The Structure of the Dye Containing LB Films Investigated by Infrared Spectroscopy

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We have investigated the orientation and thermal motion of the hydrocarbon chains in the mixed LB films of the ternary systems consisting of merocyanine (MS), deuterated arachidic acid (C_{20}-d), and deuterated n-octadecane (AL_{18}-d) with the molar ratio [MS] : [C_{20}-d] : [AL_{18}-d] = 1 : 2 : x (x = 0, 1, 2, 3, 4, 5) by means of polarizing infrared transmission spectroscopy. The band widths of the CH_2 anti-symmetric and symmetric stretching modes of the hydrocarbon chain of MS decrease with increasing x. The orientation angle γ, which is the angle between the long axis of the hydrocarbon chain and the normal to the film plane, changes approximately from $25°$ down to $17°$ with increasing x. These results suggest that the thermal motion of the hydrocarbon chain of MS is hindered by the AL_{18}-d molecules added, that the J-aggregate is accompanied by the thermal motion of the hydrocarbon chain of MS, and that the H-aggregate is accompanied by the highly packed state of the hydrocarbon chains of MS and AL_{18}-d.

Key words: merocyanine dye, H-aggregate, ternary system, LB films, thermal mobility, orientation, infrared spectroscopy

1. INTRODUCTION

The merocyanine dye with a benzothiazole, a rodanine ring and a stearyl side chain (MS, see Fig. 1) is of great interest as one of the film forming materials in the Langmuir-Blodgett (LB) films because of the potential for realizing organic solar cells and optical memory media.[1-3]

It is well known that LB films of the MS - arachidic acid (C_{20}) binary system show a sharp absorption peak at 590 nm, when they are prepared using the aqueous subphase containing Cd^{2+}.[4,5] The absorption band shows the characteristics of the J-band, with its absorption maximum red-shifted from that of the monomer band (540 nm).[4,5] The aggregation state of MS can be however drastically changed, when an appropriate third component is introduced into the system. For the monolayers at the air/water interface, for instance, H. Nakahara and D. Möbius have observed a blue-shifted band of an MS-containing ternary system.[6] The band was however of transient nature and no attempt has come to our knowledge to conserve it in the LB films. Recently, we have found that a pronounced blue-shifted band at 505 nm is induced when n-octadecane (AL_{18}) is added to the MS - C_{20} binary system. This band is stable enough, indicating that the MS aggregation state in the LB films can be easily controlled by adding the AL_{18} molecules as the third component. The blue-shifted band at 505 nm is caused by an H-aggregate, which has been concluded by the energy shift, the sharpness, and the in-plane anisotropy of the band.[7-10] In order to reveal the mechanism of individual MS aggregates, it is important to characterize their structures.

In this paper, we have investigated the orientation and thermal mobility of the hydrocarbon chain of MS by means of the polarizing infrared transmission spectroscopy. A model by P.-A. Chollet [11] is
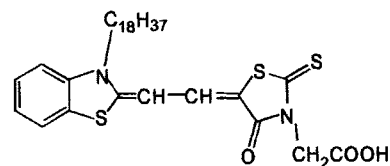

Fig. 1. Chemical structure of MS.

introduced in order to estimate the tilt angle of the long axis of the hydrocarbon chains against the film plane. We have also discussed the correlation between the aggregation state of the MS dye and the thermal mobility of the hydrocarbon chain of MS. Deuterated C_{20} (C_{20}-d) and deuterated n-octadecane (AL_{18}-d) are used to separate the infrared bands due to the hydrocarbon chain part of MS.

2. EXPERIMENTAL

MS, C_{20}-d, and AL_{18}-d were used as the film forming materials. MS, C_{20}-d, and AL_{18}-d were purchased from Hayashibara Biochemical Laboratories Inc. Kankoh-Shikiso, C/D/N Isotopes, and Cambridge Isotope Laboratories Inc., respectively. MS, C_{20}-d, and AL_{18}-d were dissolved in the freshly distilled chloroform with the molar mixing ratio of 1 : 2 : x (x = 0, 1, 2, 3, 4, 5). The concentration of MS was of the order of 10^{-4} M. The LB films were prepared by the standard vertical dipping method. The aqueous subphase and the deposition conditions were the same as given in our previous papers.[6-9] A CaF_2 substrate precoated with five monolayers of cadmium arachidate (CdC_{20}) was used.
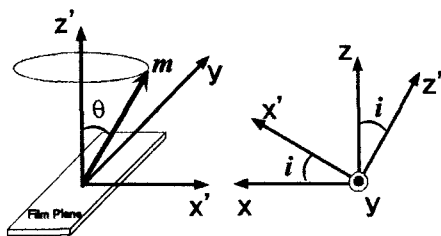
Fig. 2. The configuration of the vector m corresponding to the sum of the transition moments of the CH_2 anti-symmetric or symmetric stretching modes. (X', Y, Z') and (X, Y, Z) refer to the Cartesian coordinates with respect to the film and the incident light, respectively, where Y axis corresponds to the dipping direction and Z axis is taken along the direction of the incident.

All the LB films were of Y-type with a transfer ratio around unity.

The infrared absorption spectra were measured by a JASCO FT/IR-300 spectrometer. The spectrometer was purged with the nitrogen gas to minimize the absorption due to water vapor. The infrared absorption spectra were recorded at a 4 cm^{-1} spectral resolution by coadding 100 scans.

Through the experiments, the polarizing transmission absorption spectra $A_{\parallel}$ and $A_{\perp}$ of the mixed LB films were measured by a linearly polarized light with the electric vector parallel and perpendicular to the dipping direction, respectively. The linearly polarized light was introduced with an inclination angle i between the direction of the incident beam and the normal to the film plane. Fifty-layered mixed LB films deposited on both sides of the substrates were used as the samples.

3. THEORETICAL BACKGROUND

In order to estimate the tilt angle γ of the long axis of the hydrocarbon chains against the film plane, a model proposed by P.-A. Chollet [11] is introduced. In the model, the effects of the refractive index, the reflection, and the optical rotation of the electromagnetic wave due to the organic thin films are properly taken into account to provide the quantitative information about the molecular orientation.

As shown in Fig. 2, the polar angle of the vector m corresponding to the sum of the transition moments of CH_2 anti-symmetric (or symmetric) stretching mode is defined by θ, where it is assumed that m distributes uniformly with respect to Z' axis. The direction of the incident beam of the linearly polarized light is along Z axis with its electric vector in X-Y plane, where i is the inclination angle. In the case, the dichroic ratio R $(=A_{\parallel} / A_{\perp})$ is deduced as,

$$R = \frac{\frac{1}{2}\left\langle \sin^2\theta \right\rangle \left[n_3 \cos\ i + n_2\sqrt{1-\left(\frac{n_1}{n_3}\right)^2 \sin^2 i} \right]}{\left\{ n_1 \cos\ i + n_3\sqrt{1-\left(\frac{n_1}{n_3}\right)^2 \sin^2 i} \right\}\left[\frac{1}{2}\cos\ i\left\langle \sin^2\theta \right\rangle\sqrt{1-\left(\frac{n_1}{n_3}\right)^2 \sin^2 i} + \left\{\frac{n_3 n_1^3}{n_2^2}\right\}\sin^2 i\left\langle\cos^2\theta\right\rangle \right]} \tag{1}$$

where n_1, n_2, and n_3 refer to the refractive indices of the air, the LB films, and the CaF$_2$ substrate, respectively. In the present study, n_2 is approximated by the refractive index of the hydrocarbon chains, i.e., $n_2 = 1.5$. The tilt angle γ of the long axis of the hydrocarbons from Z' axis can be obtained referring to,

$$\cos^2\theta + \cos^2\theta' + \cos^2\gamma = 1 \tag{2}$$

where θ and θ' represent the tilt angles of the transition moment vectors m and m' corresponding to the CH_2 anti-symmetric and symmetric stretching modes, respectively. It is noted that m and m' are orthogonal to each other as a matter of course, and that the both are orthogonal to the long axis of a hydrocarbon chain in its *trans-zigzag* conformation.

4. RESULTS AND DISCUSSIONS

Let us first examine the tilt angle γ of the long axis of the hydrocarbon chain of CdC$_{20}$ in the CdC$_{20}$ LB film.

Fig. 3(a) shows the polarizing infrared absorption spectra $A_{\parallel}$ of the CdC$_{20}$ LB film. The bands at 2915 cm^{-1} and 2848 cm^{-1} are assigned to the CH$_2$ anti-symmetric and symmetric stretching modes, respectively. The lower peak maximum positions of the two bands (2915 cm^{-1} and 2848 cm^{-1}) are characteristic of all-*trans* conformation of the hydrocarbon chain of the C$_{20}$Cd LB film. It is noted that R-values of the bands at 2915 cm^{-1} and 2848 cm^{-1} remain approximately unity when the direction of incident infrared beam is perpendicular to the film plane ($i = 0°$). The results coincide with the assumption of the uniformly distributed vector m (or m') with the polar angle θ (or θ').

Fig. 3(b) shows the dichroic ratio R of the CH$_2$ anti-symmetric stretching band in the CdC$_{20}$ LB films plotted against the inclination angle i. The solid curves refer to the inclination-angle-dependence of the dichroic ratio R calculated using eq. (1); (i) $\theta = 10°$, (ii) $\theta = 30°$, (iii) $\theta = 50°$, (iv) $\theta = 70°$, (v) $\theta = 80°$, (vi) $\theta = 83.5°$, (vii) $\theta = 90°$. The best least squares fit is obtained for $\theta = 83.5°$.
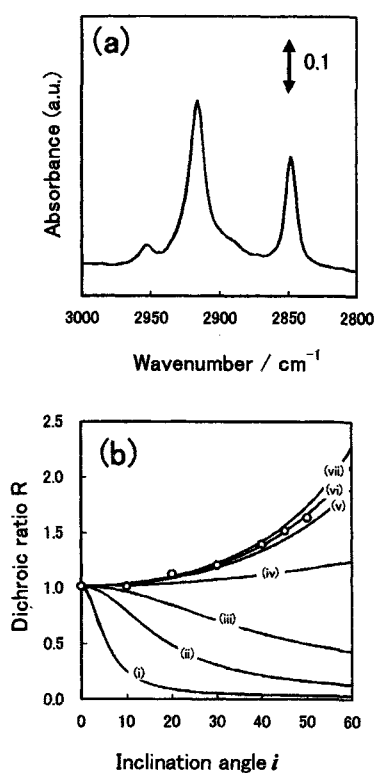
Fig. 3(a). The polarizing infrared transmission spectra $A_\parallel$ of the CdC_{20} LB films. (b). The dichroic ratio R of the CH_2 anti-symmetric stretching band for the CdC_{20} LB films plotted against the inclination angle i. The solid curves refer to the inclination-angle-dependence calculated using eq. (1); (i) $\theta = 10°$, (ii) $\theta = 30°$, (iii) $\theta = 50°$ (iv) $\theta = 70°$ (v) $\theta = 80°$ (vi) $\theta = 83.5°$ (vii) $\theta = 90°$.

Fig. 4(a). The polarizing infrared transmission spectra $A_\parallel$ of the mixed LB films with the molar mixing ratio of [MS] : [C_{20}-d] : [AL_{18}-d] = 1 : 2 : x. (b). The tilt angle γ of the long axis of hydrocarbon chain of MS plotted against the molar mixing ratio of x.

For the dichroic ratio R of the CH_2 symmetric stretching band, the best least squares fit is obtained for $\theta' = 81.5°$ repeating the above procedure. Using eq. (2), we obtain $\gamma = 10.9°$, which is about 1/3 of our previous estimate [10], but comparable to 7° reported for the CdC_{18} LB films by J. Umemura and his collaborators [12]. It is therefore suggested that the previously adopted model is too simplified to obtain quantitatively reliable estimates.

Fig. 4(a) shows the polarizing infrared transmission spectra $A_\parallel$ of the mixed LB films of MS - C_{20}-d - AL_{18}-d ternary system with the molar mixing ratio [MS] : [C_{20}-d] : [AL_{18}-d] = 1 : 2 : x (x = 0, 1, 2, 3, 4, 5). The two major absorption bands at 2920 cm^{-1} and 2850 cm^{-1} are due to the CH_2 anti-symmetric and symmetric stretching modes, respectively. The two bands originate from the hydrocarbon chain of MS. In Fig. 4(a), it is clearly found that the widths of the two bands change with the molar mixing ratio x. In general, the broad widths of the two bands due to the CH_2 anti-symmetric and symmetric stretching modes are characteristic of the disordered state of the hydrocarbon chain, while the narrow ones indicate that the hydrocarbon chain is in a highly ordered state. Through the course from $x = 0$ to x
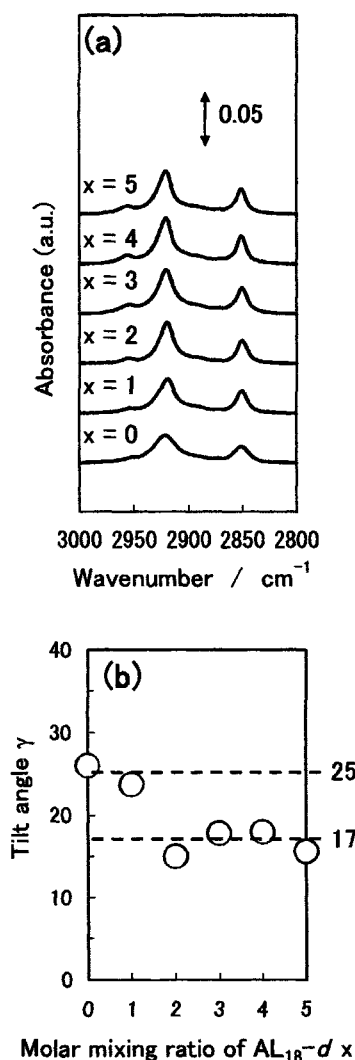
=2, the widths of the both bands decrease, indicating that the motion of the hydrocarbon chain of MS is hindered by mixing AL_{18}-d as the third component. In the region from $x = 2$ to $x = 5$, the widths of the bands remain unchanged, indicating the constant mobility of the hydrocarbon chain of MS. The x-dependence of the widths will be further discussed in a separate paper.

Fig 4(b) shows the x-dependent tilt angle γ of the long axis of the hydrocarbon chain of MS in the ternary LB films against the film plane. The value of angle γ is estimated to be around 25° at $x = 0$. The γ-value decreases with increasing x through the course from $x = 0$ to $x = 2$, and then it remains approximately the same, ca. 17°, in the region from $x = 2$ to $x = 5$, showing the constant orientation of long axis of the hydrocarbon chain of MS with respect to the film plane. It is noted that

these γ-values for MS are apparently larger than the above obtained value (γ=10.9°) for the hydrocarbon chain of CdC$_{20}$.

In the following, a tentative explanation will be given to the x-dependence of γ observed for the hydrocarbon chain of MS in the mixed LB films of the binary and the ternary systems.

For the binary system of MS and C$_{20}$ (i.e., x=0), it has been reported that the LB film is inhomogeneous and composed of the MS-rich and the C$_{20}$-rich domains. The hydrocarbon chain with the *trans-zigzag* conformation is known to have the cross section of 0.2 nm^2. The hydrocarbon chain of MS may then occupy an area of 0.2/cosγ, if the occupied volume is assumed to remain constant irrespective of γ. The value estimated is 0.221 nm^2 for γ=25°, which is about 37 % of the occupied area of the chromophore of an MS molecule, 0.6 nm^2, at the air/water interface.[8,13]

From the thermodynamic viewpoint, the state of aggregation in general is governed by the compromise between the enthalpy and the entropy terms. In the present case, the enthalpy may increase when the van deer Waals interaction among the hydrocarbon chains is weakened, and the entropy may increase with the thermodynamic weight due to the deviation, both configurational and motional, from the *trans-zigzag* conformation in the empty space allotted to each chain. It is therefore plausible to consider that the hydrocarbon chain of MS in the binary system is not in the highly ordered state with the *trans-zigzag* conformation but in the thermally active state with *gauche* conformations.

For the ternary system with the molar mixing ratio [MS] : [AL$_{18}$-d] : [C$_{20}$-d] = 1 : 2 : x (x = 1, 2, 3, 4, 5), the estimated occupied area of the MS hydrocarbon chain decreases down to 0.2/cos17° =0.209 nm^2 as the AL$_{18}$-d content increases up to x=2, and then it tends to saturate remaining constant. This is consistent with our previous remark that the AL$_{18}$-d molecules tend to fill the empty space of MS molecules to cause the change in the aggregation state of the chromophores.[8,9] The empty space may contain the AL$_{18}$-d molecules up to two in number, each enhances the van deer Waals interaction and reduces at the same time the space allotted to the hydrocarbon chain of MS, resulting in the more highly packed state of the hydrocarbon chains of MS and AL$_{18}$-d with their thermal motion being hindered.

As mentioned in Introduction, the LB film of the MS - C$_{20}$ binary system is known to show the red-shifted band at 590 nm due to the J-aggregate.[4,5] We have found that the mixed LB films of the MS - C$_{20}$ - AL$_{18}$ ternary system exhibits the blue-shifted band at 505 nm.[7-10] The blue-shifted band at 505 nm is observed with the molar mixing ratio [MS] : [C$_{20}$] : [AL$_{18}$] = 1 : 2 : x (x = 0.5, 1.0, and 1.5), and we concluded that the blue-shifted band is due to the H-aggregates. For $x \geq 2$, the position of the blue-shifted peak has been found to shift from 505 nm up to 520 nm with increasing x, indicating that the aggregation number decreases gradually, i.e., the size of aggregates changes from that of a fully developed H-band to that of an oligomer or a dimer.[7-10]

In this paper, we have shown the tentative results of a study on the relationship between the aggregation state of the MS dye and the orientation and mobility of the

hydrocarbon chain of MS. The J-aggregate is accompanied by the thermally active motion of the hydrocarbon chain of MS, and the H-aggregate is associated with the more highly packed state of the hydrocarbon chains of MS and AL$_{18}$-d.

5. CONCLUSIONS

We have studied the orientation and thermal motion of the hydrocarbon chain of MS in the MS - C$_{20}$-d - AL$_{18}$-d ternary systems (x = 0, 1, 2, 3, 4, 5) by means of polarizing infrared transmission spectroscopy. The band widths of CH$_2$ anti-symmetric and CH$_2$ symmetric stretching modes decrease in the course from x = 0 to x = 2. The orientation angle γ, which is the angle between the long axis of the hydrocarbon chain and the normal to the film plane, changes approximately from 25° down to 17° with increasing x. The results indicate the following: (a) the thermal motion of the hydrocarbon chain of MS is hindered by the AL$_{18}$-d molecules added; (b) the J-aggregate is associated with the thermal motion of the hydrocarbon chain of MS; (c) the H-aggregate is accompanied by the highly packed state of the hydrocarbon chains of MS and AL$_{18}$-d. These suggest that the aggregate formation is controlled by the state of hydrocarbon chain packing.

In the present paper, we have concentrated the discussion on the typical cases of the J-band and the H-band. A comprehensive study including the oligomeric and dimeric aggregates of MS is now in progress and will be published elsewhere.

6. ACKNOWLEDGEMENTS

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