Preparation and Property of Langmuir-Blodgett Film of *N,N'-ω-p*-Xylene-bis-[stearyldimethylammonium chloride]

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The fabrication of Langmuir-Blodgett (LB) film of N,N'-ω-*p*-xylene-bis-[stearyldimethylammonium chloride] (XSAC) and the adsorption of α-naphthol orange (NO) molecules onto these XSAC LB films were investigated by FTIR and UV-visible spectroscopies. It was found that the adsorption of NO molecules onto the XSAC LB film took place selectively at the molar fraction of XSAC, 0.25 and NO molecules on the LB film were almost oriented parallel to the substrate surface.

Recently, cationic LB films containing long-chain alkylammonium salts have been attracting attention because of the specific adsorbability which is different from that of anionic LB films. In the previous papers,[1-3] we have prepared the cationic LB films of distearyldimethylammonium chloride and tristearylmethylammonium chloride by applying high surface pressure, and investigated the adsorbability of dye molecules onto these cationic LB films. The results indicated that dye molecules such as α-naphthol orange and methyl orange were considerably adsorbed on these LB films.

In the present work, we studied the fabrication of the dicationic LB films which are expected to have higher adsorbability, and examined structural characterization of these LB films by IR absorption spectroscopy. Furthermore, adsorbability of dye molecules onto these dicationic LB films was investigated by UV-visible spectroscopy.

XSAC($C_{18}H_{37}N^+(CH_3)_2$-CH_2-C_6H_4-CH_2-$N^+(CH_3)_2C_{18}H_{37}$) used as the dicationic film material was kindly supplied from Kao Co. Ltd., and was used without further purification. Dye material, NO was used as adsorbate. Also, when the monolayer was transferred on a substrate, octadecane was mixed with XSAC to enhance the lateral interaction between alkyl-chains. Miscibility of XSAC and octadecane in the monolayer was examined by measuring surface pressure-area (π-A) isotherms. Multilayer deposition was carried out by the conventional vertical dipping method under the condition of 15°C and 35 $mN \cdot m^{-1}$. The orientation angle of alkyl-chain and deposited amounts of XSAC on a substrate were measured by a FTIR spectrometer (JASCO FTIR-8900) equipped with MCT detector. For the adsorption experiments, the deposited LB films were dipped into 1.0 x 10^{-4} $mol \cdot dm^{-3}$ of aqueous NO solution for a given period of time. After establishing the adsorption equilibrium, the LB film was drawn up from the aqueous dye solution and the adsorbed amounts of NO molecules on the LB film were analyzed by using UV-VIS-NIR scanning spectrophotometer (Shimadzu Co. Ltd., UV-3100PC).

Figure 1 shows the π-A isotherms of XSAC/octadecane mixed monolayers spread on distilled water at various molar fraction of XSAC (X_{XSAC}).

The monolayer of X_{XSAC}=1.0 (pure XSAC monolayer) shows the typical expanded film, and the collapse pressure of about 40 $mN \cdot m^{-1}$ was observed irrespective of X_{XSAC}. Also, the molecular areas at a constant surface pressure proportionally decreased with decreasing X_{XSAC}, and these results suggest that

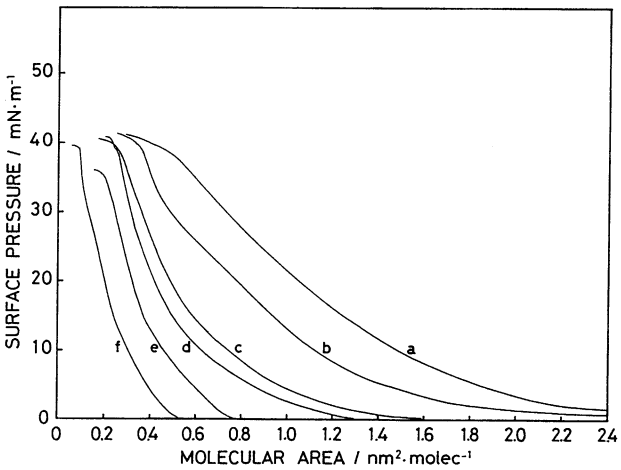

Figure 1. Surface pressure-area (π-A) isotherms of XSAC/octadecane mixed monolayers on distilled water at 20°C. X_{XSAC}; a:1.0, b:0.7, c:0.5, d:0.4, e:0.3, f:0.2

XSAC and octadecane are mixing ideally in the monolayer. Therefore, it is clear that the molecular density of XSAC does not change at any X_{XSAC}.

Figure 2 shows reflection-absorption (RA) and transmission IR spectra for 6 layers of XSAC LB film.

In transmission spectrum, three bands were observed at 2851 cm^{-1} and 2919 cm^{-1} for symmetric(υ_s) and antisymmetric stretching vibration(υ_a) of CH_2, respectively and 2954 cm^{-1} for $\upsilon_a(CH_3)$. We also measured the RA spectrum, in which five bands were observed at 2852 cm^{-1} for $\upsilon_s(CH_2)$, 2923 cm^{-1} for $\upsilon_a(CH_2)$, 2873 cm^{-1} for $\upsilon_s(CH_3)$ and 2968 cm^{-1} and 2958 cm^{-1}

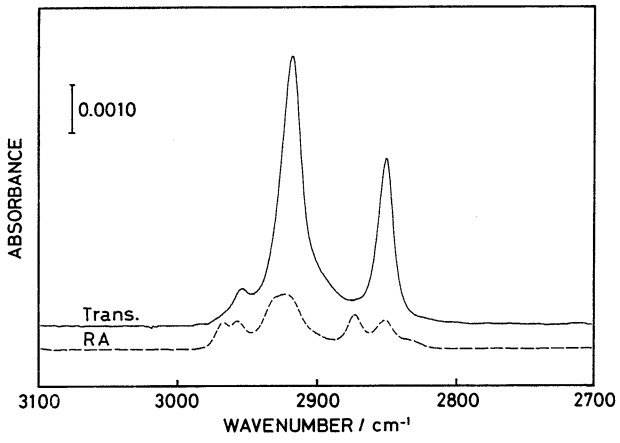

Figure 2. Infrared transmission and RA spectra of 6 layers of XSAC LB film at X_{XSAC}=0.25.

for $\upsilon_a(CH_3)$. The C-H symmetric and antisymmetric stretching vibration band were weakly observed in RAS, in which the electric field vector is perpendicular to the substrate, while these bands were strongly appeared in the transmission spectrum. This indicates that the alkyl-chain is nearly oriented perpendicular to the substrate surface. From the dichroic ratio between these IR transmission and RAS intensities, the orientation angle of alkyl-chains in the XSAC LB film could be evaluated quantitatively.[4] These angles of alkyl-chains in XSAC LB film were calculated to be about 4~11° from surface normal.

By using these LB films, the adsorption experiments were carried out. The amount of NO molecules adsorbed on the LB film surface was evaluated from the absorption intensity of UV-visible spectra. Figure 3 shows the relationship between the peak area at 474 nm of UV-visible absorption spectra and X_{XSAC}.

In this figure, although the first layer of XSAC LB film was ionically interacted with the glass surface, the adsorption of NO was appreciably found on the monolayer, and moreover, adsorbability of NO depended on X_{XSAC} at 5 or 9 layers.[5] Particularly, the maximum adsorption of NO was occurred at X_{XSAC}=0.25. Therefore, the adsorption characteristic of NO molecules was especially investigated for the distinctive state observed at X_{XSAC}=0.25.

For these LB films, polarized UV-visible absorption spectra were measured to estimate the orientation of NO molecules. The results are shown in figure 4.

In the case of spectra measured with p-polarized light, peak intensity did not change with variation of incident angles but the peak maximum indicated slightly blue shift, whereas in the case of s-polarized light, the peak intensity increases but is independent on the peak maximum. Since the long axis of NO molecule was assumed to be parallel with the transition moment of the molecule as shown by the molecular stracture in figure 4, above results indicated that the long axis of NO molecules were distributed almost parallel to the LB film surface. Moreover, tilt angles could be calculated from dichroic ratios of these spectra.[6] The tilt angles of NO molecules were about 70~80° from the surface normal.

By taking account of these orientation data, the amounts of XSAC and NO in adsorbed LB films can be obtained. The results are shown in Table 1.

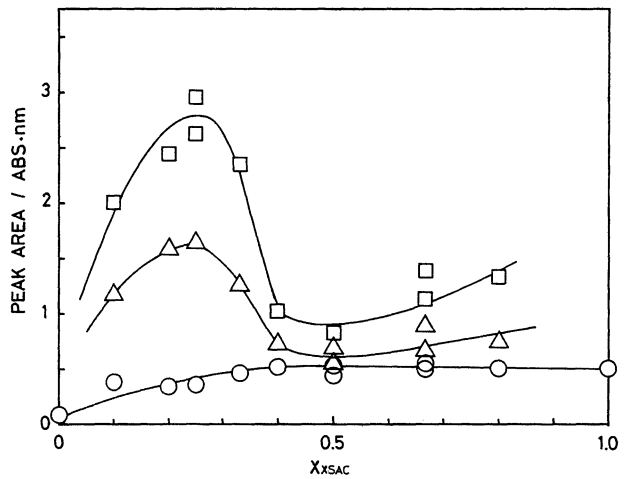

Figure 3. The adsorption characteristic of NO on XSAC LB film at various X_{XSAC}. ○: monolayer, △: 5 layers, □: 9 layers

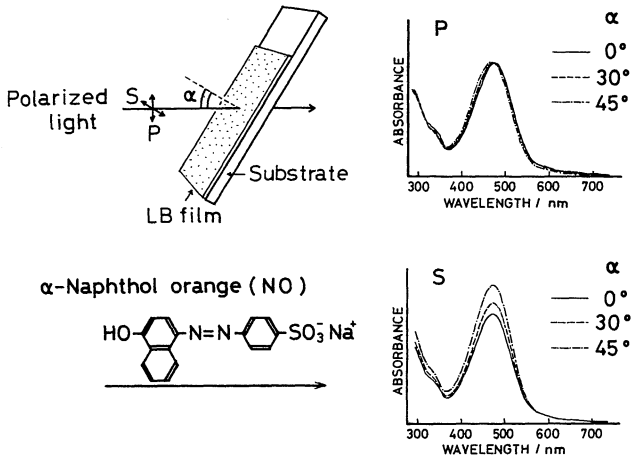

Figure 4. Polarized UV-visible spectral changes after adsorbing NO on XSAC LB films. α is an angle between the direction of incident light and the normal direction of the substrate.

Table 1. Molecular ratio of NO to XSAC in NO adsorbed LB films.

X_{XSAC}	Molecular ratio, XSAC : NO
0.25	1.00 : 1.07
1.00	1.00 : 0.65

NO was adsorbed on 9 layers of XSAC LB films at 20° C.

The molecular ratio of NO to XSAC was calculated to be 1 : 1 for the LB film prepared at X_{XSAC}=0.25, and 1 : 0.65 at X_{XSAC}=1.0. The decrease of adsorbed ratio of NO to the XSAC LB film is considered to be due to the difference in composition of the LB film. Accordingly, these results suggest that the sulfonate and hydroxyl groups in NO molecules interact with ammonium groups in the XSAC molecules. As a result, the NO molecules probably penetrated into the XSAC LB film, and laid in polar head group moieties of XSAC molecules in LB film.

In the present work, it can be concluded that 1) the monolayers of XSAC could be easily transferred onto a solid substrate by the addition of octadecane, 2) the adsorption of NO on the XSAC LB film took place selectively at X_{XSAC}=0.25, 3) NO molecules adsorbed on the LB film were tilted about 70~80° from the normal of substrate surface and 4) in the case of X_{XSAC}=0.25, NO molecules interacted with XSAC molecules at the ratio, XSAC : NO =1 : 1.07.

References and Notes

1 K. Tajima, M. Takahashi, and K. Kobayashi, *Thin Solid Films*, **178**, 381 (1989).
2 M. Takahashi, K. Tajima, and K. Kobayashi, *Thin Solid Films*, **221**, 298 (1992).
3 M. Takahashi, K. Kobayashi, and K. Tajima, *J. Jpn. Soc. Colour Mater.* **66**, 461 (1993).
4 J. Umemura, T. Kamata, T. Kawai, and T. Takenaka, *J. Phys. Chem.*, **94**, 62 (1990).
5 The number of layers conventionally indicates the operation times corresponding to the number of down or up stroke.
6 H. Akutu, Y. Kyogoku, H. Nakahara, and K. Fukuda, *Chem. Phys. Lipids*, **15**, 222 (1975).