



Effect of Wilhelmy Plate Material on Hysteresis of Langmuir Film Isotherms

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Langmuir isotherms and their hysteresis for monolayers of octadecanoic acid, octadecylamine and octadecanethiol were measured at 25 °C using an automated Langmuir trough. Surface pressures were measured with Wilhelmy plates made of platinum plate, filter paper and microscope slide cover made of glass. Hysteresis curves for octadecylamine on Pt plate and glass indicate that after the first compression, the contact angle increases. During subsequent cycles, the contact angle remains constant. For the Wilhelmy plate made of filter paper, the hysteresis curves are reversible for all the three substances, showing that the contact angle remains constant during all the cycles. For octadecanoic acid and octadecanethiol, adsorption on both Pt and glass is comparatively small, since subsequent isotherms differ only slightly from the first.

Key Words: Langmuir isotherms, Octadecanoic acid, Octadecanethiol, Hysteresis curves.

INTRODUCTION

Measurement of surface pressure-area isotherms of insoluble films on air-water interface is an established technique, which is useful, inter alia, for determining the orientation of the spread amphiphile molecules on the interface, for testing the stability of the surface film and for studying reactions between surface films and the subphases¹⁻⁸. In this experiment, the most commonly employed instrument is a modified Langmuir-Adam film balance. The modifications to the original film balance include automatically recorded, computer-controlled mechanized motion of barriers, electromechanical measurement and recording of surface pressure⁹.

In a typical experiment, a known amount of solution of a film-forming compound is spread on the surface of water between two surface barriers using a micro syringe. The solvent is allowed to evaporate and one of the barriers is moved towards the other, decreasing the area available to the monolayer. The surface tension is measured using a tensiometer with a Wilhelmy plate dipping into the aqueous phase. The barrier position and hence the available area and the surface tensions are recorded. The process continues till the monolayer collapses. A plot of surface pressure (decrease of the surface tension from the surface tension of the pure liquid) *versus* the area available to the monolayer is known as the surface pressure-area isotherm at any particular temperature.

The value measured by the surface balance depends on the contact angle between the Wilhelmy plate and the substrate water. The force on the plate is given by:

$$F = \rho_p g l w t - \rho_l g l w t + 2\gamma(t + w) \cos\theta \quad (1)$$

where ρ_p and ρ_l are the densities of the plate and the liquid respectively. γ is the liquid surface tension, θ is the contact angle of the liquid on the solid plate and g is the acceleration due to gravity. The air phase has been neglected in this equation, since its density is negligible. The length, width and thickness of the plate are, respectively, l , w and t .

The force, F , is measured with a microbalance. The balance is zeroed before measurement, so the first two terms on the right hand side of eqn. 1 are eliminated from the equation. If the contact angle, θ , is zero, $\cos\theta = 1$, the difference in downwards force, ΔF , experienced by the Wilhelmy plate in pure water and the film-covered water is given by:

$$\Delta F = 2(\gamma' - \gamma)(t + w) \quad (2)$$

here γ' and γ are the surface tensions of pure water and the film-covered water. The difference $\gamma' - \gamma = \pi$ is defined as the surface pressure of the film. If the thickness, t , is negligible compared to the width, w , eqn. 2 reduces to:

$$\Delta F = 2(\gamma' - \gamma)w = 2\pi w$$

During an experiment, w is constant, so the force measured is proportional to the surface pressure and through a calibration procedure its value can be changed to surface pressure. In case the contact angle, θ , has a value other than zero, the measured force will not give the correct value of the surface pressure.

If after the compression, the available area is increased causing the monolayer to expand and the cycles repeated, a hysteresis profile is obtained. The hysteresis curves indicate

the changes that have taken place with the repeated compression and expansion of the monolayer.

In the present work, isotherms and hysteresis of monolayers of octadecanoic acid, octadecanethiol and octadecylamine have been measured using Wilhelmy plates made of platinum, glass and filter paper.

EXPERIMENTAL

The automated Langmuir film balance used in this study was manufactured by Nima Technology, Coventry, England. The trough was made from a single slab of PTFE (or Teflon) with two PTFE barriers. Near one barrier was a measuring balance from which was hanging a Wilhelmy plate, which dipped into the aqueous phase. The force on the plate was measured by a microbalance, which displayed the reading on a computer screen. The speed at which the barrier was moved to compress the monolayer could be varied. The monolayer was compressed at a speed of $10 \text{ cm}^2/\text{min}$. The instrument displays a graph between the area available to the monolayer and the surface pressure.

The inside of the trough was cleaned with soapy water, followed by thorough rinsing with distilled water. It was then cleaned with hexane using tissue paper. Finally it was thoroughly rinsed with copious amounts of triply distilled water. The triply distilled water was prepared by taking distilled water and redistilling it in a two-stage all-quartz still. Commercial octadecanoic acid, octadecyl amine and octadecanethiol were recrystallized from hexane and their solutions prepared. The concentration of octadecanoic acid was $2.229 \times 10^{-3} \text{ M}$, that of octadecylthiol was $4.174 \times 10^{-3} \text{ M}$ and for octadecyl amine it was $2.0248 \times 10^{-3} \text{ M}$. The solutions were prepared in pure hexane for the first two and for the amine 5 mL of ethanol was added to the solvent hexane.

The measurements were made at a constant temperature of 25°C , by allowing the substrate water to come to this temperature by storing it in a water bath. Blank runs on pure water and with spread pure solvent were made to ensure that there was no surface impurity.

Wilhelmy plates made of three different materials were used. They were: a platinum plate, a filter paper and a glass microscopic slide cover. The platinum plate and the filter paper was each of the dimensions $10 \text{ mm} \times 10 \text{ mm}$, while the glass slide cover was $18 \text{ mm} \times 18 \text{ mm}$. To clean the platinum plate, it was heated to red hot to burn off the impurities clinging to it. The filter paper was used without any treatment. The glass slide cover was cleaned with a solution of chromic acid (potassium dichromate in concentrated sulfuric acid) followed by thoroughly rinsing with copious amounts of triply distilled water.

Measurement of hysteresis: To measure hysteresis curves, the monolayer was compressed and before it collapsed, the motion of the barrier was reversed to start expansion. This was done by changing the sign of the speed of the barrier to negative. After the monolayer expanded fully to the point where the compression had originally started, the sign of the speed was changed back to positive to compress the monolayer to repeat the cycle. Similarly, several cycles were recorded.

RESULTS AND DISCUSSION

The hysteresis curves for the three substances with each Wilhelmy plate are given in Figs. 1-9. For the Wilhelmy plate

made out of a filter paper, the hysteresis curves showed that the isotherms were reversible. Except for a small amount of loss of film material, the curves were superimposable. This shows that the contact angle of water with the filter paper did not change from one cycle to the next. This held for all the three substances studied.

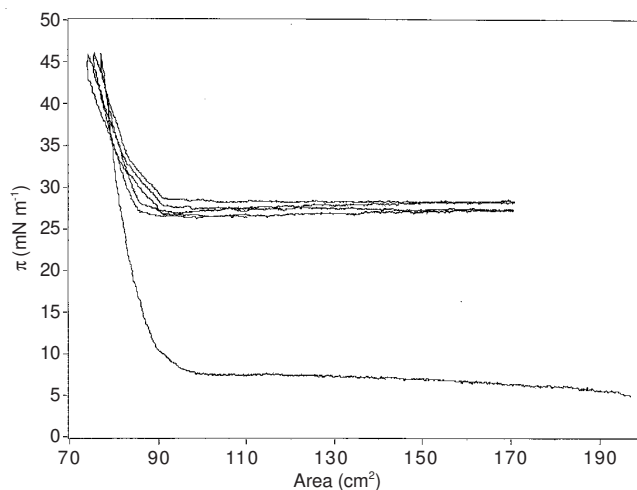


Fig. 1. Hysteresis curves of octadecylamine monolayer over water 25°C , using Pt Wilhelmy plate. $35 \mu\text{L}$ of 2.0248 mM solution spread. Speed of compression = $10 \text{ cm}^2/\text{min}$. The first cycle is the one with the lower baseline. Subsequent cycles are shifted up wards and they progressively shift left because of the loss of material (Ref. 10)

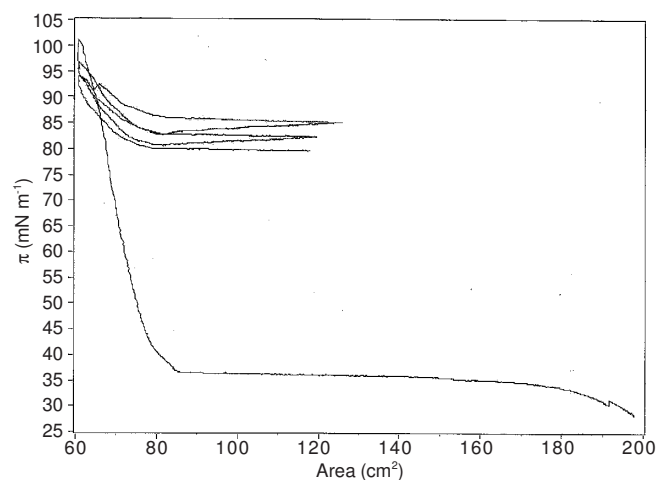


Fig. 2. Hysteresis curves of octadecylamine monolayer over water 25°C , using glass slide cover as the Wilhelmy plate. $25 \mu\text{L}$ of 2.0248 mM solution spread. Speed of compression = $10 \text{ cm}^2/\text{min}$. The first cycle is the one with the lower baseline. Subsequent cycles are shifted up wards and they progressively shift left because of the loss of material (Ref. 10)

The behaviour with filter paper contrasts markedly with glass and platinum, particularly for octadecyl amine. For the amine, with glass slide cover and with Pt plate, instead of the isotherm beginning with a flat region as with the filter paper, the surface pressure curve continuously rises gently, before it reaches the region where it starts to increase steeply. This continuous gentle increase is caused by the adsorption of the amine on the Wilhelmy plate surface leading to a progressive increase in the contact angle, which in turn causes an increased surface pressure to be registered according to eqn. 1 when $\theta > 0$. This

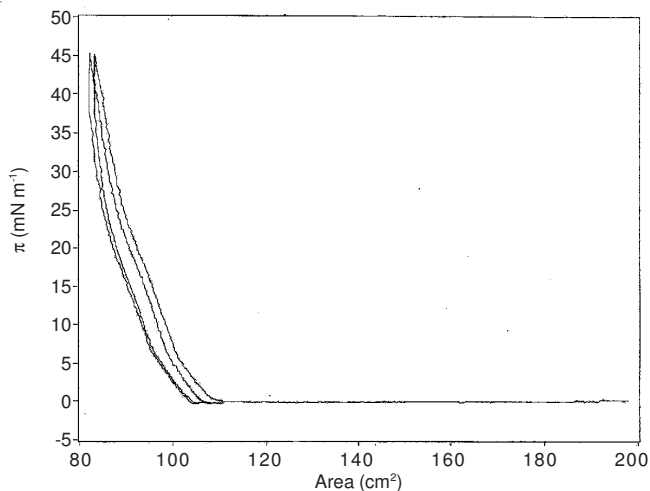


Fig. 3. Hysteresis curves of octadecylamine monolayer over water at 25 °C, using filter paper Wilhelmy plate. 35 μ L of 2.0248 mM solution spread. Speed of compression = 10 cm^2/min . The first cycle is the one at the right. Subsequent cycles shift to lower areas because of the loss of film material to evaporation and dissolution

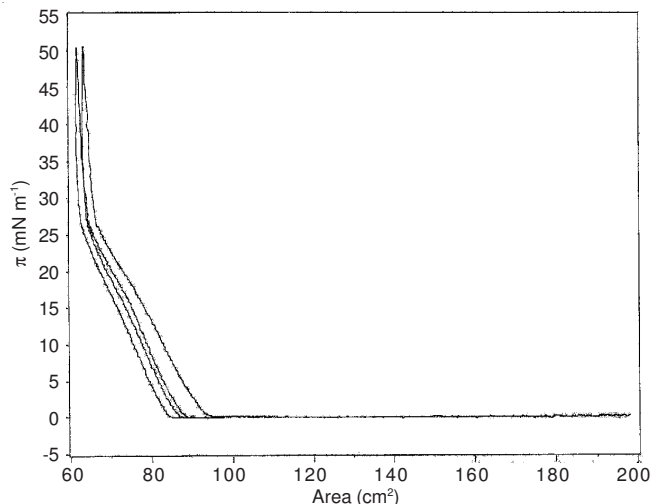


Fig. 6. Hysteresis curves of octadecanoic acid monolayer over water at 25 °C, using filter paper Wilhelmy plate. 25 μ L of 2.2287 mM solution spread. Speed of compression = 10 cm^2/min

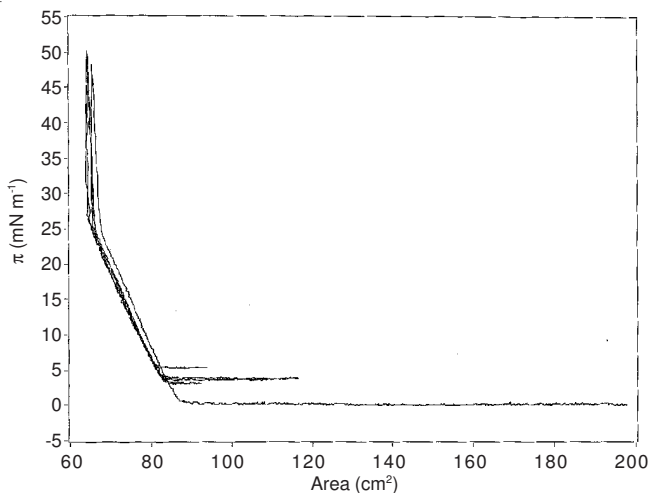


Fig. 4. Hysteresis curves of octadecanoic acid monolayer over water at 25 °C, using Pt Wilhelmy plate. 25 μ L of 2.2287 mM solution spread. Speed of compression = 10 cm^2/min

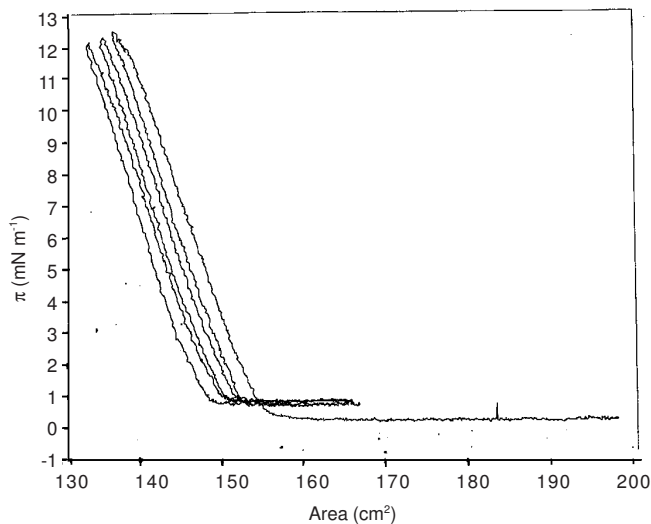


Fig. 7. Hysteresis curves of octadecanethiol monolayer over water at 25 °C, using Pt Wilhelmy plate. 25 μ L of 4.1735 mM solution spread. Speed of compression = 10 cm^2/min

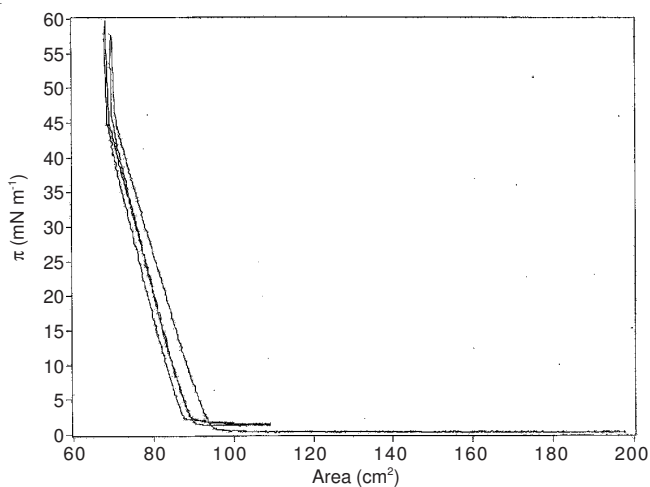


Fig. 5. Hysteresis curves of octadecanoic acid monolayer over water at 25 °C, using glass Wilhelmy plate. 25 μ L of 2.2287 mM solution spread. Speed of compression = 10 cm^2/min

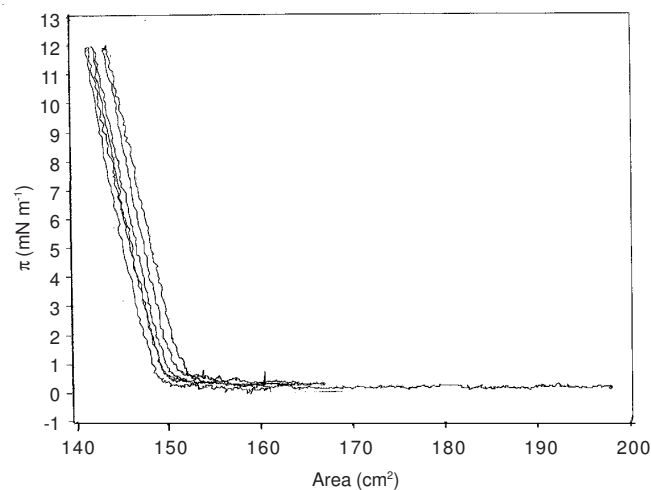


Fig. 8. Hysteresis curves of octadecanethiol monolayer over water at 25 °C, using glass Wilhelmy plate. 25 μ L of 4.1735 mM solution spread. Speed of compression = 10 cm^2/min

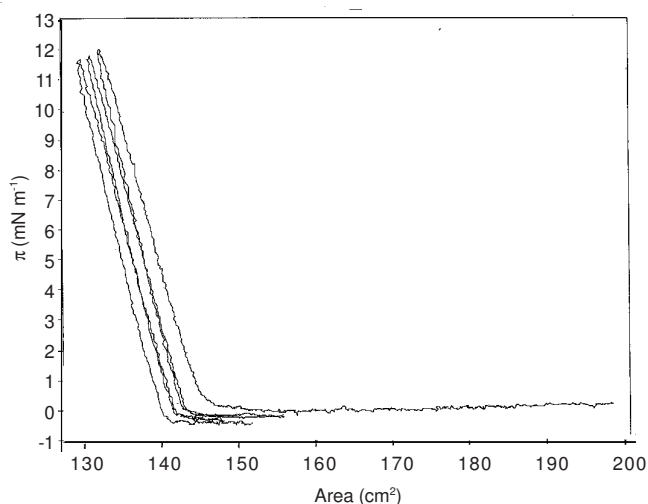


Fig. 9. Hysteresis curves of octadecanethiol monolayer over water at 25 °C, using filter paper Wilhelmy plate. 25 μ L of 4.1735 mM solution spread. Speed of compression = 10 cm^2/min

interpretation is confirmed by the hysteresis curves. During hysteresis measurements of the amine with platinum plate and glass, the baseline of the second cycle does not coincide with that of the first cycle. When the monolayer is expanded, the surface pressure does not reach zero on full expansion. Instead, what should be the region of zero surface pressure (the baseline on full expansion) shows a pressure over 20 mN/m .

This behaviour is peculiar to octadecyl amine. For octadecanethiol measured with glass and platinum plate, the subsequent cycles in hysteresis curves show a relatively small difference (Figs. 7 and 8) from the first. With glass and with platinum the deviation is very small compared to the case for the amine. This leads to the conclusion that the contact angle of the Wilhelmy plate remains constant after the first cycle, which in turn implies that octadecanethiol does not get adsorbed significantly either on glass or on platinum surface during the measurements.

Similarly, octadecanoic acid displays a small difference in isotherms measured subsequent to the first cycle. The

conclusion is that the contact angle does not change significantly, which implies that octadecanoic acid too does not get adsorbed sufficiently on either glass or platinum surface. This is confirmed by the fact that the earlier portion of the isotherm is a straight line, with the surface pressure remaining constant before it starts rising steeply.

The hysteresis behaviour also shows that for the systems studied there was some loss of the monolayer material over time as indicated by the shift of the isotherms to lower area/molecule in successive cycles. This loss is caused by evaporation and dissolution of the monolayer material in the subphase¹⁰.

Conclusion

Octadecylamine coats platinum and glass surface changing the contact angle between water and the Wilhelmy plate, which leads to erroneous values of the surface pressure. This causes an irreversible behaviour observed during the hysteresis studies. The hysteresis curves with filter paper Wilhelmy plate on the other hand show reversible behaviour. Octadecanoic acid and octadecanethiol show reversible hysteresis curves on all three types of material. Hysteresis shows that the loss of monolayer material during the experimental timeframe is minimal.

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