

Phase Separation In Langmuir Monolayers: Stearic and Elaidic Acid

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Introduction: Stearic acid is a prototypical molecule for Langmuir monolayer studies and the structure of these Langmuir films has previously been determined using x-ray scattering techniques. Elaidic and oleic acids, which are nearly identical to stearic acid, except for a double bond in the middle of the alkane chain, exhibit very different isotherms. The structure of these films has hereto never been investigated.

For stearic acid monolayers with zero surface pressure ($>24\text{\AA}^2/\text{molecule}$) previous x-ray scattering studies have shown that there is coexistence between a tilted condensed phase and a liquid expanded phase. Below this critical area, stearic acid monolayers exhibit a tilted orthorhombic structure whose tilt continuously decreases to zero and remains untilted prior to the collapse of the monolayer. For pure elaidic and oleic acids, the surface pressure increases from zero at about 55\AA^2 [1], corresponding to a molecular area that is twice that of stearic acid. For mixtures of elaidic and stearic acid, thermodynamic studies of these monolayers suggest mixing whereas for stearic and oleic acid they suggest phase separation.

Methods and Materials: X-ray reflectivity and grazing-incident angle diffraction(GID) studies were carried out using the BNL/Harvard Liquid Spectrometer at $\lambda=1.53187\text{\AA}$ and an x-ray Langmuir trough. Monolayers were spread on a pure water sub-phase from a fatty acid solutions solubilized in chloroform (typically 50-100 micro liters of a 1 mM solution). Measurements were carried out at either fixed area or constant pressure. In the case of elaidic and oleic acid, rapid pressure changes at fixed area necessitated constant pressure measurements.

Results: GID results are shown in the figures for a stearic acid monolayer and for a monolayer composed of a 1:1 mixture of stearic and elaidic acid. Both were obtained at an average surface pressures of $\sim 8\text{ mN/m}$. In the case of stearic acid this corresponds to a coverage of $\sim 22\text{\AA}^2/\text{molecule}$ and for the mixed monolayer this corresponds to a coverage of $\sim 30\text{\AA}^2/\text{molecule}$. The diffraction pattern, with the higher wavevector peak on the $L=0$ axis, and the lower peak off the $L=0$ axis is characteristic of a nearest-neighbor tilt with an area of about $\sim 22\text{\AA}^2$, determined from the lattice constants, in agreement with the isotherm area. For both samples, as the surface pressure is increased the off-axis peak position decreases, corresponding to a smaller tilt. At sufficiently high surface pressure $\sim 30\text{ mN/m}$ only a single peak is observed, corresponding to an untilted phase.

Conclusions: Our results show that the structure of mixed elaidic and stearic acid monolayer films exhibit the same GID patterns at the same surface structure, albeit at different molecular areas. This strongly suggests that the two components have phase separated where the stearic acid regions are ordered and the elaidic acid regions are disordered. These results are in contrast to the results of Fehrer[1] that found mixed monolayers. If the two components had indeed mixed to form an ordered structure, then the molecular area would have been closer to $30\text{\AA}^2/\text{molecule}$ and not the value of $22\text{\AA}^2/\text{molecule}$ calculated from the GID pattern. Subsequent Brewster Angle Microscopy studies provide support to our findings of phase separation.

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References

[1] A.I. Fehrer, R.D. Collins, T.W. Healy, Aust. J. Chem **30**, 511 (1977)

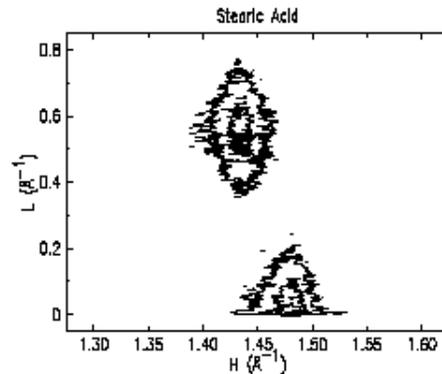


Figure 1. Grazing incident angle diffraction pattern from a monolayer of stearic acid at $\sim 8\text{ mN/m}$ at $15\text{ }^\circ\text{C}$.

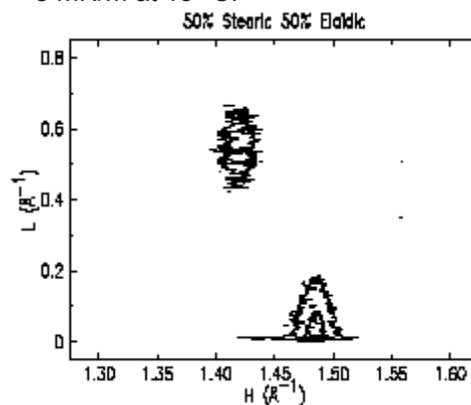


Figure 2. Grazing incident angle diffraction pattern from a monolayer of 1:1 mixture of elaidic and stearic acid at $\sim 8\text{ mN/m}$ at $15\text{ }^\circ\text{C}$.