arranged in ordered states.^{1,2)} This technique includes two steps; (i) the formation of a stable monolayer film at the air-water interface, and (ii) the transfer of the film onto a solid substrate. A typical film-forming molecule consists of a hydrophilic part (functional moiety) and a hydrophobic part (long alkyl chain), and both hydrophilicity and hydrophobicity of the molecule play an important role in each step.³⁾ In this case, intermolecular interaction between the hydrophobic parts effective in forming the monolayer is the relatively weak dispersion force between the long alkyl chains. Therefore, the introduction of a mesogenic unit into the hydrophobic part is of special interest because of its anisotropic large polarizability corresponding to the strong dispersion force. Although there are already some works on the structure of monolayers or LB films of amphiphiles containing mesogenic units, they are concerned with the orientation of the mesogenic units.⁴⁻⁷⁾ More interesting is, however, that the introduction



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of a mesogenic unit into the hydrophobic part will open up the possibilities of controlling the orientation of the functional moiety by modifying the hydrophobic part.

This study describes the effect of introducing phenylcyclohexyl group into the hydrophobic part of amphiphilic dye molecules on the structures of monolayers at the air-water interface and LB films on solid substrates.

The amphiphilic cyanine dye molecules, 1 and 2, were synthesized according to Sondermann⁸⁾ with slight modifications. The amphiphilic squarylium dye 3 was synthesized as described previously⁹⁾ and 4 with slight modifications. Surface pressure-area (π -A) isotherms were measured at 290 K by using a Langmuir trough with a barrier speed of $1 \times 10^{-3} \text{ nm}^2(\text{molecule})^{-1} \text{ s}^{-1}$. Chloroform was used as a spreading solvent. Icosanoic acid is converted to its cadmium salt (5) and the counter anions of cyanine dyes (1 and 2) are replaced by Cl^- on the aqueous subphase containing $4 \times 10^{-4} \text{ mol dm}^{-3}$ of CdCl_2 and $5 \times 10^{-5} \text{ mol dm}^{-3}$ of KHCO_3 (pH=6.0). The deposition of the mixed monolayers of 1-4 with 5 was carried out as described previously¹⁰⁾ at 25 mN m^{-1} except that the dipping speed was $20 \text{ mm}(\text{min})^{-1}$ for mixed monolayers of 2 with 5.

Surface pressure-area isotherms of 1-4 are shown in Fig. 1. Two striking features caused by the introduction of phenylcyclohexyl group are presented in this figure. First, the limiting areas per molecule which are obtained by extrapolating the linear portions in relatively high pressure regions increase. The limiting areas of 1 and 3 are 0.57 and 0.58 nm^2 , respectively, while those of 2 and 4 are 0.68 and 0.72 nm^2 , respectively. The limiting areas of 1 and 3 are governed by the hydrophilic part since the cross-sectional area per normal hydrocarbon chain is 0.20 nm^2 . This suggests that the limiting areas of

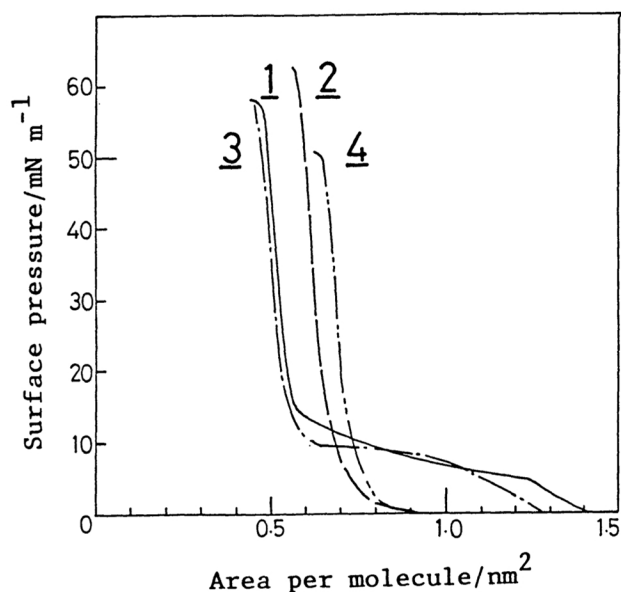


Fig. 1. Surface pressure-area isotherms of 1-4 at 290 K.

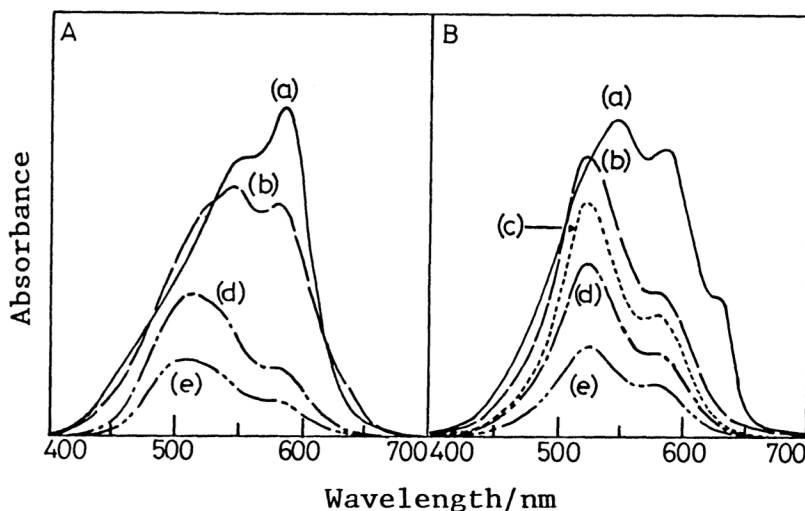


Fig. 2. Absorption spectra of mixed LB films of (A): 1 with 5, and (B): 2 with 5. The molar mixing ratios r are, (a): 3/1, (b): 1/1, (c): 1/3, (d): 1/5, and (e): 1/10.

2 and 4 are governed by the hydrophobic part which is bulkier than the normal hydrocarbon chain, although there is also a possibility that the change in the orientation of the chromophore gives rise to an increase in the limiting area. Secondly, the expanded phases observed for 1 and 3 at low pressures are not to be seen for 2 and 4. This is qualitatively explained by the stronger dispersion force between the mesogenic units which leads to a larger number of molecules present in one cluster at the air-water interface. This will reduce the value of q of the state equation at low pressures, $\pi(A-A_0)=qRT$, where A_0 is an excluded area and the other symbols represent their usual meanings.³⁾ Consequently, π - A isotherms will rise at the areas near to A_0 's.

The transfer of a monolayer of a pure dye was unsuccessful except 3. Therefore, 5 was used as a matrix. The mixed monolayers of 1 with 5 with a molar mixing ratio $r=1/3$ was, however, not transferred onto a solid substrate under the present conditions. Figure 2 shows the absorption spectra of mixed LB films of 1 and 2 with 5. The state of chromophore of 1 and even the deposition manner strongly depend upon r except in the region $r \leq 1/5$. On the contrary, the absorption spectra of mixed LB films of 2 with 5 are almost the same in shape when $r \leq 1/1$. This is also due to the stronger dispersion force between the molecules of 2 leading to the less miscibility of 2 with 5 than that of 1 with 5. This decrease in miscibility is also observed for mixed LB films of 4 with 5 compared to those of 3 with 5. The absorption spectra of chloroform solutions of 1 and 2 show a sharp peak at ca. 570 nm. Therefore, the 520-nm peak for $r \leq 1/1$ is attributed to H-like aggregate because the flow orientation described later will not occur if this peak is due to a small aggregate such as an isolated dimer.

In-plane spectral anisotropy is observed for mixed LB films of 2 with 5 in contrast to the case of mixed LB films of 1 with 5 in which there is no in-plane anisotropy to be seen. Typical polarized spectra are shown in

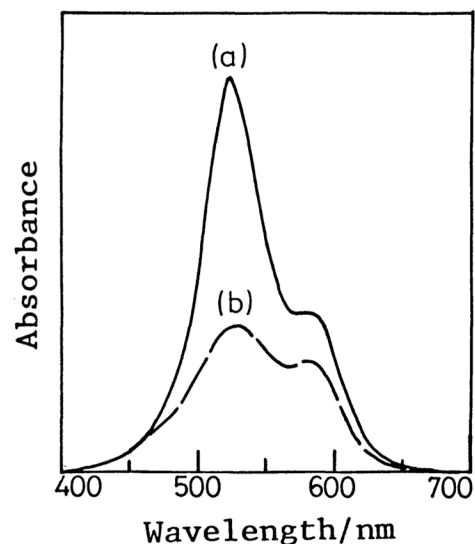


Fig. 3. Polarized absorption spectra of mixed LB films of 2 with 5 ($r=1/3$). The electric fields of polarized light are parallel (a) and perpendicular (b) to the dipping direction.

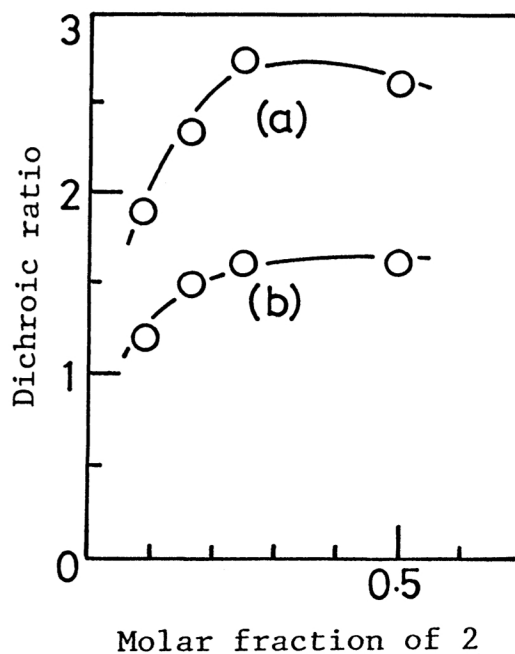


Fig. 4. Dichroic ratio as a function of molar fraction of 2. (a): 520-nm peak, (b): 580-nm peak.

Fig. 3 for $r=1/3$. It is noted that the transition dipole moment of the chromophore tends to be lined up along the dipping direction. This tendency is more prominent for the 520-nm peak than for the 580-nm peak. The dichroic ratio obtained from the peak heights is plotted against molar fraction of 2 in Fig. 4. The values for the 580-nm peak are near to unity and the observed in-plane anisotropy may be due to the overlapping of the 520-nm peak.

This in-plane anisotropy is not due to in-plane anisotropic arrangement of molecules at the air-water interface but to the flow orientation during the deposition process.¹¹⁾ This is verified by the following experiments. The trough used was a rectangular one with a barrier moving from one end to the other. If the molecules are already arranged anisotropically at the air-water interface before transferring to a solid substrate, the dichroic ratio should be different depending upon whether the solid substrate is parallel or perpendicular to the moving direction of the barrier. The dichroic ratios are, however, the same irrespective of the direction of the solid substrate. Therefore, at least the chromophore of 2 responsible for the 520-nm peak exists at the air-water interface as a low-dimensional crystallite elongated along one of the crystallite axes,¹¹⁾ which is realized by the stronger dispersion force. In this case, the orientation of the crystallite of the molecule 2 is governed by the velocity gradient and the Brownian motion upon the water surface during the deposition process. The detailed discussion on the dichroic behavior is now in progress.

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