

## **Experimental Study of Densely Packed Thin Film of Octadecanoic Acid at Air–Water Interface**

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## Abstract

The surface pressure-area ( $\pi$ -A) isotherm of Octadecanoic Acid (OA) was obtained by using Langmuir balance technique. The characterization of two dimensional thin film of OA was carried out in term of  $\pi$ -A isotherm and rigidity. There has been plenty of work reported on the studies for L and LB film on solid substrates. However, formation of densely packed thin film of OA before the first compression with respect to initial surface pressure and effect on final surface pressure after the compression for high surface density initially loaded has not been investigated at the A-W interface. As areal density of the molecule on water surface increases before the first compression started, the nature ( $\pi$ -A) isotherm and behavior of the 2-D film changes..

## 1. Introduction

When surfactant molecule spread at the A-W interface, it form Langmuir monolayer or in some cases leads to formation of multilayer. The Langmuir monolayer of water-insoluble, single chain amphiphiles with simple polar groups can exist in different phases depending on the surface density, temperature and surfactant structure. Two dimensional thin Langmuir films are having wide range of application in various fields. The Langmuir-Blodgett (LB) technique is well known to be an attractive method for preparing high-quality ordered thin films. In order to form defect free LB films, the properties of the monolayer and condition of the possibility of quantitative transfer must be carefully investigated. Fatty acid Langmuir monolayer like OA monolayer on pure water have been well studied and different phases have been observed under area (A) of compression [1]. Existence of these different phases can be inferred from the changes in the slope of the  $\pi$ -A isotherm [2], Brewster angle microscopy (BAM) [3] and X-ray diffraction [2]. The surface pressure-mean molecular area ( $\pi$ -A) isotherm of Octadecanoic acid (OA), was obtained by using Langmuir technique.  $\pi$ -A isotherm obtained for various loading with increase in amount of OA at air-water interface.

## 2. Experimental Section

### A. Materials

Octadecanoic acid (C<sub>17</sub>H<sub>35</sub>COOH, 99%) (purity 99%) were purchased from Sigma-Aldrich Chemical Company. Octadecanoic acid and Chloroform was used without further purification. All other reagents used were of analytical grade. Chloroform (99.9%) was used as a solvent and

Milli-Q water was used as subphase (resistivity > 18.0 M $\Omega$  cm at 25 °C). All the experiments were done at 25.0  $\pm$  0.1 °C, in a dust free environment. AR grade acetone was used for cleaning purpose of the trough and barrier.

### B. Method

Experiments were conducted in a Langmuir mini-trough system (KSV instruments Ltd., Finland) having trough size 324 X 75 mm. The subphase temperature of the experiments was set at 25  $\pm$  0.1 °C and the subphase temperature controlled with a thermostat (PolyScience Digital Controller, USA). All the measurements were performed at 25 °C. The trough was made of teflon and moving barrier was made of Derlin. A Whilhelmy plate method was used for surface pressure measurements with accuracy 0.01 mN.m<sup>-1</sup>. The Langmuir balance was enclosed in a glass box to avoid air disturbance as well as dust particles. Prior to spreading of OA solution on the subphase, LB trough and barriers were cleaned with acetone (AR Grade) and rinsed by Milli-Q water several times. After cleaning the trough and the barrier, they were fitted in the appropriate positions. Milli-Q water was then poured into the trough till the barriers were in contact with the water. Any contamination, which may have been present on the surface of water, was removed by bringing barriers close together so that the surface area was minimized and then withdrawing the top layer of the subphase with the help of a suction pump (SP20, KSV instrument, Finland). The procedure was repeated until the surface pressure recorded at the minimum area was < 0.01 mN/m. 20  $\mu$ L of the solution, containing 1 mg.mL<sup>-1</sup> of Octadecanoic acid in chloroform, was then spread dropwise on water surface using a gastight Hamilton microsyringe. After complete spreading of the solution, 30 minute of time was provided for the solvent to evaporate before the start of the measurements. This period was sufficient for chloroform evaporation [4, 5]. The pH of the Milli-Q water was  $\approx$  6.5 (due to CO<sub>2</sub> dissolution). After solvent evaporation, the monolayer were compressed at a speed of 10 mm.min<sup>-1</sup> [6] and expansion rate 5 mm/min was kept constant. The data for the surface pressure as a function of mean molecular area was recorded. Triplicate runs were conducted in order to check the reproducibility of surface pressure measurements in all cases.

## 3. Results and Discussion

### A. $\pi$ -A isotherm Measurement

Figure 1 depicts  $\pi$ -A isotherms of OA insoluble monolayer at the A-W interface. The results obtained in our studies are consistent with the literature [4, 7, 8]. The isotherm shows two linear curves. Initially the surface pressure constant is and nearly zero then increases linearly, after which it increases sharply at lower mean molecular area before collapsing. In both these regions, the isotherm seems to have a different slope.

The lower region has slope less than upper region. The change in slope indicates some rearrangement of the molecules at the A-W interface, most probably from a flat orientation to a vertical orientation. After this rearrangement, the slope again increases sharply, indicating the formation of the compact solid phase. It was observed that the collapse pressure of the OA monolayer at the A-W interface on our studies was little bit less than reported in literature [8]. The characterization of the  $\pi$ -A isotherm in term of compressibility factor was reported in literature [9].

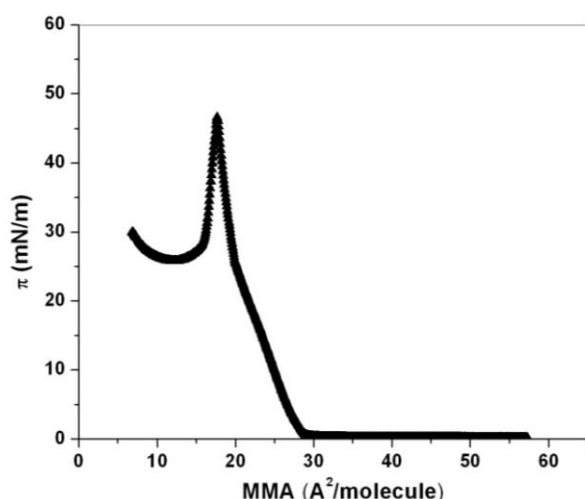


Figure 1:  $\pi$ -A isotherm of Octadecanoic acid at air-water interface (Temperature 25°C, compression rate 10 mm.min<sup>-1</sup> waiting time = 30 min.)

### B. Effect of Increasing Areal Mass Density on Initial Surface Pressure

The effects of increasing areal mass density of OA on  $\pi$ -A isotherm on water surface was studied as shown in Figure 2. With the increase in density of the OA molecules from spreading solution,  $\pi$ -A isotherm shifted towards left in gases and liquid state. When surface pressure reached 47 mN.m<sup>-1</sup>, monolayer get collapse. It is observed that mean molecular areas with different spreading amount at air-water interface were different which means might be number of OA molecules play a role in  $\pi$ -A isotherm. More amount of OA added, more of

OA molecules remain on the surface. However, the collapse pressures observed nearly the same in all cases but surface pressure after collapse is different for different amount of spreading solution of same concentration. There might be chances of multilayer formation in presence of large amount of molecule on surface. In the present study, the isotherm was found to be highly reproducible under identical experimental conditions. In order to understand the role of number of molecule of OA on surface, isotherms were recorded by increasing the amount of spreading solution (Figure 2). It is observed that as the surface density of OA molecule increases by loading the high amount of solution on water surface, the  $\pi$ -A curve did not overlap with the previous  $\pi$ -A curve after 40  $\mu$ g of loading of OA. The effect of increasing surface density of OA on initial surface pressure  $\pi$ -A isotherm at air water interface was studied as shown in Figure 3.

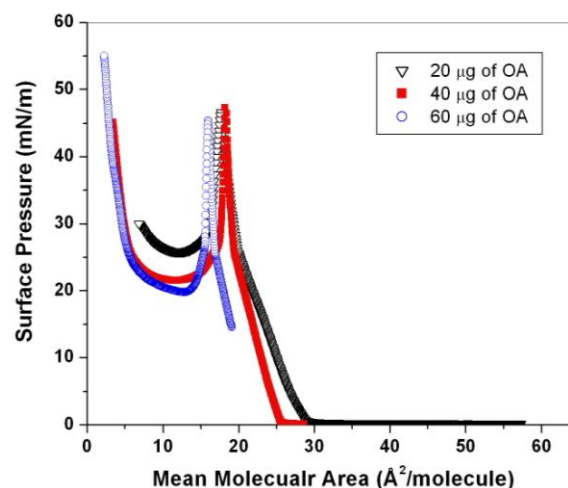


Figure 2: Effect of areal mass density of OA loaded on water surface (compression speed = 10 mm.min<sup>-1</sup>, waiting time = 30 min. Temperature 25°C)

With the increase in number of molecules of OA from spreading solution on water surface before starting the compression it is observed that  $\pi$ -A isotherm shifted towards left. It was found that in case of 60  $\mu$ g of OA loaded, the initial surface pressure of  $\pi$ -A isotherm raised by some value which indicates that more OA molecules existed in layer, but in case of 40  $\mu$ g loading does not found any increases in initial surface pressure. The initial surface pressure vs. OA amount loaded on subphase showed a sigmoidal shape (Figure 3). As the quantity of OA on subphase increases, it was found that initial surface pressure ( $\pi$ ) increases slowly followed by rapid rise and then again slowly. Almost all the  $\pi$ -A isotherm of OA monolayer shows the same maximum surface irrespective of the quantity added on the surface.

The surface pressure after collapse of monolayer found to be different for different amount of spreading at interface.

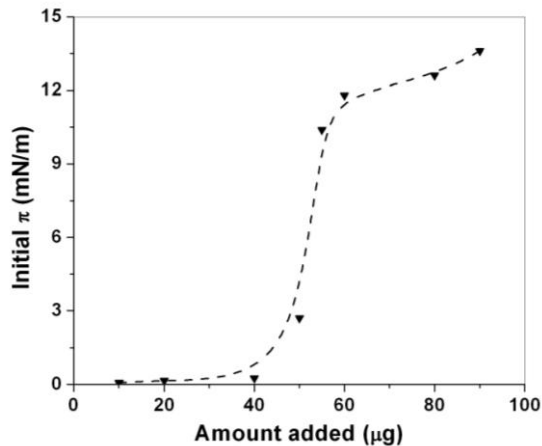


Figure 3: Effect of increase in surface density of OA on water surface on initial surface pressure (compression speed = 10 mm.min<sup>-1</sup>, waiting time = 30 min. Temperature 25°C)

#### 4. Conclusion

The Langmuir monolayer of OA at air–water interface was prepared successfully for various surface densities. The surface density of OA molecule increased initially before the first compression by increasing the amount of OA on water surface. The optimum condition, such as surface density of the OA i.e. amount of OA loaded on water surface was studied. It is observed that with increasing the amount of OA on water surface,  $\pi$ -A isotherm shifted towards left in gases and liquid state. Almost all the  $\pi$ -A isotherm of OA Langmuir film shows the equal final surface pressure irrespective of the surface density initially loaded on water surface. The surface pressure after collapse of monolayer found to be different for different amount at interface.

#### 5. References

- [1] G. L. Gaines, " " *Insoluble Monolayers at Liquid-Gas Interfaces*.: Interscience, New York, 1996
- [2] VM Kaganer, H Mohwald, and P Dutta, *Reviews of Modern Physics*, **1999**, 71(3), 779-819.
- [3] GA Overbeck, and D Mobius, *Journal of Physical Chemistry*, **1993**, 97(30),7999-8004.
- [4] LVN Avila, SM Saraiva, and JF Oliveira, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, **1999**, 154(1-2), 209-217.
- [5] GY Wen, B Chung, and TH Chang, *Polymer*, **2006**,47(26), 8575-8582.

[5] HS Wang, *Vibrational Spectroscopy*, **2004**, 34(1), 169-173.

[7] S Kundu, and D. Langevin, , *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 2008. **325**(1-2): p. 81-85.

[8] YS Kang, DK Lee, and YS Kim, *Synthetic Metals*, **2001**, 117(1-3),165-167.

[9] RS Bhande, YA Landge, PA Giri, *Journal of Chemical and Pharmaceutical Research* accepted for publication, **2012**,5(4)