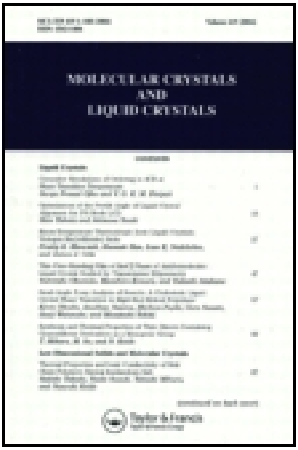

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Blue-Shifted Band in LB Films of Merocyanic-Arachidic Acid-N-Alkane Ternary System

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Blue-Shifted Band in LB Films of Merocyanic-Arachidic Acid-N-Alkane Ternary System

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The layered structure of the LB films of merocyanine (MS)-arachidic acid (C_{20})-n-octadecane (AL_{18}) ternary system has been studied by means of the X-ray diffraction technique. Besides the homogeneously-stacked films of ternary system, heterogeneously-stacked films composed of alternate stacking of bilayers of the mixed system and the pure C_{20} were fabricated for comparison. Two different regimes are recognized in the X-ray diffraction profiles of the homogeneously-stacked films, indicating that the MS-MS and the C_{20}-C_{20} bilayer unit cells are responsible for the lower-order and the higher-order peaks, respectively.

Keywords: merocyanine LB film; ternary system; X-ray diffraction measurement

INTRODUCTION

We have found a blue-shifted band in the mixed LB films of merocyanine dye (MS, Fig. 1), arachidic acid (C_{20}) and n-alkane (ALn). The blue-shifted band located around 505 nm can be assigned to H-aggregates of the dye molecules[1]-[4], while the 590-nm red-shifted band for the MS-C_{20} binary system is referred to as a J-band[5]-[8]. We have examined the associated layered structure by means of the surface pressure - area isotherm and the X-ray diffraction measurements. Two different regimes have been recognized in the X-ray diffraction profiles[4], while three different bilayer unit cell species may be considered to exist in the phase-separated system[5]-[8].

In this paper, in order to identify the origin of the two different regimes, we have compared the X-ray diffraction profiles of the conventional LB films of the ternary system and the heterogeneously-stacked films composed of the alternate stacking of bilayers of the ternary system and the pure C_{20}, containing only two among the three possible unit cell species.

EXPERIMENTAL

The merocyanine dye (MS), arachidic acid (C_{20}) and n-octadecane (AL_{18}) dissolved in the freshly distilled chloroform with a mixing ratio $[MS]:[C_{20}]:[AL_{18}]=1:2:2$ and C_{20} in chloroform, were used as the spreading solutions for the ternary and the pure C_{20} monolayers, respectively. The monolayers on the aqueous subphase containing Cd^{2+} ions were transferred onto a glass substrate hydrophobized with 1,1,1,3,3,3-hexamethydisilazane at a surface pressure of 25 mN/m with a dipping speed of 25 mm/min using the vertical dipping method as reported previously[11]-[16]. All the resultant LB films were Y-type with a transfer ratio of about unity. The X-ray diffraction measurements were carried out by the ordinary $\theta-2\theta$ scan method with a CuKα source ($\lambda=1.5418$ Å) operated at 30 kV and 30 mA using a Shimadzu XD610 X-ray diffractometer, immediately after the sample preparation. Fifty-layered LB films were used.

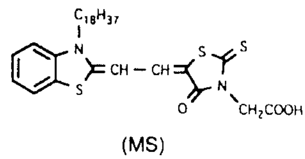

FIGURE 1 Chemical structure of merocyanine dye (MS).

RESULTS AND DISCUSSION

Figures 2(a) and (b) show the X-ray diffraction profiles for a homogeneously-stacked LB film of the mixed monolayers and a heterogeneously-stacked LB film of the alternate stacking of bilayers of the ternary system and the pure C_{20}, respectively. It is well known for various Y-type Cd-salt LB films that Cd^{2+} ions give the stronger X-ray scattering than any other constituents involved, and that a diffraction peak of odd order is stronger in intensity than the adjacent even-ordered peaks[19]. The diffraction peaks up to the 11th are seen in each figure, where the peak at $2\theta \approx 3^\circ$ is assigned as the 2nd order to lead to a reasonable estimate of the Cd-Cd spacings. The peaks of the heterogeneously-stacked film in Fig. 2(b) are higher in intensity than the corresponding ones of the homogeneously-stacked film in Fig. 2(a) for $2^\circ < 2\theta < 18^\circ$. Two different regimes are recognized in the present 2θ range. For $2\theta < 9^\circ$, each peak in Fig. 2(b) is located slightly lower in angle than the corresponding peak in Fig. 2(a), while, for $2\theta > 9^\circ$, no significant difference is seen in the peak position.

Figures 3(a) and (b) show the Cd-Cd spacing plotted against the X-ray diffraction order n for the homogeneously-stacked and the heterogeneously-stacked LB films, respectively, where the 2nd-order peak with lower accuracy is eliminated from each figure. The solid and the dashed lines denote the

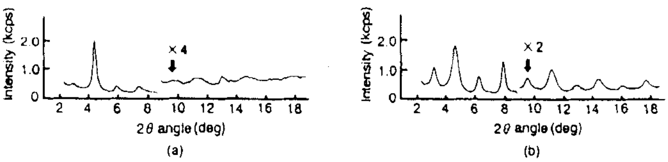

FIGURE 2 The X-ray diffraction profiles of the MS-C_{20}-AL_{18} ternary system. (a) The homogeneously-stacked films of the ternary system. (b) The heterogeneously-stacked films composed of alternate stacking of bilayers of the ternary system and the pure C_{20}. The molar mixing ratio in the ternary system [MS]:[C_{20}]:[AL_{18}]=1:2:2.

average values of Cd-Cd spacings for n≤5 and n>5, respectively. In each case, the average value for n≤5 is greater than that for n>5 which remains constant (about 55 Å).

The results of the X-ray diffraction measurements can be interpreted as follows: the MS-C_{20} binary system is known to form heterogeneous monolayers, where MS molecules are phase-separated from C_{20} molecules to form the J-aggregate. If we assume that MS and C_{20} are also phase-separated

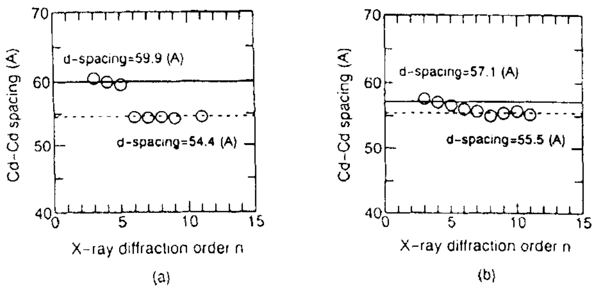

FIGURE 3 Cd-Cd spacing plotted against the X-ray diffraction order n for the MS-C_{20}-AL_{18} ternary system. (a) The homogeneously-stacked films of ternary system. (b) The heterogeneously-stacked films composed of alternate stacking of bilayers of the ternary system and pure C_{20}. The molar mixing ratio in the ternary system [MS]:[C_{20}]:[AL_{18}]=1:2:2. The dotted and dashed lines show the average values of Cd-Cd spacing for n≤5 and n>5, respectively.

from each other in the present ternary monolayers, there are three types of bilayers, (1) (CdC_{20}-$C_{20}Cd$), (2) (CdC_{20}-MSCd) and (CdMS-$C_{20}Cd$), and (3) (CdMS-MSCd) in the homogeneously-stacked films. But there are only two types of bilayers, i.e., Types (1) and (2), in the heterogeneously-stacked films.

The average Cd-Cd spacings for n>5 are 54.4 and 55.5 (Å) for the homogeneously-stacked (Figs. 3(a)) and the heterogeneously-stacked (Fig. 3(b)) LB films, respectively, each of which is comparable to the value of pure C_{20} LB films (55.2 Å, typically)[9]. This suggests that the X-ray scattering for n>5 in both types of films is mainly due to (CdC_{20}-$C_{20}Cd$) (Type (1)) bilayer unit cells which are more or less associated with structural disorders inherent in the mixed system.

According to the earlier works[5]-[8], each MS molecule in MS-C_{20} binary films has an empty space which can roughly accommodate two straight-chain hydrocarbons. In the previous papers[3],[4], we have indicated from the analysis of π-A isotherms that the empty spaces are fully filled with AL_{18} molecules at the molar mixing ratio of [MS]:[C_{20}]:[AL_{18}]=1:2:2. Further, it is suggested that the space filling by AL_{18} is responsible for the increase in the Cd-Cd spacing observed for n<5 which is assignable to Type (2) or Type (3) bilayer unit cell

In the heterogeneously-stacked films, the average Cd-Cd spacing of 57.1 Å for n<5 should be due to Type (2) heterogeneously-stacked bilayer unit, since no Type (3) bilayer unit cell is formed in the present heterostructure. This value is about 2 Å greater than that of the pure C_{20} bilayer or Type (1) unit cell (55.2 Å, typically) but about 3 Å smaller than the average value for n<5 of the homogeneously-stacked films (59.9 Å). It is therefore indicated that Type (3) bilayer unit cell is responsible for the Cd-Cd spacings obtained for the lower-order diffraction peaks in the homogeneously-stacked films.

References

[1] Y. Hirano, H. Sano, J. Shimada, H. Chiba, J. Kawata, Y.F. Miura, M. Sugi and T. Ishii, Mol. Cryst. Liq. Cryst., **294,** 161 (1997).
[2] Y. Hirano, J. Kawata, Y.F. Miura, M. Sugi and T. Ishii, Thin Solid Films, **327–329,** 345 (1998).
[3] Y. Hirano, K.N. Kamata, J. Kawata, Y.F. Miura, M. Sugi and T. Ishii, Mol. Cryst. Liq. Cryst., **322,** 111 (1998).
[4] Y. Hirano, K.N. Kamata, J. Kawata, Y.F. Miura, M. Sugi and T. Ishii, submitted.
[5] M. Sugi, T. Fukui, S. Iizima and K. Iriyama, Mol. Cryst. Liq. Cryst., **62,** 165 (1980).
[6] S. Kuroda, M. Sugi and S. Iizima, Thin Solid films, **99,** 21 (1983).
[7] H. Nakahara and D. Möbius, J. Colloid and Interface Sci., **114,** 363 (1986).
[8] H. Nakahara, K. Fukuda, D. Möbius and H. Kuhn, J. Phys. Chem., **90,** 6144 (1986).
[9] A. Matsuda, M. Sugi, T. Fukui, S. Iizima, M. Miyahara, Y. Otsubo, J. Appl. Phys., **48,** 771 (1977).