# A Reflection Spectroscopic Study of Surface Pressure Gradients in Monolayers of Long Chain Fatty Acids

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Compression of long chain fatty acids generates gradients in surface pressure similar to but smaller than those reported previously for polymer monolayers. These have been investigated by reflection spectroscopy and surface pressure measurements for the monolayers at the air/water interface. The gradient increases sharply in the condensed state and is dependent on the chain length of the compounds chosen. The spreading as well as the compression techniques affect the gradient formation and a pressure gradient implying inhomogenity in the monolayer is always present. © 1995 Academic Press, Inc.

## INTRODUCTION

Monolayers spread at the air/water interface can provide an ideal model for phase transition effects and therefore have attracted considerable attention. Fatty acids and lipid molecules often show various monolayer phases at the air/water interface. Such monolayers have been used as a model for two-dimensional phase transitions and have been widely used in both experiment and theory (1–7). In most of these studies it has been assumed that the simple long chain fatty alcohols and acids form homogenous and defect-free condensed states leading to a uniform monolayer at the air/water interface. Radiotracer and surface potential studies on some long chain alcohols and octadecanoic acid have indicated that differences arise in compression and expansion isotherms depending on the measuring positions and velocity of area change (8, 9).

Reflection spectroscopic studies and surface potential measurements carried out on lipids and dye monolayers at the air/water interface have shown that a surface pressure gradient is formed during compression (10, 11). Recently Peng and Barnes have reported such pressure gradients in polyvinyl stearate and polymethyl methacrylate (12, 13). In this study, reflection spectroscopy and surface pressure have been used to investigate such gradients in long chain fatty acid monolayers at the air/water interface. Reflection spec-

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troscopy is based on the enhanced interfacial light reflection technique developed by Grüniger et al. (14). The advantage of using this technique is that it allows in situ measurements. It has been used to study the interaction of different monolayer-forming materials with a variety of subphases (15–17).

The results indicate that a surface pressure gradient is formed during compression and depends on the chain length of the material. It also depends to some extent on the spreading and compression techniques.

## EXPERIMENTAL METHODS

The long chain fatty acids were obtained from Sigma Chemie and the samples were 99.9% pure. Chloroform was used as the spreading solvent. For all the samples, concentration of the stock solutions were in m$M$. Deionized distilled water from Milli-Q Millipore was used for the subphase. All the experiments were done at 22°C. The surface pressure as a function of molecular area was measured using discontinuous compression with the interruption lasting 2 min. The compression speed was 0.01 nm/mol/min. The monolayers were formed in a circular PTFE trough. The surface pressure was measured using a 20-mm-wide filter paper Wilhelmy balance.

The reflection spectrometer used for the measurement under normal incidence of light was similar to that described earlier (14). The reflectivity measurements were done simultaneously with the surface pressure and the wavelength used was 548.3 nm (Sodium D-line).

The reflection spectrometer measured the difference in the reflectivity $\Delta R$ of the water–air interface covered by a monolayer and a clean reference surface. At least three reproducible results were obtained for each experimental pattern.

The spreading and the fiber optic position for the $\Delta R$ measurement are indicated by f for the position near the fixed barrier, e for the even position, and m for the moving barrier end.

## RESULTS AND DISCUSSION

Following the Fresnel equations, $\Delta R$ is proportional to the surface layer thickness at wavelengths where the mole-
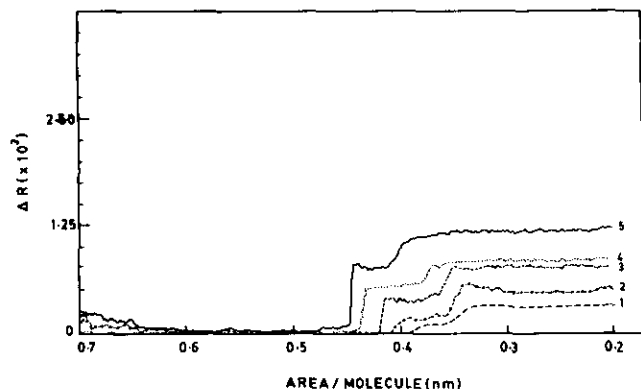
FIG. 1. R–Surface area plot for fatty acid monolayers for chain lengths corresponding to: 1, 14; 2, 15; 3, 17; 4, 18; and 5, 20 carbon atoms.

cules do not have any absorption (10). For the sake of brevity, the $\Delta R$–$A$ isotherms for the long chain fatty acid monolayers are shown in Fig. 1. It is seen that the lift-off area where the $\Delta R$ signal starts to rise is a function of the chain length of the fatty acid molecules. Here the position of the optic fiber is near the fixed barrier and the spreading of the solutions was done at that end (position f).

Figure 2 (A) and (B) shows plots of the lift-off area as a function of the chain length for different positions of the optic fiber and at different spreading positions. In all the cases the recorded reflection intensity values were highest near the moving barrier (position m) and decreased toward the fixed end (position f), clearly indicating a surface pressure gradient which was formed as compression proceeded. It is also seen that the gradient developed earlier when the solution was spread close to the moving barrier than when it was spread evenly from the fixed end.

Figure 3 shows the surface pressure gradient vs surface pressure plot. It shows the presence of a marked surface pressure gradient for the films in the condensed phase and that the apparent surface pressure at m is always higher than at f. We can attribute this to the horizontal displacement of the Wilhelmy balance along the compression direction. Such a displacement could lead to a decrease in the measured force value and an apparent increase in the recorded surface pressures so that the actual values are smaller than the recorded values. This is in agreement with the reflection spectroscopic data and the study of shear viscoelastic properties of monolayers of some polymers, octadecanol and behenic acid (18).

It is seen that the measured surface pressure should depend on the position of the Wilhelmy plate. The observation that the spreading mode affects the formation of the surface pressure gradients clearly indicates that after it is spread and before compression the monolayer is not homogeneous. Subsequent compression increases the inhomogeneity. The results also indicate that the longer the chain length, the greater the inhomogeneity of the monolayer formed during
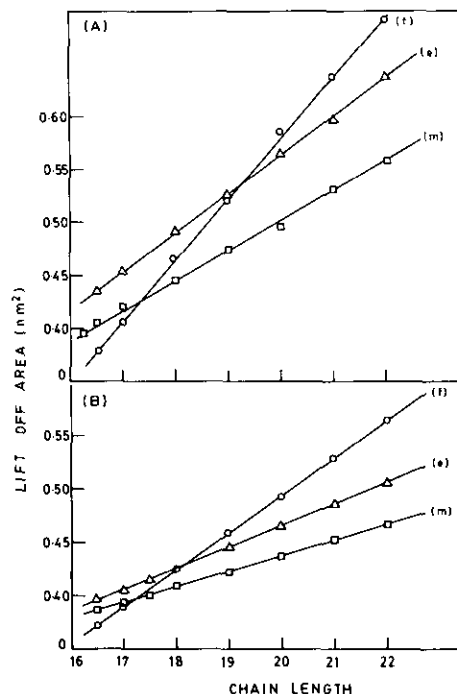


FIG. 2. Lift-off area vs chain length for positions of optic fiber at: m, moving barrier; e, even; and f, fixed barrier. (A) Spreading position at m and (B) at f.

compression. Such effects have been reported for the polymer monolayers also (12, 13).

The recently developed method of Malcolm (19), which uses the symmetric compression mode to improve the flow of the monolayer during compression, may give surface pressure values independent of the Wilhelmy balance position. Such a measurement also might lead to a better understanding of the inhomogeneity in simple monolayers.
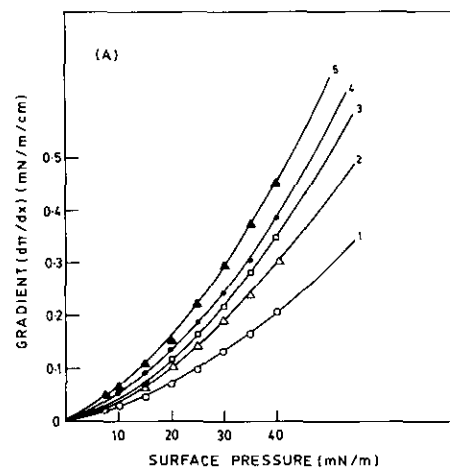


FIG. 3. Surface pressure vs surface pressure gradient for the different fatty acid monolayers for the spreading position at m.

## ACKNOWLEDGMENT

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