Study the Behavior of π-A Isotherm with Increasing Amount of Octadecanoic acid at Air–Water Interface

R. S. Bhande[#], Y. A. Landge and P. A. Giri

Department of Chemical Engineering, Finolex Academy of Management and Technology, Ratnagiri, M.S., India
_____

ABSTRACT

The surface pressure-mean molecular area (π-A) isotherm of surfactant was obtained by using Langmuir balance technique. Characterization of 2-D Langmuir film of Octadecanoic acid (OA) was carried out in term of π –A isotherm and surface pressure–compressibility (π–C_S) curve. There has been plenty of work reported on the studies for Langmuir monolayer and Langmuir Blodgett film monolayer or multilayer sampled on solid substrates. However, effect of increasing in amount of surfactant with respect to initial and final surface pressure of on π -A isotherm not been investigated at the air-water interface. Surface pressure–compressibility (π–C_S) curves of OA monolayer obtained from the surface pressure area data. The compressibility characterized the phase transition of film more clearly during the monolayer compression and is deemed to be more sensitive for intermolecular interactions especially for their changes. The phase transition point of OA monolayer was shown clearly by a peak in π–C_S curve.

Keywords: Langmuir film, OA, Surface pressure, Isotherm, Compressibility,
_____

INTRODUCTION

When surfactant molecule spread at the air-water 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 monolayers like Octadecanoic acid monolayers 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 π-A isotherm [2], Brewster angle microscopy (BAM) [3] and X-ray diffraction [2]. The surface pressure-mean molecular area (π -A) isotherm of Octadecanoic acid (OA), was obtained by using Langmuir technique. π-A isotherm obtained for various loading with increase in amount of OA at air-water interface. There has been plenty of work reported on the studies for Langmuir monolayer and Langmuir Blodgett film with OA but with increasing the loading of OA at air water interface not been investigated.

_____

EXPERIMENTAL SECTION

A. *Materials*

Octadecanoic acid (C$_{17}$H$_{35}$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 MΩ cm at 25 °C). All the experiments were done at 25.0 ± 0.1 ^{0}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 ± 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^{-1}. 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 µL of the solution, containing 1 mg.mL^{-1} 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 ≈ 6.5 (due to CO$_2$ dissolution). After solvent evaporation, the monolayer were compressed at a speed of 10 mm.min.$^{-1}$ [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.

RESULTS AND DISCUSSION

A. *π-A isotherm Measurement*

Figure 1 depicts *π* -A isotherms of OA insoluble monolayer at the air–water 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 slop less than upper region. The change in slope indicates some rearrangement of the molecules at the air–water 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 Octadecanoic acid monolayer at the air-water interface on our studies was little bit less than reported in literature [8].

B. *Effect of Increasing Loading on Initial Surface Pressure*

The effect of increasing loading of OA on π-A isotherm at air water interface was studied as shown in Fig. 2. With the increase in number of molecules of OA from spreading solution, π-A curve shifted towards left. It was found that the initial surface pressure of *π–A* isotherms increased, in case of 60 µg of OA loaded which indicated that more OA molecules existed in layer but in case of 40 µg amount initial surface pressure does not show any increased. The initial surface pressure vs. OA amount loaded on subphase showed a sigmoidal shape (Figure 2). As the quantity of OA on subphase increases, it was found that initial surface pressure (π) increases slowly followed by rapid rise and then again slowly. Almost all the π-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.
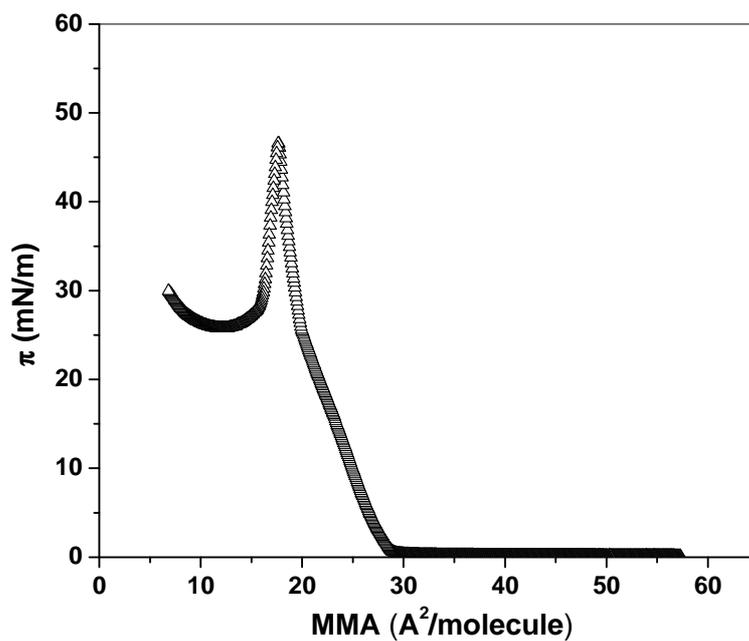
_____

Figure 1: π-A isotherm of Octadecanoic acid at air-water interface (Temperature 25°C, compression rate 10 mm.min⁻¹ waiting time = 30 min.)
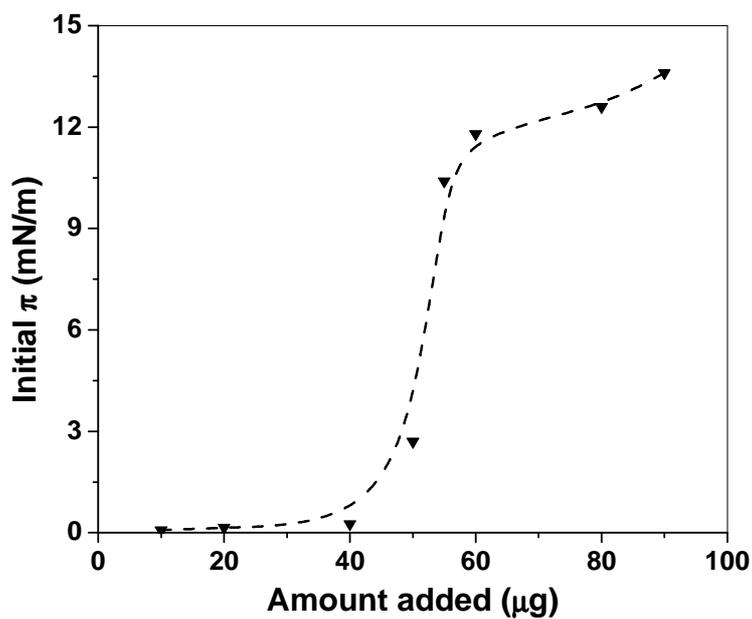

Figure 2: Effect of amount of OA loaded on subphase on initial surface pressure (compression speed = 10 mm.min⁻¹, waiting time = 30 min. Temperature 25°C)

C.　Static Compression Modulus

The compressibility coefficient is defined as following equation:

$$C_S = -\frac{1}{A}\left(\frac{\partial A}{\partial \pi}\right)_T$$

(1)

_____

Where *A* is the mean molecular area which is calculated automatically by Langmuir–Blodgett Trough according to the OA amount added into subphase and π is the corresponding surface pressure. It is expressed as m.mN^{-1}. The compressibility coefficient is often interpreted as its reciprocal form ($K' = 1/C_S$), originally defined as the surface compressional modulus, which is a measurement of the compressional elasticity of the film [9].

The typical surface pressure–area (π–*A*) isotherms shown in figure 1 and surface pressure–compressibility (π–C_S) curves of OA film are shown in following figure 3. Compared with conventional surface pressure isotherm, the compressibility characterized the phase transition of film more clearly during the monolayer compression and is deemed to be more sensitive for intermolecular interactions especially for their changes. Figure 3 shows the phase transition point of OA layer by a peak in π–C_S curve. The surface pressure of the phase transition ranges from 25 to 35 mN.m^{-1}, according to the π–C_S curve. The maximum compressibility about 0.75 m.mN^{-1} has been observed.
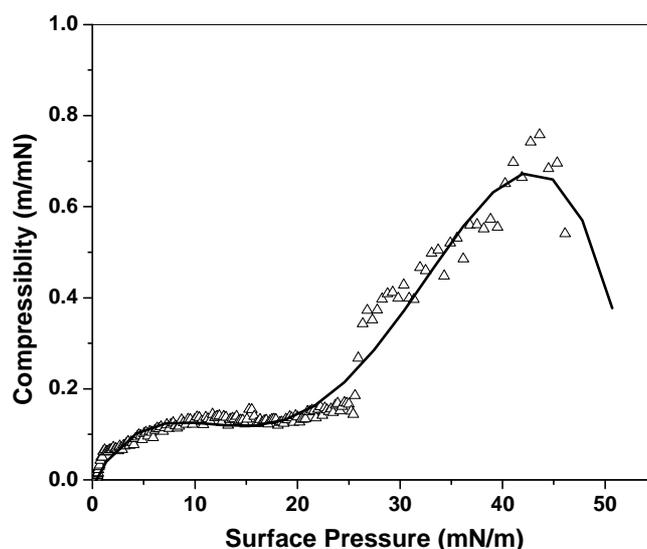

Figure 3 Surface pressure–compressibility (π–C_S) curves of OA monolayer at air water interface (compression speed = 10 mm.min^{-1}, waiting time = 30 min. Temperature 25°C)

CONCLUSION

In this research, OA Langmuir monolayer was formed successfully by spreading OA solution directly air-water interface. The optimum condition, such as amount of OA loaded on subphase was studied. It is observed that with increasing the amount of OA on water subphase, π-A isotherm shifted towards left. Almost all the π-A isotherm of OA monolayer shows the same final surface pressure irrespective of the amount added at air water interface. The surface pressure after collapse of monolayer found to be different for different amount at interface. The compressibility of OA film during compressing process indicates that phase transition occurred. The maximum compressibility about 0.75 m.mN^{-1} has been observed.

REFERENCES

[1] GL 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.
[6] 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] F Behroozi, Langmuir, **1996**, 12(9), 2289-2291.