Salt Effects on the Degradation of a Self Assembled Monolayer



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A Senior Comprehensive Project

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Dr. David Statman

Pledge:

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Abstract

When a drop of water is placed on top of a hydrophobic or hydrophilic surface, forces act upon the water molecules in the drop and either push it away to minimize contact and make the drop bead up or it pulls it closer and flattens out the droplet. By looking at the contact angle the drop makes with the surface, we can determine how hydrophobic/philic the surface is. The goal of this experiment is to use two self assembled monolayers as the surface. The hydrophobic substrate are octadecanethiol and the hydrophilic one are mercaptoundecanoic acid. Then use contact angle measurements to observe how the monolayers degrade and lose their hydrophobicity over time as they are exposed to different concentrations of multiple salt solutions.

Introduction

Water is essential to life. That alone can be easily seen when we observe the human body. An adult is typically 60% water, and if that is not enough to prove water's importance, simply look at the world we inhabit, which is 71% covered in water. Despite how essential and how prominent of a role it plays in all organisms lives, there is still much we don't quite understand about water. Water is a very unique liquid, so it's not so simple to understand. For example: when compared to similar liquids, water has a much greater surface tension, a higher heat capacity and an intricate network of bonds that break and reform almost instantly. These same hydrogen bonds will rearrange themselves when they are exposed to hydrophobic particles in order to minimize their contact. The bonds will reform around the particle and it will enclose it if the particle much smaller than the bulk water. A similar effect will happen when the hydrophobic material is much larger than the water. However, since the material is too large to fit inside the

spacing of the bonds, the water will constrict on itself in order to once more minimize its contact with the material and thus creating a depletion layer. In our lab we study the interaction between water and hydrophobic as well as hydrophilic materials. This gives us better understanding into how these interactions work, and also lets us observe these surfaces and measure their stability.

Two solutions are widely used for experimental research as well as protective coatings, the hydrophilic solution, mercaptoundecanoic acid and the hydrophobic octadecanethiol which is particularly helpful when used to coat and protect against water degradation. However, since nothing will last forever, the monolayers formed from the solutions will also begin to degrade and breakdown. The rate of this breakdown can be affected by what it's exposed to, for example, salt exposure. Such as a monolayer coating on equipment found near the sea, or a study of the monolayers inside of a biological solution. Even though these solutions are used often, there is still some concern with regards to their rates of degradation and how those rates are affected by outside sources. An experiment where we look into how much faster a substrate degrades due to salt will bring clarity to how stable these solutions' monolayers are. Such results will aid in more accurate and efficient use of the substates in lab settings as well as aid in knowing which sort of hydrophobic coating will be most useful in commercial use.

Theoretical Background

Although the experimental component of this lab is not extremely intricate, there will still be a number of theoretical principles one should know in order to understand the meaning of the results. For one, a scientist should always have a comfortable understanding of whatever materials they are working with. In this case, those materials are water, octadecanethiol and mercaptoundecanoic acid. Even though there is still much to be learned about water, there is also

much that we already know. With the whole experiment revolving around the interactions of our two monolayers with water, it would be ridiculous to not first try understand as much as possible about water's known interactions and structure.

Properties of Water

Hydrogen Bond

Although water is overall neutral, it has a dipole moment due to the high electronegativity of the oxygen that pulls the shared electrons more strongly and causing a higher electron density around it. Due to the dipole moment caused by the partial charges, the opposite poles from separate molecules can attract one another, forming hydrogen bonds, as shown below.

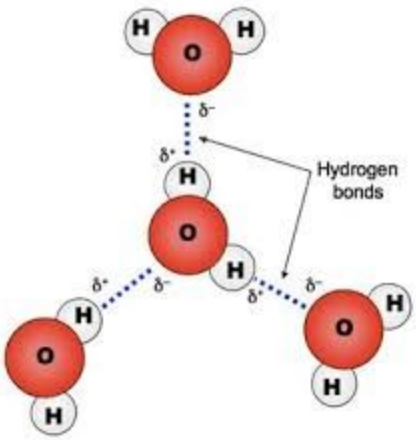


Figure 1: Hydrogen Bonds. This figure is a visual representation of how hydrogen bonds to oxygen due to the formed dipoles. Taken from www.chemistscorner.com

As can be inferred by its name, hydrogen bonds are a unique characteristic to this element, bonding to the partial negative charge of Oxygen, Nitrogen and Fluorine. This one of a kind features allows water to perform actions that cannot be seen in other forms of liquids that

can aid in explaining the development of organisms. Water is a polar molecule, simply meaning it has a dipole present, and thus can interact in a special way with other molecules. Inside of our water molecules, there are also two lone electron pairs on the hydrogen, which give water its bent shape. These lone electron pairs make the oxygen side of the molecules even more negative and allow hydrogen to attract to it more strongly. This interactions is weaker than a covalent bond but stronger than a normal dipole to dipole attraction. In order to measure just how hydrophobic a molecule is, the contact angle between a drop of water and a substrate is measured.

When a water droplet is on a surface, it will typically stay in place while maintaining a semi spherical shape rather than just forming a puddle. This due to the hydrogen bonds and its distribution of forces associated with the bonds. As it can be seen in the figure below, the spherical shape is caused by the molecules at the very edge of the water, because the number of hydrogen of bonds that can be formed is greatest towards the center, the molecules at the extremes experience a net radially inwards force (Yuan 2013).



Figure 2: Force Distribution of a Droplet. When water is in drop form, every molecule is subject to a range of forces, where the center experiences zero net force but the extremities have a radially inward pull. Taken from Yuan.

Contact Angle

The contact angle is measured by making a tangent line right where the water and the surface meet, and it is measured from the center of the droplet outward, as can be seen in figure 3. The molecules that make contact and are near the surface can interact with it, changing the shape. With a hydrophobic surface, the water will want to minimize the amount of contact that it makes with the surface, forcing the droplet to bead up even more thus raising the contact angle. When the contact angle is raised to a high contact angle beyond 90°, then the surface is categorized as hydrophobic, while below 90° is hydrophilic (Yuan 2013). Since the hydrophobicity of the surface is directly correlated to this contact angle, any change to it would also mean a change in the surface's hydrophobicity. Given this relationship, my project consists of monitoring the change of the contact angle as the surface is exposed to different concentrations of salt over time. As the angle changes, we can directly relate this to the degradation of the substrate and assess its stability in the presence of salt.

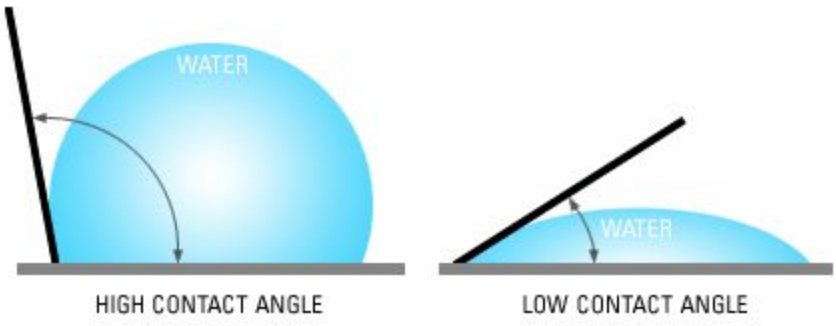


Figure 3: Contact Angle. If the water droplet forms a low contact angle which is below 90° then the surface is hydrophilic, however, if the angle is greater than that, it is considered a high contact angle and hydrophobic. Taken from: https://innovareacademics.in/journals/index.php/ijcpr/article/view/18892/10951

Depletion Layer

While on a hydrophobic surface, water will minimize its contact with it, receding and forming an area at the interface where the density of water molecules is incredibly reduced. The width of this layer can range from 2-4 Å (Poynor 2006), and due to its size, its has been very difficult to measure, causing uncertainty as to whether or not this layer exists. In Figure 4 (a) is a simple illustration for the depletion layer, where the gray is water and the white zone around the two rectangular objects are their respective depletion layers. Within close proximity, two depletion layers will form a low density "bridge" between them, and the difference in pressures will begin to pull the two objects into the area. This phenomenon results in a net attractive force between two like hydrophobic particles.

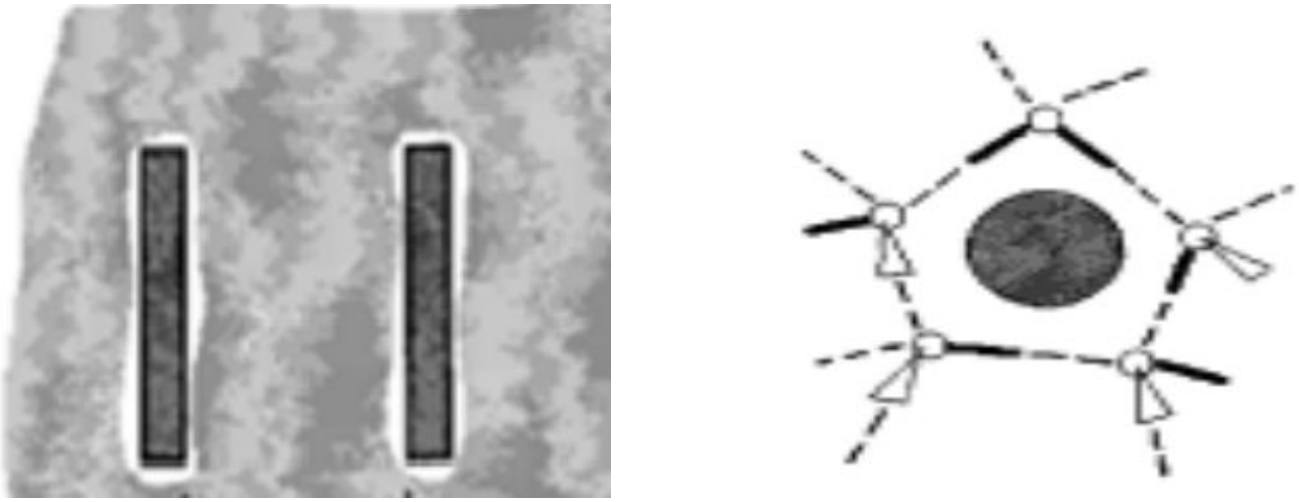


Figure 4: Depletion Layer. **(a)** A large hydrophobic particle inside of bulk water will create a low water density layer surrounding it (left). **(b)** This layer is caused by the hydrogen bonds arranging themselves to surround the particle with their bonds (right). Taken from Lum

Inside of bulk water, like shown Figure 4 (b) , when a small hydrophobic particle is submerged in water and the depletion layer encases the object due to the hydrogen bonds being a very ordered. The bonds will break and reform in a way that the object is left inside of empty space. This arrangement maximizes the number of bonds the hydrogens are forming, while minimizing its contact with the object. As the bonds rearrange, they organize the system and reduce its entropy, making it unfavorable for the system to do. However, the combination of electrostatic forces, thermal energy at room temperature, and released energy from when the bonds break all allow for the bonds to go into entropically unfavorable state. The energy of the system is used to form the bonds, lowering its energy state and making an energetically favorable state.

Self Assembled Monolayer (SAM)

The monolayers that were created and used in my lab consisted of either 11-mercaptoundecanoic acid (MUA) or 1- octadecanethiol (ODT). After dissolving these compounds in ethanol, gold slides were placed in this solution and left to soak so that it may bind to the slide and form a layer. They're called self assembled because no energy needs to be inputted to the system in order to cause this layer to bind, however, several factors can affect its formation, such as the temperature. The optimal temperature is above 25°C to reduce the amount of defects that will form in the monolayer (Love 2005). Our lab had an average temperature that varied very slightly around 24°C. Another factor is the soaking time of the substrate in the solution. The suggested soak time to get stable physical properties of the SAM is 12-18 hours (Love 2005). The solution will can begin to bind to the surface in minutes, however in order to

form a dense stable monolayer for experimental use, several hours of soaking would be required. Both of these solutions consist of a sulfide group that undergo the following reaction with gold (Rajalingam 2008):

$$Au + R\text{-}SH \rightarrow Au\text{-}SR + \tfrac{1}{2} H_2$$

Hence, gold is optimal coating on these slides in other to form the monolayer with no external energy, but also gold is a relatively inert element (Love 2005). It won't casually react with external elements, this will keep the contact angle from changing due to any undesired reactions. Below is a figure showing how the monolayer will bind to the gold slide. The thiol groups are the head groups that will bind to the gold.

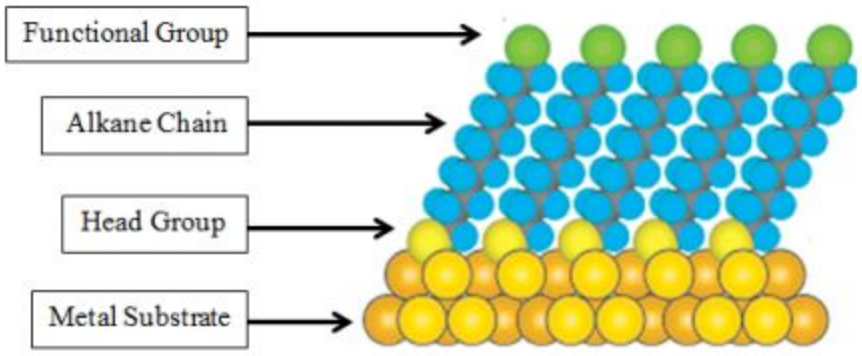


Figure 5: Self Assembled Monolayer. The headgroup contains sulfides that bonds to the gold substrate, the alkane chain is a chain of carbons and the functional group will vary depending on the compound. A carboxyl group for MUA and Methyl group for ODT. Taken from Love

Octadecanethiol (ODT)

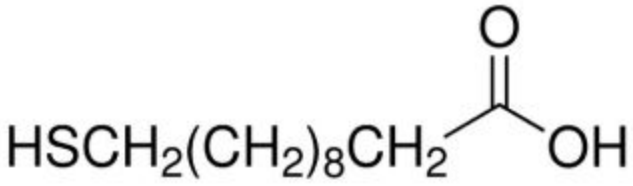
ODT is a thiol, and has the sulfide in its head group that reacts to gold. It also has an alkane chain which is a carbon chain made up solely of single bonds (its chemical formula given below).

$$CH_3(CH_2)_{16}CH_2SH$$

Due to its nonpolar nature, it is subject to London forces, which are induced dipole to induced dipole interactions (Atkins 2010). As electrons are always in motion, at any given instance there is a difference in charge density and thus a momentary dipole. Normally this dipole doesn't have very strong interactions. However when in contact with a strong polar molecule, such as water, a dipole will be induced causing the ODT to be attracted to water, but also to the other induced dipoles of the same solution. The strength of this attractive force is dependent on how many electrons there are, the amount of contact that is made between the two molecules and it is inversely proportional to the distance between the two objects (Atkins 2010). The shape of ODT is a long rod, giving it a lot of surface area where it will come in contact with water and form a dipole. Even though there will be interactions between the ODT and water, because of the short range of London forces, there is very little pull on the distant water molecules. The closer neighboring ODT molecules however are influenced enough by London forces to cause an attraction. Due to this, the ODT will attract to itself, and not a polar molecule like water, giving it its hydrophobic properties.

Mercaptoundecanoic Acid (MUA)

MUA is also a thiol, however, this molecule has a polar functional group. Of course, it is subject to London forces, as are all molecules, but due to the carboxyl polar group, it has a permanent dipole. As the sulfide head group bonds to the gold slide, the dipole to dipole interactions between the functional group and the dipole in water will cause an attractive force. Since this dipole attraction is greatly dependent on distance, as the water and MUA attract one another and get closer, the attraction itself will get stronger and this giving MUA is hydrophilic properties (Atkins 2010). This electrostatic interactions is inversely proportional to the distance, and the attraction to the substrate will largely affect the contacting water molecules than the further ones in the bead of water. Since the attraction is to those molecules at the bottom, this causes the water to spread out more along the substrate and flatten out the droplet and decrease contact angle.



Scanning Electron Microscope (SEM)

For a SEM, a beam of electrons is focused on a small area and moved over each point of the object you wish to scan. The electron current which then comes back from the object is collected and amplified and used to modulate the brightness of a cathode-ray tube that follows behind the beam of electrons. If any aspect of the object causes the returning electron current to

change while it passes over any given point, that variation will be reflected as a brightness discrepancy (Smith 2004).

Methodology

Using previous comp projects on similar experiments as well as a set-up proposed by Guillaume, I've derived procedures that will result in the necessary data whilst being simple and easy to follow.

Making Solution

Unlike my predecessors, my project will consists of having a single concentration of ODT and MUA while only varying the concentration of NaCl that they shall be soaking in. ODT and MUA have molecular weights of 286.59 g/mol and 204.37g/mol respectively. Using these values, we can see that we will need 286.59g of ODT to form a 1 Molar solution in a 1L beaker. However, our desired concentration is 0.1M inside of a 100mL flask, thus we only need to measure out 2.866g and 2.044g for our two solutions. Since the solutions are solid and in powder form, they were first weighed out in the appropriate amounts and then dissolved in a flask of ethanol. In order to make sure that compounds properly dissolve, we place the flask into an ultrasonicator for 15 minutes. After that is done, the vial must sit for a couple of hours to assure that a precipitate does not form. A similar procedure is done for the NaCl solution; for a 0.1M solution in a 100ml with molecular weight 58.44g/mol, we need to measure out 0.584 g for every 0.1M that the desired concentration is changed. The NaCl is dissolved in millipore water and then also placed into the ultrasonicator.

Forming the Monolayer

Due to the self assembling nature of our monolayers, in order for it to form, we need simply place the gold slide in a vial of the solution for the desired amount of time. After enough time has passed, the slide is removed from the vial and rinsed fives on each side with ethanol. The monolayer slide is then placed into another vial filled with more ethanol and put into the ultrasonicator for 10 minutes to further rinse is. Afterwards, the slide is removed and rinsed once more, 5 times on each side with ethanol. With that, the monolayer will have properly bonded to the gold slide and is ready for measurements and can be seen when exposed to a drop of water. Gold will normally just cause the drop to puddle but with the monolayers bonded, the typically beading of the drop will become very visible. For the salt exposure portion of the comp, the monolayer slide is stored in a vial containing a specified concentration of salt solution and is then monitored at set amount of times.

Measuring Contact Angle

Before the slide is placed in any of the slide solutions, an initial measurement of zero soak time is taken as a control. This measurement is taken by dripping a drop of millipore water onto the gold slide then using a camera to zoom in through a freestanding lens to take a photo of the drop on the slide. The more accurate values of the contact angle is measured when the photos are put into the ImageJ software. Initially, the slide were removed from the solution to take measurements every half hour for the first three hours, afterwards it was done once every 24 hours from the starting time until 8 days.

Camera Setup

My camera setup is shown below in Figure 6. The camera used is a Cannon Power Shot ELPH 100HS, that zooming in through a freestanding double convex lens with a focal length of 75mm. The freestanding lens was placed approximately 4.3cm away from the camera lens which in turn was approximately 7cm away from the apparatus where the slide was placed. This apparatus is then 19.2cm away from the diffuser box which is the only other source of light when measurements are taken and all other lights are turned off. On the apparatus is a dropper which is used to dispense approximately 15μL onto the slide, and the height of the dropper is adjusted so that the needle remains within the drop after is it dispensed. The camera zooms in and focuses, taking five photos each time a measurement is made. The slide is then cleaned with lens paper and replaced into its vial of salt solution.

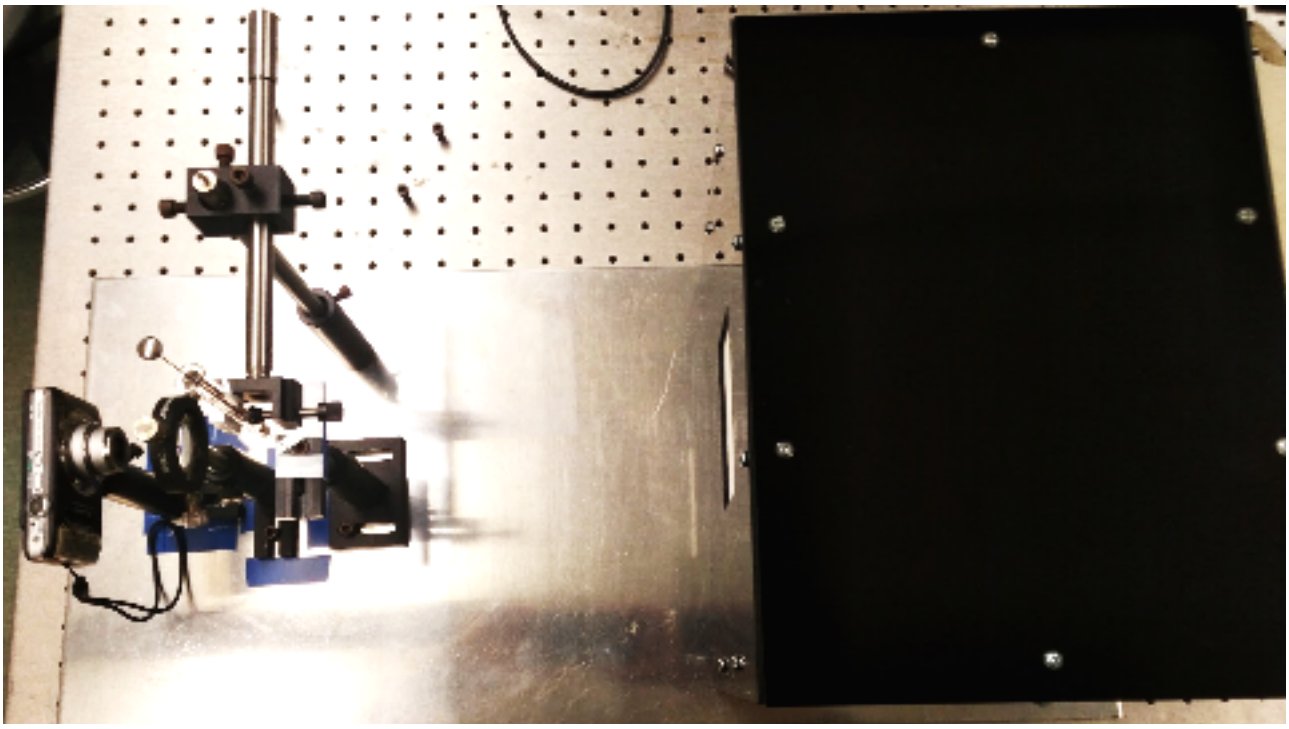


Figure 6: Experimental Setup. This is the setup used to take measurement in our lab, consisting of a camera, syringe, freestanding lens, a rigid platform and a light diffuser box.

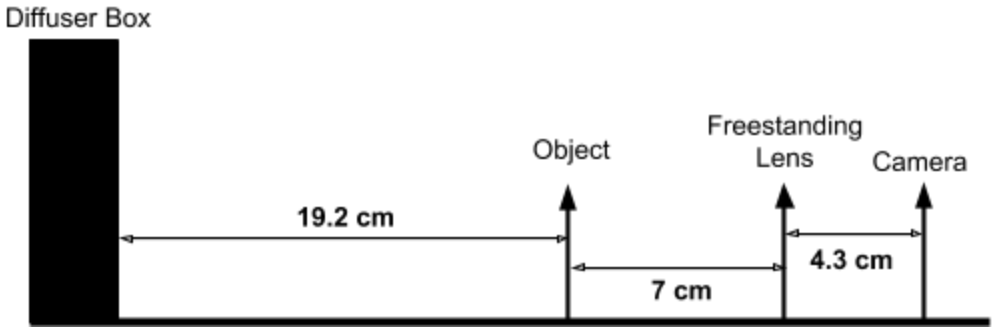


Figure 7: Experimental Setup (2). This figure is a simple model of the previously shown setup, showing the distances between each of the objects. Not drawn to scale.

ImageJ

The taken photos are then converted into black & white as required by the ImageJ software. Once the photos are moved into this program, I can manually add points along the curve of the water droplet called the DropSnake method (Stalder 2006). Once an appropriate number of points have been placed, the first point can be clicked again in order to calculate the contact angle. A measurement for the both the left and right side will appear on the upper left corner of the photo as shown below. With the 5 photos we will have 5 different measurements which were averaged out and taken into account for error calculations.

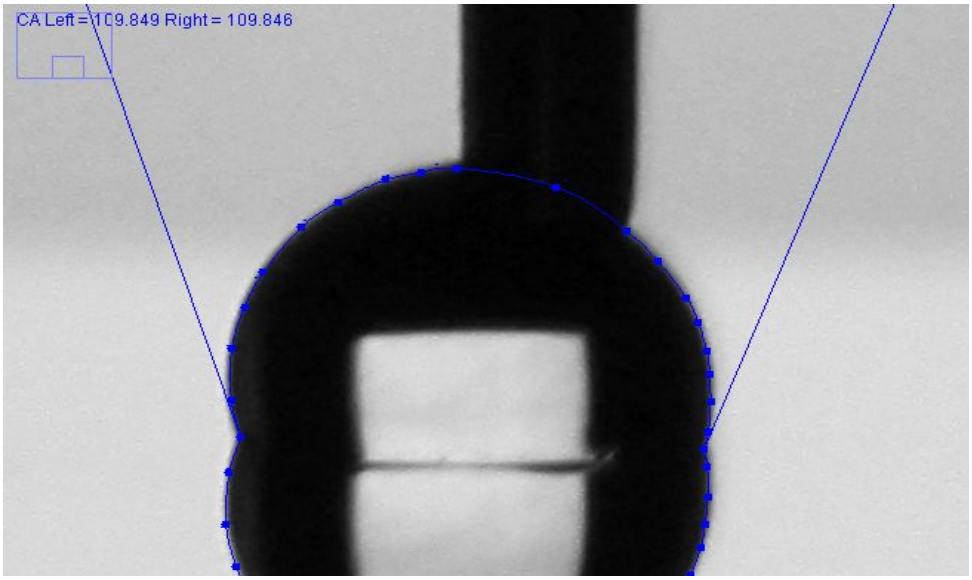


Figure 8: ImageJ Trace. This is a drop of water on a 0.5M NaCl soaked slide with a left contact angle of 109.849° and a right contact angle of 109.846°.

Results and Graphs

For this experiment, the ODT and MUA monolayers were formed on top of the gold slides and then soaked in different concentrations of different salts. The three salts tested were NaCl, NaBr, and KCl all with the concentrations of 0.5M, 1.0M and 1.5M. The original plan was to expose both the MUA and ODT slides to all three salts however, due to running out of time before the arrival of materials, the experiment was reduced to exposing both ODT and MUA to NaCl but only ODT to both NaBr and KCl. They initial measuring points was to be every half hour for the first three hours and then once every 24 hours, as can be seen in tables 1a, 2a, 2b. However, after some consideration, it was determined that more focused was needed in the initial 12 hours rather than just the initial three and the measurement points was changed to every three hours for the first 12 hours and then again once every 24 hours after that. The graphed change in angle is calculated using $\Delta\theta_n = \theta_{0\ hrs} - \theta_n$.

NaCl Solutions

Table 1a: ODT in 0.5M NaCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	111.092	0	0.425
0.5	108.427	2.665	0.478
1	108.773	2.319	0.312
1.5	106.599	4.493	0.415
2	106.098	4.993	0.623
2.5	105.094	5.997	1.049
3	105.510	5.581	1.011
24	103.367	7.725	0.699
48	102.145	8.947	0.664
72	101.324	9.768	0.435
96	101.045	10.047	0.279
120	101.384	9.708	0.407
144	101.495	9.597	0.534

Table 1b: ODT in 1.0M NaCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	112.273	0	0.381
3	108.400	3.873	0.613
6	105.0121	7.261	0.592
9	104.419	7.855	0.494
12	103.941	8.332	0.566
24	102.0068	10.267	0.554
48	101.1871	11.086	0.409
72	100.8245	11.449	0.364
96	100.4734	11.800	0.366
144	99.3716	12.902	0.411

Table 1c: ODT in 1.5M NaCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	105.087	0	0.419
3	104.0916	0.995	0.521
6	104.0543	1.032	0.466
9	101.3125	3.774	0.392
12	101.4993	3.587	0.315
24	100.9957	4.091	0.445
48	100.1858	4.901	0.462
72	100.74759	4.339	0.386
96	99.3386	5.748	0.492
144	98.1165	6.970	0.645

Contact angle measured was recorded five times, having an independent angle for the lefts and the right, and was then averaged for each side and once more between the remaining two averaged. The shown error is the standard deviation of the mean.

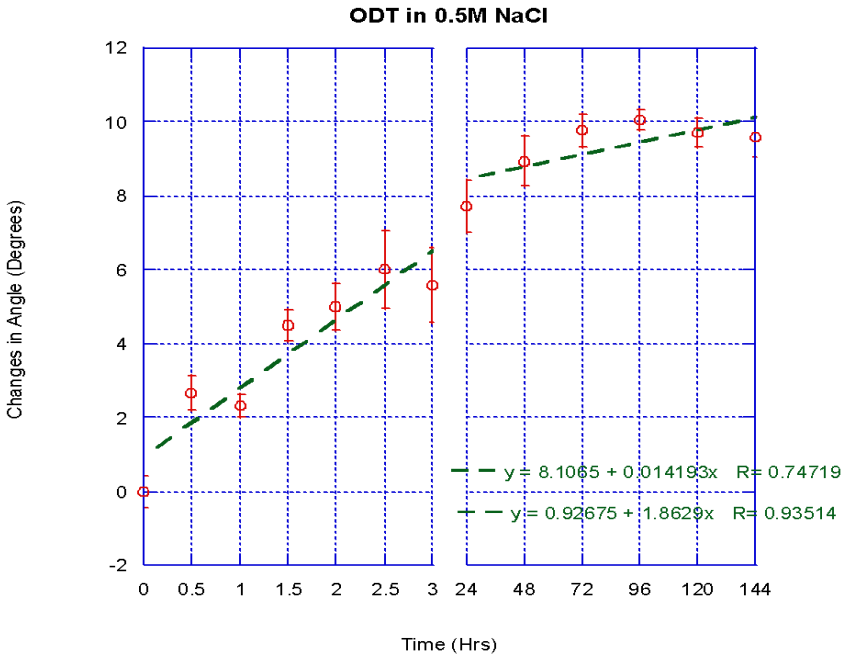


Figure 9. Graph of ODT exposed to 0.5M NaCl

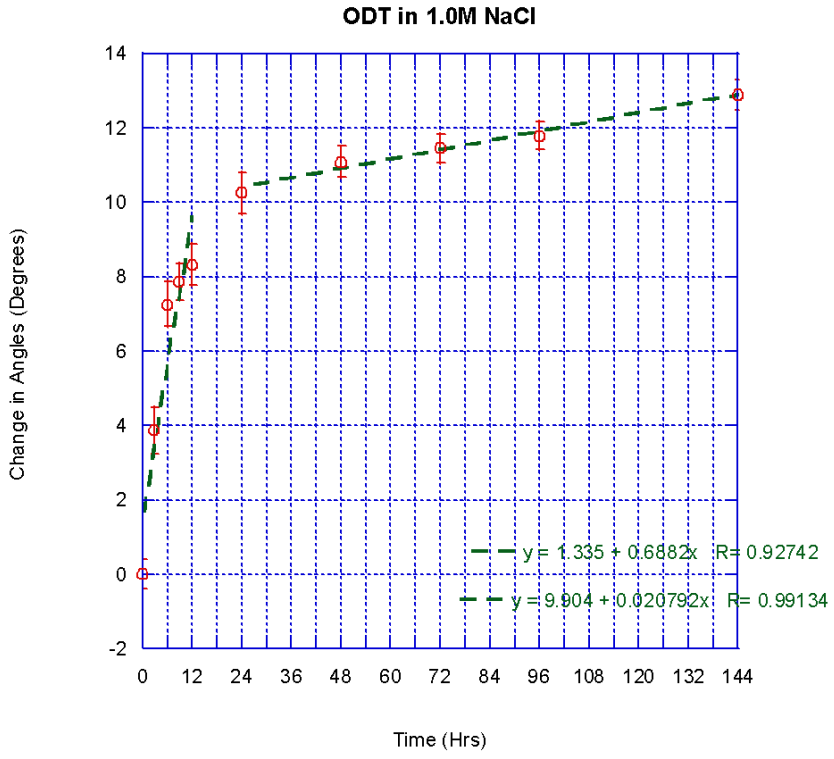


Figure 10. Graph of ODT exposed to 1.0M NaCl

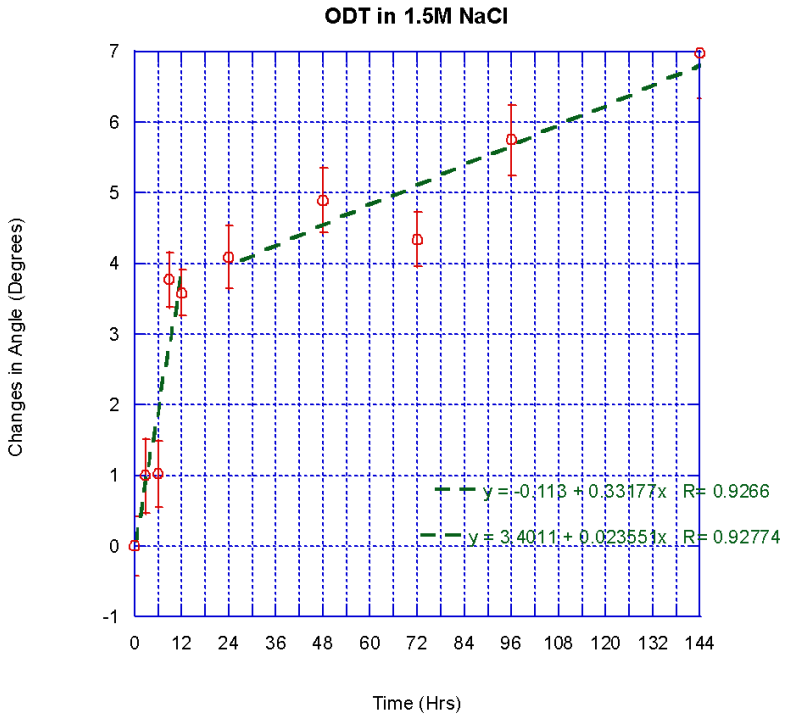


Figure 11. Graph of ODT exposed to 1.5M NaCl

Between the three concentrations there was an average of 9.823 degrees change to the contact angle after 144 hours and for the sets that measured the first 12 hours, there was an average of 5.959 degrees of change. No direct correlation between the concentration quantity and the contact angle change cannot be established from this set of experiments since when raising the concentration from 0.5M to 1M increases the amount of angle change and how much more the monolayer degrades, however, increasing concentration from 1M to 1.5M actually increases the contact angle change significantly, going even lower than the 0.5M solution.

Table 2a: MUA in 0.5M NaCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	46.126	0	2.707
0.5	58.098	-11.972	2.776
1	65.632	-19.506	0.742
2	66.650	-20.524	0.633
3	65.505	-19.379	0.677
24	69.681	-23.555	1.066
48	73.272	-27.146	0.976
72	79.302	-33.176	0.298
96	79.604	-33.478	0.317
120	77.260	-31.134	0.601
144	80.836	-34.710	0.767

Table 2b: MUA in 1.0M NaCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	45.701	0	0.389
0.5	53.362	-7.661	0.602
1	53.5166	-7.815	0.574
2	55.112	-9.411	0.506
3	56.9569	-11.256	0.516
24	60.2127	-14.511	0.660
48	63.3169	-17.616	0.863
72	64.9744	-19.273	0.844
96	66.0218	-20.321	0.804
120	67.88261	-22.181	0.733
144	70.8568	-25.156	0.455

Contact angle measured was recorded five times, having an independent angle for the lefts and the right, and was then averaged for each side and once more between the remaining two averaged. The shown error is the standard deviation of the mean.

In tables 2a there are several points in the data where the degradation does not seem to follow its typical trend, this because during measurements, one side of the contact angles was occasionally extremely lower than other, one of the possible reasons for this occurrence is that when slide was placed down for the measurements, the surface may have not been properly wiped leaving lint or dust-like particles. This would tilt the slide and cause the water to lean one side, causing one angle to noticeably alter and disrupt the average.

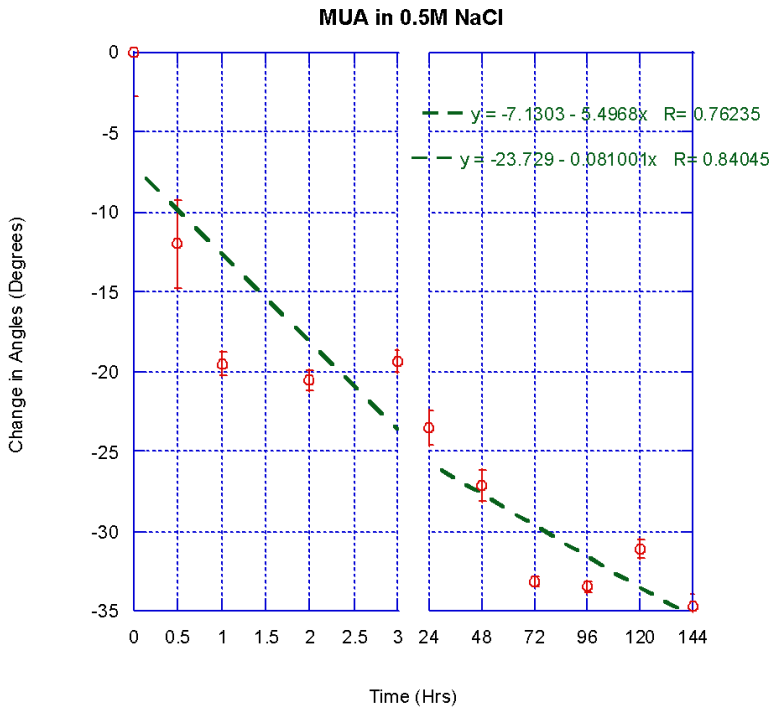


Figure 12. Graph of MUA exposed to 0.5M NaCl

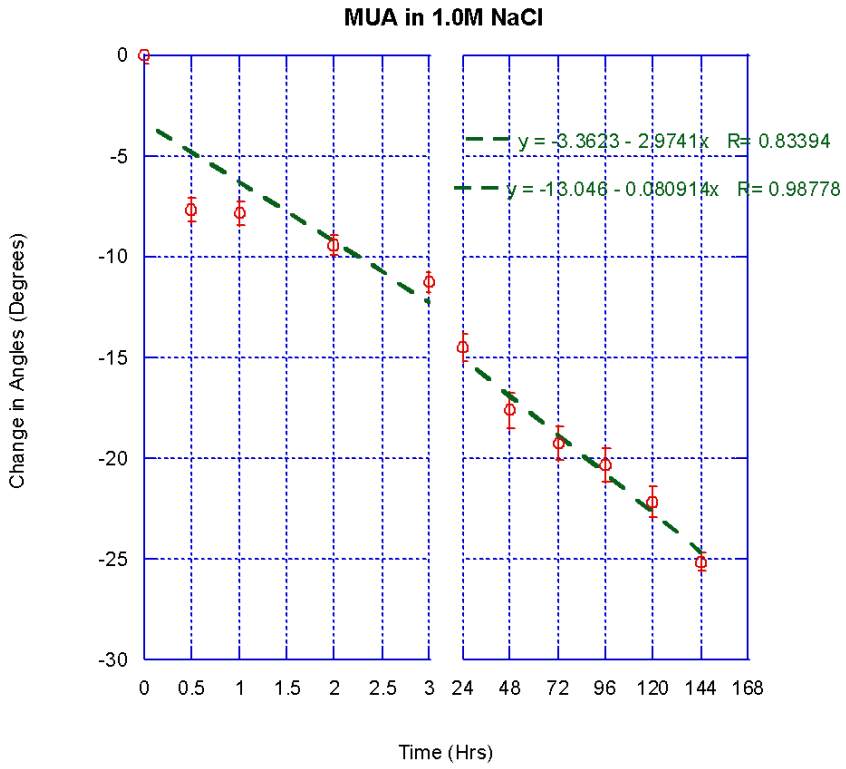


Figure 13. Graph of MUA exposed to 1.0M NaCl

Comparing the quantity but not the sign of the angle change for MUA in NaCl to that of the ODT, the MUA had usually degraded twice as much as the ODT did. Likely due to its molecular structure and size, MUA was much more susceptible to degradation of NaCl and suffered much more damage. The data for 1.5M was omitted due to corruption of the original raw data that made the information unretrievable and the experiment was not able to be redone in time.

NaBr Solutions

Table 3a: ODT in 0.5M NaBr

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	98.777	0	0.246
3	101.960	-3.183	0.376
6	99.638	-0.861	0.661
9	97.538	1.238	0.835
12	95.878	2.899	0.843
24	94.731	4.045	0.761
48	94.520	4.256	0.511
72	94.904	3.873	0.419
96	93.721	5.056	0.451
144	92.905	5.872	0.307

Table 3b: ODT in 1.0M NaBr

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	105.697	0	0.249
3	104.639	1.058	0.430
6	102.422	3.275	0.547
9	102.005	3.692	0.525
12	102.292	3.405	0.483
24	102.792	2.905	0.521
48	102.399	3.297	0.489
72	101.810	3.887	0.370
96	100.650	5.046	0.460
144	100.905	4.792	0.490

Table 3c: ODT in 1.5M NaBr

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	104.323	0	0.487
3	102.805	1.518	0.554
6	102.931	1.392	0.386
9	102.659	1.664	0.413
12	101.610	2.713	0.497
24	100.804	3.519	0.538
48	100.047	4.276	0.569
72	99.725	4.598	0.526
96	98.999	5.324	0.428
144	98.162	6.162	0.525

Contact angle measured was recorded five times, having an independent angle for the lefts and the right, and was then averaged for each side and once more between the remaining two averaged. The shown error is the standard deviation of the mean.

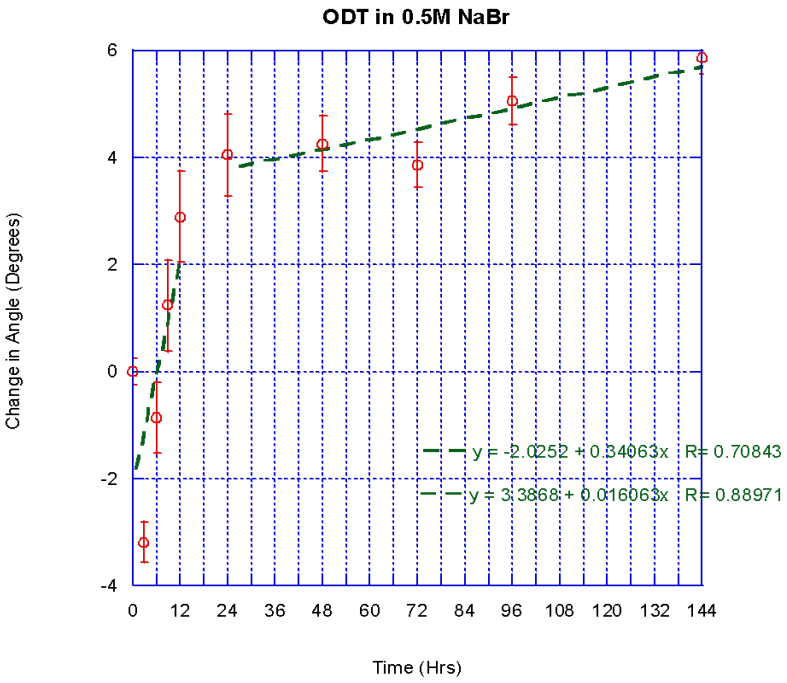


Figure 14. Graph of ODT exposed to 0.5M NaBr

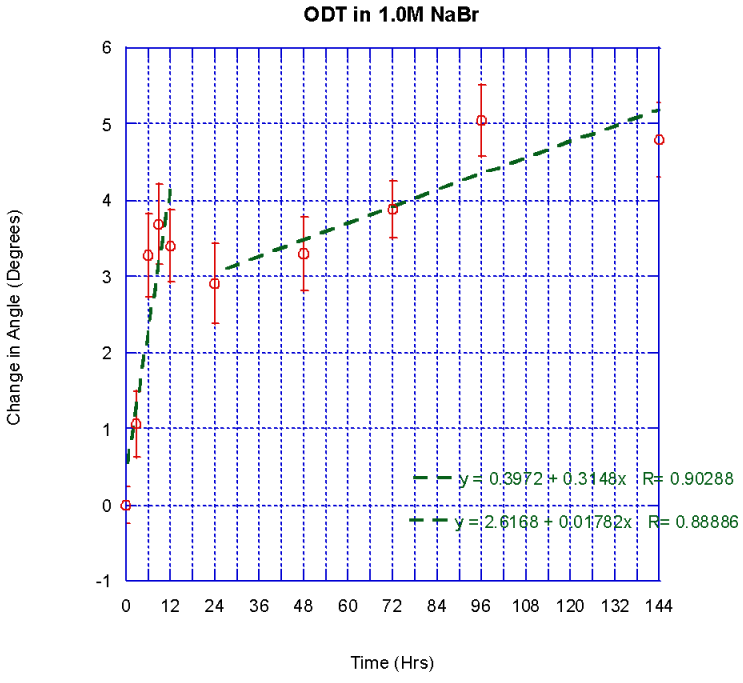


Figure 15. Graph of ODT exposed to 1.0M NaBr

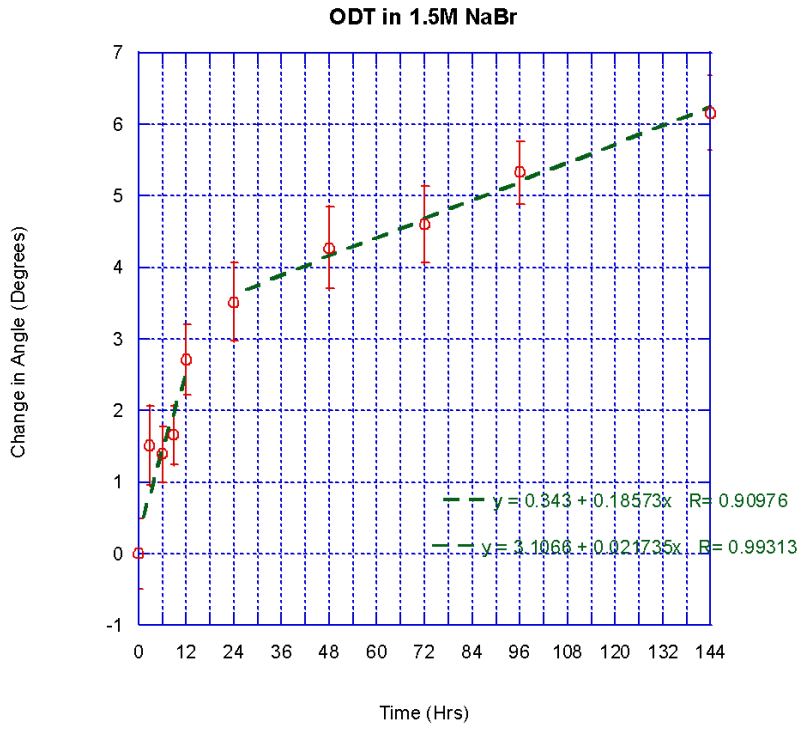


Figure 16. Graph of ODT exposed to 1.5M NaBr

The NaBr solutions averaged in the first 12 hours of 3.004 degrees of change to the contact angle and 5.608 degrees after 144 hours of soak times had passed. Unlike the NaCl, all three solutions has a similar range of value for their angle change with a small deviation. When specifically looking at the trendline's slope for after 24 hours (bottom equation of the line) there is an increasing trend as the concentration is increased as well. The quantity of the overall change for this solution was similar to the values recorded for the 1.5M concentration of NaCl. I believe this to be simply coincidental specifically because the 1.5M NaCl was particularly lower values than the other two measurements. A combination of humidity in the lab, difficult to see dust particles on the slide during measurements or a slightly unlevel stand could have contributed this particular instance of a smaller angle change in 1.5M NaCl.

KCl Solutions

Table 4a: ODT in 0.5M KCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	108.185	0	0.351
3	105.030	3.156	0.444
6	104.416	3.769	0.379
9	103.387	4.798	0.453
12	103.838	4.347	0.424
24	103.325	4.860	0.423
48	102.443	5.743	0.456
72	103.955	4.230	0.344
96	103.295	4.890	0.476
144	102.131	6.055	0.661

Table 4b: ODT in 1.0M KCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	106.376	0	0.233
3	105.302	1.074	0.348
6	104.814	1.562	0.604
9	103.801	2.575	0.583
12	103.941	2.435	0.488
24	103.751	2.625	0.513
48	102.025	4.351	0.375
72	100.716	5.660	0.383
96	99.326	7.050	0.443
144	100.002	6.374	0.404

Table 4c: ODT in 1.5M KCl

Time (hrs)	Angle (Degrees)	Change in Angle (Degrees)	Error in Angle (Degrees)
0	94.736	-	0.318
3	104.969	0	0.342
6	104.339	0.630	0.641
9	103.162	1.807	0.766
12	101.505	3.464	0.621
24	99.054	5.915	0.660
48	100.071	4.898	0.762
72	98.299	6.670	0.532
96	98.316	6.653	0.469
144	98.226	6.743	0.490

It should be noted that for the 1.5M KCl solution, the initial measurement prior to salt exposure was omitted when calculating change in angle and plotted. Since the initially was significantly lower than the following measurement as well as lower than everyone of the next measurement, it was determined that the initial angle was distorted due possibly to the level of the stand or barely visible dust particles in the slide. As such, the 3 hours exposure was treated as the control measurement for calculations.

Contact angle measured was recorded five times, having an independent angle for the lefts and the right, and was then averaged for each side and once more between the remaining two averaged. The shown error is the standard deviation of the mean.

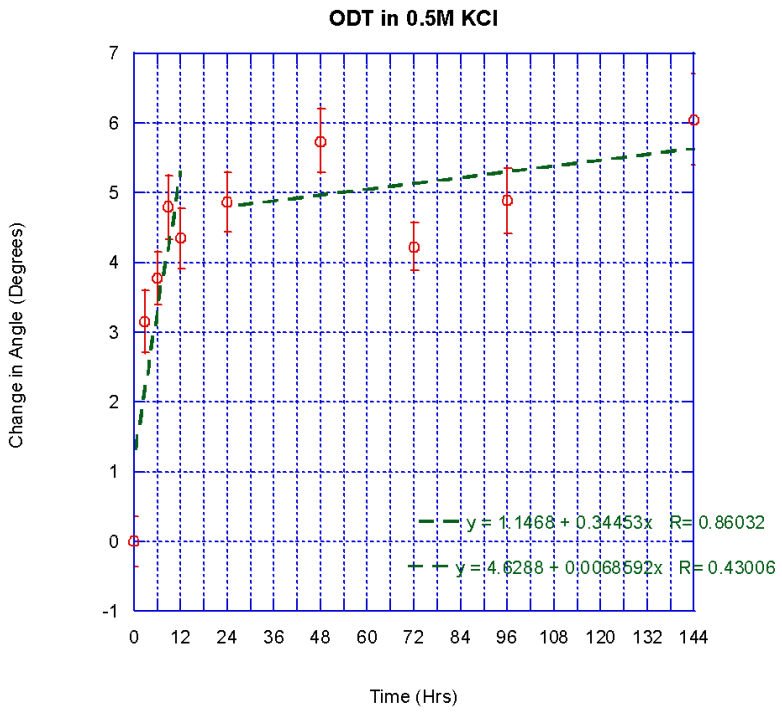


Figure 17. Graph of ODT exposed to 0.5M KCl

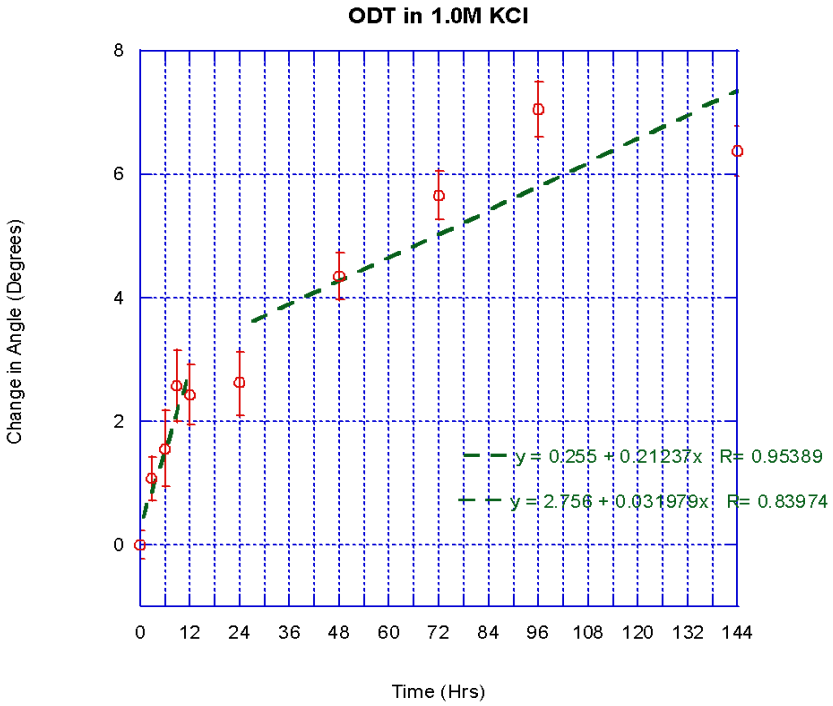


Figure 18. Graph of ODT exposed to 1.0M KCl

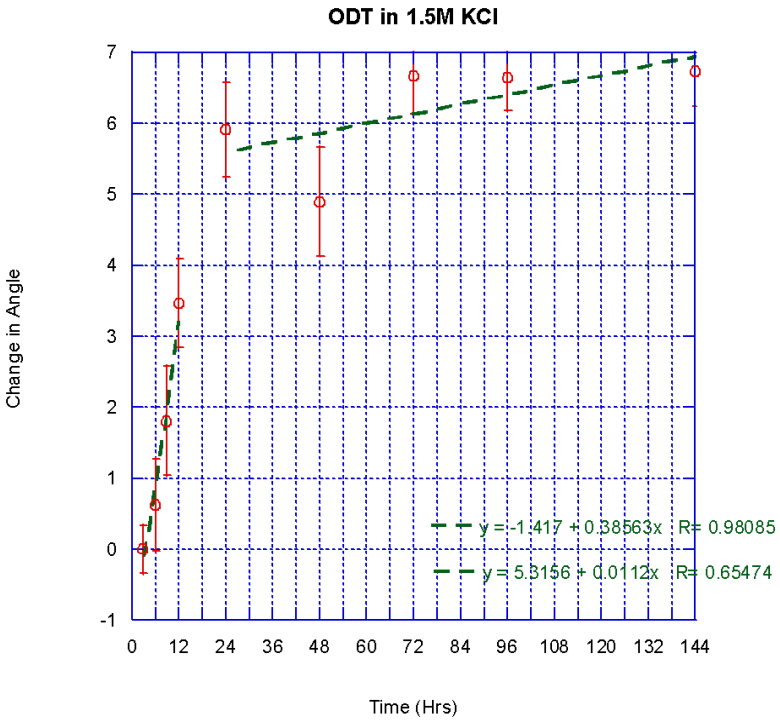


Figure 19. Graph of ODT exposed to 1.5M KCl

In the initial 12 hours, there was a 3.415 degree change to the contact angle and after the final 144 hours, the total change had increased to 6.391 degrees. Unlike the other two solutions, followed a trend where when the concentration was increased there was also a small increase in the total amount of angle change after 144 hours. KCl produced the most stable final results with and angle change within 0.4 of a degree from the following concentration.

Discussion of Results

This discussion will focus mainly on ODT since it was exposed to all three solutions. From the final total change in the angles for each of the solution, I was unable to determine any specific correlation between concentration the the amount of angle change, except the case of KCl where there was a small increase in the degradation rate as well as the increase in the post 24 hour degradation rate of the NaBr solutions. However, it became very visible that when exposed to NaCl, the monolayer degraded much faster and quickly became less hydrophobic especially when compared to KCl and NaBr. Both of the last two salts had a smaller degradation rate in the 12 hrs window and over the course of the full 144 hours. I believe the reason why those 2 salts were able to degrade the monolayer less than NaCl was due to ionic radius. NaCl is the smallest of the three and allows more possibility for the ions to find itself in the spacing between the molecular spacing in the ODT and begin to separate it from itself. According the averages, NaBr produce that smallest change in contact angle, in the following image, the ionic radii is shown and the difference of size can be seen.

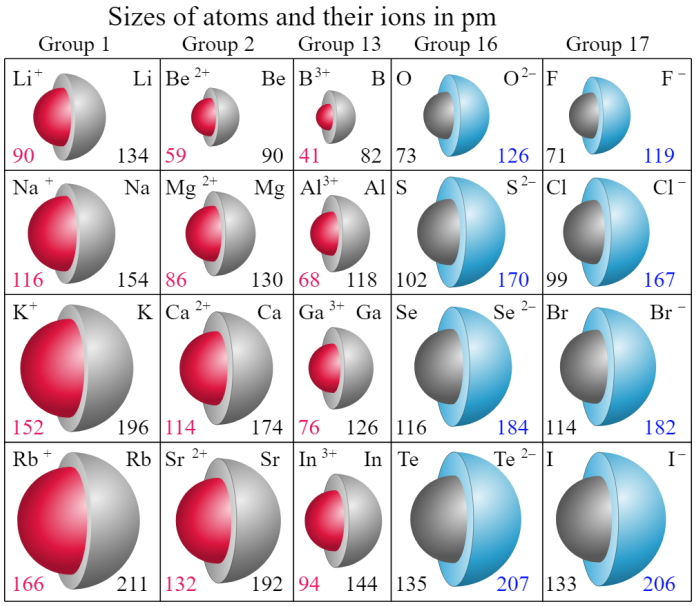


Figure 20. Table showings the atomic radius of element normally (in black), the ionic radius of the cations (in red) and the ionic radius of anions (in blue). Taken from: https://ch301.cm.utexas.edu/section2.php?target=atomic/bonding/ionic-radii.html

Although the normal atomic radius of potassium is significantly greater than the bromide, when they become ionic and exchange their electrons, the bromide increases in radii and becomes larger than both the ions of potassium and chloride. However, since there will still be a presence of sodium in the bromide solution, degradation will still take place given the small ionic radius of the sodium that will break down the monolayer. In order to observe what occured to the monolayer more closely we took a look at a much smaller scale through the use of a scanning electron microscope.

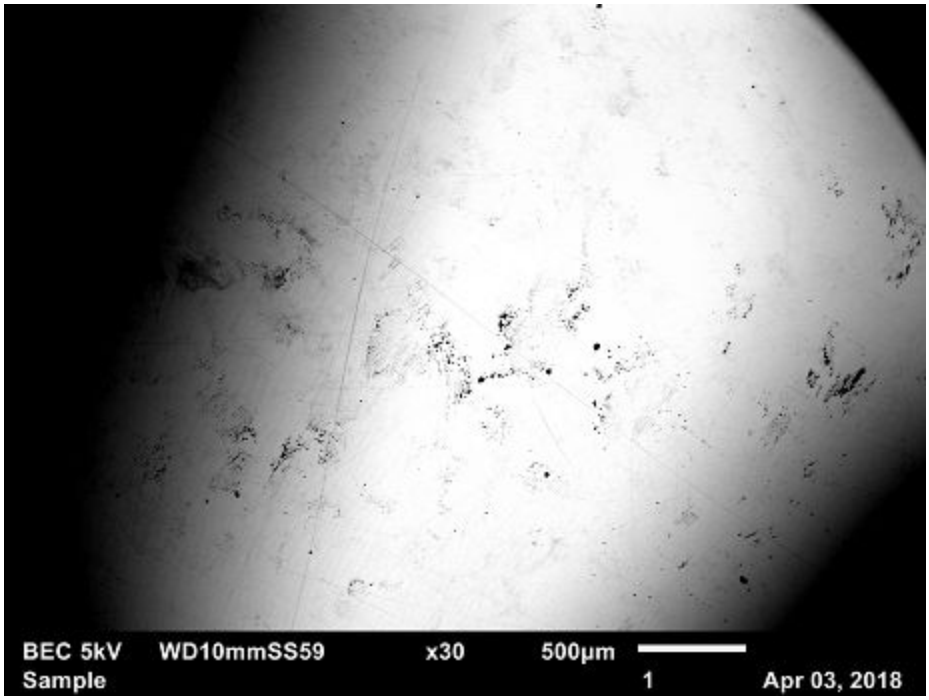


Figure 21. SEM imaging of an ODT slide exposed to 1.5M NaCl for 144 hours.

The SEM uses difference in contrast and brightness in order to image certain "distortions" on the surface of the object. In this case, the very dark spots are areas where the monolayer has experience "pitting" and the salt is degrading those areas most strongly and eating away at the layer. The SEM reflects points further from the observer as darker zones and the closer points are white. This shows the dark spots as literally holes inside of the monolayer As shown in Figure 21, the NaCl produce a lot of very dark spots on the surface of the slide, and much like the other slides, there was no uniformity in the distribution of the pitting. We can also see a lot of area of gray shading which is zones of much more superficial degradation, where only the very top of the monolayer was being damaged and not pitted through.

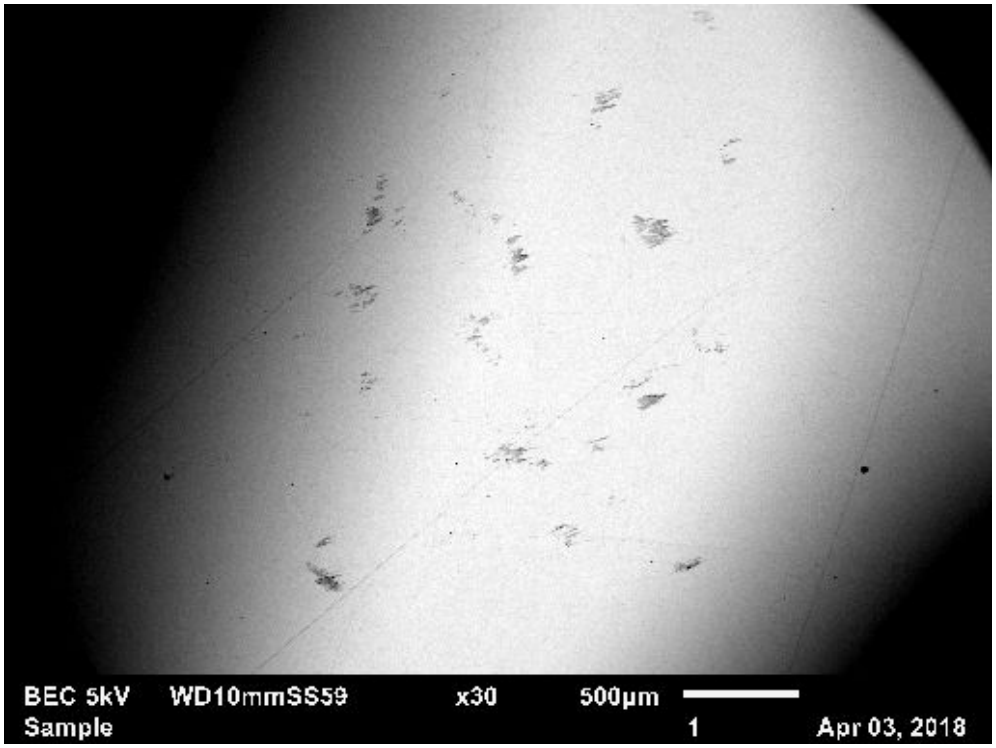


Figure 22. SEM imaging of an ODT slide exposed to 1.5M KCl for 144 hours.

When comparing this KCl slide to the previous NaCl, we see a very obvious lack of pitting in this image but still a fair amount of superficial degradation on the ODT. Due to both the potassium ion and the chloride ion being decently sized, there was very little opportunity for the ions sneak inside the atomic spacing and break ODT layer deeply. However, the superficial degradations zones are separated but grouped together in a more uniform fashion than in any of the other slides.

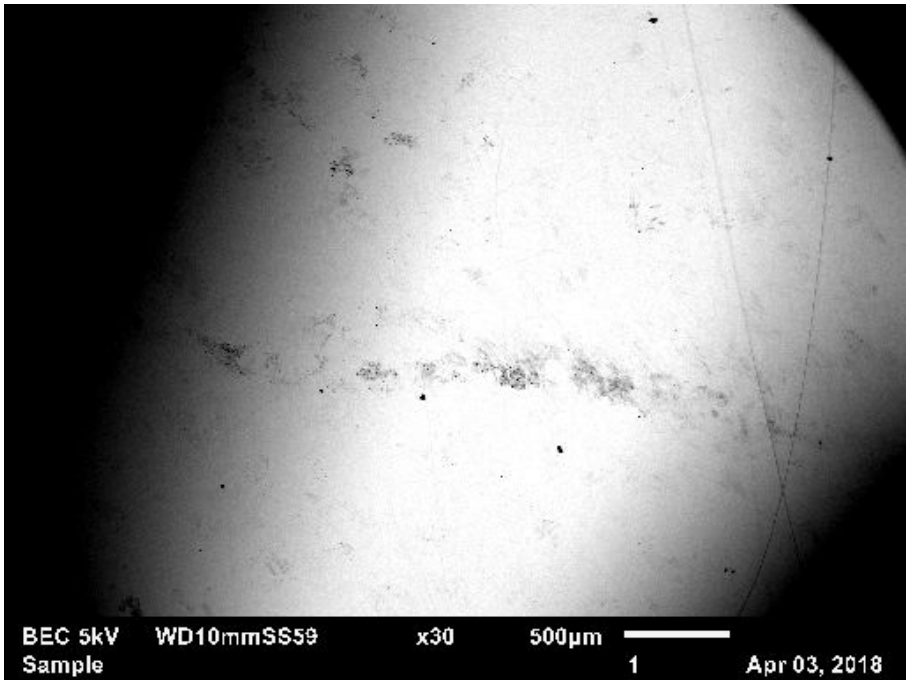


Figure 23. SEM imaging of an ODT slide exposed to 1.5M NaBr for 144 hours.

Surprisingly, even though the NaBr had on average less of a change to the contact angle than the KCl, this slide shows a similar amount of superficial degradation but a slight increase of pitting. This slide was specifically the 1.5M solution of NaBr, which happened to have degraded about the same amount as the 1.5M KCl slide. For these particular slides, the degradation happened to be very similar amounts, however, the sodium ion in the NaBr was able to pitt the monolayer more frequently and increase the number of dark spots in the slide.

These images not only help determine how each of the salts affected the slides differently, but also reinforced the theory that the salts were physically eating away at the monolayer. The presence of the pitts promote the hypothesis of the salt being able to get into the monolayer and “drill” into it. The ions being able to fall inside the molecular spacing of the ODT would inevitably cause pitting similar to what was seen in the SEM images, in order to fully

confirm that this is the case, we would require a full chemical analysis of the ODT to determine the molecular spacing in each of the bonds and determine whether or not any of the ions can fit inside it. Another future step would be to use the SEM from the initial creation of the slide prior to exposure, to determine the uniformity of the monolayer formation to accommodate for the possibility that some of the monolayer degradation was not caused by the salt but rather that the slide originally started at a certain state of pitting. The SEM could also be used at sevel measurements points to see how quickly the monolayer begins to breakdown within the first 12 hours of the experiments.

The SEM can also be utilized to confirm salt build up during measurements. With the previous figures from the SEM, there was no noticeable build up of salt on the monolayer since all points of interest were dark spots which were digged in spots on the layer. However, if salt does manage to build on the slide it is possible for the salt to dissolve into the water droplet used for measurement. I performed a small experiment in my lab where I measured the contact angle made by different droplets on the same monolayers. I used a pure water droplets and three others with a 0.1 M solution of NaCl, NaBr and KCl. The NaCl droplet had slightly higher contact angles but the NaBr and KCl both ranged around ten whole degrees greater than the pure water droplet. If salt finds its way inside of the water droplet the contact angle made will be overestimated and data will be skewed. The SEM can be used to confirm there is indeed no build up on the surface.

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