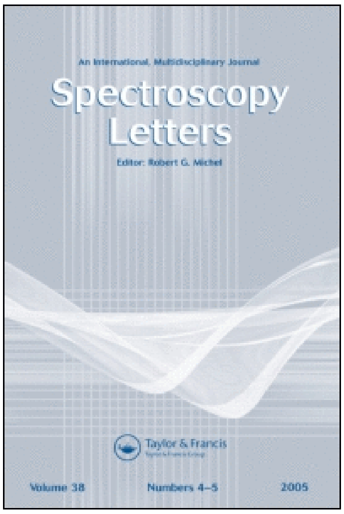

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MOLECULAR ORIENTATION AND AGGREGATION IN THE LANGMUIR-BLODGETT FILMS OF 4-[4'-(4"- DECYLOXY PHENYLAZO) NAPHTHLOXY] BUTYL TRIMETHYLAMMONIUM DEXTRAN SULFATE STUDIED BY ULTRA-VIOLET AND INFRARED SPECTROSCOPY

Keywords: LB films, amphiphiles, Azo, Naphthalene.

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Abstract:

Infrared transmission, Reflectance-Absorption (RA) and Ultra-Violet (UV) spectra were measured for mono- and multi-layers Langmuir-Blodgett (LB) films of 4-[4'-(4"-decyloxy phenylazo)naphthloxy] butyl trimethylammonium bromide formed with SDS to study the molecular orientation and aggregation. The results indicate that the compound do not aggregate in the LB films, and the alkyl tail is nearly perpendicular to the substrate surface and the chromorphore part adopts trans-zigzag conformation. These results also suggest that the molecular orientation and aggregation are not depend upon the number of monolayers. The

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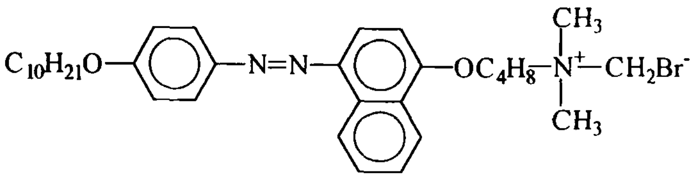
comparison of infrared transmission and RA spectra indicates that the hydrocarbon chain is nearly perpendicular to the substrate surface, but the two rings in the chromophore part are tilted considerably from the surface normal.

Introduction

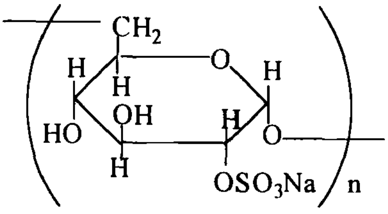
A great deal interesting has been devoted to the Langmuir-Blodgett (LB) films of some materials which have potential applications in optical information storage, light switching devices, nonlinear optical devices, etc.. And the structural characterization of these materials have become more and more important for understanding the structure-function relationship.[1-3] In order to understand their interesting properties, it is very important to investigate molecular orientation, aggregation and structurein in LB films [4,5]. In this paper, we focused our attention to a new azobenzene-containing amphiphiles compounds which with slight modification in the chromorphric part[6], 4-[4′-(4″-decyloxy phenylazo)naphthloxy] butyl trimethylammonium bromide, the structure is represented in Figure 1 (abbrevied as $C_{10}AzoNaph(1,4)C_4N^+Br^-$), studying the molecular orientation and aggregation in LB films by Ultra-Violete (UV) and Infrared spetra (IR).

Experimental Section

The sample $C_{10}AzoNaph(1,4)C_4N^+Br$ was synthesized as reported previously [6]. Sodium dextran sulfate (SDS; MW 50 000) used in this research was purchased from Nakarai Chemicals, Ltd., Japan, and was highly pure grade. Ion - free water was purified by a double distiller before experiments. A LB device with a Wilhelmy balance[7] was employed for the surface pressure - area (π-A) isotherm measurements as well as LB fabrications. The monolayer was obtained by spreading chloroform solution of $C_{10}AzoNaphC_4N^+Br$ (1 mg/ml) on the surface of a doubly distilled water containing SDS in a concentration of 10 mg/L. After evaporation of the solvent, the monolayer was compressed at a constant rate of 10 cm^2/min up to the surface of 30 mN/m. The π-A isotherm showed that the monolayer were solid condensed films at this pressure. The LB films were transferred onto CaF_2 plate at a dipping and raising speed of about 10 mm/min.



$C_{10}AzoNaph(1,4)C_4N^+ Br^-$



SDS

Figure 1. The Struture of $C_{10}AzoNaph(1,4)N^+Br^-$ and SDS

The layers was transferred with the vertical dipping method [8]. The above procedure were carried out at 20 ± 1°C.

The CaF_2 substrates have been cleaned by ultrasonication in a CQ500 Model cleaner in distill water, ethanol, acetone, chloroform, acetone, ethanol, and distill water for 5 min respectively, and then washed with large amount of distilled water[8].

Infrared measurements were made by a Bruker IFS66V FT-IR spectrometer equipped with a MCT detector. Spectra of LB fillms were taken at 4 cm^{-1} resolution and generally several hundred scans were accumulated for acceptable signal/noise. UV-vis absorption were recorded on a Shimadzu UV-3100 spectroscopymeter, and the slit is 2 nm.

Results and Discussion

1. UV-vis absorption spectra of $C_{10}AzoNaph(1,4)C_4N^+$ - SDS LB films: Our previous study indicates that the molecule of

C_{10}AzoNaph(1,4)$C_4N^+Br^-$ on SDS solution can form stable monolayer because the hydrophilic head group of its can be associated with the sulfanate group of SDS through electrostatic interaction to make insoluble polyion complexes[9]. Figure 2 shows the Ultraviolet-visible (UV-Vis) absorption spectra of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ in chloroform solution (a) and one- to seven-monolayers of C_{10}AzoNaph(1,4)C_4N^+ - SDS (b-e). Two absorption band at 243 nm and 392 nm in the spectra of LB films are assigned to the π - π^* transition of the trans-azobenzene chromorphore with the transition moment roughly parallel to the short axis and the long axis, respectively. Comparison of two absorption spectra at 243 nm and 392 nm enables us to discuss the orientation of azobenzene chromorphore in the LB films[10]. The relative intensity of the band at 243 nm is much stronger than that of the band at 392 nm in the spectrum of LB film. This result suggests that the azobenzene chromorphore is oriented nearly perpendicular to the substrates surface.

UV absorption spectra of the one- to seven-monolayer of C_{10}AzoNaph(1,4)C_4N^+-SDS LB films (in figure 2,b-e) are very similar to each other except for band intensities which increase almost in line with increasing the number of monolayer, *n*, suggesting that chromorphoric part structure of LB films changes little as a function of *n* value. And that these spectra are very similar to the spectrum of C_{10}AzoNaph(1,4)C_4N^+Br in solution indicate that the composite dose not form molecular aggregation in the LB films. In general, azobezene-containing amphiphilic molecules easily form H-aggregation in LB films [11]. Thus, in this respect, C_{10}AzoNaph(1,4)C_4N^+-SDS LB films shows different property. Probably, the presence of naphthalene ring and/or SDS make the formation of H-aggregation difficult.

2. Infrared spectra of LB films of C_{10}AzoNaph(1,4)C_4N^+ - SDS: Figure 3 (a), (b) and (c) show infrared absorbance spectra of C_{10}AzoNaph(1,4)C_4N^+-SDS LB film, C_{10}AzoNaph(1,4)$C_4N^+Br^-$ in solid state, and that of SDS in solid state, respectively. In Figure 3 (b) intense bands at 2923 and 2851 cm^{-1} are assigned to

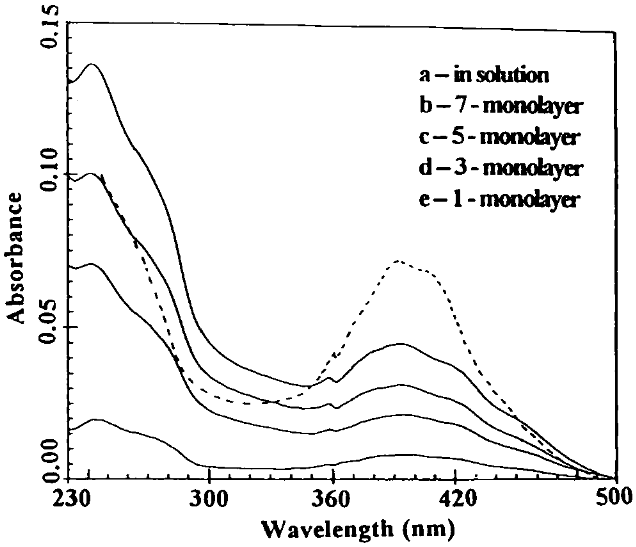


Figure 2. UV-Vis absorbance spectra of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ in cholorform solution (a), 7,5,3,1-monolayer LB films of C_{10}AzoNaph(1,4)C_4N^+-SDS (b-e).

CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chain (both the alkyl tail and the chain bonded to the ammonium groups). In 3(a) these two bands are appeared at 2920 and 2850 cm^{-1} . It is well known that vibrational frequencies of CH_2 antisymmetric and symmetric stretching bands of ethylene chain are very sensitive to the degree of its conformational order [12,13]. When the methyiene chain takes a trans-zigzag conformation, the bands appear near 2918 and 2848 cm^{-1}. The bands due to CH_2 antisymmetric and symmetric stretch mode of the alkyl in LB film are closed to 2918 and 2848 cm^{-1}, indicates that C_{10}AzoNaph(1,4)C_4N^+ - SDS assumes largely trans-zigzage conformation but include some gauche conformation. This indicates that the alkyl tail is too short to take highly ordered structure in LB film. Comparison of the infrared spectra in Figure 3(b) with that of azobenzene[14,15], and naphthylene derivatives enables us

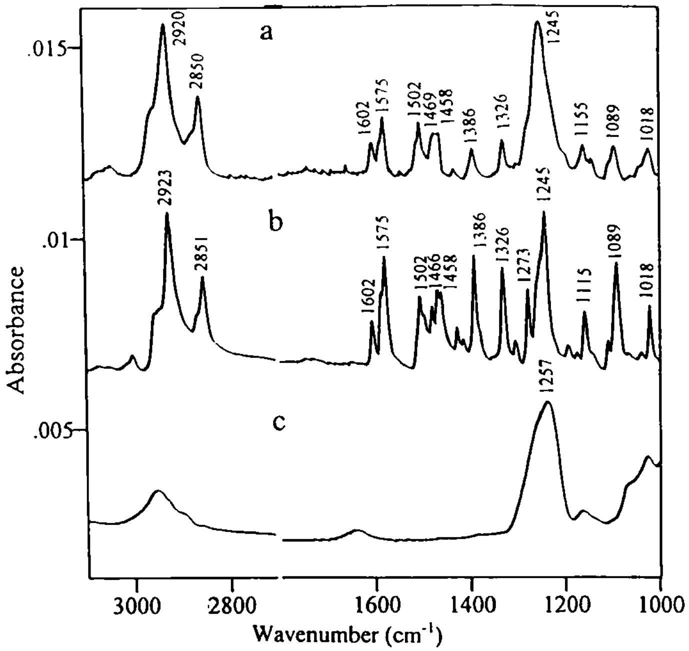


Figure 3. FT-IR spectra of C$_{10}$AzoNaph(1,4)C$_4$N$^+$-SDS LB films (a), C$_{10}$AzoNaph(1,4)C$_4$N$^+$Br$^-$ (b) and SDS (c) in solid state.

to propose vibration assignments for bands in 800-800 cm^{-1} region. In Figure 3(b), bands due to ring stretching mode of phenyl group are identified at 1602, 1508 cm^{-1}, respectively, in analogy with those of azobenzene derivatives[14]. Judging from the difference between the infrared spectra of azobenzene and naphthyl derivatives, we may assume that a band groups at 1575 and 1502 cm^{-1} are ascribed to another ring stretching mode of the naphthyl group.

A medium feature group near 1466 and 1458 cm^{-1} are assigned to a CH$_2$ deformation mode of the hydrocarbon chain, which is sensitive to the intermolecular interaction and thus often used to distinguish the lateral packing of the chains: its single appearance is characteristic of *n*-paraffins with a hexagonal

Table 1. Assignments of vibrational frequency of C_{10}AzoNaph(1,4)C_4N^+Br in a solid state, five-monolayer LB films of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ formed with SDS.

LB films	Azonaph in solid	Assignment
2920	2924	CH_2 asym. stretching mode
2850	2852	CH_2 sym. stretching mode
1602	1602	phenyl ring C-C stretching mode
1575	1575	naphthyl ring C-C stretching mode
1509	1508	phenyl ring C-C stretching mode
1502	1502	naphthyl ring C-C stretching mode
1469	1466	CH_2 deformation mode
1458	1456	CH_2 deformation mode
1387	1386	naphthyl ring deformation in plane
1326	1324	phenyl ring deformation in plane
1245	1249	=C-O- stretching mode
1155	1155	=C-N= stretching mode
1089	1089	phenyl ring-O-C stretching mode
1018	1018	naphthyl ring-O-C stretching mode

subcell packing, while the splitting band (near ~1473 and ~1463 cm $^{-1}$) is indicative of an orthorhombic subcell packing[16,17]. The appearance of the splitting deformation band in the spectrum of C10AzoNaph(1,4)C4N$^+$-SDS LB films appear in the 1466 and 1458 cm^{-1}, it therefore concluded that the alkyl chain is in a hexagonal subcell packing in the film.

A medium band at 1386 cm^{-1} (Figure 3b) is assigned to a in plane ring stretching mode, is characteristic of the naphthalene ring[18,19], and band at 1326

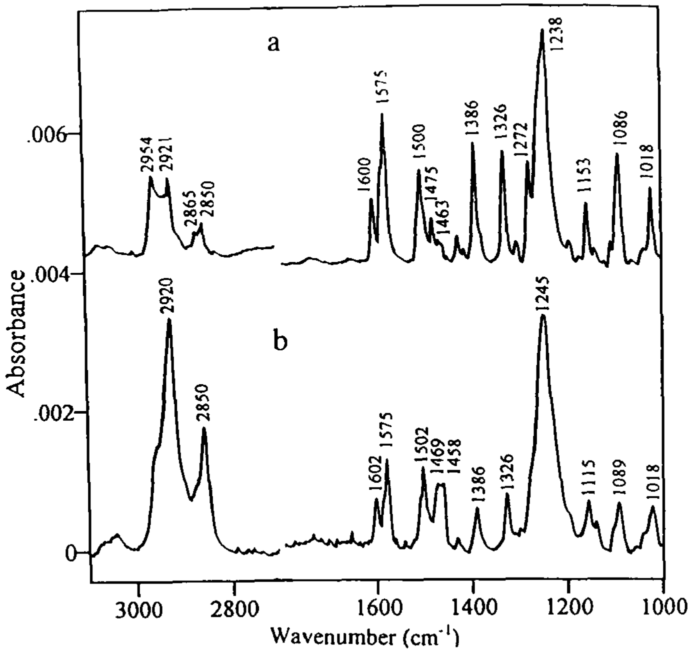


Figure 4. IR reflection-absorption spectra (a) and FT-IR transmission spectra (b) of five-monolayer LB films of C_{10}AzoNaph(1,4)C_4N^+-SDS.

cm^{-1} is the corresponding mode of phenyl ring. These two band can be seen in the Raman spectra of its.

A band at 1273 cm^{-1} in figure 2b, assigned to a ring stretching mode, is characteristic of naphthalene ring[18,19]. It seems that bands near 1249 and 1089 cm^{-1} arise from phenyl ring =C-O-ring asym. and sym. stretching mode respectively.

Of note in figure 3 (a), frequencies of these in LB films are very close to that for a solid state (KBr tablet), indicating that the structure of the chromorphoric part of molecule changes little between the LB films and solid state. Table 1 summarizes the assignments of vibrational frequency of

C_{10}AzoNaph(1,4)$C_4N^+Br^-$ in a solid state, and five-monolayer LB films of C_{10}AzoNaph(1,4)$C_4N^+Br^-$ formed with SDS.

IR reflection-absorption spectra (RAS) were also measured for five-monolayer LB film of C_{10}AzoNaph(1,4)C_4N^+-SDS (in figure 4a) . Comparison the transmission and RA spectra of the five-monolayer films reveals that the bands due to CH_2 antisymmetric and symmetric stretching modes; and that of CH_2 1469 cm^{-1}, are much stronger in the former and weak in the latter. These observations suggest that the hydrocarbon chain are 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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