

# **Studies on Monolayers and Multilayers of Mesogenic Amphiphilic Molecules**

by  
*P. Viswanath*

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Jawaharlal Nehru University  
for the award of the degree of  
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***Raman Research Institute  
Bangalore 560 080  
India***

# CERTIFICATE

This is to certify that the thesis entitled **Studies on Monolayers and Multilayers of Mesogenic Amphiphilic Molecules** submitted by P. Viswanath 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 award of any other degree or diploma.

Prof. N. Kumar

(Center Chairperson)

Director

Raman Research Institute

Bangalore 560 080 - INDIA

Prof. Kattera A. Suresh

(Thesis Supervisor)

# 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 for the award of any degree, diploma, membership, associateship, fellowship or any other similar title of any University or Institution.

(Prof. Kattera A. Suresh)

(P. Viswanath)

Liquid Crystal Laboratory

Raman Research Institute

Bangalore 560 080 - INDIA

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## List of Symbols Used Frequently in the Thesis

$\pi$	Surface Pressure
$\gamma_0$	Surface Tension of Water
$\gamma$	Surface Tension of Water in the Presence of Monolayer
$A/M$	Area per Molecule
$A_0$	Limiting Area per Molecule
$\pi_c$	Collapse Pressure
$t$	Temperature
$A_n$	Normalised Area
$\pi_n$	Normalised Surface Pressure
$L_1$	Low Density Liquid
$L'_1$	Low Density Liquid with Untilted Molecules
$L_2$	High Density Liquid
$D_1$	Three Layer Domains
$D_2$	Optically Flat Multilayer Domains
$D_3$	Lens Shaped 3D Domains
$F$	No. of Degrees of Freedom of a System
$C_b$	No. of Components in Bulk
$C_s$	No. of Components at the Interface
$P_b$	No. of Phases in Bulk
$q$	No. of Monolayer Phases at the Interface
$d$	Thickness of a Domain
$\mu'$	Effective Refractive Index
MF	Mole Fraction
$ E $	Compressional Elastic Modulus
$A_{id}$	Ideal Area per Molecule
$A_{12}$	Experimentally Determined Area per Molecule
$A_{exc}$	Excess Area per Molecule
$\Delta G_{exc}$	Excess Gibbs Free Energy
$\theta$	Contact Angle
$S$	Spreading Co-efficient
$I_n$	Normalised Fluorescent Intensity

## List of Materials Used in the Experiment

Ch	Cholesterol
ChA	Cholesteryl acetate
ChH	Cholesteryl heptanoate
ChO	Cholesteryl octanoate
ChN	Cholesteryl nonanoate
ChL	Cholesteryl laurate
ChM	Cholesteryl myristate
ChP	Cholesteryl palmitate
ChS	Cholesteryl stearate
ChOl	Cholesteryl oleate
ChOC	Cholesteryl oleyl carbonate
ChB	Cholesteryl benzoate
ChHC	Cholesteryl hydro cinnamate
8CB	Octylcyanobiphenyl
7CB	Heptylcyanobiphenyl
6CB	Hexylcyanobiphenyl
EPPH	p-(p-Ethoxy phenylazo phenyl hexanoate)
7AOB	Diheptylazoxybenzene
NBDHDA	4-(Hexadecyl amino)-7-nitrobenz-2 oxa-1,3-diazole
NBDSA	4-(octadecanoic acid)-7-nitrobenz-2 oxa-1, 3-diazole

# Preface

This thesis deals with studies on the characterisation of phases, interactions between the polar head groups, complex formation, structural transitions and phase transitions in Langmuir monolayers. The amphiphilic molecules when spread at air-water(A-W) interface form insoluble mono-molecular layer [1, 2]. These are referred as Langmuir monolayers. They are ideal systems to study many physical properties in two dimensions(2D). They also mimic biological systems. The monolayers can also be transferred to substrate. These are called Langmuir -Blodgett(LB) films. An understanding of the interactions between the molecules in the monolayer is required to fabricate functional devices like bio-sensors which employ LB films.

Many different phases in Langmuir monolayers have been reported [2]. The richness in phase diagram is of scientific interest and it has been studied using various experimental, theoretical and simulation techniques. Broadly, the phase sequence on increasing the surface density of the molecules can be classified as: gas( $G$ ),  $L_1$ (low density liquid),  $L_2$ (high density liquid) and  $S$ (solid).

Surface manometry is a method used to study the Langmuir monolayers. Here, the surface pressure( $\pi$ ) is measured as a function of area per molecule(A/M) which is the inverse of surface density at constant temperature. The area per molecule is usually varied by compressing the monolayer with a barrier. The surface pressure,  $\pi$ , is given by,

$$\pi = \gamma_0 - \gamma \quad (1)$$

where,  $\gamma_0$  is the surface tension of the pure water and  $\gamma$  is the surface tension of water in the presence of the monolayer. These surface pressure( $\pi$ )-area per molecule(A/M) isotherms provide valuable information on the phase transitions in the monolayers. A kink in the isotherm signifies a phase transition. A plateau in the isotherm indicates a coexistence of many phases or multilayers.

There are other techniques used to study the monolayers. They are epifluorescence microscopy, Brewster angle microscopy, ellipsometry, surface potential studies, surface second

harmonic generation, grazing incident x-ray diffraction and miscibility.

Many structures of the monolayer phases have been identified using xray diffraction techniques and miscibility. In literature, as many as 17 different phases have been reported [2, 3]. According to Crisp's phase rule [4] for a 2D mixed monolayer, the degrees of freedom,  $F$ , at constant temperature and external pressure is given by,

$$F = C_b + C_s - P_b - q + 1 \quad (2)$$

where,  $C_b$  is the number of components in the bulk,  $C_s$  is the number of components in the interface,  $P_b$  is the number of bulk phases and  $q$  is the number of monolayer phases in equilibrium with one other. This phase rule accounts for the simultaneous existence of many phases that occur in monolayers and mixed monolayers.

Some mesogenic(liquid crystal forming) amphiphilic molecules also form Langmuir monolayers. The evolution of 2D monolayer to 3D multilayers with compression is quite interesting in system which has smectic liquid crystalline mesophase. Recent studies indicate some similarities between the collapse behavior in liquid crystalline materials and pulmonary lung surfactant at the A-W interface [5]. We have undertaken a systematic study of monolayers and multilayers using surface manometry, epifluorescence and Brewster angle microscopy and reflection microscopy techniques. Here we focus on the amphiphilic molecules which are liquid crystalline in nature. In chapter-1, we have presented the type of materials that form Langmuir monolayers and the various techniques employed by us to study them.

Chapter-2 deals with systematic studies on the Langmuir monolayers of cholesteryl derivatives. Our studies on the short chain esters of cholesterol, indicated the formation of a stable monolayer. Though cholesterol(Ch) and cholesteryl acetate(ChA) have similar molecular cross-sectional areas, the high density phase,  $L_2$ , found in Ch and ChA were very different. In ChA, the  $L_2$  phase was highly crystalline in nature because of the presence of weakly polar ester group. The esters, cholesteryl heptanoate and cholesteryl octanoate did not form stable monolayers and yielded 3D crystals. We found an interesting behavior in

the  $\pi$ -A/M isotherm of cholesteryl nonanoate. This is shown in Figure 1. Here, the limiting

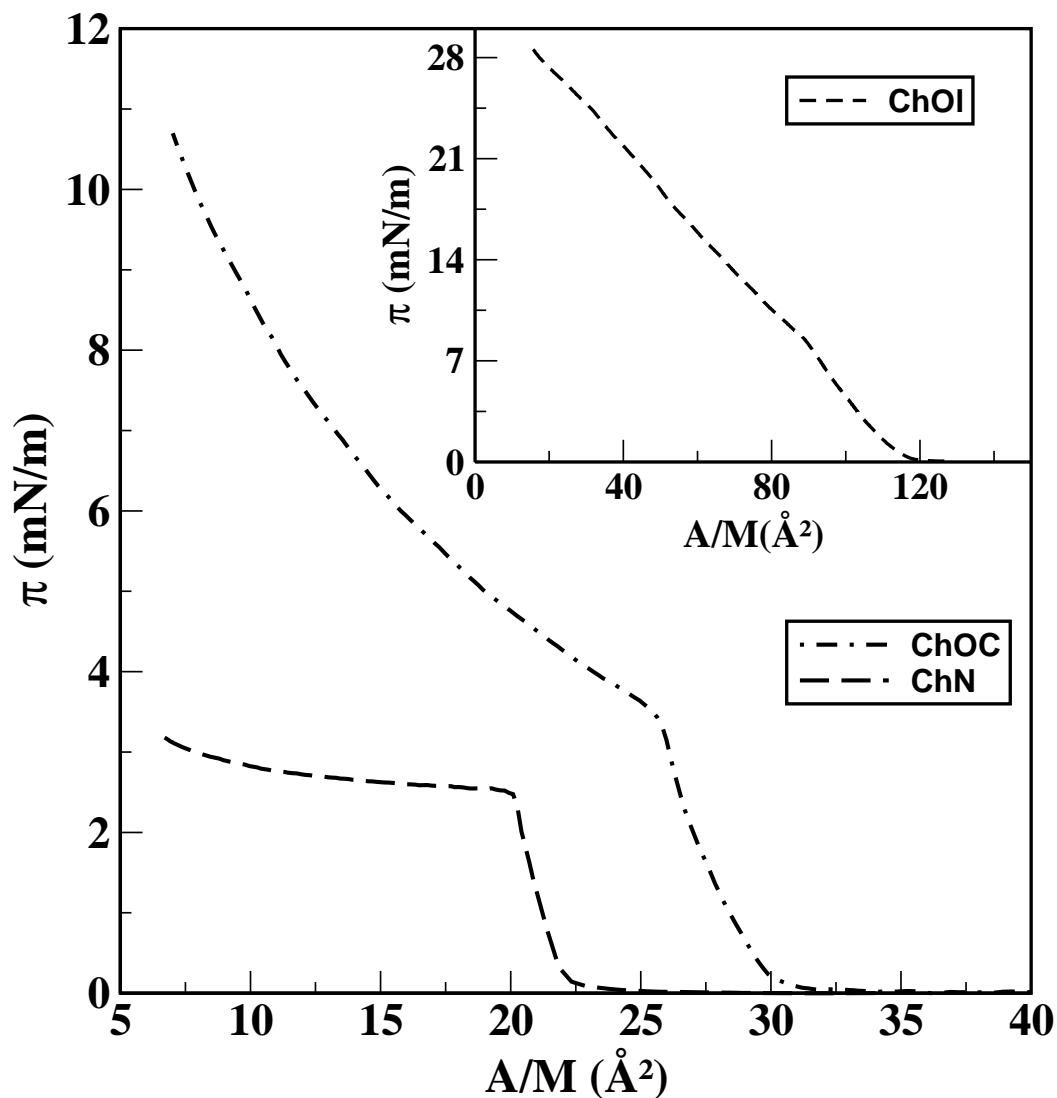


Figure 1: Surface pressure( $\pi$ ) - area per molecule( $A/M$ ) isotherms for cholesteryl nonanoate(ChN) and cholesteryl oleyl carbonate(ChOC). The inset shows the  $\pi$ - $A/M$  isotherm for cholesteryl oleate at a temperature,  $t=25$  °C.

area per molecule,  $A_0$ , corresponded to that of a bilayer. Our epifluorescence and Brewster angle microscopy(BAM) studies showed that these bilayers are fluidic in nature. The BAM images of ChN are shown in Figure 2. For ChN monolayer, the heating caused by the probe laser beam melts the bilayer phase yielding  $G$  phase. Normally, one expects the  $G$  phase to decrease in area with compression. However, in this case, the effect was so dominant that the  $G$  phase continued to grow even during compression. This sequences of melting are shown in Figures (2(b) to 2(f)). Further compression of the ChN led to the formation of uni-

form bilayer (Figure 2(g)). At still lower values of A/M, the bilayer collapsed to 3D circular metastable domains(Figures 2.15(h) and 2.15(i)). Under reflection, we found in the collapsed

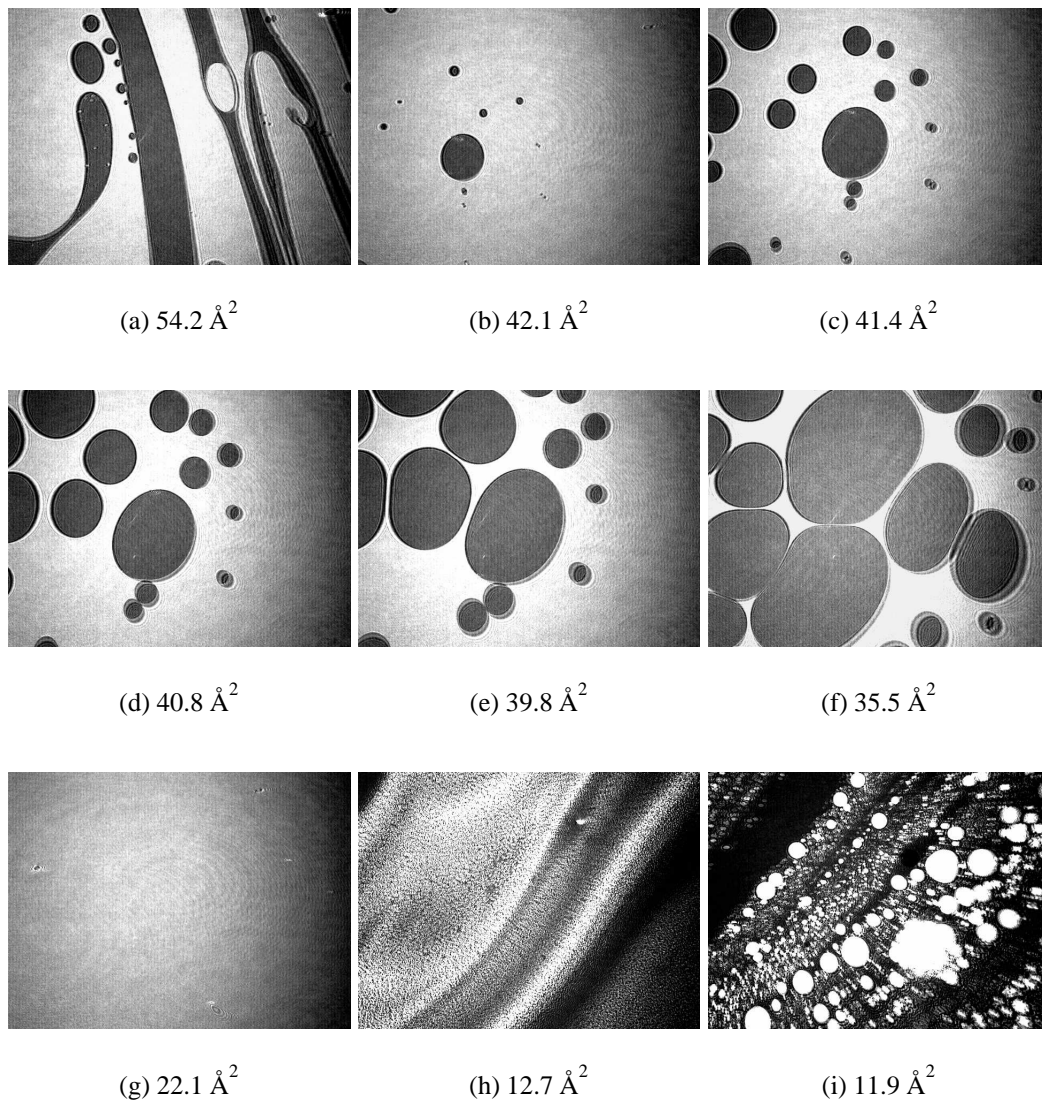


Figure 2: Brewster angle microscopy images of cholesteryl nonanoate. Figure(a) shows the presence of coexistence of gas(dark) and bilayer phase(bright background). Figures(b) to (f) show the growth of gas domains(dark) due to laser heating. Figure(g) shows the homogeneous and uniform bilayer phase. Figure(h) shows the collapsed state. Here the bright dots represent the 3D liquid domains. Figure(i) shows the collapsed state at lower A/M. Here bright dots coalesce to form bigger circles which tend to crystallize in time. Scale of each image is  $6.4 \times 4.8 \text{ mm}^2$ .

state, 3D circular metastable domains transforming to branched and dendritic crystals. The behavior of cholesteryl laurate was found to be similar to that of cholesteryl nonanoate. However, in ChL the 3D crystals formed even at higher area per molecule(A/M). The monolayer

behavior of cholesteryl myristate, cholesteryl palmitate and cholesteryl stearate were very different. They exhibited 3D crystals although they yielded high surface pressures with low limiting area per molecule( $A_0$ ) value. Interesting behavior was seen for cholesteryl benzoate where the  $A_0$  corresponded to that of a bilayer. Our microscopy studies on these bilayers showed irregular and sharp boundaries indicating they were crystalline in nature. Our studies on cholesteryl oleate showed stable monolayer. The  $\pi$ -A/M isotherm indicated a large limiting area for this molecule(Figure 1). In bulk, in cholesteryl esters, based on xray techniques, three different packings have been reported [6]. Their studies indicated that the interactions between different parts of the molecules are responsible for these packings. They are cholesteryl-cholesteryl, cholesteryl-chain and chain-chain interactions. For the esters, cholesteryl caproate to cholesteryl octanoate, cholesteryl-cholesteryl interactions dominate. For the intermediate esters, cholesteryl nonanoate to cholesteryl laurate, cholesteryl-chain interactions dominate. For still higher homologue of cholesteryl esters, cholesteryl tridecanoate onwards chain-chain interactions dominate. Our studies indicated that the packing of cholesteryl esters at the A-W interface have a good correlation with their bulk packing.

In chapter-3, we discuss the polar head group interactions between cholesterol(Ch) and octylcyanobiphenyl(8CB). Both these materials are amphiphilic and form stable monolayers. Based on our  $\pi$ -A/M isotherm studies, we find two collapse pressures. The lower collapse pressure,  $\pi_{c(8CB)}$ , characteristic of 8CB, varied after 0.6 mole fraction(MF) of Ch in 8CB. The higher collapse pressure,  $\pi_{c(Ch)}$ , characteristic of Ch is independent of composition. Our epifluorescence studies indicated a clear phase separation into cholesterol rich(grey)  $L_2$  phase and octylcyanobiphenyl rich(bright)  $L_1$  phase. We observed 8CB rich multilayer domains above the  $\pi_{c(8CB)}$  and 3D crystals of Ch above  $\pi_{c(ChA)}$ . Based on our surface manometry, epifluorescence, reflection and Brewster angle microscopy studies, we have constructed the phase diagram for Ch-8CB mixed monolayer. This is shown in Figure 3. Here, we clearly find a phase separation between  $L_1$  and  $L_2$  phases in the range 0.1 to 0.9 MF of Ch in 8CB. We attribute this immiscibility to the role of polar head group interactions between the OH group of Ch and CN group of 8CB. Here, the interactions between the hydrophobic groups

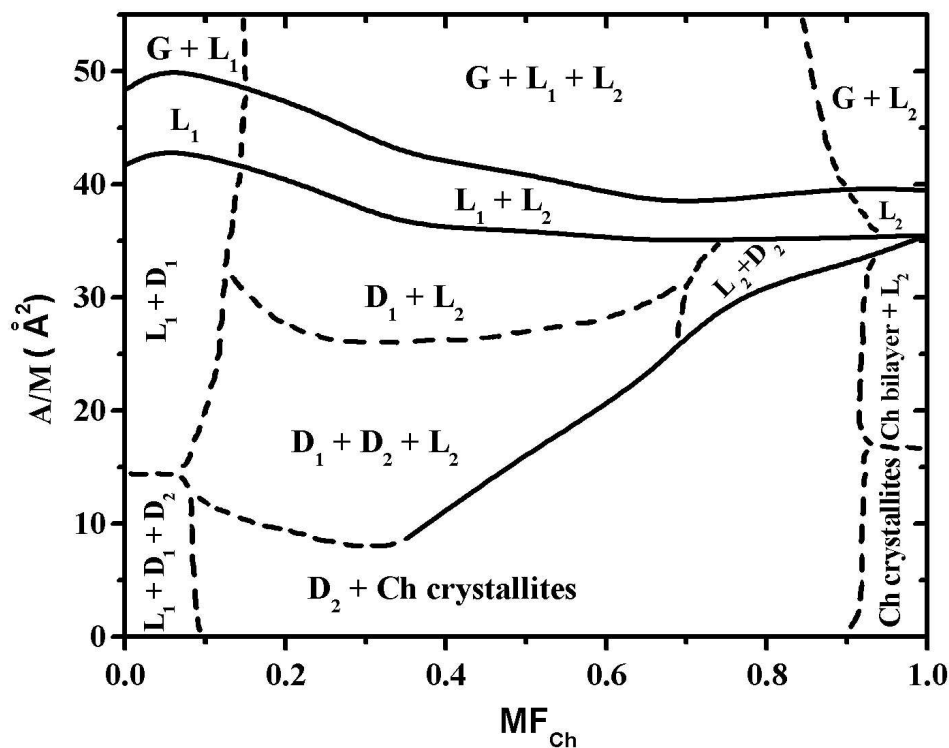


Figure 3: Phase diagram of Ch-8CB mixed monolayers with increasing mole fraction(MF) of Ch in 8CB at 22 °C.

do not play an important role. In Ch monolayer, the rigid skeleton along with OH group is normal to the A-W interface. The OH polar group easily forms hydrogen bonding with water. In the 8CB monolayer, the biphenyl core along with the CN polar group is tilted at the A-W interface. The presence of a strong tilted CN dipole alters the local hydrogen bonded network and tends to orient the dipoles of water molecules. This orientational mismatch between OH and CN groups at the A-W interface is the most probable reason for the immiscibility found in our studies in the Ch-8CB mixed monolayer.

Chapter-4 describes our study on the mixed monolayer of a weakly polar cholesteryl acetate(ChA) with a strongly polar 8CB. Here, the ChA has the same hydrophobic rigid skeleton as that of cholesterol but with a weakly polar ester group. Here, we find the collapse pressure behavior to be very different from the Ch-8CB mixed system. In ChA-8CB system, the lower collapse pressure,  $\pi_{c(8CB)}$ , was found to increase gradually with composi-



tion of ChA and the higher collapse pressure,  $\pi_{c(ChA)}$ , was independent of composition. Our epifluorescence studies showed only  $L_1$  phase below  $\pi_{c(8CB)}$  at all compositions(except at the extreme limits). However, above  $\pi_{c(8CB)}$ , we find multilayer( $D_2$ ) domains coexisting with the  $L_1$  phase. Above  $\pi_{c(ChA)}$ , 3D crystals of ChA were observed. We attribute this miscibility to less solvation of the weakly polar OCO group in ChA which possess a smaller hydration number when compared to the OH polar group in Ch. In ChA, the weakly polar ester group acts only as an hydrogen bond acceptor having relatively fewer hydrogen bonds with water molecules. The OCO group of ChA can also interact with the CN group of 8CB through dipole-induced dipole interactions favoring the miscibility. The immiscibility observed above  $\pi_{c(8CB)}$  may be due to the weak interactions between the hydrophobic cores.

In chapter-5, we discuss the mixed monolayer study on a donor azo dye and an acceptor molecule at the A-W interface. We have studied on the azo dye, p-(p-ethoxy(phenylazo phenyl) hexanoate), EPPH, with 8CB. The surface manometry studies indicated a strong reduction in the A/M for the mixed monolayer. The excess area per molecule,  $A_{exc}$  was found to be negative indicating an attractive interactions between the molecules in the mixed monolayer. This is shown in Figure 4. The  $A_{exc}$  was negative for all ranges of mole fraction(except at the extremum) which indicated condensation in the mixed monolayer. The maximum condensation was seen at 0.5 MF of EPPH in 8CB. The collapse pressures for the mixed monolayer were higher in the range of 0.3 to 0.7 MF of EPPH in 8CB(with maximum value of 25 mN/m at 0.7 MF of EPPH in 8CB) than the collapse pressures for the individual monolayers (15.1 mN/m for EPPH and 4.8 mN/m for 8CB). This indicated that the mixed monolayer was very stable compared to the monolayer of individual components. Based on these results, we infer that the molecules in the mixed monolayer form a stable complex. In the complex the tilt of 8CB was considerably reduced. We find the usual sharp decrease(spike) in surface pressure after collapse for EPPH. However, this trend disappeared in the mixed monolayer below 0.7 MF of EPPH in 8CB where it showed a plateau region in the  $\pi$ -A/M isotherm. The kinetics of the variation of the area per molecule with time at a low surface pressure indicates a crystallizing tendency for EPPH monolayer. However, this

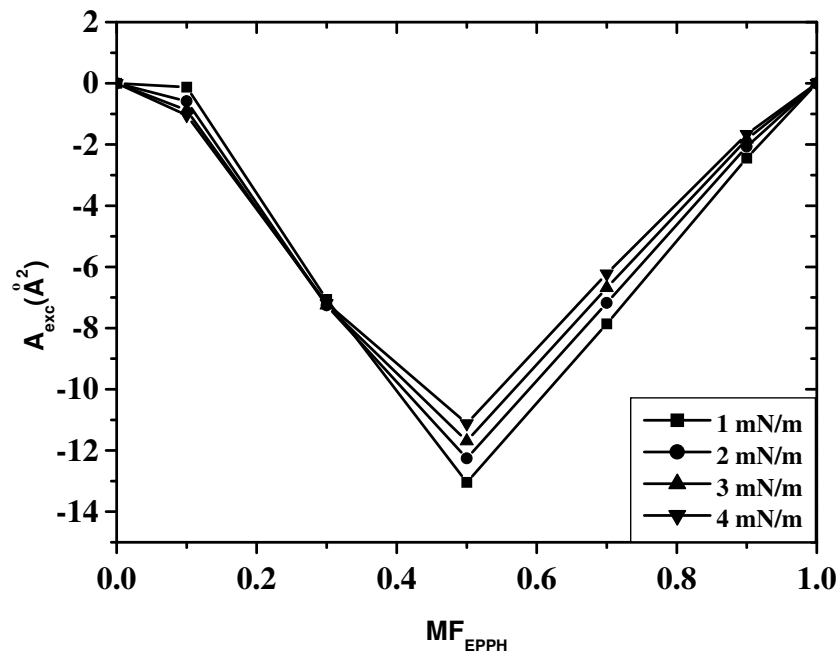
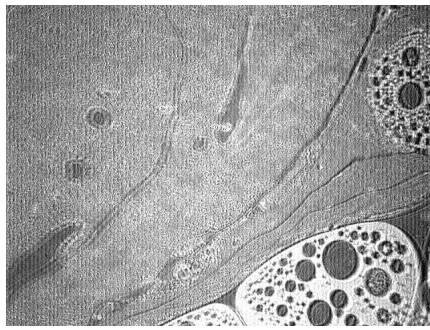


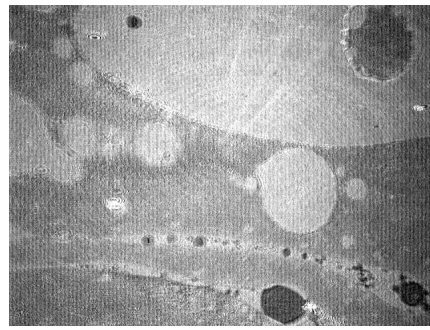
Figure 4: Plot of the excess A/M,  $A_{exc}$ , with mole fraction(MF) of EPPH. The maximum condensation is seen at 0.5 MF of EPPH in 8CB.

crystallizing tendency was inhibited by the presence of 8CB in EPPH. We have carried out UV irradiation studies on EPPH monolayer and in the mixed monolayer. The cis to trans conversion was found to occur even in the mixed monolayer indicating that the complex formation was not very strong. The study on these systems are interesting due to their various applications like photo induced phase transition, patterning and photo lithography [7].

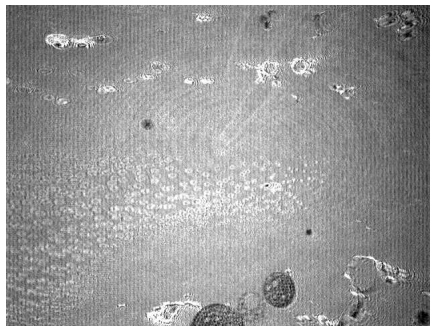
We discuss in chapter-6 on “tilted to untilted” phase transition in mixed Langmuir monolayer. Here the mesogenic weakly polar molecule, diheptyl azoxy benzene(7AOB) was mixed with 8CB. The molecule 7AOB has a weak dipole moment perpendicular to the molecular axis whereas the CN dipole in 8CB is along the molecular axis. For 7AOB, our surface manometry studies indicated a strong correlation in the monolayer formation with its bulk liquid crystalline phases. The  $\pi$ -A/M isotherm for the mixed monolayer indicated a kink. The Brewster angle microscopy studies on 7AOB-8CB mixed monolayer indicated a clear two phase region. The two phases were liquid like. This is shown in Figure 5. Here, the bright phase is  $L'_1$  and the grey phase is the  $L_1$  phase. With compression, the less dense  $L_1$  phase transformed to a comparatively denser  $L'_1$  phase. These observations were consistent with our epifluorescence microscopy results. The tilted  $L_1$  phase transformed to  $L'_1$  phase



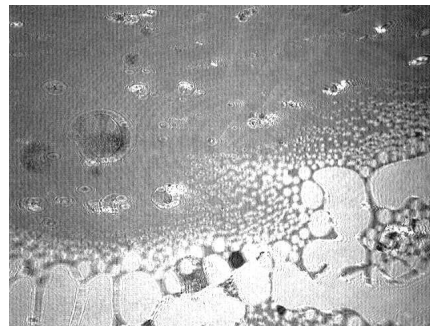
(a)  $41.6 \text{ \AA}^2$



(b)  $22.4 \text{ \AA}^2$



(c)  $18.9 \text{ \AA}^2$



(d)  $16 \text{ \AA}^2$

Figure 5: Brewster angle microscopy images for 0.5 MF of 7AOB in 8CB. Figure(a) shows the coexisting gas(dark) +  $L_1$ (grey) +  $L'_1$ (bright) phase. Figure(b) shows coexistence of  $L'_1$ (grey) phase and  $L_1$ (bright) phase with traces of gas(dark) phase. Figure(c) shows the collapsed state. Here, the predominantly present  $L'_1$  phase coexists with traces of multilayer domains(brighter) and gas phase. Figure(d) show multilayers coexisting with  $L'_1$  phase in the background. The field of view is  $6.4 \times 4.8 \text{ mm}^2$ .

which is ordered and untilted in the mixed monolayer. The magnitude of elastic modulus of the  $L'_1$  phase was higher than that of  $L_1$  phase. This indicated that the  $L'_1$  phase was more rigid compared to  $L_1$  phase. We infer based on these studies that the formation of the untilted and more ordered phase is due to the reduction in the flexibility of chains in 7AOB due to the rigid biphenyl cores of 8CB.

Chapter-7 deals with the fluorescent dye induced wetting in liquid crystal domains at the air-water interface. Understanding the “wetting-dewetting” phenomenon is of fundamental importance in physics, chemistry and biology. Wetting-dewetting on a system is important due to its various applications [8]. e.g., ink jet printers, xerox, drying of paints and spraying

of pesticides over a leaf. We have studied an amphiphilic fluorescent dye(NBDHDA) doped in a liquid crystal with n-alkyl cyanobiphenyl systems. On excitation by light of appropriate wavelength we found that the dye gets bleached. This in turn altered the surface tension of the host liquid crystal domains. For smectic multilayers at the air-water interface, we found that the layers flowed and the diameter of the smectic domains increased with a corresponding decrease in the thickness. However, under white light illumination, the thickness of multilayers increased with the decrease in diameter. This process was accompanied by the movement of dislocation fronts. This process of photo-bleaching and the recovery is shown in Figure 6. For the dye doped nematic domains at the air-water interface, under reflection microscope, we found interference rings indicating lens shaped domains. On excitation with light of appropriate wavelength, the interference rings moved towards the periphery with uniform increase in diameter. This indicated a decrease in the curvature of the domains. Under reflection, the interference rings reappeared and moved towards the centre indicating an increase in the curvature. The domains nearly regained their original diameters. We attribute these phenomena to a surface tension gradient created during photo-bleaching and absorption by the fluorophore. This results a concentration and temperature gradient leading to Marangoni flow in liquid crystal domains.

Some of the work described in chapters 3 and 4 of this thesis have been published: *Polar head group interactions in mixed Langmuir monolayers*, P. Viswanath and K. A. Suresh, Phys. Rev. E, **67**, 061604, 2003.

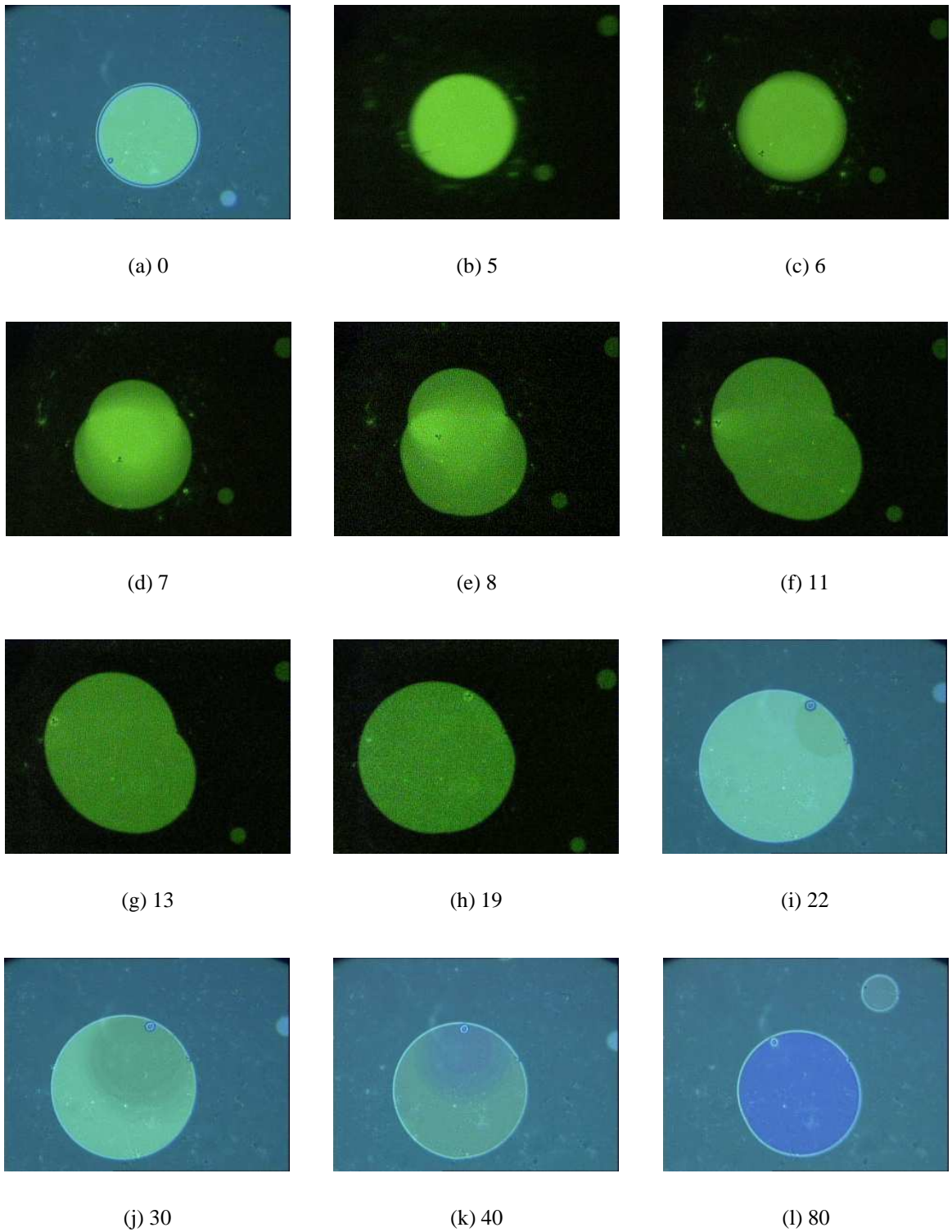


Figure 6: Microscopy images showing the evolution of smectic domain doped with fluorescent dye as a function of time. Figure(a) represents the initial image taken under reflection. Figures(b to h) were taken under epifluorescence. Here, the diameter of smectic domains increases. Figures(i to l) were taken under reflection where a decrease in diameter due to the movement of dislocation fronts was observed. Scale of each image is  $190 \times 140 \mu\text{m}^2$ .

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