
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Properties of Bilirubin/Stearic Acid Mixed Monolayer and Multilayers

Jian-Ming Ouyang [a] , Chuan Li [a] & Wei-Han Ling [a]
[a] Department of Chemistry, Jinan University, Guangzhou, 510632, P.R. China

Version of record first published: 24 Sep 2006

To cite this article: Jian-Ming Ouyang, Chuan Li & Wei-Han Ling (1999): Properties of Bilirubin/Stearic Acid Mixed Monolayer and Multilayers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 129-132

To link to this article: http://dx.doi.org/10.1080/10587259908023394

*Mol. Cryst. and Liq. Cryst.*, 1999, Vol. 337, pp. 129-132
Reprints available directly from the publisher
Photocopying permitted by license only





# Properties of Bilirubin/Stearic Acid Mixed Monolayer and Multilayers

JIAN-MING OUYANG, CHUAN LI and WEI-HAN LING

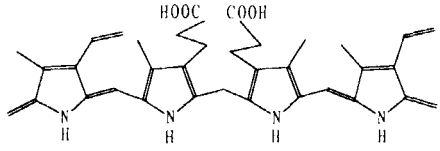
*Department of Chemistry, Jinan University, Guangzhou 510632, P.R.China*

A study is reported on monolayer and LB films obtained by mixing stearic acid and bilirubin at different molar ratios. The observed additivity of the areas of the films components is attributed to the conformational changes of BR in monolayers. Low-angle X-ray diffraction result showed a Bragg peak with a *d*-value of 4.97 nm, corresponding to a Y-type film.

*Keywords:* bilirubin; mixed monolayer; Langmuir-Blodgett films

## INTRODUCTION

Black-pigment gallstones are the products of abnormal biomimeralization in mammal bodies. The main components are calcium bilirubinate, copper bilirubinate etc.[1]. The structural organization and biophysical properties of bilirubin molecules in ordered molecular assemblies are similar to those in biological membrane system. Therefore, if bilirubin or its derivatives can be incorporated in ordered molecular films, these ordered system may have potential applications in mimicking the mineralization processes and in investigating the structure of bilirubin, which is believed to play a very important role in the properties of bilirubin and its salts.[2,3]




SCHEME 1 The molecular structure of BR.

## EXPERIMENTAL

Bilirubin was obtained from Sigma Chemical Co. All the other chemicals were of A.R. grade. The formation of air-water monolayers and deposition of the LB films were carried out according to a previous paper.[4] The components of monolayers were mixed immediately before the experiment.

## RESULT AND DISCUSSIONS

Fig.1 shows the π -A isotherms of bilirubin (BR), stearic acid (SA), and their mixtures in different molar fractions at 25℃. Both the components (SA and BR) and their mixtures produce stable monolayers. The π -A behavior of pure SA monolayers is in agreement with literature.[5] The limiting area values ($A_0$) of BR and SA are 0.71 and 0.21 $nm^2$, respectively. As the amount of BR increases from 0 to 1.00, the isotherm not only shifts toward larger molecular areas with a lower surface pressure, but also decreases the liquid-condensed phase region. Since BR may orient in three conformational forms at the air-water interface: the erected form (Mode A, $A_0$ = 0.7 $nm^2$ by C.P.K. model[6,7]), the flat form (lying flat on the surface, Mode B, $A_0$ = 1.6 $nm^2$) and the H-bond form (Mode C, $A_0$ = 1.2 $nm^2$), the obtained area (0.71 $nm^2$) per BR molecule for pure BR monolayers indicates that BR molecules orient in a perpendicular posture to the air-water surface (Mode A).

The average area per molecule of a mixed monolayer may be calculated from the molecular areas of the components according to the additivity rule:

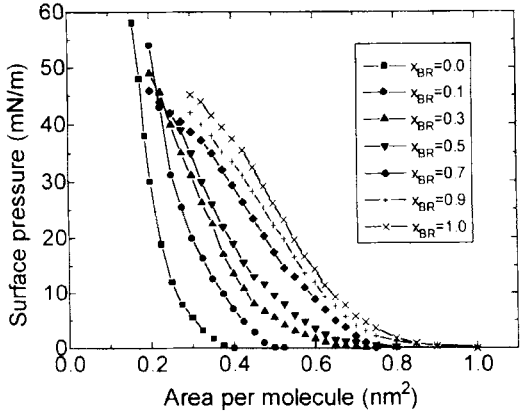



FIGURE 1 π -A curves for SA/BR mixed monolayers at different molar fractions.

$$A_{calc} = x_{BR}A_{BR} + x_{SA}A_{SA} \text{ .....at constant } \pi \quad (1)$$

where $x_{BR}$ and $x_{SA}$ are the mole fractions of BR and SA, $A_{BR}$ and $A_{SA}$ are the molecular areas of the single component monolayers and $A_{calc}$ the calculated molecular area of the mixed monolayer. Deviations from the additivity give information about the packing of the molecules.

Fig. 2 shows the measured and calculated areas per mixture molecule depending on the monolayer composition at different $\pi$ values. The results obtained show the presence of deviations from ideal behavior. These deviations change their magnitude not only with surface pressure, but also with the composition of the mixed monolayers. At the surface pressure of 6 and 18 mN/m, the measured values are markedly higher than the calculated values, especially at a molar ratio of ca. 1:2 of BR to SA. But the deviation nearly disappear when the surface pressure reaches 36 mN/m. It means that in the BR/SA monolayers with a low BR content a repulsive interaction between the two molecules or a conformational change of BR molecule have taken place at the air-water interface. It is more reasonable to assume that it is the result of orientational changes of BR at the interface during compression of the monolayer, for the reason that SA and BR are not completely immiscible according to the surface phase rule.

If the calculated area ($A_{calc}$) per molecule in Eq.(1) is replaced by the apparent area per molecule, the actual area per molecule BR might be calculated. For this purpose the area of the SA molecule has to be the same in pure as well as in mixed monolayers. Perhaps, this condition is not fulfilled completely. Nevertheless, an estimation of the area per molecule BR in mixed monolayers seems to be useful. Fig. 3 shows the apparent area per BR molecule in BR/SA mixed monolayer as a function of $x_{BR}$. For the monolayers with a low BR content ($x_{BR}$=0~0.3) the area per molecule BR (1.2 $nm^2$) is close to the face area of BR in Mode C, but it (1.2 $nm^2$) is close to the side area of BR in Mode B in the mixed monolayers with a high BR content ($x_{BR}$=0.4~1.0).

It can be seen that originating in a conformational transition, commencing at $x_{BR}$ = 0.3, BR turn from the H-bond form (Mode C) to the erected form (Mode A). In Mode C, two pairs of intramolecular hydrogen bonds exist in BR. Each of those links one of the two carboxyl groups to the contralateral pyrrolenone end ring, so that the hydrogen atoms are interposed between both oxygen atoms of the carboxyl group on the one hand and the oxygen and nitrogen atoms of the pyrrolenone ring on the other. That is, in the mixed monolayers with high BR content, BR plays an important role. It orients with side touching water (Mode A) and SA orients in the BR monolayers. However, SA plays an important role in the mixture monolayers with low BR content. In this case, BR orients with face touching water in H-bond structure (Mode C) in the SA

monolayer.

Thirty layers of the LB films of BR/SA mixture of molar ratio 1:1 was investigated by low-angle X-ray diffraction. One broad Bragg peak ($2\theta$=1.775°) was observed, showing a periodic structure of the films. The average layer spacing for the mixed LB films was calculated by Bragg diffraction formula $2d\sin\theta = n\lambda$ to be: 4.97 nm, being nearly twice that of the stearic acid long chain, indicating *Y*-type films.

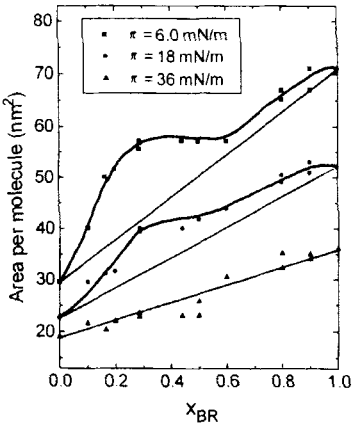



FIGURE 2 Molecular area of the BR/SA mixed films determined at π =6, 18, and 36 mN/m as a function of $x_{BR}$.

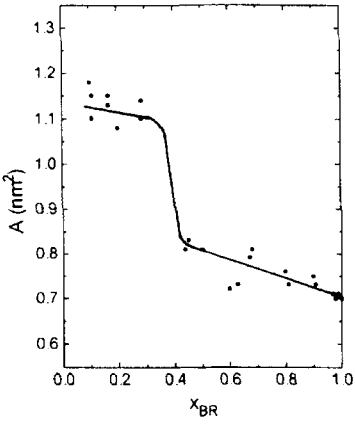



FIGURE 3 Apparent area per BR molecule in BR/SA mixed monolayer as a function $x_{BR}$.

**Acknowledgments**

This research work was granted by a Key Project of Science and Technology from the Education Department of China and Natural Science Foundation of Guangdong Province (980898, 970635).

## *References*

[1] T. Dorner, B. Knipp and D. A. Lightner, *Tetrahedron*, **53,** 2697 (1997).
[2] R. V. Person and B. R. Peterson et al., *J. Am. Chem. Soc.*, **116,** 42 (1994).
[3] S. E. Boiadjiev, and R. V. Person, *J. Am. Chem. Soc.*, **114,** 10123 (1992).
[4] J.-M. Ouyang and Z.-H. Tai et al., Thin Solid Films, **289,** 199 (1996).
[5] G. L. Gaines, Jr., Insoluble Monolayers at Liquid-Gas Interfaces, Interscience, New York, 1966, Chapter 6.
[6] D. Kaplan and G. Navan, *Israel J. Chem.*, **23,** 177 (1983).
[7] W. S. Sheldrick, *Israel J. Chem.*, **23,** 155 (1983).