Dynamic Behavior of Self-Assembled Langmuir Films Composed of Soluble Surfactants and Insoluble Amphiphiles

DISSERTATION

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Abstract

The work presented develops a method to identify the extent to which soluble surfactants can be compressed using a Langmuir monolayer technique and use of a Langmuir Trough. Soluble surfactants are often considered incompressible, but they can be highly compressible, as with the commercial surfactant Mergital LM 11, sodium dodecyl sulfate (SDS), and even attain a collapse point, as with dodecyl trimethyl ammonium bromide (DTAB), if the subphase concentration and compression speed are within certain limits. A kinetic model is developed and parameters are fit by non-linear modeling. Subphase concentration has a large effect on relative compressibility, attaining a maximum near the shoulder of a surface tension plot. The results of the model parameters are consistent with this observed maximum. The model parameters also suggest that surfactant desorption occurs by a monomeric mechanism.

The extent to which soluble surfactants are compressible, is important to membrane penetration studies performed using a Langmuir monolayer technique. In systems containing mixtures of a lipid and soluble surfactant, it is shown that the dynamic characteristics of the soluble compression are present in the penetration studies, meaning the surfactant does not freely adsorb and desorb from the interface as is an assumption made in nearly all mixture models in current literature. The effect of soluble surfactant compression must be accounted for if accurate partition calculations are to be made.
Dedication

I dedicate this dissertation to my loving family, especially my very supportive wife Kimberly. This work would not have been accomplished without her encouragement.
Acknowledgments

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# Table of Contents

Abstract........................................................................................................................................... ii

Dedication........................................................................................................................................ iii

Acknowledgments........................................................................................................................ iv

Vita....................................................................................................................................................... v

List of Tables ......................................................................................................................................... ix

List of Figures ........................................................................................................................................ x

Chapter 1 Introduction ...................................................................................................................... 1

1.1 Compression of Amphiphile Monolayers on a Langmuir Trough............................................. 3

1.2 Model Membrane Formulation ................................................................................................ 5

1.3 Dividing Surface ........................................................................................................................ 8

1.4 Sorption Method ........................................................................................................................ 10

Chapter 2 Soluble Surfactants on Langmuir Trough .................................................................... 12

2.1 Langmuir Monolayers of Soluble Species ............................................................................. 13

2.2 Observed Maximum Compression in Soluble Species ............................................................ 14

2.3 Compression Maximum Hypothesis ......................................................................................... 17

2.4 Mathematical Model of Sorption ............................................................................................ 18
List of Tables

Table 2.1: Fitted model parameters for SDS compression ........................................... 23
Table 2.2: Relevant calculated model parameters to Section 2.5.1, additional importance
to highlighted values ........................................................................................................ 26
Table 2.3: Relevant calculated model parameters to Section 2.5.2, additional importance
to highlighted values ........................................................................................................ 29
Table 2.4: Relevant calculated model parameters to Section 2.5.3, additional importance
to highlighted values ........................................................................................................ 33
Table 2.5: Relevant calculated model parameters to Section 2.5.4, additional importance
to highlighted values ........................................................................................................ 36
Table 2.6: Model parameters found for DTAB compressions ........................................ 39
Table 3.1: Maximum pressure attained during penetration studies for differing
experimental conditions .................................................................................................... 68
List of Figures

Figure 1.1: Cartoon of LB monolayer formation ......................................................... 4
Figure 1.2: Cartoon of monolayer transfer ................................................................. 5
Figure 1.3: DPPC and POPC lipid structures ............................................................... 7
Figure 1.4: Left, Pressure Area isotherm for a typical lipid. Right, Pressure, volume
isotherms for a typical substance [3]. ........................................................................... 7
Figure 2.1: Maximum surface pressure and surface tension vs. SDS bulk subphase
concentration ................................................................................................................. 15
Figure 2.2: Maximum surface pressure and surface tension vs. DTAB bulk subphase
concentration. collapse point observed within box....................................................... 16
Figure 2.3: DTAB collapse point observed at subphase concentration 4.12 mM ............. 16
Figure 2.4: Generic titration curve with cartoon of surface ............................................. 18
Figure 2.5: Predicted surface pressure for 0.25 mM SDS compressed at 50 cm$^2$/min .... 24
Figure 2.6: Predicted surface pressure for 1.97 mM SDS compressed at 50 cm$^2$/min .... 24
Figure 2.7: Starting trough area analysis, A/Ao plotted, 1.97 mM SDS compressed at 50
cm$^2$/min ......................................................................................................................... 28
Figure 2.8: Starting trough area analysis, area plotted, 1.97 mM SDS compressed at 50
cm$^2$/min ......................................................................................................................... 28
Figure 2.9: Model parameters for SDS by concentration ................................................. 34
Figure 2.10: Successive compressions of 0.25 mM SDS at 50 cm²/min............................... 37
Figure 2.11: Successive compressions of 2 mM SDS at 50 cm²/min................................. 37
Figure 2.12: Successive compressions of 1 mM SDS at 50 cm²/min ............................... 38
Figure 2.13: Model parameters for DTAB by concentration........................................... 39
Figure 2.14: Predicted surface pressure for 4.44 mM DTAB compressed at 50 cm²/min 40
Figure 3.1: Isotherms of DPPC on subphase containing SDS. Curve marked ‘0’ is the
        isotherm of pure DPPC monolayer on water as subphase. Curves from 1 to 5 are the
        isotherms obtained over subphase containing increasing concentration of SDS in the
        subphase: 0.03 mM (1), 0.1 mM (2), 0.3 mM (3), 1 mM (4) and 2 mM (5) respectively 44
Figure 3.2: Volpo 20 structure, n≈19 ........................................................................... 47
Figure 3.3: Surface tension plot with cmc estimation for Volpo 20 ................................. 47
Figure 3.4: Compression of 1.83 g/L Volpo 20 at 50 cm²/min ........................................ 48
Figure 3.5: Penetration study DPPC over 1.83 g/L Volpo 20 ........................................... 48
Figure 3.6: Penetration study POPC over 0.52 g/L Volpo 20, initial concentration
        146 Å²/molecule .................................................................................................. 49
Figure 3.7: Penetration study POPC over 0.52 g/L Volpo 20, initial concentration
        72 Å²/molecule .................................................................................................. 49
Figure 3.8: Mergital LM 11 structure, n≈10 ................................................................. 51
Figure 3.9: Surface tension plot with cmc calculation for Mergital LM 11 .................... 52
Figure 3.10: Compression of 3.876 g/L Mergital LM 11 at 50 cm²/min ....................... 52
Figure 3.11: Compression of 0.0290 g/L Mergital LM 11 at 50 cm²/min ....................... 53
Figure 3.12: DPPC compressions over 3.86 g/L Mergital LM 11 solution .................... 53
Figure 3.13: DPPC compressions over 0.029 g/L Mergital LM 11 solution

Figure 3.14: EO-926 structure, n≈11, R is a blend of alkyl groups

Figure 3.15: Surface tension plot with cmc estimation for EO-926

Figure 3.16: Compression of 1.28 g/L EO-926 at 50 cm²/min

Figure 3.17: DPPC compressions over 1.28 g/L EO-926 solution

Figure 3.18: Procetyl AWS structure, n≈5 and ≈19 respectively

Figure 3.19: Surface tension plot with cmc estimation for Procetyl AWS

Figure 3.20: Compression of 0.932 g/L Procetyl AWS at 50 cm²/min

Figure 3.21: DPPC compressions over 0.9230 g/L Procetyl AWS solution

Figure 3.22: Relative area for DPPC over Procetyl AWS with changing expansion speeds

Figure 3.23: EO-219 structure, n≈6

Figure 3.24: Compression of 2.62 g/L EO-219 at 50 cm²/min

Figure 3.25: DPPC compressions over EO-219 (water insoluble) suspension

Figure 3.26: Relative area under the curve for Volpo 20 penetration studies into DPPC and POPC monolayers

Figure 3.27: Relative area under the curve for Mergital LM 11 penetration studies into DPPC

Figure 3.28: Relative and actual area under the curve for Procetyl AWS penetration studies into DPPC
Chapter 1 Introduction

Amphiphilic materials are of great importance in colloidal chemistry, both in understanding basic phenomena as well as manufacture of colloidal structures from a bottom up approach. Colloids are structures or molecules which have at least one spatial dimension measuring between 1 nm and 1 µm. Amphiphiles are molecules that contain at least two chemically distinct regions, one that is compatible with the surrounding phase, generally a solvent, while the other is less compatible. This physical structure means amphiphiles often occupy the interface between two dissimilar phases which stabilize that interface. Liquid/liquid or liquid/gas interfaces are the two most commonly studied with respect to amphiphiles, but there has been increased work in supercritical fluids. In the presence of only one fluid phase, they can create a whole range of different micellar structures, often colloidal in size. Of more importance to this work is amphiphilic behavior at the interface which forms between air and water. This surface, as well as all others, can be considered colloidal as it has a thickness which is different from zero, resulting in a real, continuous density profile, not a discontinuous step. This makes studying interfaces challenging as it blurs the very definition of an interface.

Gibbs suggested that the interface be based on one species, usually the solvent, and considered a step change positioned at a point \( x \) where the overcompensated error in one domain would be balanced out by the undercompensated error in the other domain. It can
then be said, using this step model and a dividing surface located at $x$, that the surface excess, denoted $\Gamma$, for this component is zero. Any deviation from this step model, through the transition from one phase to the other, would then result in either a positive, a higher species aggregation than what is expected, or negative, lower species aggregation, surface excess. Due to the decision to use the step model, surface excess has units of molecules per unit area, neglecting the finite thickness of the actual interface.

In the air/water systems most important to this work, amphiphiles are composed of hydrophobic, hydrocarbon chains or tails, and hydrophilic, highly polar head groups, and are denoted as surfactants. These surfactants have high surface excesses as a result of the hydrophobic effect, water’s tendency to exclude nonpolar, or nonpolar portions of, molecules. A water molecule is capable of forming four very strong hydrogen bonds in four different directions. When water is placed next to the nonpolar tail or equally the surface, it necessarily loses its full bonding capabilities. This makes it easier for a surfactant to be brought to the surface, with its tail oriented away from the aqueous phase, than bulk water molecules. Increasing this surface excess effect are the beneficial van der Waals forces between the tail groups which are also a driving force for micelle formation beyond a certain bulk concentration of monomer surfactant called the critical micelle concentration ($\text{cmc}$). The phenomenon which is observed by these amphiphiles can be exploited and studied in a Langmuir trough, giving rise to model cellular membrane studies and interactions as well as novel techniques for ultra-thin film development.
1.1 Compression of Amphiphile Monolayers on a Langmuir Trough

A Langmuir trough, and its precursors, are one of the oldest molecular approaches in creating highly controllable colloidal structures at a gas/liquid interface. The technique allows for creation of monolayers at the interface which can be transferred or even used as an ultra-thin film coating by passing a substrate through the self-assembled molecular monolayer. These thin films are commonly produced from insoluble species which are confined to the gas/liquid interface. A movable barrier allows for the available surface area to change while prohibiting any surface species from escaping under it, as shown in the Figure 1.1 cartoon, achieving a variation of surface concentration or, equivalently, average area per molecule. When the desired area per molecule is reached, a solid substrate is passed through the interface allowing for transfer of the self-assembled monolayer shown in Figure 1.2.

These monolayers are useful in surface treatments, modeling cell membranes, and advanced electronics, but are currently limited to insoluble, often lipid like molecules. Soluble species are considered to quickly desorb from the surface, leaving no appreciable compression. However, as shown later, there are certain conditions which lead to considerably higher surface excesses than what is found within equilibrium conditions alone.

An important interpretation of surface tension is thought of as the energy required to bring a molecule from the bulk phase to the interface. There are energy barriers associated with this movement and the higher the barrier, the higher the surface tension. Soluble surfactants decrease the surface tension in aqueous systems because they
disproportionally aggregate at interfaces compared to bulk concentration stabilizing hydrogen bonding in water at the surface. If fully understood, these energy barriers, along with the use of a Langmuir trough, can be manipulated to create a nonequilibrium state where a much larger surface excess of soluble surfactant is obtained than what is achieved at equilibrium. If the energy barriers are successfully exploited, this nonequilibrium interface could be transferred to a solid substrate in a similar manner as traditional insoluble species. The exploited energy barriers are likely affected by various conditions including type of soluble surfactant, surfactant cmc, bulk concentration, and temperature.

Figure 1.1: Cartoon of LB monolayer formation
1.2 Model Membrane Formulation

Methods of creating elementary membranes for penetration studies involve depositing a known amount of the lipid 1,2-dipalmytoyl-sn-glycero-3-phosphocholine (DPPC), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC), or a mixture of both [1] to the air/water interface within a Langmuir trough. As structurally shown in Figure 1.3, the largest difference between the two lipids is the rigid double bond in POPC which is not present in DPPC. This kink produces vastly different observations within the compression studies. Deposition on the air/water interface is done using a chloroform solution, with the chloroform quickly vaporizing due to its low vapor pressure. The area per lipid molecule is then adjusted by moving the trough barriers which is capable of producing a packing of lipidic molecules, molecules/area, similar to those found in nature with similar chemical potentials [2].

During the barrier movement, the lipids are normally compressed to form the monolayer. Surface tension, force per unit length, is measured during this compression and thermodynamic properties can be obtained from the resulting data collection, a

Figure 1.2: Cartoon of monolayer transfer
surface pressure-area (π-area) isotherm. This isotherm is analogous in nearly every way to a P-V isotherm, including phase transitions as shown side by side in Figure 1.4. Important to this work is the analogy between reversible work and area under the curve.

It is seen that each isotherm passes through all three ‘phases,’ gas, liquid, and solid. After a monolayer reaches a solid state, further compression will result in a collapse point either forming three-dimensional structures, the monolayer is piling up on itself no longer a monolayer, or the monolayer is forced into the subphase creating micellular structures. The pressure response is generally seen as a sudden drop in surface pressure or a horizontal plateau.
Figure 1.3: DPPC and POPC lipid structures

Figure 1.4: Left, Pressure Area isotherm for a typical lipid. Right, Pressure, volume isotherms for a typical substance [3].
1.3 Dividing Surface

A surface is the interface between two different phases of matter. Although commonly thought of as 2-dimensional, a surface is actually 3-dimensional, with continuous rather than step changes in properties with movement from one bulk phase across the interface into the other bulk phase. This makes surface chemistry difficult without a rigid definition of the interface. Surface excess is closely related to the two dimensional concentration of a component located at an interface and is calculated by choosing a location for the interface and calculating the difference in overestimated and underestimated concentrations in each of the two phases. Gibbs chose this location for the interface such that the surface excess of the solvent in question would be equal to zero. The location of the interface would then be set for all other species in question. The Gibbs equation, which is used later, gives a quantitative relationship between surface excess and surface tension.

There are two ways to conceptualize of surface tension, as the force acting along a three-domain contact line, force per length, and as the surface free energy, energy per area. Each are equally valid and sometimes one is invoked over the other for clarity, and this has led to a number of ways to measure surface tension. The two methods used in this work are the Wilhelmy plate method and bubble pressure tensiometry.

The Wilhelmy plate method is quite simple and uses the idea of surface tension as a force along a contact line. A small rectangular paper plate made from a type of filter paper is lowered into the aqueous solution, a 0° contact angle is achieved, and the force acting on the plate is measured, corrected for gravity and buoyancy effects, then divided
by the contact length of the contact line, approximated to be twice the width of the paper plate. This method works most efficiently when measuring a difference in surface tensions as gravitational and buoyant forces do not need to be corrected. This is defined as surface pressure, $\pi$, and is defined as

$$\pi = \gamma_o - \gamma$$

where $\gamma_o$ is a known reference surface tension, often that of the pure water/air interface at standard temperature and pressure, and $\gamma$ is the surface tension as measured by the Wilhelmy plate.

Bubble pressure tensiometry uses interfacial energies to derive a thermodynamic relationship between surface tension and the pressure differential across a curved interface known as the Laplace equation, and is as follows,

$$\Delta P = \frac{2\gamma}{r}$$

where $\Delta P$ is the pressure difference across the curved surface and $r$ is the radius of curvature for a spherical surface. In the technique, gas is continuously bubbled from a capillary into a solution and an electrical transducer monitors the pressure within the formed bubble. Bubbles are formed in a second much larger capillary to determine the hydrostatic liquid pressure in order to obtain the pressure differential. Most bubble tensiometry is used with the maximum bubble pressure in mind rather than measuring the bubble radius. Due to the nature of the contact line formed between the capillary wall, the aqueous phase, and the gas, the maximum bubble pressure occurs when the radius of the bubble equals the radius of the capillary forming the bubble. A narrow capillary allows
that no correction is needed to account for nonspherical bubbles. This method cannot measure the surface tension effect which is the result of an insoluble species.

Dynamic surface tension has been extensively studied to expand the knowledge about how surface tension, and thus surface concentration of various soluble species changes with time in respect to a change in surface area. These dynamic effects are primarily the result of energy barriers, sorption kinetics, and diffusive limitations. Various methods of measurement are available and have been used to study the dynamic effects of many species: maximum bubble pressure method [4], drop volume method[5], inclined plate method [6], reversed funnel method [7], and Langmuir trough isotherms [8-11]. While most of the work done in this field is with respect to dynamic effects of surface tension in a newly formed surface, that is surfactant adsorption, the effect of changing adsorption suggests that there are parameters which can be manipulated to change the rate of desorption from an equilibrated surface in order to maximize the non-equilibrium surface excess of a soluble species. This leads to the idea of a set of optimum parameters which gives rise to the highest likelihood of thin film formation using a modified Langmuir Blodgett method.

1.4 Sorption Method

Sorption models fall into three broad categories, sorption kinetic limited, diffusion limited, or a combination of the two within a transition window[12]. Adsorption and desorption are each viewed as a two stage process, sorption and diffusion. When a molecule desorbs from a surface, it first must desorb from the interface into a small
sublayer which is formed, then it must diffuse from the sublayer out into the bulk. The opposite is true for adsorption.
A ‘compressible’ monolayer is one where the packing density of molecules confined at an interface can be changed systematically by varying the available surface area. This is accomplished by moving a barrier that sweeps the confined molecules on the surface while allowing soluble species in the subphase to free move beneath the barrier. Although this method is traditionally viewed as applicable only to insoluble amphiphiles, a number of previous studies have shown that soluble species can be compressed into monolayers given certain conditions [11, 13-15]. The key point for insoluble species is that this is a dynamic phenomenon; given sufficient time, such as an extremely low compression rate, no compression of the species at the interface would be observed. To understand this phenomenon, consider the fact that there exists an energy barrier which must be overcome for a soluble species to desorb from an air/water interface. Decreasing available area faster than the rate at which desorption occurs will cause a buildup of soluble species into a more traditional monolayer. However there is some disagreement of what conditions are of most importance to the compressibility of soluble surfactants ranging from critical micelle concentration [13] to intermolecular forces within the formed monolayer [14]. The following work expands the consideration to include bulk surfactant concentration.
2.1 Langmuir Monolayers of Soluble Species

When creating Langmuir monolayers with a soluble species, the subphase is replaced with a solution containing the species of interest. The subphase, rather than being ‘inert’ water, now interacts with the surface through the soluble surfactants in solution. Isotherms are produced in the same manner as with insolubles and the surface pressure is measured identically. However, when performing an isotherm, intuition as well as experimentation [16] suggests that a faster barrier speed results in a higher degree of compression, or higher surface pressure, as there is an energy barrier which must be overcome by the candidate soluble species in order to desorb into the subphase from the air/water interface.

The isotherms studied in this work were all performed in the same Langmuir trough, with a maximum workable area of 260 cm$^2$ and a minimum area of 55 cm$^2$. The solutions of interest were loaded into the trough and permitted to equilibrate for approximately 15 minutes. The barriers were then closed and the surface aspirated to remove contaminants. Upon opening the barriers, the solution was permitted to make sufficient progress toward equilibrium for 30 minutes before the isotherms were performed. The barrier speed was chosen to be a moderate 50 cm$^2$/min in both compression and expansion. Expansion was immediate upon complete compression, as the emphasis in this study is the compression phase of the isotherm. A 3 minute wait time was established between successive isotherms.

The free exchange of the soluble species between the surface and the bulk means that when new surface is created, as with the expansion step in an isotherm, the candidate
species must adsorb to the surface as opposed to simply spreading out. This takes a considerably longer time in comparison with an equilibrium surface excess often taking three or more hours to be established [17]. However, substantial progress toward equilibrium happens within the first few minutes of a newly created surface. While equilibrium may not be established at the onset of compression, the available surface area will promptly decrease to some value which is equivalent to the true equilibrium surface excess, with very little experimentally introduced error. This allows successive isotherms to be performed without significant wait periods.

2.2 Observed Maximum Compression in Soluble Species

Previous work shows that sodium dodecyl sulfate (SDS) compression at the air/water interface is highly dependent on bulk concentration as seen in an adapted Figure 2.1 [16]. Further, dodecyl trimethyl ammonium bromide (DTAB) has since been shown to exhibit similar behavior when compressed, even leading to a solid phase collapse point as indicated in Figure 2.2 and shown in Figure 2.3. In addition, the effect of barrier speed on the compression is as expected.

Both soluble species are capable of producing significant surface pressures, attaining values similar to lipidic compression, within a certain range of bulk concentrations, beginning at low compression at low concentrations, increasing to a maximum with increasing bulk concentration, and finally decreasing back to very low compression at bulk concentrations exceeding the cmc. When compared to the included surface tension curves, the compression maximum is attained for each SDS and DTAB at a concentration
slightly higher than the characteristic shoulder which many surface tension curves exhibit.

Each set of isotherms were started at the same open area and compressed to the same closed area. The value taken as the maximum was taken at an identical area for each species as opposed to the absolute maximum attained. This allowed for results to be directly comparable despite small variations in the trough area.

Figure 2.1: Maximum surface pressure and surface tension vs. SDS bulk subphase concentration
Figure 2.2: Maximum surface pressure and surface tension vs. DTAB bulk subphase concentration. Collapse point observed within box.

Figure 2.3: DTAB collapse point observed at subphase concentration 4.12 mM
2.3 Compression Maximum Hypothesis

The work conducted expands on the previously observed maximum compression for soluble surfactants. It is hypothesized that all soluble surfactants can be compressed to a degree, in an unequilibrated state, and each of these will have a maximum compressibility window of bulk-phase concentrations. The nature of surface tension effects with respect to changing bulk phase concentration has led to this hypothesis. Figure 2.4 shows an idealized titration curve for surface tension vs. bulk surfactant concentration. Area A shows an increase in surface excess due to increasing bulk concentration with very little surface tension change. In area B, the surface excess has reached a constant maximum value, indicated by the constant slope, but the surface tension continues to decrease because of increased surfactant activity due to increased bulk concentration. Area C is above the critical micelle concentration where surface excess is again constant. Surface tension is also constant because the concentration of the monomeric form of the surfactant is constant due to micelle formation. For maximum compressibility, it is best to start out with a large initial surface concentration. However, increasing bulk concentration decreases the energy barrier required to overcome for desorption from the surface to happen. This leads to a hypothesized and observed maximum compressibility in the A to B transition area.
2.4 Mathematical Model of Sorption

Current thermodynamic methods of calculating surface excess, Pethica’s Equation, Barnes’ Equation, Magalhaes’ Equation, and the Partial Molar Area Method, all include the assumption that the chemical potential of the soluble surfactant species is the same at the interface and in the bulk solution, i.e. equilibrium. The method of soluble surfactant compression is inherently nonequilibrium based, thus different methods must be determined to calculate surface excess. It is proposed that a kinetic approach to explaining the sorption occurring during soluble surfactant compression is an adequate
first step. A general mole balance, assuming no bulk flow, is written over the air/water interface:

\[
\frac{dN_i}{dt} = r_i A
\]  

(2.1)

Where \( N_i \) is the number of moles of species \( i \), \( r_i \) is the rate of sorption of species \( i \), and \( A \) is the air/water interfacial area. There is no true flow of bulk material within the compression of an interface. As species adsorb and desorb from the surface it changes the chemical makeup of the surface through time. This sorption can be included within the reactive term, in a sense producing, adsorbing, or consuming, desorbing, the interested species. This is especially important because it is shown that adsorption rate is quicker as surface concentration is low \[17\]. Follows is a hypothesis that desorption rate would also be dependent upon surface concentration, quicker with a higher surface concentration. This allows for any sorption law to be used for \( r_i \) of the form

\[
r_i = \left[ k_{\text{adsorption}}(T, E_{i, \text{adsorption}}) \right] \left[ \text{fn}(\Gamma_i) \right] \\
+ \left[ k_{\text{desorption}}(T, E_{i, \text{desorption}}) \right] \left[ \text{fn}(\Gamma_i) \right]
\]  

(2.2)

The rate constants \( k_{\text{sorption}} \) can be expressed through the Arrhenius equation, where activation energy, \( E_{i, \text{sorption}} \) may be a function of bulk concentration, as the energy barrier of sorption is affected by bulk concentration. Bulk concentration is considered to be constant within individual experiments due to the relatively small amount of surfactant being transferred to the bulk and the ability of an equal amount of surfactant to absorb behind the barrier. Sorption being a function of bulk concentration follows from the discussion of the surface tension titration curve in Section 2.3.
Assuming that surface excess, $\Gamma$, is equivalent to the 2D surface concentration, the number of moles of species $i$ can be written using the product of surface excess and area as such:

\[
\frac{d(\Gamma A)}{dt} = r_i A
\]  \hspace{1cm} (2.3)

Both surface excess and area change with time. Expanding the differential using the product rule and rearranging we are left with,

\[
\frac{d\Gamma}{dt} = r_i - \frac{\Gamma \, dA}{A \, dt}
\]  \hspace{1cm} (2.4)

The technique used for area change, $a_o$, yields a constant change in area with respect to time, which can be substituted into Equation 2.3 yielding:

\[
\frac{d\Gamma}{dA} = \frac{r_i}{a_o} - \frac{\Gamma}{A}
\]  \hspace{1cm} (2.5)

Realizing that net desorption will occur during compression and assuming that this net desorption follows a first order kinetic method, solving the differential we obtain:

\[
\Gamma = \Gamma_o e^{k_{\text{desorption}} \frac{a_o}{A_o} (A - A_o) - \ln \left( \frac{A}{A_o} \right)}
\]  \hspace{1cm} (2.6)

where $\Gamma_o$ is the initial surface excess calculated from equilibrium surface tension measurements and the Gibbs Isotherm. While Gibbs Isotherm is only applicable to dilute binary solutions and depends on the ionic nature of the species in question, this approximation will be good enough for this analysis as it is more interested in the desorption constant. While $\Gamma$ is typically defined as the equilibrium surface excess, one can imagine a situation where a nonequilibrium surface excess can arise from changes in surface area over a noninfinite time span. The only unknown in this equation is
However, surface excess cannot easily be calculated under non-equilibrium conditions but can be considered proportional to measured surface pressure, $\pi$ under equilibrated conditions [18]. It is hypothesized that this proportional relationship continues to hold fairly well under non-equilibrium compression of the surface, which introduces one additional unknown, a proportionality constant $P$,

$$ (\gamma_o - \gamma) = \pi = P(\Gamma_o - \Gamma) \quad (2.7) $$

yielding the final fitted equation:

$$ \pi = P \cdot \Gamma_o \left(1 - e^{-\frac{k_{desorption}}{a_o}(A-A_o) - \ln\left(\frac{A}{A_o}\right)}\right) \quad (2.8) $$

The values of $P$ and $k_{desorption}$ were fitted to various bulk concentrations of SDS and DTAB, as well as various barrier speeds, and starting trough areas. In addition, any error introduced in calculating $\Gamma_o$ will be incorporated into the proportionality constant and the quantity $(P \cdot \Gamma_o)$ is of more interest.

### 2.5 SDS Modeling

Modeling was performed using JMP® Pro 9.0.0 64-bit Edition Nonlinear Fit. Each compression isotherm performed with SDS was solved by the Analytic Gauss-Newton method, convergence criterion was 1E-5, and confidence limits were found with an alpha of 0.050.

Due to the nature of the modeling Equation 2.8, $k_{desorption}$ has the possibility of becoming an insignificant parameter. When modeling SDS concentrations above approximately 2 mM, the model showed instability, unable to nicely converge due to the
very small values returned for $k_{\text{desorption}}$. Upon examination of the iterative steps taken, the solver oscillated between positive and negative values for $k_{\text{desorption}}$, then returned parameter values with standard error ten or more times larger than the returned value. This term is multiplicative in the exponent, and simple sign changes result in a very different fit. It was decided that the large error in the parameters would result in a parameter which includes a possible value of zero. This would mean the parameter is insignificant and upon manually fixing $k_{\text{desorption}}$ to zero, the models fit very nicely just using the parameter $P$ and the effect of changing area. A summary of the parameters calculated for SDS compression are given in Table 2.1 and a sample of the fits are shown in Figure 2.5 and Figure 2.6. Variables studied include subphase concentration, compression number, compression speed, and initial starting area. Two additional quantities were calculated, $(P \cdot \Gamma_o)$ and $k_{\text{desorption}}/a_o$, in order to additionally understand the ability of the model to describe observed phenomena.
<table>
<thead>
<tr>
<th>concentration (mM)</th>
<th>comp-</th>
<th>Gamma,a,o</th>
<th>a,o (cm²/mM)</th>
<th>A,o (cm²)</th>
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Table 2.1: Fitted model parameters for SDS compression
Figure 2.5: Predicted surface pressure for 0.25 mM SDS compressed at 50 cm$^2$/min

Figure 2.6: Predicted surface pressure for 1.97 mM SDS compressed at 50 cm$^2$/min
2.5.1 Compression Speed Analysis with SDS

It was expected that as barrier speed is increased the surface pressure will increase due to the finite desorption rate at which the soluble species can be removed from the surface. This was observed previously with SDS [17], and reinforced with DTAB observations as previously shown in Figure 2.3. It was also hypothesized that among different compression speeds, the rate of desorption would remain constant and that the division by the compression rate might approximately correct for the experimentally changed compression rate. However, for the five sets of experiments presented in Table 2.1 and singled out within Table 2.2 with nonzero and nonnegative \( k_{\text{desorption}} \) values performed at different compression speeds, it was found that no set of experiments resulted in \( k_{\text{desorption}} \) constants which had overlapping 95% confidence intervals, and were thus not statistically different from one another. Whereas the confidence intervals of the combined term \( k_{\text{desorption}}/a_o \) were calculated and found that in 3 of the 5 sets of experiments presented, compressions performed at 0.25, 0.5, and 1.97 mM, \( k_{\text{desorption}}/a_o \) values were not statistically different from one another. It was also found that in a 4th set of experiments, again at 1.97 mM, 2 of 3 individual compressions had the same \( k_{\text{desorption}}/a_o \) through overlapping confidence intervals. These results are important as they suggest that the term \( k_{\text{desorption}}/a_o \) in the model seems to follow the original hypothesis, yet it is experimentally observed that compression speed has a significant effect on surface pressure below the cmc of SDS. This suggests the model, as written, incorrectly describes the relationship between compression speed and surface pressure. While differential area and area ratios are within the model, there is no time dependence
incorporated in these terms. Regardless, the model is still able to fit the data well with differing compression speeds. Given this observation, the proportionality constant, $P$, may be incorporating this behavior in some way.

An interesting observation in 3 of the 5 experiments presented is that the fit parameter $P$ increases, then decreases with speed increasing. It is difficult to explain this observation as $P$ has no physical meaning to the system as it was introduced as a way to relate surface excess to surface pressure. Also, within one case, the 0.5 mM compressions, two calculated $P$ values had overlapping 95% confidence intervals, meaning they are statistically indistinguishable.

| concentration (mM) | comp. number | Gamma,o | a,o (cm²) | A,o (cm²) | P | Approx Std Error | Lower CI | Upper CI | k (1/min) | Approx Std Error | Lower CI | Upper CI | k/a,o | Lower CI | Upper CI | 0.5 1 5.97E-04 | 0.0 280.1 5.68E-05 1.28E-05 3.60E-05 8.87E-05 3.47 0.0473 3.37 3.56 -0.0091 -0.0675 -0.0712 | 0.25 1 5.97E-04 | -100 279.7 1.78E-05 6.12E-06 8.45E-06 2.46E-06 7.40 0.1153 7.10 7.71 -0.0740 -0.0750 -0.0711 | 0.25 1 5.97E-04 | -200 282.9 1.20E-05 5.46E-06 4.74E-06 2.95E-06 14.9 0.367 14.1 15.6 -0.0743 -0.0767 -0.0781 | 0.5 1 5.97E-04 | -50 279.7 10.0 0.641 8.44 11.3 1.17 0.0129 1.14 1.20 -0.0234 -0.0229 -0.0239 | 0.5 1 5.97E-04 | -100 279.6 13.6 1.35 11.5 15.9 2.24 0.0863 2.17 2.31 -0.0224 -0.0217 -0.0231 | 0.5 1 5.97E-04 | -200 283.0 10.0 1.32 7.78 12.9 4.69 0.110 4.48 4.91 -0.0235 -0.0224 -0.0245 | 1.97 1 6.29E-03 | 0.25 161.8 394 4.06 486 403 8.84E-02 7.91E-03 6.92E-03 8.84E-02 7.91E-03 6.92E-03 | 1.97 1 6.29E-03 | 0.1 161.9 351 3.34 345 358 0.103 1.81E-03 0.0998 0.107 -4.16E-03 -3.99E-03 -4.28E-03 | 1.97 2 6.29E-03 | -25 161.7 352 3.34 345 358 0.103 1.81E-03 0.0998 0.107 -4.16E-03 -3.99E-03 -4.28E-03 | 1.97 2 6.29E-03 | -50 161.6 421 5.39 410 432 0.178 4.76E-03 0.169 0.187 -3.56E-03 -3.37E-03 -3.75E-03 | 1.97 2 6.29E-03 | -100 161.9 375 8.65 359 394 0.400 0.0173 0.365 0.434 -4.00E-03 -3.65E-03 -4.34E-03 |
| Table 2.2: Relevant calculated model parameters to Section 2.5.1, additional importance to highlighted values |

### 2.5.2 Starting Area Analysis

One source of error when attempting to replicate presented data may include the size of trough used. When performing experiments with lipids and insoluble species this is not generally considered a significant source of error. However, soluble species behave very
differently than insoluble species and some conventional thoughts likely do not hold. In order to test if Langmuir trough dimensions would have an effect on the experiments performed, a starting area of one half the maximum trough size was chosen as a comparison. If starting area has no effect, we should observe no difference between the compression curves. Shown in Figure 2.7 are the results of such an experiment performed at 1.97 mM and 50 cm²/min compression speed. It is observed that there is a rather large difference between the two curves. When simply area is plotted against surface pressure as in Figure 2.8, the difference is still observed. It is interesting to note that with 50% less compression area, large surface pressures are attained. To further attempt to explain these observations, the previous model was fitted to the data. The results of the fit are shown in Table 2.3. The only statistically insignificant parameter, $k_{\text{desorption}}$, found was within the first compression, that which was shown in Figure 2.7 and Figure 2.8. The proportionality parameter was about twice the value for the half trough than for the full trough. This suggests that the method by which the different physical parameters of Langmuir troughs are accounted for in the model is not straight forward, but partially contained within the proportionality constant. Which suggests the proportionality constant is not as simple as what has been accepted as a first approximation, but rather a form of chemical potential may better relate surface pressure and surface excess.
Figure 2.7: Starting trough area analysis, A/Ao plotted, 1.97 mM SDS compressed at 50 cm$^2$/min

Figure 2.8: Starting trough area analysis, area plotted, 1.97 mM SDS compressed at 50 cm$^2$/min
Table 2.3: Relevant calculated model parameters to Section 2.5.2, additional importance to highlighted values

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2.5.3 Subphase Concentration Analysis

It is observed that compression seems to be dependent on subphase bulk concentration. The relevant model parameters have been presented in Table 2.4 and in graphical form in Figure 2.9. It is interesting to note that the two parameters, $k_{\text{desorption}}$ and $(P \cdot \Gamma_o)$, as well as the modeled parameters seem to be inversely correlated. In fact in every case which returned non zero, real values, the correlation of estimates, between $k_{\text{desorption}}$ and $P$, calculated by JMP® were less than -0.9 and most less than -0.99, indicating an inverse correlation even within one single experimental set. This suggests that the model, as written, may be able to be simplified to a single fit parameter.

The parameter $k_{\text{desorption}}$ seems to attain a maximum at concentrations near 0.25 mM. Above concentrations of around 2 mM, as indicated earlier, $k_{\text{desorption}}$ approaches zero, and becomes statistically insignificant. At even higher concentrations, around 12 mM, it attains negative values, which is nonsensical the way the model has been derived. At low concentrations, the desorption rate is low due to the incredibly small initial concentration of SDS found at the surface. The available surface can be decreased by quite a large amount before there is significant desorption.
As bulk concentration increases, this desorption rate increases due to increasing initial surface concentration. At some point, experimentally observed at approximately 0.25 mM, this rate of desorption peaks and begins to decrease. It is consistent with the maximum pressure hypothesis presented in Section 2.3 that a peak in desorption rate would not coincide with the observed maximum pressure attained near 2 mM as a high desorption rate would make it difficult to attain high pressures. We continue to see fairly low maximum compressions at 0.25 mM near 1 mN/m because the desorption rate is relatively high. As the desorption rate falls, the maximum compression increases to a maximum around 2 mM SDS. As the maximum compression increases, the surface excess, $\Gamma$, is increasing, changing the environment from which a surface molecule must desorb. At relatively low $\Gamma$, a surfactant molecule is surrounded by mostly water molecules, but as $\Gamma$ increases, surfactant-surfactant interactions increase. These interactions likely contribute to an increasing energy barrier to desorption as the surfactant molecules must be encased in a hydration shell in order to desorb. These interactions would create di-, tri-, or n-mers which have even higher energy barriers to desorb as a single unit. This suggests $k_{\text{desorption}}$ is a measure of monomer desorption only. At the end of the compression, when the barriers stop and reverse direction, rapid desorption is observed as previously shown [16]. When the constant force of decreasing available interfacial area is stopped, the n-mers which were created are able to more easily separate, once again decreasing the energy barrier for desorption. The model was not attempting to describe such behavior and a different mechanism describing the decrease in surface excess upon compression completion is needed.
As bulk SDS concentration is increased above 2 mM, $k_{\text{desorption}}$ approaches zero as previously mentioned. Also, at concentrations above 2-3 mM, there is a transition into the linear region of the surface tension plot, indicating a constant, maximum, equilibrium surface excess. Once this point has been reached, the starting composition of the interface no longer changes. All compressions above 2-3 mM SDS start with identical experimental parameters concerning only the interface. Continued increases in bulk concentration are responsible for observed changes. This is likely an upper bound limitation to the model as the maximum pressure still decreases.

Further application of the model to even higher bulk concentrations shows a transition to negative calculated $k_{\text{desorption}}$ values at concentrations above the cmc. The physical meaning of the desorption constant, leads to this being a nonsensical result as that would mean adsorption to the surface as the interfacial area is decreasing. This is further observation that the model breaks down at higher bulk concentrations.

Additionally, the bulk phase is assumed to be a constant, homogeneous sink for interfacial surfactant molecules. With changing bulk concentration, this may not be accurate. Regional micelles could be forming in the sublayer at bulk concentrations lower than the proper cmc. If regional micelles are forming as soon as 2-3 mM SDS concentration, this type of explanation would begin to challenge the typical thought that bulk micelles are not surface active. Due to the nearly non-existent compression observed above the cmc, this type of approach to explaining the observed phenomenon may hold merit.
Ultimately, this is a fundamentally different type of compression from lipid monolayer studies. Much of the theory which apply to insoluble lipid compression may not directly apply to systems of soluble surfactants.
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Table 2.4: Relevant calculated model parameters to Section 2.5.3, additional importance to highlight values.
2.5.4 Compression Number Analysis

Successive compression isotherms were performed at various bulk concentrations of SDS. It was hypothesized that upon successive compressions, the parameters would be unchanged. That is, the nature of soluble surfactants being able to freely move back and forth between the interface and bulk would result in each successive compression being identical to the previous. Additionally, 3 minutes of wait time were included between compressions at maximum interfacial area, or open on the Langmuir trough to allow for a more equilibrated state to occur before successive compressions. It was observed that the difference between such successive compressions is little as shown representatively in Figure 2.10 for 0.25 mM SDS, Figure 2.11 for 1 mM SDS, and Figure 2.12 for 2 mM SDS. The relevant model parameters have been presented in Table 2.5, which includes 14
runs at 12 different experimental conditions. For each model parameter, $k_{\text{desorption}}$ and $P$, 7 of the possible 16 pairs of compressions were found to be statistically insignificant from one another, due to overlapping 95% confidence intervals. For the most part these were found within the same successive compressions, but there are examples where $k_{\text{desorption}}$ and not $P$ was found insignificant, and vice versa. In many other sets of compressions the 95% confidence intervals were very close to one another without overlapping, possibly meaning that the calculated parameters may be found to be insignificant in a replication of the experimental parameters.
Table 2.5: Relevant calculated model parameters to Section 2.5.4, additional importance to highlighted values

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<th>A,o (cm2)</th>
<th>P</th>
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<th>Lower CL</th>
<th>Upper CL</th>
<th>k (1/min)</th>
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Figure 2.10: Successive compressions of 0.25 mM SDS at 50 cm$^2$/min

Figure 2.11: Successive compressions of 2 mM SDS at 50 cm$^2$/min
2.6 DTAB Modeling

Modeling was again performed using JMP® Pro 9.0.0 64-bit Edition Nonlinear Fit. Each compression isotherm performed with DTAB modeled was solved by the Analytic Gauss-Newton method, convergence criterion was 1E-5, and confidence limits were found with an alpha of 0.050.

As with the SDS, at concentrations higher than the ‘shoulder’ on the surface tension plot, the parameter $k_{\text{desorption}}$ approached zero. Model parameters are shown in Table 2.6 and graphically shown in Figure 2.13. A sample of the fit is shown in Figure 2.14. There are no discernible trends associated with the fitted parameters for DTAB compression as there seemed to be with SDS. It is possible that the concentration window was too small as the study with DTAB was focused more on the compressibility maximum, then the collapse point once it was discovered.

Figure 2.12: Successive compressions of 1 mM SDS at 50 cm²/min

![Successive compressions of 1 mM SDS at 50 cm²/min](image)
The model, in its current form, cannot, and did not intend to, predict or model the behavior observed in the collapse point near 4 mM, previously presented in Figure 2.3.

Table 2.6: Model parameters found for DTAB compressions

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<th>A.o (cm²)</th>
<th>Gamma*P</th>
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<th>Upper CL</th>
<th>k (1/min)</th>
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<td>13</td>
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Figure 2.13: Model parameters for DTAB by concentration
Figure 2.14: Predicted surface pressure for 4.44 mM DTAB compressed at 50 cm$^2$/min
Chapter 3 Soluble Surfactant Interactions with Lipid Monolayers

Model membranes can be studied by Langmuir monolayer compression, creating a planar, half bi-layer, the air/water interface, composed of lipid molecules found within membranes. Such molecular interactions confined to a 2D plane are beginning to be understood [16, 19, 20] and the knowledge expanded to areas such as soluble surfactant interaction with cell membranes [1, 2]. This technique provides a highly controlled experimental setting where manipulation of the membrane can closely be monitored. The manner in which soluble surfactants interact with membranes is important to many industries ranging from cell culture, to drug delivery, to cosmetics. Surfactants typically disrupt the structure of lipid assemblies, sometimes so severely that they cause cell lysis. In cellular culture, cell lysis is occasionally intentionally executed in order to retrieve cell contents.

The cosmetic industry has a special concern as cell lysis is one of the mechanisms which elicit epidermal inflammation [21]. Skin irritation tests must be performed by industry in order to protect its customers as well as provide a safe desired product. Currently there are many ways to perform skin irritation studies including human tissue models, animal testing, and human patch tests [22]. A downside to the previous methods and tests are that they require complex biological systems in which changing a single variable often has the effect of changing other characteristics of the system. This makes it difficult to identify at a more fundamental level why specific surfactants lead to certain
effects. A new method to screen for skin irritation can be thought of by observing the effects interested species have on the formation of a model lipid membrane at the air/water interface within a Langmuir trough. Such a system is able to explore molecular interactions in a much simpler manner in which variables can independently and systematically be manipulated, resulting in a less complicated cause and effect system. The presented work in Chapter 3 was partially funded by a cosmetics company and all surfactants studied were provided by the company due to a particular interest in those compound mixtures.

Experiments of this sort can be performed in various ways. By using a sweep method on a multi-compartment trough [23], a lipid monolayer can be assembled within one compartment at a gas/liquid phase, and then transferred, intact, to another compartment where the penetration study is to be conducted. Another method involves a single compartment trough, where a lipid monolayer is again assembled, but then the soluble surfactant is injected within the bulk liquid phase, allowing for the penetration study to be conducted [1]. A final method, which was used in this study, involves assembling a lipid monolayer at the gas/liquid interface of a solution of the soluble species for which the penetration study is desired [1].

A Langmuir trough was used in the study. The trough was filled with a solution of the surfactant of interest in a particular study. The trough was then permitted to equilibrate and any insoluble impurities to migrate to the air/water interface. The trough was closed, and the surface aspirated to remove any impurities which may be a part of the interface. The trough was opened to a maximum possible area of 280 cm$^2$ and permitted to equilibrate for at least 20 minutes, until no change in surface pressure was observed. The
tension sensor was zeroed which resulted in a known reference surface tension, that of equilibrated surface tension at the given surfactant concentration. The lipid of interest was deposited from a 1 mg/ml solution prepared in chloroform using a micro-syringe. Deposition volumes were either 22.5 µL or 45 µL. The system was permitted to equilibrate for 30 minutes then the mixed monolayer was compressed at 5 cm²/min with varying expansion speeds. The system was permitted to again equilibrate for 30 minutes before each successive compression was performed.

Previous work involving the compression of DPPC in the presence of sodium dodecyl sulfate (SDS) illustrates the interaction between the two at the air/water interface as shown in Figure 3.1 [16]. As the DPPC is compressed into a more packed monolayer it displaces SDS from the surface, into the subphase, arriving at a collapse point which is believed to contain very little SDS regardless of the bulk subphase concentration. Various thermodynamic models can be used to estimate the SDS concentration present within the monolayer. A key assumption in this analysis is that the compression rate is slow enough that the soluble component freely moves from surface to subphase, not attributing to the observed change in surface pressure. The work associated with removing soluble species from the surface is considered negligible in such a condition. As the experiments described below show, this is not always the case.

The soluble surfactants used within this study for penetration studies are ethoxylated alcohols, the types that are typically found in cleaning products and cosmetics. Polyethoxylate chains (-OCH₂CH₂-)ₙ are nonionic but highly hydrophilic, and so when attached to an appropriate hydrophobic group, the resulting molecule is generally surface active. Compared to the other two soluble surfactants studied here, DTAB and SDS, these
polyethoxy hydrophilic groups are considerably larger. These large headgroups lead to steric effects not typically observed with ionic surfactants.

It is currently thought that there is a limit to penetration studies using this method of creating a model membrane over a solution of the interested species as they require interested species be water soluble at the desired testing concentration. This limits the current usage of the method somewhat as many surfactants in cosmetics and lotions are not appreciably water soluble.

![Figure 3.1: Isotherms of DPPC on subphase containing SDS. Curve marked ‘0’ is the isotherm of pure DPPC monolayer on water as subphase. Curves from 1 to 5 are the isotherms obtained over subphase containing increasing concentration of SDS in the subphase: 0.03 mM (1), 0.1 mM (2), 0.3 mM (3), 1 mM (4) and 2 mM (5) respectively.](image)

3.1 Volpo 20

Volpo 20 is a trademarked polydisperse mixture of ethoxylated alcohols with structure shown in Figure 3.2. The cmc of Volpo 20 was estimated to be approximately
0.14 g/L from the break point of the somewhat unconventional air/liquid surface tension measurements using a bubble tensiometer shown in Figure 3.3. Typical surface tension curves have three regions of linear relationship on a log scale as shown in the ideal case in Figure 2.4. The curve for Volpo 20 seems to have only two regions of linear relationship, with possibly a condensed middle region where surface excess is constant with increasing bulk concentration. The estimated cmc is presuming that the resolution of the surface tension graph is not high enough to observe the typical transition which indicates a cmc.

A solution of Volpo 20 was then made at the concentration of 1.83 g/L, well above the estimated cmc in order to minimize any compression effect due to the soluble surfactant, as previously detailed in Chapter 2, which may not be negated by slow, near equilibrium, compression. Also by choosing a Volpo 20 concentration above the cmc it is proposed that equilibrium surface excess is more rapidly attained as is the case with SDS [17]. Figure 3.4 shows the extent of compression a Volpo 20 solution exhibits at a moderate compression speed, 50 cm²/min. This allows the observed phenomena to be attributed to DPPC alone or DPPC/surfactant interaction.

Penetration studies depositing DPPC over the 1.83 g/L Volpo 20 solution were then performed, as shown in Figure 3.5. Compression speeds were ten times slower than with just Volpo 20, 5 cm²/min with the intent that compression effects due to the soluble species alone would be further mitigated and the interaction between soluble species and insoluble would also be minimized. DPPC was deposited on the surface with an initial area per molecule of 148 Å²/molecule, isotherms were made with a wait time of 30 minutes between cycles. There is an observed shift in the compressions to a lower
apparent surface area value, which to some extent is normally expected. A large shift is normally indicative of molecular interactions which do not dissociate upon expansion [1]. However in this case, DPPC alone does not show as much shift when above water, suggesting that the Volpo 20 is affecting the DPPC monolayer in some way. A highly probable alternative mechanism for this phenomenon is by solublizing, thus removing, the DPPC from the surface.

The area under these compression curves is analogous to the area under a pressure-volume curve, each giving the work done during the compression. As time elapses, the work required for compression decreases, suggesting that there are fewer DPPC molecules available for compression. An analogous system could be represented as a piston with a slow leak. In compression of a piston with a slow leak, the higher the pressure inside the piston becomes, the larger the flow rate out of the leak. Additionally if the compression of the piston stops, the pressure within the piston will eventually equilibrate to atmospheric conditions.

Penetration studies depositing POPC over similarly concentrated subphases of Volpo 20 were also conducted. Recall from the structure of DPPC and POPC which was shown in Figure 1.3 that the main difference between the two lipids is a double bond within one of the carbon chains. This double bond had a dramatic effect on the penetration studies performed. POPC was deposited at two different initial concentrations, 146 Å²/molecule and half that at a higher concentration of 72 Å²/molecule, however the compressions were remarkably similar as shown in Figure 3.6 and Figure 3.7 respectively. The most remarkable observation is that the initial concentration seems to effect the second and higher isotherm compressions. The system,
after the initial compression, behaves very much like a soluble surfactant. This may be because Volpo 20 also contains the double bond ‘kink’ that POPC does in the surfactant tail. Also to note is that the compression is greatly diminished compared to POPC alone. This suggests that membranes with a large POPC makeup would be very easily disrupted by Volpo 20.

Figure 3.2: Volpo 20 structure, n≈19

![Volpo 20 structure diagram]

Figure 3.3: Surface tension plot with cmc estimation for Volpo 20
Figure 3.4: Compression of 1.83 g/L Volpo 20 at 50 cm²/min

Figure 3.5: Penetration study DPPC over 1.83 g/L Volpo 20 at 5 cm²/min
Figure 3.6: Penetration study POPC over 0.52 g/L Volpo 20, initial concentration 146 Å²/molecule

Figure 3.7: Penetration study POPC over 0.52 g/L Volpo 20, initial concentration 72 Å²/molecule
3.2 Mergital LM 11

Mergital LM 11 is a trademarked polydisperse mixture of ethoxylated alcohols with Figure 3.8 showing the structure. The cmc of Mergital LM 11 was calculated to be near 2.5 g/L from air/liquid surface tension measurements using a bubble tensiometer and linear fitting as shown in Figure 3.9. A solution of Mergital LM 11 was then made at the concentration of 3.86 g/L, well above the cmc, again in attempt to minimize any compression effect due to the soluble surfactant, as well as attain rapid equilibrium surface excess. Figure 3.10 shows the very small, less than 1 mN/m, compression which this Mergital LM 11 solution exhibits at a moderate compression speed, 50 cm²/min. This suggests the observed phenomena can be attributed to DPPC alone or DPPC/surfactant interaction as opposed to appreciable surfactant/surfactant interactions. A second solution of Mergital LM 11 was also made below the CMC at a concentration of 0.029 g/L, near where a suspected ‘maximum compressibility’ exists for Mergital LM 11 compressions alone as explained in Chapter 2. Figure 3.11 shows the considerably higher compressibility, 6-8 mN/m, with this solution, an observation which shows up again within the penetration studies discussed later. This increased compressability is in agreement with the hypothesis which was presented in Section 2.3

Penetration studies depositing DPPC over Mergital LM 11 solutions were performed each with an initial DPPC concentration of 74 Å²/molecule for both solution concentrations. The results are shown in Figure 3.12 and Figure 3.13. Compressions of DPPC alone have been added to figure so the effect of the soluble surfactant can be seen. It is important to note that the reference point for calculating π, surface pressure, are
different for each of 3 conditions, high, low, and no Mergital LM 11, but rather the compressions relative to one another are most important. When the subphase concentration is above the cmc, the compression looks more like that of normal DPPC, whereas compression with the subphase concentration below the cmc exhibits compression of the soluble species. This leads to the idea that calculations attempting to identify the surface excess of the soluble component as in penetration studies would benefit from knowledge and integration of soluble surfactant isotherms.

There is a larger observed shift in the compressions to a lower apparent surface area value in DPPC compression over Mergital LM 11 as compared with Volpo 20. This larger shift is likely attributed to a higher solublizing effect than what is seen with Volpo 20. It is possible that this phenomenon is attributable to molecular interactions preventing dissociation of the surface active molecules upon expansion of the area. In either case, it follows that Mergital LM 11 would likely disrupt membranes containing DPPC more than that of Volpo 20.

Figure 3.8: Mergital LM 11 structure, n≈10
Figure 3.9: Surface tension plot with cmc calculation for Mergital LM 11

\[ y = -8.531 \ln(x) + 43.805 \]
\[ R^2 = 0.9974 \]

\[ y = -0.342 \ln(x) + 36.245 \]
\[ R^2 = 0.3876 \]

CMC \( \approx \) 2.5 g/L

Figure 3.10: Compression of 3.876 g/L Mergital LM 11 at 50 cm\(^2\)/min

\[ y = -0.342 \ln(x) + 36.245 \]
\[ R^2 = 0.3876 \]

CMC \( \approx \) 2.5 g/L
Figure 3.11: Compression of 0.0290 g/L Mergital LM 11 at 50 cm²/min

Figure 3.12: DPPC compressions over 3.86 g/L Mergital LM 11 solution
Inset: Relative area under compression curves
3.3 EO-926

EO-926 is a third ethoxylated alcohol studied. Its structure is shown in Figure 3.14. The cmc of EO-926 was estimated to be near 0.3 g/L from the somewhat unconventional air/liquid surface tension measurements using a bubble tensiometer as shown in Figure 3.15. A solution of EO-926 was then made at the concentration of 1.28 g/L, sufficiently above the estimated cmc. Figure 3.16 shows the relatively small compressibility EO-926 exhibits, at this solution concentration, a maximum compression near 2.5 mN/m, under a moderate barrier speed, 50 cm²/min, which is very comparable to Volpo 20 compression.

Penetration studies depositing DPPC over the EO-926 solution were performed with an initial DPPC concentration of 148 Å²/molecule as shown in Figure 3.17. Also within the figure is the relative area under each curve. The surface pressure increases more
gradually, indicating that the compression of the subphase, EO-926, may be contributing to the compression. We see a large drop in relative area after the first compression then the isotherms nearly overlap one another. This is likely a result of molecular rearrangements and interactions of the surface active molecules which do not completely dissociate upon expansion. The phenomena is also seen in the repeated isotherms. There is little drift of these isotherms which likely indicates that the DPPC is not being removed from the surface at a rate which is hypothesized to be the primary cause of the shift with Mergital LM 11.

Figure 3.14: EO-926 structure, n≈11, R is a blend of alkyl groups
Figure 3.15: Surface tension plot with cmc estimation for EO-926

Figure 3.16: Compression of 1.28 g/L EO-926 at 50 cm²/min
3.4 Procetyl AWS

Procetyl AWS is a trademarked collection of molecules which also contains an ethoxylated portion as shown in Figure 3.18, in addition there is a polypropylene unit. The cmc of Procetyl AWS was estimated to be near 0.25 g/L obtained by surface tension measurements using a bubble tensiometer. The somewhat unconventional plot is shown in Figure 3.19.

A solution of 0.932 g/L Procetyl AWS was made, sufficiently above the estimated cmc. Figure 3.20 shows the relatively small compressibility Procetyl AWS exhibits, at this solution concentration, a maximum compression near 1.5 mN/m, under a moderate barrier speed, 50 cm²/min, which is very comparable to Volpo 20 and EO-926 compressions.
Penetration studies were performed on a solution of 0.923 g/L Procetyl AWS. DPPC was deposited with an initial concentration of 148 Å²/molecule and compression was performed at 5 cm²/min. The results are shown in Figure 3.21. The successive compression shapes are very similar to Mergital LM 11 and EO-926.

Penetration studies depositing DPPC over the EO-926 solution were performed with an initial DPPC concentration of 148 Å²/molecule as shown in Figure 3.17. Also within the figure is the relative area under each curve. The surface pressure increases more gradually, indicating that the compression of the subphase, EO-926, may be contributing to the compression. We see a large drop in relative area after the first compression then the isotherms overlap one another. First analysis suggests this is a result of molecular rearrangements and interactions of the surface active molecules which do not completely dissociate upon expansion, however experiments completed where average surface age differed from those shown in Figure 3.17 follow a nearly identical relative area vs time, or surface age after lipid deposition. The time difference is introduced in the expansion speed of the isotherms produced and is shown in Figure 3.22. This nearly identical behavior has two implications, the data suggest the previous hypothesis involving molecular rearrangements to describe the observed shift in successive compressions is incorrect and the expansion speed in isotherm construction may not matter.

Area under an isotherm compression curve, as discussed previously in Section 3.1, is a measure of the work required to decrease the available surface area to a specified amount. A decreasing area under the curve of successive isotherms of an insoluble, lipidic species is indicative of a decrease in the work required to decrease that surface area. This decrease in required work is often attributed to molecular rearrangements
which are established upon compression which in turn makes it easier, requiring less work, upon successive compressions. However in this case we do not see the same decrease in work upon successive compressions, but rather observe a clear time dependence. This time dependence, following nearly the same curve for these two different experimental parameters, suggests that the decrease in work required for compression is likely due to the removal of lipid from the surface rather than the normal explanation involving intermolecular forces creating loosely aggregated molecules which do not disassociate upon expansion. This experimental evidence gives more recognition to the previous hypotheses of solublization of the lipid membrane.

When performing penetration studies such as presented in this work, the expansion segment of the isotherms produced are less useful than the compression segment, due to poor reproducibility and large observed hysteresis effects and thus have not been presented in this work. However the results and discussion of Figure 3.22 show that the relative area under the curve seems to be independent of the expansion speed. Due to the extremely slow compression speed, 5 cm²/min, penetration experiments take many hours to complete when expansion speed is equated to compression speed. This result suggests that this experiment can be performed by using quick expansion following compression, possibly being extended to other soluble species as well.
Figure 3.18: Procetyl AWS structure, $n$≈5 and ≈19 respectively

Figure 3.19: Surface tension plot with cmc estimation for Procetyl AWS
Figure 3.20: Compression of 0.932 g/L Procetyl AWS at 50 cm²/min

Figure 3.21: DPPC compressions over 0.9230 g/L Procetyl AWS solution
3.5 Insoluble Surfactant Penetration Study

It was hypothesized that this penetration study technique would only give meaningful results for water soluble species. There are a great number of water-insoluble species used in the cosmetic industry, of which degree of skin irritation is still a desired metric. EO-219, a mixture of soluble and insoluble species of which the structure is shown in Figure 3.23, was selected as a preliminary species. As there is no meaningful micelle concentration and there was uncertainty about what would be measured using bubble tensiometry, surface tension plots were not produced. Instead a high concentration, relative to the others used in this study, was chosen for compression and penetration studies performed. A suspension at the concentration of 2.62 g/L of EO-219 was prepared. During overnight mixing, a milky white substance floated to the top of the
volumetric flask. This was likely foam, and the layer was poured off. During compression in the Langmuir trough, a similar phenomenon was again observed. It was questioned that this could be insoluble droplets which were floating to the surface. In either case, the surfactant in question still had an insoluble component, and its overall concentration was unknown.

Isotherms were performed on the water insoluble EO-219 in the same manner as the previous species. Compression spikes initially, then is fairly constant around a very small 1 mN/m. This phenomenon may be attributed to observation that the white floating substance aggregated near the Wilhelmy plate. What may have been measured is more of a liquid/liquid surface pressure due to the aggregation. Initially the aggregation would cause a change in the surface pressure, but further compression does not change the liquid/liquid surface tension, thus would have no effect. These results are shown in Figure 3.24.

Prior to penetration studies, the surface was aspirated to remove any phase separated droplets that many have risen to the surface. DPPC was added in the same way as previous, to a surface concentration of 148 Å²/molecule. Upon deposition the DPPC solution in chloroform did not quickly spread as it did with all other subphases. This delayed spreading of the DPPC did not seem to matter as compressions were, again, started 30 minutes after deposition as shown in Figure 3.25. It is important to note the scale of the surface pressure axis is much smaller than previously, indicating very little compression was observed. It is also observed that the surface pressure initially spikes as observed with EO-219 alone, however to a much lesser degree. This brings into question the hypothesis that what was previously being measured was a liquid/liquid surface
pressure, because upon further decrease in area, further compression due to the presence of the DPPC was noted. There is no definite progression with subsequent compressions, seemingly random and independent of previous compressions.

Given these results, the preliminary study of water insoluble species penetration is inconclusive. The usefulness of the Langmuir monolayer technique for partially soluble surfactant mixtures of indeterminate composition appears to be quite limited.

![Chemical Structure](Figure 3.23: EO-219 structure, n=6)
Figure 3.24: Compression of 2.62 g/L EO-219 at 50 cm²/min

Figure 3.25: DPPC compressions over EO-219 (water insoluble) suspension
3.6 Penetration Study Metrics

This preliminary study of real surfactants has shown that it is not easy to obtain consistent data with industrial surfactants, complicated mixtures of similar molecules. Those used in this study are a mixture of many similarly structured molecules, and are not a uniform structure. Notwithstanding, there is a desire for characterizing the behavior of these substances and attempting to correlate those findings with biological studies, namely skin irritation. Metrics have been derived from the previous experimentation and follow.

As previously described, area under the curve is an important metric indicating the work required to move the barriers on the Langmuir trough. This work arises due to compression of insoluble species, compression of and subsequent desorption of the soluble species and compression of the interaction between the insoluble and soluble species. Because the reference point for each compression is slightly different, absolute areas are not easily compared across different subphases. Changes in work required for compression arise from one of the three indicated sources.

The work associated with compression and desorption of soluble species would not necessarily change from one compression to the next due to the free exchange of surfactant between the surface and the bulk subphase solution. Given that the compression conditions are the same from isotherm to isotherm, this work is not expected to vary greatly. This is further seen by reexamining the repeated compressions of Figure 3.10, Figure 3.11, and Figure 3.16. These compressions were performed at a much faster compression rate, 50 cm²/min as opposed to 5 cm²/min, and with a much shorter wait.
time between compressions, 3 minutes as opposed to 30 minutes. Given the small
difference in successive compressions under these conditions it is seen that work to
compress these soluble surfactants is very similar. Thus any difference cannot be
significantly explained by the soluble surfactant compression. This reasoning can loosely
be applied to the interaction compression. Since the soluble species is free to move
between surface and bulk solution, it is thought that the work, from this source would
also be the same between successive compressions given equivalent experimental
parameters.

This leads to any difference observed to be due to differences in lipid compression.
As previously discussed in length in Section 3.4, lipid-lipid interactions changing from
compression to compression is an unlikely explanation and more likely is the
solublization and physical decrease in available lipid at the surface for compression. It
follows that if a soluble surfactant were able to solubilize and remove lipids from an
interface, it may cause cell death at a higher rate than a soluble surfactant which cannot.
The relative areas under the curves were calculated in each penetration study.

Maximum obtained pressures were also noted for each run, shown in Table 3.1 as the
values may be correlative to biological studies which were not part of this work. These
are metrics are easy to obtain from a single experiment which is a benefit if any sort of
biological screening process is desired.
3.6.1 Relative area for Volpo 20

Volpo 20 was the only soluble surfactant in which penetration studies were performed for both DPPC and POPC. The areas under the curves were calculated, the area under the first curve was set to 1 and subsequent compressions were compared to the first compression. The results are shown in Figure 3.26.

It is important to note that the two uppermost curves are penetration studies into DPPC at the same initial concentration, 148 Å²/molecule and identical compression patterns, both compressing and expanding at 5 cm²/min with 30 minute wait at open. The difference is the subphase concentration of Volpo 20 which was used for the penetration, 1.83 g/L and 0.469 g/L, both well above the estimated cmc. These two curves suggest that penetration studies performed above the cmc will have a similar area under the curve vs time plot. If this is true, one explanation is that the interface containing DPPC is exposed to the same monomeric surfactant concentration subphase for bulk concentrations above the cmc for Volpo 20. Above the cmc the free monomeric, non-
micellar, concentration of the bulk is constant, as the micelles act as a source or sink for the monomeric form of the surfactant. It is possible that the only interaction the DPPC monolayer has is with the monomeric form. This is in agreement with the normal assumption that micelles are non-surface active.

The other two curves are for that of Volpo 20 penetration into a POPC monolayer. In this comparison, the key differences, apart from the slight difference in subphase concentration, is the initial concentration of POPC is double for the lower curve. Also the expansion step in the upper curve is ten times faster than the bottom, more concentrated POPC, curve. The first compression of the isotherms occur at the same average time, it is the second compression which begins sooner for the faster expansion run. The work required to compress the system with more initial POPC is lower when compared to the first compression with less initial POPC. This is counterintuitive as more POPC on the surface should require a higher work to compress. It is important to recall that the nature of this comparison is that each is comparing the area to the first compression. Reexamining Figure 3.6 and Figure 3.7 shows that the compressions past the first are relatively similar. In addition, they resemble Figure 3.4 very well. One explanation is that much of the POPC is leaving the surface and what is left after initial compression is a surface mostly devoid of POPC. The reason for the larger drop in relative area for the higher initial POPC would simply be because the work required for compression 1 was much higher for this set of conditions. Another reason for the large decrease in area could be that aggregates are forming among the POPC, almost fully excluding the Volpo 20, which do not dissociate upon expansion within this time scale. This would mean that
compression is mostly due to the Volpo 20 alone, in the areas outside the POPC domains which were formed.

Alternatively, this phenomenon could be a result of time effects as the second compression started earlier for the lower POPC trial than the double POPC trial. However it is shown later, in Section 3.6.4, that this does not seem to matter for the combination of DPPC and Procetyl AWS, thus it is thought this may not be the cause here.

**Figure 3.26:** Relative area under the curve for Volpo 20 penetration studies into DPPC and POPC monolayers

### 3.6.2 Relative Area for Mergital LM 11

The relative areas under the curves has already been shown in Figure 3.12 and Figure 3.13 within the inset. These are reproduced, and plotted on the same axis in Figure 3.27 to aid in comparison. Each penetration study had the same initial concentration of DPPC
at the surface, $74 \text{Å}^2$/molecule, and differ only in expansion speed and subphase concentration. In this study one was well above the calculated cmc, 2.5 g/L, and one below, near the shoulder of the surface tension plot, 3.86 g/L and 0.029 g/L Mergital LM 11 respectively.

Again, as with the Volpo 20, the expansion speed was changed along with the subphase concentration. The difference in plots could be attributed to the time difference between compressions, however it is shown, in Section 3.6.4, that this does not seem to matter for the combination of DPPC and Procetyl AWS, thus it is thought that time may not be the cause here. Further, the plots do not initially follow the same curve as they did with Volpo 20, so the difference can be more easily attributed to the subphase concentration.

The change in subphase concentration seems to be a large factor in the difference in curves. As seen from Figure 3.27, the work required for successive compressions of the DPPC monolayer on a subphase above the cmc decreases more rapidly than below the cmc. As seen with the Volpo 20 experiments, as long as the subphase is above the cmc, there is little difference in the decreased required work upon successive compressions which was attributed only to the monomeric form of the surfactant interacting with the monolayer. The data presented is consistent with this monomeric view as the solution above the cmc has a higher surfactant monomer concentration than the solution below the cmc. The higher monomeric concentration allows for more interaction with the DPPC monolayer, solubilizing more DPPC, resulting in a lower relative work of compression upon subsequent compressions.
3.6.3 Relative Area for EO-926

Few penetration studies were performed with EO-926, and the relative area curve is located within the inset of Figure 3.17. The interesting thing about this experimental work is that the sharp decrease in relative area, work of compression, seen is similar to that of Volpo 20 penetration into POPC. The difference being that after the initial compression with EO-926, subsequent compressions still achieve high surface pressures. Where the Volpo 20 seemed to remove nearly all the POPC from the surface after the first compression, the EO-926 seemed to either remove a specific amount of DPPC and no more, or did not remove the DPPC, but rather assisted in rearrangement of the monolayer such that, upon expansion, a gas phase was not achieved.
3.6.4 Relative Area for Procetyl AWS

Procetyl AWS penetration studies were the most identical upon repetition. A decrease in breadth of variables studied was substituted for repeatability. Relative area, along with actual area, data is presented in Figure 3.28. For each of these penetration studies, the subphase concentration and initial DPPC concentration were identical, within accepted error. The only change was the expansion rate. This leads to different surface pressure vs. time profiles. In addition, the initial conditions were the same for each experiment, making the reference state for calculating surface pressure, $\pi$, the same. This means that the area under the curve are directly comparable, and shown.

First it is noted that the actual areas for each experiment are quite similar to one another, as expected. The repeatability of commercial surfactants is sometimes a difficult hurdle to overcome. Due to these similar results, and the only variable to change between experiments being expansion speed, it suggests that expansion speed is not important and that area under successive compressions is more a function of time than of expansion speed. This also indicates that the hypothesis that the decrease in work through successive compressions is due to physical removal of lipid from the surface may be valid, and that it is a function, at least in part, of surface age.
3.7 Conclusions of Penetration Studies

The presented work shows that for systems containing an insoluble amphiphilic lipid and a soluble surfactant, the surfactant does not freely adsorb and desorb from the interface but rather has a significant effect on surface pressure measurements. This is of special importance to thermodynamic models used to calculate the molecular makeup of such a surface as virtually all models in current literature use the assumption that soluble species are free to adsorb and desorb from the interface. These mixed amphiphile surfactant surfaces are just beginning to be better understood and it is important to identify the limitations of current methods.
In this limited study, the commercial surfactant Mergital LM 11 follows the hypothesis presented in Section 2.3. This is important in minimizing the compression effects at the interface or exploiting those effects.

The monomer concentration seems to be the only important factor in changing the penetration studies. Thus, studies performed above the subphase cmc will have the same results. This is important in minimizing cost of studies if a screening process were developed.

Additionally, expansion speed does not seem to affect penetration, but rather surface age is the most important variable of which to be aware. This would allow any screening process to make efficient use of equipment time.
Chapter 4 Conclusions and Further Work

Further understanding of soluble surfactant compression has been presented here, however there still are areas which are lacking understanding. The starting area analysis showed that different compression behavior was produced when starting the compression from half the trough dimensions. This behavior was not easily explainable by a simple shift of the compression, or by using a proportional area. Further work could explore trough width and possibly barrier speed in traditional units of length/time in attempt to explain the observations. Understanding this behavior would allow for easier reproducibility and transferability of conditions which maximize compression potential for soluble surfactants.

This work has helped expound on the conditions which allow for maximal surface pressure to be obtained with a soluble surfactant. The next step is to see if under these optimal conditions if it is possible to transfer a soluble species using a modified Langmuir-Blodgett technique. This would especially be interesting with regard to the collapse point observed in DTAB compression.

The work done with mixed amphiphilic lipids and soluble species presented many hypotheses attempting to explain observed phenomena. Testing these many hypotheses were not part of the limited study and could be further developed quite easily by film transfer and AFM or XPS analysis of the surface created. Alternatively, XPS techniques are becoming more advanced to the point that fluid interfaces are starting to be studied.
When the technique is developed, this would be an excellent application, as fluid interfaces have traditionally been so difficult to characterize chemically.

As discussed, the current model has limitations at higher concentrations. With these limitations in mind, different kinetic models can be proposed and tested for predictability. In addition, many current models which calculate partitions of mixtures of insoluble amphiphiles and soluble surfactants contain the assumption that the soluble species freely adsorbs and desorbs from the interface. The previous work has shown this not to be the case. Work on creating a model which incorporates the dynamic behavior of soluble surfactant compression will further expand knowledge in the area.

The screening for possible penetration studies as a substitute for biological skin irritation studies seems to be promising. Further development of soluble surfactant compression needs to occur in parallel with the continued penetration work. In addition, it should be investigated as to biological skin irritation study’s correlation with the data and conclusions presented in this work.
Appendix A List of Equipment and Supplies

The following is a list of equipment used within the previous work. General lab supplies have been omitted.

- Sensadyne Bubble Tensiometer, Model# PC500-LV, Serial# 470
- Langmuir-Blodgett Trough, NIMA Technology, Model# 611, Serial# 087
- NIMA TR516 DAQ Software
- JMP® Pro 9.0.0 64-bit Edition
- PowerSpec PC, Microcenter Inc., Windows Vista, Serial# V20102082038
- Mega-Pure System, Barnstead, Version# MP-1, Model# A440267, Serial# 674930897328
- Various Lipid Species, Avanti Polar Lipids Inc.
- Sodium Dodecyl Sulfate, Aldrich
- Dodecyl Trimethyl Ammonium Bromide, Aldrich
- Surfactant samples from cosmetics company
Bibliography


