CHEMISTRY LETTERS, pp. 1307-1310, 1987.

Host-Guest Complexes of an Amphiphilic β-Cyclodextrin and Azobenzene Derivatives in Langmuir-Blodgett Films

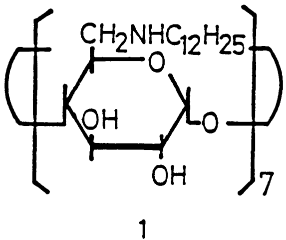
Motoo TANAKA, Yasuko ISHIZUKA, Mutsuyoshi MATSUMOTO, Takayoshi NAKAMURA, Akira YABE, Hiroshi NAKANISHI, Yasujiro KAWABATA,*
Hisao TAKAHASHI,+ Shoji TAMURA,+ Waichiro TAGAKI,+
Hiroo NAKAHARA,++ and Kiyoshige FUKUDA++
National Chemical Laboratory for Industry, Yatabe, Ibaraki 305
+ Department of Applied Chemistry, Faculty of Engineering,
Osaka City University, Sugimoto 3, Sumiyoshi-ku, Osaka 558
++ Department of Chemistry, Faculty of Science, Saitama
University, Urawa, Saitama 338

Langmuir-Blodgett films of host-guest complexes were fabricated for the first time using heptakis(6-dodecylamino-6-deoxy-)-β-cyclodextrin (1) and 4-(4-dimethylaminophenyl)azobenzoic acid. The guest molecule is included in the cavity of 1 with its long axis perpendicular to the film surface.

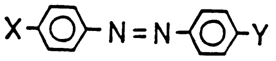
Cyclodextrins (CD's) are unique molecules consisting of several glucose units with a cavity inside of the cylindrical structure and various organic molecules are included in the cavity to form host-guest complexes.[1)] A wide variety of applications are expected when host-guest complexes are fabricated in Langmuir-Blodgett (LB) films. For example, a functional dye without long alkyl chains can be incorporated as a guest which is in a specific environment in the cavity and isolated by the host molecules.

We have demonstrated that long alkyl sulfinyl or sulfide derivatives of β-CD are fabricated as LB films.[2)] Azobenzene derivatives are known as typical guest molecules for CD's in aqueous solutions. In addition, the host-guest complexation has been confirmed for an amphiphilic β-CD derivative, heptakis(6-dodecylamino-6-deoxy-)-β-cyclodextrin (1), and 4-(4-dimethylaminophenyl) azobenzoic acid (2) in the chloroform solution.[3)] This report provides the first example of LB films of host-guest complex.

The amphiphilic β-CD (1) was synthesized as repoted in the previous paper.[4)] Commercially available azobenzenes (2-6) were used without further purification. Chloroform solutions (1.0×10^{-4} mol dm^{-3}) of 1 and azobenzenes except 3 were mixed and spread on pure water. For 3, a chloroform



1



2 : X = NMe_2 , Y = COOH
3 : X = NMe_2 , Y = SO_3Na
4 : X = H , Y = COOH
5 : X = NMe_2 , Y = H
6 : X = H , Y = H

solution of 1 was stirred with powder of 3 for 10 min and the filtrate was spread on pure water. Surface pressure-area (F-A) isotherms were measured at a compression speed of 8×10^{-3} nm^2 (CD molecule)$^{-1}$ s^{-1} at 290 K. The monolayers were deposited onto quartz slides precoated with five monolayers of cadmium icosanoate. Polarized absorption spectra of the deposited films were measured as described previously.[5)]

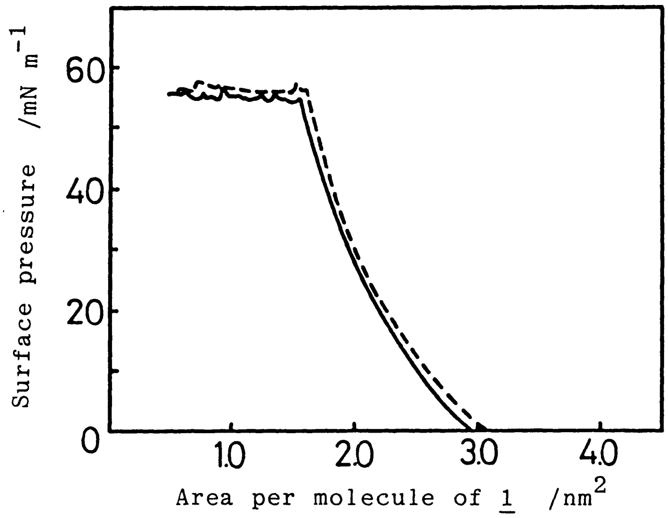


Fig. 1. F-A isotherms of CD (——):pure 1, (----):eqimolar mixture of 1 and 2.

Figure 1 shows F-A isotherms of pure **1** (solid line) and an equimolar mixture of 1 and **2** (dotted line). The monolayer of pure 1 is stable up to 55 mN m^{-1}. The limiting area of **1** (ca. 2.5 nm^2) strongly suggests that the base of cylindrical cyclodextrin residue is parallel to water surface in analogy with the sulfinyl derivative (-S(O)- instead of -NH- of **1**).[2)] The F-A isotherm of the mixture of 1 and **2** is identical with that of pure 1. Each monolayer was deposited on a hydrophobic quartz surface as a Y type film at 30 mN m^{-1} up to 100 layers. The LB film of the mixture has yellow color, showing that 2 is incorporated into the film.

Several methods are known to confirm the formation of host-guest complex, e.g., X-ray analysis of single crystal, induced circular dichroism spectra in solution, chemical shift in NMR spectra in solution, wavelength shift in UV-VIS spectra of guest molecule in water.[1)] In the case of ultra thin films, however, these techniques are difficult to be applied.

Quantitative analysis of **2** in the LB film was carried out to determine the molar ratio of 1 and **2**. The LB film prepared from the equimolar mixture of 1 and 2 was dissolved into chloroform by sonification. The number of molecule **2** obtained from the optical density of the solution was compared with the number of molecules 1 calculated from the molecular area at 30 mN m^{-1}. Molar ratio of 1:1 was found to be maintained even in the LB film. Other azobenzenes (3-**6**) together with 1 were also adopted to build up multilayers. Absorption spectra showed that **3** and **4** were incorporated into the films, but no appreciable amounts of 5 and **6** were detected.

The relationship between the structure of azobenzenes and their ability to be incorporated into the LB films indicate an important role of salt formation between the amino moiety (-NH-) of **1** and the acidic ones such as -COOH and $-SO_3H$ of azobenzenes. This is further supported by the fact that a sulfinyl derivative of **1** could not incorporate 2 into the LB films.

However, the host-guest complex formation is also essential for azobenzenes to be included in the LB films. When N-methyloctadecylamine or mixtures of N-methyloctadecylamine and methyl octadecanoate were used instead of 1, the resulting LB films showed no signal of 2 in the absorption spectra. A probable structure of the host-guest complex of 1 and 2 is illustrated in Fig. 2. This model is in good agreement with that in a chloroform solution, in which the formation of host-guest complex of 1 and 2 was confirmed by chemical shifts of **2** in NMR spectra and by induced circular dichroism. The strong host-guest complexation was observed together with the salt formation between the amino residue (-NH-) of 1 and the carboxyl group of **2**.3)

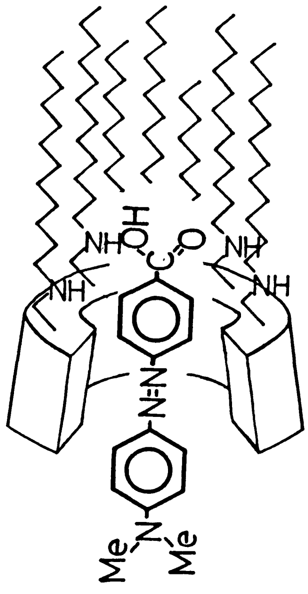


Fig. 2. Probable structure of 1 and 2 in the LB films.

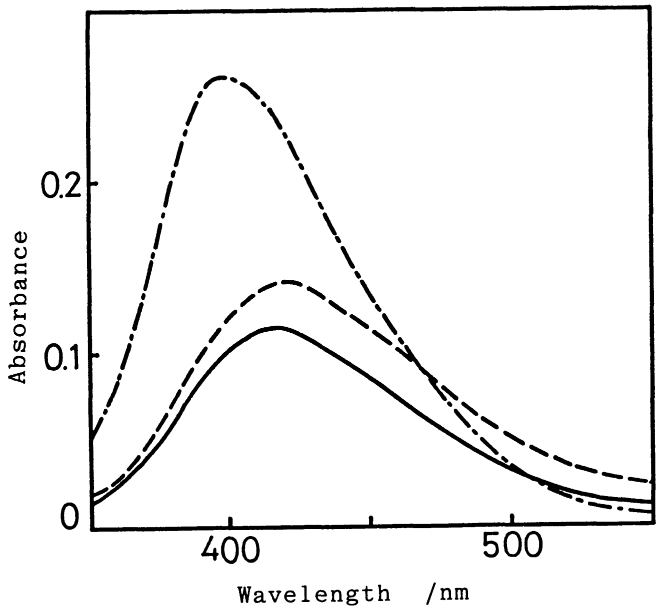


Fig. 3. The absorption spectra of the LB films of equimolar mixture of 1 and **2** (50 layers on both sides), (———):perpendicular incidence, (— — —):45° with s-polalized light, (—·—): 45° with p-polarized light.

Figure 3 shows absorption spectra of the LB film (50 layers on both sides) obtained from an equimolar solution of 1 and 2. In the case of perpendicular light incidence, the peak was observed at 417 nm (solid line). Polarized spectra at the incident angle of 45° were also measured to determine the orientation of 2 in the film. S-polarized light (electric vector perpendicular to the incident plane) gave the same λ_{max} at 417 nm (broken line). However, p-polarized light (electric vector in the incident plane) gave a peak at 400 nm (dash-dotted line) and the absorbance was significantly larger than that in the former case. Since the visible band is ascribed to the transition moment along the long axis of azobenzenes, the above results suggest that the major part of the molecule 2 is almost perpendicular to the film plane as shown in Fig. 2, although minor part may have somewhat different orientation. Induced circular dichroism of the LB film (20 layers on both sides) (solid line) was measured with the perpendicular incidence (Fig. 4). The spectral shape is similar to that obtained in a chloroform solution (broken line). The similarity of both spectra may afford an additional evidence for the formation of host-guest complex, although there remains some complications as for the interpretation of induced circular dichroism spectra of thin films.

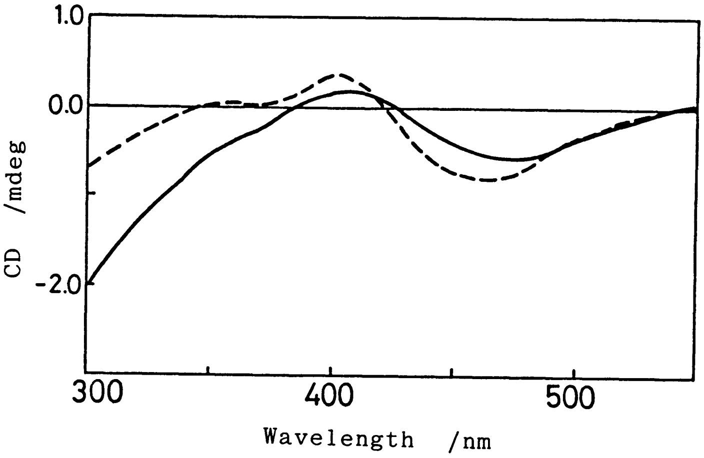


Fig. 4. Induced circular dichroism spectra of **1** and 2,(———):LB films (20 layers on both sides) of equimolar mixture of **1** and 2, (- - -): chloroform solution of **1** and 2, 2x10^{-3} and 2x10^{-4} mol dm^{-3}, respectively, cell length 1 mm.

In conclusion, mixtures of β-cyclodextrin 1 and azobenzene derivatives were deposited as LB films from chloroform solutions through the formation of monolayers on a water surface. Azobenzene derivative 2 in the LB films is included inside of the cavity of 1 to form a host-guest complex accompanied with salt formation and the long axis is oriented perpendicular to the film surface. This is the first example of the LB films composed of the host-guest complex. Azobenzenes, without long chains, were incorporated in LB films with highly ordered structure. Further work will be done to clarify the detailed structure of the host-guest complex and to develop the application of this unique structure for optical memories in the LB films. The study on the formation of the host-guest complex at air-water interface with guest molecules dissolved in the subphase is also in progress.

We would like to thank Drs. M. Sugi, and E. Manda for informative comments and discussion.

References

1) M. L.Bender and M.Komiyama, "Cyclodextrin Chemistry," Springer Verlag, New York (1978).
2) Y.Kawabata, M.Matsumoto, M.Tanaka, H.Takahashi, Y.Irinatsu, S.Tamura, W.Tagaki, H.Nakahara, and K.Fukuda, Chem. Lett., 1986, 1933.
3) Y.Kawabata, Y.Ishizuka, H.Nakanishi, H.Takahashi, S.Tamura, and W.Tagaki, Proc. of The 5th Symposium on Cyclodextrin, Dec. 1986, Kyoto.
4) H.Takahashi, Y.Irinatsu, S.Kozuka, and W.Tagaki, Mem. Fac. Eng. Osaka City Univ., 26, 93 (1985).
5) Y.Kawabata, T.Sekiguchi, M.Tanaka, T.Nakamura, H.Komizu, M.Matsumoto, E.Manda, M.Saito, M.Sugi, and S.Iizima, Thin Solid Films, 133, 175 (1985).

(Received April 1, 1987)