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Formation and Deposition of Monolayers of Amphiphilic β-Cyclodextrin Derivatives

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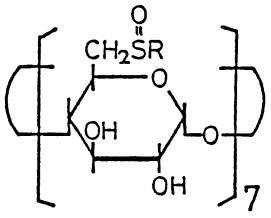
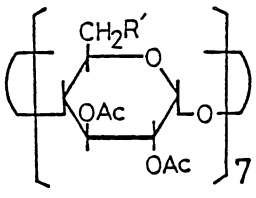
Stable condensed monolayers of four different amphiphilic derivatives of β-cyclodextrin were formed on a water subphase. The base of the cylindrical cyclodextrin residue was found to be parallel to the water surface. Langmuir-Blodgett films were obtained for three derivatives.

Langmuir-Blodgett (LB) films are interesting molecular assembly systems characterized by the ultra thin thickness and the high degree of alignment of the molecules. Developments of a new class of monolayer-forming materials are indispensable to utilize this unique system for practical purposes.[1] A new scope of application will be given by using cyclodextrins(CD's) consisting of several glucose units with a cavity inside of the cylindrical structure. They act as hosts for various kinds of guests such as organic molecules as well as inorganic ions.[2] With this object in view we synthesized some heptakis(6-alkylsulfinyl-6-deoxy-)-β-cyclodextrins and a sulfide analog, and examined their capabilities of the formation of stable monolayers and the deposition as the LB films.

Synthesis of the materials presented here will be reported in a separate paper.[3] Figure 1 shows the pressure-area (F-A) isotherms of the CD's(**1**-**5**) at 290 K. The monolayers of CD's were spread from chloroform solutions (2.0×10^{-4} mol dm^{-3}) on pure water. The extrapolated areas per molecule at zero pressure (A_0's) of **1**, **2**, **4**, and **5** were 2.17, 2.23, 2.53, and 2.59 nm^2, respectively, and the monolayers were stable at least up to 55 mN m^{-1}. The monolayer of **3** was unstable and no condensed phase was observed probably due to the insufficient alkyl chain length.



1: R=$C_{12}H_{25}$
2: R=C_8H_{16}
3: R=C_4H_9



4: R'=S(O)$C_{12}H_{25}$
5: R'=S$C_{12}H_{25}$

The observed values of the A_0

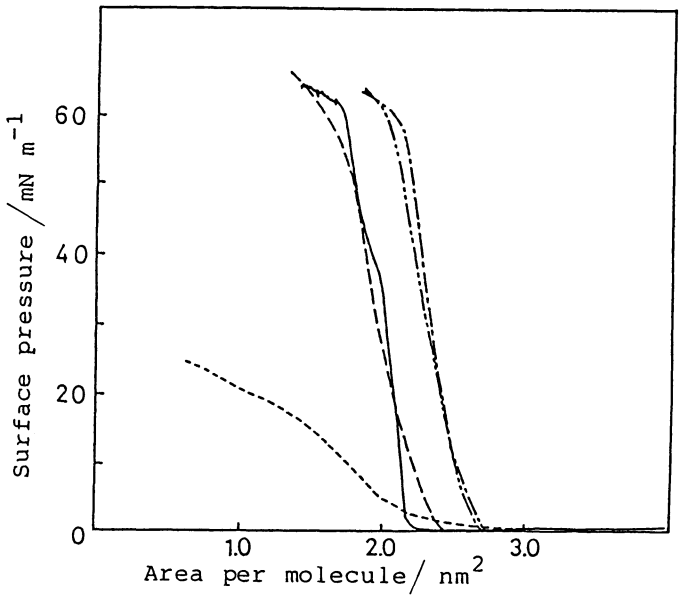


Fig. 1. F-A isotherms of the CD's; (———):1, (— — —):2, (------):3, (—·—):4, (—··—):5.

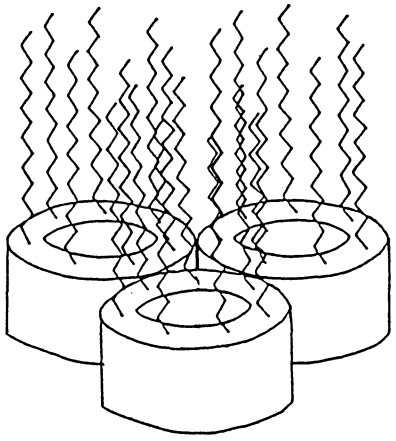


Fig. 2. Schematic representation for the arrangement of CD molecules on water surface.

indicate that the base of the cylindrical part is parallel and the alkyl chains are perpendicular to the water surface. The external diameter of unsubstituted β-CD is 1.54 ± 0.04 nm and the height is 0.79-0.80 nm, according to Saenger.[4] The area of the base of a β-CD molecule is calculated to be 1.77-1.96 nm^2, which corresponds to 1.95-2.16 nm^2 if we assume the closest packed structure in the two dimentional layer. The A_0 value of 2.17 nm^2 observed for **1** is in good agreement with the caluculated value. The substitution of secondary hydroxy groups with acetyl ones increased the A_0 value from 2.17 to 2.53 nm^2 (cf., the A_0's of **1** and **4**). The removal of oxygen from the sulfinyl group to sulfide did not change A_0 (cf., A_0's of **4** and **5**). These results have substantiated that A_0 is governed by the rigid cylindrical part of the molecule. Figure 2 shows a plausible arrangement of the CD molecules on a water surface. The deposition of the monolayers of the CD's except **3** was attempted at 30 mN m^{-1} using glass slides precoated with 5 layers of cadmium eicosanoate. The LB films, characterized as Y type, were obtained for **1**, **4**, and **5**. The monolayer of **2** was not deposited under these conditions. Attempts to introduce guest molecules into the LB systems of CD's are in progress.

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References

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