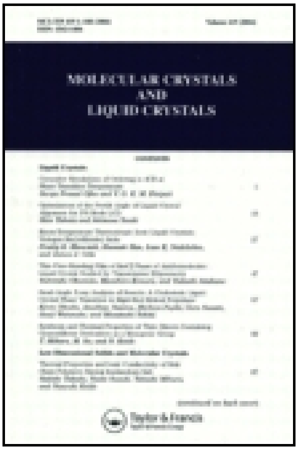

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Behaviors of Long-Chain Bifunctional Molecule, α, ω-13, 16-dimethyloctacosanedioate dimethylester (C_{30}DME), at the Air-Water Interface

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The conformational change of α, ω-13, 16-dimethyloctacosanedioate dimethylester (C_{30}DME) at the air-water interface was studied by changing the surface pressure. The surface pressure (π)-surface area (A) isotherm of C_{30}DME indicates that the structure of C_{30}DME changes from linear to reverse U-shape with the increase of surface pressure. The conformational change of C_{30}DME was confirmed by several instruments such as an ellipsometer, a Reflection-Absorption IR (RA-IR), and an atomic force microscope (AFM).

Keywords: bolaamphiphile; Reflection-Absorption IR; reverse U-shape

INTRODUCTION

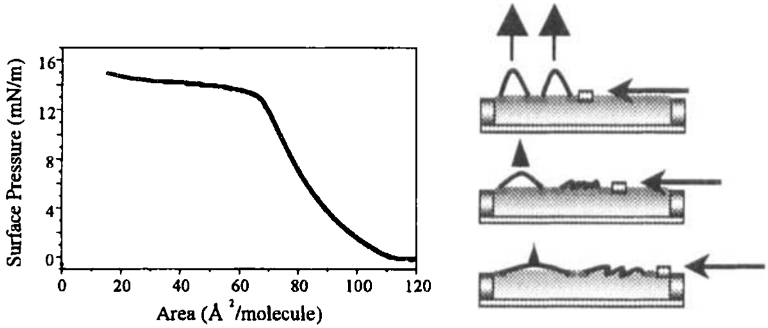
C_{30}DME, bolaamphiphile, is a major structural fatty acyl component of the membrane lipids in a strict anaerobic thermophilic bacterium, *Thermoanaerobacter Ethanolicus*. This unusual structure has been considered to explain thermophilicity (65℃) of this bacterium, though its exact molecular behavior at the air-water interface or in a membrane still remains to be unknown. Bolaamphiphile describes the molecules in which two polar head groups are linked covalently by a hydrophobic chain, saturated hydrocarbon.[1] Compared to the case for single-headed amphiphiles, the second head-group generally induces higher solubility in water, higher critical micelle concentration (cmc), and lower aggregation numbers.[2] While the study of monofunctional amphiphilic molecules are prevailed at the air-water interface, there have fewer reports on bolaamphiphiles.[3] The π-A isotherm of C_{30}DME differs from that of typical monofunctional amphiphiles. So, many researchers have discussed the formation of a reverse U-shape monolayer of bolaamphiphiles by observation of long plateau regions in the isotherms, but there have not been further discussions.[4] Herein we aim to report a conformational model of C_{30}DME molecule at the air/water interface with the increase of surface pressure by using several instruments such as an ellipsometer, an AFM, and a RA-IR.

EXPERIMENTAL

C_{30}DME was synthesized in the membrane of the cell of bacteria and isolated using flash column chromatography as described elsewhere.[5] Spectroscopic grade chloroform was purchased from Aldrich and used to make spreading solution for the Langmuir-Blodgett deposition. LAUDA FW-2 (LAUDA instruments, Germany) was used to get the π-A isotherms and LB films. The compression speed of the barrier was 20 cm^2/min. The C_{30}DME LB films were deposited vertically at surface pressures of 1, 6.5, and 14 mN/m with dipping speed of 5 mm/min on hydrophilic substituted silicon wafers for the ellipsometry or on mica substrates for AFM measurements. The Rudolph automatic-nulling ellipsometer, Auto EL2, was used to measure the thickness of the multilayer of the LB film with operating wavelength, 632.8nm, and angle of incidence, 70°±0.02. The experimental errors in the values of the phase difference (Δ) and azimuth (ψ) were less than 0.03 and 0.02, respectively. AFM measurements were performed on autoprobe CP (Park Scientific Instruments) using a 100μm scanner with a pyramidal Si_3N_4 tip. A 1μm×1μm section of the LB film was scanned in the contact mode. All film depositions were performed at a constant temperature at 20±0.5℃. RA-IR spectra were obtained by a Bio-Rad FTS-6000 interferometer working on the mid-infrared region. A cryogenic MCT detector was used as a detector. The infrared beam was guided onto the water surface by an external reflection unit. The spectra were measured at an incident angle of 20° to the surface. The resolution was 2 cm^{-1} and 256 interferograms were used to plot the IR spectra.

RESULTS AND DISCUSSION

C_{30}DME generates very stable and reproducible monolayer at the air/water interface as in Figure 1(a). The isotherm shows the broad increase of surface pressure in a wide region from 110 Å^2/molecule to 65 Å^2/molecule and has a long plateau region below 65 Å^2/molecule at 14 mN/m. The onset area at 110 Å^2/molecule and the transition area at 65 Å^2/molecule indicate the linear shape and the reverse U-shape with two hydrophilic ends of C_{30}DME anchored on the water subphase, respectively.

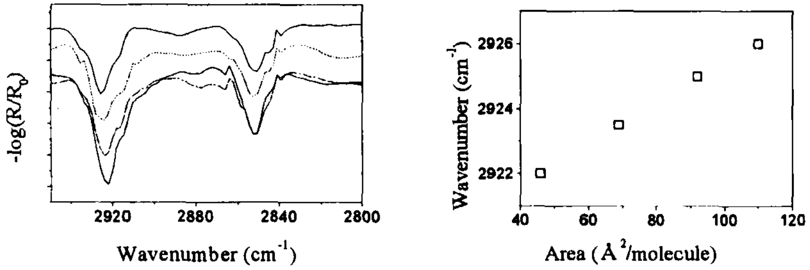


(a) (b)

FIGURE 1. (a) π-A isotherm of C_{30}DME at 20℃, (b) The schematic illustration for the conformational change of C_{30}DME.

The thickness of the monolayer was 7.9, 10.7, and 18.1 Å for the surface pressure 1.5, 6.5, and 14mN/m, respectively. Layer thickness at each surface pressure is increased to the half of the contour length of the C_{30}DME, 39.4 Å. And the surface roughness was measured by AFM; 3.25, 3.85, and 2.77 Å for the surface pressure 1.5, 6.5, and 14mN/m, respectively, which indicates increased and decreased surface roughness by increasing the surface pressure. At low surface pressure, the molecules are laid down at the air/water interface and make smooth surface. However, by increasing the surface pressure, the molecules start to bend and generate inhomogeneous layers with different layer thickness. At high surface pressure, the compact monolayer was formed and the roughness is lowered again. Figure 1 (b) illustrates these conformational changes of C_{30}DME monolayer at the air/water interface.

Figure 2 is the RA-IR spectra of C_{30}DME monolayer as the surface area is decreased. The IR spectra show the shift of CH_2 asymmetric stretching band from 2926 to 2920 cm^{-1} as the compressed surface area.



(a) (b)

FIGURE 2. (a) RA-IR spectra of C_{30}DME at the air/water interface, (b) wavenumber shift of CH_2-asymmetric stretching band as a function of surface area.

The shift to the lower wavenumber indicates the conformational change to the highly ordered structure.[6] Compared to the π-A isotherm of C_{30}DME monolayer, the RA-IR spectra and thickness (max. 18.1Å) measurement indicate the increment of highly ordered reverse U-shape molecules by increasing the surface pressure. These results coincide with the molecular dimensions provided by the molecular dynamic calculations.[7]

Acknowledgments
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