STUDIES ON THE PHASE TRANSITIONS AND MOLECULAR CONFORMATIONS IN LANGMUIR MONOLAYERS

by

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Thesis submitted to Jawaharlal Nehru University
for the award of the degree of
Doctor of Philosophy.

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CERTIFICATE

This is to certify that the thesis entitled Studies on the Phase Transitions and Molecular Conformations in Langmuir Monolayers submitted by Amitabha Bhattacharyya, for the award of the degree of DOCTOR OF PHILOSOPHY of Jawaharlal Nehru University is his original work. This has not been published or submitted to any other university for any other degree or diploma.

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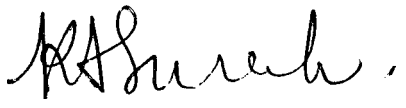
DECLARATION

I hereby declare that this thesis is composed independently by me at the Raman Research Institute! Bangalore, under the supervision of Prof. Kattera A. Suresh. The subject matter presented in this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title.



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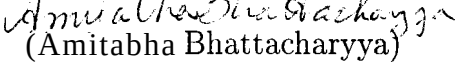

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Symbols used frequently in the thesis

	Surface Pressure
γ	Surface Tension
A_m	Area per molecule.
T	Temperature.
D_1	Three Layer Domains.
D_2	Optically flat 3D domains.
D_3	Lens shaped 3D domains.
χ_{SA}	Molar Concentration of SA.
f	No. of degrees of freedom of a system.
C^B	No. of components in bulk.
C^S	No. of components confined to the interface.
P^B	No. of phases in bulk.
q	No. of phases in the monolayer.
$P_\perp$	Surface Dipole Moment.
ΔV	Surface Potential.
d	Thickness of a Domain.
μ'	Refractive Index.
ε	Elastic Constant.
μ	Chemical Potential.
a	Activity.
ϕ	Surface Area Fraction.
x	Mole Fraction.
ΔH_{mix}	Residual Enthalpy of Mixing.
W	Dispersion Interaction Energy.
π^*	Value of π corresponding to Molecules being expelled from the Interface.
A_m^*	A_m corresponding to π^*.

Preface

This thesis deals with studies on phase transitions and molecular aggregations in Langmuir monolayers. Amphiphilic molecules spread at the air - water interface to form a mono-molecular film called a Langmuir monolayer. In this thesis, the word monolayer refers to Langmuir monolayer, unless stated otherwise. The monolayers behave like two – dimensional (2D) systems and are interesting, both from the scientific and industrial point of view.

Monolayers exhibit many different 2D phases. The typical phase sequence, seen on increasing the surface molecular density of the monolayer is gas, liquid-expanded (LE), liquid-condensed (LC) and solid. Monolayers are one of the easily realisable 2D systems. They exhibit extremely rich phase diagrams and unusual pattern formation. Also, this makes them interesting in view of many theories like the Kosterlitz – Thouless dislocation mediated melting in 2D.

In analogy with pressure in a three – dimensional (3D) system, the relevant parameter for a monolayer is the surface pressure. The surface pressure (π) of a monolayer is given by

$$\pi = \gamma_o - \gamma \qquad (1)$$

where γ_o = surface tension of pure water, and

γ = surface tension of water with the monolayer.

A plot of π as a function of area per molecule *(A,)* at a given temperature is a π–***A,*** isotherm. These isotherms are equivalent to the pressure – volume diagrams for 3D systems. The study of these isotherms is called surface manometry and it provides valuable information about the phase transitions in the monolayers.

In addition to surface manometry, monolayers are also studied using techniques like epifluorescence microscopy, Brewster angle microscopy, surface potential studies, surface second harmonic generation, miscibility studies and so on.

Monolayers of fatty acids and alcohols have been studied in great detail using these and other sophisticated techniques like high energy x-ray diffraction. Based on these studies as many as 17 different phases have been identified for the monolayers. To describe the different phases of these monolayers, a different and more elaborate nomenclature has been developed on the basis of the above mentioned studies. In this nomenclature, the LE phase is called L_1. The LC phase is called the L_{2d} or L_{2h} depending on the structure. The solid phase is again subdivided into many other phases. Chapter 1 provides the background material for the problems described in this thesis.

Some liquid crystal forming molecules are also amphiphilic and they form monolayers. In case of molecules which exhibit smectic phase in bulk, the monolayer generally transforms smoothly into a multilayer structure on decreasing &. The mechanism and nature of this transition has been a topic of great interest.

Our studies are conducted with a home made Langmuir trough, using the techniques of surface manometry and epifluorescence microscopy. We also use reflection and polarising microscopy to characterise the 3D or multilayer domains that are formed. In this thesis, we describe our work on a few interesting problems. These are briefly described below.

In Chapter 2 we consider our studies on multilayer formation in a liquid crystal monolayer. We have studied the monolayers of 4' - n - octyl - 4 - cyanobiphenyl (8CB), a liquid crystal forming molecule. In bulk, 8CB shows the following phase sequence

$$Crystal \xrightarrow{20.5^{\circ}C} SmecticA \xrightarrow{33.3^{\circ}C} Nematic \xrightarrow{41.5^{\circ}C} Isotropic.$$

It is known that 8CB monolayers exhibit the usual gas and LE phases. A compression of the gas – LE two phase monolayer leads to a pure LE phase. On further

compression, a first order transition from the LE phase to a 3 layer structure is seen. A probable mechanism for this transformation has also been suggested by previous investigators.

Our investigations indicate that the LE to 3 layer (D_1) transformation is not a true phase transition. On further compression of the LE – D_1 co-existence phase, there is a formation of much thicker 3D structures, before the LE to D_1 transformation is complete. In this transformation there is a co-existence of domains of many different thicknesses. From our studies we find the sequence of phases on compression to be:

$$\text{gas} \longrightarrow \text{gas} + \text{LE} \longrightarrow \text{LE} \longrightarrow \text{LE} + D_1 \longrightarrow \text{LE} + D_1 + \text{3D domains.}$$

We have also employed the techniques of fluorescence microscopy, reflection and polarising microscopies to study these 3D domains. We find that the 3D structures formed at the air - water interface on compressing the monolayer have liquid crystalline order. These domains show the same phase sequence as seen in bulk 8CB. The transition temperatures are somewhat lower, as indicated below

$$Smectic A \xrightarrow{28^{\circ}C} Nematic \xrightarrow{36^{\circ}C} Isotropic.$$

We suggest that this decrease in transition temperatures is due to the presence of water molecules within the molecular layers of these domains. Further, the 3D domains are flat in shape upto 28°C and convex lens shaped at higher temperatures. The flat domains are in smectic A phase while the convex lens shaped domains are in nematic or isotropic phase, depending on the temperature.

Chapter 3 dwells upon interface roughness and ordering in liquid crystal films. In order to have a better understanding of the molecular order in the D_1 and multilayer domains of 8CB, we have carried out high resolution x-ray studies on 8CB films transferred onto glass substrate. In our studies, the 8CB films are transferred using a technique where the substrate is placed horizontally. The glass substrate is placed under water and the monolayer is spread and stabilised at the air – water interface. After this, the water is removed slowly using a siphon,

so that the monolayer gets lowered on to the glass substrate, thus forming films on the glass surface. We confirm by microscopic observations that the molecular order is preserved on transferring it to the glass surface. In another technique for monolayer transfer to a horizontally placed substrate, the monolayer is spread on water in a conical trough, the substrate is placed under the water and the water drained out using a tap at the bottom of the trough. It may be mentioned here that liquid crystal films on a solid substrate prepared by techniques like surface treatment, spin - coating etc. do not preserve any order of the molecules.

The transferred films have been studied using high resolution x-ray reflectivity. On cooling the substrate to temperatures corresponding to the crystal phase of 8CB, the reflection features of the D_1 film disappear, indicating a dewetting of the substrate. Wetting is achieved again only on heating the sample to high temperatures comparable to isotropic temperatures of bulk 8CB.

Also, the surface roughnesses at the air - film and the film - glass interfaces are conformal in the nematic and isotropic temperatures. This conformality weakens in the smectic temperatures and reduces exponentially as the temperature approaches the crystallisation point.

The subject matter of Chapter 4 is phase induction and phase separation in a mixed monolayer. We have studied the mixed monolayers of 8CB and stearic acid (SA). A monolayer of a fatty acid like SA exhibits a phase sequence of

$$\text{gas} \rightarrow \text{LE} \rightarrow \text{solid} \rightarrow \text{collapsed state.}$$

As already stated, the monolayer of 8CB exhibits the phase sequence of:

$$\text{gas} \longrightarrow \text{gas} + \text{LE} \longrightarrow \text{LE} \longrightarrow \text{LE} + D_1 \longrightarrow \text{LE} + D_1 + \text{3D domains.}$$

Thus the monolayers of the individual compounds do not exhibit the LC phase. The phase diagram of the mixed monolayer has been studied in detail. The complete phase diagram at 23°C is shown in Fig 1. In our studies of the mixed monolayer, we observe the induction of the LC phase over a concentration range from 3% to 95% SA in 8CB. We propose that the presence of the shorter chain length 8CB molecules reduces the effective chain length of the mixed monolayer

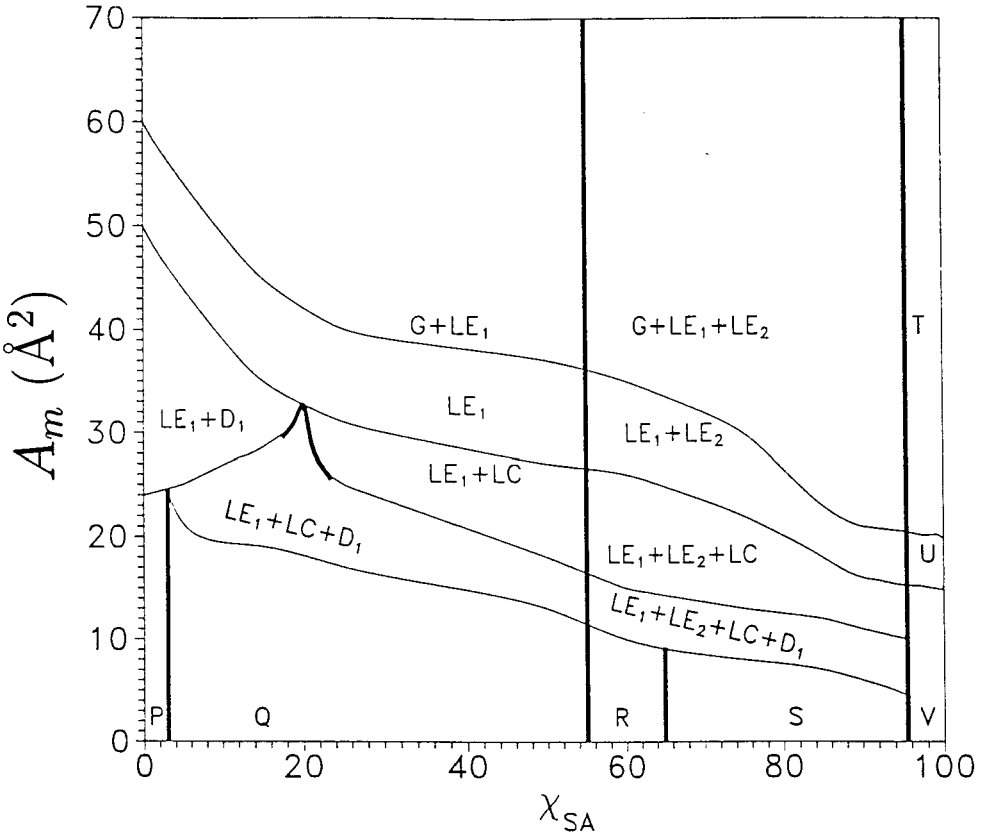

Figure 1: The phase diagram of the mixed monolayer of 8CB and SA at 23°C. [Key: P = LE_1+ D_1+ D_2, Q = LE_1+ LC + D_1+ D_2, R = LE_1+ LC + D_1+ D_3, S = LE_1+ LE_2+ LC + D_1+ D_3, T = gas + LE_2, U = LE_2, V = collapsed state.]

and this may be inducing the LC phase.

Interestingly, we find a phase separation of the LE phase itself into two liquid expanded phases, one of which (LE_1) is 8CB rich and the other (LE_2) is SA rich. This phenomenon is observed for 55% to 95% SA in 8CB. Such a phase separation has not been reported in the literature to our knowledge. Also, there is a co-existence of three stable phases in the mixed monolayer. According to Crisp's phase rule for 2D systems, such a three phase co-existence is allowed only for a two component system.

In addition, there is a formation of D_1 and thicker (D_2 and D_3) domains. For a concentration of SA less than 80% in 8CB, the 3 layer D_1 domains appear before the LC phase as area per molecule is reduced. On the other hand, for higher concentrations of SA, the LC phase appears first. This indicates a subtle balance of the hydrophilic head - subphase and hydrophobic tail - subphase interactions.

An earlier work on the same mixed monolayer reports a phase seggregation of the monolayer on increasing the surface density. In this seggregated state,

all the 8CB molecules are squeezed out of the interface and settle above the SA monolayer. From our studies, we infer that there is only a partial seggregation of the 8CB molecules.

The last Chapter of the thesis deals with the unusual features in the $\pi - A$ isotherms of a polymer monolayer. Since chain length plays a crucial role in deciding the structure of monolayers of small molecules like 8CB and SA, we have undertaken studies on monolayers of long molecules like polymers. In particular, we have probed the monolayer of a liquid crystal siloxane polymer LCP1. This polymer exhibits the Smectic C phase over the temperature range -7.2°C to 72°C.

In earlier studies on some polymer monolayers, a strong compression expansion hysteresis in the $\pi - A$ isotherms has been reported. From surface manometric studies, we find that the LCP1 monolayer exhibits a very pronounced compression – expansion hysteresis. In addition, there are some unusual features in the isotherms. In the compression cycle of the isotherm, there is a decrease in π (Fig 2, A, $\sim 700 Å^2$). This decrease is compression rate dependent at 25°C. Also, there is an increase in π in the expansion cycle of the isotherm. This increase is of the order of 0.5 to 0.7 dyne/cm, well above the error bar. It occurs only at 25°C.

Epifluorescence studies indicate that the LCP1 monolayer exhibits many interesting phases that appear like bright spots (BS), melted stripe (MS), striations, foam, and irregular shaped (IS) domains. All these phases are 3D structures. The phase sequences exhibited by the LCP1 monolayer on compression at different temperatures are given below.

T = 25°C: gas → gas + LE → LE → LE + BS → LE + BS + striations → LE + MS.

T = 35°C: gas → gas + LE → LE → LE + BS → LE + IS.

The phase sequences on expansion are different.

T = 25°C: MS + LE → MS + gas → foam + gas → BS + gas.

T = 35°C: IS + LE → IS + gas → BS + gas.

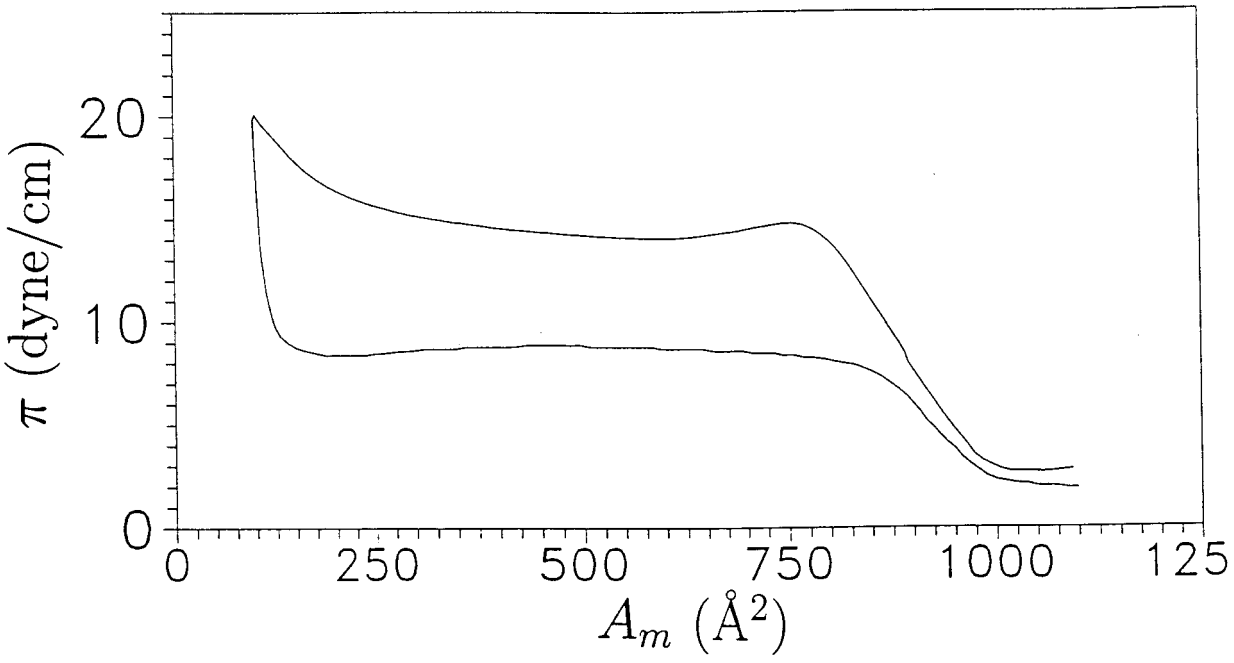

Figure 2: The π – **A,** isotherm of LCP1 monolayer at air - water interface at 25°C obtained by surface manometry.

The hysteresis in the π **– A,** isotherms indicates that the high density structures like BS, MS, IS etc. are more stable than the LE phase. This is supported by the fact that there is an LE – gas trasition on expanding an MS – LE co-existence monolayer.

The decrease in π in the compression cycle of the isotherm appears to indicate that a minimum surface density of molecules is required for the nucleation of the BS domains. Once the nucleation starts, the process continues on its own. As a result, there is a depletion of molecules at the interface, leading to a drop in π.

We suggest that the increase in π on expansion is due to a delayed melting of the MS domains. Due to this delayed melting there is a depletion of molecules at the interface, which results in a decrease in π. When the MS domains start melting, molecules are released to the interface and this increases the surface pressure. Such an increase in π in an expansion isotherm has not been reported in the literature to our knowledge.

Many of the results presented in this thesis have been published in the following papers:

1 *"Formation of Liquid Crystalline Phases from a Langmuir Monolayer.", K. A.* Suresh and A. Bhattacharyya, *Langmuir, 13*, 1377 (1997).

2 *"Phase Diagram of a Liquid Crystal Siloxane Polymer at Air Water Interface.", A.* Bhattacharyya and K. A. Suresh, *Mol. Cryst. Liq. Cryst., 299*, 193 (1997).

3 *"Novel Phase Diagram of a Mixed Langmuir Monolayer of Octylcyanobiphenyl and Stearic Acid.",* A. Bhattacharyya and K. A. Suresh, *Europhys. Lett., 41*, 641 (1998).

4 *"Unusual Features of the Surface Pressure - Area Isotherms of a Siloxane Polymer at the Air-Water Interface.", A.* Bhattacharyya and K. A. Suresh (manuscript under preparation).