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Preparation and Spectroscopic Study of Langmuir-Blodgett Films of 4-[4(-(4(-Decyloxy Phenylazo) Naphthloxy] Butyl Trimethylamimonium Dextran Sulfate

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PREPARATION AND SPECTROSCOPIC STUDY OF LANGMUIR-BLODGETT FILMS OF 4-[4(-(4(-DECYLOXY PHENYLAZO) NAPHTHLOXY] BUTYL TRIMETHYLAMIMONIUM DEXTRAN SULFATE

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Abstract: 4-[4(-(4(-decyloxy phenylazo) naphthloxy] butyl trimethylammonium bromide can form a stable monolayer on the subphase of an aqueous sodium dextran sulfate solution. Infrared transmission, reflection-absorption and ultraviolet-visible spectra have been measured for the one- and multi-layer LB films to study the molecular orientation and aggregation in the films. It was found that the title compound does not form molecular aggregation in the LB films. The alkyl tail is nearly perpendicular to the substrate surface and adopts largely trans-zigzag conformation.

INTRODUCTION

Much attention has been paid to Langmuir-Blodgett (LB) films of azobenzene-containing amphiphilic molecules because they show potential applications in optical information storage and light switching devices[1-2]. In order to understand their interesting properties at the molecular level, it is very important to investigate molecular aggregation, orientation and structure in the LB films. In this paper, we report a spectroscopic study on molecular orientation and aggregation in LB films of a new azobenzene-containing ammonium amphiphile, 4-[4(-(4(-decyloxy phenylazo)naphthloxy] butyl trimethylammonium bromide (Figure 1; abbreviated as C_{10}AzoNaph(1,4)$C_4N^+Br^-$).

EXPERIMENTAL

The sample, C_{10}AzoNaph(1,4)$C_4N^+Br^-$, was synthesized by the method reported previously[3]. Sodium dextran sulfate (SDS; MW 50,000) was purchased from Nakarai

Chemicals Ltd., Japan.

A LB device[4] with a Wilhelmy balance was employed for the surface pressure - area (π-A) isotherm measurements as well as LB fabrications. A chloroform solution of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ (1 mg/mL) was placed onto an aqueous subphase containing SDS (10 mg/L). After evaporation of the solvent, the monolayers were compressed up to the surface pressure of 30 mNm^{-1} (293K). The LB films were transferred onto CaF_2 plates at the surface pressure of 30 mNm^{-1}. The π-A isotherm showed that the monolayers were solid condensed films at this surface pressure.

IR measurements of the LB films were made by a Bruker IFS66V FT-IR spectrometer equipped with a MCT detector. The spectra were obtained at 4 cm^{-1} resolution and generally several hundred scans were coadded for acceptable signal to noise ratio. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer.

RESULTS AND DISCUSSION

Figure 1(a) and (b) show surface pressure - area (π-A) isotherms of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ on the surface of pure water, and an aqueous solution of sodium dextran sulfate(SDS), respectively. It can be seen from curve a that the surface pressure increases slowly with the compression on pure water. This indicates that it can not form a stable interfacial monolayer because of the high water solubility of the head group of this amphiphile, and that the LB fabrication is impossible on pure water surface. If the aqueous solution of an anionic polymer is selected as the subphase, an insoluble composite layer at the air-water interface is expected. The aqueous solution of SDS proved to be proper subphase in which the hydrophilic head group of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ may be associated with the sulfonate group of SDS through electrostatic interactions to make insoluble polyion complexes. As can be seen from curve b, the composite C_{10}AzoNaph(1,4)C_4N^+-SDS layer shows features characteristic of a stable monolayer .

Ultraviolet-visible absorption spectra of one- to five-monolayer LB films of C_{10}AzoNaph(1,4)C_4N^+-SDS are very similar to the spectrum of C_{10}AzoNaph(1,4)$C_4N^+Br^-$

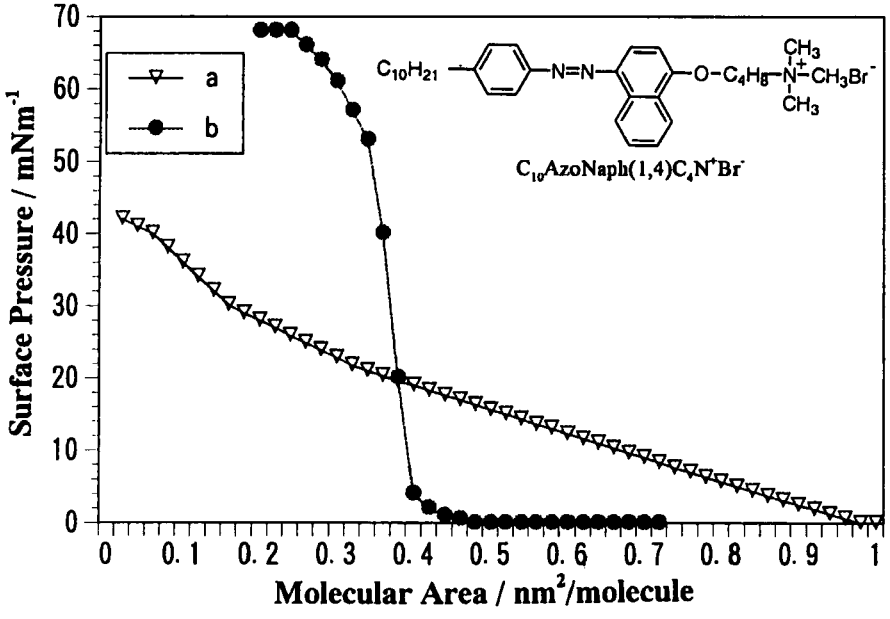

FIGURE 1. π-A isotherms of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ on the surface of pure water(a) and the solution of SDS(b). (pH; 6.5, 297 K)

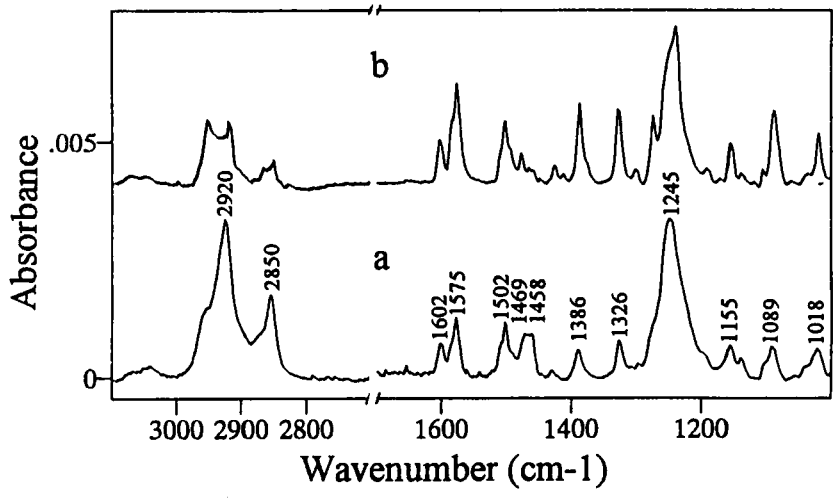

FIGURE 2. Infrared transmission(a) and reflection-absorption(b) spectra of five monolayer LB films of C_{10}AzoNaph(1,4)C_4N^+-SDS.

in a chloroform solution, suggesting that the composite also does not form molecular aggregation in the films. In general, azobenzene-containing amphiphilic molecules easily form H-aggregates in LB films[5]. Thus, in this respect, C_{10}AzoNaph(1,4)C_4N^+-SDS shows different property. Probably, the presence of naphthalene ring and/or SDS make the formation of H-aggregates difficult.

Figure 2 (a) and (b) show infrared transmission and reflection absorption (RA) spectra of five monolayer LB films of C_{10}AzoNaph(1,4)C_4N^+-SDS, respectively. Bands at 2920 and 2850 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chain (both the alkyl tail and the chain bonded to the ammonium groups). The frequence of the CH_2 stretching bands are sensitive to the conformation of a hydrocarbon chain. The above frequencies suggest that the hydrocarbon long chain of C_{10}AzoNaph(1,4)C_4N^+ assumes largely trans-zigzag conformation but may include some gauche conformation. Probably, the alkyl tail is too short to take highly ordered structure.

The intensities of the CH_2 stretching bands and those of the CH_2 scissoring bands near 1460 cm^{-1} are much stronger in the transmission spectrum than in the RA spectra. This result suggests that the hydrocarbon chain is nearly perpendicular to the substrate surface. Bands at 1602, 1575 and 1502 cm^{-1} are due to the stretching modes of the aromatic rings. The intensities of these bands are similar between the infrared transmission and RA spectra, indicating that the two rings are tilted considerably from the surface normal.

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