

**RELAXATION MECHANISM IN METHYL STEARATE MONO-
LAYER FILMS AT THE AIR/WATER INTERFACE**

by


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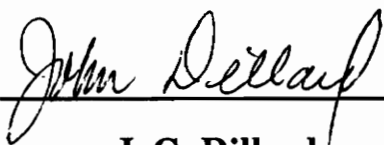
in

Chemistry

Approved By



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(ABSTRACT)

A monolayer film of methyl stearate was compressed until catastrophic film collapse took place. Surface pressure relaxation was then followed as a function of time. Investigation involving the effects of film compression beyond the collapse pressure revealed an important process involved in the surface pressure relaxation mechanism. When the monolayer is compressed beyond the collapse pressure and then held at a constant area, the surface pressure relaxation, in a plot of surface pressure vs time, was delayed during the initial stage of the process. A similar delay in the surface pressure relaxation was also observed for a monolayer film of methyl stearate when it was compressed and held at 40 mN/m, below the collapse pressure, for some time before allowing it to relax under a constant area condition. A relaxation mechanism has been proposed to explain the delay phenomenon observed during the surface pressure relaxation at constant area: At collapse, the monolayer film buckles and folds over to form bilayer molecular channels (ridges and ribbons). The ridges and ribbons act as a reservoir for monolayer material to make up for lost molecules at the air/water interface due to the growth of a bulk (crystalline) phase under a constant area condition.

The results from temperature dependence studies as well as from the area-relaxation experiments strongly support the proposed relaxation mechanism. The

Langmuir-Blodgett films of methyl stearate, deposited before and after the catastrophic film collapse, revealed interesting structural features of the collapsed film.

The experimental results from the pressure-time, area-time, and pressure-area isotherms strongly suggest that the methyl stearate monolayer film undergoes an organized film collapse. This work helps to better understand the relaxation mechanism in monolayer films at the air/water interface.

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CHAPTER - 1

INTRODUCTION

1.1 Thesis Statement

The molecules of the monolayer film which were expelled out of the air/water interface during an organized film collapse, return to the air/water interface when the monolayer film is allowed to relax on its own under a constant area condition.

It is well known that monolayer films at the air/water interface of long chain fatty acids and some other materials like cholesterol undergo organized film collapse when compressed beyond their respective collapse pressures. The monolayer molecules are lifted away from the air/water interface to form ridges and ribbons on the top of the monolayer during the organized film collapse. It has long been speculated that ridges and ribbons (if attached to monolayer) may act as reservoirs to replenish film molecules lost by some means from the monolayer at the air/water interface. But, no direct evidence had been obtained to support this hypothesis. In the present work, the author has made efforts to accumulate and present enough evidence that will definitely strengthen, if not confirm, the aforesaid speculation.

1.2 Proposed Study

In Chapter 1, general background on insoluble monolayer films is provided. A brief introduction on the historical development in monolayer film research is given. The monolayer film materials and their properties, such as, the monolayer film states, the monolayer film stability and the relaxation mechanisms in monolayer films are discussed in great detail. Also discussed in this chapter are the potential uses of the

monolayers in some areas of the sciences of technological importance.

Chapter 2 deals with the experimental methods. The working principles of the film balance used for the present investigation are briefly explained. The sample preparation and the monolayer film forming techniques are described. The data collection methods for isotherms, the pressure-area, the pressure-time and the area-time are explained. The transfer of methyl stearate films from the air/water interface to the glass slides, the Langmuir-Blodgett (LB) film technique, has also been described.

The experimental results and the discussion of the results are given in Chapter 3. The results are presented under four main categories: Pressure-area isotherms; Pressure-time isotherms; Area-time isotherms and the Langmuir-Blodgett films. Based on the experimental results a complete surface pressure relaxation model is suggested which describes the surface pressure relaxation mechanisms at the microscopic level.

In Chapter 4, the results from the present investigations are summarized. And continuing further from the present work a few research ideas have also been suggested which will further enhanced and improve our understanding of the proposed relaxation mechanisms in the insoluble monolayer film.

1.3 Insoluble Monolayer Film - Historical Background:

The usefulness of insoluble film forming materials has been known for a long time. A recorded classic example of ancient applications of spread films is the use of oils for calming the rough stormy seas, in AD 429 and ca 651 [1]. The calming effect of oil on the rough sea was attributed to the holiness of the oil.

Benjamin Franklin was the first to carry out the scientific demonstration of the calming effects of oils on a water surface. In his classic experiment carried out some time in 1770 - 1771, he added a teaspoonful of olive oil to one end of the Clapham

pond which spread swiftly on the water surface to cover about half an acre. A number of experiments were performed of this kind throughout the late 18th century and in to the 19th century, with the most prominent work being that of Lord Rayleigh. Rayleigh investigated the change in surface tension of the water caused by the contamination due to the surface film of insoluble oils. He was the first to believe that such oil films on the water surface are only one molecule thick. But he couldn't develop a method of his own to confirm his idea. It was Miss Agnes Pockels, working on her kitchen table, who developed a method to systematically monitor the variations in the surface tension of water contaminated with the oil as a function of the surface concentration of the oil. Her work was published in 1893, the first ever reported pressure-area isotherms, the isotherms which are now commonly used to characterize the insoluble film forming materials.

The work of Lord Rayleigh and Miss Pockels stirred a lot of interest among the scientific community of that time. Devaux, Hardy, Harkins, and Langmuir were among the prominent scientists to take up this area of research [1,2]. Devaux measured, with the help of additional tools, the thickness of such spread film and found them to be of the order of molecular dimension. From the work of Hardy it was clear that oils without the polar functional group(s) cannot spread on the water surface.

The historical development of insoluble monolayer film research during the 18th and the 19th centuries has been covered concisely in many books [1,2]. All of this early work contributed a lot to the understanding of the insoluble monolayer film, but the real progress in this area was made in the early 20th century from the work of Irving Langmuir.

In 1917, Irving Langmuir further developed the technique employed by Pockels, to measure the surface pressure of the insoluble monolayer film [3]. This device is

quite often also referred as the Langmuir film balance. Using the film balance, he carried out many experiments with the insoluble monolayers. From experiments involving long-chain fatty acids, he concluded that the films on the water surface are only one molecule thick and that the cross-sectional area occupied by the molecule is about 20 \AA^2 per molecule. From such investigations he also concluded that the polar end of the molecule is in contact with the water and that the long hydrocarbon chain part is oriented vertically upwards, away from the water surface. With his work, a strong theoretical and experimental foundation was laid for the insoluble monolayer film research.

Other than Langmuir's work, greater understanding of the insoluble monolayer films was provided during the first half of the 20th century from the work of Harkins, Schaefer, Rideal, Schulman, Adam and Frumkin to name few. The book by Harkins is a good source of information about the work carried out during this period on the insoluble monolayer films [4]. Gaines has summarized the work carried out up to the early 60s of this century in his classic monograph entitled " Insoluble Monolayers at Liquid-Gas Interfaces" [2]. Gaines, further reviewed the work up to the early 70s [5]. The work done during the period 1972-1977 is extensively covered by Barnes in the Specialist Periodical Reports on colloid science [6,7]. Further, an excellent source of references on recent work involving insoluble monolayers is provided by Adamson [3], Roberts [1] and Ulman [8].

1.4 Insoluble Monolayer Film Properties:

1.4.1 Materials

In order to form a stable insoluble monolayer film on a liquid subphase, the monolayer material must possess certain characteristic physical and chemical proper-

ties. First, the material must be substantially insoluble in the subphase. Sometimes it is possible for the material that has an appreciable solubility in the subphase to form a relatively stable film on the subphase surface provided that the solubilization process is kinetically slow. For example, the solubility of stearic acid in water is reported to be 0.0029 g per 1000 g of water [9], yet the amount as small as 1 mg when spread on the surface of the water (500ml) contained in a trough with a exposed surface of 550 cm², forms a stable film without any detectable loss due to solution of the film [2].

Some of the simplest classes of materials that are capable of forming a stable monolayer films are long chain acids, alcohols, amines and esters. The molecules of such materials consist of a long linear hydrocarbon chain with polar head-groups at one end. The long hydrocarbon chain imparts a hydrophobic character while the polar groups imparts a hydrophilic character to the molecules. In order to form a stable film on the water surface the molecules must possess the right balance between hydrophobicity and the hydrophilicity. For example, a straight-chain acid with 14-carbon atoms in the chain is sufficient to form an insoluble monolayer film on the water surface. On the other hand if the polar group on the molecule is a sulphonic group (SO₃⁻) then even if there are 16 carbon atoms in the chain, the solubility will be too great and no monolayer will form.

The absence of polar groups in long-chain hydrocarbons does not allow hydrocarbons to spread on the water surface and thus such compounds do not form stable monolayers. But when the long-chain hydrocarbons, for example, 28-carbon alkane, are introduced on the mercury subphase they spread out rapidly to form an insoluble monolayer [10]. This is because mercury has a very high surface energy (surface tension), the strong dispersion forces acting between alkane molecules and the mercury surface enables the alkane molecules to spread out and lie flat on the mercury surface.

Therefore, the nature of the subphase is also very important in determining the ability of film materials to form an insoluble monolayer film. Water has been extensively used as subphase for monolayer film studies but some non-aqueous subphases, such as, mercury and hydrocarbon liquids have also been used in a limited way.

In order to form a stable insoluble monolayer film, the film material must also be a non-volatile in the temperature range of interest. Many film materials may be stable at any given temperature in the bulk phase but when they are spread out on the subphase surface they become so thin that they may be susceptible to evaporation.

Some film forming materials do not have the inherent properties to form an insoluble monolayer film but they can still be made to form an insoluble monolayer film with the help of another material which normally would form an insoluble monolayer film. For example, n-hexadecane, when present alone forms a lense on the water surface but when it is mixed with long-chain acids it spreads out on the water surface to form a mixed monolayer film [11].

Another important part of the insoluble monolayer film forming process is the use of the spreading solvent. The spreading solvent is used to spread the film forming material on the subphase surface. The spreading solvent must be volatile enough to evaporate within a few minutes after the sample is introduced to the water surface, but at same time it should be stable enough to allow the preparation of the solution of any desired concentration with a great degree of accuracy. The spreading solvent, such as, chloroform, hexane and benzene are commonly employed in the preparation of the solutions of the film forming materials. These solvents are volatile and have a very high spreading coefficient. Among others, the solubility of the film forming materials in a given spreading solvent is also a very important criterion in the solvent selection. Sometimes a mixture of spreading solvents is used for some film materials

that are difficult to dissolve in any one solvent. In fact it is a very common practice, especially in studies involving the complex biological molecules, to use a mixture of spreading solvents. Another desirable property of the solvent is that it should be insoluble in the subphase or its solubility should be negligibly small. If the solvent is soluble in the subphase then the chances are good that it might influence the surface properties of the subphase.

1.4.2 States of Monolayer Films

In general a insoluble monolayer film at the air-water interface can exist in three different states, namely, the gaseous, the liquid, and the solid states. A typical pressure-area isotherm of the methyl stearate monolayer film obtained from the present work is shown in Figure 1.1.

In the gaseous state the molecules are far apart from each other and hence the average area occupied per molecule is very large compared to the size of the individual molecules. The molecules in the gaseous monolayer state lie almost flat on the subphase. In this state, films supposedly obey the two-dimensional perfect gas law, $\pi \sigma = kT$, where σ is the area in \AA^2 per molecule, k is the boltzmann constant, π is the surface pressure, and T is the temperature. As in the case of the three-dimensional gas theory where a perfect gas law is obeyed only at a very low pressure and at a very large volume, the two-dimensional gas law is followed by the insoluble monolayer film at a very low surface pressure and at a large value of area per molecule only. It was found in some cases that the surface pressure as low as 0.001 mN/m may not be low enough to satisfy the two-dimensional perfect gas law [3].

As the monolayer film in the gaseous state is compressed, the area per molecule (molecular area) decreases as the available trough area becomes increasingly smaller, and the area occupied by a single molecule becomes increasingly significant compared

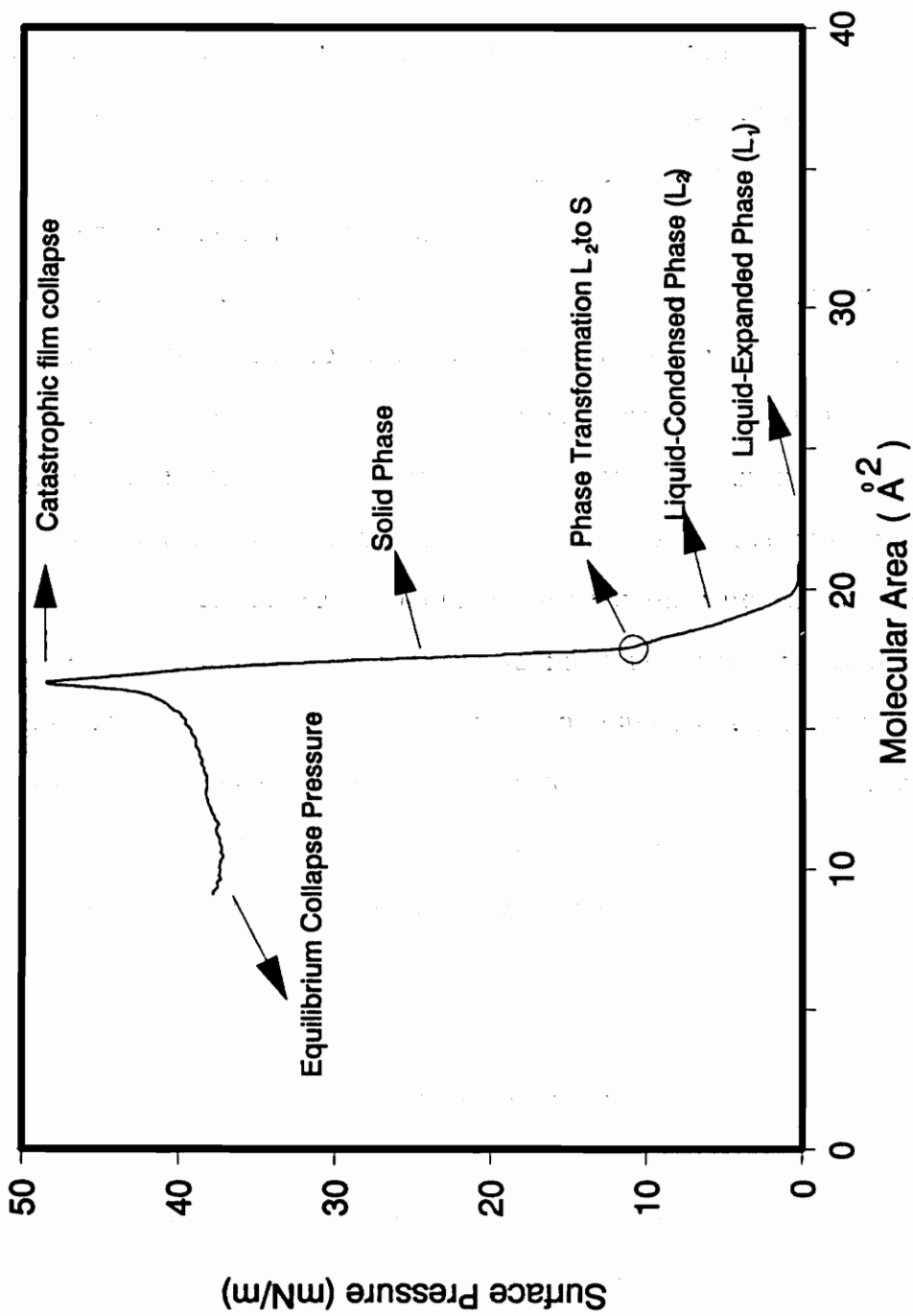


Figure 1.1 A typical pressure-area isotherm of methyl stearate monolayer film, at 291.7K.

to the total area available to the monolayer film. Under such conditions the behavior of the spread film deviates considerably from the two-dimensional perfect gas law. Different equations have been suggested, similar to the van der Waals equation of states, for the three-dimensional system. Each of them has their merits and demerits and are found to be useful only under certain specific conditions [2].

When the monolayer film is still further compressed, it undergoes a phase transition from the gaseous state to the liquid state. The surface pressure at which this transition takes place is a function of the material and the temperature. In the liquid state, the molecules are much closer to each other than in the gaseous state but are still not close enough to have a closely packed and a well aligned configuration at the air/water interface. The hydrophobic part of the molecules is randomly oriented away from the water surface while the polar group is in contact with the water. The liquid state has been further divided into sub-classes - the liquid-expanded state (L_1) and the liquid-condensed state (L_2). The extrapolated molecular area at zero surface pressure, for a single-chain molecule in the L_1 state is about 50 \AA^2 . The L_1 state has a relatively higher compressibility ($2 \text{ to } 7 \times 10^{-2} \text{ m/mN}$) [4] than the bulk (three-dimensional) liquid phase. The L_2 state is comparatively less compressible than L_1 . Upon further compression, the monolayer film in the L_1 state, before going into the L_2 state, undergoes a phase transition to an Intermediate state (I state), which has a very high film compressibility ($2.2 \times 10^{-1} \text{ m/mN}$). The monolayer film compressibility in the L_2 state is relatively lower ($k = 5 \text{ to } 10 \times 10^{-3} \text{ m/mN}$) [4]. Depending upon the temperature and the material in use, all or some of the different liquid states may show up in the pressure-area isotherm.

Upon further compression, the monolayer film in the liquid-condensed state undergoes a phase transition to a state of very low compressibility, the solid state. The

film compressibility in the solid state, $k = 0.0005$ to 0.0001 m/mN [4], is comparable to that of the bulk (three-dimensional) solid phase. The pressure-area behavior is effectively linear and exhibits the steepest slope. The linear portion in the solid state region of the pressure-area isotherm when extrapolated to the molecular area at zero surface pressure gives what is known as the Pockels point. This area corresponds approximately to the cross-sectional area of the hydrocarbon chain. This suggests that the hydrocarbon chains of these molecules in the solid states are closely packed.

The different states of monolayer films just described above give a simplified picture. There may exist a variety of complex monolayer structures which are characteristics of a particular film material. For example, three different condensed phases, the condensed solid (CS), the solid (S) and the superliquid (LS) with a vertical chain arrangement were found in the condensed state alone in monolayer films of long-chain ethyl esters [12,13].

1.4.3 Monolayer Film Stability

A complete understanding of monolayer film stability is vital for progress to be made in the use of the insoluble monolayer films for various applications in micro-electronics, biosensors, optics, and subphase evaporation control [68]. Monolayer films of long alkyl chain acids, alcohols and esters have also been used as models for the more complex biological architectures. The study of monolayer film stability of simple molecules will help to describe the behavior of complex biological system that form bilayers and serve as ion gates in cells.

1.4.3.1 Surface Pressure

When an insoluble film forming material is introduced to a water surface the material spreads rapidly on the water and lowers its surface energy. The reduction in

surface energy of the water due to the presence of a film forming material gives rise to surface pressure. The surface pressure is equal to the lowering of surface tension of the pure solvent, $\pi = \gamma_0 - \gamma$, where γ and γ_0 are the surface tension of water with and without film, respectively. As the film density on the water surface increases, either by the addition of more insoluble film forming material or by compression, the surface pressure increases. For a given film material, there is a limit to which the surface pressure can rise. A point is reached when further compression of the monolayer results in the expulsion of the film forming materials from the air/water interface. This process of fast monolayer film collapse is known as catastrophic film collapse. The collapse pressure corresponding to the catastrophic film collapse is thus defined as the "highest surface pressure to which a monolayer film can be compressed without a detectable expulsion of film forming molecules to form a new phase" [2]. The collapse pressure is dependent not only on the film material type but also on the experimental factors such as temperature, film compression rate and the previous history of the monolayer film [2,14]. In recent studies it was found that the nature of the pressure-area isotherms, including the collapse pressure, can be varied greatly at constant temperature by changing the "time of observation" [15,16].

In contrast to the catastrophic film collapse which takes place at the collapse pressure, a slow monolayer film collapse takes place when the monolayer film is compressed above the equilibrium spreading pressure but below the collapse pressure, that is in the metastable region.

1.4.3.2 Equilibrium Spreading Pressure

When a sample of crystalline insoluble film forming material is introduced to a water surface, the film material spreads on the water surface to an extent until it attains a characteristic constant surface pressure. This constant surface pressure at which the

monolayer film material is in equilibrium with the bulk phase is known as the equilibrium spreading pressure, which is temperature dependent. The equilibrium spreading pressure is often a difficult value to obtain on a reasonable time scale because in most cases the approach to equilibrium between the bulk phase and the monolayer is a very slow process [1]. Because of this, a monolayer film can be compressed to a much higher surface pressure than the equilibrium spreading pressure without breaking the integrity of the monolayer film. Thermodynamically, a film compressed above its equilibrium spreading pressure cannot be stable and will have a natural tendency to aggregate and form a bulk phase. The equilibrium spreading pressure for methyl stearate was earlier obtained [17] by two different methods that yield different results, 18.6 mN/m and 24.6 mN/m at 294.1 K. The value of 18.6 mN/m was obtained by putting a relatively large amount of bulk phase on the water surface and then allowing it to reach an equilibrium with the spread monolayer film. The equilibrium spreading pressure of 24.6 mN/m was obtained by compressing a spread monolayer film of methyl stearate to film collapse, followed by surface pressure relaxation at constant area until a relatively constant value was obtained. The reason behind this discrepancy in the values for the equilibrium spreading pressure of the same film material is still not well understood.

1.4.3.3 Relaxation Mechanisms

The mechanisms by which monolayer films, compressed above the equilibrium spreading pressure, are transformed into a bulk phase has been under investigation for several years. However, this process is still far from being understood. Monolayers compressed above their equilibrium spreading pressure undergo area-relaxation under a constant surface pressure condition or surface pressure-relaxation under a constant area condition [18-23]. This relaxation process is mainly associated with the trans-

formation of a two-dimensional monolayer film into a three-dimensional (bulk) structure. The formation of a bulk phase and its subsequent growth enables a monolayer film to lower its stress level and ultimately achieve an equilibrium state.

In the past, efforts were made to develop kinetic growth models to explain bulk-phase growth in monolayer films based on growth models developed for three-dimensional systems [17,24,25]. Recently, Vollhardt and co-workers have developed a theoretical three-dimensional film growth model that takes into account different possible geometries for the growing nuclei [26-29]. The model was successfully applied to explain the three-dimensional film growth of stearic acid at the air/water interface. The model is applicable only when the experiment is carried out under constant surface pressure conditions. This growth model has yet to be tested on other systems.

Although attempts are being made to model area-relaxation at constant surface pressure in the metastable region, little work has been done to explain surface pressure relaxation at constant area. The reason probably lies in the fact that the monolayer relaxation phenomenon can be quantitatively described for constant surface pressure conditions [17,30].

Most surface pressure-relaxation experiments have involved monolayer film relaxation in the metastable region. Here, a monolayer film is compressed to a desired surface pressure in the metastable region, and the decrease in surface pressure is followed as a function of time under a constant area condition. If the film is compressed above its equilibrium spreading pressure, the surface pressure continues to decrease at constant area until it attains a thermodynamically stable equilibrium state, the equilibrium spreading pressure.

Some work has involved stepwise film compression and relaxation, where a film is compressed and allowed to relax completely before compressing it again to a higher

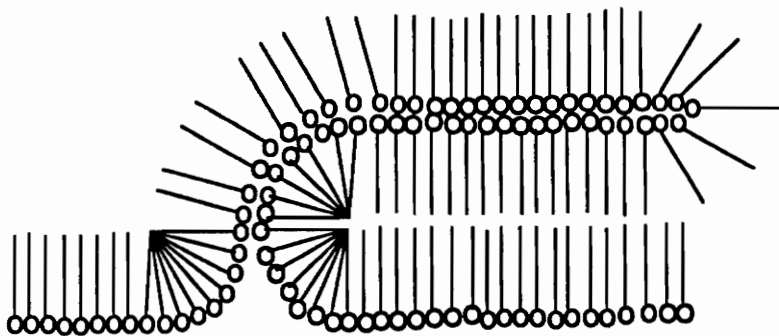
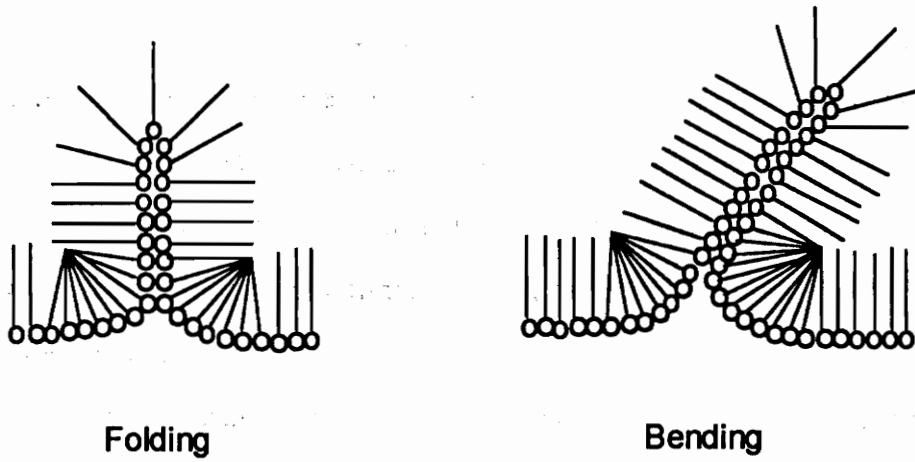
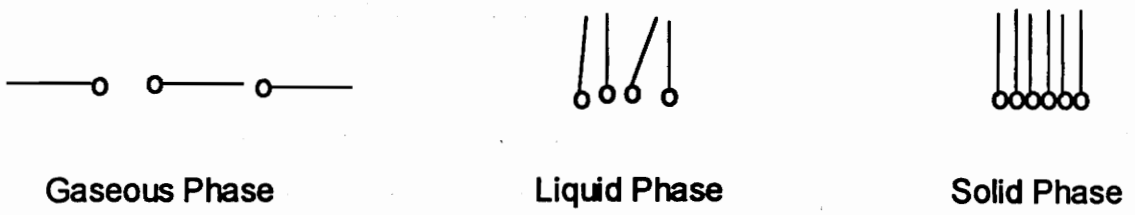
surface pressure [31-34]. After each compression step the surface pressure is monitored as a function of time at constant area. Although work has been done to explain the kinetics of surface pressure relaxation at constant area, a satisfactory description of the mechanistic details involved in the process has not been reached. Also, a major problem in interpreting the kinetics of surface pressure relaxation lies in the fact that the monolayer film passes through a series of different thermodynamic states during the relaxation process [17]. Additionally, little work involving surface pressure relaxation in films compressed beyond the collapse pressure has been reported [32,35]. One of the objectives of the present work is to investigate in detail the surface pressure relaxation processes for monolayer films compressed beyond the collapse pressure.

It is well known that when a monolayer film is compressed to collapse pressure, a catastrophic film collapse takes place. During the catastrophic film collapse a two-dimensional monolayer film is transformed into a three-dimensional film structure. The molecules that are expelled from the air/water interface to form a three-dimensional phase on top of the monolayer film may develop into a crystal or remain as a floating lens and grow as the monolayer film is further compressed beyond the collapse pressure [36]. The three-dimensional film formation during catastrophic film collapse is believed to occur via a folding and buckling mechanism (Figure 1.2), where a two dimensional monolayer film is buckled to form a three dimensional film structure in the form of the ribbons and/or vesicles [37,38]. Ries was the first to propose such a film collapse mechanism for the monolayer film of n-hexatriacontanoic acid at the air/water interface [37]. Electron micrographs of these catastrophically collapsed monolayer films transferred to solid supports revealed many long flat ribbon-like structures. The thickness of such ribbon-like structures was estimated to be about two molecules thick. Based on such observations Ries proposed that during film com-

pression the film rises from the surface along the line of rupture and folds over with a head to head arrangement. The resulting structure is essentially a bilayer (two molecules thick) which may then fall on the underlying monolayer film to produce a tri-layer structure (Figure 1.2). Similar collapsed film structures were observed in the mixed film of n-hexatriacontanoic acid and polyvinyl acetate [39]. Also, the presence of ribbon-like structures in the collapsed monolayer film of cholesterol [40] and isoleucine-gramicidin B [41], a membrane channel-forming antibiotics, indicates that such structures are not specific to fatty acids only.

In studies involving 2-hydroxytetracosanoic acid, the ribbon-like structures were not found in the micrographs of the collapsed film but instead tall ridges or folds were found in abundance [38]. It was speculated at that time that the ridges may act as reservoirs which may supply the replacement molecules to the monolayer film at the air/water interface from where molecules are lost by some means [38]. The ribbon-like structures may also act as a reservoir provided they are still attached to the monolayer film. Once broken or detached from the monolayer film the ribbon-like structures will cease to function as reservoirs. In earlier studies with fatty acids and cholesterol, ridges were found in the monolayer films before the appearance of two molecule thick ribbon-like structures in the collapsed film but were smaller in numbers [37,39,40].

In a recent study it was demonstrated that the organized film collapse in the monolayer film of stearic acid is greatly influenced by the subphase pH [42]. The organized monolayer film collapse is also a function of the film material. For example, the catastrophic film collapse in a lecithin monolayer film is not an organized film collapse. The collapsed film structure were found to be irregular, unlike the ribbons or platelet structures observed in the collapsed monolayer film of cholesterol [40].



Continuous expansion of monolayer molecules via molecular channel

Figure 1.2 A schematic diagram of the monolayer film collapse [41].

Multilayer film formation was also observed during catastrophic film collapse in a monolayer film of ethyl stearate but the nature of such collapsed phase has not been addressed [12].

1.5 Scope of the Present Work

As discussed above, the organized monolayer film collapse results in a multi-layered film structure, but the nature and the structure of the collapsed phase has not been investigated in any detail. In particular, the influence of the collapsed film structures, such as, ridges, Bi- and tri-layer film structures (ribbons) on the relaxation process has not been addressed. Ries has long speculated that the ridges and ribbons (if attached to the monolayer films) could act as a source of film materials to replenish the molecules lost from the monolayer film via different means from the air/water interface, but, to date no experimental evidence has been reported that supports such speculation.

No thorough investigation has been carried out to see how a monolayer film relaxes under a constant area condition following compression beyond its collapse pressure, and what molecular processes accompany such relaxation. A clear understanding of such a molecular process and its influence on the relaxation phenomenon is vital for any three-dimensional film growth model to be successfully developed.

The present work was undertaken mainly to investigate the relaxation behavior of monolayer films compressed beyond their collapse pressures. In particular, evidence for an organized film collapse and a test of Ries's speculation have been pursued. Surface pressure relaxation isotherms at constant area, area relaxation isotherms at constant surface pressure, and pressure-area isotherms have been obtained to aid in characterizing the relaxation mechanisms in the monolayer films of methyl stearate. Temperature dependent studies were also performed.

Methyl stearate, was selected as a model film-forming for a number of reasons. First, the long chain acids, alcohols and esters essentially represent the same class of insoluble film material, so any of these should be representative. Second, esters are not sensitive to pH fluctuations as are carboxylic acids. Third, little data have been reported for organized film collapse in monolayer films of fatty esters.

1.6 Potential Uses

The mechanistic and the kinetic aspects of relaxation in collapsed monolayer films are important not only for the understanding of the fundamental process of the nucleation and growth of 3-dimensional structures from 2-dimensional monolayers, but also for technological implications in the processes such as evaporation control in water reservoirs, boundary lubrication, channel gating in biological membranes, and the spreading kinetics of the Lung surfactant. The importance of such investigations and their potential application in some areas of science are discussed below.

Lung Surfactant

Dipalmitoyl phosphatidylcholine (commonly known as DPL) is found in the lung along with pulmonary surfactant. The presence of pulmonary surfactant is very important in stabilizing the lung alveoli and for reducing the work of breathing [43]. In order for pulmonary surfactants to be effective as a lung alveoli stabilizer, the presence of DPL which generates a very high dynamic surface pressure (lowering of the surface tension at the interface) at the interface is vital during the lung compression cycle [43]. But the DPL molecules lost from the interface during lung the compression cycle must be able to re-penetrate the interface in sufficient numbers during the lung expansion cycle in order for it to be effective for the next compression cycle. It was found during the laboratory studies that at temperatures comparable to that of the body, the post collapse film structure of the DPL monolayer film is stable enough that

it does not allow DPL molecules to re-enter the interface [44,45]. Experiments have been carried out to characterize the influence of a second surface active component, such as cholesterol or unsaturated phosphatidylcholines (also present in the lung), on the re-penetration behavior of the DPL molecules [46]. It was found that the mixtures of DPL and cholesterol as well as DPL and phosphatidylcholines resulted in a greater degree of re-spreading of the surface film in the post collapse relaxation regime. However, the exact molecular processes that are responsible for such an enhanced degree of relaxation is still not properly understood. Earlier Ries et.al. [40] obtained electron micrographs of the collapsed monolayer film of cholesterol, the ribbon-like and platelet structures as expected for the organized film collapse were found. It is therefore possible that the presence of cholesterol in a mixture with DPL might have resulted in an organized film collapse when the monolayer film is compressed past the collapse pressure, thus enabling the film materials in the collapsed film to go back to the air/water interface through molecular channels. There possibly may be other reasons responsible for the post-collapse enhancement of surface pressure relaxation in the mixed film of DPL with the cholesterol, so more work needs to be done to investigate especially the structure and the nature of the collapsed film in the mixed films of DPL and cholesterol. A complete understanding of the film collapse mechanism of such films at the air/water interface will provide further insight into the function of the lung surfactant.

Evaporation Control

The utility of monolayer films of long chain acids, alcohols and esters for water evaporation control has long been recognized [47-53]. A monolayer film of methyl stearate held at 11 mN/m was found to reduce the rate of water evaporation by 12% [48]. In general the effectiveness of the monolayer films in retarding water evaporation

depends on two basic facts: 1) the existence of strong intermolecular forces of attraction between the spread monolayer film materials and 2) the strong adhesive forces between the subphase and the film material. It is for these reasons that it is expected that substances containing double bonds or other irregular structural properties would not form good evaporation retarding films because the amphiphiles would not pack well in monolayers. Though the influence of molecular architecture and surface pressure on evaporation retardation has been investigated, there has been little work done to investigate the kinetics of re-spreading of the collapsed film on the water surface. It should be expected that the evaporation retarding monolayers on the reservoir (water) surfaces would frequently break down (collapse) due to water rippling or some other disturbances. Thus, the kinetics of film re-formation would be important to the overall retardation efficiency of the film.

Efforts should therefore be made to investigate relaxation mechanisms and relaxation kinetics in the monolayer films in order to be able to have a greater degree of control over the monolayer relaxation process which can then be exploited towards these ends.

CHAPTER - 2

EXPERIMENTAL METHODS

2.1 Instrumentation, the Film Balance

A picture of the Film Balance used in the present study is shown in Figure 2.1. The Joyce-Loebl Langmuir Mini Trough was used to obtain the pressure-area, pressure-time, and the area-time isotherms. It was also used to deposit the Langmuir-Blodgett films on the glass slides.

The Langmuir-Trough essentially consists of a stainless steel trough with a Teflon coating to make it hydrophobic and chemically inert. The trough holds the liquid subphase upon which the monolayer film is formed. A constant perimeter barrier is used to manipulate the total area available to the spread monolayer material. The film barrier, with a width of 2 cm, is made up of PTFE coated glass fiber and is mounted above the trough such that it is half submerged in the subphase. The total water surface area available to the spread monolayer film material is manipulated by moving the film barrier forward or backward. Using the speed setting switch on the instrument the speed of the barrier can be adjusted. The trough has a maximum water surface area of 506 cm² when the film barrier is completely open, and a minimum area of 71 cm² when the film barrier is in the closed position.

The Wilhelmy plate technique is employed to measure the surface pressure produced by the spread monolayer film [2]. The Wilhelmy plate is a thin plate of width one cm and negligible thickness. The thin plate can be metal, (usually platinum), quartz or simply filter paper. In the present investigation filter paper was used. The

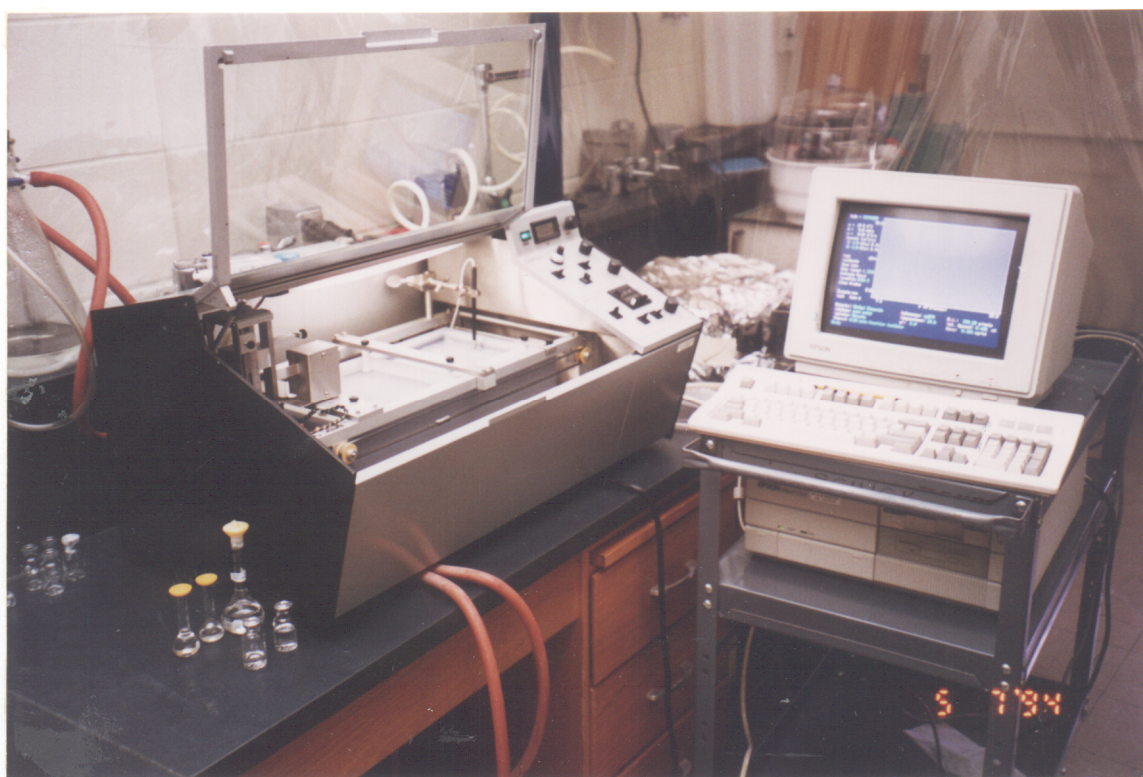


Figure 2.1 The film balance (Joyce-Loebl Minitrough).

Wilhelmy plate is about 4 cm long and is attached to a microbalance. The plate is hung vertically and partially submerged in the water subphase. The surface pressure produced by the spread insoluble film alters the force experienced by the Wilhelmy plate. The relationship between the surface pressure and the force experienced by the Wilhelmy plate is described as [1]:

$$F = \rho_p lwtg - \rho_0 twhg + 2\gamma(t+w)\cos\theta \quad (1)$$

Where, F is the downward force acting on the Wilhelmy plate. The ρ_p , l , w , t , and h are the density, length, width, thickness, and the height (length of the submerged part) of the plate, respectively. The g is the gravitational constant. The ρ_0 and γ are density and surface tension of water, respectively. The θ is the contact angle between Wilhelmy plate and water (usually zero).

There are three forces acting on the partially submerged Wilhelmy plate - the gravitational force, the surface tension acting downwards, and the buoyancy force acting upwards due to the displaced water.

From equation 1 the net change in force on the Wilhelmy plate, in the presence of the spread film material is given by,

$$\Delta F = 2(\gamma_0 - \gamma)(t + w) \quad (2)$$

Where γ and γ_0 are the surface tension of water with and without the spread film, respectively.

The surface pressure is defined as:

$$\pi = \gamma_0 - \gamma \quad (3)$$

So, for a Wilhelmy plate of a negligible thickness and a width of 1 cm, we have from equation (2) and (3):

$$\Delta F = 2\pi \quad (5)$$

Therefore, the force experienced by the Wilhelmy plate is twice the actual surface

pressure.

The film balance also has the capability to deposit Langmuir-Blodgett films. The deposition process is completely automated. The deposition speed, stroke depth, and the surface pressure of the monolayer film can be set to any desired value.

2.2 Sample Preparation and Monolayer Formation

Methyl stearate was purchased (Sigma, 99% purity), and was used without further purification. Optima grade Chloroform (Fisher scientific) was used as spreading solvent. No surfactant impurities were detectable in the chloroform by film-balance measurements.

A solution of methyl stearate in chloroform (12.3 mM) was prepared. The concentration of solution is subject to uncertainties in weighing very small amounts. About 3% uncertainty in concentration was observed based on fluctuation in Pockel's point determinations. All glassware used in generating and storing the spreading solutions were cleaned in a Nochromix solution (Fisher Scientific) for 2 days, followed by rinsing with large quantities of high purity water, including one 10-min rinse using an ultrasonic bath. The glassware was air dried in a class 100 environment.

High purity water used for cleaning and for subphase preparation was produced by a Barnstead Nanopure Bioresearch-grade purification system, which provides Type-I water with an 18-M Ω resistivity and no detectable surface-active impurities. The aqueous subphase used consisted of pure water (pH 6.8). The film balance is located in a class 100 clean room. Monolayers were deposited at the air/water interface by using a gastight syringe to spread 20 μ l of sample solution, unless otherwise specified. Data collection was delayed for 10 min in order to ensure the complete evaporation of the chloroform. The temperature of the water subphase was varied using a ther-

mostated circulator (Fisher Scientific) which regulated the temperature of the trough assembly within $\pm 0.1^\circ\text{C}$. The trough is hollow, allowing circulation of thermostated water.

2.3 Isotherms

The pressure-area, pressure-time, and area-time isotherms were obtained by using a computer interfaced Joyce-Loebl Minitrough system. The spread monolayer was compressed continuously at a constant compression rate of $0.05\text{-}0.09\text{ \AA}^2\text{ sec}^{-1}\text{ molecule}^{-1}$.

2.3.1 Pressure-Area Isotherms

The pressure-area isotherms were obtained for a range of temperatures 291.6 K to 306.5 K. Balance was put into the pressure-area isotherm mode and the spread Monolayers of methyl stearate were compressed at a constant rate, and surface pressure data was recorded at an interval of $0.1\text{ \AA}^2\text{ molecule}^{-1}$. Data collection was carried out until a little beyond the collapse pressure. At each temperature, at least three independent measurements were made to check the reproducibility.

2.3.2 Pressure-Time Isotherms

A spread monolayer film was compressed until a desired surface pressure was reached, the film compression was stopped and relaxation at constant area was monitored as a function of time. The surface pressure data was recorded every 5 seconds for more than 8000 seconds. The isotherms were obtained under different experimental conditions such as, temperature, surface pressure, and overcompression ratio. The overcompression ratio ($\text{OR} = A_{\pi_c}/A_f$) is defined as a ratio of the monolayer film area corresponding to the collapse pressure (A_{π_c}) to final monolayer area when the film compression is finally stopped (A_f).

2.3.2.1 Overcompression Ratio

A monolayer film of methyl stearate was compressed to a surface pressure below the collapse pressure and was allowed to relax at a constant area. The surface pressure was monitored as a function of time and pressure-time isotherms were obtained for monolayers compressed to a number of different maximum surface pressures.

The pressure-time isotherm data for monolayers of methyl stearate compressed beyond the collapse pressure were obtained by methods similar to those described for film compressed below the collapse pressure, where in this case the initial compression was continued directly to an area corresponding to a particular overcompression ratio. Here the reference area was taken to be the area corresponding to the collapse pressure. The collapse pressure, however, is a function of the nature of the film material and other experimental factors such as temperature, film compression rate and pre-history of the monolayer film. The exact collapse pressure is a very difficult quantity to predict [2,14]. Typically, the collapse pressure vary slightly ($< 5\%$) from run to run, primarily as a result of mechanical fluctuations in the compression rate. Therefore, repeat runs are performed in order to determine statistical uncertainties. Additional uncertainty in the overcompression ratio was introduced by the 5-second time intervals used for collecting the pressure-time plots. It was not always possible to detect the precise collapse pressure in real time. However subsequent analysis of the digitized data could be used to accurately determine the film collapse pressure in most cases. Typically, film collapse was followed by a significant drop in surface pressure (Figure 2.2). Greater uncertainty was obtained for data collected at 306.5 K because the surface pressure maintained a constant value following the film collapse, thus increasing the uncertainty in the point of collapse. The effect of over compression ratio was studied at each of the temperatures, 297.8 K, 300.7 K, 303.7 K and 306.5 K. Temperature effects were

studied in greater detail for an overcompression ratio of 1.01. Pressure-time isotherms were obtained at six temperatures, 291.7 K, 294.9 K, 297.8 K, 300.7 K, 303.7 K and 306.5 K.

2.3.3 Area-Time Isotherms

2.3.3.1 Before Catastrophic Film Collapse

Area-Time isotherms were obtained by the following procedure: After depositing the spreading solution and with the barrier fully open, the instrument was set to constant pressure mode with the set point already defined and with a low gain setting. The barrier then began compressing the film. The low gain setting results in a film compression rate of approximately $0.04\text{-}0.08 \text{ \AA}^2 \text{ sec}^{-1} \text{ molecule}^{-1}$. As the surface pressure began to rise and approached the set point value, the gain setting was slowly increased to maximum sensitivity. The preset constant surface pressure was maintained throughout the experiment while the change in film area as a function of time was recorded. Area-relaxation data were collected at intervals of 10 seconds until the barrier had reached its minimum area position.

2.3.3.2 After Catastrophic Film Collapse

The area-time isotherms collected for monolayers compressed beyond the collapse pressure were also obtained. All the area-time isotherms were obtained at a constant surface pressure of 40 mN/m. For these experiments, monolayers were compressed using the manual mode. Upon film collapse, the compression was stopped and the surface pressure was allowed to relax to a desired value. When the desired surface pressure was reached, the instrument was switched to the auto mode which maintained the preset surface pressure by adjusting the barrier position. The change in monolayer area was then monitored as a function of time. Area relaxation data

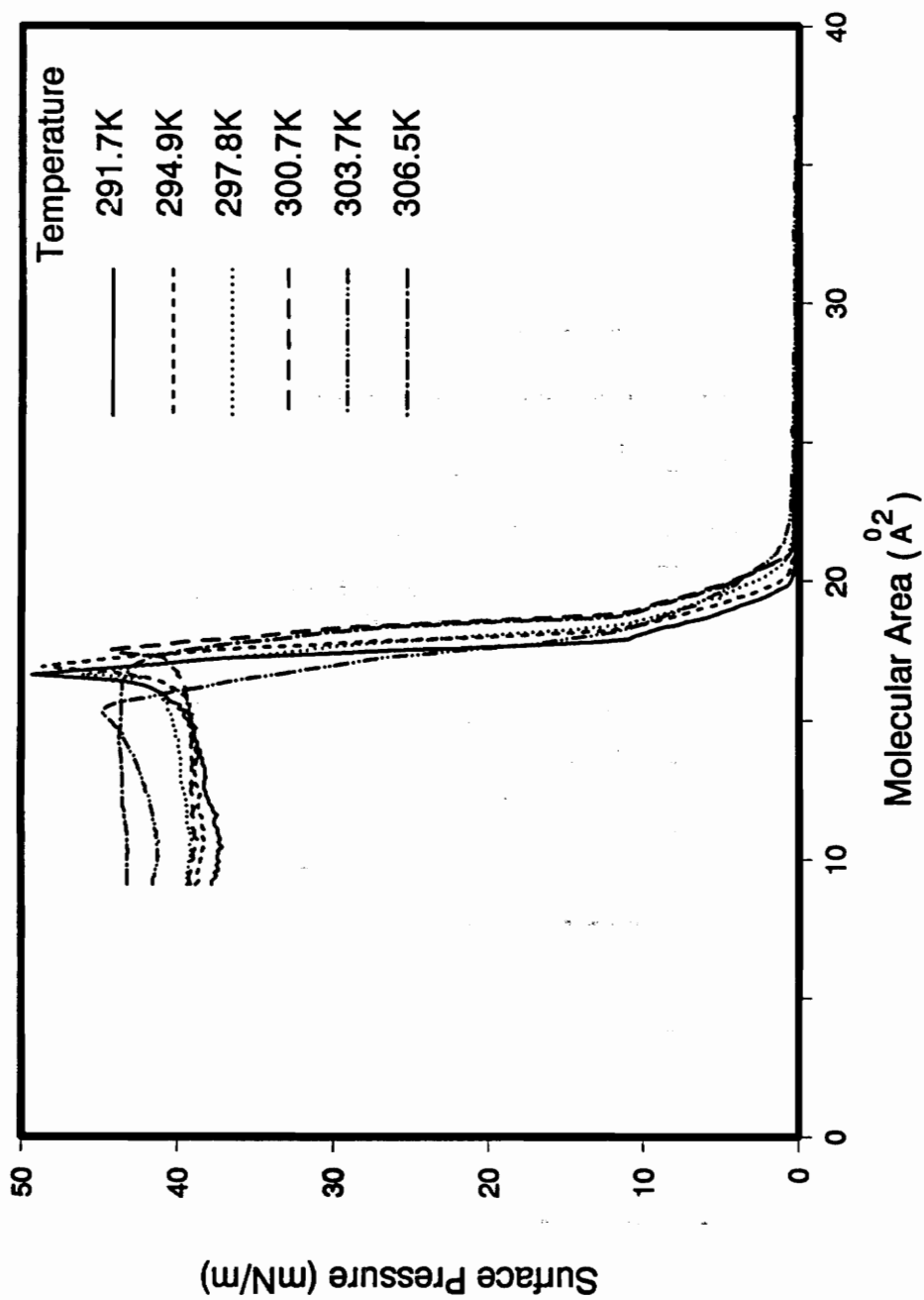


Figure 2.2 Pressure-area isotherms of methyl stearate monolayer film at different temperatures.

were recorded at time intervals of 10 seconds.

2.4 Langmuir-Blodgett Films

An insoluble monolayer film transferred from the air/water interface onto a solid substrate is known as a Langmuir-Blodgett film. Successful deposition typically indicated by a transfer ratio of one, which is defined as A_1/A_s , where A_s is the substrate area containing the transferred film and A_1 is the decrease in trough area observed during the deposition.

The Langmuir-Blodgett films were deposited on 75 x 25 x 1 mm microscope glass slides (Fisher brand). The glass slides were cleaned according to the procedure described for the glassware cleaning in the sample preparation section 2.2 (Sample Preparation and Monolayer Formation). Before introducing the monolayer material to the water surface, a clean glass slide was immersed in the water subphase such that only 30 mm length of the slide was below the water surface. The sample solution was then spread on the water surface and, after allowing 10 minutes for the solvent to evaporate, the film was compressed to the desired surface pressure. The barrier mechanism was then set to auto mode, and the film was transferred onto the slide by slowly withdrawing the slide by using the dipping assembly. Since the surface pressure is maintained constant during the LB film deposition, the trough area must decrease to compensate for the film removed from the air/water interface. Monolayer transfer was accomplished using the vertical dipping method [2,54] with speeds of about 8 mm/min.

CHAPTER - 3

RESULTS AND DISCUSSION

3.1 Pressure-Area Isotherms

Pressure-area isotherms observed for methyl stearate at different temperatures are shown in Figure 2.2. The basic features of the isotherms are in close agreement with those reported earlier [55]. On compression, the monolayer film undergoes a phase transition from L_1 to L_2 at about $21 \text{ \AA}^2/\text{molecule}$. A subsequent transition to the solid phase occurs upon reaching a surface pressure of about 11.0 mN/m . Further compression of the film results in a sharp rise in the surface pressure that ultimately leads to catastrophic film collapse. Typically after the film collapse there is a rapid drop in surface pressure that eventually levels off at a steady value (equilibrium collapse pressure).

Based on the Ries model of film collapse, it is apparent why a steady state surface pressure is reached following collapse. At collapse, the monolayer film buckles and folds over to form bilayer molecular channels. The presence of such molecular channels in the monolayer films allows the hydrophobic planes of the two sides of the collapsed film to slip passed each other easily (Figure 1.2), and thus provides an energetically favorable path to lift film molecules from the air/water interface upon further compression.

The steadiness of the post-collapse pressure is an indication of continuous lifting of monolayer molecules from the air/water interface. It has been suggested for the monolayer film of ethyl stearate that the equilibrium collapse pressure represents a

transition process in which the monolayer film is continuously transformed into bilayers [12]. The magnitude of the steady state surface pressure after the film collapse is a function of the balance between the rate at which the material is lifted from the air/water interface and the rate at which the film is compressed. At any given temperature in the present work, the steady state surface pressure was found to vary moderately from run to run due to small variations in compression speed.

From pressure-area isotherms, molecular areas corresponding to Pockels points for both the solid and L₂ phases were determined at different temperatures. The observed Pockels point and their 95% confidence intervals (determined from multiple independent experiments) are given in Table 3.1. Also given in the table are collapse pressure and surface pressures corresponding to the phase transition from L₂ to solid.

Irrespective of the temperature, the ratio of the extrapolated area of the L₂ phase to the extrapolated area of the solid phase was found to be constant, 1.09 ± 0.01 . This suggests that the two condensed phases have two well defined molecular orientation at the air/water interface. The hydrophobic chain orientation in the solid phase, and in the L₂ phase for methyl stearate monolayers were reported earlier to be close to 0° and 27°, respectively with respect to the surface normal [55].

The monolayer film compressibility in the solid state region was determined to be in the range of 0.001 to 0.003 m/mN at different temperatures. The film compressibility was measured in the surface pressure range of 15-30 mN/m. At surface pressure above 30 mN/m, a partial collapse of the film is suspected. Thus the pressure-area data above 30 mN/m were not considered for calculating the film compressibility. The surface pressure range, 15-30 mN/m was also used to get the Pockel's point at different temperatures.

Table 3.1. The numerical data of characteristic points on the pressure-area isotherms, at different temperatures are reported at 95% confidence interval.

Temperature (K)	Pockels Point Solid Phase \AA^2 / molecule	Pockels Point Liquid-condensed Phase \AA^2 /molecule	Surface Pressure Corresponding to LC-S Transition (mN/m)	Surface Pressure Corresponding to LE-LC Transition (mN/m)	Collapse Pressure (mN/m)
291.7	18.1 +/- 0.8	19.8 +/- 0.6	11.4 +/- 0.9	0.4 +/- 0.2	49.0 +/- 2.3
294.8	18.1 +/- 0.5	19.6 +/- 0.1	12.0 +/- 0.4	0.7 +/- 0.3	48.9 +/- 0.5
297.8	18.8 +/- 0.3	20.4 +/- 0.4	10.9 +/- 1.5	0.8 +/- 0.1	45.8 +/- 1.0
300.7	19.2 +/- 0.3	20.7 +/- 0.5	11.3 +/- 1.0	0.5 +/- 0.3	44.1 +/- 2.0
303.7	18.7 +/- 1.8	20.4 +/- 1.8	10.9 +/- 1.2	0.5 +/- 0.4	44.9 +/- 0.2
306.5	19.0 +/- 1.7	20.9 +/- 1.6	11.2 +/- 0.9	0.6 +/- 0.2	43.3 +/- 1.2

3.2 Pressure-Time Isotherms

The pressure-time isotherms were obtained for the monolayer films of methyl stearate compressed both below as well as above collapse pressure. The isotherms were obtained under different experimental conditions, such as, temperature, surface pressure, and overcompression ratio.

3.2.1 General Features

A typical surface pressure relaxation isotherm for a methyl stearate monolayer compressed beyond the collapse pressure is shown in Figure 3.1. For the ease of understanding, the different parts of the isotherm have been labeled. The time, $t=0$, on the isotherm corresponds to the point at which film compression is stopped. The initial sharp drop in surface pressure, represented by **a**, is due to molecular rearrangement in the collapsed film. The sharp drop in surface pressure is followed by a plateau region (**b**) in which the rate of relaxation is extremely slow. The plateau region is immediately followed by region **c** where the rate of relaxation increases. The surface pressure range in region **c** corresponds to the solid phase region of the pressure-area isotherm. A subtle break in the continuity of region **c** is observed near 27 mN/m. Presently, the origin of this feature is unclear. Following region **c** a discontinuity is observed at about 11.0 mN/m (labelled **d**). This point represents a phase transition taking place in the monolayer film, from S to L_2 state. The surface pressure relaxation below the phase transformation point is represented by region **e**, which is in the L_2 state regime of the monolayer film.

Sims and Zografis have previously reported pressure relaxation at constant area for methyl stearate monolayers compressed to film collapse at 298.2 K [19,56]. They attributed the relaxation mainly to expulsion of film molecules from the air/water

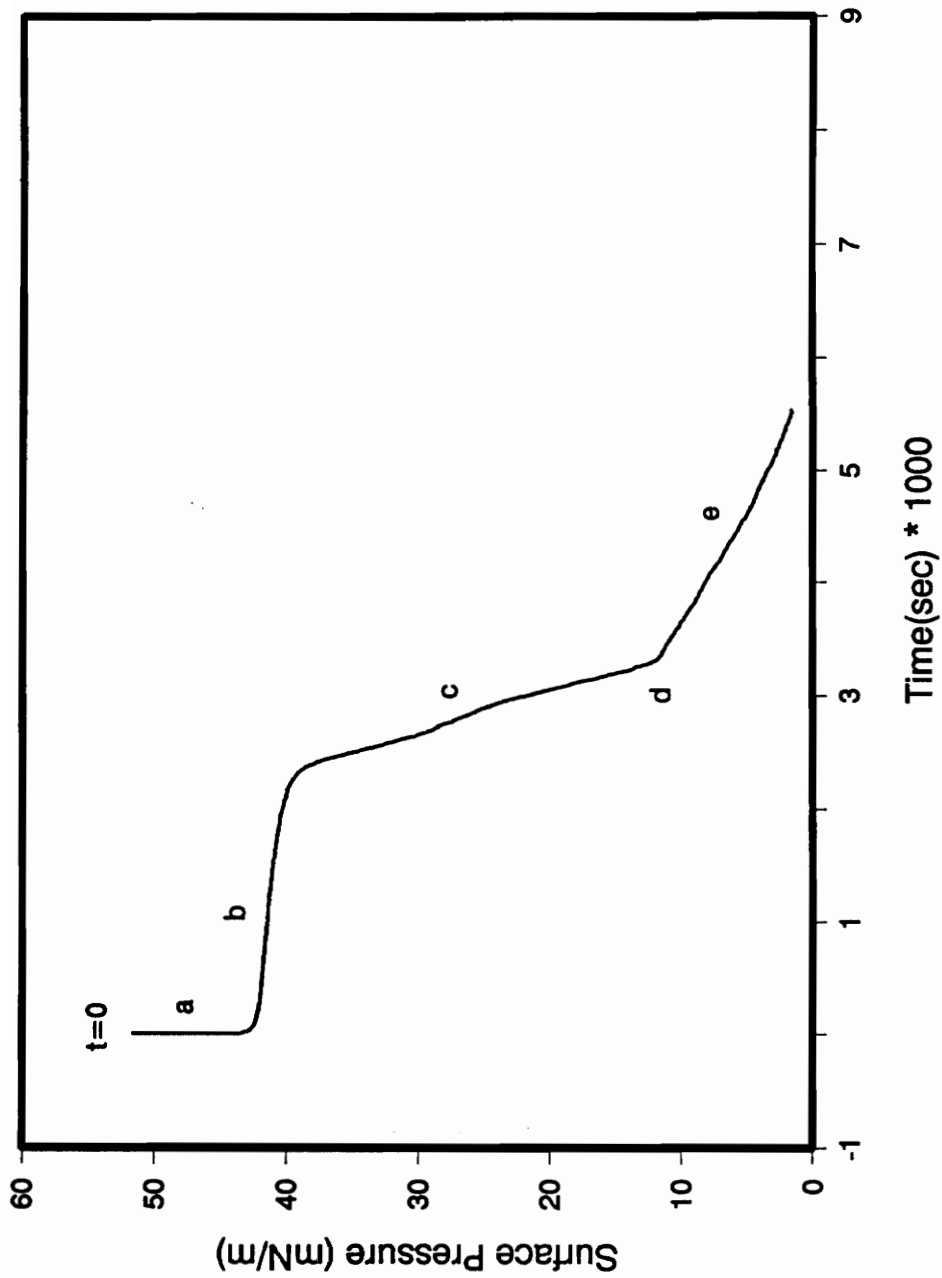


Figure 3.1 Pressure-time isotherm of a methyl stearate monolayer compressed beyond the collapse pressure. a) molecular rearrangement immediately after the film compression was stopped, b) plateau, c) accelerated relaxation in the solid phase regime, d) S/L₂ transition point and e) relaxation in the L₂ phase regime.

interface and the formation of three-dimensional lens structures. However, neither the nature of such lens structures nor of the various features of the relaxation isotherm was addressed. The limited amount of data given in these earlier reports is in qualitative agreement with the more complete data reported here. Furthermore relaxation was followed for only about 20 minutes after film collapse [56]. Therefore, only regions a and b in the relaxation curve (Figure 3.1) were observed.

Other possible sources of surface pressure loss with time are evaporation of monolayer material and its dissolution. As a part of the present investigation, material loss due to evaporation was checked at 297.7 K. This was done by comparing the pressure-area isotherms obtained for the spread monolayers of methyl stearate, where the data collection was delayed for various times up to 30 minutes following monolayer spreading. The extrapolated molecular areas corresponding to the solid regions of the isotherms were found to be equal within experimental uncertainty. Thus, there is no loss of the film material in a 30 minute period due to either dissolution or evaporation. It is therefore concluded that evaporation or dissolution effects are minor contributors to the features of the relaxation isotherms.

3.2.2 Surface Pressure Relaxation Mechanism - A Qualitative Model

As discussed in section 3.1, bi-molecular thick channels are formed during film collapse according to the Ries model [41], see Figure 1.2. If film compression is continued beyond the collapse pressure, more film material would be lifted away from the air/water interface into the molecular channels and deposited on the top of the monolayer film to form multilayered structures. This is an example of organized film collapse. The greater the extent of film compression (higher overcompression ratio), the greater will be the amount of film material present on the top of the monolayer in the form of ridges and/or ribbons. The ridges are formed during the film compression

and constitute a bi-molecular thick film raised above the air/water interface. As the monolayer film is compressed further these ridges grow taller finally bend over and fall on the top of the monolayer film to form ribbons.

During relaxation after the film compression is stopped, a sharp initial drop in the surface pressure is observed (Figure 3.1). The sharp initial drop in the surface pressure is followed by plateau region. It has been reported that bulk phase nuclei are formed in the metastable region, well before the collapse pressure is reached [56]. Thus during all phases of relaxation, monolayer material will be consumed by a growing bulk phase at the air/water interface.

Ries had earlier suggested that the ridges, ribbons, and other structures formed during the film collapse could serve as a reservoir to replace the film materials lost from the monolayer [38]. He further proposed that these structures could serve as reservoirs only if they were attached to the underlying monolayer film. In light of these arguments it is logical to postulate that as film material is consumed by the growing bulk phase at the air/water interface, molecules from reservoir structures can be transported back to the air/water interface through molecular channels to replenish the monolayer. This process of monolayer replenishment would maintain a steady level of surface concentration of the film molecules in the monolayer at the air/water interface, and thus would maintain a constant surface pressure until the reservoir structures are depleted. After all the film material from the reservoir structures has returned back to the air/water interface, further growth of the bulk phase results in a decrease in the surface concentration of film molecules and the surface pressure begins to drop. Indeed, this scenario accounts for the observation of a plateau region and subsequent accelerated decrease of surface pressure (Figure 3.1).

The pressure range associated with relaxation immediately following the plateau

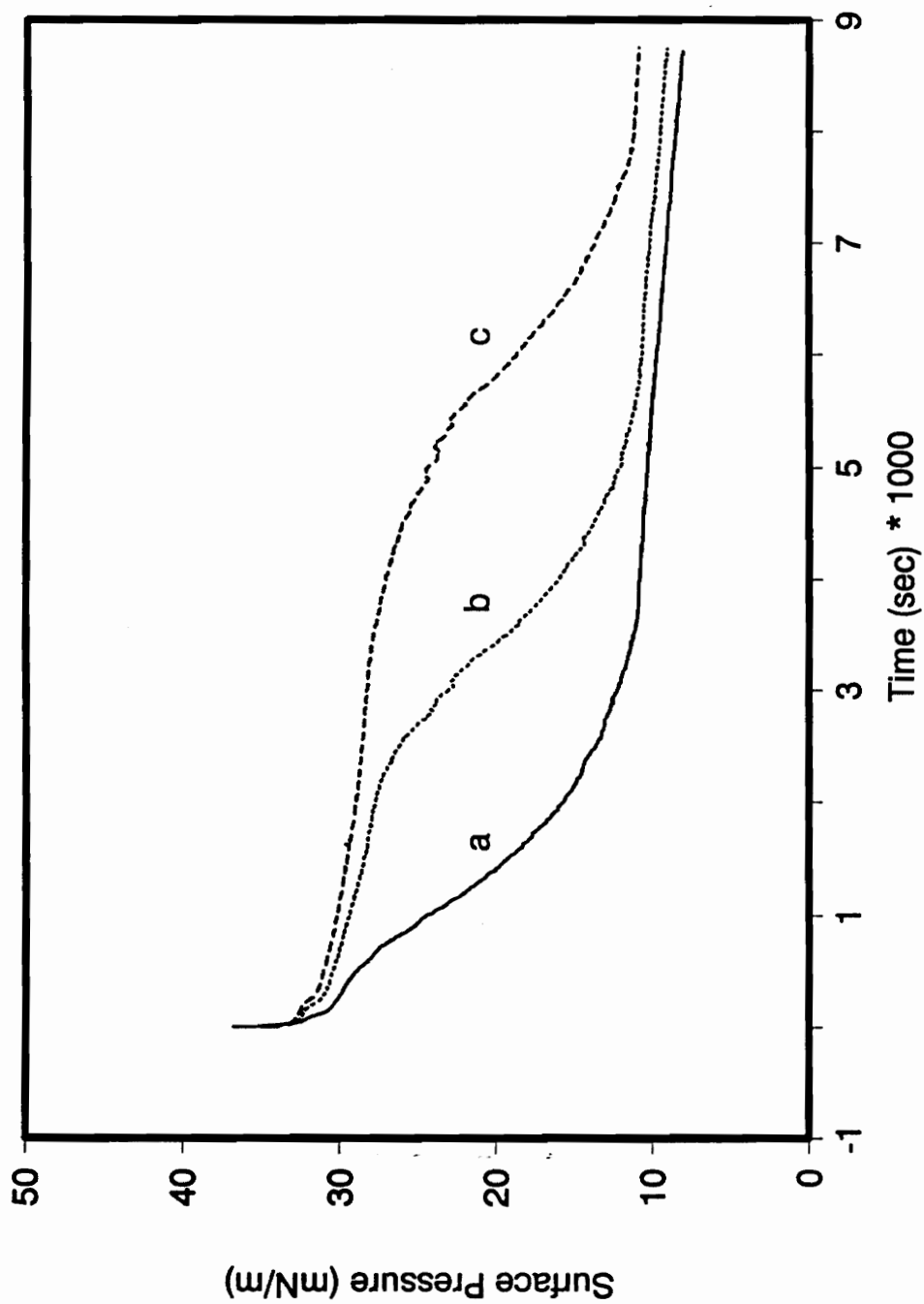


Figure 3.2 Pressure-time isotherms of methyl stearate monolayers for different overcompression ratios at 297.8 K: a) OR = 1.010 ± 0.007 ; b) OR = 1.046 ± 0.009 ; c) OR = 1.074 ± 0.010 .

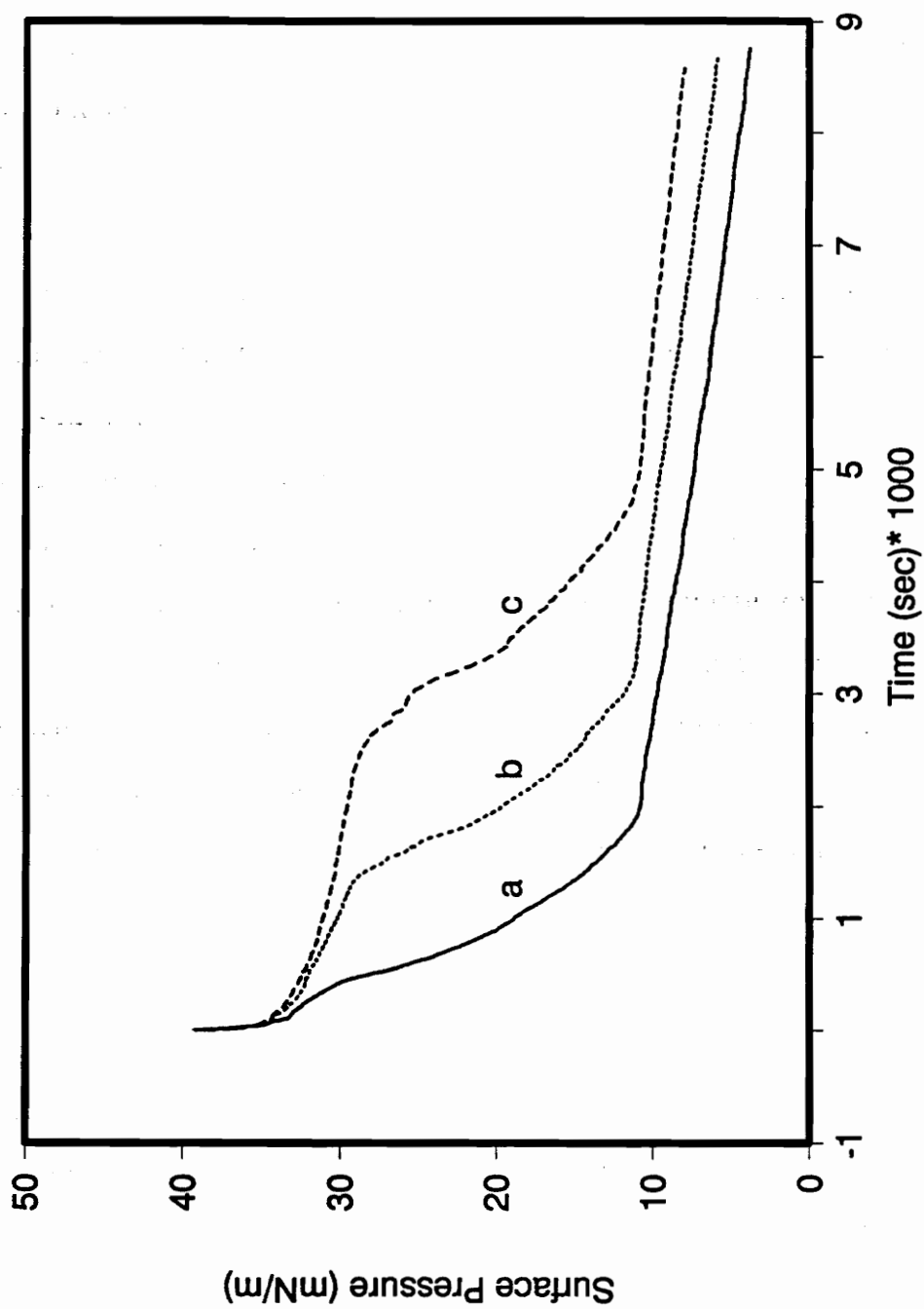


Figure 3.3 Pressure-time isotherms of methyl stearate monolayers for different overcompression ratios at 300.7 K: a) OR = 1.011 ± 0.008 ; b) OR = 1.034 ± 0.013 ; c) OR = 1.079 ± 0.007 .

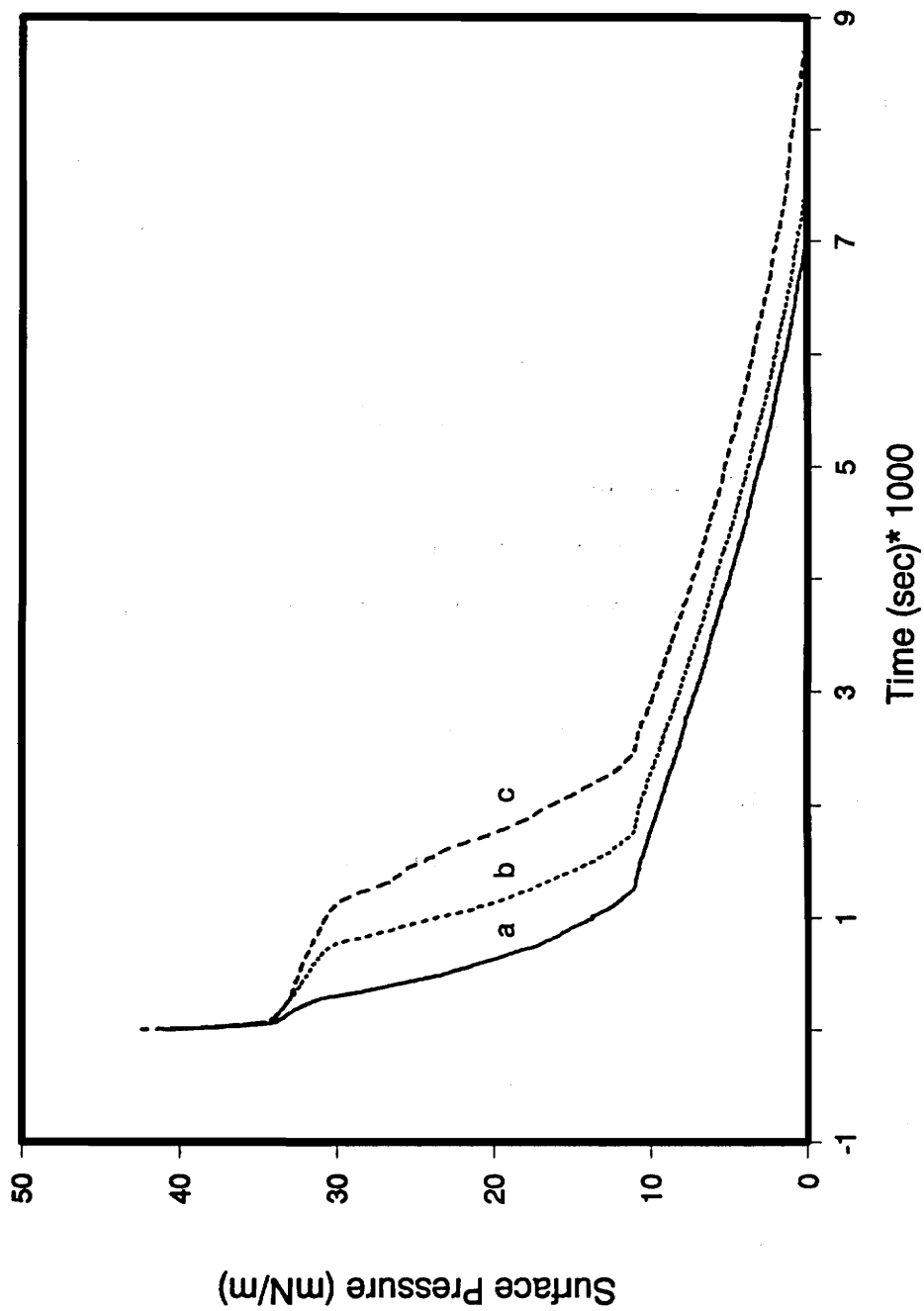


Figure 3.4 Pressure-time isotherms of methyl stearate monolayers for different overcompression ratios at 303.7 K: a) OR = 1.008 ± 0.006 ; b) OR = 1.040 ± 0.011 ; c) OR = 1.090 ± 0.010 .

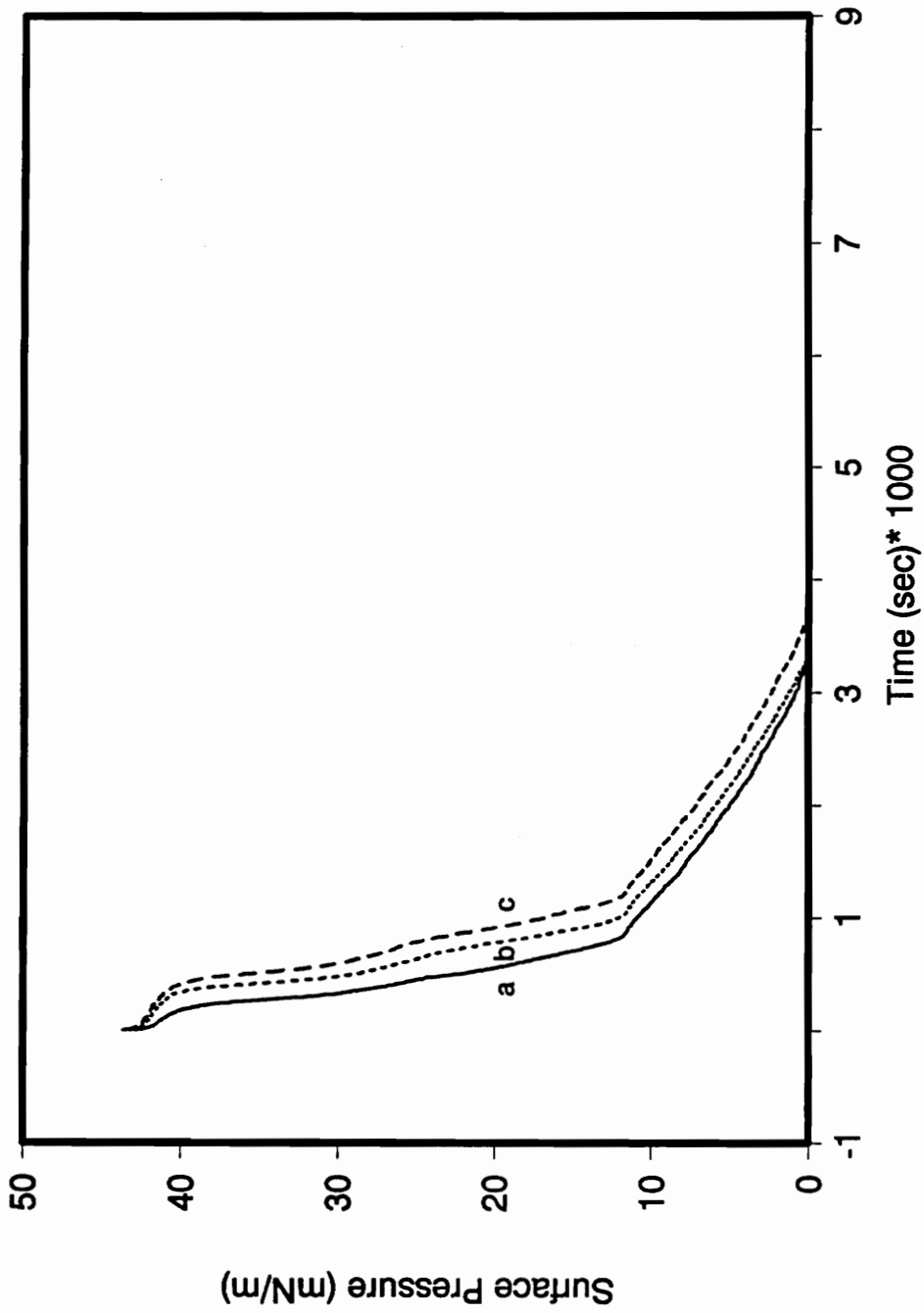


Figure 3.5 Pressure-time isotherms of methyl stearate monolayers for different overcompression ratios at 306.5 K: a) OR = 1.019 ± 0.010 ; b) OR = 1.031 ± 0.013 ; c) OR = 1.070 ± 0.011 .

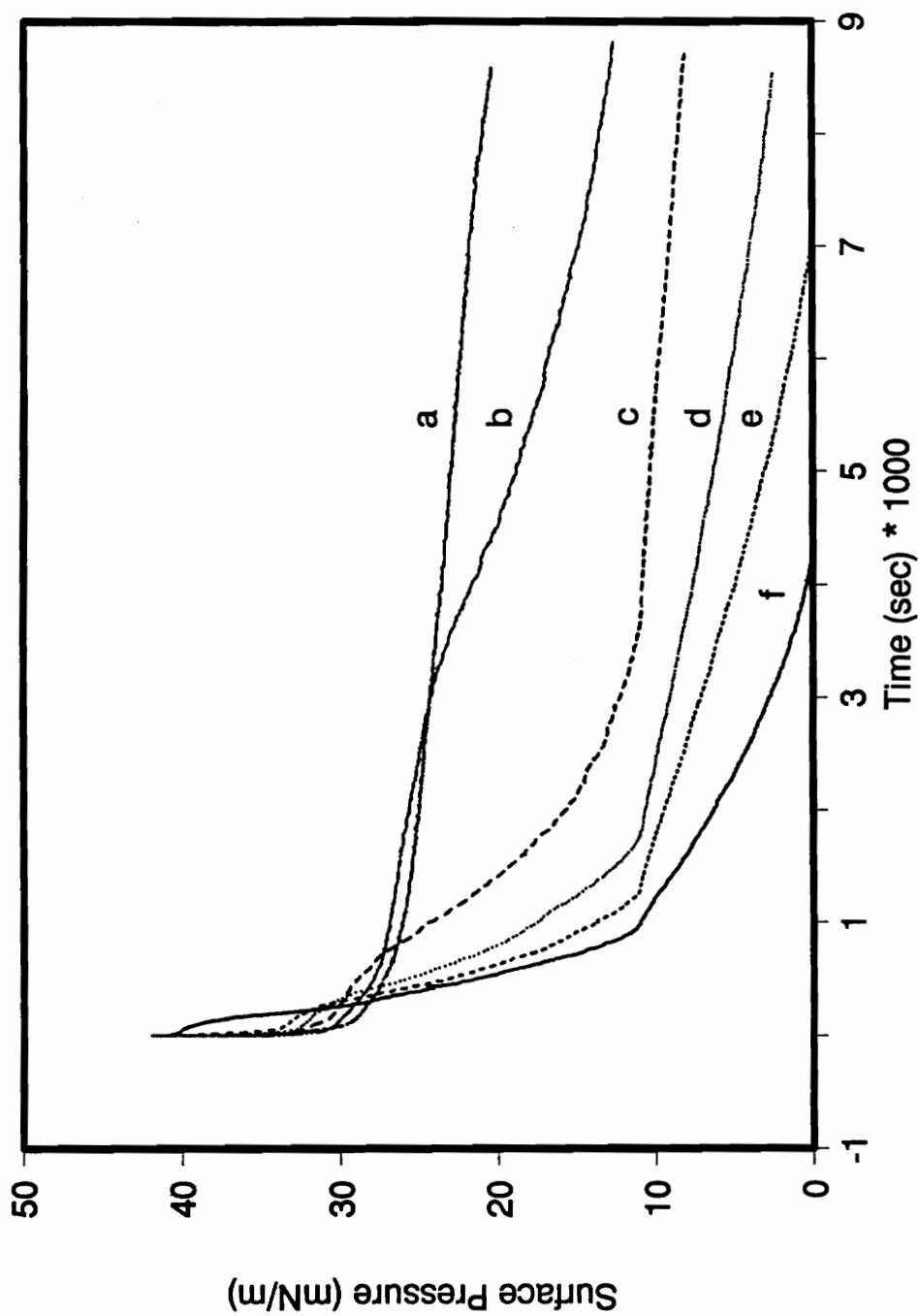


Figure 3.6 Pressure-time isotherms of methyl stearate monolayer film compressed to catastrophic film collapse, at different temperatures - a) 291.7 K, b) 294.9 K, c) 297.8 K, d) 300.7 K, e) 303.7 K and f) 306.5 K.

region corresponds to the solid phase region of the monolayer in pressure-area isotherms. A break is observed in the pressure-time isotherms near 27 mN/m (Figure 3.1). This feature is more prominent at higher overcompression ratio than at lower overcompression ratio for a given temperature, and overall is more prominent at higher temperature (Figures 3.2-3.5). This break in the pressure-time isotherm has a correspondence in the pressure-area isotherms where a similar break is observed in about the same surface pressure range (Figure 2.2). The significance of this break cannot be reconciled from the present investigation. However, earlier work has shown that esters can exhibit multiple solid-like phases - solid, solid-compressed, and super-cooled liquid depending on the size of the terminal alkyl group and temperature [57]. It is therefore possible that the break in the pressure-time isotherm may be an indication of a phase transition between the different solid-like phases of the monolayer.

As the bulk phase grows still further, the surface concentration will become low enough to correspond to the L_2 phase. Indeed, a discontinuity is observed in the relaxation curves at about 11.0 mN/m, corresponding very closely to the pressure of the L_2 -S transition observed in the pressure-area isotherms (Figure 2.2). The rate of surface pressure relaxation decreases in the L_2 phase of the monolayer.

3.2.3 *Below V_s Beyond Collapse Pressure*

The surface pressure relaxation isotherms for methyl stearate monolayer film compressed to the same extent beyond the collapse pressure at different temperatures are shown in Figure 3.6. Relaxation isotherms for films compressed to 40 mN/m, below the collapse pressure, and immediately allowed to relax under a constant area condition at different temperatures are shown in Figure 3.7. When these two figures are compared the most notable observation is the absence of the plateau region in the isotherms of monolayers compressed below the collapse pressure. Other than the

plateau region, all other features of the isotherms are the same, including a sharp break in the pressure-time isotherm at about 11.0 mN/m. At any given temperature, irrespective of whether the monolayer film was compressed above or below the collapse pressure, the isotherms were superimposable in the liquid-condensed region. This suggests that irrespective of the pre-history of the film compression, the surface pressure relaxation mechanism is the same in this region of the isotherm.

In order to determine the stability limit of the monolayer film below the collapse pressure, methyl stearate monolayers were compressed to different surface pressures, 40, 30, 22, 10 and 6 mN/m and allowed to relax at constant area. These pressure-time isotherms were obtained at 297.8 K and are shown in Figure 3.8. It is observed that the surface pressure decreases rapidly at constant area when the monolayer is compressed above the L₂-S transition surface pressure. This observation is consistent with earlier work on methyl stearate where the same observation was noted during step-wise compression experiments [19].

It was also observed that it is not necessary to compress the monolayer film beyond the collapse pressure to see plateau in the pressure-time isotherm. A methyl stearate monolayer was compressed to 40 mN/m and held at constant pressure for long enough to get the desired area-relaxation ratio. The film was then allowed to relax at constant area. Surface pressure relaxation isotherms obtained at 297.8 K and at three different area-relaxation ratios are shown in Figure 3.9. The area-relaxation ratio (A_0/A) is defined as the ratio of molecular area at the beginning of the constant pressure condition to that at the end. The isotherms are similar in every respect to those obtained for the monolayers compressed beyond the collapse pressure, shown in Figure 3.2. The isotherms in Figure 3.9 were obtained at the three area-relaxation ratios, 1.01, 1.03 and 1.07. These area-relaxation ratios were selected specifically for comparison with

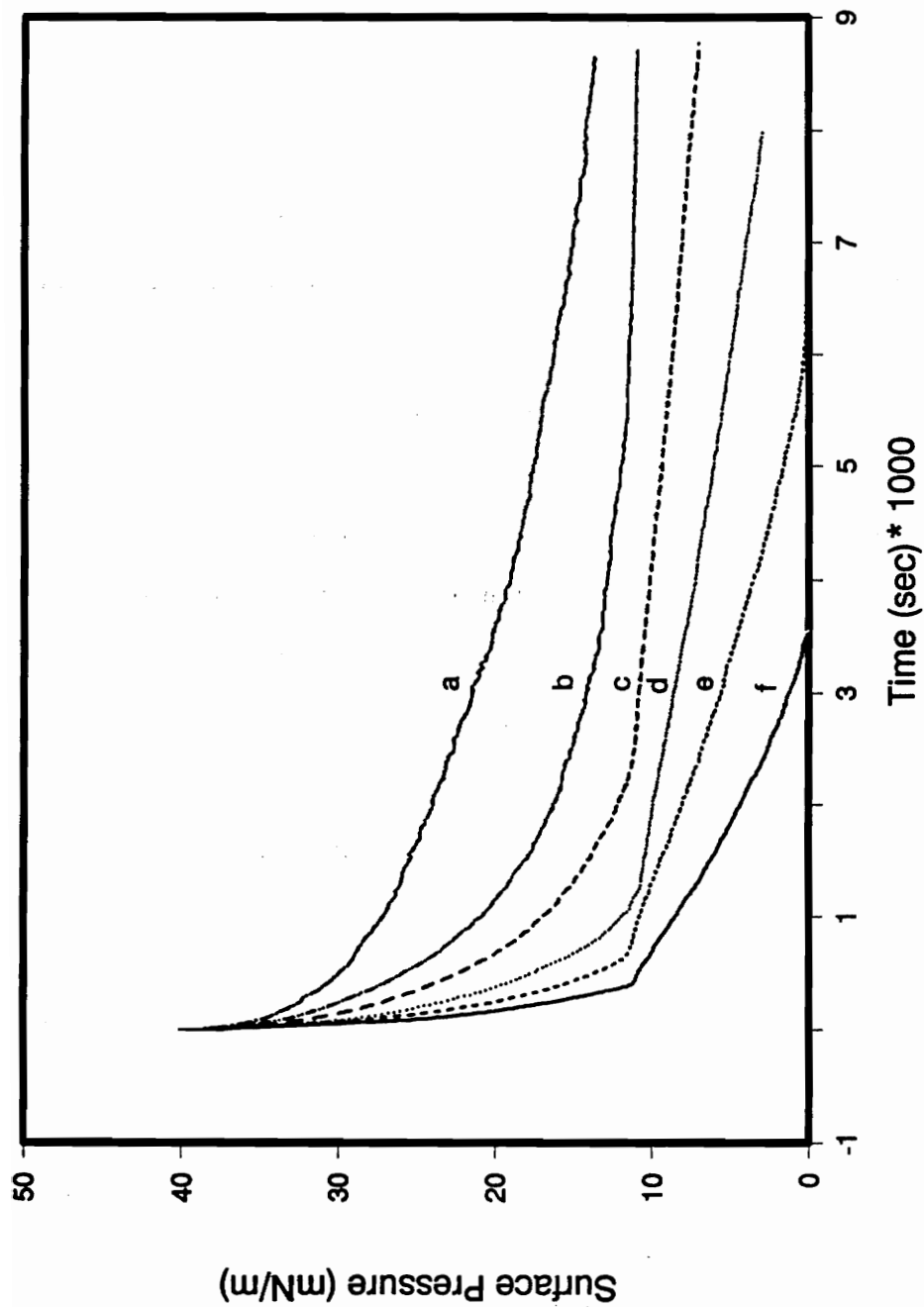


Figure 3.7 Pressure-time isotherms of methyl stearate monolayer film compressed to 40 mN/m, below the collapse pressure, at different temperatures - a) 291.7 K, b) 294.9 K, c) 297.8 K, d) 300.7 K, e) 303.7 K and f) 306.5 K.

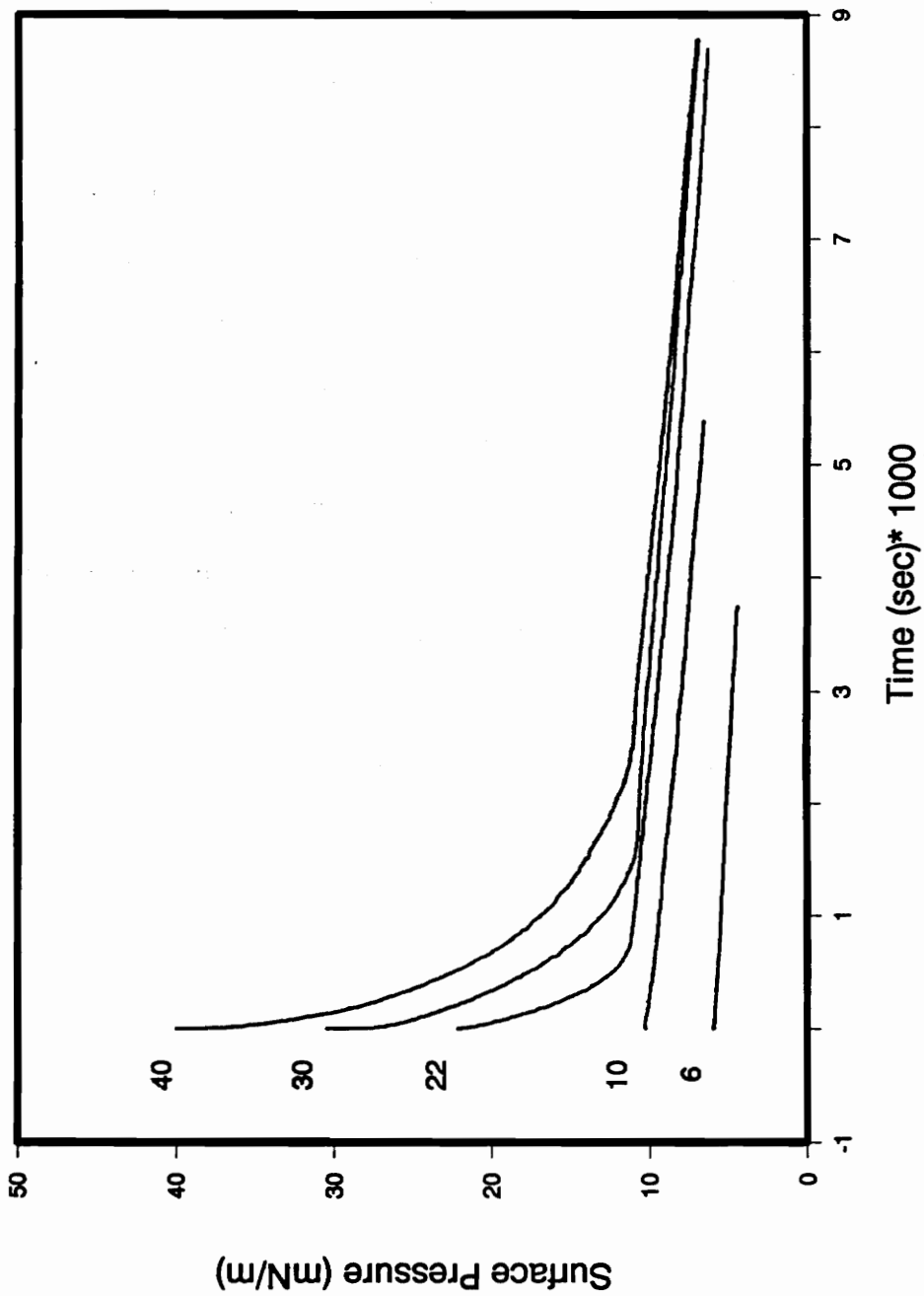


Figure 3.8 Pressure-time isotherms of methyl stearate monolayer film compressed to different surface pressures below the collapse pressure, at 297.8 K.

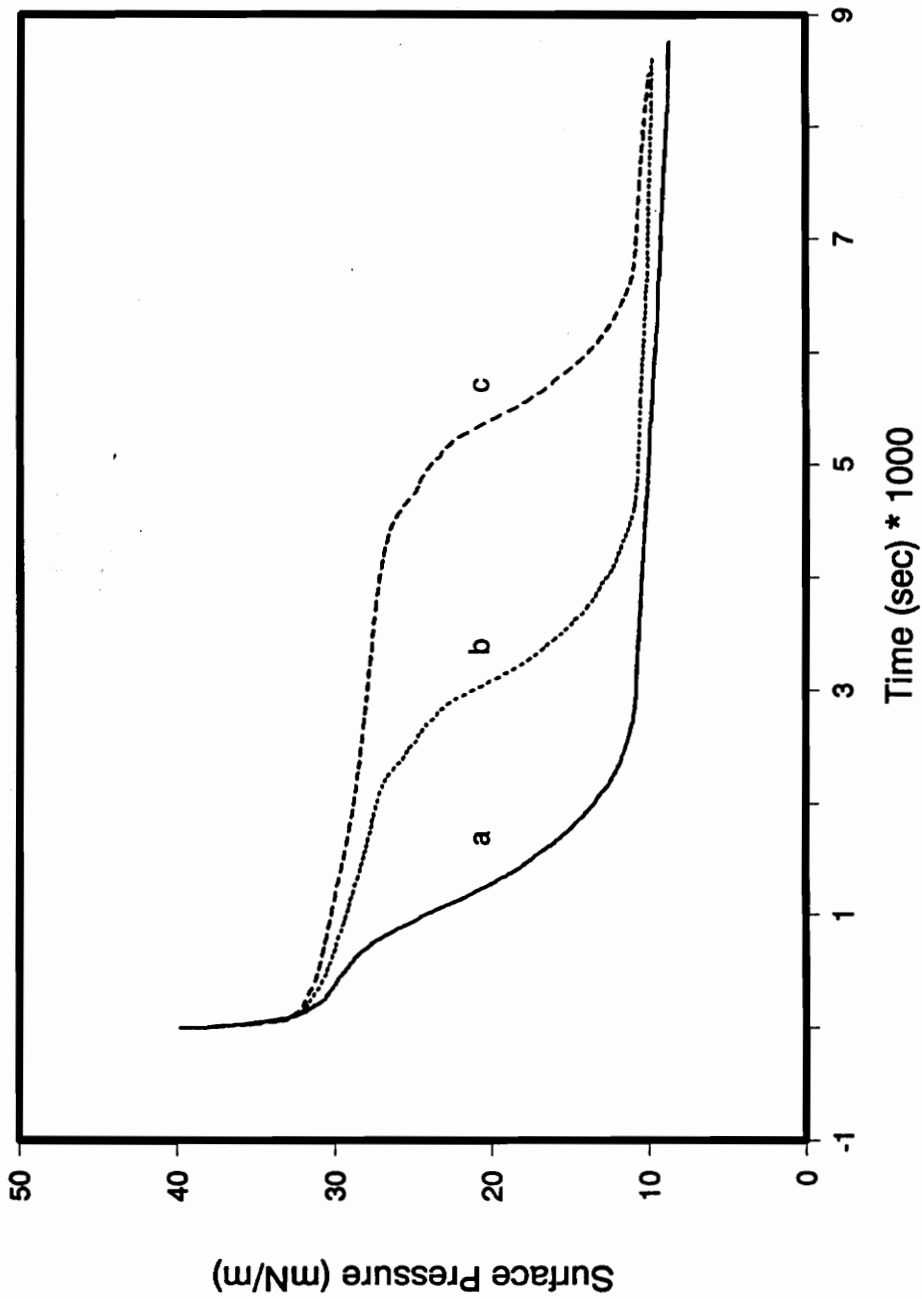


Figure 3.9 Pressure-time isotherms of methyl stearate monolayer film after it was held and allowed to age at 40 mN/m, below the collapse pressure, to different extents defined by the area-relaxation ratio (A_0/A_t): a) 1.007, b) 1.030 and c) 1.070.

post-collapse relaxation experiments (Figure 3.2). The observed similarities, of the isotherms suggests that the molecular process responsible for the plateau region relaxation behavior occurs in both pre- and post-collapse compressed films. This suggests that the molecular channels similar to one in the post-collapsed film are formed during area-relaxation at constant pressure. But, the absence of the plateau region in the pressure-time isotherms (Figure 3.7) for monolayers that were not allowed to age at 40 mN/m below the collapse pressure would then indicate that the molecular channels are not formed spontaneously at surface pressure below the collapse pressure: There is an incubation period associated with the molecular channel formation.

It should be noted that the overcompression ratio and the area-relaxation ratio are both measures of the extent of area-relaxation, the difference lying in the condition under which these measurements are made. The area-relaxation ratio is measured under a constant pressure condition whereas the compression factor is not. Nevertheless, a compression factor of 1.01 and a area-relaxation ratio of 1.01 would both mean a 1% reduction in the monolayer film area from a reference point. The reference point for the overcompression ratio is the area corresponding to the collapse pressure. The reference point for the area-relaxation ratio is the area corresponding to the set surface pressure.

3.2.4 Influence of Overcompression Ratio

The influence of overcompression on the constant area relaxation of methyl stearate monolayers is illustrated by Figures 3.2-3.5. For a given temperature, the relaxation process was a function of the overcompression ratio. The greater the ratio, the greater is the initial delay (plateau region) in the corresponding pressure relaxation curve. All other features of the isotherms were found to be independent of overcompression, including the S-L₂ phase transition occurring at a surface pressure of

about 11.0 mN/m.

The lengths of the plateau regions and the intermediate regions between the plateau and S-L₂ transition point were determined graphically for different temperatures and are plotted as functions of the overcompression ratio in Figures 3.10-3.13. The relaxation-time between the Plateau and the S-L₂ transition appears to be independent of the overcompression ratio. The relaxation-time corresponding to the plateau region was also determined and found to increase with overcompression ratio. These observations are consistent with the proposed relaxation mechanism. As discussed earlier, higher overcompression will increase the amount of film material lifted from the air/water interface to form ridges and other structures. Therefore, the supply of monolayer replenishing material from these reservoirs (Section 3.2.2) will lengthen the plateau regions. In order to establish a quantitative relationship between the plateau relaxation-time and the overcompression ratio, the overcompression ratio and the plateau relaxation-time would need to be known precisely. The plateau relaxation-time can be easily determined from the isotherm with a great degree of accuracy. However, as explained in section 2.3.2.1 the overcompression ratio is difficult to determine (or reproduce) precisely.

For a given temperature, the rate of relaxation in the L₂ region of the isotherm was found to be independent of overcompression ratio.

3.2.5 Influence of Temperature

Pressure-time isotherms of overcompressed methyl stearate monolayers (OR = 1.01) at different temperatures are shown in Figure 3.6. The overall relaxation time decreases with increasing temperature. The plateau region in particular exhibits a dramatic decrease in duration with increase in temperature. The phase transition pressure for S-L₂ remains at about 11.0 mN/m apparently independent of temperature.

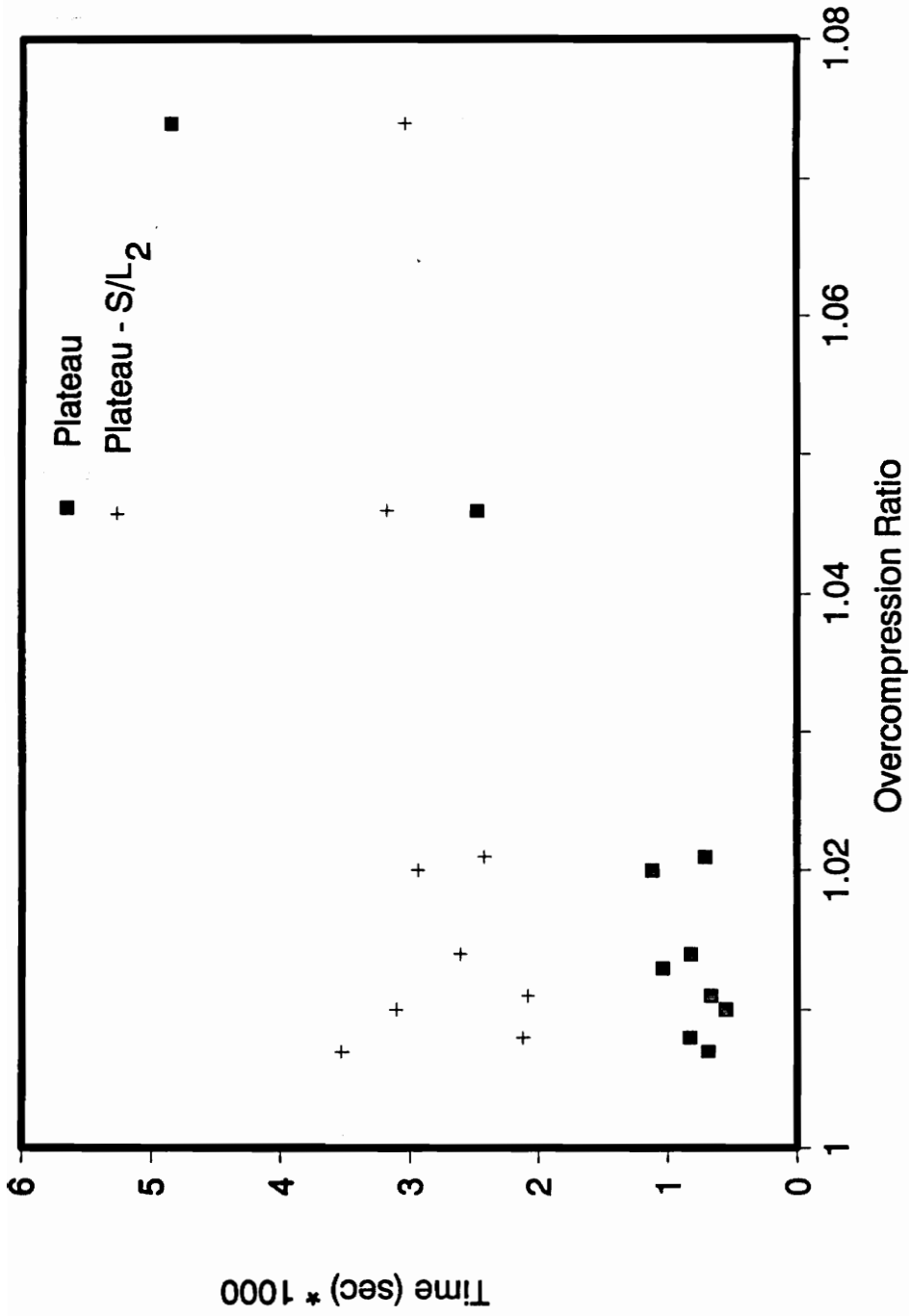


Figure 3.10 The influence of the overcompression ratio on the relaxation-time in the plateau region, and in the region between the plateau and the S/L₂ phase transition point, at 297.8 K. Each point represents a different isotherm.

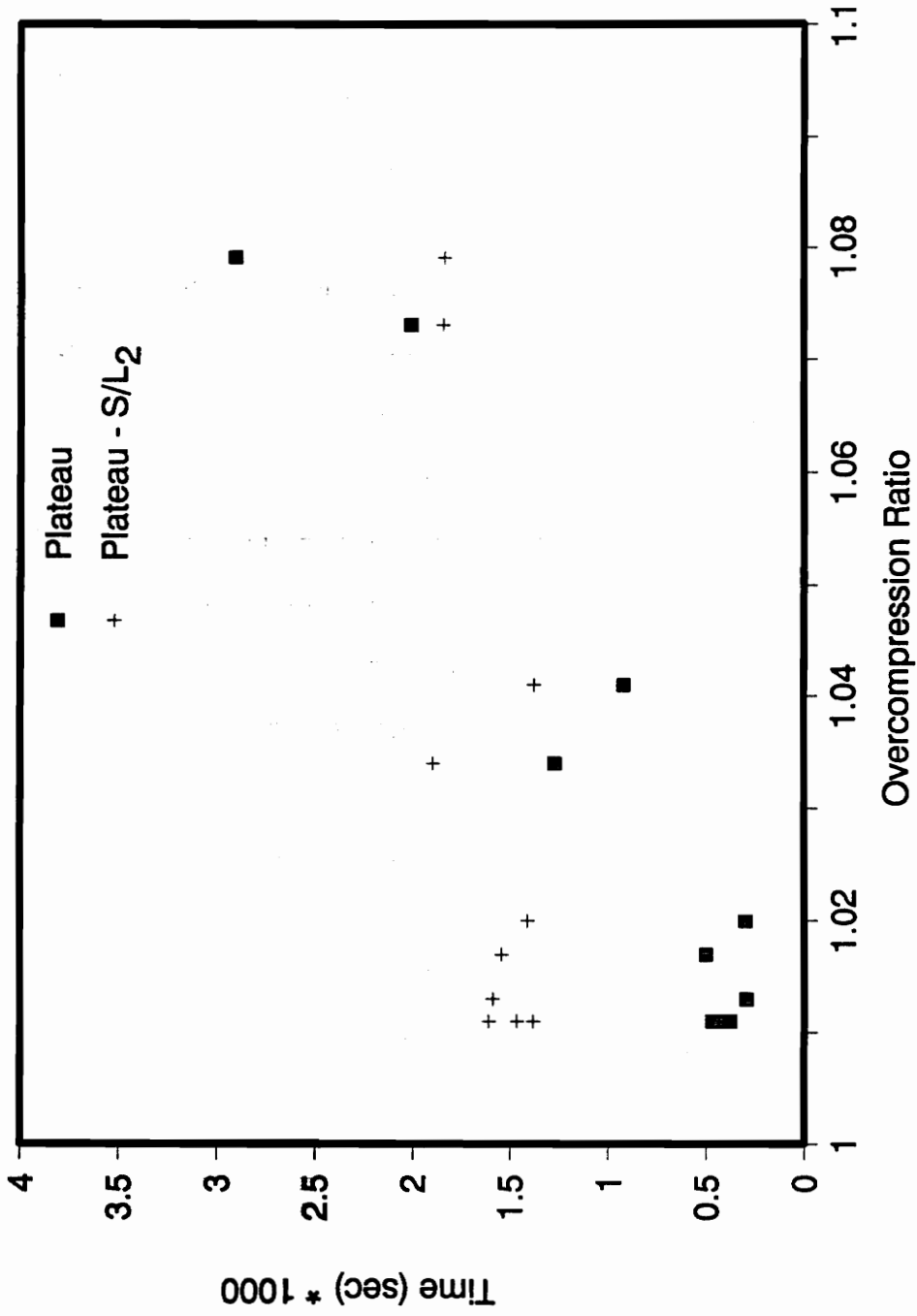


Figure 3.11 The influence of the overcompression ratio on the relaxation-time in the plateau region, and in the region between the plateau and the S/L₂ phase transition point, at 300.7 K. Each point represents a different isotherm.

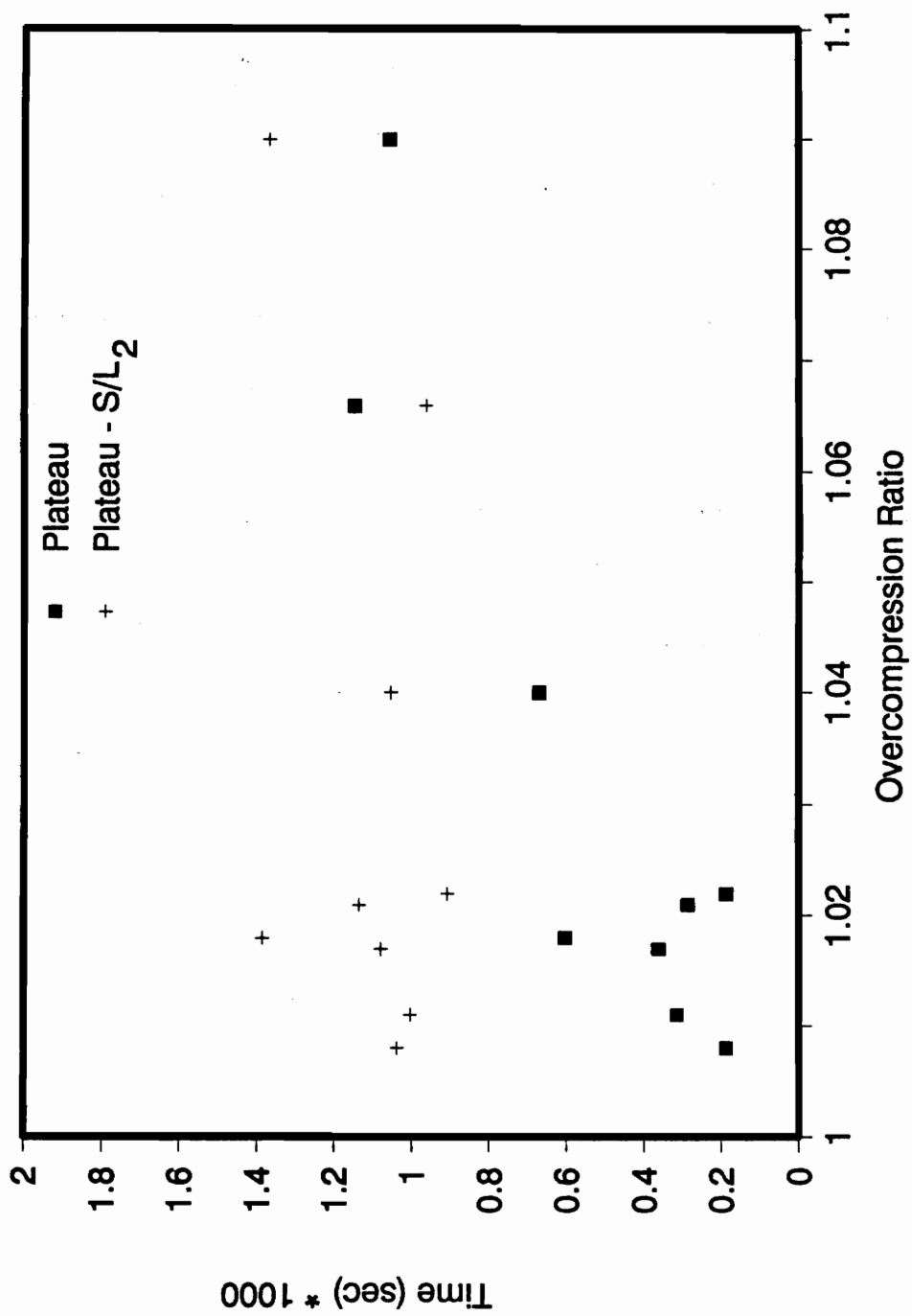


Figure 3.12 The influence of the overcompression ratio on the relaxation-time in the plateau region, and in the region between the plateau and the S/L2 phase transition point, at 303.7 K. Each point represents a different isotherm.

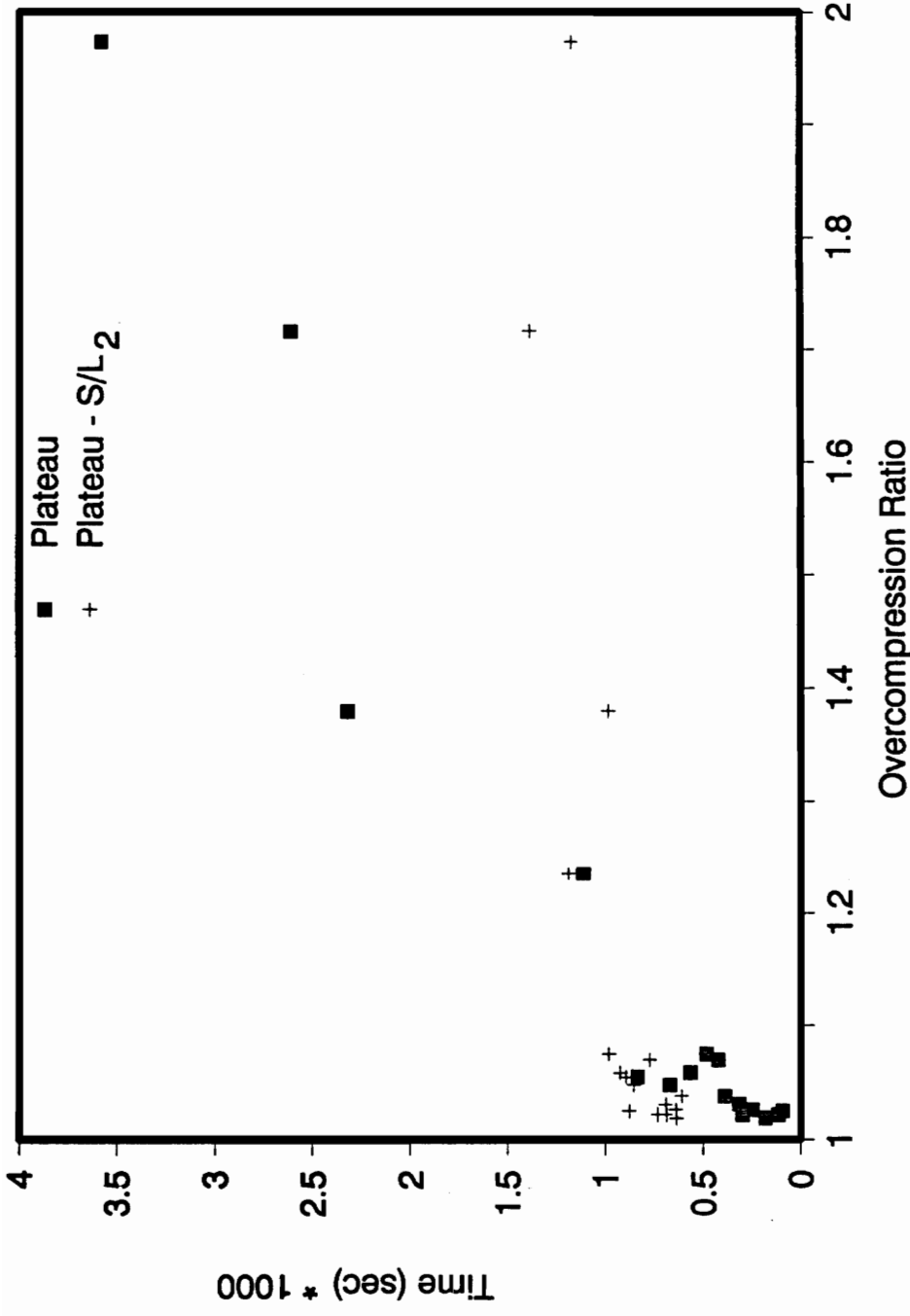


Figure 3.13 The influence of the overcompression ratio on the relaxation-time in the plateau region, and in the region between the plateau and the S/L2 phase transition point, at 306.5 K. Each point represents a different isotherm.

It should be noted, however, that the relaxation at temperatures 294.8 K and 291.8 K are too slow to reach the surface pressure of 11.0 mN/m during the planned experimental period.

Since the amount of film material lifted from the air/water interface during the film collapse should be temperature independent, a decrease in the duration of the plateau region at higher temperature would suggest a faster consumption of film into the growing bulk phase. Thus the film reservoirs would be depleted more quickly. At lower temperature, 291.8 K, the plateau region is quite long, which indicates a much slower bulk phase growth.

The growth of the bulk phase is dependent upon two basic process, the transport of monolayer material to the growing bulk phase and its subsequent transformation. The transformation process may involve adsorption and reorientation of the reacting species, and therefore is expected to have a relatively higher activation energy. Therefore, at higher temperature, greater thermal motion speeds up the bulk phase growth.

The plateaus were in general found to have a non-zero slope. The small decrease in surface pressure with time in the plateau region would suggest that the rate at which film molecules at the air/water interface are removed and added to the growing bulk phase nuclei is higher compared to the rate at which the film molecules are transferred back to the air-water interface from the molecular reservoirs.

3.2.6 Influence of Pre-Existing Bulk Phase

In order to investigate the influence of pre-existing bulk phase on film collapse and relaxation behavior, four consecutive compression/relaxation cycles were performed on a single monolayer at 297.8 K. For each cycle, compression was taken to collapse at about 45 mN/m (OR = 1.01), and relaxation was monitored well past the

S-L₂ transition. The results are shown in Figure 3.14. In general, all the features of the pressure-time isotherms were found to be the same in each of the four cycles. The duration of the plateau region as well as that of the solid region, were found to be the same in each cycle. Furthermore, the collapse pressure did not vary much from cycle to cycle. The non-varying collapse pressure is consistent with earlier studies carried out on methyl stearate monolayers by Sims and Zigrifi [19]. The similarities in the relaxation behavior between the cycles suggest that the films behave essentially as immiscible mixed monolayers and that the presence of bulk phase material does not affect the monolayer properties.

3.3 Area-Time Isotherms

The representative area-relaxation isotherms for methyl stearate monolayers with different pre-relaxation history are shown in Figure 3.15 and the data are summarized in Table 3.2. All monolayers were over compressed (OR = 1.01) and allowed to relax at constant area to different surface pressure values. Then the monolayers were compressed to and maintained at constant surface pressure of 40 mN/m. The subsequent constant pressure relaxation was faster for monolayers relaxed to 35 or 30 mN/m than it was for monolayers relaxed to 20 mN/m. Interestingly, the area-relaxation exhibited by the monolayer relaxed to 20 mN/m was comparable to that of a monolayer compressed directly to 40 mN/m (pre-collapse) and maintained at constant pressure. The monolayer relaxed to 25 mN/m following collapse exhibited an intermediate relaxation behavior. Note that the surface pressures 35 mN/m and 30 mN/m are above, and 25 mN/m and 20 mN/m are below, the surface pressure range in which the plateau region is observed at this temperature (297.8 K). In fact, the plateau region ends at about 25 mN/m at 297.8 K (Figure 3.2).

Longer area relaxation times for monolayers relaxed to surface pressures below

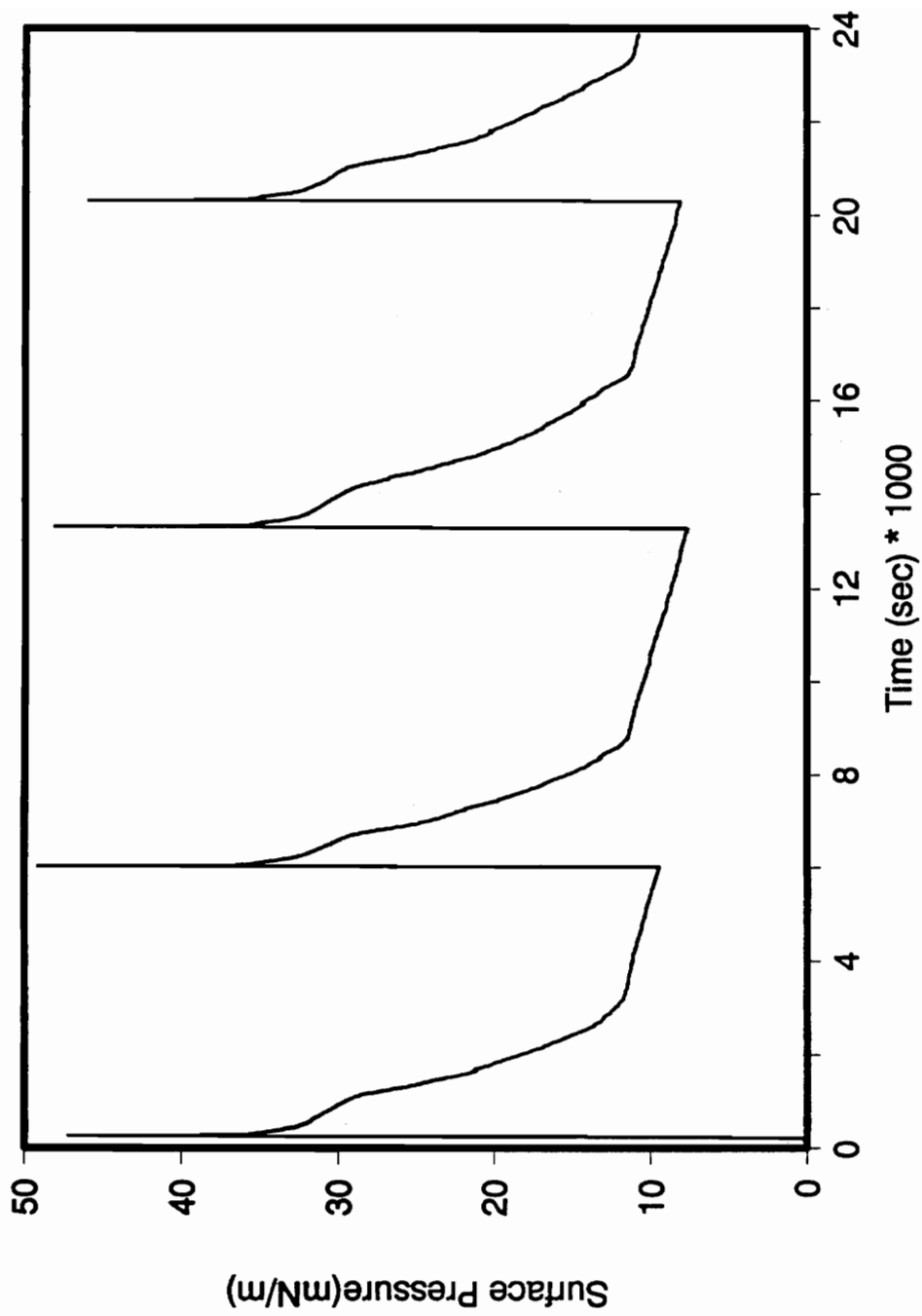


Figure 3.14 The influence of pre-existing bulk phase on the surface pressure relaxation behavior of the methyl stearate monolayer film, at 297.8 K.

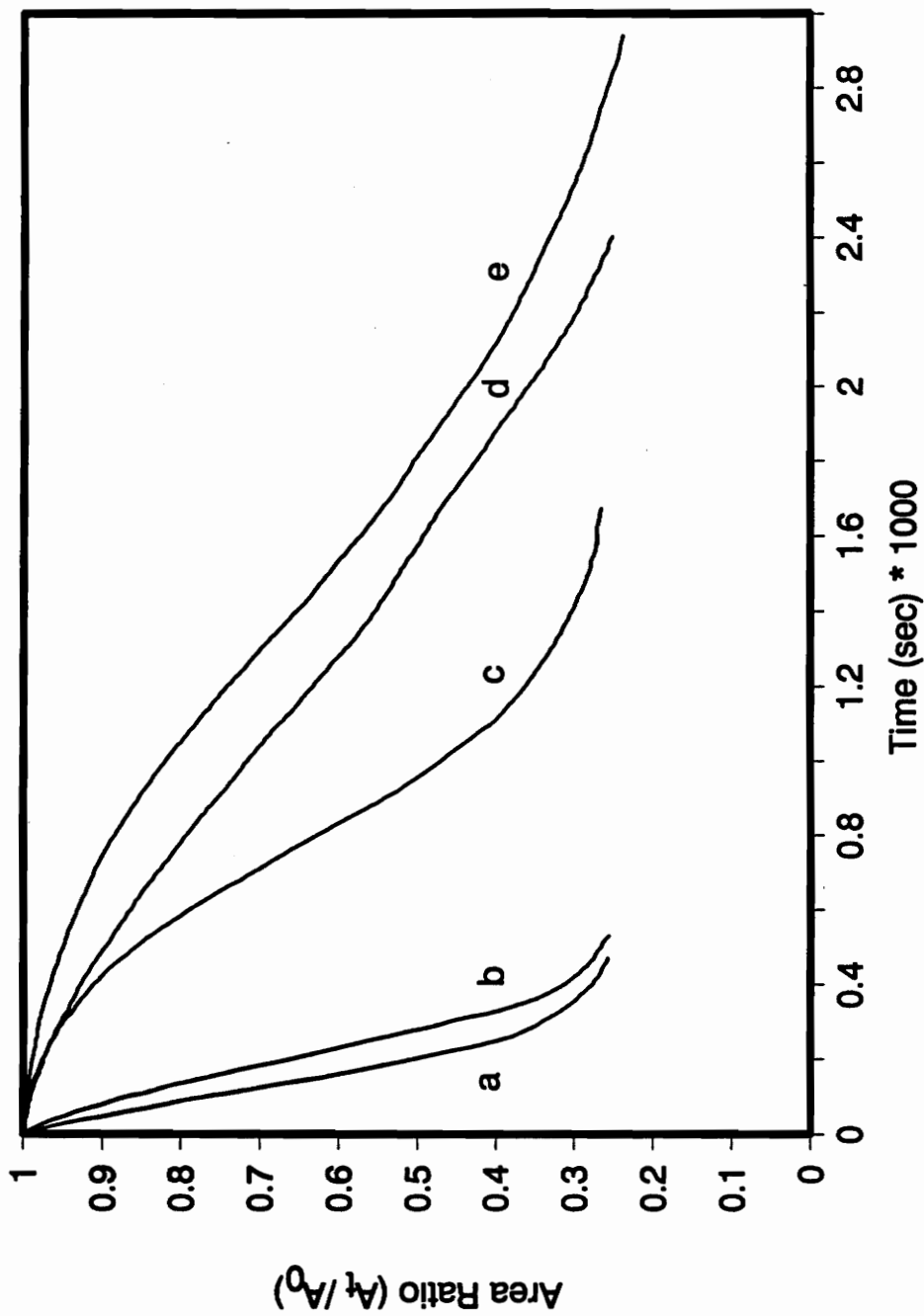


Figure 3.15 Area-relaxation isotherms of methyl stearate monolayers at 297.8 K, at 40 mN/m. Where **a**, **b**, **c**, and **e**, correspond to monolayer films compressed to collapse pressure followed by relaxation at constant area to 35, 30, 25 and 20 mN/m, respectively. An area-relaxation isotherm of monolayers compressed directly to 40 mN/m, below the collapse pressure is represented by **d**.

Table 3.2

Area relaxation-times for methyl stearate monolayers with different pre-relaxation history, at constant pressure of 40 mN/m, at 297.8 K. The errors in mean are reported at 95% confidence interval.

Area Relaxation (%)	Time (seconds)						
	10	20	30	40	50	60	70
Samples							
Sample-1	537 +/- 56	861 +/- 81	1130 +/- 92	1371 +/- 94	1646 +/- 139	1959 +/- 216	2327 +/- 208
Sample-2	77 +/- 59	121 +/- 76	171 +/- 108	217 +/- 132	272 +/- 165	331 +/- 203	438 +/- 271
Sample-3	69 +/- 48	114 +/- 80	156 +/- 105	197 +/- 132	239 +/- 160	287 +/- 191	384 +/- 255
Sample-4	413 +/- 24	579 +/- 24	703 +/- 24	823 +/- 20	965 +/- 46	1157 +/- 157	1471 +/- 178
Sample-5	704 +/- 238	1024 +/- 323	1288 +/- 391	1541 +/- 436	1806 +/- 448	2137 +/- 423	2568 +/- 212

- Sample-1 :** Area-relaxation in methyl stearate monolayer film at 40 mN/m, below the film collapse.
- Sample-2 :** Area-relaxation at 40 mN/m in methyl stearate monolayer film which was subjected to film collapse followed by surface pressure relaxation to 35 mN/m.
- Sample-3 :** Area-relaxation at 40 mN/m in methyl stearate monolayer film which was subjected to film collapse followed by surface pressure relaxation to 30 mN/m.
- Sample-4 :** Area-relaxation at 40 mN/m in methyl stearate monolayer film which was subjected to film collapse followed by surface pressure relaxation to 25 mN/m.
- Sample-5 :** Area-relaxation at 40 mN/m in methyl stearate monolayer film which was subjected to film collapse followed by surface pressure relaxation to 20 mN/m.

the plateau region and shorter relaxation times for those relaxed to pressures above the plateau region can be attributed to the absence and presence, respectively, of molecular channels in the collapsed film structures. As discussed in section 3.2.2, the plateau regions of pressure-time isotherms are indications of the presence of molecular channels (bi-trilayers, ribbons, and ridges), which act as reservoirs for replenishing monolayer material to the air/water interface during the surface pressure relaxation. During surface pressure relaxation, the reservoirs are depleted by the end of the plateau region.

Now, it should be noted that during monolayer film compression the presence of such molecular channels in the collapsed monolayer film will provide an easy escape route for the molecules in the monolayer to escape the air/water interface. Since during area-relaxation under a constant surface pressure condition, any small fluctuation in the set constant surface pressure value would cause the film barrier to move in order to maintain the constant surface pressure, the presence of molecular channels in the monolayer film would make it almost impossible to maintain any constant surface pressure without the monolayer film being compressed continuously. This leads to a shorter relaxation time. The area-relaxation at constant pressure for a monolayer containing molecular channels is mainly due to the expulsion of monolayer material from the air/water interface into the molecular channels. These interpretations support a theoretical model in which slow film collapse at constant surface pressure is attributed to the formation and growth of such molecular channels [25]. In the absence of molecular channels the area-relaxation would be governed by the formation and growth of a bulk phase and would therefore occur significantly slowly.

The relaxation-time for the film that was allowed to relax to 25 mN/m after the film collapse, which is about the end of the plateau region, showed an intermediate

behavior. This is probably due to the fact that some relatively small number of molecular channels are still present in the partially relaxed film.

It was shown in section 3.2.3 that the molecular channels are also formed at the pre-collapse pressure, but there is an incubation period associated with it. Therefore, in the absence, initially, of molecular channels, the area-relaxation at constant pressure for monolayers compressed to 40 mN/m (below collapse pressure) is expected to be much slower during the initial stages of the relaxation process (Figure 3.15 d). It is interesting to note that the observed relaxation-time for the monolayer film which was allowed to relax to 20 mN/m after the film collapse is comparable to the one in which the area-relaxation was carried out before the film collapse, at 40 mN/m (Table 3.2). This is due to the disappearance of molecular channels from the monolayer film which was allowed to relax to 20 mN/m (below plateau region) after the film collapse.

3.4 Langmuir-Blodgett Films

The Figure 3.16 a, shows a glass slide supported LB film of a methyl stearate monolayer deposited immediately after the surface pressure reached a constant surface pressure of 40 mN/m (below the collapse pressure). No features could be seen under the optical microscope. The transfer ratio for such film was found to be close to unity, which indicates the monolayer transferred intact to the glass slide. When the monolayer was allowed to age for about 20 minutes ($A/A_0 = 0.66$, see Figure 3.15 d) at 40 mN/m before depositing, many features could be seen as shown in Figure 3.16 b. The observed features consist of elongated platelet-like structures (bulk phase). Ribbons or other the vesicle-type structures are not seen. It is understandable that the ribbons and other reservoir structures are too small (a bi-molecular structure of methyl stearate is expected to be less than 5 nm in thickness) to be observed on the LB film.

Langmuir-Blodgett films of methyl stearate, deposited immediately after the

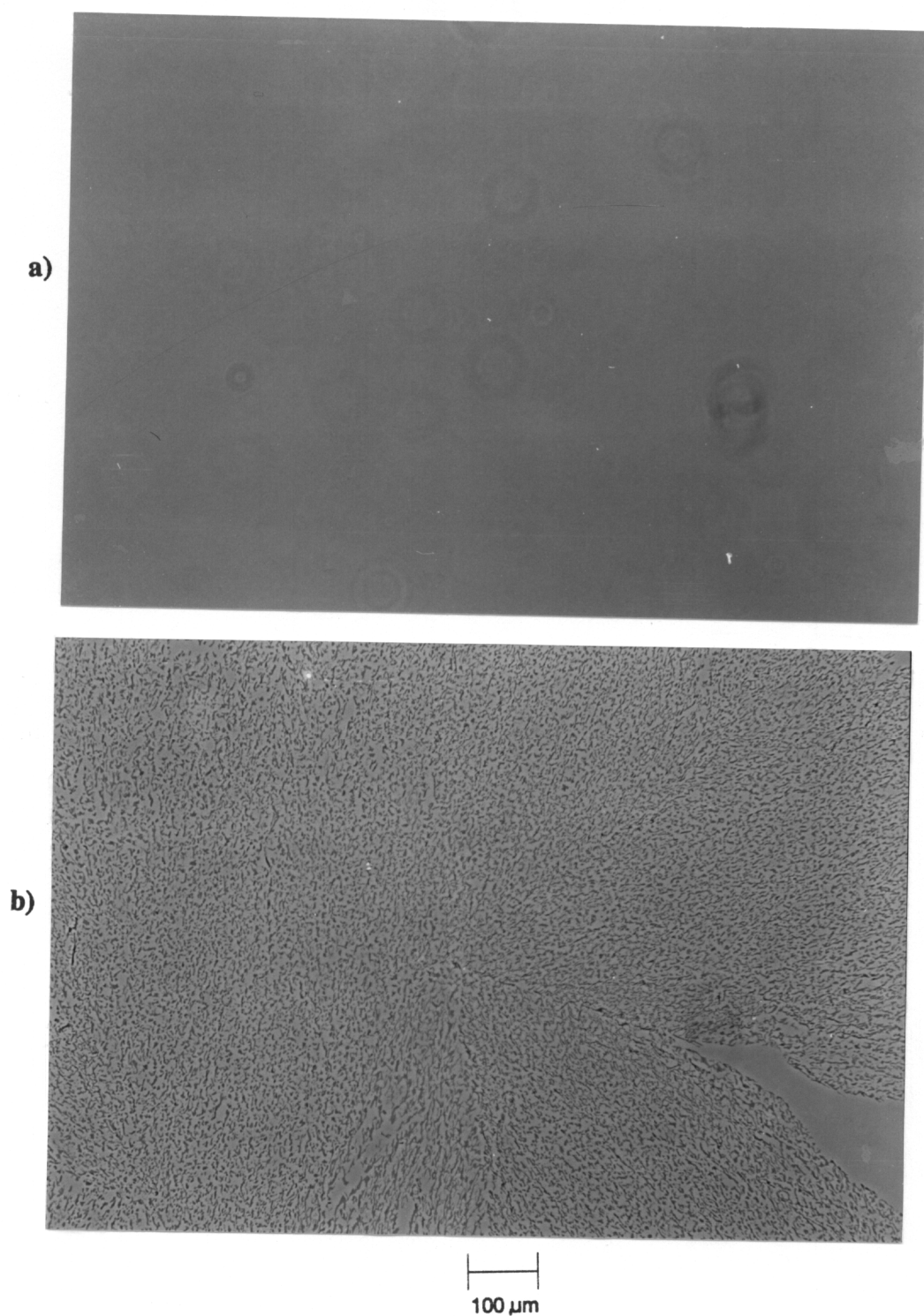
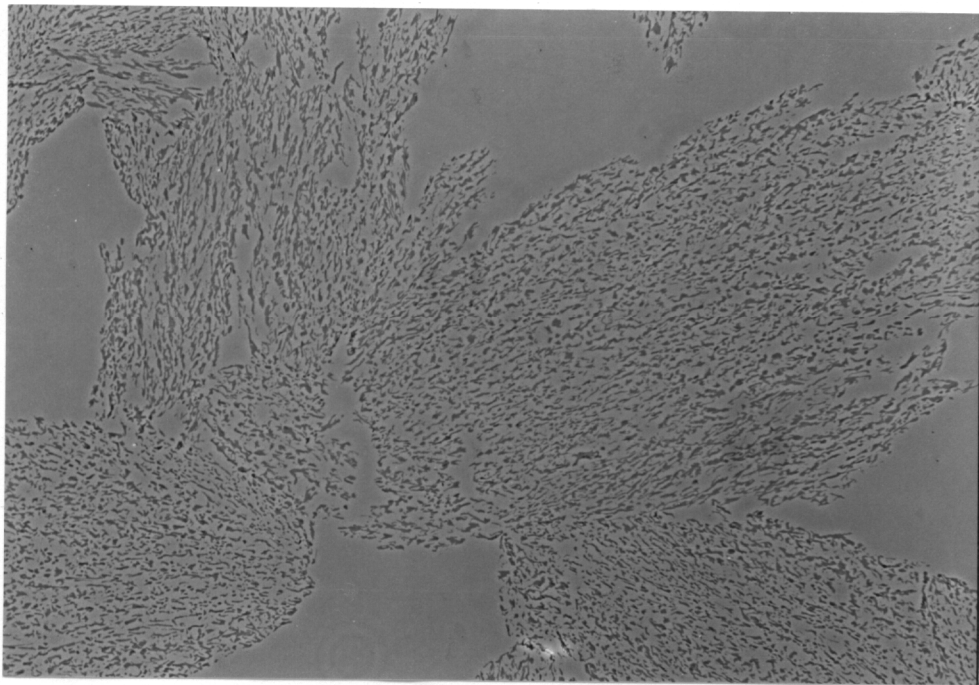
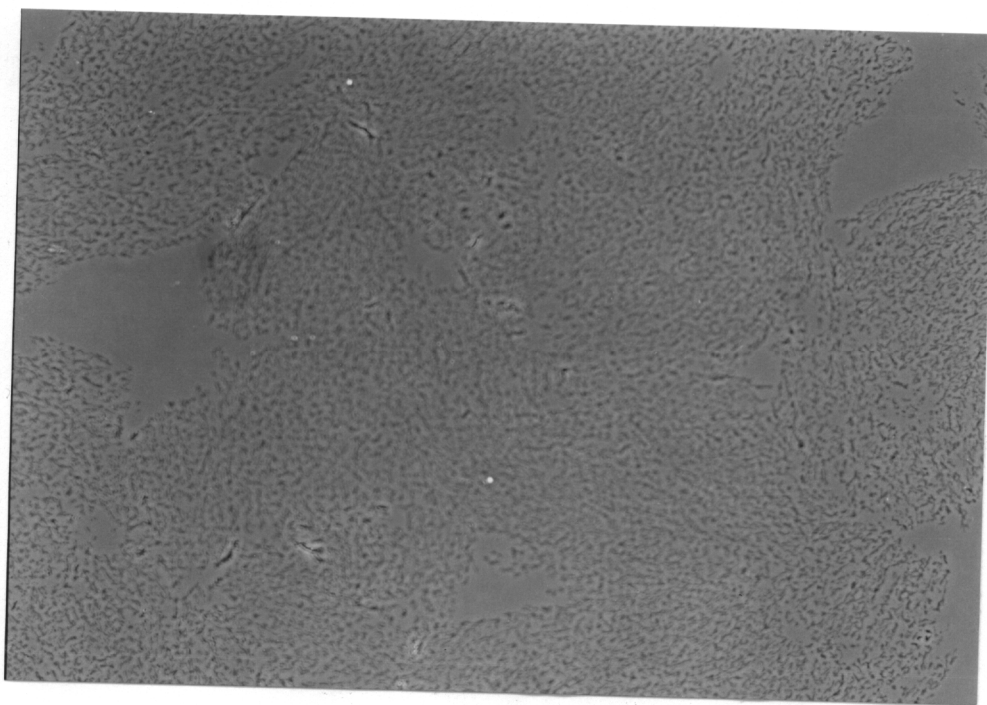


Figure 3.16 The optical micrograph of a methyl stearate monolayer film which was a) not allowed to age at 40 mN/m and b) allowed to age at 40 mN/m (area-relaxation ratio, $A_0/A_t = 1.51$), below the collapse pressure.



100 μm

Figure 3.17 The optical micrographs of the collapsed monolayer film of methyl stearate (OR = 1.021) showing elongated platelet structures.



100 μm

Figure 3.18 The optical micrographs of methyl stearate monolayer film which was allowed to relax to 20 mN/m after the catastrophic film collapse and then recompressed back to a catastrophic film collapse followed by relaxation to 40 mN/m - numerous platelets could be seen.

catastrophic film collapse ($OR = 1.021$) at 40 mN/m, also had platelet structures (Figure 3.17). These structures were essentially of the same nature except for the fact that they seem to be slightly bigger in size compared to the LB films in which the monolayer film was allowed to age at 40 mN/m (below the collapse pressure).

In another experiment a LB film of methyl stearate was obtained that was subjected to (i) catastrophic film collapse, (ii) constant area relaxation to below the S-L₂ phase transition, and (iii) re-compression to a constant surface pressure of 40 mN/m. The platelets were not observed in the LB monolayers. However, upon re-compression to a second film collapse, and constant area relaxation to 40 mN/m, the platelets reappeared (Figure 3.18). The absence of platelets in the LB film of monolayers recompressed to 40 mN/m, below the second film collapse, would then suggest that the platelets which were initially present after the first collapse fused together over the period of time (relaxation at constant pressure) to form a huge bulk phase which would be difficult to transfer on the glass slide. The reappearance of platelets in the LB film following a second film collapse may be due to reformation of the platelets from the remaining monolayer material.

In order to find out exactly how these platelets behave during surface pressure relaxation after the film collapse, one could monitor in-situ the relaxation process using an optical microscope. Alternatively one could deposit collapsed monolayers of methyl stearate on glass slides at different surface pressures following collapse and relaxation. The deposited LB films could then be compared to determine any changes in the appearance, size, and number of platelets. This approach was attempted, but no monolayers could be deposited for $\pi < 30$ mN/m.

CHAPTER - 4

CONCLUSIONS AND FUTURE WORK

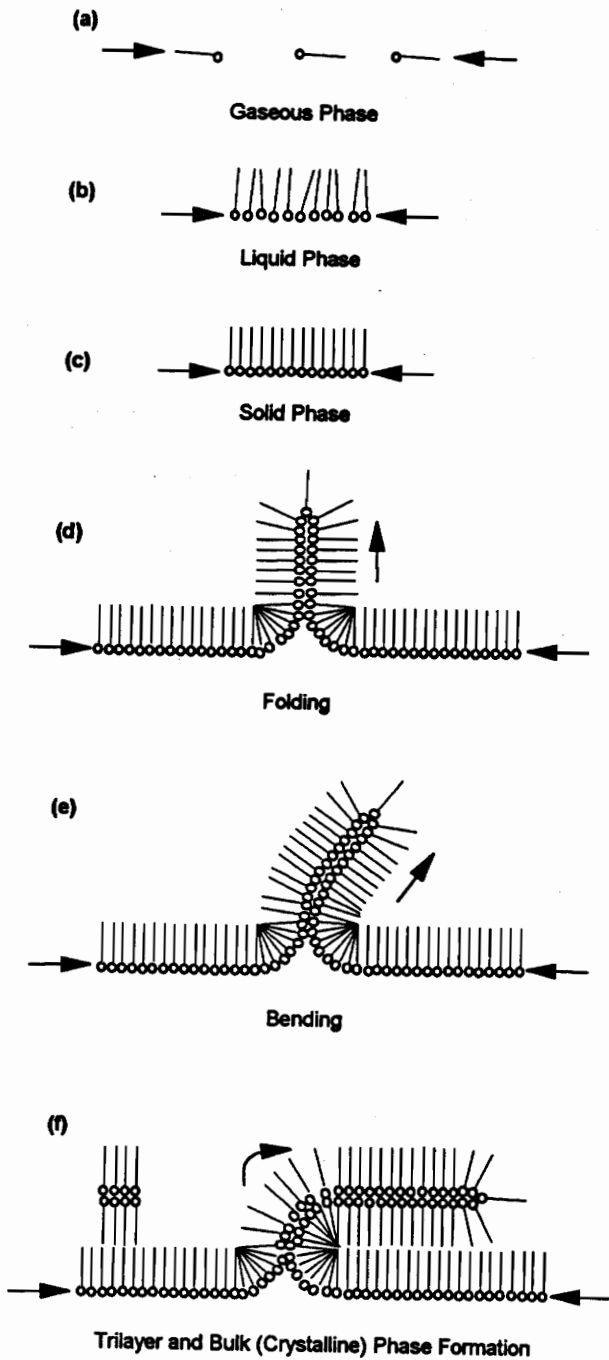
4.1 Conclusions

From the experiments reported in this work, a sequence of molecular processes associated with the monolayer film collapse and its subsequent relaxation at constant area emerges as shown schematically in Figure 4.1.

Upon compression the monolayer undergoes phase transition from a gaseous phase to liquid phase to solid phase in that order (**a** through **c**). The monolayer finally buckles and folds over to form tall ridges (**d**) when compressed past the collapse pressure. The ridges continue to grow taller with further compression of the monolayers beyond the collapse pressure, finally it bends (**e**), falls over on the top of the underlying monolayer film to form a tri-layer film and a ribbon is formed (**f**). Thermodynamically, formation of a crystalline bulk phase is favorable whenever a monolayer film is compressed beyond its equilibrium spreading pressure (ESP), so nucleation of a crystalline bulk phase is imminent (**f**).

The molecular processes associated with the post-collapse relaxation at constant area are shown in Figure 4.1(**g-j**). The ridges and ribbons function as molecule reservoirs to replenish the material lost to the bulk phase. As the bulk phase grows, the film molecules from the reservoirs are transferred back to the air/water interface, and thus the ridges and ribbons become smaller in size (**g-i**). As long as the reservoirs are present, the surface concentration in the purely monolayer areas, and thus the observed surface pressure, will remain constant. This situation corresponds to the plateau region

Collapse



Relaxation

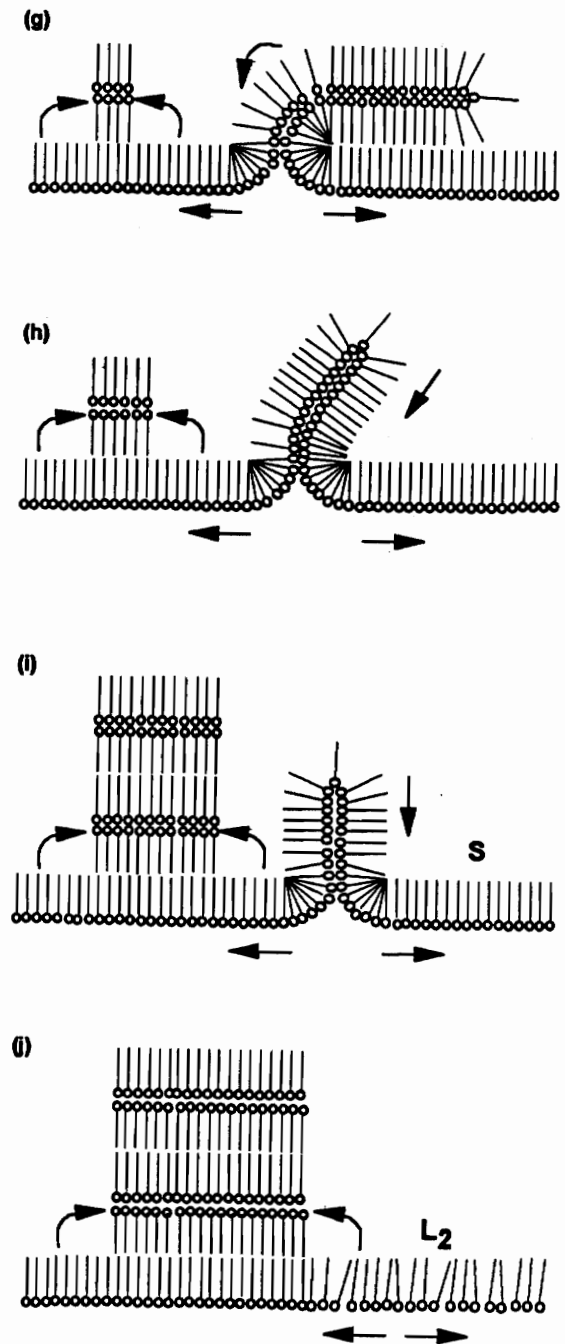


Figure 4.1 A schematic diagram of the monolayer film collapse and its subsequent relaxation at constant area.

in the pressure-time isotherms (see section 3.2.2). Once the reservoirs are depleted, further growth of the bulk phase results in a decrease in surface concentration of the monolayer and results in a higher rate of pressure decrease. The monolayer then proceeds back through the various phases ($S \longrightarrow L_2 \longrightarrow L_1$, etc.) until the ESP is reached (j).

Relaxation curves of methyl stearate monolayers compressed to and aged at 40 mN/m (below the collapse pressure) revealed that plateau regions are not specific to previously collapsed films. This observation suggests that the ridges and ribbons are formed even when the monolayer film is compressed to below the collapse pressure. The absence of plateau in the pressure-time isotherms of monolayers compressed to 40 mN/m, but not aged, implies that there is an incubation period associated with the formation of such multilayered structures below the collapse pressure.

4.2 Future Work

This work has permitted a qualitative understanding of the surface pressure relaxation processes in the collapsed film of methyl stearate at the air/water interface. In order to better quantitate the processes, experiments need to be designed to obtain in-situ information regarding monolayer structures during relaxation. One possible method would be to monitor, using an optical microscope and fluorescent probe molecules, the fine microstructural details of the monolayer at the air/water interface. Fluorescence microscopy has proven to be a very useful tool in understanding the monolayer phase transitions [58,59] and has also been used to elucidate the lateral structures of the monolayer films [60,61].

The thickness and other molecular level information such as the molecular arrangements in the platelets of methyl stearate could be obtained using an Atomic Force Microscopy. In a recent study, the Atomic Force Microscopy (AFM) was utilized

to elucidate the collapsed film structure of the lipid monolayer films [62]. The catastrophically collapsed film structure in the LB films of magnesium stearate was indeed found to be three layers thick, as expected for a monolayer film which buckles and folds over. In another study, the usefulness of the AFM techniques for the direct observation of molecular arrangements in the fatty acid monolayers was demonstrated [63]. A similar AFM investigation should therefore be carried out on the platelet structures found in the collapsed film of methyl stearate to firmly establish the exact nature of the molecular arrangements.

Alternatively, Brewster Angle Microscopy (BAM) could be used to monitor, in-situ, the film collapse in methyl stearate monolayer film at the air-water interface. BAM has been found to be a very useful non-destructive technique to visualize the monolayer film collapse [64,65]. This technique is especially useful in monitoring the formation and growth of the bulk phase [66,67]. As far as the work presented here is concerned, BAM technique may be used to extract more detailed information about the behavior of the bulk phase during relaxation processes. Firstly, one can monitor the formation and the growth of the bulk phase during compression. Secondly, the behavior of platelets could also be monitored.

Continuing further from the work presented here one can further investigate the influence of many factors such as subphase pH, the nature of the polar head group, and the hydrocarbon chain-length, on the observed delay in constant-area relaxation in the monolayer film. Depending upon various factors, the monolayer films may or may not undergo an organized film collapse during the film compression. Therefore, the surface pressure relaxation isotherms may or may not exhibit a plateau region. For example, one could carry out the work presented here with fatty acid monolayers at different subphase pH. It is expected that at higher pH, for example at $\text{pH} = 7.0$, the

presence of ionized carboxyl groups would disrupt the specific alignment of the headgroups at the air/water interface and therefore would hinder the organized film collapse of the monolayer film at the air/water interface. On the other hand, at subphase pH = 2.0, it has been demonstrated that fatty acid monolayers undergo organized film collapse [42]. Therefore one would expect to see a plateau in the surface pressure relaxation isotherm for the monolayer film compressed beyond the collapse pressure at subphase pH = 2.0, but not at pH = 7.0.

These studies are important and must be undertaken to thoroughly investigate the influence of various factors on the nature of collapse and relaxation behavior of monolayer films.

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Vita

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