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Molecular Orientation and Domain Formation in Surface Monolayers of Azobenzene-Containing Amphiphiles and Their Polyion Complexes[1]

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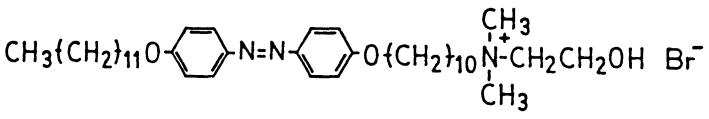
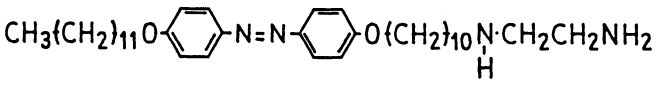
Examination of the surface monolayer on pure water or on aqueous polyanion of two azobenzene-containing compounds by the pressure-area isotherm and absorption spectroscopy established the controlled formation of surface microcrystals, islands, liquid expanded films, and condensed films.

The monolayer behavior at the air-water interface of azobenzene-containing amphiphiles has been studied by several groups. Heesemann examined the surface orientation of aliphatic chain-appended azo dyes,[2] and Nakahara and Fukuda prepared a series of substituted azobenzenes and discussed the relation between the mode of the alkyl-chain substitution and the molecular orientation of the monolayer.[3] Saito and coworkers[4] examined the monolayer and multilayer characteristics of azobenzene-containing fatty acids. Shimomura and Kunitake found that absorption spectra of aqueous dispersions of azobenzene-containing ammonium bilayers varied extensively depending on the component structure and the membrane physical state.[5] These bilayer-forming amphiphiles were subsequently shown to form stable monolayers especially in the form of polyion complexes.[6]

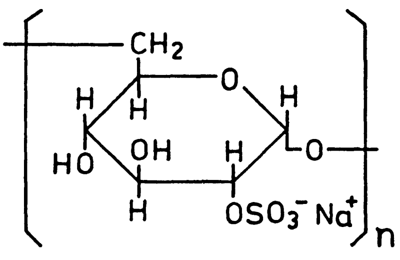
In this paper, we report on the absorption spectral observation of surface monolayers of azobenzene-containing amphiphiles, which reflects structural changes of the monolayers due to the extent of compression and/or complexation with an anionic polymer in the subphase. Azobenzene amphiphiles, $C_{12}AzoC_{10}N^+$(1) and $C_{12}AzoC_{10}\cdot ED$(2), have been described : the former compound forms bilayer dispersion in water,[4] and the latter cannot be dispersed in water by itself and forms



1 $C_{12}AzoC_{10}N^+$



2 $C_{12}AzoC_{10}ED$



Dextran Sulfate
molecular weight 50000

separate domains in a bilayer matrix.[7)]

The pressure-area isotherms of the surface monolayer(π-A curve) were measured with a computer-controlled film balance(San-esu Keisoku Co., model FSD-20). Absorption spectra were obtained by a photodiode array-equipped spectrometer (Otsuka Electronics, model MCPD-100). The tip of a Y-type optical fiber was fixed vertically at a position 2-3 mm above the water surface. A tilted black plate was placed in the Langmuir trough below the optical fiber in the reflectance mode, and a mirror was placed instead on the bottom of the trough in the absorption mode.

Figure 1A displays π-A curves of 1 and 2 on pure water(Milli Q system, Millipore Co.) at 20 °C. The spreading samples were prepared in a 7:1:2 mixture(by volume) of benzene, ethanol, and methylene chloride. The monolayer of 1 possesses a transition from the liquid expanded film to the condensed film, and the molecular area estimated by extrapolation of the solidus line to the zero surface pressure is 0.42 $\text{nm}^2\cdot\text{molecule}^{-1}$. On the other hand, 2 produces simply a condensed monolayer with molecular area of ca. 0.28 $\text{nm}^2\cdot\text{molecule}^{-1}$. This value is identical with that obtained for a stearylamido-substituted azobenzene,[3)] and is somewhat larger than the cross section(ca. 0.20 $\text{nm}^2\cdot\text{molecule}^{-1}$) of the vertically oriented hydrocarbon chain. The much larger molecular area of the former compound is characteristic of the ammonium monolayer.

Figure 1B is a comparison of π-A curves of 1 on pure water and on aqueous dextran sulfate(1 x 10^{-4} unitM, 1 M = 1 mol dm^{-3}). The portion of the π-A curve on pure water that corresponds to the liquid expanded state disappears on dextram sulfate probably due to complexation with this anionic polymer.

These monolayer behaviors are consistent with the spectroscopic observation. Figure 2 compares reflectance spectra of the monolayers of 1 and 2 under progressive compression. The monolayer of 1 gives λ_{max} at 365 nm at a low surface pressure(6 $\text{mN}\cdot\text{m}^{-1}$), but it shifts to 335 nm with increasing pressures. These two values agrees closely with that of the molecularly-dispersed(isolated) compound and that of the crystalline bilayer dispersion, respectively. The spectral shifts are reversible with respect to the surface pressure change. It is indicated, therefore, that the surface chromophore is transformed from non-interacting arrangements to the crystalline packing upon compression. In contrast, the monolayer of 2 gives λ_{max} at 303 nm even under very low surface pressures(e.g., 0.2 $\text{mN}\cdot\text{m}^{-1}$), and it does not shift with increasing pressures. This monolayer apparently forms crystalline surface dispersions even without compression. The surface monolayer of 1 displays very different spectral pattern in the presence of dextran sulfate. When the surface area per molecule is larger than 0.6 nm^2, the absorption intensity(λ_{max} 360 nm) fluctuates extensively. As the surface pressure starts to build up by further compression, the spectral fluctuation disappears and the intensity is enhanced. The λ_{max} then shifts to 340 nm. This shift is also observed on pure water.

The intensity fluctuation clearly indicates the formation of monolayer islands which are drifting on water. Their sizes are estimated not to be much smaller than the size of the optical fiber (1 mm diameter). The island formation is seen very clearly by the time course of absorbance, as demonstrated in Fig. 3. The stock

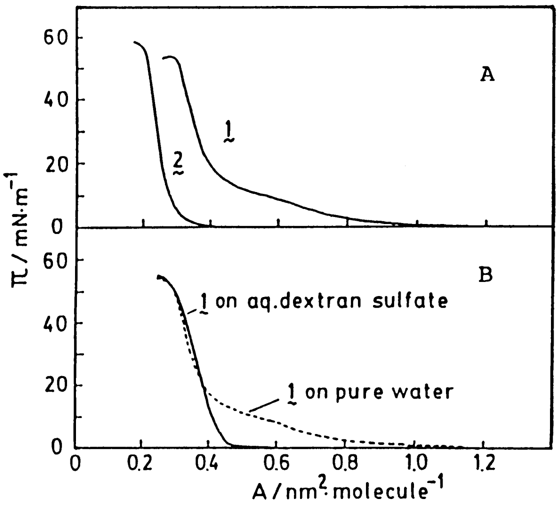


Fig. 1. Π-A curves of 1 and 2 at 20 °C.
A: on pure water.
B: on aq. dextran sulfate(1×10^{-4} unitM).

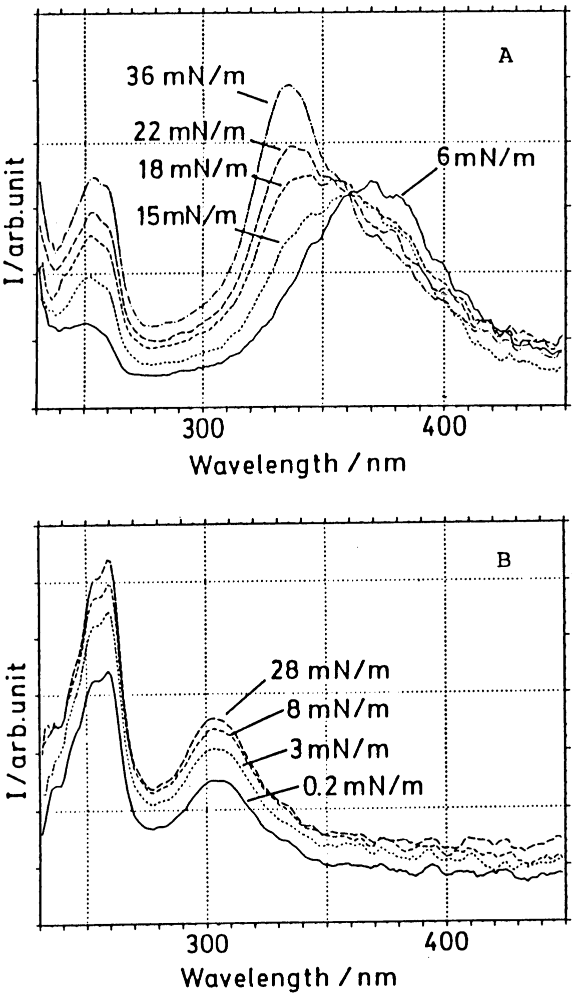


Fig. 2. Reflectance spectra of surface monolayers on pure water at 20 °C. A: 1, B: 2.

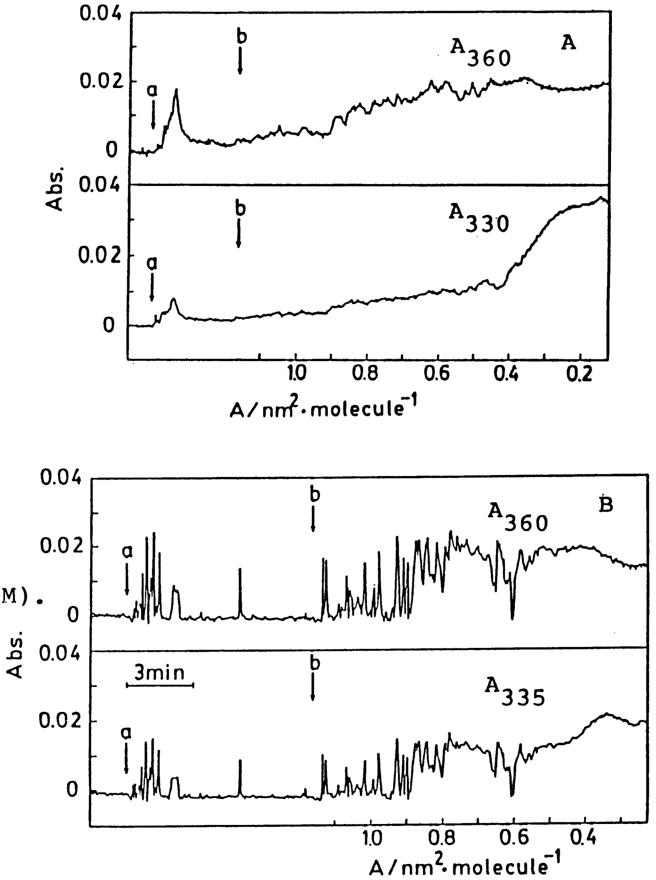


Fig. 3. Time course of absorbance (in the reflectance mode) of the monolayer 1 at 20 °C.
a, spreading of the stock solution.
b, start of compression.
A: on pure water.
B: on aq. dextran sulfate.

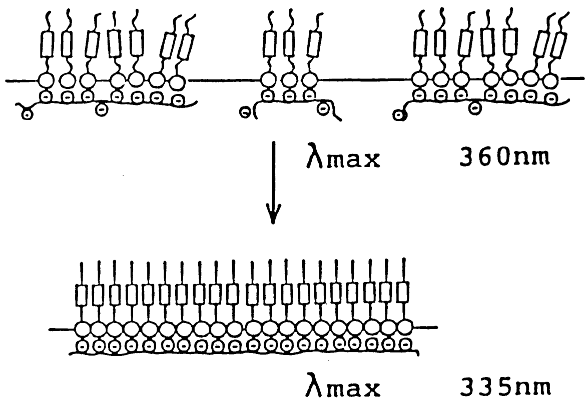


Fig. 4. Schematic illustraions of a polyion-complexed monolayer. Transformation of mobile domains to a compressed continent.

solution of 1 was dropped at several locations of the trough (at a in Fig. 3), and let to spread for a few minutes prior to compression. Remarkably different spectral behavior was observed between the monolayer on pure water and that on aqueous dextran sulfate. On pure water, absorbances (A_{360} and A_{330}) increase gradually with compression, and A_{330} becomes greater than A_{360} at the later stage in agreement with the λ_{max} shift shown in Fig. 2A. In contrast, spike-like absorbance changes due to the drifting monolayer island are found soon after spreading and in the initial stage of compression, in the presence of dextran sulfate. As the compression proceeds, the spike appears more frequently and coalesces at ca. 0.9 nm^2 $molecule^{-1}$. At 0.5 nm^2 $molecule^{-1}$, the sharp fluctuation is gone, and A_{335} gradually increases at the expense of A_{360}. The chromophore packing in the island is considered to be loose since λ_{max} is situated at 360 nm. These islands are compressed to form larger continents with a concomitant orientational change of the chromophore. A schematic illustration of this situation is given in Fig. 4. Heesemann(2) reported similar intensity fluctuations on pure water due to island formation.

In conclusion, we showed that simultaneous examination of absorption spectra and the pressure-area relation is very useful for characterization of surface monolayers. The surface monolayer of azobenzene-containing compounds and the corresponding Langmuir-Blodgett films are drawing strong attention because of their optical and other functions.[4,8-12] The present study indicates that their assembling properties can be controlled by molecular design and complexation.

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