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Spectroscopic and Structural Studies on Adsorption of Azo Dye in Cationic Langmuir–Blodgett Films

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The monolayer properties of octadecylamine at various pHs on the Naphthalene Red (NR) aqueous solution were studied from the measurements of surface pressure–area isotherms. It was observed that the presence of the azo dye substituted with the –OH group (NR) in the subphase affects the compressibility of the octadecylamine monolayer. The adsorbability of the cationic Langmuir–Blodgett (LB) films was investigated by NR as an adsorbate. The cationic LB films before and after the azo dye adsorption were characterized by UV–vis absorption and emission spectroscopy, polarized visible absorption, X-ray diffraction, FTIR spectroscopy, and atomic force microscopy. Strong dipole–dipole interaction between the NR molecules in functionalized LB films was observed in accordance with the exciton model. It was found that the adsorption of the azo dye induced rearrangement of the layer structure of the cationic LB films where the hydrocarbon chains of the amine molecules exhibited an interdigitated structure and the azo dye molecules adsorbed in the LB films were oriented in an edge-on configuration. Furthermore, the substituent position of the –OH group of NR plays a crucial role in the different ways on the orientation of the other azo dyes in organized assembly.

Organized molecular systems are of considerable interest both from fundamental and practical points of view.[1] The study concerning the adsorption on the Langmuir–Blodgett (LB) films has attracted much attention in recent years as the adsorption phenomenon is largely related to the properties of the LB film and the adsorption of molecules is controllable in molecular assemblies through its process. The LB technique allows one to prepare LB films containing water-soluble molecules.[2] On the adsorption process, ionic interaction is a strong attractive force between adsorbent and adsorbate. For this reason, an ionic adsorbent is expected to have high adsorbability for oppositely charged ionic substances. Attention has been focused on cationic LB films containing long-chain alkylammonium salts and alkyl-amine for their specific adsorbability which is not expected from the characteristics of anionic LB films.[3,4] Adsorption behaviour on the cationic LB films is considered to be governed also by various interactions, namely hydrophobic and dipole–dipole interactions in addition to the ionic interaction. Cationic film materials interact strongly with a variety of materials such as surfactants, polymers, dispersed materials, proteins, biological colloids, and lipids and then their mechanisms are very important in practical applications.[5] Formation of LB films of long-chain amine salts offers comparable, as well as complementary advantages in contrast to the fatty acid soaps which seem to be unusable for certain purposes such as incorporation of acid sensitive molecules.[6] The monolayer of octadecylamine is analogous to that of stearic acid but the deposition of cationic material monolayers to solid substrate is somewhat difficult,[7] which may be due to the ionization of the amino group to the ammonium ion. LB films of long-chain alkylamines were prepared by weakening the charge repulsion among the polar head groups, and by determining suitable deposition conditions like the pH, temperatures and the anionic dye concentration of the aqueous subphase, and the surface pressures.[8,9] These films were found to retain their cationic properties. Site-selective binding of the anionic molecules is possible by ionic adsorption process on these cationic films. However, little information is available about the specific adsorbability of the cationic materials. Recently, the authors have investigated with fabrication of organized molecular films containing functional dyes such as Alizarine Violet (AV) and Sulforhodamine B (SRB) in cationic LB films.[10,11]

Among various azo dyes, in this work we study on the adsorption behavior of Naphthalene Red (NR) on the octadecylamine LB film instead of α-Naphthol Orange (NO) and Methyl Orange (MO) used in the previous work by Takahashi et al.[9] The azo dyes have been of immense interest as one of the film forming materials due to their interesting functional properties such as *cis-trans* isomerization and also the potential application for a molecular switch and optical memory.[12,13] Moreover the different orientation types of the azobenzene chromophores in the interfacial films were controlled by variation in numbers and substituent positions of the long alkyl chain.[14] These systems have extensive applicability as a model for dye aggregates; they can also act as probes designed for molecular organizations with photoelectric functions. In this paper, we report on the adsorption behaviour of Naphthalene Red on the octadecylamine LB film. The interaction between the dye and the long chain cationic material at the air/water interface indicated the change in compressibility of the monolayers. Different spectroscopic methods have been used to elucidate the adsorption behaviour and the photophysical properties of the azo

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dye in functionalized LB films. Furthermore, the orientations of the azo dyes in organized assembly are strongly dependent upon the chromophores such as the –OH substituent at different positions. This remarkable change in orientation of the anionic azo dye molecules in organized assemblies occurs due to the change in the hydrophobic behavior of the molecule in contrast to the previous works.[9] Also a strong dipole-dipole interaction has been found in the NR molecules adsorbed on LB films. On adsorption of the dye in the cationic film the change in the layer structure has been observed by X-ray diffraction analysis. Morphological and topographic changes on the mono- and multilayers of octadecylamine films on adsorption of the anionic azo dye were studied by atomic force microscopy (AFM).

Experimental

Octadecylamine and Naphthalene Red (NR) were purchased from Tokyo Chemical Industry ltd. Octadecylamine were recrystallized several times from ethanol solutions. NR was used as received, however the purity was checked by electronic absorption spectroscopy. The molecular structures are given in the insets of Figs. 1A and B. Distilled water (pH $\approx$ 5.8 at 20 °C) deionised by a Milli-Q water purification system and having a resistivity of 18.2 MΩ-cm was used. The pH's of the aqueous subphase were varied at about 10.3 and 3.1 with addition of $NaOH_{aq}$ and HCl_{aq}, respectively just before the measurements. Octadecylamine was dissolved in choloroform and was used as the spreading solution. The monolayers were spread from a chloroform solution on the distilled water and various pH's aqueous subphase, and on the aqueous NR solution (1×10^{-4} M). After allowing fifteen minutes for the chloroform to evaporate, the monolayer at the air/water interface was compressed slowly. Surface pressure - area isotherms were measured by a Langmuir-type film balance (Lauda) at 20 °C and various pH's. The octadecylamine monolayers formed on the distilled water subphase (pH $\approx$ 10.3, $T = 20$ °C) were compressed to a surface pressure of 45 mN/m and subsequently the monolayer was transferred by the LB technique onto the solid substrate. The dipping rate was 7 mm/min for both up and down strokes. Sufficient time for drying the film in air was given in the subsequent transferring the monolayers to the solid substrate. Quartz plates were used as substrates for UV-visible absorption and emission spectroscopy. Calcium fluoride (CaF_2) plates, coated by five layers of cadmium arachidate to make the surface hydrophobic were used for transmission FTIR measurement. Glass plates coated with iron(III) stearate were used for X-ray diffraction. Adsorption of the azo dye was determined by immersing the octadecylamine LB film into the aqueous solution (1×10^{-4} M, pH $\approx$ 6.2) of NR for a given period of time. We used the NR-adsorbed octadecylamine LB films for spectroscopic and structural studies. The electronic absorption spectra of the LB films were recorded on a Hitachi U-3210 spectrophotometer. Fluorescence emission spectra of the LB films were recorded on a Hitachi MPF-3 fluorescence spectrophotometer. FTIR spectra were measured with a Perkin-Elmer FTIR spectrophotometer with a TGS detector. Values of the long spacing for the layered structures of the built-up films on glass plates were measured by an X-ray diffractometer (Rigaku, Rad-B, Cu $K\alpha$ radiation, 40 kV, 30 mA) equipped with a graphite monochromator. AFM images were recorded on a Seiko SPA300 in air and under ambient conditions. We used microfabricated rectangular Si_3N_4 cantilevers with integrated pyramidal tips with a given force constant of 0.09 N/m.

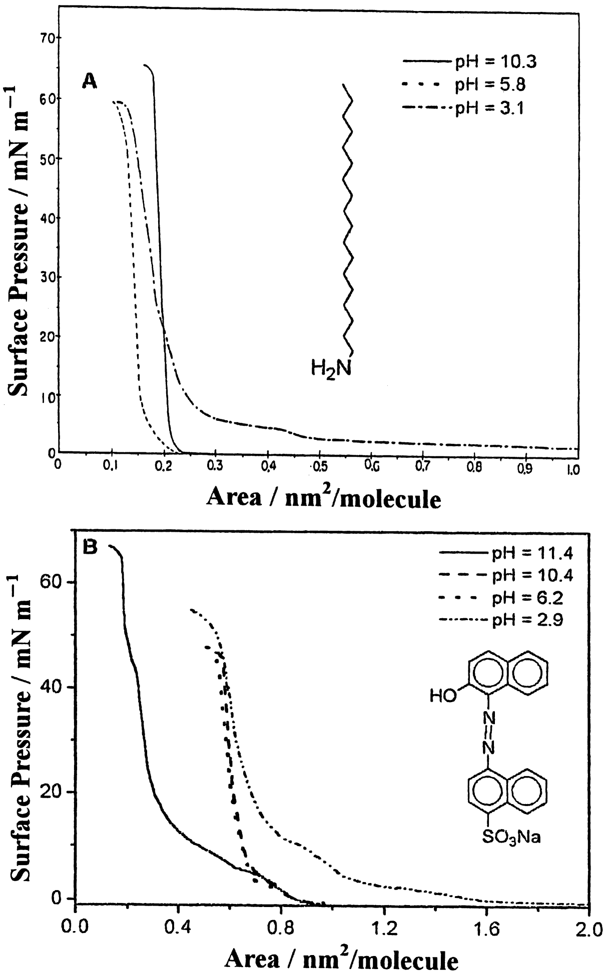

Fig. 1. (A) Surface pressure–area isotherms of octadecylamine monolayers on a distilled water subphase at pH 3.1 (with HCl_{aq}), 5.8 (pure water), and 10.3 (with $NaOH_{aq}$). (B) Surface Pressure–area isotherms of octadecylamine monolayer on NR aqueous subphase (1×10^{-4} M) at different pH's of 3, 6.2, 10.4, and 11.4. Insets show the molecular structures of octadecylamine and NR molecules in panel A and B, respectively.

Results and Discussion

1. Monolayer of Long Chain Alkylamine on Aqueous Subphase Containing NR Dye.

Figure 1A shows the surface pressure versus area per molecule (π–A) isotherms of the octadecylamine monolayer on the aqueous subphase at various pH values. When the octadecylamine monolayer was spread on the just distilled water (pH = 5.8) without any ions, it is apparent the long-chain amine forms a condensed monolayer with a relatively small molecular area, which can be considered to be due to a little hydrophilicity of the amino-group, being hydorated only in part. It is evident that protonation of octadecylamine occurs in the acidic region, leading to formation of an expanded monolayer with large compressibility at about pH 3 with HCl_{aq}, whereas a typical condensed phase behavior was observed at pH 10.3 with $NaOH_{aq}$. These isotherms are well consistent with those in the early works.[8,9,15] The value of pK = 9.9 for a long-chain amine monolayer was estimated from measurements of surface potential changes of the monolayers by Betts and Pethica.[15] At basic pH the protonation of the amino group in the octadecylamine molecule is practically forbidden.[15] These results were confirmed by IR spectra of the deposited films obtained at different pH's of the aqueous subphase. Figure 1B presents π–A isotherms of the octadecylamine monolayer on the aqueous subphase containing NR molecules (1×10^{-4} M/L). Comparing Fig. 1B with Fig. 1A, it is clear that the presence of NR dye in the aqueous subphase expands the monolayer of the long-chain amine and affects their compressibility, i.e. the slope of the isotherms in different ways. These results suggest that the octadecylamine molecule is interactive with the NR molecule. The calculated molecular areas of NR for edge-on and flatwise orientations are 50 Å^2 and 150 Å^2, respectively.[16,17] It was reported that the NR molecule appears to penetrate the film among the protein chains.[18] In the present case (Fig. 1B), the extrapolation to zero surface pressure gives a molecular area of 73 Å^2 approximately for pH of 10.4 on the aqueous subphase containing NR whereas a molecular area of 22 Å^2 has been obtained on the distilled water subphase without NR (Fig. 1A, pH 10.3). It seems that the NR molecule causes the slope less steep, this change may be due to a penetration of dye molecules with nearly vertical orientation, between the long-chain amines of the monolayer at a pH of 10.4. In addition, the monolayer on the aqueous subphase reveals a decrease in the molecular area at pH 11.4. The equilibrium constant of the complex formation can be quite large due to ionic interaction and in the process the NR adsorption on the amine monolayer considerably occurs upto pH 10.4. At higher pH of 11.4, the adsorption of the anionic dye is limited because the degree of ionization of the amino group has decreased.

2. Spectroscopic Studies of NR on Cationic LB Films. Figure 2 shows the UV-vis absorption spectra of the NR dye in ethanol (1×10^{-5} M) with the peak at 512 nm in the 350–600 nm region. This band is assigned to the π–π^* transition moment of the NR molecule which is parallel to the long axis of the azo chromophore.[19] The absorption bands centered at 230 nm corresponds to the $^1L_a \leftarrow {}^1A$ transition whereas the band at 323 nm represents the $^1L_b \leftarrow {}^1A$ transition of the naphthalene chromophore.[20] The absorption spectra of the cationic LB films of different numbers of layers containing the NR molecules show the absorption bands in the 370–600 nm region. The electronic absorption spectra for the LB films in the long wavelength region with band at 425 nm and a shoulder at 590 nm are markedly different from the solution spectrum suggesting the closer association of the molecules in the LB films that resulted in the formation of two-dimensional aggregates. The change in the absorption spectra of LB films with respect to those in solution can be explained in terms of the intermediate strength exciton coupling theory.[21] In accordance with the exciton model[20] the dipole-dipole interaction between the neighboring molecules results in the generation of an exciton band which is considered to be located either above or below the monomer exciton band. In the present case, new exciton bands in LB films containing NR molecules have been developed at 425 nm and a shoulder at 590 nm. The magnitude of the spectral shift is expressed as:

$$\Delta\nu = \frac{2}{hc}\left(\frac{N-1}{N}\right)\frac{\mu^2}{r^3}\left(1-3\cos^2\alpha\right) \tag{1}$$

where $\Delta\nu$ is spectral shift in wavenumber from the linear aggregate to the monomer, h is the Planck's constant, c is the velocity of light, N is the number of monomers in the aggregates, μ is the transition dipole moment, r is separation distance between the molecular centers and α is angle between the dipole moment of the molecules and the line joining the center of the neighboring molecules in the aggregates. We used this model to estimate the aggregates in LB films qualitatively. According to this equation, a red-shift in the absorption spectra occurs for $\alpha < 54.7°$, while for $\alpha > 54.7°$ a blue-shifted band is observed. In the present case a blue-shifted band at 425 nm in NR adsorbed LB films compared to the monomer band at 512 nm in solution; the comparison suggests a rather vertical orientation of the transition moment along the long axis of the NR molecule in dye adsorbed functionalized LB films. On the other hand, the absorption bands in the 282 and 317 nm occurred in ethanol solution are slightly red-shifted in LB films and the intensities of the vibronic bands of the naphthalene chromophore corresponding to the ^1L_a and ^1L_b state respectively, changed somewhat in the LB film compared to that in solution. This indicates the role of molecular ordering in the LB films.

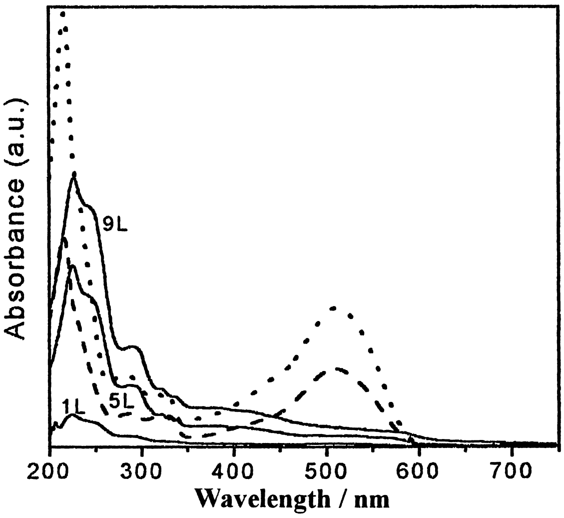

Fig. 2. Absorption spectra of NR in aqueous solution (dashed line), ethanol (dotted line), and NR adsorbed octadecylamine LB film for different numbers of layers (solid line).

Figure 3 shows the emission spectra of NR in ethanol (1×10^{-5} M) with a band centered at 595 nm ($\lambda_{ex} = 500$ nm) that corresponds to the S_1–S_0 transition and is directed parallel to the long axis of the molecule. The fluorescence spectrum of the 9 layer octadecylamine LB film adsorbed in the NR solution (1×10^{-4} M) shows a broad band centered at 620 nm and a shoulder at 665 nm. The fluorescence spectrum of the NR molecules in LB films is red-shifted and broadened compared to that in the solution. The red-shift and broadening of the emission spectrum suggests aggregation of the NR molecule in the cationic LB films. The excitation spectra of NR in the ethanol and NR-adsorbed LB films obtained by monitoring the band maximum of the fluorescence emission are also shown in Fig. 3. The excitation spectrum of NR in the ethanol shows a

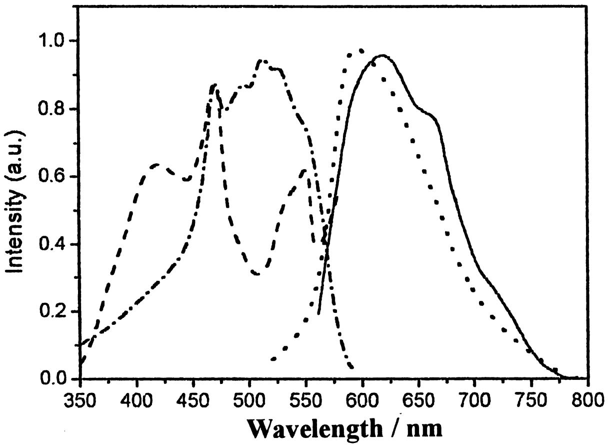

Fig. 3. Emission spectra of NR in ethanol (·········) and NR in nine layer LB film (————). Excitation spectra of NR in ethanol (—•—•—) and NR in LB film (– – – –).

broad band in the region 450–570 nm with some vibronic bands. The dye adsorbed LB film spectrum in the 400–570 nm region, on the other hand, shows distinct bands 417, 470 and 548 nm of the transition moment directed parallel to the long axis of the molecule. The large difference observed between the excitation spectra of NR in the ethanol and in the cationic LB films suggests the molecular association, packing, and site-specific orientation of the NR molecules in the organized films. In the excitation spectrum of LB films a clearly blue-shifted band at 417 nm in comparison with the solution excitation spectrum also suggests the strong dipole–dipole interaction of the molecules in the organized assembly. The excitation spectrum further indicates the vertical orientation of the long axis of the NR molecules complementing isotherm studies at the air–water interface. In other words, the octadecylamine LB film has an appropriate microenvironment to facilitate the well-organization of the NR molecules.

3. Adsorption Behavior of NR on Cationic LB Films. It is expected that the transferred LB film of octadecylamine is capable of interacting with the NR molecule in the aqueous solution as observed from the isotherm measurements. Different numbers of layers of LB films of octadecylamine were deposited on the quartz substrate at a pH of 10.3 to evaluate the adsorbability of the LB films by using the NR molecule as an adsorbate. Adsorption behaviour of NR has been monitored by immersing the octadecylamine LB films onto the aqueous solution of NR (1×10^{-4} M) for a particular period of time. To quantify the amount of adsorption of NR molecules in the cationic LB films, UV-vis absorption spectra of the NR adsorbed on nine-layered octadecylamine LB films have been measured. UV-vis absorption spectra of the NR adsorbed on nine layered octadecylamine films at various immersing times are given in the inset of Fig. 4. The adsorption characteristic of NR is shown in Fig. 4. The intensity of the absorption peak increased with increasing the immersing time and the adsorption equilibrium is achieved after approximately 60 minutes. Since the intensity of absorption corresponds to the adsorbed amount of NR molecules in the LB films, this indicates that the adsorbed amount of NR gradually increased with increasing immersing time. In the first step of the adsorption process, the NR molecules move toward the octadecylamine LB film in a fast diffusive process. After this period, the few adsorbed molecules must change their conformation in order to make room for the other molecules. This is a slow process because the steric and electrostatic hindrance must be overcome. The quantitative dependence of adsorption amount of NR in the octadecylamine LB film was also determined by monitoring the UV-visible absorption spectra of the dye-adsorbed LB film for different numbers of layers. It has been found that the specific adsorbability of NR increases with increasing the number of layers (up to 9 layer). The adsorbed amount of the NR dye shows a constant absorbance above nine layers. This suggests that the NR adsorption quantitatively occurs with the deposited amount of cationic material on the substrate. With increasing the number of octadecylamine layers, it has been observed that the complete adsorption of the NR dye required longer immersing time. Therefore, the penetration of the NR dye into the cationic LB film is rate-determining step in the adsorption process.

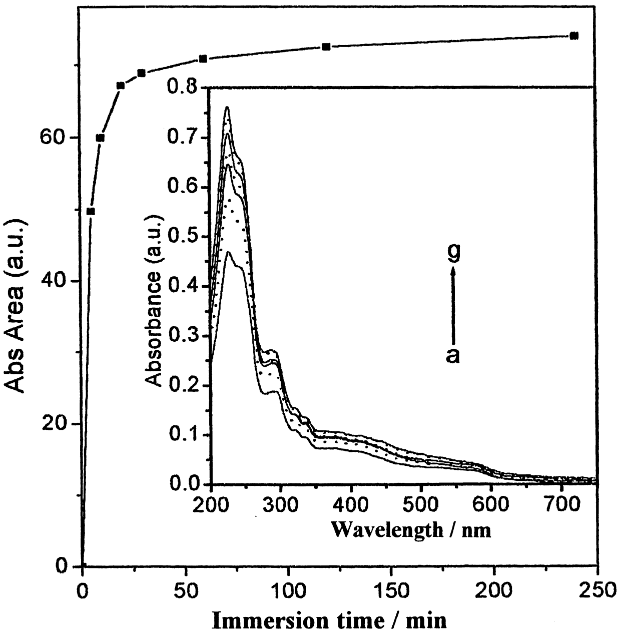

Fig. 4. Adsorption isotherm of NR in nine layer octadecylamine LB film: absorbance area versus immersion time. Inset presents the UV-vis absorption spectra of the dye adsorbed on 9 layer octadecylamine LB film at various immersion time (a) 5, (b) 10, (c) 20, (d) 30, (e) 60, (f) 120, and (g) 240 minutes.

4. Orientation of the Adsorbed NR Molecule in Cationic LB Films. The UV-visible absorption of NR in the LB films from the π–π^* transition is sensitive to the direction of polarization of an incident light, which enables the use of polarized light to probe the structural anisotropy within the films. Polarized visible absorption[23,24] or infrared transmission[25] and attenuated total reflection spectroscopy[26] can provide an indication of the order and orientation of the LB films deposited on solid substrate. In the present case, the orientation of NR molecules in the LB films has been estimated by polarized visible absorption spectra. The electric vector, parallel to polarization direction, of the incident radiation is perpendicular or parallel to the

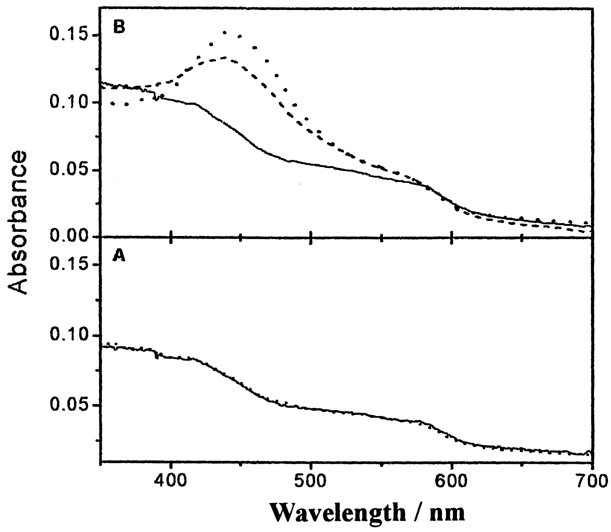

Fig. 5. Polarized absorption spectra of NR adsorbed octadecylamine LB film at an incidence angle of (A) 0° and (B) 45°. Solid and dotted line indicate the absorption spectra for *s*- and *p*-polarized light, respectively. Dashed line indicates the spectra for unpolarized light.

dipping direction. Figure 5 illustrates the spectra measured for nine layers of NR adsorbed octadecylamine LB films at two incident angles. At the normal incidence ($i = 0°$), the absorption intensities for the *p*- and *s*-polarized lights are almost same, suggesting the vectors representing the transition dipole moments along the long-axis of the NR molecules are uniformly distributed over the film surface and make a constant angle with the surface normal (uniaxial orientation). When the film is tilted 45° away from the normal direction, the absorption under the *p*-polarization mode is the strongest, while that under the *s*-polarization mode is the weakest. These observations suggest the preferential order and arrangement of the NR molecules in cationic LB films. A band centered around 443 nm as clearly evident from Fig. 5B, was observed for the *p*-polarized light and unpolarized light further suggesting the specific orientation and strong dipole–dipole interaction between the chromophores of NR molecules in LB films. This anisotropic behavior of the blue-shifted band in LB films also indicate that the angle between the dipole moments of the molecules with the line joining the center of the neighbouring molecules in the linear aggregates is greater than 54.7°. Molecular orientation of the NR molecule in the octadecylamine LB film was evaluated by considering the four-phase system. Phase 1 is the incident air phase, phase 2 is the LB film containing the NR molecule, phase 3 is the quartz substrate, and phase 4 is air. Assuming the uniaxial orientation of the transition dipole moment with the angle θ toward the surface normal, the ratio between *p*- and *s*-polarized intensities is given by[27,28]

$$\frac{A_p}{A_s} = \frac{n_1\cos i + n_3\cos r}{n_1\cos r + n_3\cos i}\left\{\cos i\cos r + \frac{2n_1^3 n_3\sin^2 i}{n_2^4\tan^2\theta}\right\} \quad (2)$$

where the refractive indices of four phases are $n_1 = 1.00$ (air), $n_2 = 1.50$ (LB film), $n_3 = 1.54$ (substrate), i is the angle of incidence at the LB film, r is the angle of refraction at the interface of LB film and substrate that can be evaluated from $n_1 \sin i = n_3 \sin r$, and θ is the tilt angle of the transition dipole moment of the NR dye chromophore with respect to the surface normal. Since the direction of the transition dipole moment of the NR chromophore is assigned along the long axis, this measurement shows that the NR chromophore is tilted at an angle of 28° from the surface normal. This tilt angle (28°) and the mean molecular area of octadecylamine on the NR aqueous subphase from the π–A isotherm (73 Å^2 at pH 10.4) suggest that the NR chromophores are arranged nearly perpendicular to the substrate surface. It is worth to note that the orientation of the azo dyes at the air/water interface and LB films are remarkably different depending upon the nature of the molecule, the hydrophobicity–hydrophilicity of the –OH group and their substituted positions, according to the facts that α-Naphthol Orange molecules adsorbed in cationic LB films are oriented in a lying-flat configuration[9] whereas the NR molecule are oriented in an edge-on configuration although the structure of the molecules are very much similar. As confirmed by the polarized electronic absorption spectra, this can occur due to two plausible reasons: (i) NR molecule is a rigid rod like molecule which is preferentially oriented to accommodate between the octadecylamine molecules and (ii) the difference in position of the –OH group at the end opposite to the sulfonate group changing the hydrophilic nature of the NR molecule compared to the α-Naphthol Orange molecule.

5. Structural Characterization of NR-Adsorbed Octadecylamine LB Films. The regular transfer of octadecylamine monolayer on the calcium fluoride (CaF_2) plate was confirmed by FTIR transmission spectra of the octadecylamine LB films of different number of layers. Figure 6 shows the FTIR transmission spectra for eight layers of octadecylamine on a CaF_2 plate before and after the NR adsorption. The IR transmission spectrum of crystalline NR in KBr pellet has also been presented in Fig. 6C for comparison. The CH_2 symmetric and antisymmetric stretching vibration bands due to the hydrocarbon chains of the octadecylamine molecule appear at 2850 and 2919 cm^{-1} respectively and these absorbances increased lin-

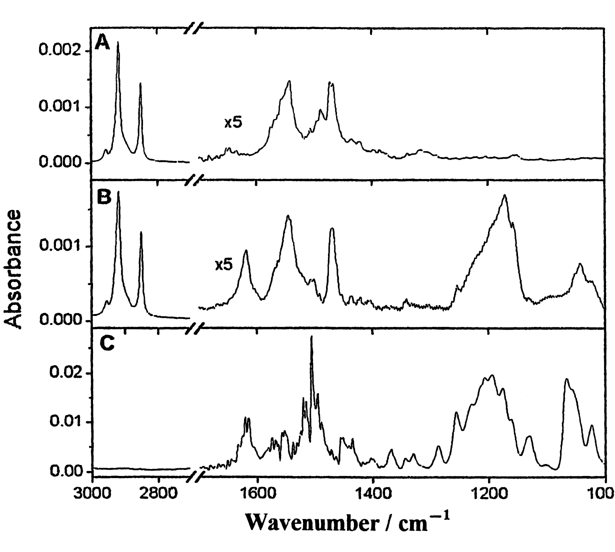

Fig. 6. FTIR transmission of spectra of (A) octadecylamine LB film, (B) octadecylamine LB film after NR adsorption and (C) NR in KBr pellet.

early with increasing number of layers. Most of the hydrocarbon chains take a *trans* zigzag conformation with a little *gauche* characteristic.[29,30] In Fig. 6B, the bands due to the NR molecule are observed in addition to those of octadecylamine. The bands at 1400, 1465, and 1535 $\mathrm{cm^{-1}}$ are assigned as the N=N stretching, $\mathrm{CH_2}$ bending and NH bending, respectively. The absorbance of these bands in LB films are changed in comparison to the absorbance of NR molecule in KBr pellet, which is due to the specific orientation of the NR molecules after adsorption in the cationic LB films. The band at 1435 $\mathrm{cm^{-1}}$ is assigned as $\mathrm{B_1}\omega$ of ring vibrations in plane, polarized along the short-axis of the azo dye ring where as the band at 1616 $\mathrm{cm^{-1}}$ is assigned as $\mathrm{A_1}\omega$ of ring vibrations in plane, polarized along the long-axis of the azo dye ring.[25,31–33] The band in the region 1020–1040 $\mathrm{cm^{-1}}$ appears for the $\mathrm{S{=}O^-}$ stretching vibration which is present in Figs. 6B and 6C. The neutral $-\mathrm{NH_2}$ group (Fig. 6A) in octadecylamine LB film was changed to $\mathrm{NH_3^+}$ (Fig. 6B) after immersing the film in the NR aqueous solution (pH $\approx$ 6.2). The band of $\mathrm{NH_3^+}$ group seemed to be overlapped to those of the strong ring vibration. The bands in the region 1130–1160 $\mathrm{cm^{-1}}$ (Figs. 6B and 6C) is due to symmetric stretching of the $-\mathrm{SO_2^-}$ bands. Reflection-absorption FTIR spectroscopy[9] revealed that the hydrocarbon chain of the octadecylamine molecule made a tilt angle of 4.5° with the surface normal, suggesting to a nearly perpendicular orientation of the octadecylamine molecule to the film surface. On the other hand, a tilt angle of 13.5° for the hydrocarbon chains was observed on the azo dyes adsorbed in the cationic LB films.

In order to elucidate the periodic structure of the NR adsorbed octadecylamine LB films, X-ray diffraction (XRD) measurements were carried out. Figure 7 shows the XRD patterns of the immersing time dependence of ten layers of the NR-adsorbed octadecylamine LB films. The XRD profiles of octadecylamine LB films with several reflections indicate the presence of a highly order layer structure. On adsorption of the NR dye in the octadecyl-amine LB film new peaks appeared and the intensity of these peaks increased with increasing the immersion time. On the other hand, the peaks observed for the octadecylamine LB film before the NR adsorption become smaller and disappear if the adsorption of NR is completed (Figs. 7B and 7C). This suggests the rearrangement of the layer structure in the octadecyl- amine LB film. We obtain the layer-by-layer distance of 5.23 nm and 3.74 nm for the octadecylamine LB film before and after the NR adsorption respectively. The layer-by-layer distance of 5.23 nm represents a bilayer thickness, as the length of the octadecylamine molecule in fully stretched configuration is 2.4 nm. The reason that the bilayer thickness is larger than twice the length of the octadecylamine molecule is the presence of water layer and counter ions to screen the mutual charge repulsion of the headgroups. However, on the NR adsorption the bilayer thickness has been decreased considerably.

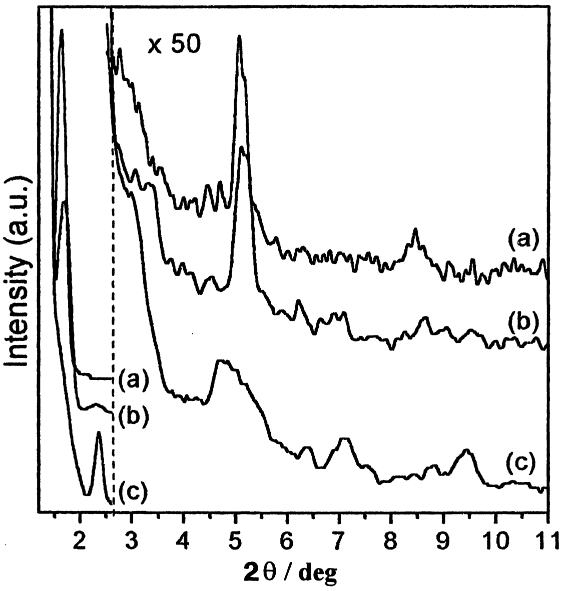

Fig. 7. XRD profiles of octadecylamine LB film at different immersing time in NR solution (a) 0, (b) 10, and (c) 69 min.

6. Interdigitated Structure of Azo Dye-Adsorbed LB Films. Based on the spectroscopic studies and XRD measurements as discussed above, the probable molecular arrangements of the octadecylamine LB films before and after the NR adsorption are presented in Fig. 8. A Y-type multilayer struc-

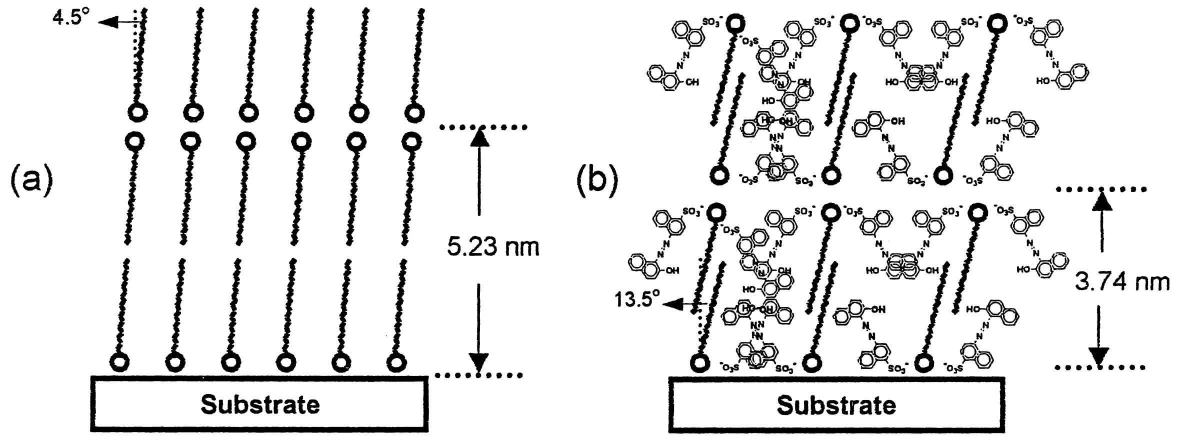

Fig. 8. Schematic presentation of (a) Y-type multilayered octadecylamine LB film, (b) NR adsorbed octadecylamine LB film.

ture of the octadecylamine LB film where the hydrocarbon chains are almost aligned vertically is observed. In this case, it can be assumed that the sulfonate group at the terminal position of the NR molecule interacts with the amine group of the octadecyamine molecule. Thus, the NR molecules in the LB films are considered to be arranged and oriented as shown in Fig. 8b, with the sulfonate group linked with the $-NH_2$ group of octadecylamine and the opposite end of the NR molecule allowed to be in nearly parallel to the hydrocarbon chain. It is most likely that NR fits between the void space among the hydrocarbon chains of octadecylamine and such a molecular arrangement is favorable for ionic interaction between the cationic and anionic groups. Molecular areas of octadecylamine and NR molecules and their interactions at the air/water interface as obtained by the isotherm measurements also demonstrated these type of molecular arrangements. The decrease in the bilayer thickness of octadecylamine on the NR adsorption with the change in the layer structure observed by XRD measurements can be discussed on the basis of an interdigitated structure where the hydrocarbon chains overlapped as illustrated in Fig. 8b. Adsorption of the dye into the LB films is considered to increase the intermolecular distance between the long-chain amine molecules along the substrate surface plane. As mentioned above, the isotherm studies also showed the expansion of the molecular area of octadecylamine on the NR molecular subphase. For this reason, the LB films probably compensate the lack of lateral interaction and rearranged as an interdigitated layer structure on the azo dye adsorption. Steady state absorption and emission spectroscopy pointed a strong dipole–dipole interaction as discussed earlier indicating presence of more than one to one correspondence of the NR and octadecylamine molecules. New exciton bands observed in the absorption and excitation spectra of the NR adsorbed in LB films are considered to have occurred owing to the interaction of the two or more NR molecules in the organised assembly as schematically illustrated in Fig. 8b.

7. Atomic Force Microscopic Studies of the Surface Structure of the NR Dye Adsorbed in the Octadecylamine LB Film. AFM images have been obtained to characterize the surfaces and the morphology of the cationic LB films by adsorption of the anionic NR dye. The LB films have been deposited on freshly cleaved mica for AFM measurements. Figure 9 shows the AFM images of the octadecylamine LB films of 1, 5 and 9 layers before and after the NR adsorption. The single layer LB film of octadecylamine deposited on mica forms a uniform flat surface as shown in Fig. 9a. With increasing the number of layers a texture of small gathering islands with some surface roughness occurred. The AFM image of five layered LB film of octadecylamine on mica as given in Fig. 9b reveals a fairly flat surface except somewhat undulating surface with a surface roughness of about 2 nm. On the other hand, the image obtained for nine layered LB film of octadecylamine gives more or less a flat surface with a few small islands and hole. It seems from the images of octadecylamine as exhibited in Figs. 9a, 9b, and 9c that with increasing the number of layers of the LB films of octadecylamine, numbers of

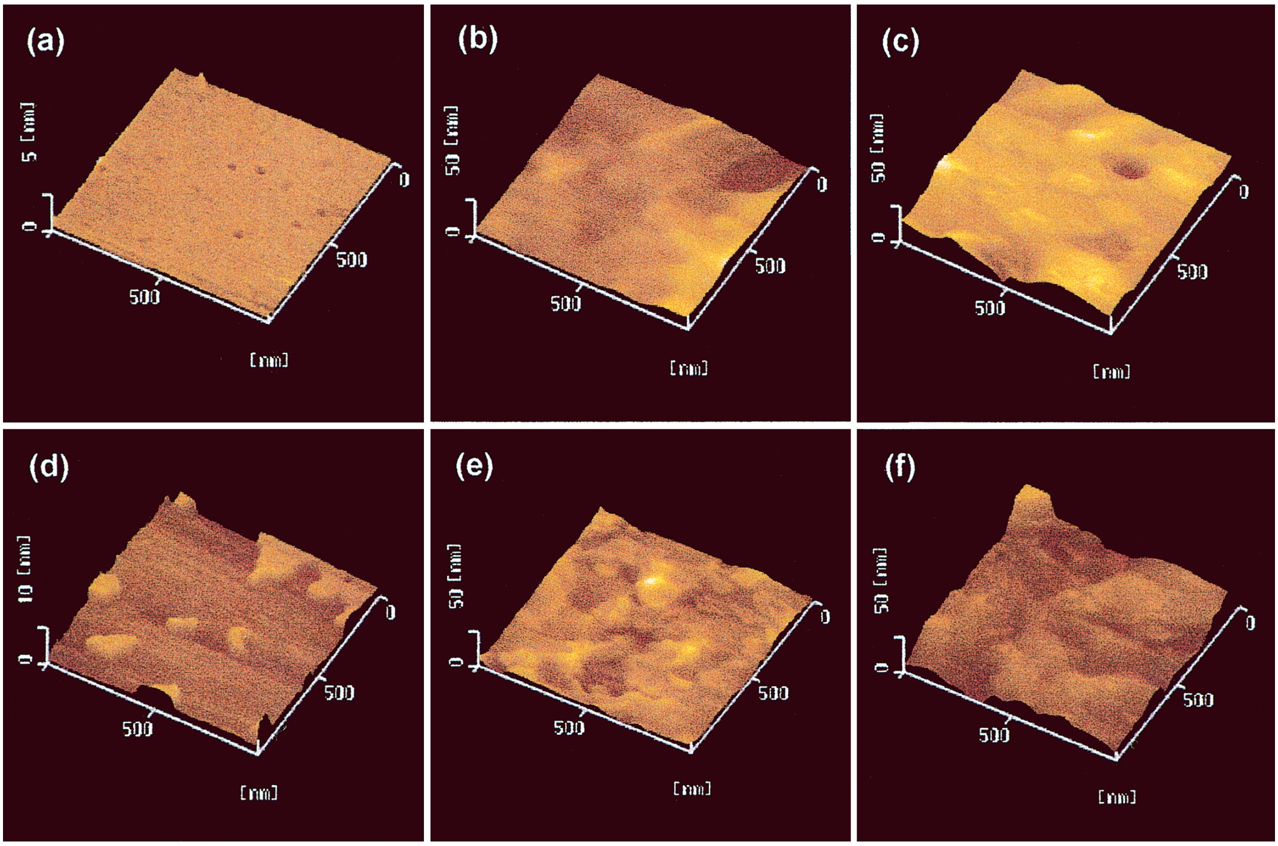

Fig. 9. AFM micrographs of octadecylamine LB film on mica (a) 1 layer, (b) 5 layer, and (c) 9 layer; (d) 1 layer (e) 5 layer, and (f) 9 layer film after adsorption in NR solution (1×10^{-4} M).

small domains exists which possibly occurred during the drying process of the deposited multilayers on the substrate. On alkaline subphase, the octadecylamine molecule can form islands like its fatty acid analogue[34] due to the lateral interaction between molecules. When the NR molecule is adsorbed in the cationic LB film, a typical change in the layer structure is observed as depicted in Figs. 9d, 9e, and 9f. The most striking feature is the distinctive growth of islands coming out from the monolayer phase after the adsorption of NR dye. During the isotherm measurements, an expansion of the molecular area of octadecylamine was observed on the aqueous subphase containing the azo dye. For this reason, it seems that on the dye adsorption perfect planar surface structure of the monolayer could not be maintained. The images for NR adsorbed multilayered LB films of octadecylamine as given in Figs. 9e and 9f consist of more patches which are different in size (100–200 nm) and are randomly distributed, thus indicating reorganization of the layer structure in the LB films. It is also apparent from the images 9e and 9f that the domains and islands are pushed out from substrate surface and arranged in tiers. Thus, the dye adsorbed multilayered films can be considered as a piled up film of the dye adsorbed monolayers. Although the AFM images of the dye-adsorbed LB films exhibits some disordered distribution of the patches, however the parallel arrangement of the layer structures are maintained.

In conclusion, the monolayer characteristics of a cationic long-chain amine molecule at the air-water interface were studied in presence of an anionic azo dye at the subphase. The water-soluble anionic azo dye has been incorporated in the cationic LB films. Adsorption behaviour of the anionic azo dye onto the cationic LB film was investigated by electronic spectroscopy. Polarized visible absorption spectra of the π–π^* transition suggested the specific orientation of the NR molecule in the LB film. On the adsorption of the NR molecule in the octadecylamine LB film, rearrangement of the layer structure was observed from the low angle X-ray diffraction measurements. These cationic LB films took an interdigitated bilayer structure on the adsorption of NR. AFM images elucidated the changes in morphological structures of the cationic LB films on the adsorption of the azo dye. The information on the ionic interaction and the molecular arrangement is expected to provide a better understanding of the adsorption behaviour of various adsorbates on cationic LB films. Orientations of the azo dye in functionalized LB films are strongly dependent upon the kinds of the end groups and their positions. Finally, these self-organizations of the anionic dyes in cationic monolayer and multilayered films are considered to be an important parameter for its application in chemical sensors and devices.

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