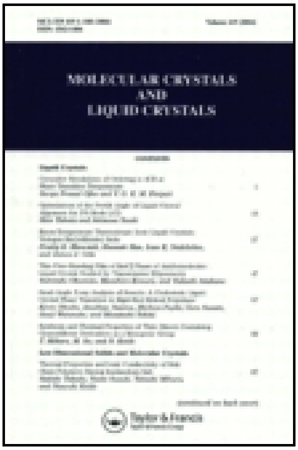

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Direct Visualization of Collapse Process of Porphyrin Monolayers and Porphyrin Exclusion from Mixed Monolayers at the Air-Water Interface

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DIRECT VISUALIZATION OF COLLAPSE PROCESS OF PORPHYRIN MONOLAYERS AND PORPHYRIN EXCLUSION FROM MIXED MONOLAYERS AT THE AIR -WATER INTERFACE*

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Abstract The collapse process of porphyrin monolayers at the air-water interface was studied by Brewster angle microscopy and by compression-recompression isotherms. It was found that the start of collapse observed by BAM is accordant with that measured by compression-recompression isotherms. The behavior of mixed monolayers was studied also and the results showed that porphyrin islands were excluded from mixed monolayers at 35mN/m.

INTRODUCTION

Porphyrins, as highly conjugated molecules, have been widely used as film materials because of their chemical stability and other various properties.[1,2] In this paper, the behavior of 5,10,15,20-tetra-(p-isoamoxycarbonphenyl)porphyrin monolayers at the air-water interface was studied by Brewster angle microscopy(BAM) and π-A isotherm. In particular, we try to characterize the start of collapse for porphyrin monolayers by BAM and by compression-recompression isotherms. The behavior for mixed monolayers of porphyrin and arachidic acid was studied also. It could be directly observed that porphyrin islands were excluded from mixed monolayers at the pressure of 35 mN/m.

EXPERIMENTAL SECTION

5,10,15,20-tetra-(p-isoamoxycarbonphenyl)porphyrin was synthesized and purified as described previously.[3] This material is capable of forming stable monolayers on water. Chloroform was used as the spreading solvent for both porphyrin monolayers and mixed monolayers. The subphase was deionized and double distilled water. Compression-

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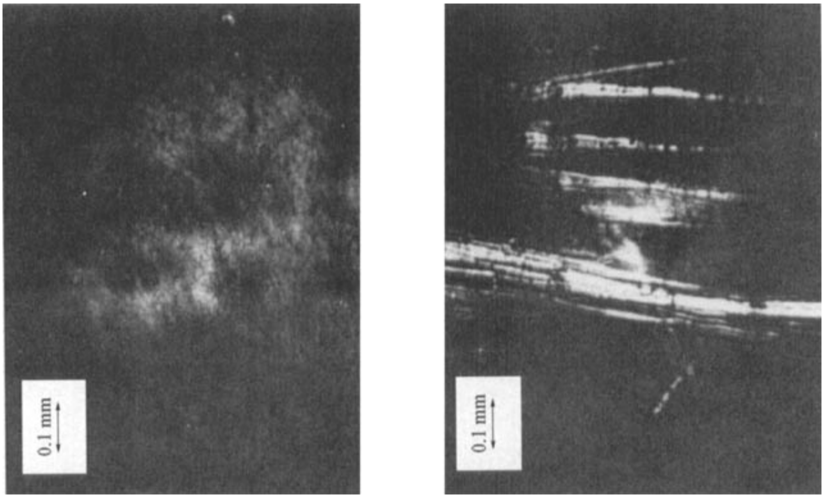
recompression isotherms were carried out by KSV-5000 Instruments. The images of BAM were obtained by BAM-2, manufactured by Institute of Photographic Chemistry, Chinese Academy of Sciences.

RESULTS AND DISCUSSIN

The images of monolayers were observed by BAM at different pressures. From images of monolayers, it was found that whether crumples (bright lines on the pictures) appeared in monolayers or not depending on pressures. Some crumples were observed in monolayers when the pressure was 40mN/m or higher, and no crumples were observed when the pressure was lower than 40mN/m. Fig.1 presented the characteristic pictures of monolayers at 20mN/m and at 40mN/m when monolayers were compressing, respectively. It was clear that crumples arose from collapsed monolayers and monolayers started to collapse at the pressure of 40mN/m.



20mN/m 40mN/m

FIGURE 1 Images of monolayers at 20mN/m and at 40mN/m, respectively.

It is of great interest that crumples were still observed after collapsed monolayers expanded to zero pressure. Fig.2 presented the picture of collapsed monolayers after expanded to zero pressure. This result indicated that crumples could not re-spread entirely when collapsed monolayers expanded. The existence of crumples would result in the decrease in areas of monolayers at any pressures when recompressing. The deccrease in areas of monolayers maybe had an effect on recompression isotherm. Typical compression-recompression isotherms of porphyrin monolayers were shown in Fig.3. It was shown that whether the tops of compression isotherms and that of recompression isotherms were coincident or not depending on the pressures. The tops of compression isotherms and that of recompression isotherms were coincident below the pressure of 40mN/m or were not coincident over 40mN/m. This result indicated that the collapse process of porphyrin monolayers could be characterized by compression-recompression isotherms.

FIGURE 2 Image of collapsed monolayers at zero pressure before recompression

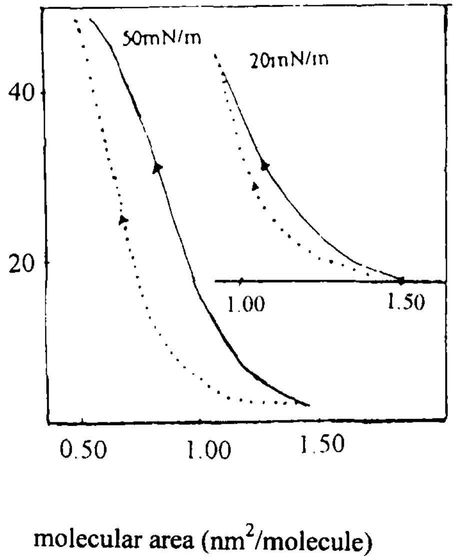


FIGURE 3 Compression (__) and recompression (.....) isotherm of porphyrin monolayers

Porphyrin and arachidic acid mixtures in $CHCl_3$ were used as the spreading solution. The molar ratios of porphyrin to arachidic acid were 1:1, 1:2, 1:4, 1:8 and 1:16 respectively. The Soret bands in the absorption spectra both for LB monolayers of porphyrin and for LB monolayers of mixtures(1:1, 1:2, 1:4, 1:8, 1:16) are at 425nm. Those are different from the Soret band in solution. This suggested that Porphyrin could not exist in mixed monolayers as individual molecule. Porphyrin maybe existed in mixed monolayers as porphyrin islands. It was not distinguished porphyrin islands from arachidic acid islands by BAM below the pressure of 35mN/m.

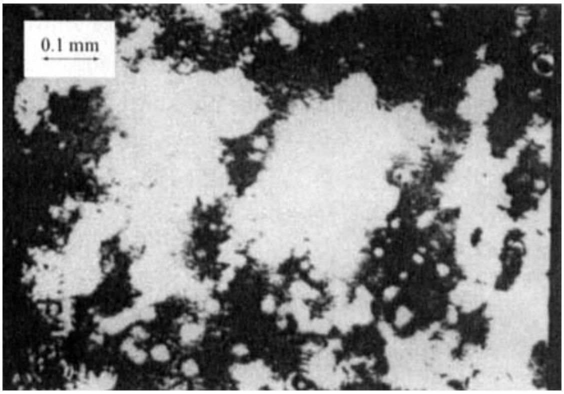


FIGURE 4 Image of porphyrin islands in mixed monolayers at 35mN/m

When molar ratio of porphyrin to arachidicacid was 1:4, it was observed that some islands, the bright areas as shown in Fig.4, were excluded from mixed monolayers at 35mN/m. It was the value of 35mN/m that corresponded to the break in the π-A isotherm. Simlar results were obtained when molar ratio were 1:8 and 1:16 respectively. It was found that the ratios of porphyrin to arachidic acid had an effect on the areas of islands that were excluded from mixed monolayers. The higher the content of porphyrin was, the larger the areas of islands were. This results revealed that it was porphyrin islands that were excluded from mixed monolayers. M.Vandevyver has reported that porphyrins were excluded from mixed monolayers.[4] When molar ratio was 1:1 or 1:2, the phenomenon that porphyrin islands were excluded from mixed monolayers was not observed. Above experimental results could be explained as follows. Arachidic acids were not excluded from mixed monolayers because of strong interaction between the carboxyl group of arachidic acid and water. If the ratio was 1:1 or 1:2, porphyrin islands occupied the most areas of mixed monolayers and the areas of arachidic acid in mixed monolayers were too few to exclude porphyrin from mixed monolayers.

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