

REGULATION OF THE AGGREGATED STRUCTURE OF CYANINE DYES IN  
LANGMUIR-BLODGETT FILMS USING BILAYER-FORMING AMPHIPHILES

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Aqueous cyanine dyes were adsorbed onto the monolayer of dialkylammonium amphiphiles at the air-water interface. The composite monolayer was successfully transferred on a glass substrate by the conventional Langmuir-Blodgett method, and the adsorbed cyanine dyes were shown to assume J-like aggregation.

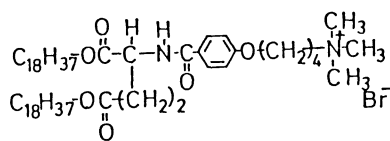
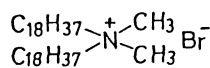
Regulation of the chromophore orientation in Langmuir-Blodgett (LB) films would be indispensable for their applications to electronic or optical purposes. The orientation and aggregated structure of dyes in LB films and their electric properties have been studied.<sup>1-4)</sup> In this letter, we show a new way of regulation of the aggregation of cyanine dyes in LB films using bilayer-forming materials.

Dialkylammonium amphiphiles form bilayer structures (vesicles and lamellae), when they are dispersed in water.<sup>5)</sup> Cyanine dyes are bound to the surfaces of the dispersed bilayers and can form J-like aggregates.<sup>6)</sup> This is also true in the corresponding cast bilayer films.<sup>7)</sup> Therefore, we expected that the J-like aggregation would also occur on the monolayer of dialkylammonium amphiphiles at the air-water interface.

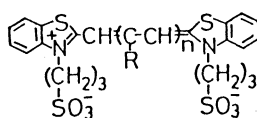
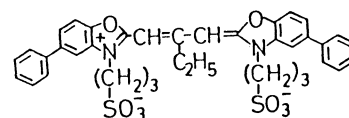
Dialkylammonium amphiphile (1)<sup>8)</sup> was used as a supporting material which forms a monolayer at the air-water interface and adsorbs dyes. Another amphiphile (2) was also used for comparative experiments. Five anionic cyanine dyes (3-7) purchased from Nippon Kanko Shikiso Co. were employed. Dialkylammonium amphiphile 1 in chloroform ( $4.1 \times 10^{-4}$  M) was spread at 20 °C on distilled water, or on aqueous cyanine dye 3 ( $3.5 \times 10^{-7}$  M), and surface pressure-area isotherms were measured with a Wilhelmy-type film balance (Kyowa Kagaku Co. HBM-AP).

Figure 1 shows the surface pressure-area isotherms for dialkylammonium amphiphile 1 monolayers. The monolayers formed condensed films at surface pressures larger than  $20 \text{ mN m}^{-1}$  on both distilled water and the cyanine dye 3 solution. The limiting area, determined by extrapolation of the isotherm of the condensed phases to zero pressure, did not depend on the presence or absence of dye 3 in the subphase, giving a value of  $70 \text{ Å}^2 \cdot \text{molecule}^{-1}$ . This observation indicates that the structure of the monolayer is not distorted by the adsorbed cyanine dye. In other words, the dye molecules are not incorporated into the monolayer but adsorbed on the monolayer surface.

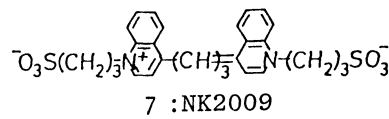
## Dialkylammonium amphiphiles

12

## Cyanine dyes

n=1 R=CH<sub>3</sub>4 : NK2039  
n=1 R=H5 : NK2011  
n=2 R=H

6 : NK1952



7 : NK2009

Subsequently, the monolayers with adsorbed cyanine dyes were transferred as follows. A glass substrate, which was rinsed with ethanolic KOH and distilled water in turn, was dipped in a subphase which contained  $3.5 \times 10^{-7}$  M of cyanine dye 3. Then, a monolayer of dialkylammonium amphiphile 1 was spread on the cyanine dye solution. The monolayer was compressed at  $30 \text{ mN m}^{-1}$  and was allowed to stand for 15 min to adsorb cyanine dye 3. The composite monolayer was transferred on the substrate by the conventional LB technique. The first monolayer was collected by withdrawing the substrate. The substrate coated with monolayers was dried for 10 min in dry air before each down-stroke deposition. Absorption spectra of monolayers and multilayers on substrates were measured between each withdrawal and dipping with a UV-visible spectrophotometer (Hitachi 330). Measurements of fluorescence spectra were carried out with a fluorescence spectrophotometer (Hitachi 650-40). The same procedure was carried out on the several combinations of supporting materials 1-2 and dyes 3-7.

The absorption spectrum of the transferred composite monolayer of amphiphile 1 and dye 3 is shown in Fig. 2. The absorption band (solid line) is sharp and located at 570 nm, which is 25 nm longer than the wavelength of the monomer band obtained in a highly diluted methanol solution (dotted line). The fluorescence spectra of the monolayer was observed (Table 1). Its bandwidth was narrow and the Stokes shift very small, demonstrating that cyanine dye 3 adsorbed on the monolayer assumes J-like aggregation.<sup>9)</sup> Not only the cyanine dye 3, but other cyanine dyes 4-7 were found to form J-like aggregates under the same conditions (Table 1).

One should note that not all monolayers of dialkylammonium amphiphiles can promote the formation of the J-like aggregate of cyanine dyes. In the case of dialkylammonium amphiphile 2, which is one of the simplest bilayer-forming materials, the monolayer certainly adsorbed cyanine dye 3 at the air-water interface, but the adsorbed dye did not produce J-like aggregates. The absorption spectrum was very broad (broken line in Fig. 2). Other dyes, which were adsorbed on this monolayer, did not form J-like aggregates, except for the case of dye 6.

The capability of cyanine dyes to assume specific aggregation in adsorbed states on silver halides or in aqueous solutions has been known to depend on molecular structures of the dyes.<sup>9)</sup> One should note that all cyanine dyes in

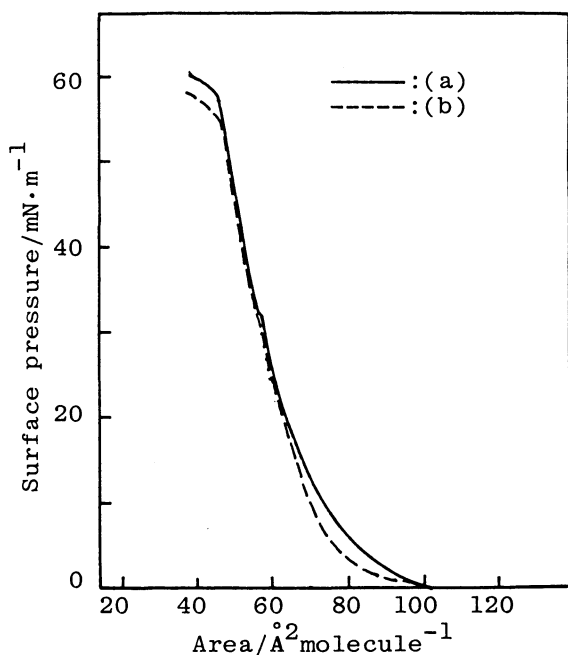


Fig. 1. Surface pressure - area isotherms of 1. (a) : on distilled water, (b) : on a cyanine dye 3 aqueous solution.

Table 1. Absorption and fluorescence maxima of transferred composite monolayers of amphiphile 1 and cyanine dyes

Dye	Absorption max./nm		Fluorescence max./nm
<u>3</u>	570	(545) <sup>a)</sup>	580
<u>4</u>	582	(558) <sup>a)</sup>	590
<u>5</u>	710	(654) <sup>a)</sup>	720
<u>6</u>	550	(505) <sup>a)</sup>	558
<u>7</u>	725	(708) <sup>a)</sup>	-

a) The dye in methanol.

Table 1 form J-aggregates, when they are adsorbed on the monolayer 1. Types of aggregation of the adsorbed dyes are independent of the molecular structures of dyes. In contrast, the aggregated structures of adsorbed cyanine dyes depend on the specific structure of the monolayer. Probably, the surface structure may play an important role. A very similar interpretation has been given in the case of bilayer membranes dispersed in water.<sup>6)</sup>

Multilayer films of the composite monolayer of amphiphile 1 and cyanine dye 3 could be prepared by repeating the transfer procedure. When the concentration of the cyanine dye in a subphase was  $3.5 \times 10^{-7}$  M, three layers were successfully

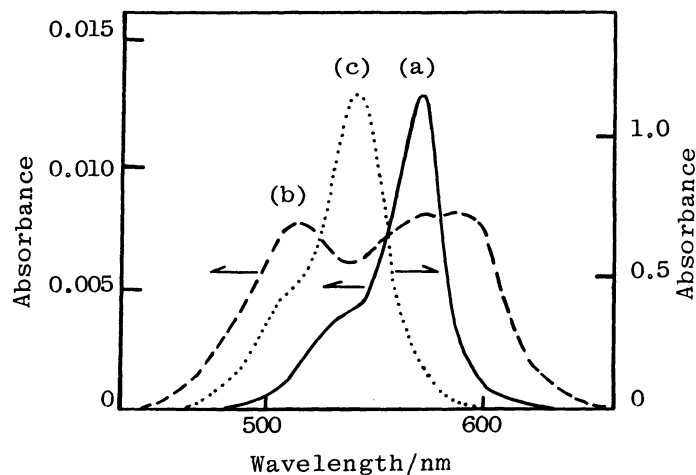


Fig. 2. Absorption spectra of single composite monolayer of amphiphiles and cyanine dye 3 on a glass substrate. (a) : amphiphile 1, (b) : amphiphile 2. (c) shows absorption spectrum of cyanine dye 3 in methanol.

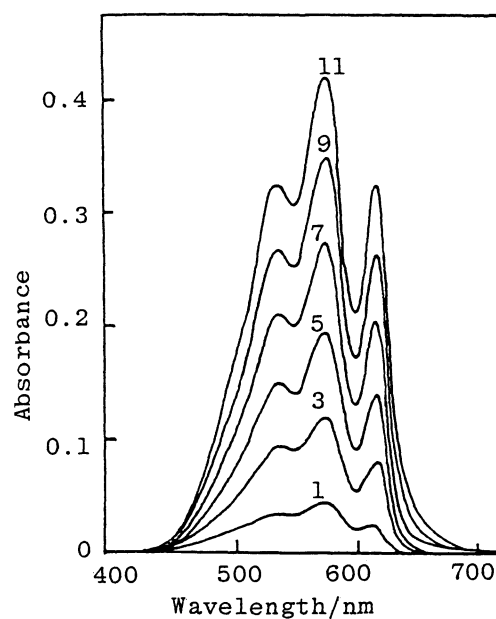


Fig. 3. Absorption spectra of type 2 multilayer (amphiphile 1 and cyanine dye 3). The numerals show the number of transferred monolayers.

transferred on a glass substrate; the increase of absorbance at 570 nm was observed with repeated depositions (type 1 multilayer). In the subsequent dipping, however, the absorbance did not increase. More than 3 monolayers could not be transferred on a substrate under these conditions. Then the concentration of the cyanine dye in the subphase was increased to  $1.9 \times 10^{-6}$  M. In this case, the absorbance of the multilayer increased linearly with the number of collection as shown in Fig. 3 (type 2 multilayer). In addition to the 570 nm band due to J-like aggregates, however, absorption bands appeared at 530 nm and 615 nm. Undoubtedly, the dye molecules with different aggregated structures exist in the collected multilayers. The increase in the dye concentration in the subphase enabled the preparation of multilayers with any thickness.

A small angle X-ray diffraction experiment (Rigaku Denki Rotaflex R-200, CuK $\alpha$ ) on the type 2 multilayer proved the presence of regular stacking of monolayers. The long spacing of the multilayer was 98 Å, which is 15 Å longer than the calculated bimolecular length of dialkylammonium amphiphile 1 (83 Å). This fact suggests that dye molecules are located between the polar groups in layered amphiphile molecules.

In this letter, we showed that cyanine dyes adsorbed on the monolayers at the air-water interface assume J-like aggregation, when amphiphiles with proper molecular structures are selected. Moreover, the multilayers with adsorbed dyes are prepared by the conventional LB technique. Several investigators have reported that cyanine and merocyanine dyes with long alkyl chains formed J-aggregates in the LB films.<sup>1,3)</sup> In our adsorption method, cyanine dyes with various molecular structures formed J-like aggregates without covalent attachment to long alkyl chains.

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#### References

- 1) H. Bücher and H. Kuhn, Chem. Phys. Lett., 6, 183(1970).
- 2) K. Fukuda and H. Nakahara, J. Colloid Interface Sci., 98, 555(1984).
- 3) M. Sugi, T. Fukui, and S. Iizima, Mol. Cryst. Liq. Cryst., 62, 165(1980).
- 4) D. Möbius, Mol. Cryst. Liq. Cryst., 52, 253(1979).
- 5) T. Kunitake and Y. Okahata, J. Am. Chem. Soc., 99, 3860(1977).
- 6) N. Nakashima, R. Ando, H. Fukushima, and T. Kunitake, J. Chem. Soc., Chem. Commun., 1982, 707.
- 7) N. Nakashima, R. Ando, and T. Kunitake, Chem. Lett., 1983, 1577.
- 8) The amphiphile was prepared according to the following paper: T. Kunitake, N. Nakashima, M. Shimomura, Y. Okahata, K. Kano, and T. Ogawa, J. Am. Chem. Soc., 102, 6642(1980). Elemental analysis. Found : C, 66.91; H, 10.42; N, 2.54%. Calcd for C<sub>55</sub>H<sub>101</sub>N<sub>2</sub>O<sub>6</sub>Br·H<sub>2</sub>O: C, 67.11; H, 10.55; N, 2.85%.
- 9) A. H. Herz, Adv. Colloid Interface Sci., 8, 237(1977).

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