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Abstract

This senior comprehensive project focused on the design and modification of an experimental apparatus used for measuring contact angles on hydrophobic and hydrophilic surfaces. Additionally, this project focused on four separate slide stability investigations involving measuring the contact angle as a function of time: 100% 11-mercaptoundecanoic acid (MUA), 100% octadecanethiol (ODT), 35% MUA / 65% ODT, and 40% MUA / 60% ODT. Each investigation studied the interaction of the different monolayers when exposed to three separate media: air, Millipore water, and ethanol. Investigations took place over a period of two weeks for each study. It was shown that the contact angle for all four self-assembled monolayers (SAMs) was stable when exposed to air. On the contrary, the contact angle was unstable as a function of time when exposed to Millipore water and ethanol for extended periods of time. Significant changes in the contact angle measurements occurred after approximately two to three days of total exposure time to the respective media based on an important subject in physics and chemistry: energy favorability. These results have implications in how sample slides are prepared and handled in the laboratory such as performing Surface Plasmon Resonance Spectroscopy (SPR) and refreshing slides using ethanol.

Introduction & Background

Lao Tzu, an ancient philosopher, said, "Nothing in this world is softer and weaker than water. But for attacking the hard, the unyielding, nothing can surpass it. There is nothing like it." Lao Tzu's paradox describes how water can be ordinary, yet impressive at the same time. For example, the water molecule is composed of two hydrogen atoms and one oxygen atom (H_2O). However, this simple molecule is known as the "universal solvent" because of its powerful ability to dissolve compounds. Researchers study the vastly complex interactions between water and various surfaces to greater understand its unusual characteristics. One of these unusual characteristics is the depletion layer that results when water interacts with a hydrophobic surface.

Characterizing a Surface:

Water, when placed on a surface, will either spread out or bead up. The word "hydrophobic" is derived from two Greek roots: "hydros" refers to water, and "phobic" implies a fear or aversion (Poynor, 2006). Therefore, a hydrophobic surface is a surface that water does not care to interact with. What determines if a drop of water will spread out or bead up? In 1805, Thomas Young derived an equation to explain the forces present on a drop of liquid placed on a surface (Stalder et al., 2006). This equation is as follows:

$$\gamma^{SV} - \gamma^{SL} = \gamma^{LV} \cos\theta, \quad (1)$$

where γ^{SV} is the solid-surface free energy, γ^{SL} is the solid-liquid interfacial free energy, γ^{LV} is the liquid-surface free energy, and θ is the contact angle (Lamour et al., 2010).

There are three cases from Eqn. 1 that describe how a drop of water will interact with the surface. If the surface energy (γ^{SV}) is greater than the surface tension (γ^{LV}), the contact angle will drop to 0° as adhesion takes over. If the surface has a high surface

energy, yet lower than the water's surface tension, the drop will interact with the surface by forming a contact angle between 0° and 90°. Lastly, if the surface energy is low, then the contact angle will be large (Lamour et al., 2010).

Surface Tension & Contact Angle:

Water forms a network of hydrogen bonds at the elementary level. In a pure liquid, each molecule in a drop of water is pulled equally in all directions by nearest neighbors. Molecules that are near the surface of the drop do not have this opportunity and are pulled inward, causing an internal pressure. Consequentially, the drop of water will contract to maintain the lowest surface energy (γ^{LV}) possible. In terms of a hydrophobic surface, it is more energetically favorable for water to interact with itself than to interact with the surface.

The contact angle is a measurement taken from the surface to the line tangent on the drop. The contact angle determines if a surface is deemed "hydrophobic" or "hydrophilic." A hydrophobic surface has a contact angle greater than 90°, while a hydrophilic surface has a contact angle less than 90°. These measures are illustrated below in Figure 1.

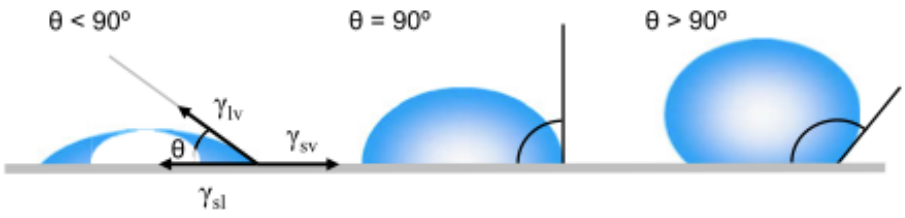

Figure 1: Contact angle measures formed from interaction with a surface. The three interfaces in Young's Equation are shown in θ<90°(Yuan & Lee, 2013).

The Interaction of Gold & Sulfur:

Researchers studying hydrophobic and hydrophilic surfaces choose gold-coated slides because sulfur (S) bonds easily to gold (Au). For Surface Plasmon Resonance (SPR), researchers choose the gold-coated slides because gold will not oxidize as easily as other metals such as silver (Ag). Organic thiols (organothiols) are composed of sulfur, hydrogen, and oxygen groups. Gold has a high electron affinity for sulfur, meaning that the relationship is energetically favorable based on the amount of energy released when gold interacts with sulfur. Gold has an electron affinity of $+223\frac{kJ}{mol}$, while sulfur has an electron affinity of $+200\frac{kJ}{mol}$. The positive sign indicates a release of energy. Once the gold-sulfur interaction takes place, an evenly distributed monolayer attaches to the sample slide. Also, another indicator for the likelihood of gold's interaction with sulfur is based on electronegativity, the tendency for an atom to attract nearby electrons. Gold has electronegativity of 2.6 while sulfur has an electronegativity of 2.5. Therefore, it is likely for gold and sulfur to attract electrons from each other to form a covalent bond (Atkins & Jones, 2010).

A Closer Look at Thiols:

Thiols form uniformly distributed hydrophobic or hydrophilic layers on gold-coated slides, but sometimes form at tilted angles as shown in Figure 2. Ulman describes how studies involving biphenyl $(C_6H_5)_2$- and naphthyl $(C_{12}H_{14}N_2)$-containing alkanoic acids $(C_nH_2O_2)$ display chain tilting possibly due to the large cross sectional area of molecules, binding geometry, binding energy, and preparation process (1996). These studies use carboxyl-terminated chains, self-assembled to silver and copper-coated slides. A hydrophobic monolayer results from a methyl-terminated (CH_3) thiol, and a

hydrophilic monolayer results from carboxyl-terminated (COOH) thiols. For example, octadecanethiol (ODT) is a methyl-terminated, hydrophobic monolayer, and 11-mercaptoundecanoic acid (MUA) is a carboxyl-terminated, hydrophilic monolayer.

Another possible explanation for the thiol thilting could be from a steric effect. When an atom or molecule comes close to another atom or molecule, it experiences an attraction or repulsion due to the "electron cloud" distribution. The atom or molecule occupies its own space, and when another atom or molecule tries to occupy the same space, it experiences repulsion. Perhaps this is the cause of the thiol tilting. The thoils could be orienting to each other in a particular geometry based on the repulsions caused by the steric hindrance (DasGupta, 2013).

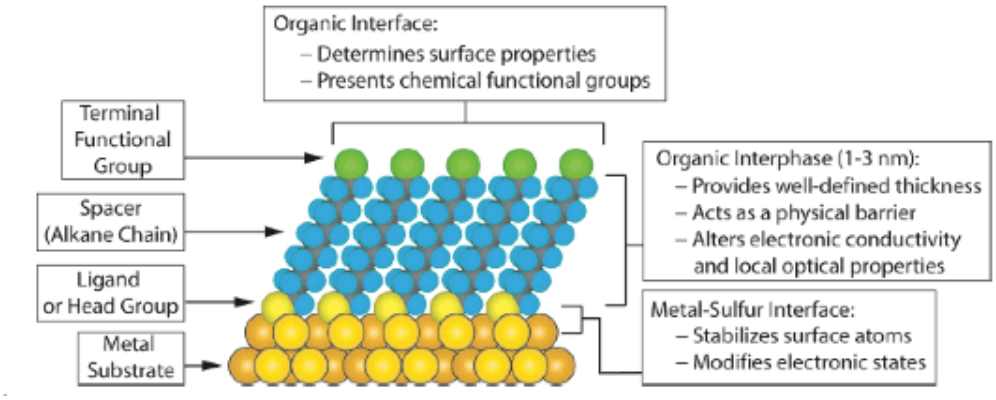

Figure 2: Example of organothiols attached to a gold-coated surface. The interaction relies on the strong electron affinity of gold and sulfur. The yellow atoms attached to the blue atoms represent sulfur binding to gold. Also, the thiols attach at angles tilted from the normal plane of the gold slide (Love, Estroff, Kreibel, Nuzzo & Whitesides, 2005).

Different Methods to Measure Contact Angles:

Contact angle measurement can be differentiated into three groups: static, advancing, and receding contact angles. In general, static contact angles have an uncertainty of ±3° due to the technician's skills and experiment conditions (Stalder et al., 2006). Most researchers instead use dynamic contact angle measurements (receding and advancing) such as the tensile method shown in Figure 3. In this method, the drop of liquid is set into motion by enlarging and decreasing the size of the droplet. An enlarged droplet is called an advancing contact angle, while a decreasing droplet demonstrates a receding contact angle. The difference of the advancing contact angle and the receding contact angle provides an important quantity: the contact angle hysteresis. The contact angle hysteresis can be used to describe how clean or homogenous a surface may be. Chemical impurities, dust, and surface roughness all affect the contact angle hysteresis.

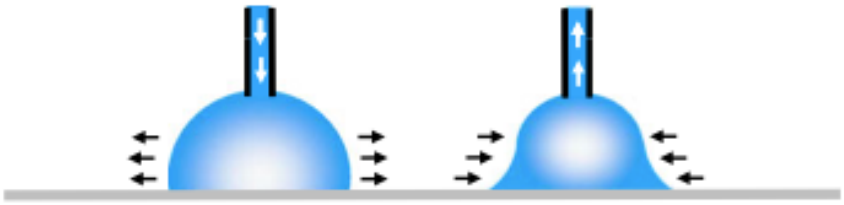

Figure 3: Advancing (left) and receding (right) contact angles as liquid is added and drawn out via an irrigation needle (Yuan & Lee, 2013).

Through the years, researchers have developed many methods to determine the contact angle. Some methods involve direct measurement, while others use indirect measurement. In the 1960s, Ramé Hart Instrument Company manufactured the first telescope goniometer (Yuan & Lee, 2013). This instrument is a very simple design using a lamp and protractor eyepiece as shown in Figure 4. A micropipette drops liquid onto the

horizontal surface for study; then the operator simply aligns the drop in the eyepiece to read the contact angle. This method is beneficial if the researcher is not too concerned with precision. The telescope goniometer method has an uncertainty of about ±2°, which is much greater than other methods that offer accuracy to the tenths and even hundredths of a degree. Impurities can enter the sample through the exposed surface design. In addition, another drawback of this method is that it is hard, if not impossible, to measure contact angles less than 20° because of the flatness of the drop (Yuan & Lee, 2013).



Figure 4: A photo of a Ramé Hart telescope goniometer used for measuring contact angles. The light source is at the far right of the image, the angle protractor on the far left, and the sample slides rest in the middle (Yuan & Lee, 2013).

The Wilhelmy balance method is an indirect way to measure contact angles. A vertical plate is submerged in the liquid of interest, and a balance detects the change in weight. The total detected force on the balance is given by

$$F = \gamma^{lv} p \cos\theta - V\Delta\rho g, \qquad (2)$$

where V is the volume of the displaced liquid, $\Delta\rho$ is the difference in density between the liquid and air, and g is the acceleration due to gravity. Once the surface tension and solid perimeter are known, the contact angle can be indirectly calculated (Yuan & Lee 2013). An advantage of this method is that the contact angle measure depends on lengths and weights, which carry a smaller uncertainty. In addition, the operator can use different wetting speeds by varying the rate in which the plate is submerged. On the other hand, the surface must encounter a uniform cross-sectional area during submersion, and the slides must have the same geometrical arrangement on all sides. The Wilhelmy Balance method may be tough for researchers studying anisotropic systems. Also, more liquid must be used compared to the telescope goniometer method (Yuan & Lee 2013).

A relatively new method in measuring contact angles is the Drop Shape Analysis method presented by Bashforth and Adams. This method balances the forces between gravitational effects and surface tension effects. Gravity causes a dispersion of the interactive forces within the sample of water, which can lead to a less spherical shape. Conversely, surface tension aids the sample of water in retaining its spherical shape. The balance between these two competing effects is demonstrated by the Laplace equation:

$$\frac{\theta}{2} = \tan^{-1}\left(\frac{h}{d}\right), \tag{3}$$

where h represents the height of the drop and d represents the diameter. The Drop Shape Analysis method is useful for small drops, but not for large drops which are more greatly affected by gravity (Yuan & Lee, 2013).

The Depletion Region:

A region of uniform, low density forms when water is placed upon a hydrophobic surface. Poynor et al. demonstrates through x-ray reflectivity that a 2-4Å low-density depletion regions forms around a water droplet when placed in contact with an octadecyltriethoxysiloxane (OTE) hydrophobic surface. Poynor et al. shows that a depleted region exists whether or not the water was degassed or aerated before placed in contact with the hydrophobic surface. Other researchers question the effect of water orientation with regards to the depletion layer. Water orientation could cause an electron deficiency at the surface of the water droplet, which may account for the presence of a low-density depletion region (Ocko, Dhinojwala, & Daillant, 2008). However, the hydrogen bonds present in water molecules allow for a wide distribution of orientations. Experiments maintain that water reorientation is not the cause of electron density depletion at the water-hydrophobic interface (Poynor, Hong, Robinson, & Granick, 2008).

Is there a correlation between the contact angle and the width of the low-density depletion region? Computer simulations from numerous researchers show no conclusive evidence (Chattopadhyay et al, 2010). Different models depend on different input parameters, which can significantly impact the presence of a large or small depletion layer, or no depletion layer at all. In general, one would expect a larger contact angle to demonstrate a larger depletion layer. Chattopadhyay et al. report a linear relationship between the equivalent width of a zero-density gap and advancing contact angle. The equivalent width of a zero-density gap is

$$D_{eq} = \frac{D(\rho_{H20} - \rho_{dep})}{\rho_{H20}}. \quad (4)$$

Eqn. 4 represents the product of the depleted zone width, D, and the electron density deficit relative to bulk water. This product is divided by the density of water to give D_{eq}, which can used to compare many different experimental results (Chattopadhyay et al, 2010). However, the graph of D_{eq} versus advancing contact angle shows large error bars as shown in Figure 5. A significant number of lines may be drawn through the error bars, which may result in a line of best fit that is difficult to produce. Chattopadhyay et al. describe how there are "unidentified and/or uncontrolled variables" that are difficult to take into account. One variable, for example, could be radiation damage, which can diminish the presence of a depletion layer. The study uses a low intensity bending magnet beam compared to beams sent through an undulator. A beam sent through an undulator intensifies the radiation by causing the beam to oscillate. This undulating effect is analogous to a person delivering repeated punches as opposed to a softer, pushing. Chattopadhyay et al. report that no radiation damage occurs in the first hour, which is when all the data is collected.

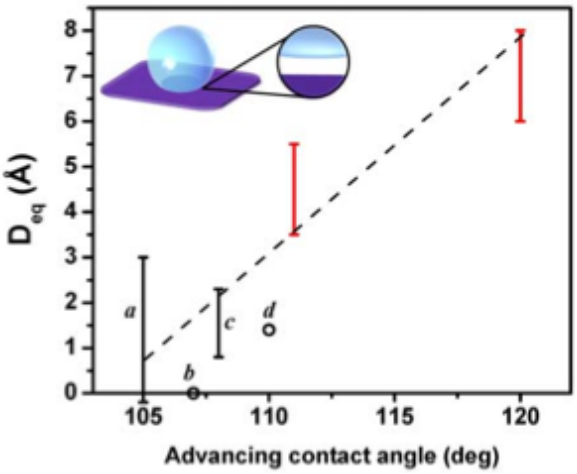

Figure 5: D_{eq} versus advancing contact angle. The general increasing pattern is the larger the contact angle, the larger the equivalent width (Chattopadhyay, 2010).

There is still much to learn about water and its seemingly unusual properties. Contact angle measurements set a foundation for further experimentation with hydrophobic surfaces such as studies in Surface Plasmon Resonance (SPR) spectroscopy. Much research is focused on understanding more about the interaction that occurs at water-hydrophobic surface interface.

Methodology

Contact angles characterize a surface as either hydrophobic or hydrophilic as described in the introduction. Measuring contact angles requires much preparation and cleaning. Any impurities that enter a sample, such as dust, will impact the contact angle measurements. Therefore, it is necessary to have as clean as an environment as possible when performing these experiments.

Organothiol Solution:

First, the solution is prepared. Depending on the type of self-assembled monolayer (SAM), different kinds of compounds can be employed such as 7-heptanethiol (C7), 11-mercaptoundecanoic acid (MUA), octadecanethiol (ODT), and mercaptoundecanol. These compounds impact how the water-surface interface acts (i.e. whether the surface is hydrophobic or hydrophilic). Ethanol acts as the solvent for all of the aforementioned compounds. The glassware used to measure the solutions is a 100 mL volumetric flask. Once the desired amount of compound is added, ethanol can be added until the flask is full. Lastly, the volumetric flask must be clearly labeled and stored in the fume hood (Statman, 2012).

Refreshing Sample Slides:

Gold-coated slides require "refreshing" as opposed to a heavy duty cleaning, as heavy duty cleaning can damage the gold-plated slides. It is necessary to wear both latex or nitrile-based gloves and disposable polyethylene gloves when handling the slides. The polyethylene gloves prevent latex powder from entering the sample. The slide is rinsed five times on each side using ethanol and placed into a beaker filled with fresh ethanol (Statman, 2012). This beaker is placed in a separate beaker filled with Millipore water. It is important to not overfill the Millipore water into the ethanol beaker. A visual description of the setup is shown below in Figure 6. Next, the "beaker-in-beaker system" is placed into the ultrasonicator for ten minutes. The ultrasonicator breaks up small impurities by projecting sound waves towards the beaker system. Lastly, the slide is rinsed five times each side using ethanol and placed in an empty beaker with a test tube cap.

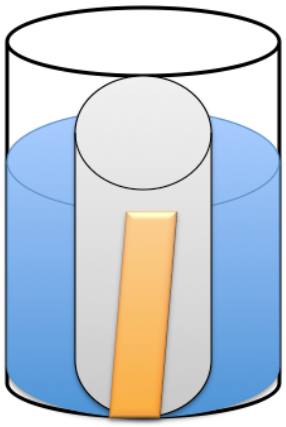

Figure 6: Visual description of the "beaker-in-beaker system." The gold-coated slide is contained within a small beaker containing ethanol. The small beaker is contained within a larger beaker containing Millipore water.

Preparing Sample Slides:

Next, the self-assembled monolayer (SAM) must attach to the gold-coated slide. Using a beaker, the gold-coated slide is submerged in the solution of interest for at least thirty minutes. After the half an hour of submersion, the slide is rinsed five times per side using ethanol. Similar to refreshing slides, the same procedure is performed once the SAM is attached. Therefore, the newly created slide must be ultrasonicated for ten minutes and rinsed again as described above. To ensure that the slide is completely dry before storage, the slide is dried using nitrogen gas by gently allowing the gas to flow over the slide. The nitrogen gas flow should be soft enough that the sample slide does not slip or fall out of the hand. Lastly, the clean slide is placed in a dry beaker with a test tube cap and stored (Statman, 2012).

The Tensile Method for Measuring Contact Angles:

The next step is to begin measuring contact angles. First, the prepared slide is placed on the slide stand with the gold-coated side facing up. Next, the dropping syringe is filled with Millipore water after priming it at least three times. The syringe is placed in the mount perpendicular to the sample slide with the needle approximately one to two millimeters above the gold-coated slide. Next, the digital camera is placed on the camera stand with the sample slide in focus. The lamp (40-Watt light bulb) is turned on and placed under the diffuser box. The lamp heats up very quickly, so the lamp should be left under the diffuser box for a long period. All overhead laboratory lights must remain off to prevent any stray radiation from affecting the digital photo. A schematic is shown in Figure 7.

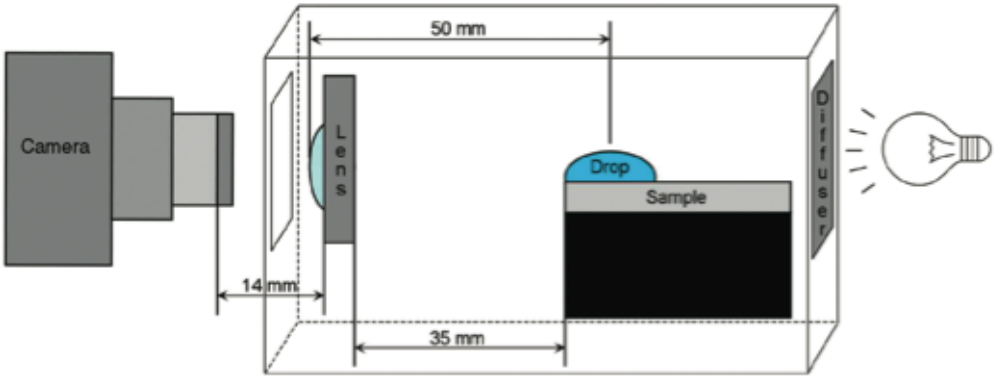

Figure 7: Schematic of the experimental apparatus adapted from Lamour et al. This shows the diffuser box overtop the sample and lens. However, the setup employed in Dr. Poynor's lab uses the diffuser box overtop the lamp instead.

The syringe is depressed to allow a small droplet of water to rest on the sample slide (about 10-15 μL). As water is added to the water droplet, the advancing contact angle is imaged. Similarly, as water is suctioned back through the needle, the receding contact angle is imaged as well. Imaging the advancing and receding contact angles is repeated as needed.

ImageJ & Analyzing:

After all the images have been documented, files are uploaded to the computer and contact angles are imaged using ImageJ (Statman, 2012). ImageJ uses a "snake-based approach" in measuring contact angles. "Snakes" are used in computer imaging for segmentation. Specifically, ImageJ uses the plugin Dropsnake to fit the shape of the water drop as shown in Figure 8. Before analyzing, image must be in black and white color.

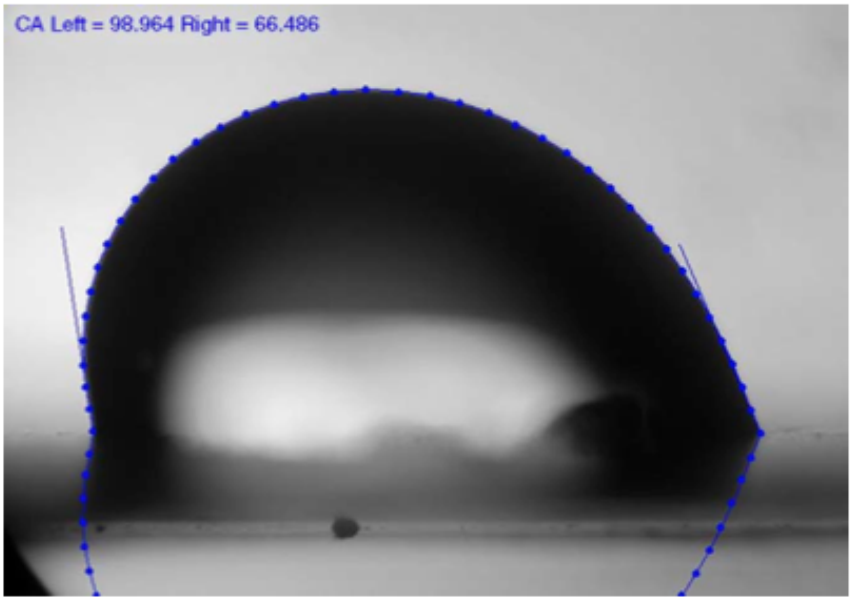

Figure 8: Photo of a drop of water analyzed by the program ImageJ. The dots connect to form a smooth fitting around the unorthodox shape of the water drop. The contact angle of the left side is 98.964°, and the contact angle of the right side is 66.486° (Stalder et. al, 2006)

Compared to other plugins such as Low Bond Axisymmetric Drop Shape Analysis (LBADSA), Dropsnake provides a smooth-fitting effect, which aids in a greater in-depth analysis of water droplets. LBADSA assumes either the shape of a circular or elliptical water drop. However, the water drop in Figure 7 fits neither the circular nor elliptical representations. This drop has an air fan pointing from right to distort the drop. Thus, the smooth fitting is appropriate for instances such as this.

To begin, the first dot is placed at the left contact point. Additional dots are placed around the contour of the drop until the last dot is placed at the right contact point. Next, dot placement is completed by clicking the first dot. There is a rough fitting of dots to the drop of water, but modifying the placement of dots can refine the fit. Dots are modified until there is a tight fit around the water drop. It is important that the second dot on the

left side and the second dot on the right side intersect the tangent lines produced from the points of contact. The upper left-hand corner of the display shows the contact angle left (CA Left) and the contact angle right (CA Right).

Cleaning Glassware:

After all the contact angle measurements have been taken, the glassware can be cleaned. Cleaning takes place first in a potassium hydroxide (KOH) bath. The KOH is added to a Nalgene container approximately five centimeters high. The rest of the Nalgene container is filled with isopropyl alcohol, leaving about 5 centimeters of room to avoid splashing when uncapping. Using Teflon-taped tongs, the dirty glassware is fully submerged into the KOH bath. The dirty glassware requires soaking in the KOH bath for a minimum of seven hours. Painted surfaces can be ruined by prolonged submersion past 72 hours (Statman, 2012).

After seven hours, glassware is removed using Teflon-taped tongs and placed on aluminum foil. The glassware is rinsed using Millipore water five times and then placed into the oven for 30 minutes at a 177 degrees Celsius (350 degrees Fahrenheit). Glassware is wrapped in aluminum foil for storage when cooled.

As described above, the majority of the time is spent cleaning and preparing the slides. This is a necessary consequence to get the best possible measurements. Using proper solutions, clean glassware, and a reliable computerized contact angle measurement apparatus allows for much more precise values to characterize hydrophobic or hydrophilic surfaces.

Discussion & Results

Several improvements have been made to the contact angle apparatus to provide for a safer and possibly more accurate method of measuring contact angles: a new diffuser box and attachment to an aluminum plate for transportation. The current setup uses a method adapted from Lamour et al. Some expensive contact angle measurement devices can cost several thousands of dollars. The homemade Lamour setup is cheap and convenient while still providing precise measurements.

Construction of an Alternative Diffuser:

As described above in the methodology section, the setup originally had a cardboard box diffuser covered in aluminum foil. The aluminum foil acts in reflecting radiation from affecting the picture quality. Placing the cardboard diffuser over the 40-Watt light bulb can present a fire hazard if the box is kept overtop the bulb for prolonged periods.

Some of the thermodynamic properties to take into account for a less flammable diffuser box include the following: specific heat, conductivity, and the auto-ignition temperature. The specific heat of a material describes the amount of heat per unit mass required to raise the temperature by one Kelvin. A larger specific heat capacity allows the material to withstand higher temperatures before changing form. Thermal conductivity describes how well a material can dissipate heat. Lastly, the auto-ignition temperature is the temperature limit in which a material will spontaneously ignite due to extreme heat (Atkins & Jones, 2010).

Cardboard, a byproduct of paper, has a specific heat of 1,336 $\frac{J}{kgK}$ (Alvin, 2013). Paper also has a thermal conductivity of .05 $\frac{W}{mK}$ and an auto-ignition temperature of

505.37 K (Chung, 2013). A good alternative material to cardboard is plexiglass, which is composed of acrylic plastic. The specific heat of acrylic is 1,470$\frac{J}{kgK}$, and the thermal conductivity of acrylic is .19$\frac{W}{mK}$ (Kaysons, 2012). The auto-ignition temperature of acrylic is 673.15 K (RM Plastics Inc., 2013). Acrylic, as opposed to cardboard, is a much better material to use because the specific heat is higher by about ten percent, the thermal conductivity is four times higher, and the auto-ignition temperature is higher by 167.78 K.

I constructed a plexiglass (acrylic) box fit to the same dimensions as the current cardboard box. I used black plexiglass in order to eliminate the need for aluminum foil. The finished diffuser is shown below in Figure 9. I continue to use a piece of white paper as the actual diffuser because this so far has provided a good background for imaging the drops of water. I understand that this piece will still be flammable, however the rest of the acrylic structure will better address the heat-related issues compared to the cardboard diffuser box.

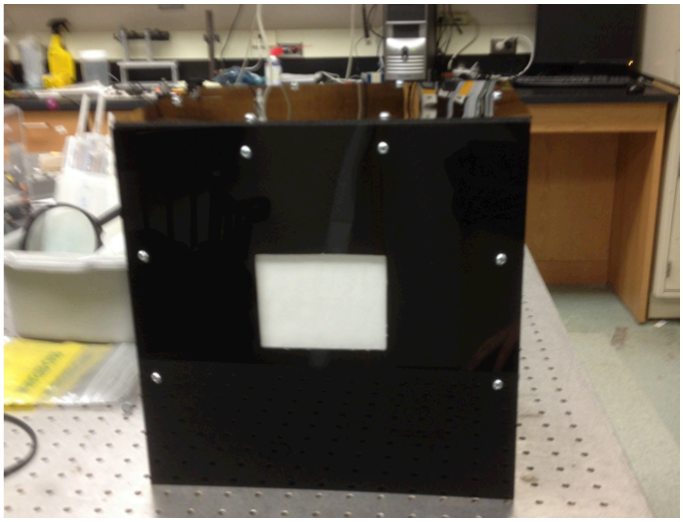

Figure 9: Image of the finished black plexiglass (acrylic) box. The central white represents the actual paper diffuser. The box is placed overtop the light source, acting as a diffuser for imaging contact angles.

Appropriate Diffuser Lighting:

Originally, the setup used a 40- Watt incandescent light bulb. This type of light bulb heats up quickly and was one of the contributing factors for the possibility of a fire hazard. I chose to change the light source to a 13- Watt compact fluorescent light (CFL) bulb based on the lower energy consumption and the smooth image background quality through trial and error. Described on the packaging, the 13- Watt CFL bulb has the equivalent 40- Watt intensity as the incandescent bulb. Other options I considered for the light source were a 7- Watt CFL and 10- Watt LED. The 7- Watt CFL produced a very bright white hue in contrast to the 13- Watt smooth white hue. The 10- Watt LED bulb concentrated too much of the light toward the top of the diffuser box.

Transporting the Setup:

Originally, the contact angle setup was attached to the large optical breadboard, and it shared the table with two other experiments. It is advantageous to have the contact angle setup be attached to a portable aluminum metal plate because when it is not in use, it can be stored in order to maximize the amount of table space. The extra free space is aesthetically pleasing as well as offering more safety in the lab.

I attached the original Thorlabs devices (i.e. the camera rod mount, sample stand, and focusing lens) to the aluminum metal plate using tapers in order to get the same sized screw holes that appear on the large lab optical breadboard. This setup allows for the current devices to be easily transferred over to the aluminum plate, and it ensures that they will have no trouble attaching in the same setup as the breadboard. Shown below in Figure 10 is a picture of the completed portable apparatus.

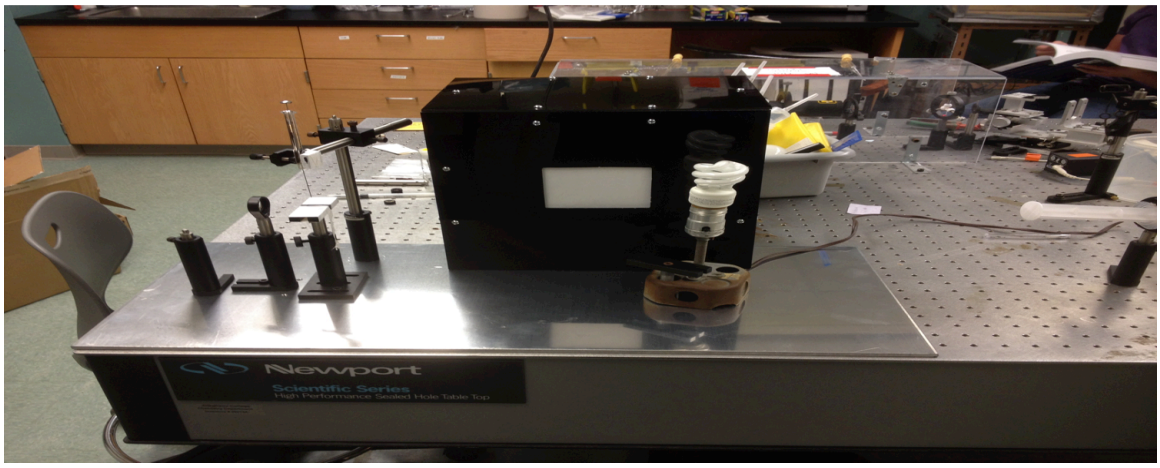

Figure 10: Photo of the finished setup. The diffuser box is placed over the lamp when the experiment is being performed. The digital camera mounts to the far left attachment.

Stability Testing Motivation:

Slides undergo different interactions after being first prepared in the lab. For example, the refreshing process for cleaning a slide involves the use of ethanol, which acts as a cleaning agent to remove any dust, impurities, or oils that the sample slide may have encountered over time. Surface Plasmon Resonance uses three separate media to investigate the depletion layer: air, Millipore water, and methanol. Additionally, the prepared slides sometimes experience long lag times on the laboratory shelves before being used in experiment. My interest and motivation lies in how these different situations potentially affect the contact angle. I have analyzed many contact angles and observed how they have changed as a function of time when exposed to different media: air, Millipore water, and ethanol. It is already known that methanol permanently damages slides, so it is excluded from my investigation.

Stability Testing Procedure Fall 2013:

1. The organic monolayer (100% ODT) is properly attached, as described in the methodology section, to one of the cut pieces of bare gold-coated slides.
2. After the organic monolayer has been properly attached, the contact angle is measured, results recorded, and the slide placed into a clean test tube filled with air, Millipore water, or ethanol depending on which test is being performed.
3. After 15 minutes, the slide is taken of the air, Millipore water, or ethanol and gently dabbed with a lens wipe for drying purposes. This is also be performed for the slide placed in air so that the experiment is the same for all media (ethanol, Millipore water, air). The exposure time is measured using a stopwatch. Also, the time is recorded when the slide is dried.
4. After the contact angle is measured, as much water as possible is suctioned up through the irrigation needle. Next, suction any residual water using the micro-capillaries, and place the slide back into the original tube containing ethanol, water, or air.
5. The contact angle is analyzed on the computer using ImageJ.
6. Steps 3-5 are repeated by varying the exposure time to ethanol, water, or air in 15-minute intervals. For example, the first sampling was performed after 15-minutes exposure, the second sampling will occur 15-minutes later (for a total exposure time of 30-minutes), the third sampling will occur 15-minutes following the second sampling (for a total exposure of 45-minutes).

7. The contact angle is measured every fifteen minutes until the exposure time reaches 2 hours (A total of 9 data points including the initial 0-minutes of exposure time).
8. After two hours exposure time has been measured and analyzed, the sampling to occur once per day (preferably at the same time each day, or close to that time). The time is recorded that the contact angle is measured. The contact angle is measured until at least 20 data points have been recorded. This should take exactly 13 days. (The first day will yield 9 data points and each subsequent day will yield one datum point until 21 data points are recorded).

Stability Testing Procedure Spring 2014:

1. The organic monolayer (100% MUA, or mixed) is properly attached, as described in the methodology section, to one of the cut pieces of bare gold.
2. After the organic monolayer has been properly attached, the contact angle is measured, results recorded, and the slide placed into a clean test tube filled with air, Millipore water, or ethanol depending on which test is being performed.
3. After 30 minutes, the slide is taken out of the air, Millipore water, or ethanol and gently dabbed with a lens wipe for drying purposes. This is also be performed for the slide placed in air so that the experiment is the same for all media (ethanol, Millipore water, air). The exposure time is measured using a stopwatch. Also, the time is recorded when the slide is dried.
4. After the contact angle is measured, as much water as possible is suctioned up through the irrigation needle. Next, suction any residual water using the micro-

capillaries, and place the slide back into the original tube containing ethanol, water, or air.

5. The contact angle is analyzed on the computer using ImageJ.
6. Steps 3-5 are repeated by varying the exposure time to ethanol, water, or air in 30-minute intervals. For example, the first sampling was performed after 30-minutes exposure, the second sampling will occur 30-minutes later (for a total exposure time of 60-minutes), and the third sampling will occur 30-minutes following the second sampling (for a total exposure of 90-minutes).
7. The contact angle is measured every thirty minutes until the exposure time reaches 3 hours (A total of 7 data points including the initial 0-minutes of exposure time). It is important to note here that, in contrast to the Fall 2013 procedure, there are two less data points compiled on the first day of testing.
8. After three hours exposure time has been measured and analyzed, the sampling occurs once per day (preferably at the same time each day, or close to that time). The time is recorded that the contact angle is measured. The contact angle is measured until at least 20 data points have been recorded. This should take exactly 14 days. (The first day will yield 7 data points and each subsequent day will yield one datum point until 20 data points are recorded).

Example of Results:

Shown below in Figure 11 is an example of some results involving the 35% MUA / 65% ODT slide submerged in ethanol for a total exposure time of (346,020 ± 326) seconds (4.01 days ± 5.43 minutes).

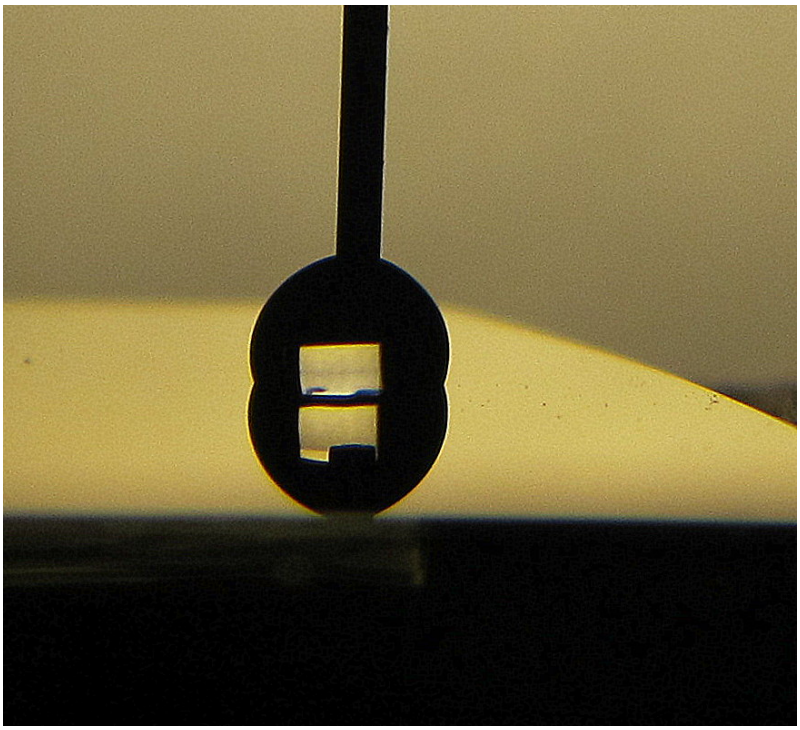

Figure 11: Image of a water drop on a 35% MUA / 65% ODT slide. This sample was submerged in ethanol after a total exposure time (346,020 ± 326) seconds. The irrigation needle down the center of the drops dispenses the amount of Millipore water in microliters.

The data associated with this sample is shown below in Table 1. The mean describes the average contact angle for this particular image. The standard deviation represents how the data points spread from the mean, and the standard deviation of the mean describes the validity of the mean. A smaller standard deviation of the mean implies a more valid or reproducible mean value (varies from 0 to 1). It is also a measure of the amount of likely

random errors that occur in an experiment. Therefore, it is an indicator to consider improving the precision of the experimental measurements (Taylor, 1982).

Image File	Contact Angle Left	Contact Angle Right
IMG_4226	100.122	101.991
IMG_4227	101.158	100.563
IMG_4228	100.628	100.223
IMG_4229	100.038	101.961
IMG_4230	101.530	100.001
IMG_4231	100.035	100.970
IMG_4232	99.620	101.418
Mean	100.7327143	
Standard Deviation	0.777072557	
Standard Deviation of the Mean	0.207681377	

Table 1: Analyzed results of 100% ODT after submersion in ethanol for (582,420 ± 692) seconds. The contact angle average is the average of the contact angle left and the contact angle right. The mean value is the average value of the contact angle averages. The standard deviation and standard deviation of the mean describe the spread and reproducibility, respectively. All values are reported in degrees.

Results for 100% ODT- Air, Millipore Water, Ethanol:

Using the Fall 2013 procedure, I performed an investigation of stability tests involving 100% ODT and three separate media: air, Millipore water, and ethanol. The Fall 2013 procedure involves testing every fifteen minutes for two hours as opposed to every 30 minutes for three hours found in the Spring 2014 procedure. The ODT monolayer was allowed 30 minutes to attach to each gold slide for all the investigations, as described in the lab manual by Ariel Statman (2012). This standardized the investigations to ensure all gold slides experienced the same amount of submersion time in the ODT solution.

The sample slides were prepared using three sections of one regular slide to reduce the amount of gold slides and chemicals used for making slides. I used the hand glass cutter in Dr. Statman's laboratory, and each piece is approximately 2.5 centimeters in length. Lastly, the slides were all stored in the respective test tube vials on the same shelf to ensure that they were subject to relatively the same environment in the laboratory. Shown below in Figures 12, 13, and 14 are the graphs of the results for 100% ODT placed in air, Millipore water, and ethanol, respectively. The following graphs display two curve fits: one for the first day of testing (shown in red) and one for the rest of the investigation (shown in blue).

Overall, the ODT monolayer was stable as a function of time when exposed to air, and unstable as a function of time when exposed to Millipore water and ethanol. Millipore water caused a significant decrease in the contact angle over the fourteen-day investigation. The results for ODT in contact with ethanol fell in between air and Millipore water: the contact angle decreased slightly. The contact angle was not

significantly affected on the first day of testing for any of the media investigated (i.e. the first nine data points in each respective graph). Significant changes in the contact angle began to occur on the third day of testing.

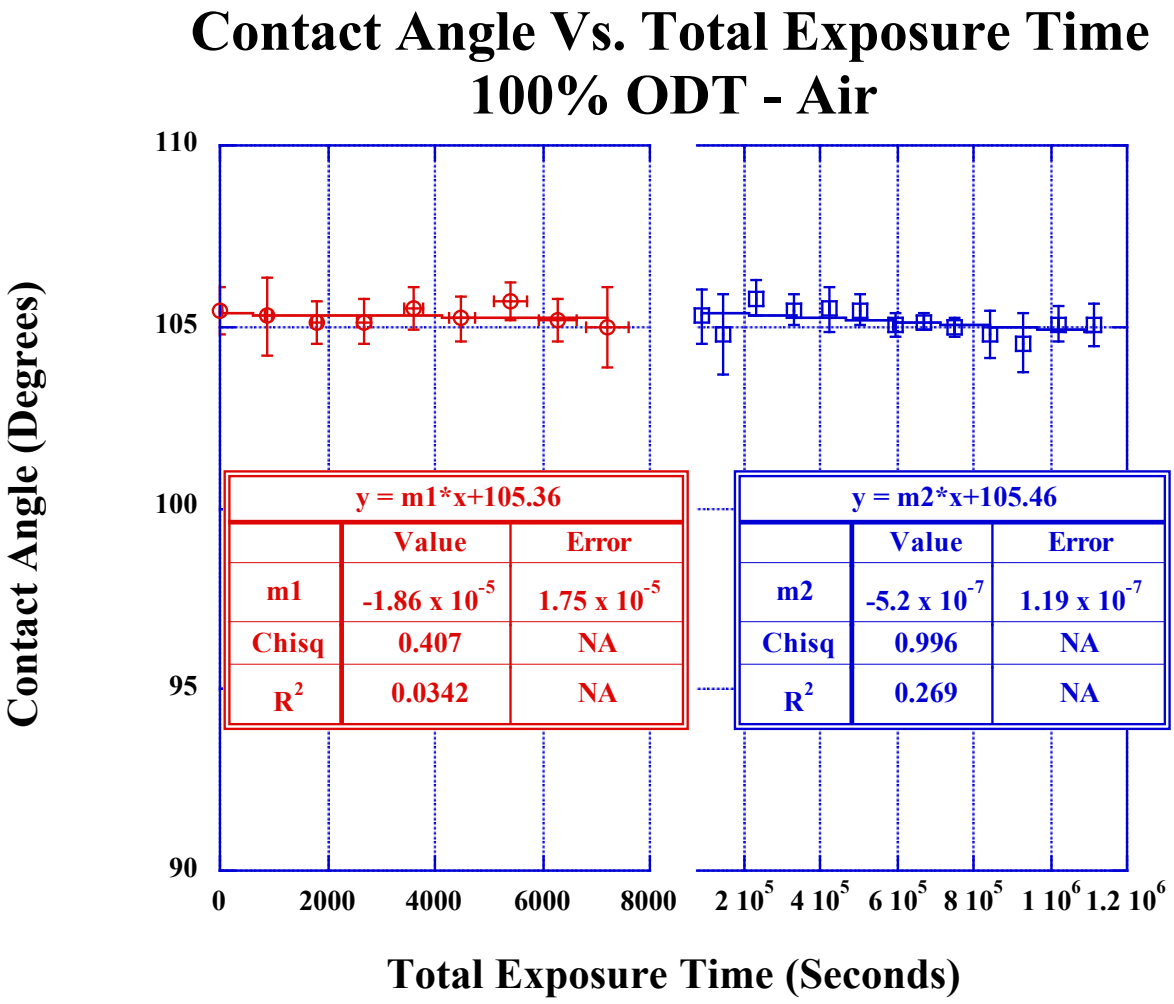

Figure 12: Graph of the Contact Angle (Degrees) vs. Total Exposure Time (Seconds). As the total exposure time progressed, the contact angle was not significantly affected. Therefore, over the course of time, 100% ODT was stable. The break in the X-axis indicates measurements being taken on a day-to-day basis instead of every 15-minutes on the first day.

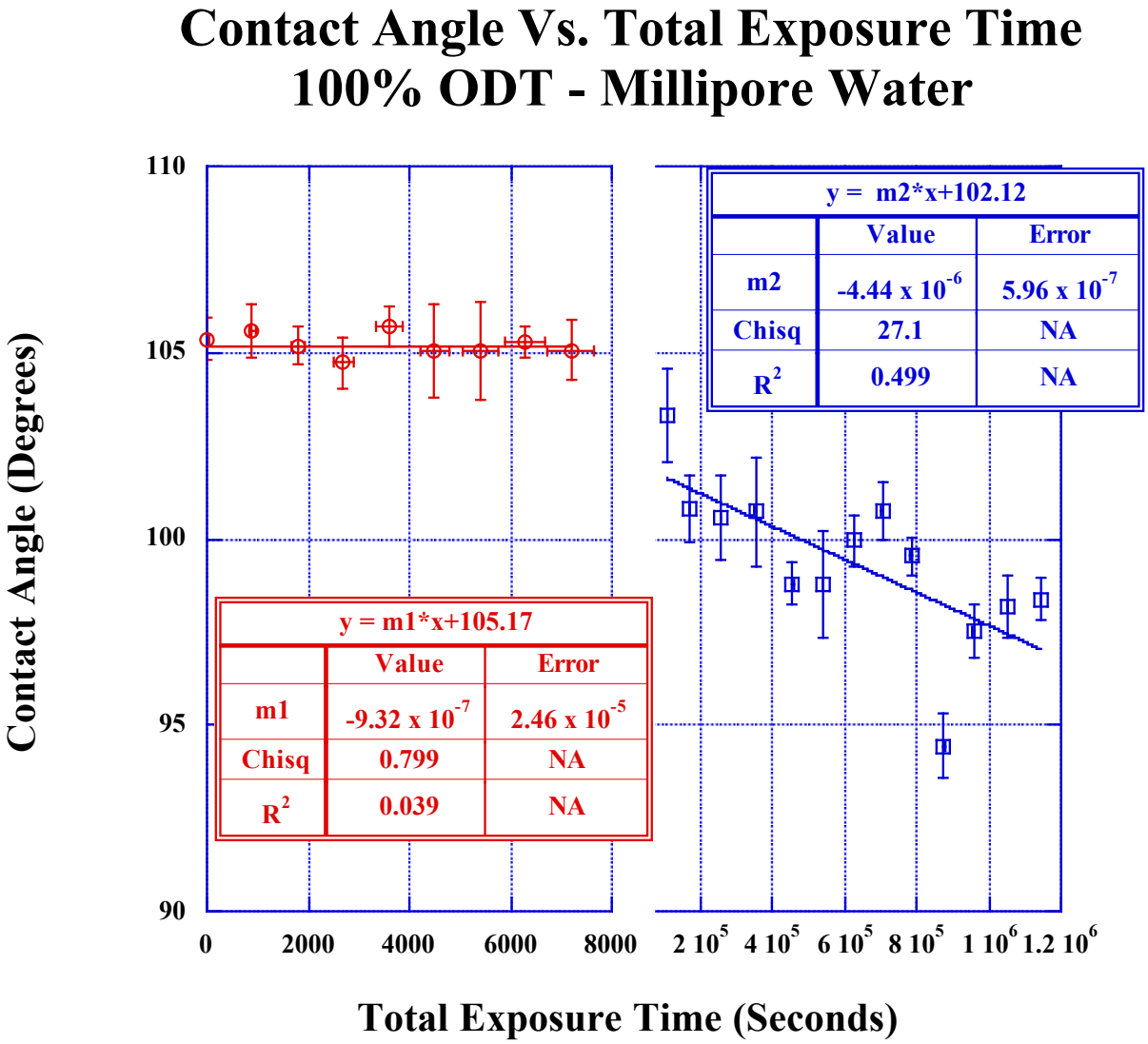

Figure 13: As Total Exposure Time increased, the contact angle decreased. Changes in the contact angle began to be significant on the third day of testing. In general, the longer 100% ODT was exposed to Millipore water, the lower the contact angle. This caused about a 5-7 degree decrease in contact angle over a period of 13 days.

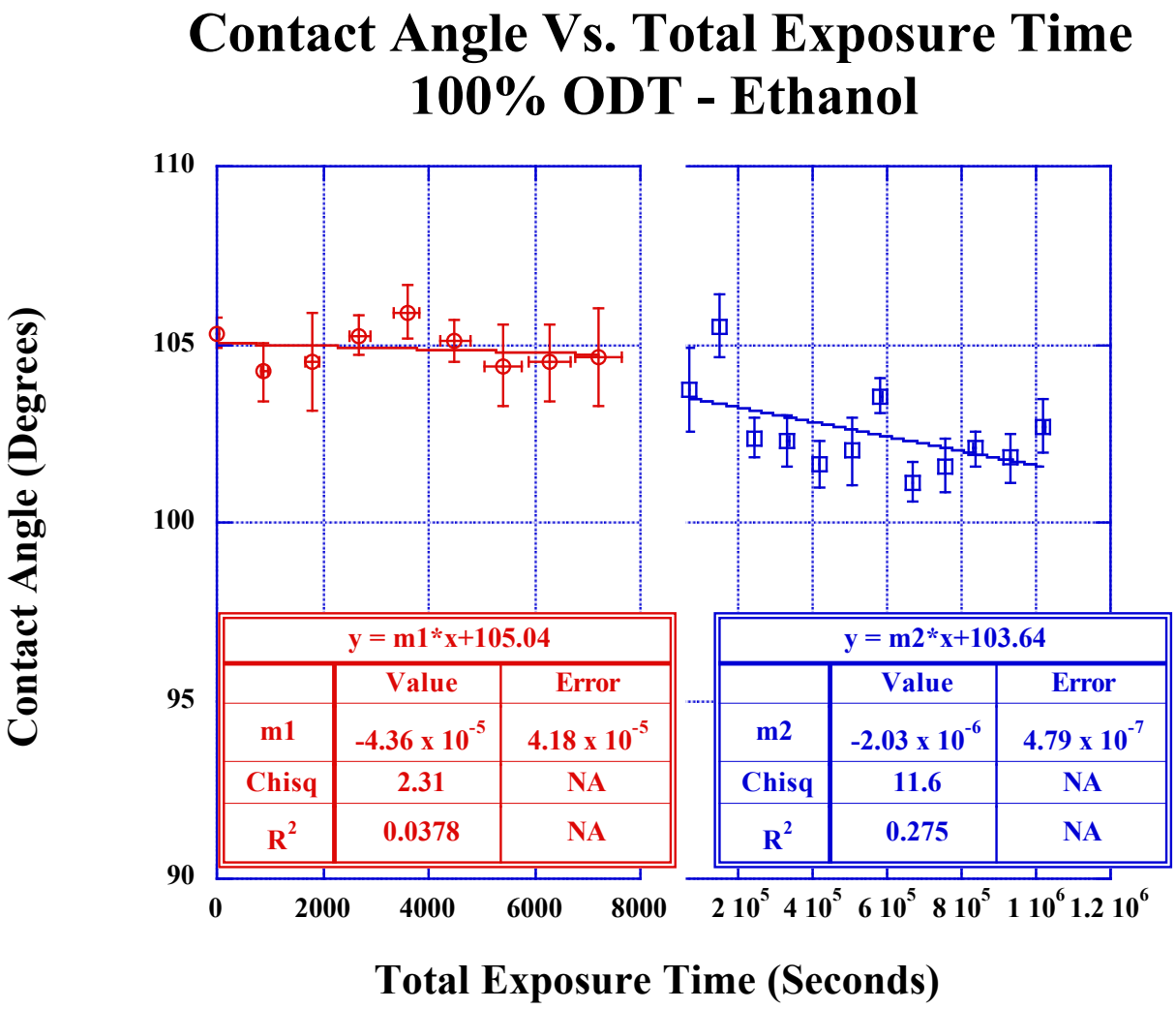

Figure 14: The contact angle decreased slightly over the course of time for 100% ODT interacting with ethanol. These results became significant near the fourth day of testing. Overall, the ethanol medium caused about a 2-4 degrees drop in the observed contact angle over a period of 13 days.

Results for 100% MUA- Air, Millipore Water, Ethanol:

In contrast to the 100% ODT sample slide investigation; the 100% MUA sample slide investigation involved using a hydrophilic monolayer. This investigation proved to be tougher than the 100% ODT investigation based on the drop placement. I experienced problems when placing the drop as shown in the provided figures. For example, on the 100% MUA slide exposed to air, there were three days over the 14-day study in which the contact angle uncertainty was out of the uncertainty range of the other data points. Drop placement errors occurred on the second, sixth, and ninth days of testing. I believe that the reason for these discrepancies occurred from the fact that the 100% MUA monolayer is hydrophilic and thus it is favorable for the drop of water to interact with the monolayer (i.e. the drop spreads out when placed in contact with the 100% MUA monolayer). As a result, the drop was distorted on the left or right side, and the contact angle measurements were skewed. Conversely, the drop placement for the hydrophobic monolayers (100% ODT, 35% MUA / 65% ODT, and 40% MUA / 60% ODT) proved to be much easier as the drop of water was repelled from the nonpolar, methyl-terminated chains. Thus, the drop appeared more symmetric and easier to render the contact angle.

100% MUA-prepared slides were stable when exposed to air over the 14-day investigation. However, when exposed to Millipore water and ethanol over the course of 14 days, the contact angle changed significantly. The contact angle for the 100% MUA slide submerged in Millipore water increased much more than the contact angle for the 100% MUA slide submerged in ethanol. This is the opposite behavior of the ODT-prepared slides for the contact angle of the ODT-prepared slides submerged in Millipore

water and ethanol decreased significantly over the 14-day investigation. The results are displayed below in Figure 15, 16, and 17.

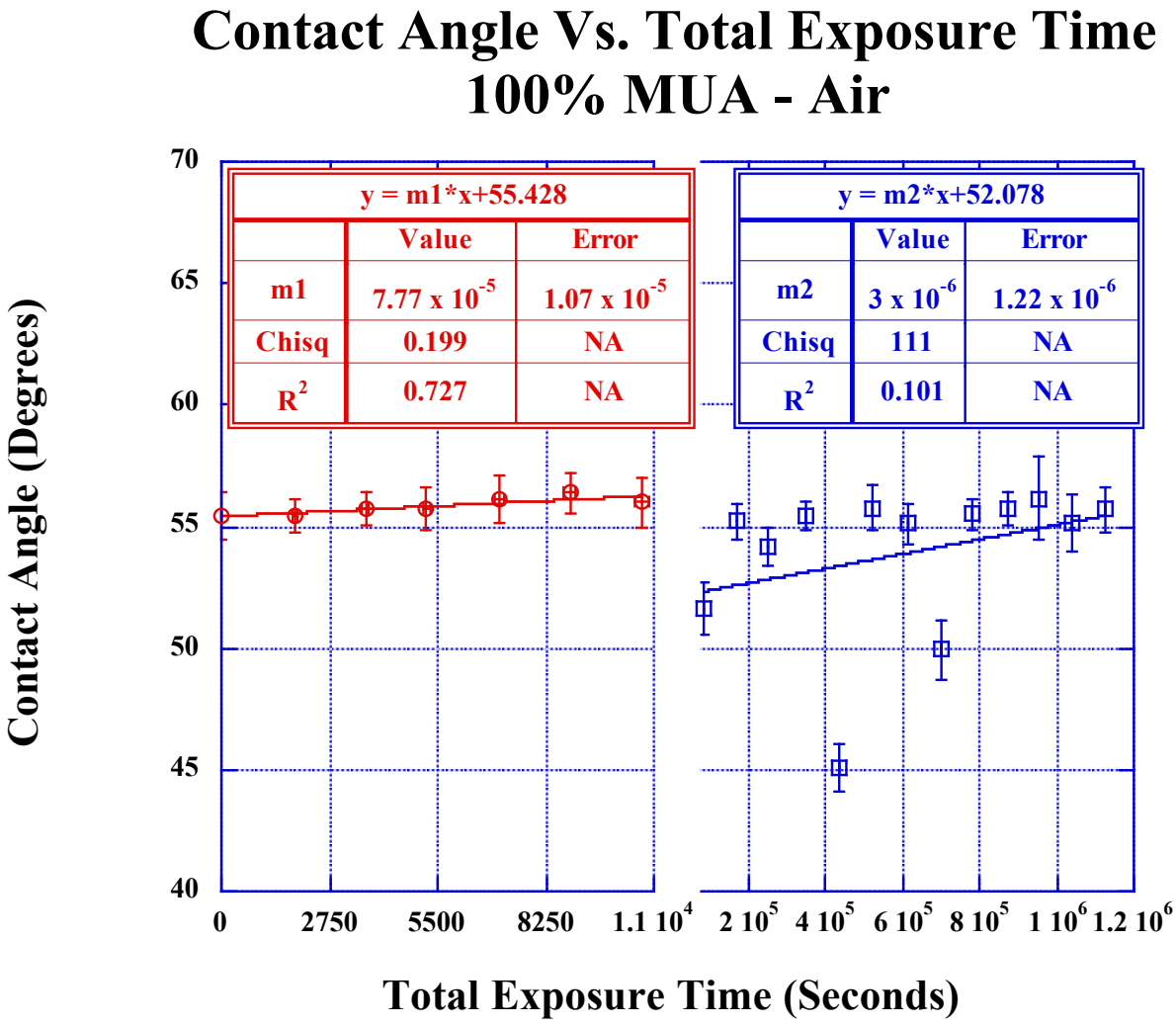

Figure 15: The contact angle of the 100% MUA-prepared remained relatively constant over the entire investigation. Outliers do exist; however these were influenced by poor drop placement on the slide. Removing the three outliers, 100% MUA was stable as time increased when exposed to air.

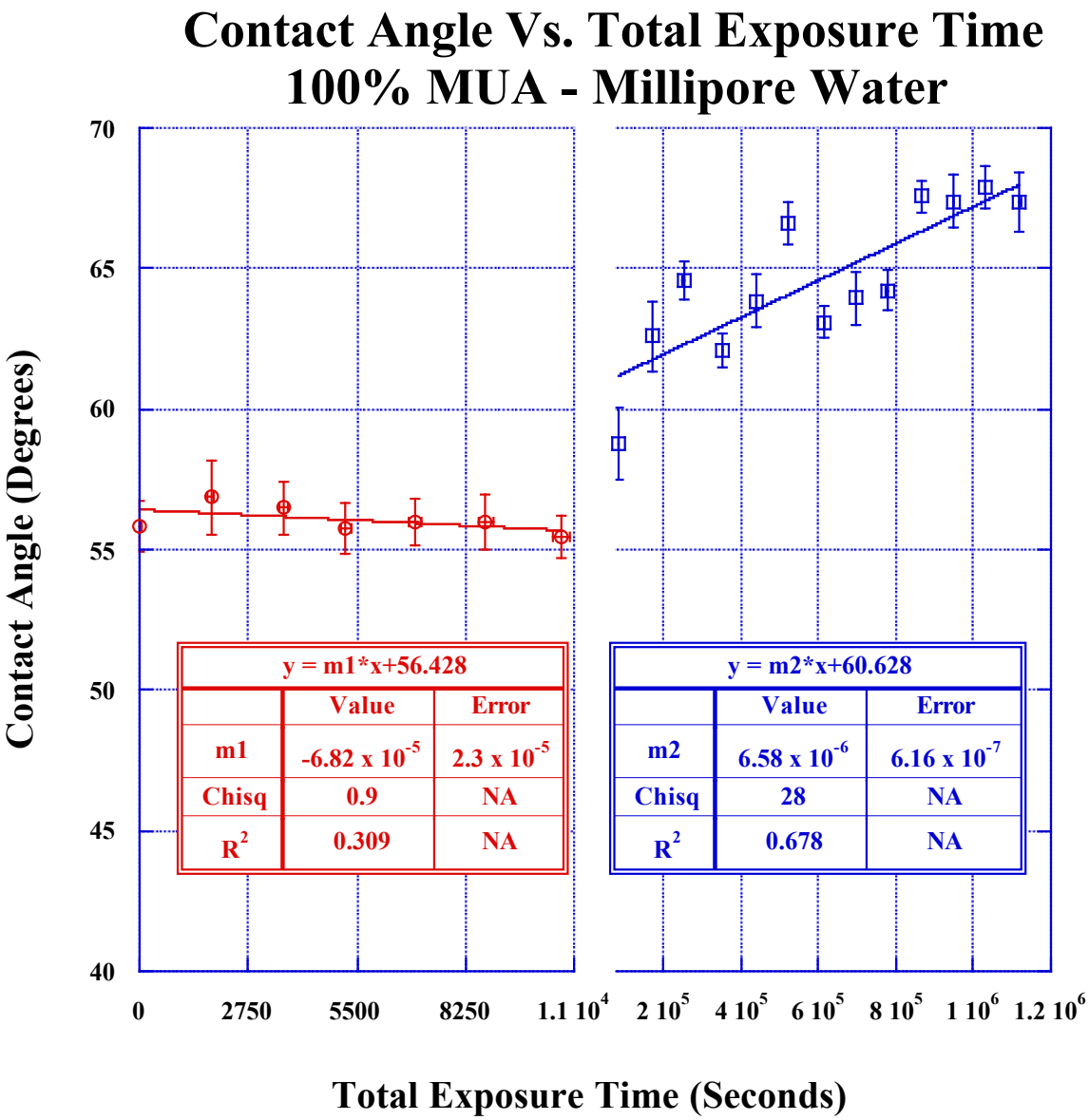

Figure 16: 100% MUA slide when submerged in Millipore water experienced a significant increase in the contact angle. The data displays stability for the first day of testing, but the contact angle increased when the slide was exposed to Millipore water for a prolonged amount of time.

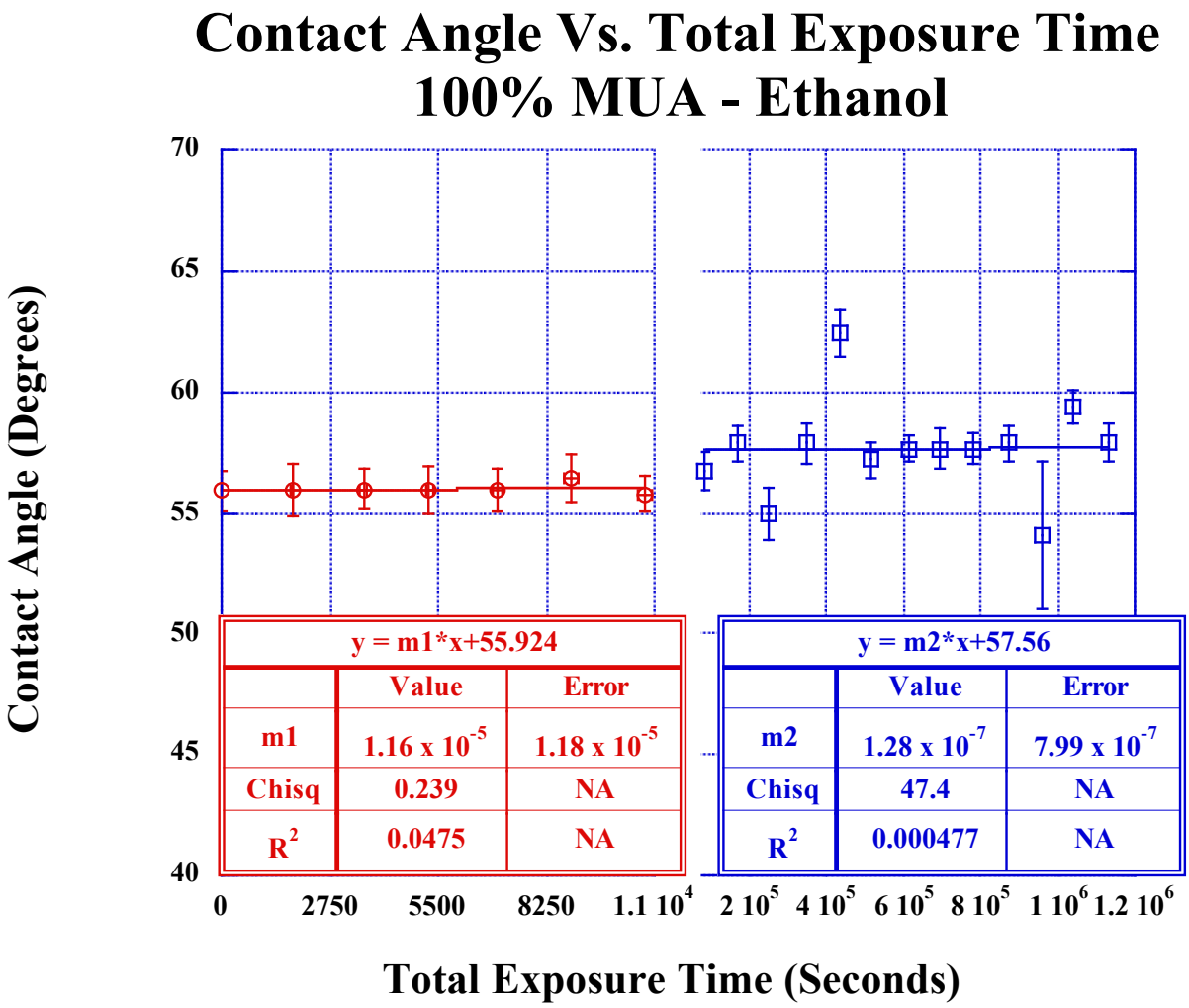

Figure 17: Ethanol caused the contact angle of a 100% MUA slide to increase by approximately 2°. The error bars on the data point for the twelfth day of testing are extremely large because of a poor drop placement in which the left side of the drop had a much larger contact angle than the right side of the drop.

Results for 35% MUA / 65% ODT - Air, Millipore Water, Ethanol:

The next two investigations involved using mixed solution slides. In this, the slide solution was composed of 35% MUA and 65% ODT and the monolayer was attached in the same manner as pure slides (i.e. 100% MUA, 100% ODT). By using mixed concentrations of hydrophilic and hydrophobic compounds, it is possible to obtain intermediate contact angles that lie between the purely hydrophilic monolayer in MUA (55.970° ± 0.828°) and the purely hydrophobic monolayer in ODT (105.44° ± 0.65°).

Using the glasscutter from Dr. Statman's laboratory, I noticed that cutting the glass slides was more difficult than I experienced in the first semester. I believe that the glasscutter was much duller than in the Fall of 2013, probably from overuse in the other experimental laboratories. As a result, the glass slides were not nearly as symmetrical for the spring investigations compared to the Fall investigations. Some pieces were sharp, and broke into smaller pieces upon cutting. Although the pieces were not symmetric to each other, it did not affect the ability of the hydrophobic monolayer to correctly attach.

Slides exposed to air demonstrated a stable contact angle over the period of the investigation similar to the 100% ODT and 100% MUA investigations. The Millipore water and ethanol decreased the contact angle significantly as time progressed. This is similar behavior to the 100% ODT slides. Figures 18, 19, and 20 show how the contact angle was affected as a function of time. Looking at these Figures, the R^2 values describe the ability to predict behavior of data. For example, the 35% MUA / 65% ODT exposed to air graph shows an R^2 value of .031194. An R^2 value equal to zero means that knowing the total exposure time (X-variable) does not help in predicting the contact angle measurement (Y-variable). Thus, the best fit curve is best described by a horizontal

line through the data points. An R^2 value equal to 1 implies that the fit perfectly predicts the behavior of the contact angle as a function of time (Taylor, 1982).

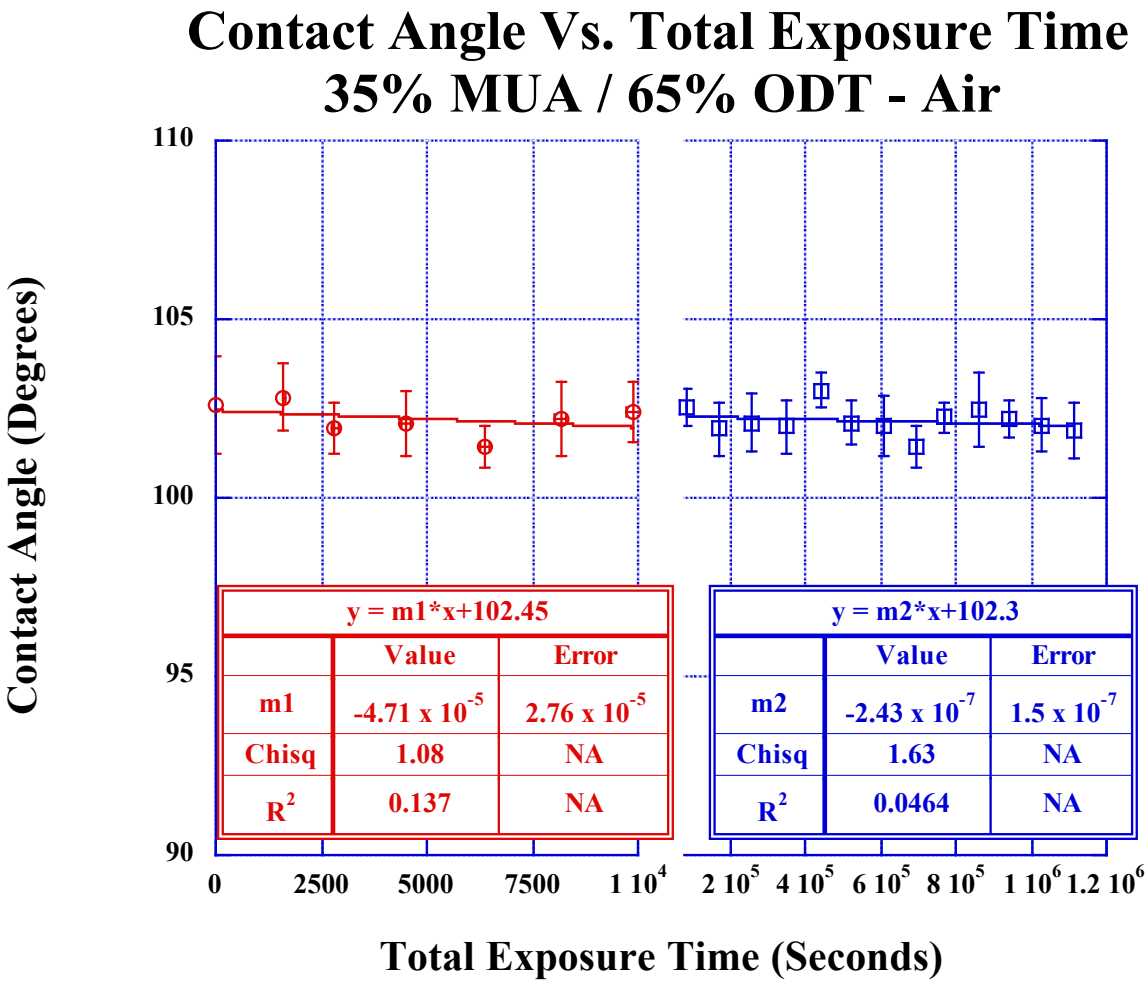

Figure 18: When exposed to air over an extended period, the contact angle for 35% MUA / 65% ODT was stable. This was the same behavior exhibited in the pure slides for 100% MUA and 100% ODT. There were some instances where the measurements differed significantly; however this could be caused by daily laboratory fluctuations such as temperature and dust.

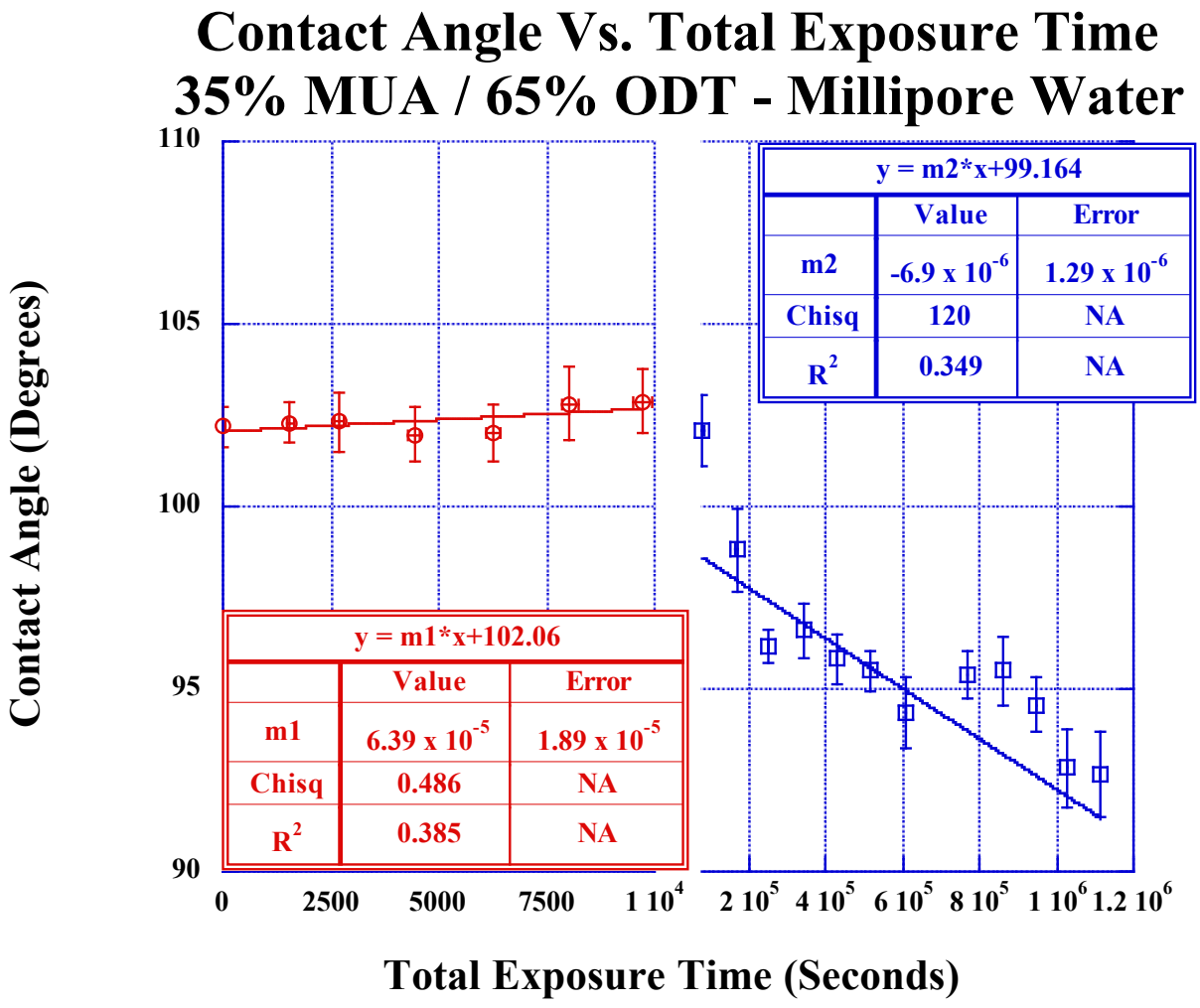

Figure 19: Millipore water caused the contact angle of 35% MUA / 65% ODT to decrease drastically over a period of 14 days. Although relatively stable on the first day of testing (the left side of the graph before the break in the X-axis), the contact angle was not stable for prolonged periods when exposed to Millipore water.

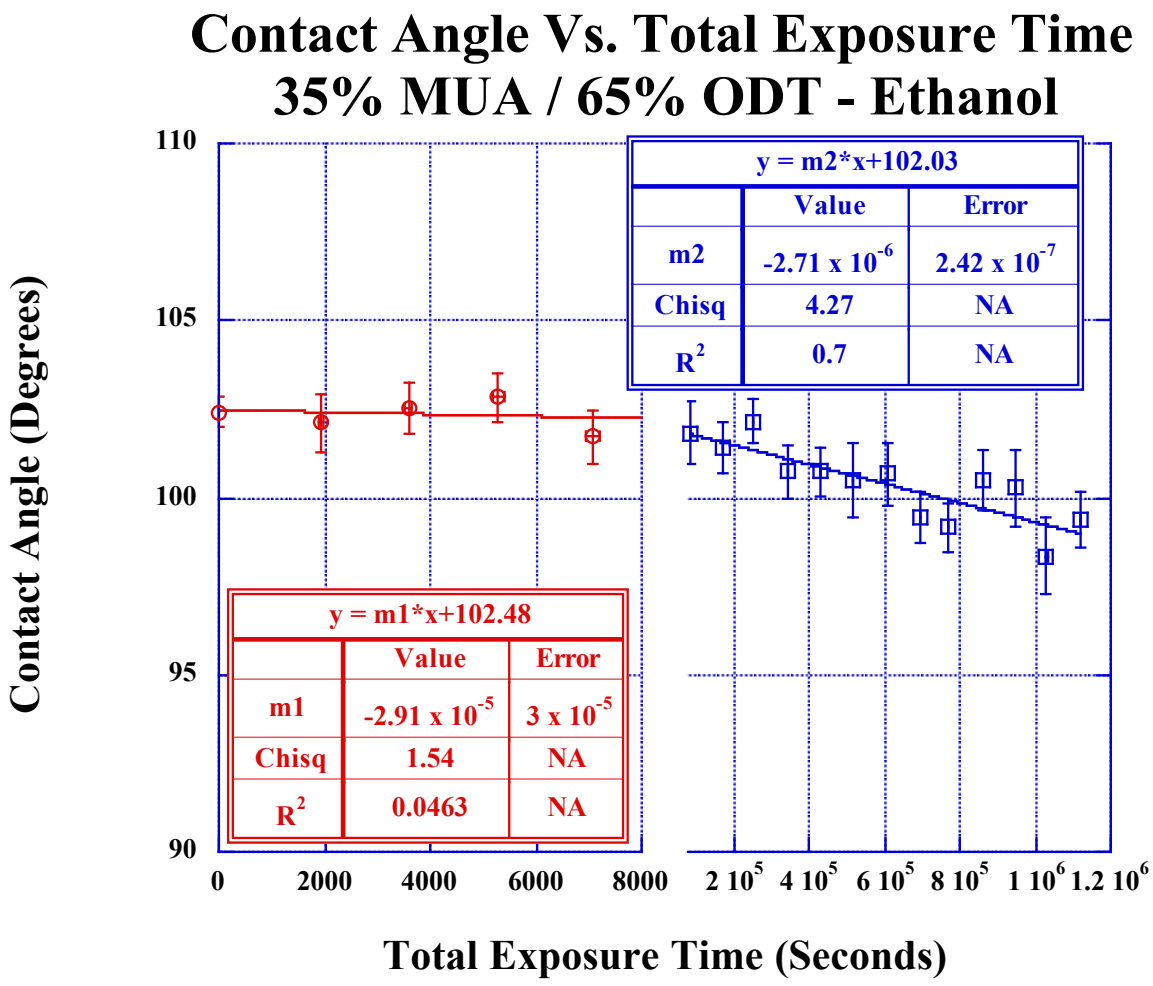

Figure 20: Similar to 100% ODT submerged in ethanol, the 35% MUA/ 65% ODT slide showed a slight decrease of about 2° over the course of the investigation. Initially, the contact angle started at (102.43 ± .41) °, and ended on day 14 at (99.38 ± .79) °.

Results for 40% MUA / 60% ODT - Air, Millipore Water, Ethanol:

The last investigation involved 40% MUA mixed with 60% ODT. The results were comparable to the previous investigation on 35% MUA / 65% ODT because they differed by only 5% in the amount of hydrophilic and hydrophobic compounds used for the making the slide solution. The reason for choosing two mixed samples with approximately the same composition of hydrophilic and hydrophobic compound was based on the fact that Dylan McNany, a fellow physics senior, researched the depletion layer using SPR for 35% MUA/ 65% ODT and 40% MUA / 60% ODT sample slides**.**

Also, as mentioned in the results for the previous investigation involving 35% MUA / 65% ODT, it was difficult to cut the gold-coated slides to symmetric pieces. The asymmetric pieces were delicate in addition to being sharp, and thus required an additional amount of time to ensure that they would not break during testing. Unfortunately, the slides used in the 40% MUA / 60% ODT investigations exposed to air and water broke when I was placing them back into their respective test tube vials. However, the broken-off pieces were small enough that there was still a large enough piece to which I could effectively place the drop of water using the irrigation needle and measure the contact angle.

Similar to the 100% ODT and 35% MUA / 65% ODT investigations, the 40% MUA / 60% ODT slides experienced a stable contact angle when exposed to air and an unstable contact angle when submerged in Millipore water and ethanol. Initially, the contact angle on the first day of testing when exposed to Millipore water was 99.344° ± 0.827°. On the last day of testing, the contact angle decreased to 93.628° ± 0.904°. These results are illustrated in the following Figures 21, 22, and 23.

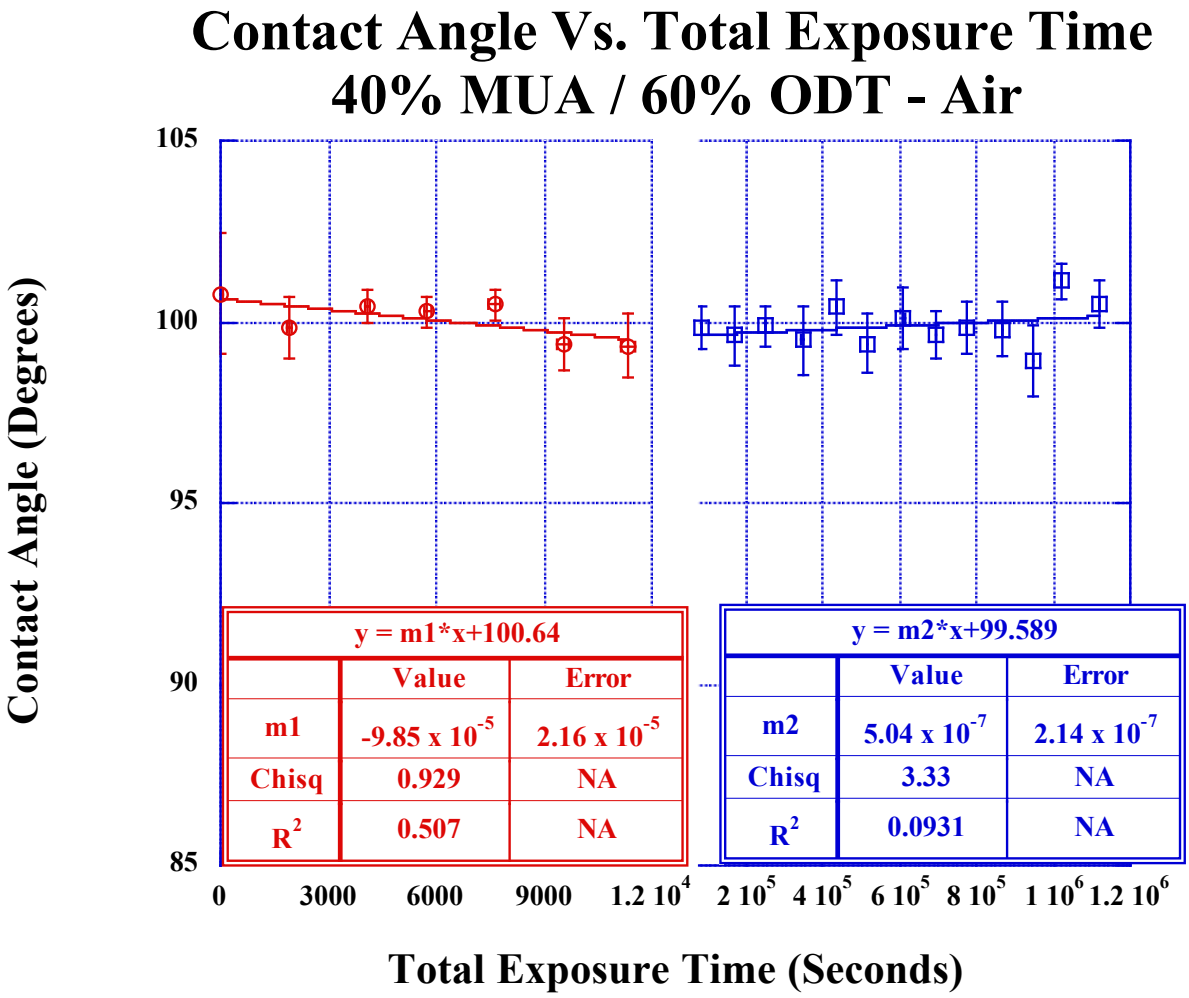

Figure 21: As demonstrated before in the pure samples and the mixed sample (35% MUA / 65% ODT), the contact angle was stable as a function of time. The starting contact angle for 40% MUA / 60% ODT was approximately 2° less than the starting contact angle for 35% MUA / 65% ODT, which makes sense because it had 5% more hydrophilic compound (or 5% less hydrophobic compound).

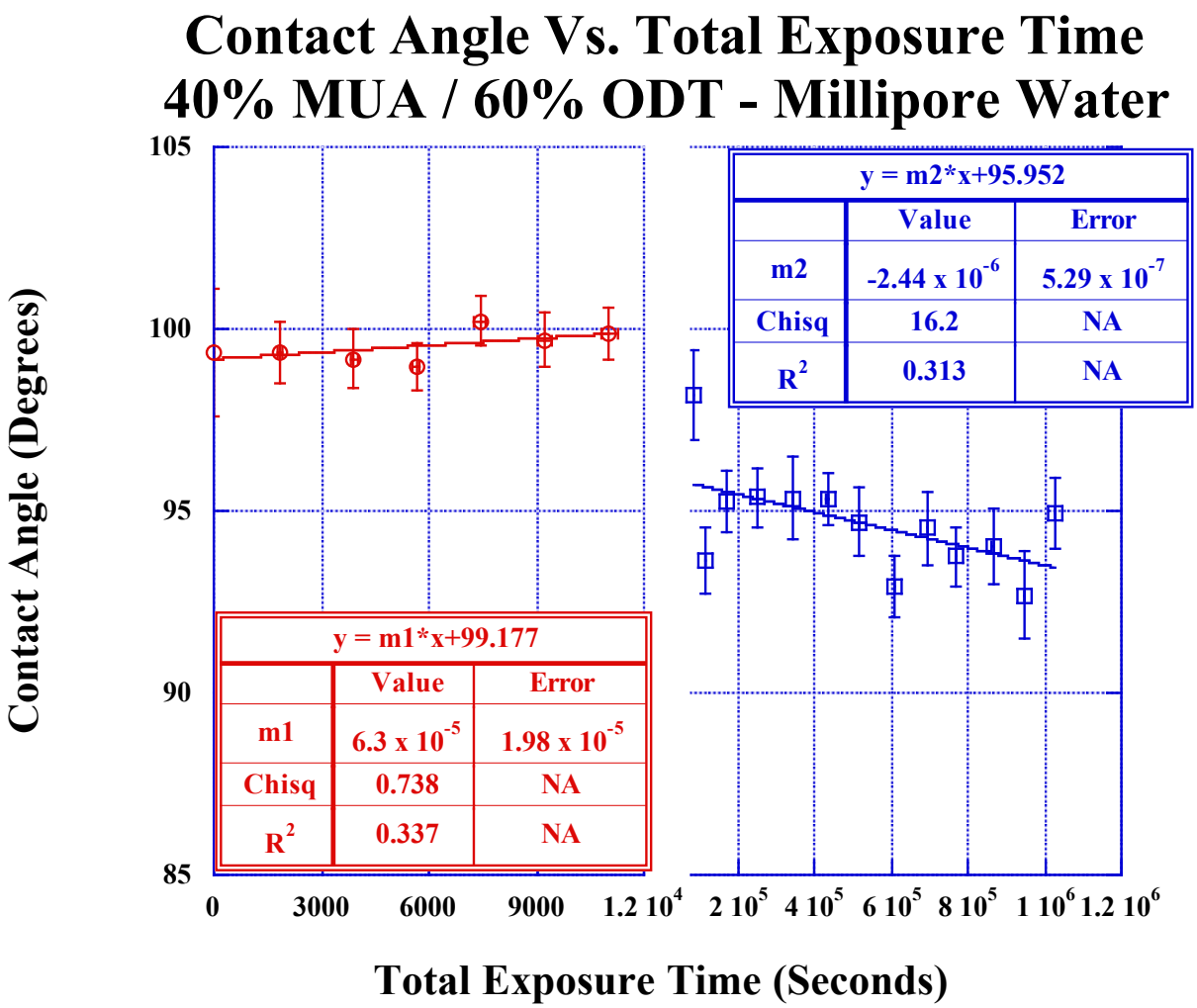

Figure 22: The contact angle of the 40% MUA / 60% ODT slide exposed to Millipore water showed a sharp decrease after the first day of testing. Therefore, when exposed to Millipore water for small periods, the contact angle remained stable; but as total exposure time increased, the contact angle decreased.

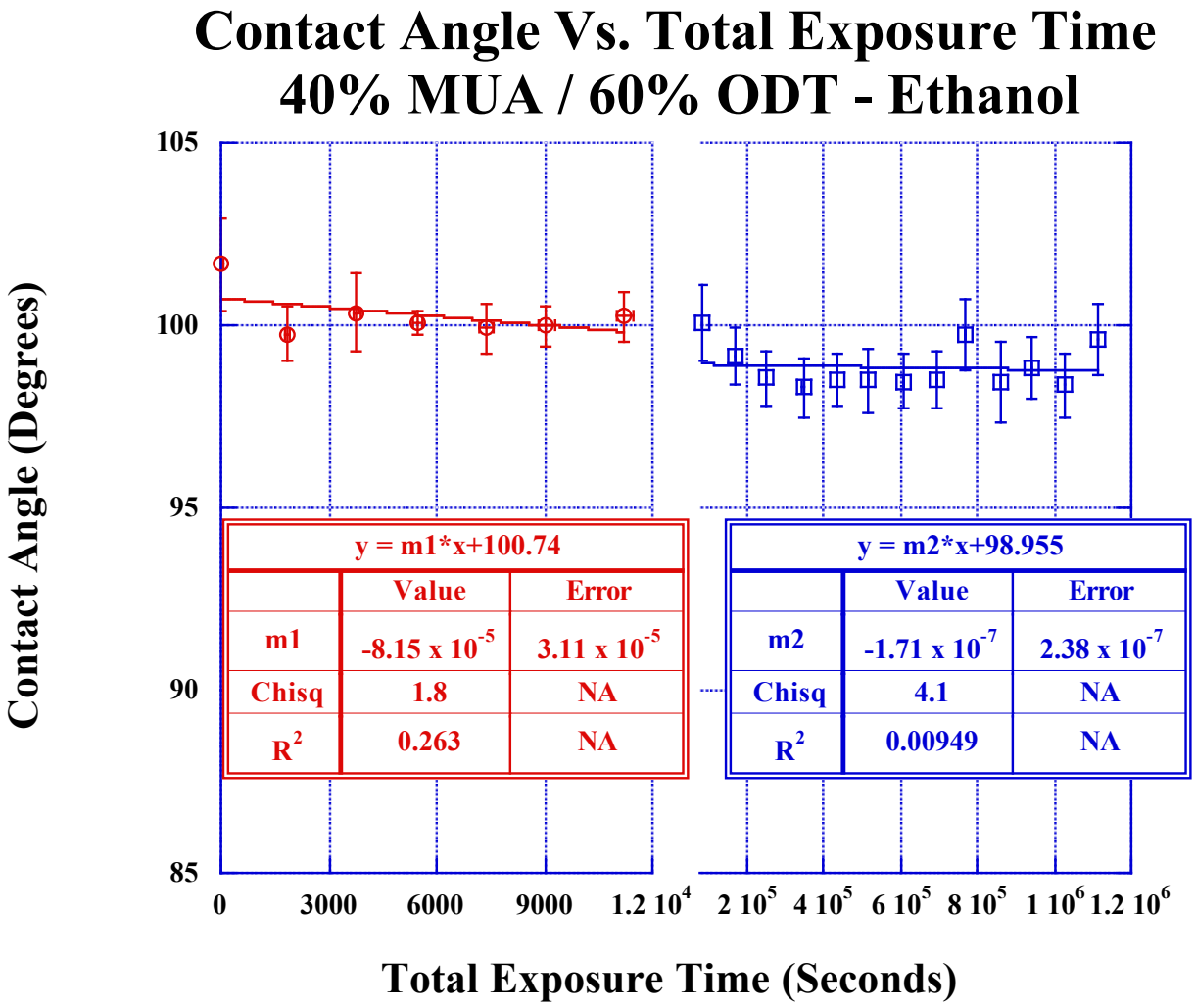

Figure 23: The contact angle slightly decreases, and the change becomes significant on the fourth and fifth days of testing. These results are comparable to the results shown in 100% ODT and 35% MUA / 65% ODT. Therefore, ethanol has a clear effect on both pure and mixed slides.

Sources & Propagation of Errors:

The uncertainties mentioned in the contact angle and the total exposure times derive from random errors and possibly systematic errors. Random errors include the day-to-day fluctuations in the lab such as any contaminants or impurities in the lab atmosphere that day or dust particles that may come into contact with the sample slide. The lens wipes provide a source of random error as sometimes the wipes leave behind fibers, which can skew the results as shown below in Figure 24.

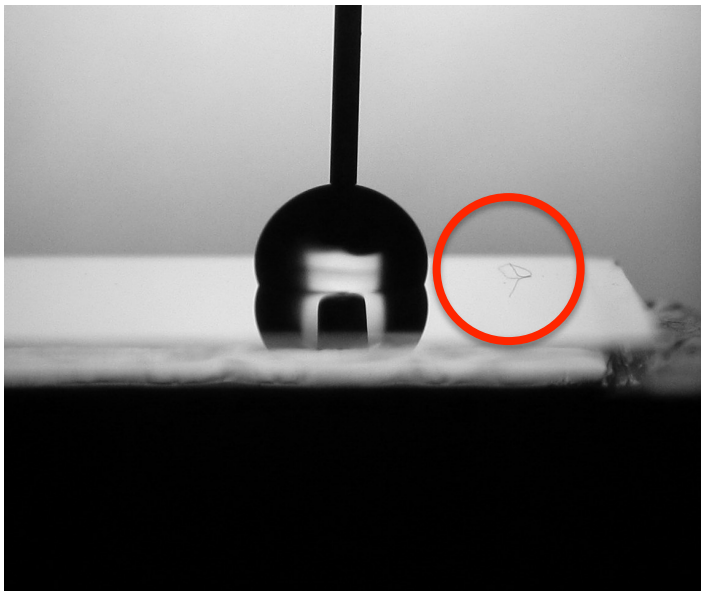

Figure 24: Example of a lens wipe fiber resting on the sample slide. The fiber appears to the right of the drop of water. If the water droplet is placed on a lens fiber, then the contact angle will be skewed.

In addition, there exists some variability in the compounds when making the respective solutions for pure and mixed slides. The operator's ability to render the triple point of contact also offers an error of definition because my ImageJ dot placement could be different from another operator's placement. Systematic errors could exist within the system such as a chromatic aberration on the convex lens or digital camera lens. These

errors are potentially difficult to distinguish if the hardware is not clearly defective. A possible method for diagnosing systematic error is by swapping out the defective hardware, replacing it with new equipment, repeating trials, then comparing results.

The contact angle uncertainty is propagated using the definition of standard deviation,

$$\sigma = \sqrt{\frac{1}{(N-1)}\sum_{i=1}^{N}(x_i - \mu)^2}, \tag{5}$$

where *N* is the total number of pictures analyzed, x_i is the individual result for the image, and μ is the average value. It is important to note that this definition of the standard deviation uses the coefficient $\frac{1}{(N-1)}$ as opposed to $\frac{1}{(N)}$. The *N-1* definition is a more conservative approach to determining the standard deviation. For example, having *N-1* in the denominator results in a larger standard deviation due to the division by a smaller number as compared to having *N* in the denominator (Taylor, 1982). The total time exposure time uncertainty is propagated assuming dependent values. For example, when propagating error for the equation,

$$x + y + z = t_{total}, \tag{6}$$

the t_{total} uncertainty would be propagated by adding each individual uncertainty of *x, y,* and *z* such that

$$\delta x + \delta y + \delta z = \delta t_{total}. \tag{7}$$

I treated the total exposure time as dependent rather than independent because each additional time step relies on the previous time step. Also, I made sure to use the same stopwatch for the entire experiment.

Analysis & Conclusion:

After performing the four slide stability investigations, it is clear that Millipore water and ethanol have a significant impact on the contact angle, thus rendering sample slides unstable over extended periods when exposed to Millipore water or ethanol. Physics, in general, seeks for an ultimate explanation for why things work the way they do. What could be the cause for instability in these sample slides? Could there be physical or chemical phenomena at work? Although the answers to these questions may be a combination of causes, it is undeniable that other research and literature can help understand the reason for slide instability.

Evans, Sharma, and Ulman present research describing the contact angle stability and the potential effect of reorganization of monolayer surfaces. The first experiment focuses on stability tests involving a self-assembled monolayer of 11-Hydroxylundecane-1-thiol (HUT). Evans, Sharma, and Ulman render the contact angles using a Rame-Hart NRL 100 goniometer. The HUT, when brought into contact with gold (Au), forms an OH-terminated monolayer. Shown below in Figure 25 is a graph of the observations for the HUT/Au monolayer. The advancing and receding contact angles increase as a function of time. This experiment uses tetrahydrofuran (THF) as the solvent for the HUT/Au-prepared slides, and it is performed testing the stability of the slide in ambient air.

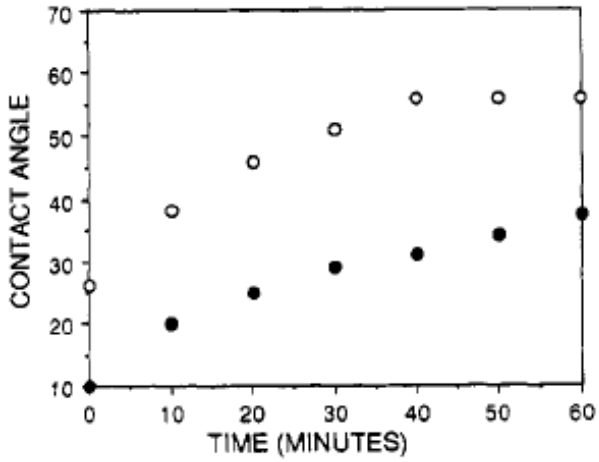

Figure 25: The contact angle for the HUT/Au monolayer experiences an increase over a period of 60 minutes. The open circles represent the advancing contact angle, while the dark, filled-in circles represent the receding contact angle (Evans, Sharma & Ulman, 1990).

Evans, Sharma, and Ulman also describe how using mixed monolayers containing larger amounts of HUT and lesser amounts of 1-dodecanethiol (DDT) shows similar, unstable contact angle behavior. Using a mixed solution of HUT and DDT allows one to introduce different amounts of carboxyl-terminated (-OH) and methyl-terminated (CH_3) thiol groups. Bain and Whitesides studied mixed monolayers using ethanol as the solvent instead of THF. They describe a "preferential adsorption" for low OH concentration solutions (i.e. hydrophobic) with respect to the OH concentration of the monolayer.

Two possible explanations put forth for the observed change in contact angle are the following: contamination and reorganization (Evans, Sharma & Ulman, 1990). Since their study was performed in ambient air, the proposed source of contamination is from hydrocarbons. This idea is based on the idea that hydrocarbons in the air like methane could be adsorbed, and thereby force the more polar OH groups to "bury" in the monolayer to reduce the surface energy. Thus, if the polar OH groups are buried in the

monolayer, then the nonpolar thiol groups will be exposed at the surface of the monolayer to form a more hydrophobic contact angle measurement.

To test if surface contamination was truly at work in their experiment, Evans, Sharma, and Ulman employ a vacuum chamber. The contact angle of a purely hydrophilic monolayer was 22°. Next, the sample was placed in a vacuum chamber, and the pressure decreased to 10^{-5} mbar. 72 hours later, the contact angle was 37°. Thus, surface contamination seems less likely compared to molecular reorganization because of the vacuum chamber environment (Evans, Sharma & Ulman, 1990).

Then, Evans, Sharma, and Ulman tried to restore the contact angle of the pure hydrophilic sample used in the vacuum chamber experiment to the original value of 22°. The sample was soaked in Millipore water for 4 days, but the contact angle did not change. However, in a separate experiment, Evans et al. observed a SAM consisting of methyl 23-trichlorosilyltricosanoate. The contact angle decreased 10° from 57° to 47°. Evans, Sharma, and Ulman describe how it is unclear why these results conflict, but offer that microscopic phenomenon is likely at work causing a reorganization of molecules within the monolayer. Their theory for the molecular reorganization was supported by X-Ray photoelectron spectroscopy (XPS), which showed reduced carboxyl content (OH) at the surface of the monolayer.

Other studies conducted in monolayer stability were performed by Laognuan, Jamison, and Lee. They describe previous research done by Bain and Whitesides in which the contact angle of a drop of water was affected by pH. Bain and Whitesides found that increasing the pH of the drop of water decreased the contact angle (1989, as cited in Laognuan, Jamison, & Lee, 2011). Porter et al. demonstrated that chain length is

important for monolayer order. It was found that in longer chain length SAMs, the monolayer demonstrated more conformational order and packing density. Shorter chain lengths exhibited greater disorder and a lowering of packing density. Porter et al. described how van der Waals forces were likely the cause for more structure and organization in the chain as a result of increased energy per chain. For example the longer the chain length, the greater the van der Waal force each molecule will experience to the neighboring chain (Porter, 2011, as cited in Srisombat, Jamison & Lee, 2011).

Kanta, Sedev, and Ralston performed an experiment in which octadecyl-phosphonic acid (OPA) formed a monolayer on a titanium surface. Kanta, Sedev, and Ralston use THF as the solvent, similar to Evans, Sharma, and Ulman. First, the contact angle was measured as a function of immersion time in OPA. Interestingly, Kanta, Sedev, and Ralston found that the contact angle increased by approximately 10° over a period of 1,000 minutes. This is best illustrated below by Figure 25.

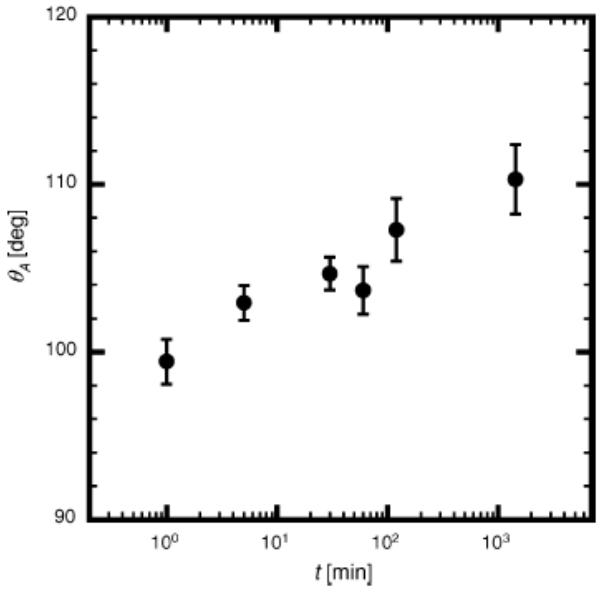

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Figure 25: The advancing contact angle measured as a function of immersion time in OPA. Interestingly, the longer the immersion time in OPA, the larger the advancing contact angle measured. This study used an OPA monolayer (2 x 10^{-4} Molar in THF solution) attached to titanium (Kanta, Sedev & Ralston, 2006).

The contact angle settled at 110°, and would not change after days of immersion. Kanta, Sedev, and Ralston describe that the reason for the increase in 10° in the advancing contact angle is due to chain ordering. For example, after minimal immersion time in the OPA, the chains are disordered; however after about 16 hours the chains have arranged themselves in a more organized fashion compared to the minimal immersion time. The longer the amount of time that the titanium surface is immersed in the OPA solution, the more structured or more ordered the chains arrange.

The same experiment was performed again, except using differing concentrations of the OPA in THF solution: 2×10^{-4} M, 2×10^{-6} M, 2×10^{-8} M, and 2×10^{-4} M at 2° Celsius. Kanta, Sedev, and Ralston found similar results to their first experiment in that the advancing contact angle increased after immersion in the OPA solution. Interestingly, the study also showed that at colder temperature (2°C), the rate of formation of the SAM is slower than at normal room temperature. These results are depicted below in Figure 26. For further stability testing, the researchers used the 2×10^{-4} M concentration because atomic force microscopy showed a much more uniform surface compared to the other concentrations.

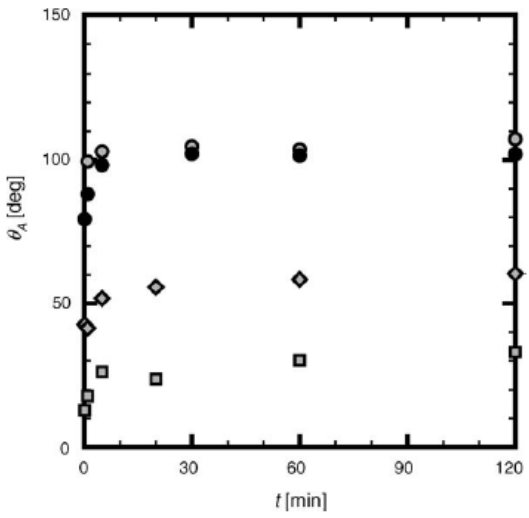

Figure 26: The shaded square is 2 x 10^{-8} M, the shaded rhombus is 2 x 10^{-6} M, the shaded circle is 2 x 10^{-4} M, and the darkened circle is the 2 x 10^{-4} M at 2°C. All exhibit an increase in the advancing contact angle measured as a function of time (Kanta, Sedev & Ralston, 2006).

Next, Kanta, Sedev, and Ralston tested the stability of the OPA monolayer (2 x 10^{-4} M) attached to titanium using exposure to different media: air, water, methanol, ethanol, acetone, cyclohexane, and toluene. The slides were immersed for 6 hours in the OPA solution. Immediately after preparing the sample slides, the contact angle was rendered to be (110 ± 2)°. Then sample slides were submerged in the respective media for 18 hours exposure time. Kanta, Sedev, and Ralston observed that the contact angle decreased slightly for toluene and acetone. For the cyclohexane, the contact angle increased slightly. On the other hand, the contact angles for the OPA slides tested in water, methanol, and ethanol decreased significantly after 18 hours exposure time to the liquids. These results are quantified below in Table 2:

Changes in water wettability of OPA SAMs on titania after 18 h exposure to various liquids

Fluid	ε (25 °C)	Water contact angle before immersion	Water contact angle after 18 h immersion	$\Delta\theta$
Air (control experiment)	1.0	110.0 ± 2.0	111.8 ± 0.9	−1.8
Cyclohexane	2.0	111.0 ± 2.4	111.6 ± 0.4	−0.6
Toluene	2.4	110.0 ± 0.5	107.8 ± 1.4	2.2
Acetone	20.7	110.8 ± 0.9	108.2 ± 2.1	2.6
Ethanol	24.3	110.5 ± 1.9	100.6 ± 1.4	9.9
Methanol	32.6	108.9 ± 2.1	91.4 ± 1.3	17.5
Water	78.5	109.5 ± 2.1	75.1 ± 3.3	34.4

Experimental conditions for the deposition were 6 h immersion in a 2×10^{-4} M OPA in THF. Advancing water contact angles and standard deviations are shown.

Table 2: Contact angle stability tests performed for OPA monolayer exposed to seven different media (dielectrics) over a period of 18 hours. The last column, Δθ, represents the decrease in the contact angle from before immersion to after 18 hours of immersion. Thus, for example air has Δθ = -1.8° because it experienced an increase in the contact angle. Similarly, water experienced Δθ = 34.4° because of a decrease in the contact angle measurement (Kanta, Sedev & Ralston, 2006).

Kanta, Sedev, and Ralston believe that the molecules of liquids (the different dielectrics employed in the experiment) slip into the openings of the adsorbed OPA monolayer, altering the shape or structure of the chains. This agrees with the aforementioned literature of Evans, Sharma, and Ulman and Laognuan, Jamison, and Lee such that the monolayers undergo an adsorption and structural reorganization, which ultimately affects the contact angle measurement.

Lastly, Kanta, Sedev and Ralston investigated the stability of monolayers with respect to heat. This study involved the use of contact angle measurements and XPS. Using OPA monolayers exposed to temperatures of 350°C, contact angle analysis showed that the contact angle was reduced to 0° from the original value of approximately 110°. XPS revealed a decrease in the amount of carbon. Kanta, Sedev and Ralston also investigated the stability of the phosphorus-titanium bond when placed in extremely high temperatures. Phosphorous existed on the surface after exposure to 800°C, but was gone

when temperature was 1,000°C. Kanta, Sedev and Ralston describe thermal decomposition of the monolayer chains (2006).

The three groups of researchers and their stability experiments seek to explain why monolayers become unstable. All three groups describe the primary cause for instability results from events at the molecular level like molecular reorganization, contamination, and chain disorder. Kanta, Sedev and Ralston go one step beyond the other researchers and seek to understand the thermal influence on monolayer stability. Using this literature as a foundation, it is possible to draw conclusions regarding why 100% ODT, 100% MUA, 35% MUA / 65% ODT, and 40% MUA / 60% ODT showed contact angle instability when exposed to three different media: air, Millipore water, and ethanol.

All four investigations showed a stable contact angle when exposed to air. For the hydrophobic samples used in the investigations (100% ODT, 35% MUA / 65% ODT, and 40% MUA / 60% ODT), Millipore water had a significant impact on the monolayer stability: the contact angle decreased considerably as a function of total exposure time. With respect to these same samples, ethanol caused the contact angle to decrease slightly. For the hydrophilic sample (100% MUA), Millipore water increased the contact angle significantly over a period of 14 days. Ethanol, acting on the 100% MUA sample, increased the contact angle slightly. Essentially, the 100% MUA samples exposed to Millipore water and ethanol experienced the opposite behavior in contact angle stability as the hydrophobic sample slides used.

Using the aforementioned literature from the three research groups, then it is clear that molecular phenomenon is at work. Why did the ODT and MUA sample slides

experience drastic changes in the contact angle as a function of total exposure time to Millipore water and ethanol? Many times in chemistry and physics, the answer comes down fundamentally to energy favorability. Based on descriptions given by Evans, Sharma, and Ulman, this appears to be the case.

Concentrating on the 100% MUA investigation, it is understood that MUA forms a hydrophilic monolayer when brought into contact with gold. It is energetically favorable for the water molecule to interact with the surface based on the description of Young's equation. The surface of the hydrophilic monolayer has a higher surface energy compared to the surface tension of the drop of water. Thus, the drop of water spreads out when placed on the MUA monolayer because the molecules in the monolayer are seeking to reduce their high energy as described by hydrophilic surfaces in Young's Equation. From Kanta, Sedev and Ralston, it can be understood that the Millipore water molecules seem to be slipping into the spaces between the MUA monolayer chains. Similarly, Kanta, Sedev and Ralston describe how ethanol, like water, is small enough to be able to penetrate into the spaces between chains. As stated before, water is a polar molecule. Ethanol on the other hand is slightly more complex. Ethanol contains an OH end, which would suggest it is a polar molecule. However, it also contains a CH_3 end, which would suggest a nonpolar molecule. Therefore, ethanol contains both a polar and nonpolar end. In order to keep the surface energy at a minimum, then according to Evans, Sharma, and Ulman, the polar OH groups may "bury" in the monolayer thus affecting the tilting of the chains (1990). The burying of polar OH groups implies a decrease in monolayer surface percentage of OH as shown in Figure 27. For the larger contact angle, there is a lower percentage of surface polar OH groups. Conversely, for the smaller contact angles, there

is a larger percentage of surface OH groups present in the monolayer (Evans, Sharma, & Ulman, 1990). Instead, it becomes more energetically favorable for the drop to interact with itself by trying to "bead up" since the surface free energy is lower than the initial state. This effect is manifest in the 100% MUA sample slide exposed to Millipore water and ethanol through an increase in contact angle as a function of total exposure time.

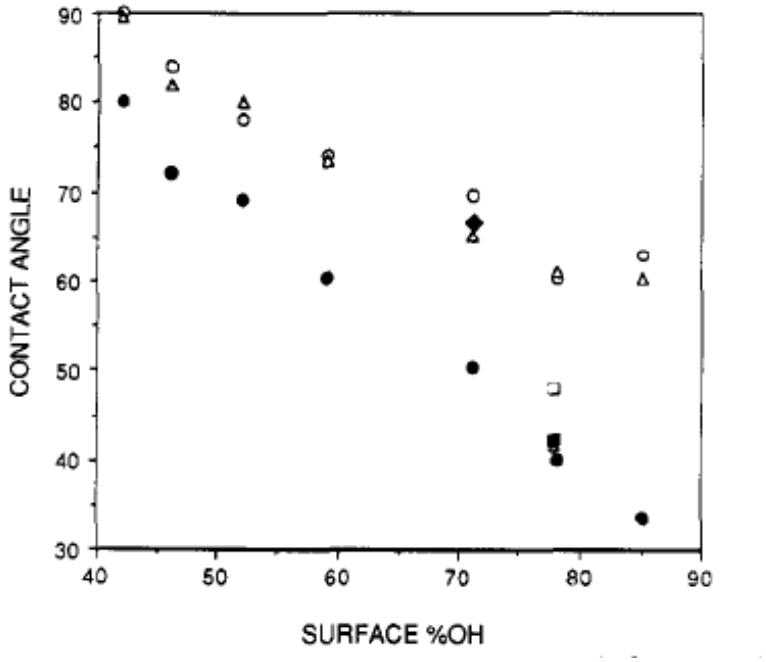

Figure 27: The contact angle is graphed as a function of surface percentage of OH. The surface percentage of OH was observed using XPS. The open circles describe samples stored at high humidity, and the triangles describe samples stored at low humidity for three days. Dark circles describe newly-prepared samples. The dark rhombus represents samples treated with acetic acid then washed before measuring. The dark square represents samples stored at -20°C, and the open square represents samples stored in a freezer then exposed to ambient air for 24 hours prior to measuring (Evans, Sharma, & Ulman, 1990).

Next, the 100% ODT, 35% MUA / 65% ODT, and 40% MUA / 60% ODT samples exhibited a decrease in the contact angle as a function of time when exposed to Millipore water and ethanol. Applying the argument put forth by Kanta, Sedev and Ralston that the smaller molecules like water and ethanol are able to penetrate the space

between chains, then it is possible to explain these three hydrophobic monolayers in the same manner as the hydrophilic monolayer presented above: energy favorability!

Since these three samples are hydrophobic as quantified by contact angle measurements, then it is reasonable to expect that the chain endings be mostly dominated by CH_3, a nonpolar molecule. Therefore, the initial surface free energy of the hydrophobic monolayer is much lower than the hydrophilic monolayer case. The nonpolar CH_3 ends of the chains do not prefer to interact with the water and consequently get "buried" deeper in the hydrophobic monolayer. With polar water and semi-polar ethanol molecules slipping in between the chains, the monolayer seeks an energy minimum but instead the surface energy increases leading to decrease in the contact angle of the hydrophobic surface when exposed to Millipore water and ethanol for extended periods.

The results of these four investigations in slide stability give insight into how to handle sample slides in the laboratory. It is safe to store sample slides on the laboratory shelf for extended periods without bringing into question the stability of the self-assembled monolayer. However, there are further implications for handling slides when performing Surface Plasmon Resonance experiments.

For example, if an SPR-water trial is performed, then the sample slide should be removed from the setup and stored in a test tube vial, where it will not be exposed to water for a long period. Specifically, a slide should not be left in contact with Millipore water on the SPR setup over a weekend as the Millipore water alters the contact angle significantly. Additionally, these results give a vote of confidence in regards to the slide refreshing process. As described in the methodology section, the slide refreshing process

uses ethanol instead of KOH to clean the surface of a slide without damaging the gold or monolayer. The results show that ethanol does not begin to have significant effects on the contact angle until approximately the third day of total exposure. Thus, refreshing the slide using ethanol should not have significant alterations to the contact angle since the exposure time is much less compared to three days.

Future Work

Investigating slide stability is an ongoing and developing research pursuit. There is a vast amount of different variables that one could study in relation to the stability of sample slides. One of the first examples I thought of was to study the contact angle as a function of temperature or possibly humidity. The temperature in the Materials Science Laboratory fluctuates frequently. Since the contact angle setup is now portable, one could move the setup to another room with controlled temperature and see how the contact angle is affected, if at all. Also, one could control the temperature of the sample slide using a hot plate as well. The sample slide could be placed in a small beaker and filled with Millipore water. Then the small beaker could be placed on a hot plate or in a bowl of ice. After measuring the temperature of the Millipore water, the contact angle could be imaged, analyzed, and graphed as a function of temperature.

Another interesting research opportunity I thought of when performing the initial 100% ODT samples involves modifying the slide preparation process. Slides are prepared by submerging a gold-plated slide in the compound of choice (ODT, MUA, or a mixture of both of them). The lab procedure, written by Ariel Statman, describes how the slide must be submerged for a minimum of 30 minutes. As I was performing my 100% ODT stability tests, I wondered how the contact angle would be affected if the slide was submerged in the compound for an extended period of time. For example, one could investigate how the contact angle changes when the slide is submerged for 1 hour as opposed to some larger amount of time such as 24 hours. Altering the total time of submersion could have implications for not only the contact angle measurements, but also for the Surface Plasmon Resonance experiments. Both experiments (contact angles

and SPR theory) work together in attempting to understand if there is a correlation between the contact angle and the thickness of the depletion layer.

There are also some design and engineering improvements that could be made to the contact angle setup. For example, the setup would be much easier to carry if there were handles attached to it, instead of having to hold it from the bottom of the aluminum breadboard. Also, the diffuser box could use some attention in regards to the corners and where the sides come together. There are some open spaces where light can escape from the diffuser box. Although the escaping light does not significantly impact contact angle imaging, the box would be more complete if as little of light as possible escaped from the box.

Appendix

Setting up the Contact Angle Apparatus:

When the contact angle setup is not in use, it can be stored away on one of the shelves. Be sure to use both hands when carrying the setup because it is heavy. However, when it comes time to set up the apparatus for testing, the Thorlabs devices need to be assembled in specific locations on the aluminum breadboard. I have drilled and tapped the approximate locations of where to attach the devices. There are additional drilled and tapped holes where one could modify the setup in the future. Furthermore, there is a tap set in the laboratory if one chooses to add more holes.

The distances used for placing the Thorlabs devices are the same distances that Lamour et al. illustrates below in Figure 28, except for the distance of the digital camera to the convex lens:

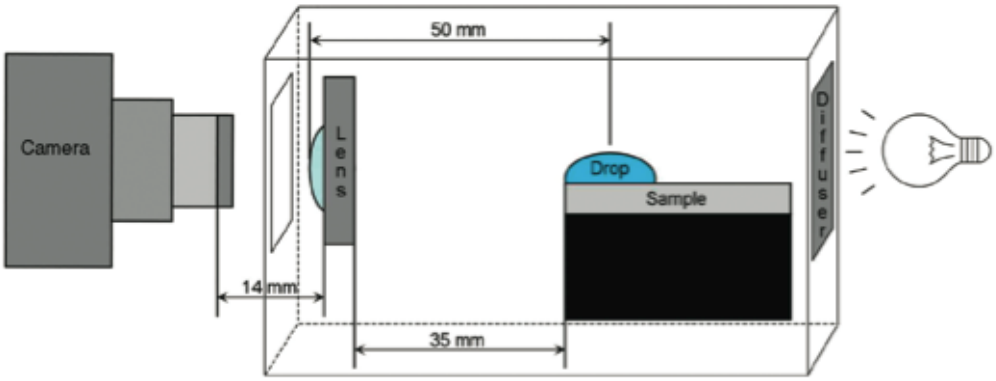

Figure 28: Illustration of the experimental setup used in Lamour et al. This is the foundation for the contact angle apparatus used in Dr. Poynor's Laboratory.

This setup is slightly modified in that the diffuser box does not rest atop the lens and sample and the focal length of the digital camera is not 14mm. The setup in Dr. Poynor's Lab places the diffuser box over the light source. The lens employed is a 50mm convex focusing lens. For the images, I rented a digital camera from the Pelletier Library with a focal length of 5.0 mm as opposed to the 14mm digital camera employed in Lamour et al.

Information for Ordering Parts:

I purchased the aluminum breadboard from http://www.cut2sizemetals.com. This site has different types of metal available for purchase, and they allow for customized cuts. I purchased the black acrylic glass for the diffuser box from a provider on eBay. I tried finding the black acrylic glass at Home Depot and local hardware shops, but neither had any in stock. The provider on eBay offered a fair price, and gave the option for up to five free cuts. The screws, L-brackets, nuts, and washers were easily obtainable from Home Depot.

The Light Source:

I experimented in the Fall 2013 with different light sources. The goal of my Fall 2013 semester was to design a new box that could eliminate the possibility of a fire. In addition to altering the diffuser box material from cardboard to acrylic glass, I chose to experiment with altering the light source. I tried using LED lamps, compact fluorescent bulbs, and the original incandescent light bulb. I found that the incandescent light source gave a good, smooth white background for the images, but it contributed a lot of heat to the diffuser box. The LED lamps were the most economical option because of low watts used compared to the incandescent and compact fluorescent bulbs. However, the LED lights provided a "sterile" and very bright white background that made analyzing the

images tough. The best option, in my opinion, was the compact fluorescent because it was economical and provided a good background for analysis. This decision is rather subjective, however, and it can surely be changed if the operator feels that a different light source is better for their visual needs.

Tips for Performing Stability Tests:

Performing the stability tests requires analyzing numerous images. I recommend using a flash drive to back up all the data. Also, prior to imaging, it is important to make sure that the contact angle setup is properly calibrated. To do this, simply use the bare gold slide and place a drop of water using the tensile method as described in the methodology section. Proceed to take a few pictures, upload them from the camera to the computer, and observe how the images appear. It is important that the images appear clear enough that one can determine the points of contact on the left and right sides of the drop, especially when having to image and analyze thousands of pictures of drops.

Also, it is important that the images have low reflection from the gold slide below. Sometimes the reflections cause the image to appear blurry, faded along the edges of the drop, or even red or blue along edges. One tip to reduce blurriness or reflection when it happens is to only adjust one Thorlabs device at a time. Altering several devices makes it difficult to identify the problem(s). After making the one adjustment, then simply repeat the process of placing a drop, imaging, and observing the drop on the computer until a sharp picture is attained. Another tip for reducing blurriness and reflection is to place the black piece of cloth in between the sample and the diffuser box. Sometimes the flash from the camera causes a reflection off of the shiny, aluminum breadboard and makes the drop appear brighter.

Renting the Digital Camera:

The Pelletier Library allows students to rent digital cameras for three days. Then, the student must renew the camera or return it. Over a two week study, I found myself having to take the camera back to the Library every few days to check it out, renew, and check back in. I had to take the camera off of the camera stand and recalibrate each time I needed to renew the camera. I suggest asking Dr. Poynor to check the camera out for some extended period of time so that one does not have to deal with calibration issues prior to imaging the sample slides. Also, make sure that the Library rents the USB cord to upload the images to the computer.

Uploading Images & Software:

When I performed my stability tests, I found the software Picasa to be very easy to work with when analyzing the images. This software is free and is offered by Google. It allows one to crop the pictures down and make them appear in only black and white. Changing the color is a necessary step before using ImageJ to analyze the contact angles. Other picture editing software do exist such as Adobe, Preview, etc.

Installing ImageJ:

The computer in Dr. Poynor's Laboratory has ImageJ installed on it currently. However, I found it much easier to install the program on my personal laptop and analyze images when I was not in the Lab. The ImageJ software can be found at the following web address: http://imagej.nih.gov/ij/download.html. The download is available for Mac OS X, Linux, and Windows operating systems. After the download is completed, it is important to download the Drop Analysis plugin for ImageJ. This plugin is necessary for rendering the contact angles. The plugin can be found at:

http://bigwww.epfl.ch/demo/dropanalysis/. Once the plugin is downloaded and installed, there appear two options: “Drop analysis- Dropsnake and “Drop analysis-LB-ADSA.” The Dropsnake option is the method I used in analyzing all of my contact angles based on the curve-fitting effect. The LB-ADSA uses a different fitting effect based on Young’s Equation.

Step-By-Step Procedure to Analyze Contact Angles:

1. Condition the irrigation needle by suctioning then dispensing Millipore water out of the syringe for three cycles.
2. Using the bare gold slide, calibrate the setup to ensure a clear image.
3. Remove the bare gold slide and place the sample slide on the stand.
4. Place a drop of Millipore water using the tensile method.
5. Image the advancing contact angle by taking approximately 7-10 images using the digital camera.
6. Upload/import the images to a computer.
7. Using Picasa (or another picture editing software), crop the images down to view the drop of water on the sample slide only.
8. Change the color of the image to black and white only.
9. Repeat steps 7-8 for every image.
10. Next, export the modified images to a folder on your desktop or flash drive
11. Using ImageJ, open one image at a time. Click on the Drop Snake plugin
12. Place the first dot on the left triple point and place dots around the edge of the drop of water until the right triple point dot. Usually 6-10 dots are necessary, but this is open to the operator’s decision if he or she prefers more dots.

13. After the last dot is placed (the right triple point), click the first dot. It should appear in red.
14. Then adjust the fit of the dot placement until a satisfactory fit is attained around the edge of the drop of water. The upper left-hand section of the screen displays the "contact angle left and contact angle right."
15. Using Microsoft Excel or Synergy Kaleidagraph, enter the name of the image file and the two measurements for the contact angles.
16. Repeat steps 11-15 for all of the images taken.
17. At the conclusion of rendering the contact angles, use the formula functions to determine the following for the contact angle:
    a. Mean
    b. Standard deviation
    c. Standard deviation of the mean
18. Save the results.

Handling the KOH Cleaning Baths:

Be sure to wear safety goggles, a lab coat, and two pairs of gloves when handling the KOH cleaning solution. The first pair should be the latex or nitrile-based gloves, and the second pair should be the disposable polyethylene gloves. The Nalgene containers can be tough to open some times, so only try to open them inside the fume hood in case of a spill. Keep the fume hood closed to the 18-inch line indicated on the left-hand side.

Also, when taking glassware out of the KOH baths after cleaning, place them on a sheet of aluminum foil. Rinse them quickly using Millipore water as described in the Methodology section. The aluminum is reactive with the KOH and produces hydrogen

gas upon contact, so it is not a good idea to allow leave the aluminum foil exposed to the KOH for long periods of time.

If the KOH bath appears a very dark brown color, then it is probably time to dispose of the bath and make a new one. Make sure to label the old KOH bath as waste. When making a new bath, place approximately one cup of KOH granules into a clean Nalgene container. Fill the rest of the container with isopropyl alcohol and allow sitting overnight before using as a cleaning bath.

Additional Notes on Cleaning Glassware:

The beakers and test tube vials are small enough to fit in the KOH containers. Do not place the plastic test tube covers into the KOH. The volumetric flasks and graduated cylinder are too big and oddly shaped. To clean the volumetric flasks and graduated cylinder, use the smaller glass funnel and pour the KOH cleaning solution into the item(s) to be cleaned. I found it to be easiest to pour the KOH into the graduated cylinder and volumetric flasks by using a separate beaker. This helps to reduce the possibility of a spill. After filling the item(s), cover the tops of the volumetric flask or graduated cylinder with aluminum foil. Then, simply follow the cleaning procedure like the other pieces of glassware. The glass tops for the volumetric flasks can be placed into the KOH containers.

Some Last Words of Wisdom:

My first three years at Allegheny College, I was set on doing the 3+2 Cooperative Engineering Program. As I ended my junior year, I changed my mind at the last moment and decided to stay for my senior year. This meant that I had to do the dreaded “comp.” After going through two semesters of comping, I am proud of my decision to stay four

years. I realized that this kind of research opportunity cannot be found at every other institution. At Allegheny, one gets the opportunity to design and perform his or her own research under the guidance of an advisor. I believe this experience has greatly prepared me for graduate school in mechanical engineering. Some last pointers or advice I can suggest are the following:

- Don't be afraid to ask questions!
    - Talk to Dr. Poynor. She is more than willing to help answer any questions about the Lab or just life in general.
- Be smart, but have fun in the Lab!
    - Play music while you work (Preferably Rolling Stones Radio)
- Ask other Poynor Lab Crew members for help.
    - Whether it is questions regarding journal articles, peer reviewing, or analyzing data, ask other students in the Lab for help.
- Remember to follow the three C's: Stay cool, calm, and collected.

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