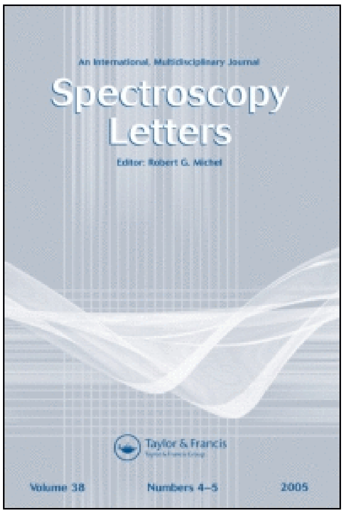

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Structure and Orientation of 1-Hydroxyl-5-Hexadecyloxy-Naphthalene LB Films Studied By UV-VIS and FTIR Spectroscopy

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STRUCTURE AND ORIENTATION OF 1- HYDROXYL -5- HEXADECYLOXY-NAPHTHALENE LB FILMS STUDIED BY UV-VIS AND FTIR SPECTROSCOPY

KEYWORDS: spectroscopy, LB films, orientation, naphthalene

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ABSTRACT

Ultraviolet-visible (UV-Vis), infrared transmission, and reflection absorption(RA) spectra have been measured for one- and multi-monolayer Langmuir-Blodgett(LB) films of $C_{16}H_{33}ONaph(1,5)OH$ at various temperature to investigate dependencies of the aggregation and phase transitions on the number of monolayers. The UV-vis spectra of the LB films have revealed that the $C_{16}H_{33}ONaph(1,5)OH$ forms aggregates in the LB film. From the temperature dependence of UV-vis absorption spectra, it is clear that the aggregate is gradual converted to monomer upto 80 °C. A comparison of the infrared transmission and

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RA spectra reveals that the hydrocarbon chains are tilted considerably in the LB film. As for the naphthalene ring part, the result suggest that the ring plane is oriented approximately perpendicular to the substrate surface. The Temperature dependence of infrared transmission spectra have been measured for 1-, 3-, and 11-monolayer LB films to investigate dependence of phase transitions on the number of monolayers. These observations show that the one-monolayer LB films does not have a clear order-disorder transition, while the three- and eleven-monolayer films have a phase transition near 60 °C. Therefore, it seems that the title angles of both the alkyl chain and chromophore part change largely concomitantly with the conversion from the aggregate to the monolayer.

INTRODUCTION

Ordered monolayer films transferred from a water surface onto a solid substrate by the Langmuir-Blodgett (LB) techniques have drawn growing interest for a recent few years[1]. This is because the LB films have a good possibility to be artificial molecular assemblies with planned structure and properties. A variety of molecular devices based on LB films have been proposed, such as films with nonlinear optical properties, photo-voltaic cells, piezoelectric and pyroelectric devices, resistance and conducting materials, and chemical and biological sensors. Investigations on thermal behaviors of amphiphilic molecules in LB films are important, because, the order-disorder transitions and annealing effects in the thin films may demonstrate specific features different from those of bulk hydrocarbon materials; the thermals behaviors are directly related to thermal stability of the organic thin films; studies may offer a new insight into functions of the thin films because those of some films are directly linked with their phase transition(2-4). In this paper, we applied the UV-vis absorption and FT-IR techniques to investigate the molecular structure, orientation, and phase transitions of the new naphthalene-containing amphiphiles 1-hydroxyl-5- hexadecyloxy -naphthalene LB films.

EXPERIMENTAL SECTION

Sample Preparation:

The 1-hydroxyl-5-hexadecyloxy-Naphthalene ($C_{16}H_{33}ONaph(1,5)OH$) was synthesized by our own lab[5].

A LB device with a Wilhelmy balance was employed for the surface pressure-area(π-A) isotherm measurements as well as LB fabrications[6]. A chloroform solution (1.0×10^{-3} M) of $C_{16}H_{33}ONaPh(1,5)OH$ was placed onto an aqueous subphase of water doubly distilled from deionized water (>12 MΩ). The temperature of the water subphase was kept at 20 °C. After the chloroform was permitted to evaporate, the monolayer was compressed at a constant rate of 20 cm^2min^{-1}. The π-A isotherm of $C_{16}H_{33}ONaPh(1,5)OH$ was shown in figure 1. The first monolayer was transferred by the vertical dipping method onto CaF_2 plates (for UV-vis and infrared transmission measurements), or gold-evaporated glass slides (for infrared reflection-absorption measurements) and the successive monolayers were transferred by the horizontal method at given pressure. The substrates used had been subjected to ultrasonifications in chloroform and then in distilled water. The transfer ratio was found to be nearly unity throughout the experiments.

Spectroscopy:

UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. For polarization measurements, a Glan-Thompson prism was used. The polarized UV beam was incident upon the LB film at the angle of 60° from the surface normal. Infrared spectra were measured on a Bruker IFS-66V spectrophotometer equipped with a liquid nitrogen cooled MCT detector. The spectra were taken at a 4 cm^{-1} resolution, and typically 512 interferograms were coadded to yield a spectra of high signal-to-noise ratio. For the FT-IR reflection absorption(RA) measurements, a home-made reflection attachment was employed at an incidence angle of 80 °, together with a KRS-5 polarizer.

To measure both UV-vis and infrared spectra at elevated temperature, the CaF_2 substrates on which the LB films had been deposited were inserted into a sample holder in a copper block that contained a ceramic heater. Temperature control contained a ceramic heater. Temperature control was achieved by using Shanghai DWT-702 temperature controller. The temperature was monitored with a thermocouple connected with the sample holder and raised by 1 °C/min.

RESULTS AND DISCUSSION

1. Surface Pressure -Area Isotherm

The surface pressure-area (π-A) isotherm of $C_{16}H_{33}ONaph(1,5)OH$ (figure 1) shows that the collapse pressure at about 45 mN/m is higher than 40 mN/m of the $C_{12}H_{25}ONaPhOC_6N(CH_3)^+Br$ and much lower than 55 mN/m of stearic acid (7). It can be extrapolated that the area occupied by the. head group of each

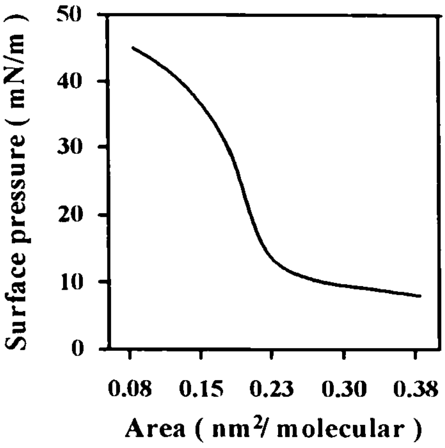

Figure 1. Surface pressure-area (π-A) isotherm of spread monolayers of the $C_{16}H_{33}ONaphOH$ on pure water at 20 °C

$C_{16}H_{33}ONaph(1,5)OH$ molecule in the solid state film is about 0.25 nm², which is smaller than the similar amphiphile $C_{12}H_{25}ONaphOC_6N(CH_3)^+Br^-$, 0.41 nm²[7] and bigger than the stearic acid, 0.2 nm². So it can be expected that the ordered arrangement of alkyl chain is lower than the stearic acid and higher than $C_{12}H_{25}ONaph\ OC_6N(CH_3)^+Br$.

2. UV-vis Absorption Spectra

Part (b) and (c) of figure 2 show UV-vis adsorption spectra of one- and eleven-monolayer LB films of $C_{16}H_{33}ONaph(1,5)OH$, respectively. In figure 2 the spectrum of $C_{16}H_{33}ONaph(1,5)OH$ in an ethanol solution is also presented as spectra (a) for comparison purpose. The UV-vis adsorption spectra of $C_{16}H_{33}ONaph(1,5)OH$ are characterized by three weak bands near 297, 315, and 329 nm and two intense bands at 230 and 245 nm. An absorption bands at 226

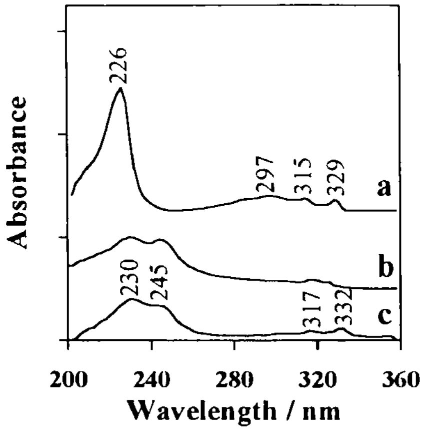

Figure 2. UV-vis absorption spectra of $C_{16}H_{33}ONaph(1,5)OH$ in an ethanol solution (a), 1-monolayer (b), and 11-monolayer LB film (c)

and 297 nm in spectrum of solution (figure 2(a)) are assigned to ^1B_b and ^1L_a of monomer which have the electronic transition moment roughly parallel to the long axis of naphthalene chromophore, while the bands at 315 and 329 nm are assigned to ^1L_a of aggregate which have electronic transition moment roughly parallel to the short axis of naphthalene chromophore. Similarly, the bands at 230 nm in spectra of figure 2(b) and (c) are assigned to ^1B_b of monomer while the bands at 245, 317, and 332 nm are assigned to ^1B_b and ^1L_a of aggregate. Of note is that a new band at 245 nm show in spectra of LB film of $C_{16}H_{33}ONaph(1,5)OH$, this new band is due to formation of aggregate in the film.

This result suggests that the monomer is the main content in the solution and much more aggregates in the LB films. Comparing the spectra of (b) and (c), it is clear that the contents of aggregates increase with the number of monlayer.

The polarized UV-vis absorption spectra of 11-monolayer LB film show that the absorption in s-polarized is much stronger than that of p-polarized. The orientation angle of chromophores were obtained by measuring the polarized UV-vis absorption spectra of 1-, 3- and 11-monolayer with the incident angle of 60 °, which are tabulated in Table 1. It is noted that the values for monolayer and multilayer LB films are almost the same, suggest that the orientation of chromophores is the similar in each monolayer.

Figure 3 depicts temperature-dependence changes in UV-vis spectra of the 11-monolayer LB film of $C_{16}H_{33}ONaph(1,5)OH$. It can be seen in figure 3, the films give a gradual spectra change. The bands at 245 nm assigned to aggregate shows a gradual intensity decrease up to 80 °C and above 80 °C, this band almost disappear, while the band at 230 nm give a gradual intensity increase upto 80 °C. Above 80 °C, the intensities of all the bands of LB film in figure 3 decrease gradually. The spectrum obtained at 110 °C is close to that of the solution. This result suggests that the aggregate breaks into monomers slowly with temperature.

The temperature-dependence spectra changes in the 3- and 11-monolayers LB films are similar to each other. The spectrum of the one-monolayer film remains unchanged upto 110 °C. This point suggests that the multi-monolayer LB films of $C_{16}H_{33}ONaph(1,5)OH$ show a phase transition near 80 °C while the one-monolayer LB film does not show a clear phase transition. Thus it is difficult to form the aggregate and also difficult for the aggregate to break into monomer in the 1-monolayer LB film.

TABLE 1. Orientation Angles of Chromophores of 1-, 3-, and 11-Monolayer LB Films of $C_{16}H_{33}ONaph(1,5)OH$

layer numbers	angle
1	31.0°
3	32.5°
11	34.0°

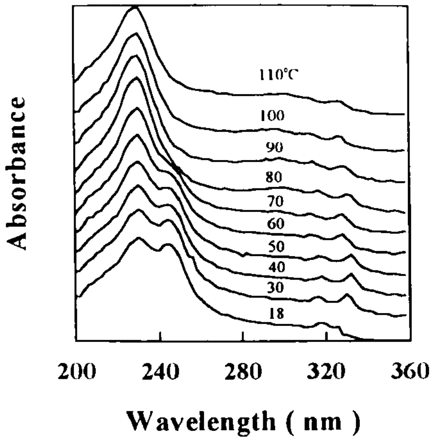

Figure 3. Temperature-dependent changes in the UV-vis absorption spectra of 11-monolayer LB film of $C_{16}H_{33}ONaph(1,5)OH$

3. Infrared Spectra

Figure 4(a) and (b) depicts the infrared transmission and infrared reflection absorption (RA) spectra of 9-monolayer LB films of $C_{16}H_{33}ONaph(1,5)OH$. An infrared spectrum of the $C_{16}H_{33}ONaph(1,5)OH$ in a solid state is also shown at the bottom of figure 4(c) for comparison. The infrared transmission spectra were also measured for 1-, 3-, 5-, 7-, and 11-monolayer LB films of the $C_{16}H_{33}ONaph(1,5)OH$. (The spectra are not show here). The assignment of the spectra are listed in Table 2.

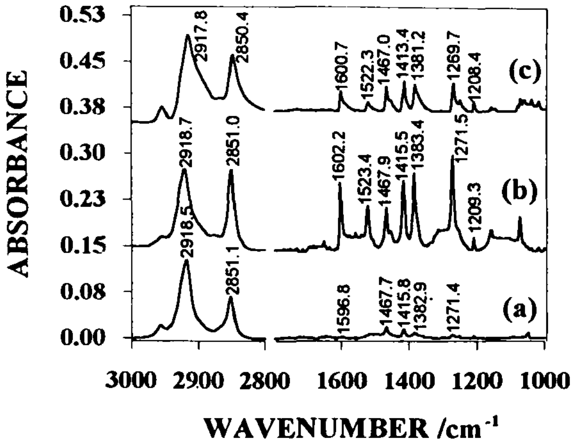

Figure 4. Infrared transmission(a) and infrared reflection absorption(b) spectra of 9-monolayer LB films of $C_{16}H_{33}$ONaph(1,5)OH and an infrared spectrum of the $C_{16}H_{33}$ONaph(1,5)OH in a solid state(c)

TABLE 2. Wavenumber of Infrared Transmission Spectra of $C_{16}H_{33}$ONaph(1,5)OH in Solid State and LB film

transmission in solid state	reflection absorption	transmission in LB films	Assignment
2953.5	2954.7	2954.6	CH_3 asym. Stretching mode
2917.8	2918.7	2918.5	CH_2 asym. Stretching mode
2850.4	2851.0	2851.1	CH_2 sym. Stretching mode
1600.7	1602.2	1596.8	ring C=C stretching mode
1522.3	1523.4		ring C=C stretching mode
1467.0	1467.9	1467.7	CH_2 deformation mode
1413.4	1415.5	1415.8	ring C=C stretching mode
1381.2	1383.4	1382.9	ring C=C stretching mode
1269.7	1271.5	1271.4	ring (=)C-O asym. stretching
1208.4	1209.3	1209.0	ring C-H def. In plane

Bands at 2918 and 2850 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chain of $C_{16}H_{33}$ONaph(1,5)OH, respectively. The frequencies of the CH_2 stretching bands are sensitive to the conformation of hydrocarbon chain; low frequencies (2920 and 2850 cm^{-1}) of the bands are characteristic of a highly ordered (trans-zigzag) alkyl tail, while their upword shift are indicative of the increase in conformational disorder, i.e. gauche conformers, in the hydrocarbon chain.(8,9) The CH_2 stretching bands appear at 2918 and 2850 cm^{-1} in the infrared spectra suggesting that the hydrocarbon chain of $C_{16}H_{33}$ONaph(1,5)OH is ordered, i.e., trans-zigzag in multi-monolayer (figure 4 a).

Of note is that the bands of the CH_2 stretching mode in the one-monolayer were appear in higher frequency. Another notable point is that the spectra of 3-, 5-, 7-, and 9-monolayer LB films are similar to each other except for band intensities which increase with the number of monolayers. This result suggest that the structure of the LB films changes little with the number of monolayer.

According to the surface selection rule in infrared RA spectroscopy, vibrational modes with their transition moments perpendicular to the surface are enhanced in a RA spectrum. Therefore the molecular orientation of the alkyl chain can be discussed from the intensities of its CH_2 antisymmetric and symmetric stretching bands(8-12). If the alkyl chain is nearly perpendicular to the substrate surface, both bands should appear strongly and weakly in the transmission and RA spectra, respectively. In contrast, if both molecular axis and plane of the alkyl chain are nearly parallel with the substrate surface, the band due to the CH_2 symmetric stretching mode is observed strongly and weakly in the transmission and RA spectra, respectively, while the band due to its antisymmetric counterpart is seen inversely. In addition, if the molecular axis of the alkyl chain is nearly parallel with the substrate surface with its molecular plane nearly perpendicular it, completely reverse spectral patterns from those right above are observed. The intensity ration of the two CH_2 stretching bands at 2918 and 2850 cm^{-1} (I_{2918}/I_{2850}) are 0.47 and 0.89 for transmission and RA spectra. This means that the CH_2 symmetric stretching bands are enhanced largely. Therefore , the observations indicate that the alkyl chain is tilted considerably in the LB film(9). The present results are in good agreement with the orientation angle calculated from polarized infrared ATR spectra(13).

As for the molecular orientation of the chromophore, the intensities of the five infrared bands show at 1600, 1523, 1415, 1382, and 1273 cm^{-1}. Bands at 1595, 1525, 1415, and 1382 cm^{-1} are assigned to the naphthalene ring stretching mode. A band at 1273 cm^{-1} is assigned to ring-O-C antisymmetric stretching mode.

The relative intensities of the five bands are very strong in the infrared RA spectrum of $C_{16}H_{33}ONaph(1,5)OH$ LB films on the Au-evaporated glass slide (figure 4b) than that in the transmission spectrum. This result suggests that the four C=C and a (=)C-O stretching modes have their transition moments nearly in the surface normal. This means that the naphthalene ring plane is oriented approximately perpendicular to the substrate surface because the above five modes are in plane vibrational modes. The relative intensity of the 1415 cm^{-1} and others bands is changed between the transmission and RA spectra (figure 4). That is because the transition moments of the four C=C stretching modes have different directions in the naphthalene ring, those are parallel with molecular axis of the naphthalene ring and perpendicular to it, respectively.

A band near 1467 cm^{-1} is attributed to a CH_2 scissoring mode of the hydrocarbon. A singlet or doublet near 1465 cm^{-1} is assigned to a CH_2 scissoring mode of the alkyl chain. The CH_2 scissoring band has been known to be sensitive to the intermolecular interaction(14,15); its singlet appearance is characteristic of n-paraffins with a hexagonal subcell packing, while the splitting of CH_2 scissoring mode is indicative of an orthorhombic subcell packing. The CH_2 scissoring mode appears as a singlet band in the spectra of the films of $C_{16}H_{33}ONaph(1,5)OH$. According, it may be concluded that the alkyl chain is in a hexagonal subcell packing in the film of $C_{16}H_{33}ONaph(1,5)OH$.

Figure 5 show infrared transmission spectral changes in the 3100-2700 cm^{-1} region for 11-monolayer LB film of $C_{16}H_{33}ONaPh(1,5)OH$ prepared on the CaF_2 plate. The corresponding spectra were measured also for the one-, and three-monolayer LB films, but the spectra are not shown here. The three-monolayer film show temperature dependent changes in the infrared transmission similar to the 11-monolayer films. In figure 6, the frequencies of the CH_2 antisymmetric stretching bands are plotted as a function of temperature for the transmission spectra of the one- and eleven-monolayer LB films. It should be point out in figure 6 that the 11-monolayer LB film shows a sharp upword shift in the narrow temperature range near 60 °C, while the one-monolayer film does not give changes in frequency.

The temperature-dependent changes in the infrared spectra of the three- and eleven-monolayer LB films of $C_{16}H_{33}ONaPh(1,5)OH$ are completely different from

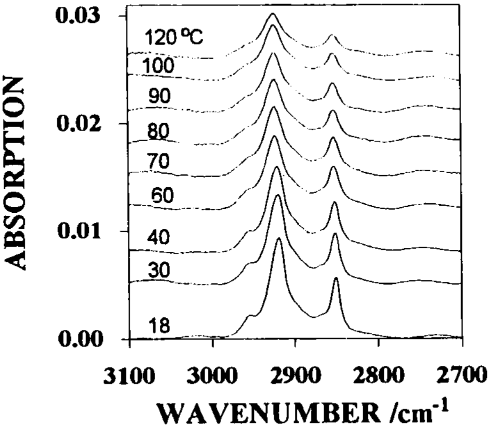

Figure 5. Infrared transmission spectral changes in the 3100-2700 cm^{-1} region for 11-monolayer LB film of $C_{16}H_{33}ONaPh(1,5)OH$ prepared on the CaF_2 plate

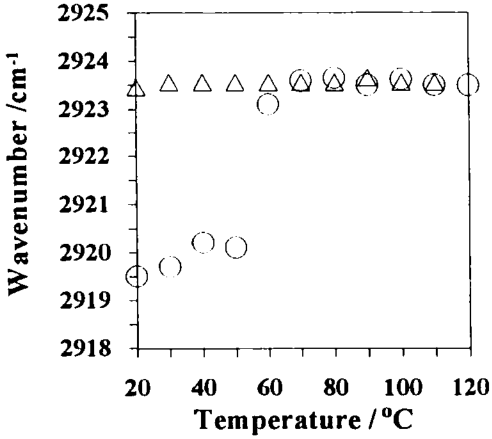

Figure 6 Temperature dependencies of the frequency of the CH_2 antisymmetric stretching bands of the one- and eleven-monolayer LB film of $C_{16}H_{33}ONaPh(1,5)OH$

those of the one-monolayer film. This difference in the thermal behavior between the one- and multi-monolayer LB films may be attributed to the interaction between the substrate and the first monolayer affects. If we compare the phase transition between the three- and eleven-monolayer LB films, it can be found that the phase transition occurs in the narrower temperature range in the eleven-monolayer LB film than in the three-monolayer. This also because the effect of the interaction between the substrate and the first monolayer.

CONCLUSION

1. The $C_{16}H_{33}ONaPh(1,5)OH$ molecules form the aggregates in the LB film, while the monolayer is the main content in the solution.
2. The aggregate gradually break into monomer upto 80 °C in multi-monolayer LB film. It is diffcult to form the aggregate and also diffcult for the aggregate to break into monomer in the one-monolayer LB film.
3. The hydrocarbon chain of LB films are tilted considerably, while the naphthalene ring plane is oriented approximately perpendicular to the substrate surface.
4. The one-monolayer LB film of $C_{16}H_{33}ONaPh(1,5)OH$ does not show a clear phase transition, while the multi-monolayer films do show a phase transition near 60 °C and 80 °C for hydrocarbon chain and naphthalene ring, respectively.

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