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Aggregated Structures of Azobenzene-linked Amphiphiles at the Air-Water Interface

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With three azobenzene-linked amphiphiles containing designed alkyl and methylene groups, spectroscopic studies on monolayer at the air-water interface were performed. The effects of the alkyl and methylene groups on the molecular orientation and aggregate states in the monolayers were shown.

Understanding of the structures and properties of monolayers at the air-water interface is of fundamental importance in the fabrication of Langmuir-Blodgett (LB) films which may be used for the construction of electronic or optical devices.[1,2] For the elucidation of the properties of monolayers, surface pressure-area isotherms (π-A curves) are usually examined, since they give comprehensive information through a relatively easy procedure.

When one deals with the amphiphiles with chromophore portions, their electronic spectra also provide abundant information on the aggregated structures. An azobenzene chromophore can be one of the most excellent probe for spectroscopic technique in monolayers:[3] It exhibits two absorptions in a ultraviolet-visible region which are attributed to the transition moments along the long and short axes.[4] The peak wavelengths and intensities of the two absorptions reflect the aggregated structures of the amphiphiles.[5] Therefore, we utilized three azobenzene-linked amphiphiles which possessed designed alkyl (tail) and methylene (spacer) groups (Fig.1) and performed a spectroscopic study on the monolayers at the air-water interface. From the variations of electronic spectra of the monolayers with applied surface pressures, we examined the aggregated states of the chromophore in the monolayers. Further, we shed light on the effect of the lengths of both the tail and the spacer on the aggregated structures in the monolayers.

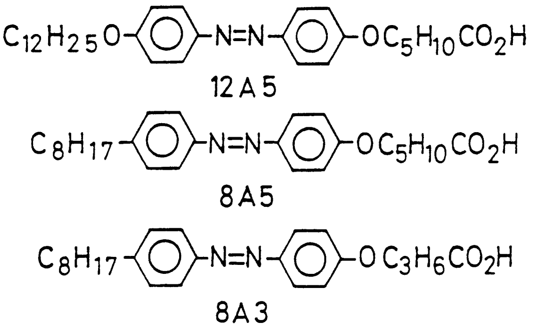

Fig. 1. Structures of the amphiphiles used in this work.

A trough which was firstly designed by Kuhn[6] was used. An optical window ($1\times10^{-4} m^2$) was placed in the bottom of the trough. The monolayer was spread from chloroform solutions on the aqueous subphase containing $BaCl_2$ ($2\times10^{-4} mol/dm^3$, pH=5.6) at 20 °C. The set-up for the measurement of an absorption spectrum is shown in Fig.2. Continuous UV light from a 30 W deuterium lamp was incident vertically to the water surface. Electronic spectra were observed at the surface pressure of 0, 5, 15, and 25 mN/m using a multichannel detector with a signal intensifier (Tracor Northern TN-6133). The spectra of the amphiphiles in hexane solution were measured using a Hitachi-330 spectrophotometer.

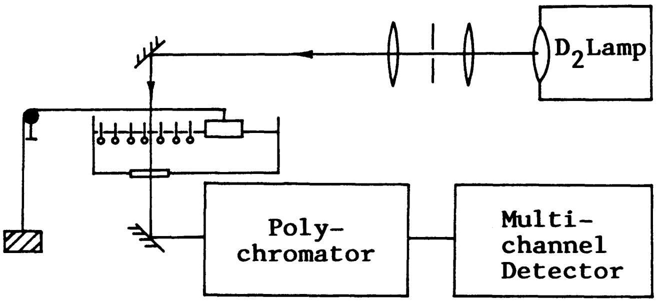

Fig. 2. Experimental set-up for the measurement of the electronic spectra of the monolayers at the air-water interface.

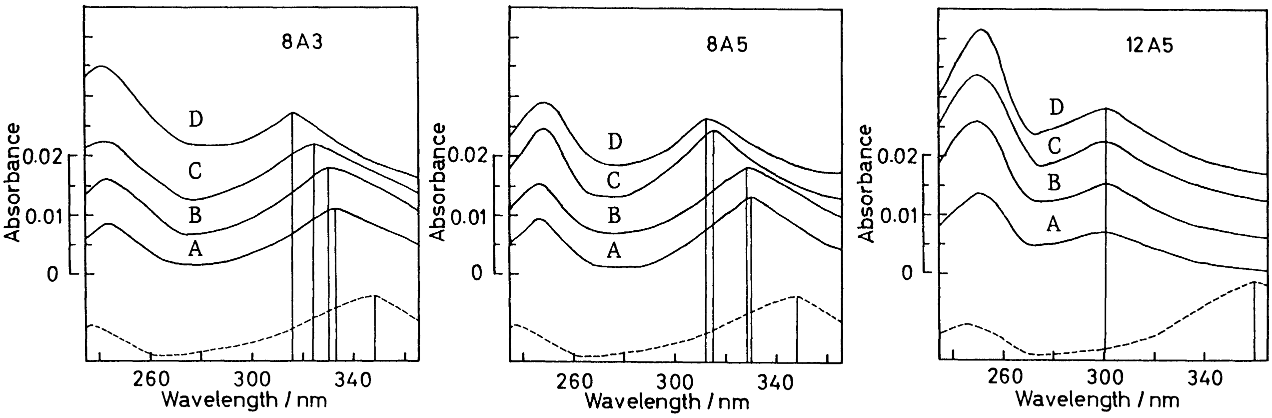

Fig. 3. Electronic spectra of the amphiphiles at the air-water interface at various surface pressures. The broken lines show the spectra in solution. Spectra were horizontally shifted. (A, 0 mN/m; B, 5 mN/m; C, 15 mN/m; D, 25 mN/m)

Figure 3 shows the change of the absorption spectrum of the monolayer of each amphiphile with change of the surface pressure. In the same figure, the corresponding spectra in solution are also shown with a broken line. At the air-water interface, the positions of the absorption maxima which are attributed to the transition moments along the long axis of azobenzene shifted to shorter wavelength, as compared with the corresponding peak in hexane solution. The extent of the shifts referred to the absorption peak in hexane solution, $\Delta\lambda$, are plotted against the surface pressure in Fig.4. The $\Delta\lambda$ values for 8A5 and 8A3 increased when the surface pressure was increased. The change of $\Delta\lambda$ was reversible; it decreased with the decrease of the surface pressure. The reversibility for 8A3 was indicated with a broken line in Fig.4. On the other hand, the $\Delta\lambda$ value for 12A5 was 60 nm which was larger than that of 8A5 or 8A3. In this case, however, no surface pressure dependence was observed.

According to the simplified molecular exciton model proposed by McRae and Kasha,[7)] these hypsochromic shifts can be explained by the parallel orientation of the transition moments along the long axis of the azobenzene chromophore (so-

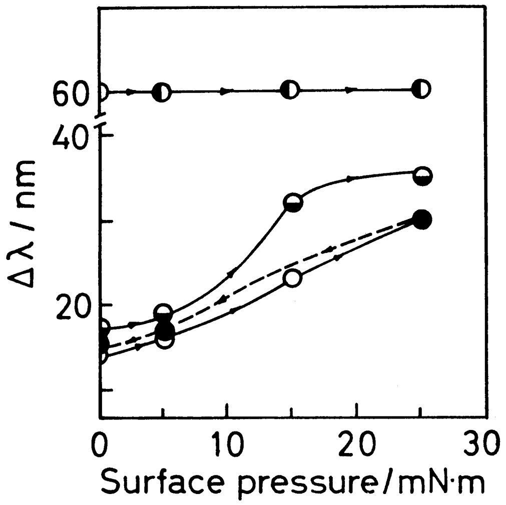

Fig. 4. Surface pressure dependence of Δλ. The broken line shows a reverse process. o,●: 8A3, ◒: 8A5, ◐: 12A5.

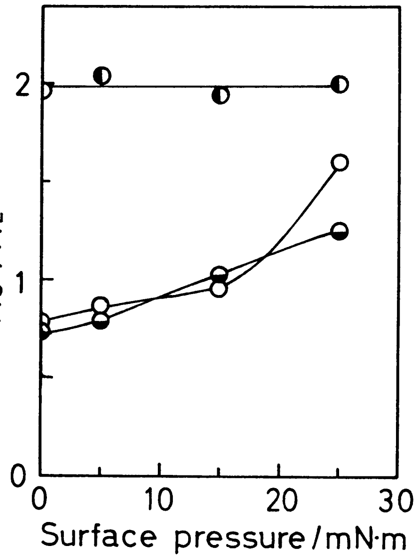

Fig. 5. Surface pressure dependence of A_S/A_L. o: 8A3, ◒: 8A5, ◐: 12A5.

called H-aggregate). Fukuda and Nakahara[8,9] showed that the tilt angle of the long axis of azobenzene chromophore from the normal direction of water surface, γ, can be estimated approximately by use of this model. A large Δλ value for 12A5 indicates that the tilt angle of 12A5 is smaller than that of 8A5 and 8A3, if one assumes that linear aggregates are formed in the condensed monolayer and that neither the number of aggregation nor the separation of the molecular centers are so different among these amphiphiles.

We showed, in a previous report,[4] that the ratio of two absorbances of an azobenzene chromophore, A_S/A_L, also gave a good measure for the orientation of the azobenzene chromophore, where A_L and A_S refer to the absorbances attributed to the transition moments along the long and short axes of the azobenzene chromophore respectively. The smaller the tilt angle of long molecular axis γ was, the larger the A_S/A_L value was. Figure 5 shows the plots of the A_S/A_L vs. surface pressure for three amphiphiles in monolayers. The A_S/A_L values for 8A5 and 8A3 increased with the surface pressure. On the other hand, the A_S/A_L value for 12A5, which was much larger than that for 8A5 or 8A3 in condensed region, exhibited no surface pressure dependence. These findings on the A_S/A_L ratios are consistent with the result from the shifts of the absorption maxima described above.

Based on these observations, we propose the possible models that describe the behaviors of the amphiphiles at the air-water interface in Fig.6. When no surface pressure is applied, 8A5 or 8A3 molecules lie with their long axes on the water surface. With the increase of surface pressure, the H-aggregate structures are formed accompanied by the rising of molecular axes up from the water surface(Fig.6(a)). On the other hand, 12A5 molecules form aggregates (domain structures) at the air-water interface immediately after the evaporation of solvent on the water surface without the application of surface pressure (Fig.6(b)). With the increase of surface pressure, the domains join together with little change of the orientation and the aggregate states.

These different behaviors of the amphiphiles at the air-water interface could be accounted for by the different lengths of the aliphatic tails in the amphiphiles. As 12A5 has a longer tail than 8A5 or 8A3 has, the tendency to strong self-aggregation turned out to appear. On the contrary, the effect due to the spacer length was not observed.

In conclusion, the orientation and aggregate states in the monolayers of 8A5 and 8A3 were found to depend on the surface pressure. In contrast, no such dependence was found in the monolayer of 12A5. In the aggregated monolayers, a longer tail in the amphiphiles favored the upright orientation of chromophores to the film plane. These findings may provide a valuable clue for the regulation of the aggregated structures in Langmuir-Blodgett multilayers through a design of the structures of amphiphiles.

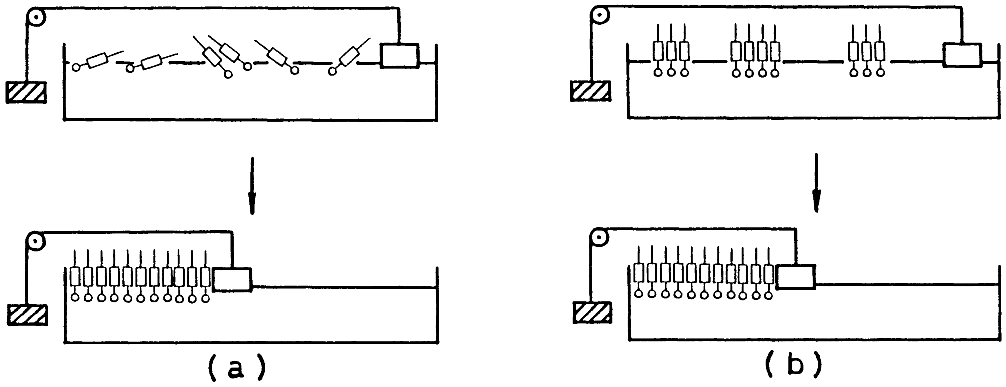

Fig. 6. The models describing the behaviors of the amphiphiles at the air-water interface. a) for 8A5 and 8A3, b) for 12A5.

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