August, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *2737—2742 (1987)* 2737

# Structure Study of Supermonomolecular Layers in Langmuir-Blodgett Films. Surface Active Squarylium Dye-Fatty Acid Binary Mixed System

Mutsuyoshi MATSUMOTO,* Takayoshi NAKAMURA, Motoo TANAKA, Tatsuo SEKIGUCHI,
Hideo KOMIZU, Sanae Y. MATSUZAKI, Eiichiro MANDA, Yasujiro KAWABATA,
Mitsuyoshi SAITO,† Sigeru IIZIMA,† and Michio SUGI†
National Chemical Laboratory for Industry, Yatabe, Ibaraki 305
†Electrotechnical Laboratory, Sakura-mura, Ibaraki 305
(Received December 25, 1986)

The structures of the Langmuir-Blodgett (LB) films of the ordinary mixed monolayer (LPF) and the supermonomolecular layer (HPF) of a surface active squarylium dye-icosanoic acid binary mixed system were examined by absorption spectroscopy. The absorption spectra of one unit layer of LPF with a molar mixing ratio ranging from 1/10 to 1/1 were almost the same, strongly suggesting that each component exists separately in the films. The LB films of two unit layers of LPF showed two peaks at 590 and 560 nm ascribed to intralayer and interlayer aggregates, respectively, besides the monomeric peak at 640 nm. The absorption spectra of one unit layer of HPF indicated a critical value of the mixing ratio 1/3.5 above which the 700-nm peak is observed. This peak is an indication of a multilayer consisting of pure **1** due to the interlayer interaction. The 560-nm peak observed for LPF is caused by a hindered interlayer interaction of the chromophores between the mixed monolayers.

Recently, the vacuum-deposited films of squarylium dyes have been investigated from the viewpoint of photovoltaic properties, whose quantum yields are high and depend not only upon the structure of the chromophore itself but also upon the packing of molecules involving intermolecular interaction and aggregate formation.[1-4] Two polymorphs are observed for a squarylium dye.[5,6] A change in the crystal form is considered to be the reason for the quick deterioration of the high solar energy conversion efficiency.[1] It is therefore important to develop a technique to obtain the desired aggregate structure.

In order to construct a system with the desired structure, i.e., suitable arrangement of molecules and aggregate formation, the Langmuir-Blodgett (LB) technique is one of the most powerful tools.[7] This technique contains a process in which a condensed phase at the air-water interface is deposited onto a substrate. Consequently, it is quite important to obtain a condensed phase with the desired structure. The desired structure is not necessarily limited to the typical condensed monolayer. In a previous paper,[8] we pointed out the technical importance of the supermonomolecular layer defined as an ordered multilayer at the gas-liquid interface.

Indeed, many studies have been categorized as concerning the supermonomolecular layer. For instance, the formation of ordered multilayers of some polypeptides at the air-water interface was observed when compressed under appropriate surface pressures.[9-11] As for 1-octadecanol, octadecanoic acid, and substituted phthalocyanine, the use of different spreading solvents leads to various structures of the condensed phases at an air-water interface.[12-15] A stable multilayer is obtained when a class of water-soluble azobenzene amphiphiles form complexes with polyanion.[16] Even more interesting are the cases where surface active azo dyes were squeezed out of the fatty acid matrices.[17,18] Selective squeezing-out of dye molecules from the mixed layer was, however, estimated mainly from *F-A* isotherms and molecular models, and the structure of the subsequent supermonomolecular layer has not yet been fully understood.

We have found, for surface active squarylium dye-fatty acid binary mixed system, that an ordinary mixed monolayer is formed under lower surface pressures (ca. 25 $mN\,m^{-1}$), and that higher surface pressures (ca. 40 $mN\,m^{-1}$) result in the supermonomolecular structure.[8,19] The structure of the supermonomolecular layer with the mixing ratio of 1/5 is characterized as a bilayer stack of a cadmium icosanoate monolayer and monolayer islands of the dye molecules squeezed out under the icosanoate monolayer. The dye molecules exist in such a manner that they are attached to the icosanoate matrix with their hydrophobic carbon chains and that the long axis of the chromophore is parallel to the film surface.

In this report, LB films with various mixing ratios were examined by absorption spectroscopy in order to clarify the supermonomolecular structure.

## Experimental

The surface active squarylium dye, 2,4-bis[3,3-dimethyl-1-octadecyl-2(3*H*)-indolylidenemethyl]-1,3-cyclobutadienediylium-1,3-diolate, (**1**) was synthesized as previously described.[20] Icosanoic acid was purchased from Eastman Kodak Co. and used without further purification. Experimental conditions where LB films were prepared were the same as those in the previous reports.[8,19] Icosanoic acid was converted to cadmium icosanoate (**2**) upon the subphase containing $4.0\times10^{-4}$ $mol\,dm^{-3}$ of $CdCl_2$ and $5.0\times10^{-5}$ $mol\,dm^{-3}$ of $KHCO_3$. Mixed LB films deposited at 25 $mN\,m^{-1}$ and at 40 $mN\,m^{-1}$ are hereafter referred to as LPF and HPF, respectively. The molar mixing ratio *r* of mixed LB films of **1** and **2** was in the range of 1/10 to 1/1. Absorption spectra of the deposited films were taken by differential spectroscopy, using the method of Kuhn et al.[21] Polarized absorption spectra were measured under four conditions described previously;[22] an incident angle of 45 or 90° to the film surface, and the electric field of the incident light parallel or normal to the dipping direction. The polarized spectra showed that all the transition moments discussed below were alomst parallel to the film surface. Absorption spectra of the solutions were measured by use of the Cary 17 DX spectrometer.

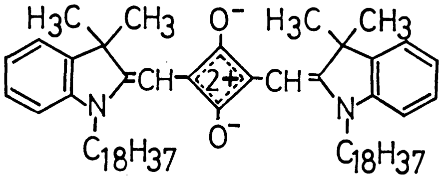
## Results and Discussion

**Two Condensed Phases at Air-Water Interface.** Figure 1 shows *F-A* isotherms of **1** (curve g), **2** (curve a), and mixed layers of **1** and **2** with the mixing ratio $r$ ranging from 1/10 to 1/1 (curves b—f). A common feature is observed for mixed layers: the first condensed phase at ca. 20—30 mN m$^{-1}$, the plateau region at ca. 30 mN m$^{-1}$, the second condensed phase at ca. 30—60 mN m$^{-1}$, and finally the collapse point at ca. 60 mN m$^{-1}$. The observed plateau region can be attributed to a transition from a monolayer in the first condensed phase to a multilayer in the second condensed phase.[9]

The mean area per molecule, $s$, is expressed as

$$s=(rs_1+s_2)/(r+1), \tag{1}$$

where $s_1$ and $s_2$ are the areas per molecule of **1** and **2**, respectively. On the plausible assumption of $s_2$ as 0.020 nm$^2$, even in the mixed layers,[8,19] the values of $s_1$ obtained were independent of the mixing ratio: 0.70 and nearly 0 nm$^2$ at 25 and 40 mN m$^{-1}$, respectively.



**1**

The former value is consistent with the molecular model when the chromophore is oriented with the long axis parallel and the short axis perpendicular to the surface. This fact indicates that an ordinary mixed monolayer is formed in the first condensed phase. In other words, the occupied area is governed by both **1** and **2**.

On the other hand, the value of $s_1$ (0 nm$^2$) under higher surface pressures indicates that the occupied area is governed by **2** alone. This strongly suggests the presence of a monolayer of **2**, which is supported by the same collapse pressure of the mixed layers with that of the monolayer of **2** (curve a). Absorption spectra of HPF with $r=1/5$ gave the model for the supermonomolecular structure.[19] This model for the squeezing-out is supported by the fact that the *F-A* isotherm of pure **1** (curve g) also shows a plateau region at ca. 30 mN m$^{-1}$ which is almost identical with that for the onset of the plateau region for the mixed layers. The large plateau region for pure **1** (curve g) suggests that the molecules **1** tend to form a multilayer at air-water interface without any detectable rise in surface pressure.

The area occupied by HPF is $ns_2'$ where $n$ is the number of the molecule **2** in the mixed films and $s_2'$ is the area per molecule of **2** at 25 mN m$^{-1}$ (0.20 nm$^2$). If the squeezed-out molecules of **1** in the above film form a monolayer under the monolayer of **2**, the area occupied by **1** will be $nrs_1'$ where $s_1'$ is the area per molecule of **1** at 25 mN m$^{-1}$ (0.70 nm$^2$). The fact that the area is governed by $ns_2'$ suggests that the layer of the squeezed-out molecules of **1** becomes a multilayer when $nrs_1'>ns_2'$ ($r>s_2'/s_1'=1/3.5$).

**Four Types of LB Films.** In order to examine the supermonomolecular structure more precisely, four types of mixed LB films were prepared for each mixing ratio. Figure 2 shows a schematic view of one or two unit layers of LPF in the first condensed phase or HPF

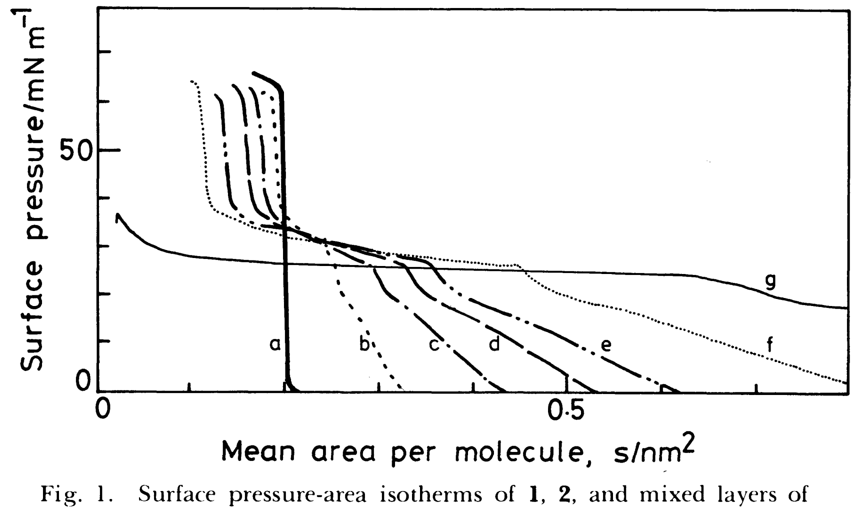


Fig. 1. Surface pressure-area isotherms of **1**, **2**, and mixed layers of **1** and **2**. a: $r=0$ (pure **2**), b: $r=1/10$, c: $r=1/5$, d: $r=1/3$, e: $r=1/2$, f: $r=1/1$, g: pure **1**. The data of a—f were reproduced from Ref. 19 by permission of Elsevier Sequoia, Lausanne.

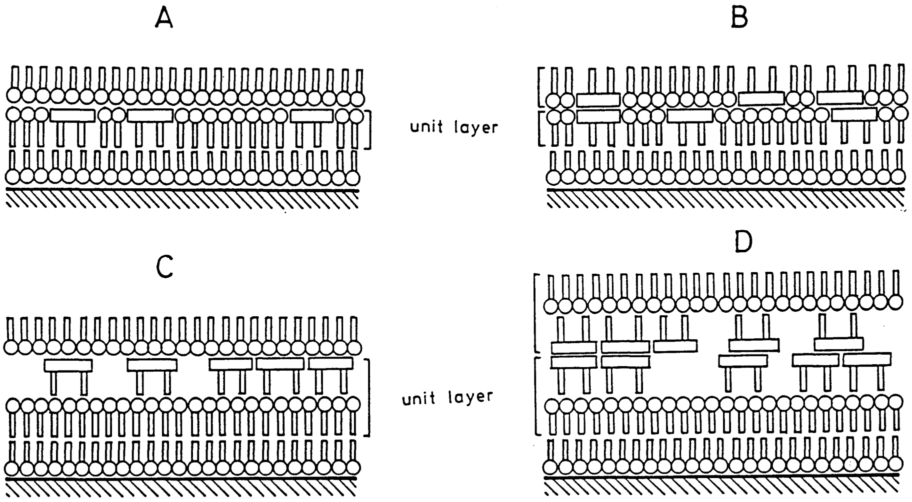


Fig. 2. Schematic view of the LB films of LPF and HPF with the mixing ratio of 1/5 deposited on a glass slide precoated with five monolayers of **2**. Only one monolayer of **2** is drawn in each case for simplicity. A: One unit layer of LPF followed by deposition of one monolayer of **2**, B: two unit layers of LPF, C: one unit layer of HPF followed by deposition of one monolayer of **2**, D: two unit layers of HPF.

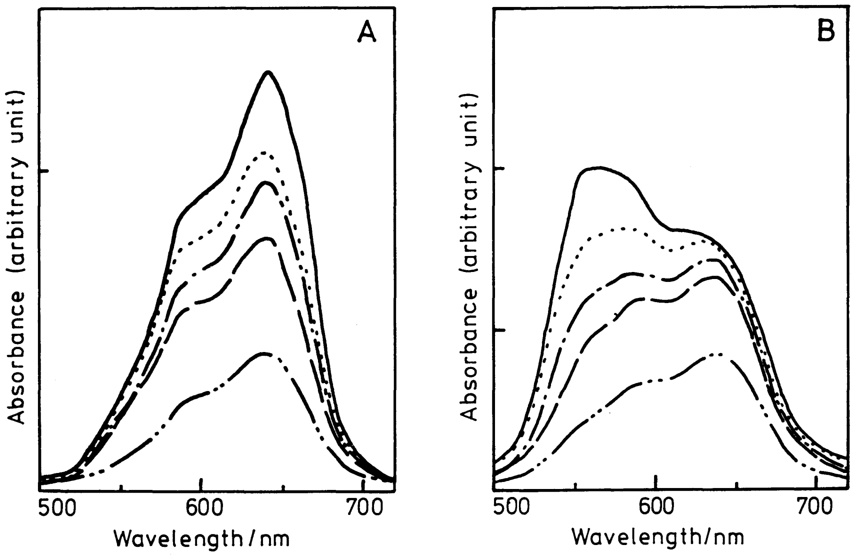


Fig. 3. Absorption spectra of one unit layer (A) and two unit layers (B) of LPF with various mixing ratios.
——: $r$=1/1, ······: $r$=1/2, —·—·—: $r$=1/3, ----: $r$=1/5, —··—··—: $r$=1/10.

in the second condensed phase with the mixing ratio of 1/5 deposited on a glass slide precoated with five monolayers of **2**. Only one monolayer of **2** is drawn in each case in Fig. 2 for simplicity.

In case A, where one unit layer of LPF is deposited on a substrate followed by deposition of one monolayer of **2**, the formation of chromophore aggregates is restricted within the same plane. Therefore, isolated molecules and intralayer aggregates with their characteristic spectra may be detected. In the case B, where two unit layers of LPF are deposited, there is a possibility of interlayer chromophore aggregation. Consequently, interlayer aggregates may be observed in addition to isolated molecules and intralayer aggregates. As is seen in this figure, LPF is an ordinary mixed monolayer whose occupied area is governed by both **1** and **2**.

In the cases C and D where one and two unit layers of HPF are deposited, respectively, the structures are quite different from those in the above two. HPF consists of dye and cadmium icosanoate segregated from each other into different layers. This gives rise to aggregates different from those in the cases A and B. The occupied area of HPF is, as is seen, governed by **2** alone.

**One Unit Layer of LPF (Case A).** Figure 3A shows the absorption spectra of one unit layer of LPF. Almost the same spectral patterns were observed for

LPF with $r$ ranging from 1/10 to 1/1. This fact strongly suggests that the molecules **1** are immiscible with the molecules **2** and that each component exists separately in the form of domains.

Each peak value of absorbance,$I$, was proportional to the area fraction of **1** in the film plane (Fig. 4). This is expressed by

$$I=I_0rs_1'/(rs_1'+s_2'), \quad (2)$$

where $I_0$ is the limiting value of $I$ when the area fraction approaches unity. This proportional relationship indicates that **1** was not dissolved into the subphase and supports the structure of the ordinary mixed monolayer.

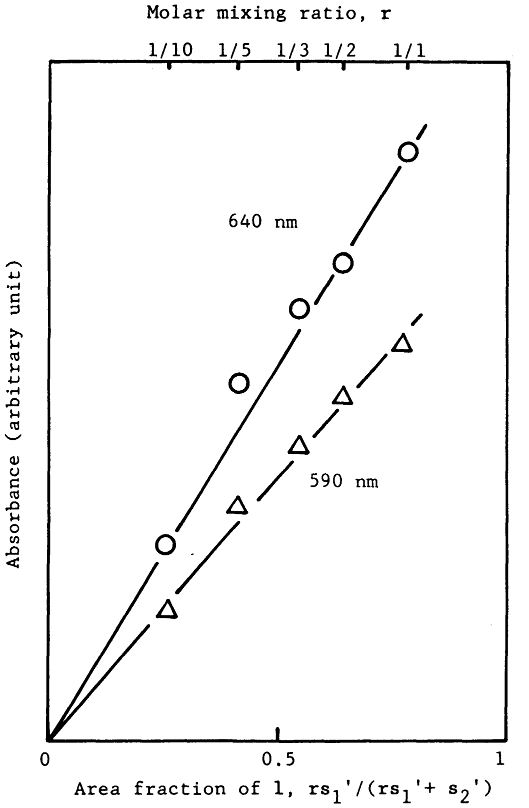


Fig. 4. Absorbance of one unit layer of LPF at each peak position as a function of area fraction of **1**. The molar mixing ratio is also shown.
○: 640 nm, △: 590 nm.

The absorption spectra of **1** in $CHCl_3$ solution ranging in concentration from $4.5\times10^{-8}$ to $1.0\times10^{-3}$ mol dm$^{-3}$ show a main peak at ca. 640 nm (The full width at half maximum is ca. 20 nm.) and a shoulder at ca. 590 nm. The 640-nm peak and the 590-nm peak as well are attributed to isolated molecules. The absorbance ratio of the latter to the former is ca. 0.2 irrespective of concentration. This indicates that these two peaks are a vibronic progression.[23,24]

In contrast to the case of chloroform solutions, the 590-nm peak observed for LB films will be ascribed to an aggregate by the following reasons, although we cannot deny the contribution from the vibronic state. Firstly, the 590-nm peak is also observed even when the monomeric peak at 640 nm is hardly found (shown later in Fig. 5B). Secondly. the absorbance ratio of the 590-nm peak to the 640-nm peak is ca. 0.7, which is much larger than the value observed in solution. Therefore, we assume that the 590-nm peak mainly originates from the side-by-side structure of the aggregate[25] formed through intralayer interaction, since the origin of the 590-nm peak does not change the context significantly.

Studies with polarized light indicated that the transition moments for both 590-nm and 640-nm peaks lie statistically in the layer plane.

**Two Unit Layers of LPF (Case B).** The absorption spectra of two unit layers of LPF are depicted in Fig.

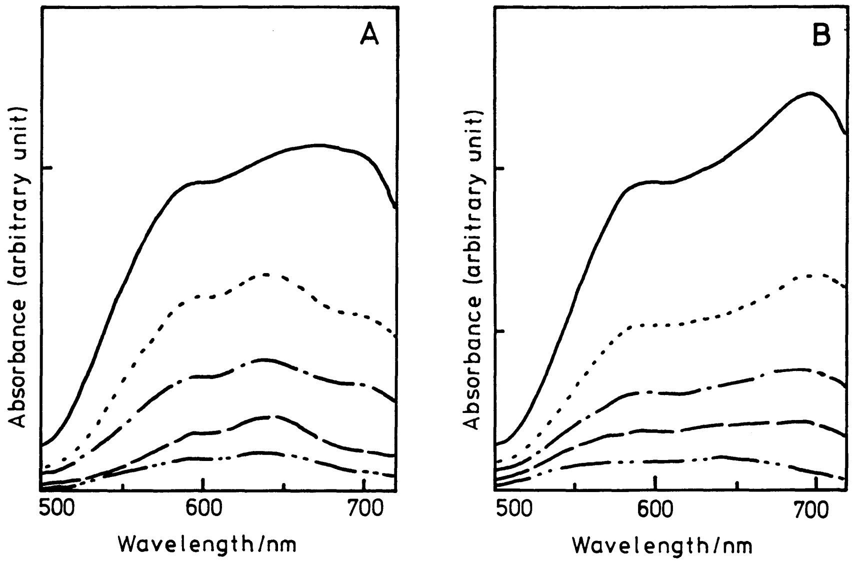


Fig. 5. Absorption spectra of one unit layer (A) and two unit layers (B) of HPF with various mixing ratios.
——: $r$=1/1, ······: $r$=1/2, –·–·–: $r$=1/3, – – – –: $r$=1/5, –··–··–: $r$=1/10.

3B. In this case, both intralayer and interlayer aggregates have the possibility of being formed. Actually, evidence for an interlayer aggregate is clearly shown in the spectra. The 560-nm peak becomes prominent with an increase in the $r$ value, which is presumably caused by the increasing occurrence of the interlayer interaction between two chromophores located in adjacent unit layers. Therefore, this peak is ascribed to the side-by-side structure of the aggregate through interlayer interaction.[26)]

Polarized spectra indicated that the transition moments for the 590-nm and the 640-nm peaks lie statistically in the film plane, whereas that of the interlayer aggregate prefers the arrangement parallel to the dipping direction (absorbance ratio of 1.2—1.3). This suggests that the chromophores are slightly rearranged during or after the deposition process when the interlayer interaction of the chromophores occurs.

**One Unit Layer of HPF (Case C).** Figure 5A shows the absorption spectra of one unit layer of HPF. In the case of $r > s_2'/s_1' = 1/3.5$, the excessive **1** should be squeezed out of the monolayer of **1** to form a complicated multilayer, since otherwise the area must be governed by $nrs_1'$. This structural change with $r$ value is schematically shown in Fig. 6.

This change is clearly detected in the absorption spectra, which is strong evidence for the validity of the supermonomolecular structure. With an increase in the $r$ value, the monomeric peak at 640 nm is relatively suppressed and the 700-nm peak emerges instead of the 560-nm peak observed for LPF. The 700-nm peak is observed only when $r$ is higher than the critical value of 1/3.5. This peak is an indication of a multilayer consisting of pure **1**. The 700-nm peak indicates the aggregate involving end-to-end interaction[25)] or J-aggregate[27)] induced by interlayer interaction within the multilayer region consisting of pure **1**.

Studies with polarized light showed that the transition moment of the above aggregate also has the tendency to be oriented parallel to the dipping direction (absorbance ratio of 1.3—1.4). This again suggests a slight rearrangement of the chromophores during or after the deposition process. The transition moments for the other peaks lie statistically in the film plane.

**Two Unit Layers of HPF (Case D).** The absorption spectra of two unit layers of HPF are shown in Fig. 5B. The feature of the similar spectral patterns for samples with $r$ ranging from 1/5 to 1/1 should be noted. Two peaks are observed at 590 and 700 nm, whereas the monomeric peak at 640 nm and the 560-nm peak are hardly to be seen.

The supermonomolecular structure is supported by the absorbances at peak positions for samples with $r$ ranging from 1/5 to 1/1. If the structures shown in Fig. 6 are valid, the absorbances should be proportional to the number of the molecule **1** per unit area because the spectral patterns are similar for these samples. The number of the molecule **1** per unit area is $nr/ns_2'$. Therefore, the absorbances $I'$ should obey the following equation:

$$I' = rI_0', \qquad (3)$$

where $I_0'$ is the absorbance when $r$ equals unity. This relationship is clearly seen in Fig. 7. This figure includes the points for the sample with $r=1/10$. It is noted that the point for the 700-nm peak is signifi-

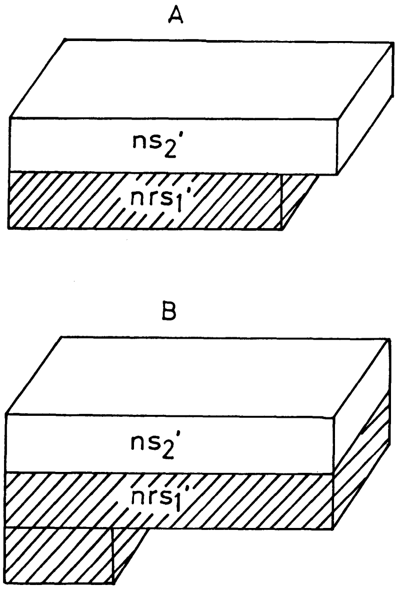


Fig. 6. Schematic view of the structural change of one unit layer of HPF with $r$ value. The portions with and without hatches represent the layers composed of pure dye **1** and pure **2**, respectively. A: $nrs_{1'} \leqq ns_{2'}$ ($r \leqq 0.20/0.70$), B: $nrs_{1'} > ns_{2'}$ ($r > 0.20/0.70$). When $r$ is small, the supermonomolecular structure is a bilayer as shown in A, while the excessive **1** and the bilayer should form a complicated multilayer in the case of $r > 1/3.5$.

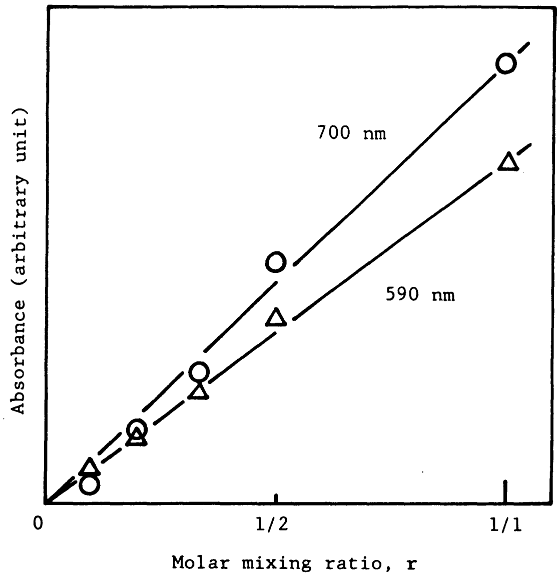


Fig. 7. Absorbance of two unit layers of HPF at each peak position as a function of the mixing ratio $r$. ○: 700 nm, △: 590 nm.

cantly deviated under the straight line. Equation 3 also indicates that **1** was not dissolved into the subphase even when compressed under higher surface pressures.

The two observed peaks are attributed to two different aggregates, as opposed to the single herringbone structure whose unit cell contains two chromophores and which possesses two allowed transitions.[24,28] This is concluded by the fact that the 590-nm peak is also observed for the case of intralayer interaction in LPF, while the 700-nm peak is found only when the multilayer consisting of pure **1** is formed. Furthermore, the transition moment for the 590-nm peak lies statistically in the film plane, while that for the 700-nm peak has a preference of being oriented to the dipping direction (absorbance ratio of 1.3—1.4). This is quite contradictory to a herringbone structure, where two allowed transitions are governed by one and the same distribution of the aggregate. In other words, if a random distribution in a plane is the case with one transition moment, this applies also to the other.

The relationship of Eq. 3 suggests that the relative ratio of occurrence of the two aggregates remains invariant for HPF with higher mixing ratios (1/5—1/1), i.e., the equilibrium between the two aggregates is held in the multilayer region consisting of pure **1**. As for HPF with $r=1/10$, the 700-nm peak is almost extinguished and the broad band covering from 550 to 650 nm remains. This suggests that the 700-nm peak is attributable to a larger aggregate than the 590-nm peak since HPF with $r=/10$ would have a considerable fraction of area which is not occupied by **1** in the mutilayer region of pure **1**.

The aggregates in HPF containing multilayers of pure **1** (case C with $r\geqq 1/3$ and case D with $r\geqq 1/5$) are not the same as those in LPF consisting of multilayers diluted by **2** (case B with all values of $r$ studied). This is reflected in the fact that the 700-nm peak emerges only for the former films and that the 560-nm peak is observed only for the latter films. The chromophores of the dyes are subjected to interlayer interaction for both cases. In contrast to the former films, however, this is more or less hindered by the molecules **2** for the latter films.

In conclusion, the desired aggregates can be obtained by the control of mixing ratio and surface pressure, which is useful in constructing molecular organizates. The method employed in this work will serve as means for clarifying other supermonomolecular structures involving interlayer interaction between chromophores.

We would like to thank Professor Kiyoshige Fukuda and Dr. Hiroo Nakahara of Saitama University for helpful comments. We also acknowledge Dr. Shinichi Kuroda, Dr. Keiichi Ikegami, and Dr. Koichi Honda for stimulating discussions.

## References

1) P. Yamln, A. P. Piechowski, G. R. Bird, and D. L. Morel, *J. Phys. Chem.*, **86**, 3796 (1982).

2) R. O. Loufty, C. K. Hsiao, and P. M. Kazmaier, *Photogr. Sci. Eng.*, **27**, 5 (1983).

3) D. L. Morel, E. L. Stogryn, A. K. Ghosh, T. Feng, P. E. Purwin, R. F. Shaw, C. Fishman, G. R. Bird, and A. P. Piechowski, *J. Phys. Chem.*, **88**, 923 (1984).

4) A. P. Piechowski, G. R. Bird, D. L. Morel, and E. L. Stogryn. *J. Phys. Chem.*, **88**. 934 (1984).

5) M. Tristani-Kendra, C. J. Eckhardt, J. Bernstein, and E. Goldstein, *Chem. Phys. Lett.*, **98**, 57 (1983).

6) M. Tristani-Kendra and C. J. Eckhardt, *J. Chem. Phys.*, **81**, 1160 (1984).

7) For example, D. Möbius, *Acc. Chem. Res.*, **14**, 63 (1981), and references therein.

8) Y. Kawabata, T. Sekiguchi, M. Tanaka, T. Nakamura, H. Komizu, K. Honda, E. Manda, M. Saito, M. Sugi, and S. Iizima, *J. Am. Chem. Soc.*, **107**, 5270 (1985).

9) T. Takenaka, K. Harada, and M. Matsumoto, *J. Colloid Interface Sci.*, **73**, 569 (1980).

10) F. Takeda, M. Matsumoto, T. Takenaka, and Y. Fujiyoshi, *J. Colloid Interface Sci.*, **84**, 220 (1981).

11) F. Takeda, M. Matsumoto, T. Takenaka, Y. Fujiyoshi, and N. Uyeda, *J. Colloid Interface Sci.*, **91**, 267 (1983).

12) H. E. Ries Jr., *Nature (London), Phys. Sci.*, **243**, 14 (1973).

13) S. Baker, M. C. Petty, G. G. Roberts, and M. V. Twigg, *Thin Solid Films*, **99**, 53 (1983).

14) G. J. Kovacs, P. S. Vincett, and J. H. Sharp, *Can. J. Phys.*, **63**, 346 (1985).

15) J. R. Fryer, R. A. Hann, and B. L. Eyres, *Nature*, **313**, 382 (1985).

16) M. Shimomura and T. Kunitake, *Thin Solid Films*, **132**, 243 (1985).

17) E. E. Polymeropoulos, D. Möbius, and H. Kuhn, *J. Chem. Phys.*, **68**, 3918 (1978).

18) J. Heeseman, *J. Am. Chem. Soc.*, **102**, 2176 (1980).

19) Y. Kawabata, T. Sekiguchi, M. Tanaka, T. Nakamura, H. Komizu, M. Matsumoto, and E. Manda, *Thin Solid Films*, **133**, 175 (1985).

20) M. Tanaka, T. Sekiguchi, Y. Kawabata, T. Nakamura, and E. Manda, *Nippon Kagaku Kaishi*, **1985**, 1516.

21) H. Kuhn, D. Möbius, and H. Bücher, "Physical Methods of Chemistry," ed by A. Weisserberger and B. W. Rossiter, John Wiley & Sons, Inc., New York (1972), Vol. 1 Part IIIB, p. 577.

22) T. Fukui, M. Saito, M. Sugi, and S. Iizima, *Thin Solid Films*, **109**, 247 (1983).

23) W. West, S. P. Lovell, and W. Cooper, *Photogr. Sci. Eng.*, **14**, 52, (1970).

24) G. R. Bird, G. Debuch, and D. Möbius, *J. Phys. Chem.*, **81**, 2657 (1977).

25) For example, J. N. Murrel, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley & Sons,

26) R. Steiger, R. Kitzing, and P. Junod, *J. Photogr. Sci.*, **21**, 107 (1973).

27) For example, H. Bücher and H. Kuhn, *Chem. Phys. Lett.*, **6**, 183 (1970).

28) C. Reich, *Photogr. Sci. Eng.*, **18**, 335 (1974).