Adsorption behavior of functional dye onto cationic Langmuir monolayers and effects of the molecular orientation on optical behavior

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The cationic monolayer properties on the pyranine aqueous subphase were studied from measurements of surface pressure-area (π-A) isotherms, *in-situ* visible spectra and observation by a Brewster angle microscopy (BAM). Pyranine molecules affect the the adsorbed behavior of monolayers for alkylamines having one or two long-chains. From the spectra, the different aggregation of pyranine molecules was observed, reflecting to the visco-elastic behavior of the monolayer. Strong dipole-dipole interaction among pyranine molecules in the Langmuir monolayer was observed for spectral shifts, which was considered with the exciton model. From the BAM images, the adsorption behavior depends upon the monolayer composition and surface pressure resulting in different visible spectra and BAM images.

Keywords : Langmuir-Blodgett Film, functional dye, Brewster angle microscopy, dye aggregate, molecular orientation

1. Introduction

Molecular organized systems have been attracted much attention in the application of electronic- and optical devices [1]. Control of the molecular arrangements is expected to provide valuable information for constructing a novel molecular device. The LB method is a candiate to controll a well-defined molecular orientation and packing [2].

Adsorption of anioinc functional dyes onto cationic LB films is an unique technique for immobilization of functional dyes in the LB film due to the ionic interactions. Changing the adsorptions condition such as pH and dye concentration in the aqeous subphase, temprature, composition in the film and substituent positions of the functional group, dye molecules in the LB film form the well-defined molecular assemblies. Cationic film substances interact with various anionic functional dye molecules [3], proteins [4], and nano particles [5]. In the previous papers, several adsorption behavior of anionic dye molecules such as alizarine violet [6], sulforhodamine B [7] and azo dye [8] onto cationic LB films were studied.

It has been reported that pyranine is a typical hydroxylarene, and the acidity is enhanced in the excited state and an increase of the acidity causes the excited-state proton-transfer (ESPT) in polar solvents [9]. K. Ray reported the ESPT reaction between octadecylamine and pyranine in the adsorbed LB film [10]. In the present work, we investigate the adsorption behavior of pyranine moleules from the aqeous solution onto cationic Langmuir monolayers at the air/water interface to examine the effect of different molecular packing in the monolayers on the dye adsorption. The adsorption manner on each cationic Langmuir monolayer has been also discussed in relation to the film elasticity. Furthermore, *in-situ* visible spectroscopy and Brewster angle microscopy (BAM) have been used to reveal the adsorption behavior of pyranine to the monolayers at the air/water interface.

2. Experiment

We used octadecylamine [ODA], gemini amphiphiles: (*p*-Phenylenedimethylene) bis (octadecyldimethyl ammonium) dibromide [*p*-PODB] and their mixture for the cationic
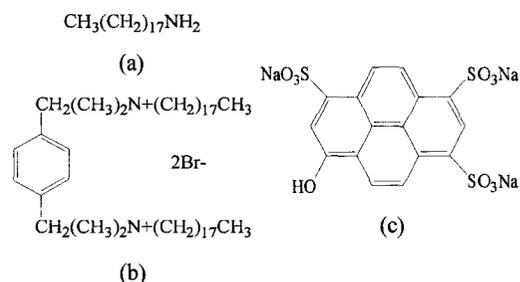
Fig.1 Structural formulas of the ODA (a), *p*-PODB (b) and pyranine (c)

film substances. Octadecylamine was purchased from Aldrich Chemical Co., Inc. and recrystalized five times from the hexane solution. The *p*-PODB was synthesized along the reference [11]. Pyranine was purchased from Acros ltd. and used as recived and the purity was checked by UV-visible absorption spectroscopy.

The surface pressusre-area (π-A) isothem was measured by a Lagmuir film balance (LAUDA, FW-2). The cationic monolayers were spread from the chlorofrom solution on the pyranine NaOHaq subphase (1×10^{-4} mol/l, pH $\approx$ 10, 20.0 °C). The monolayer was compressed at a constant velocity (46.4 cm^2/min). The *in-situ* visible spectra of Langmuir monolayers were measured using a multichannel photodetecter (Otsuka Electronics, MCPD-100). The Brewster angle microscope was equipped with a 20 mW semi-conductor laser (λ = 532 nm), an analyzer and a zooming microscope with a highly sensitive CCD camera (NFT Co., EP^3, Germany). The scale of an image was 200 μm × 100 μm. The flicker in the BAM image was due to scattering light from the instrument.

3. Results and Discussion

Fig.2-a shows π-A isotherms of the monolayers for ODA, p-PODB and the mixture ODA:p-PODB = 2:1 (in the molar raito) on the NaOHaq at 20.0 °C. The ODA monolayer exhibits a typical solid
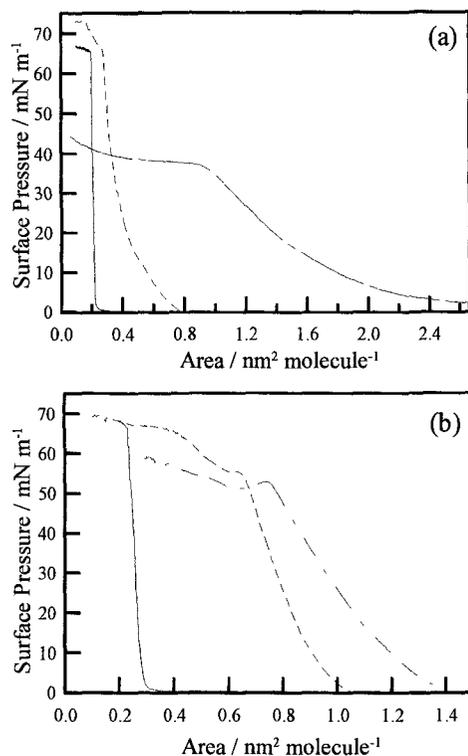
Fig.2 Surface Pressure-Area (π-A) isotherm of ODA (solid line), ODA:*p*-PODB=2:1 (dashed line) and *p*-PODB (dashed-dot line) in (a) NaOH*aq* at pH 10 and (b) 1×10-4 mol/l pyranine NaOHaq at pH 10 at 20 °C

Fig.3 *in-situ* visible spectra of pyranine molecules adosrobed onto ODA:*p*-PODB=2:1 monolayer

condensed film, whereas the *p*-PODB monolayer forms only a liquid expanded film. These behavior gave well agreetment with the previous works [8, 11]. On the other hand, their mixed monolayer (ODA:*p*-PODB=2:1) has three phases from the analysis of the film elasticity. The film elasticity is defined by [12]

$$E_s = -A(\partial \pi / \partial A) \qquad (1)$$

where A is the molecular area and π is the surface pressure. The phase at the low surface pressure below 27 mNm⁻¹ is a liquid expanded phase, in which its elasticity has nearly equal to that of the *p*-PODB monolayer. With compression, the monolayer tends to be a liquid condensed phase in the region of 27-37 mNm⁻¹. Finally, a solid condensed monolayer can be attained at the higher pressure above 40 mNm⁻¹. As the surface pressure arised, the ODA and p-PODB molecules appear to be miscible in the mixed monolayers and the ODA molecules are organized in the manner of the spaced-filled between two-alkyl chains of *p*-PODB. As a result, the rigidity of mixed monolayer was enhanced. When the monolayers were spread on the NaOH aqeous solution containing pyranine molecules (1×10⁻⁴ mol/l), the π-A isotherms were considerably changed as shown Fig.2-b. It is evident that the cationic monolayers interact with the anionic pyranine molecules and affects the molecular area and the film elasticity. This behavior suggests the formation of an ionic complex between cationic film substances and pyranine molecules. The cross-sectional area of a pyranine molecule for the edge-on and flatwise orientation are estimated to be 0.22 nm² and 0.63 nm², respectively from the CPK model, where the molecular

dimensions were assumed to be 0.93 and 0.68 nm along the long and the short axis of pyranine, respectively. At 25 mNm⁻¹, the molecular area of ODA was changed by adsorbing the pyranine molecules from 0.21 nm² to 0.26nm². The expansion of molecular area is relatively small in comparsion with the molecular area of a pyranine molecule. This fact indicates that one pyranine molecule adsorbs onto two or three ODA molecules. In the *p*-PODB monolayer, the different adsorption behavior was observed in contrast to the ODA monolayer. The molecular area of the pyranine adsorbed *p*-PODB monolayer is considerably reduced, giving the 1.2 nm² of the extraploated area from the condensed phase. From the film elatiscity, the pyranine adsorbed *p*-PODB monolayer is more rigid and this fact suggests that the *p*-PODB monolayer is considered to interact with the dye as the well-fitted molecular packing. In the pyranine adsorbed ODA :*p*-PODB =2:1 mixed monolayer, the molecular area was changed from 0.39 nm² to 0.80 nm² by adsorbing pyranine molecules at 25 mNm⁻¹. The expansion of the molecular area (0.41 nm²) suggests that the arrangement of pyranine molecules is a tilted conformation in the adsorbed monolayer.

Fig.3 shows *in-situ* visible spectra of the ODA:p-PODB=2:1 mixed monolayer immediately adsorbed pyranine molecules at various surface pressures. After spreading the mixed monolayer, an additional peak and a sholuder were appeared at 572 nm and 502 nm, respectively while the peak position was 460 nm for the pyranine monomer in the aqeous solution at pH 10. The large red shifts are due to the pyranine adsorption in the two-dimensional aggre-gates in the adosrobed monolayer. The

Fig.4   BAM image of ODA, ODA:p-PODB=2:1 and p-PODB monolayer on 1×10^{-4} mol/l pyranine NaOHaq (pH 10) at different serface pressure (size 200 μm×100 μm)

spectral shift could be considered with the exciton coupling theory due to the dipole-dipole interaction between the neighboring molecules [13].   For the dye aggregate in the monolayer, the spectral shift is expressed as ;

$$\Delta v = \frac{2}{hc}(N-\frac{1}{N})\frac{\mu^2}{r^3}(1-3\cos^2\alpha) \qquad (2)$$

where Δv is the   spectral shift in wavenumber from monomer, h is the Plank's constant, c is velocity of light, N is number of molecule in aggregate, r is distance between the molecular centers and α is the angle between the dipole moment of the molecule and the line through the center of molecules in the two-deimensional aggregate.   In accordance with the equation (2), the red shift from the monomer to the aggregates suggests rather pararell orientation of the long axis of the pyranine molecules in the monolayer. With increase of the surface pressure, the relative intensity of the band was enhanced, the shoulder band of 503 nm at 0mNm⁻¹ was reduced at 20mNm⁻¹ and disappeared at 40-50 mNm⁻¹. Instead of these spectral change, the band of 530 nm is enhanced and slightly shifted to the longer wavelength. This spectral change has been related to the different molecular enviroment for the dye aggregates.   It is well known, as a typical way, for the cyanine dye to form the J-aggregate with a red-shifted band or the H-aggregate with a blue-shifted [14].   One of the characteriztion of molecular microenviroments and packing is proposed by using the analysis of the film elasticity.   In the pyranine adsorbed ODA:p-PODB =2:1 mixed monolayer,   the film elasticity increased to nearly 150 mNm⁻¹ at the surface pressure 20 mNm⁻¹, indicating the phase change from the gas or liquid expanded to the liquid condensed phase.   And further compression induces the almost liquid condensed phase at 40-50 mNm⁻¹.   This result was well-corresponding to the spectral change of the pyranine adsorbed mixed monolayers.

The pyranine adsorbed ODA and p-PODB monolayers have also appeared at 570, 550 nm respectively.   In the case of pyranine adsorbed ODA and p-PODB monolayers, the shoulder band at 503 nm was not observed and the spectra was unchanged irrespective of the surface pressure.

The BAM image provides further information with film behavior of the dye adsorption in terms of the monolayer morphology.   Figure.4 shows the BAM image of the ODA, ODA:p-PODB=2:1, and p-PODB monoayers on the pyranine NaOHaq subphase.   The BAM images of these cationic monolayers tend to uniform homogeneous structure by the adsorption of the pyranine molecules.   Even at the 0 mNm⁻¹, the different structures could be obtained of the pyranine adsorbed ODA, p-PODB and their mixed monolayers.   The rigid condensed film with edge like domains for the ODA, fluid-expanded film with circular domains for the p-PODB and the random structure containing the expanded and the condensed phases for the mixed film were obtained.   At 25 mNm⁻¹, a large domains with a less defect for the ODA, forming the large domains for p-PODB and ordered structure for the mixed monolayers were obsereved.   And the crystallization seemed to be occured at the higher surface pressure.   The p-PODB was crystallized in the collapse by adsorption of the pyranine molecules though it's monolayer was not crystallized at the NaOH aqeous subphase without the dye.

4. Conclusion

The adsorption of the pyranine molecules to the monolayers induced with the cationic monolayer properties and the spectral change.   The behavior of visco-elasticity of the cationic monolayers is well-corresponding to the spectral change due to the dfferent dye orientation and packing in the monolayers.   And further, these results were supported by the BAM images before and after adsorbing the pyranine onto the cationic monolayers as well as changing the surface pressure.

6. References
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