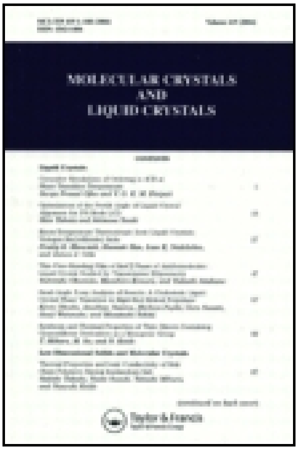

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Bilayer Formation of Two Chiral Ferroelectric Liquid Crystal Molecules at the Air-Water Interface

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To cite this article: Yan-Zhi Ren, Haishui Wang, Shiquan Xi, Yanqing Tian & Yingying Zhao (1997): Bilayer Formation of Two Chiral Ferroelectric Liquid Crystal Molecules at the Air-Water Interface, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 295:1, 97-100

To link to this article: http://dx.doi.org/10.1080/10587259708042805

Mol. Cryst. Liq. Cryst., 1997, Vol. 295, pp. 97–100
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BILAYER FORMATION OF TWO CHIRAL FERROELECTRIC LIQUID CRYSTAL MOLECULES AT THE AIR-WATER INTERFACE

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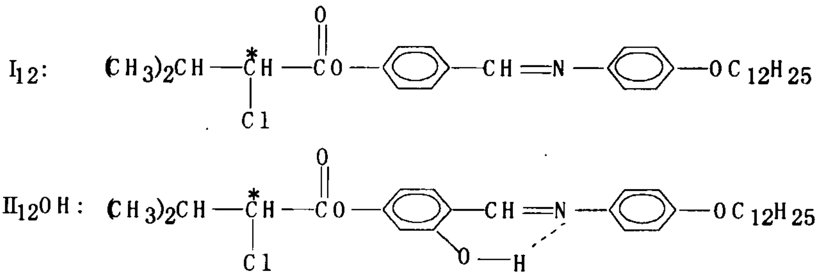
Abstract The bilayer formation behavior of two chiral ferroelectric liquid crystal molecules at the air-water interface was studied.

INTRODUCTION

Langmuir monolayers at the air-water interface have been extensively studied, while studies about multilayer formation on water are rarely reported.[1] Gruler [1] et al studied the multilayer formation of a chiral ferroelectric LC molecule on water by means of π-A isotherm. However, Gruler's molecule with the Schiff's base -N=CH- decomposes a little on water. We synthesized two molecules $II_{12}OH$ and I_{12} which are rather similar to Gruler's molecule. The molecule $II_{12}OH$ has a hydrogen bonding between the -OH and the -N=CH-, and hence is chemically stable on water.



SCHEME 1 Molecular structures of I_{12} and $II_{12}OH$

EXPERIMENTAL

Synthesis of the two compounds and their LC behavior were reported in reference 2.

The experiments were carried out with a KSV5000 film balance equipped with a surface potential (SP) meter. The surface potential was measured with a precision of 5mV, and the SP isotherm was well reproducible. The upper electrode was hung in the air and the lower electrode was immersed under water. The subphase was deionized and double distilled water. The water temperature was controlled to an accuracy of ±0.1°C.

RESULTS

$II_{12}OH$

The π-A isotherm (Fig. 1) of $II_{12}OH$ shows some typical transition points A_1 ($0.24nm^2$), A_2 ($0.12nm^2$) and A_3 ($0.04nm^2$). At the molecular area A_1, the molecule should form a tight monolayer on water. It was reported that azobenzene-containing long-chain fatty acids have an area of $0.25nm^2$ when standing vertically on water,[3] and the molecule $II_{12}OH$ is estimated to also have such an area. The molecular area A_2 is half of A_1, and the linear segment from A_1 to A_2 should reflect a transition from monolayer to bilayer.

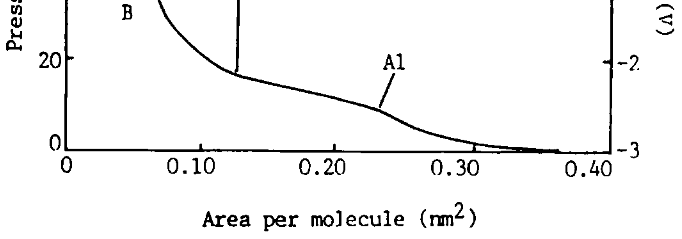
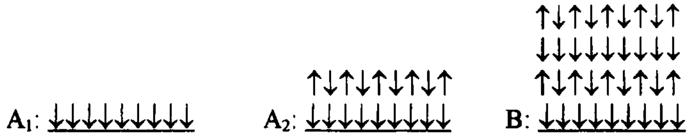


FIGURE 1 Pressure-area (bottom left) and potential-area (top right) isotherms of $II_{12}OH$ on water at 19.7°C, compressed at $6\times10^{-3}nm^2$/min. per molecule.

Polarized microscopic measurements (Zeiss Jena, 80 times) reveal that the films on water collapse at A_3 (65mN/m). The films at A_3 horizontally transferred onto quartz show crystalline domains and stripes under polarized microscope. While the films deposited at point B (40mN/m) show no images, and are uniformly dark.

X-ray diffraction measurements (Rigaku D/max rA, λ=0.154nm, CuKα) reveal that the films on water at 40mN/m have a bilayer structure. The films at 40mN/m were horizontally transferred only once onto silicon wafers. This once-transferred film has its first Bragg peak at 2θ=1.46°, with a period of 6.02nm. Since the calculated length of $II_{12}OH$ is 3.13nm, this film should be arranged in a bilayer fashion.

Surface potential measurements reveal the molecular packing manner in the bilayer. The molecule has a chiral head, which has a permanent dipole moment. The initial SP increase (Fig. 1) with compression reflects that the molecular dipole moments in the monolayer gradually stand up, with the chiral head attaching water and the hydrocarbon chains pointing to the air. (see below) The SP plateau in the range 0.27nm^2-0.12nm^2 reflects that the molecular dipole moments of the second layer must be statistically oriented on water. The number of molecular dipoles between the two electrodes should increase with compression. In order to keep the SP constant it is required that in the second layer the dipoles pointing upward be as many as the dipoles pointing downward. This is the same as Gruler's[1] bilayer structure. The final increase in SP beyond 0.12nm^2 (A_2) is small, but discernible and well reproduced. This implies that the films on water develop from bilayer to tetra-layer, with a "roll-over" mechanism.[4]



SCHEME 2 Molecular arrangement on water at points A1, A2, B of π-A isotherm

I_{12}

The surface-pressure area isotherms of I_{12}, as shown in Fig. 2, reveal that the optimal temperature for I_{12} to directly form bilayer on water is 19.7°C (the exact range is 15-22°C). The collapse area of isotherm b is 0.12nm^2, about half of the estimated cross-sectional area 0.25nm^2 of I_{12}. Isotherm b also has the longest and steepest linear solidanalogous region, among the three isotherms. At lower temperature 10.2°C (isotherm a) I_{12} tends to first form a monolayer on water, then develops into a bilayer. The molecular area at S_1 (0.12nm^2) is about half of that at S_2 (0.24nm^2). At higher temperature 29.2°C the isotherm c gives a meaningless collapse point. This temperature-dependent behavior of I_{12} is different from $II_{12}OH$, which always has a two-step bilayer formation mechanism in the range 15°C-30°C.

It is concluded that the mobility of the molecules on water surface is a crucial condition for bilayer formation. Low mobility favors a two-step mechanism and high mobility favors a one-step mechanism. The molecule $II_{12}OH$ has an additional hydroxyl group in comparison with I_{12} and hence has less mobility on water than I_{12}. At lower temperatures I_{12} has less mobility on water than at higher temperatures.

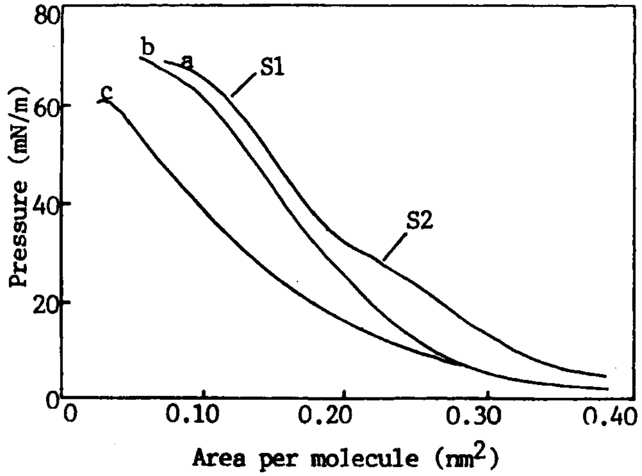


FIGURE 2 π-A isotherms of I_{12} on water. a, 10.2°C; b, 19.7°C; c, 29.2°C.

ACKNOWLEDGEMENTS

This work is supported by the National Science Foundation.

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