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Full Paper

Ionic Self-Assembly of Beryllon ll and BC18 (Benzyldimethylstearyl-ammoniumchlorid) – Synthesis, Structure, and Thin Films

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Ionic self-assembly is a way to use the button up approach, since the molecules will place themselves from down to up. In the following article this specific way were used, to build layered nanomaterial, by combining an anionic Azzo dye and a catnic surfactant. After the nanomaterial had been formed, the results showed that ionic self-assembly worked as expected with the chosen reagents. The experimental heights of the XRD and AFM matched, but they did not match with the theoretical unit cell. The unit cell had a volume, close to the actual, extracted from XRD. Through AFM, TEM and Optical Microscopy it was possible to find layered, uniform thin film. The thin film solution was too little concentrated, and therefore, the angle between the dye and glass plate could not be found.

1. Introduction

Everything from the geometrical shape of the nanomaterial to the solubility of the reactants, are all factors that may make the synthesized nanomaterial more or less effective at making a lamellar structure when processed into a thin film. The ultimate goal of ionic self-assembly is to form a product in macro size of high order through self-assembly[4]. Thin film is used for products such as solar cells and flat screens. Since ionic self-assembly is still not fully explored, we hope our project can play a part in shedding light on how we manage to create self-assembled molecules with a high molecular order.

The primary purpose of the Nano1 course is to make a map of how the different surfactants and azo-dyes form lamellar structures as thin film. This research has been taken from the former students, for this generation to build upon. This project is based on a lot of different combinations, and we're continuing the research from 2014[3].

2. Results and Discussion

2.1 – Synthesis, EA and MS

For this part, following will be presented: synthesis, both components and reaction of components. As for testing whether the actual outcome matched with the theoretical values, we had our samples go through EA and MS.Below on Figure [1] and [2] The surfactant, Benzyldime-thylstearylammoniumchlorid(BC18), **and dye, Beryllon II(Bell) is showed, which** were used in all of the tests. **In equation [1], the reaction of the** surfactant and dye (the synthe**sis) I presented, which forms the nano-material.**Surfactant and dye (the synthesis), which forms our nano-material.

$$4C_{27}H_{50}N^{+}(aq) + 4Cl^{-}(aq) + C_{20}H_{10}N_2O_{15}S_4{}^{4-}(aq) + Na_4{}^{+}(aq) \leftrightharpoons (C_{128}H_{210}N_6O_{15}S_4)_4(s) + 4Cl^{-}(aq) + Na_4{}^{+}(aq)$$

Equation [1]: The reaction of the surfactant and dye in water. .

This equation only shows the theoretic outcome. To confirm that this actually was the outcome, we did both EA and MS test.

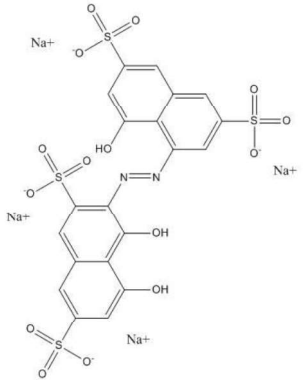


Figure [1]. Shows the dye, Bell

Notice the chosen dye has four negative sulfate groups, which of course has an effect on the results.

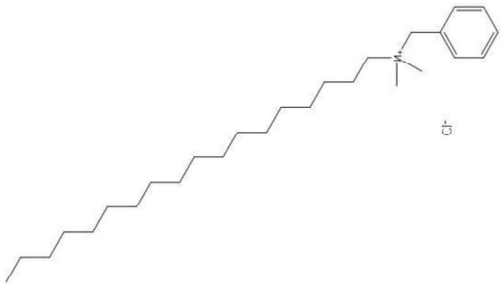


Figure [2]: Shows the result of the EA test

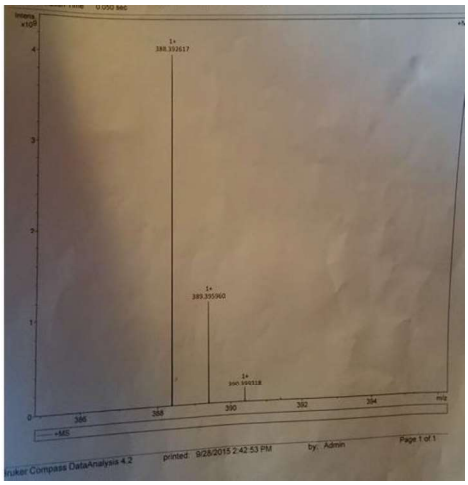
In the EA test, the examined values were at around the same amount as the theoretic values. But because it was only near, it was looked into, and it was found that the reason, it differed in the theoretic and the actual found values, could come from an extra NaCl molecule. This meant that the purity of the nano-material was affected by the NaCl molecules.

Table [1]: shows the result of the EA test

Atom	C	H	N
Theoretic Value	69.84%	9.62%	3.82%
Data	68.21%	9.20%	3.02%

As an after check, the nano material went through a MS-test, which showed that the surfactant had one positive charge and the dye had four negative charges.

This sums up that the theoretical components, was to be found in the actual nano-material.



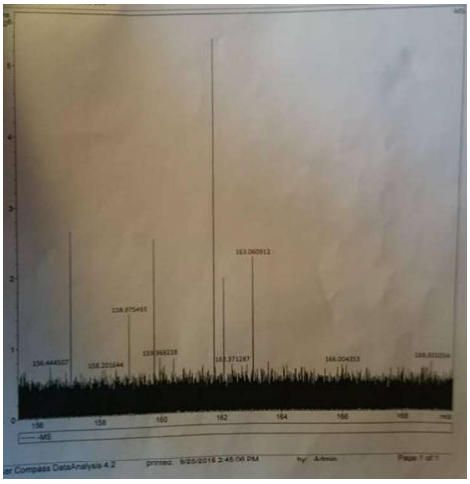


Figure [4]: MS test results showing our ESP- display

2.2 – Structure

For this part the theoretical structure is presented, determined by having the volume measured of both dye and surfactant.

The values for density or volume were not to be found, so instead of calculating the known values of the dye and surfactant, paper and pen were taken in use.

Table [2]: shows the results of the (theoretical) calculations of the surfactant and the dye

Surfactant	V	b	d	A_{Head}	A_{Tail}
	776,9 Å^3	4,2 Å	5,45 Å	50,4 Å^2	127,7 Å^2
Dye	h	b	d	V	
	27,3 Å	17,5 Å	2,4 Å	732.2 Å^3	

To keep an overview of the lengths and other measurements of the dye and surfactant, look at the table above.

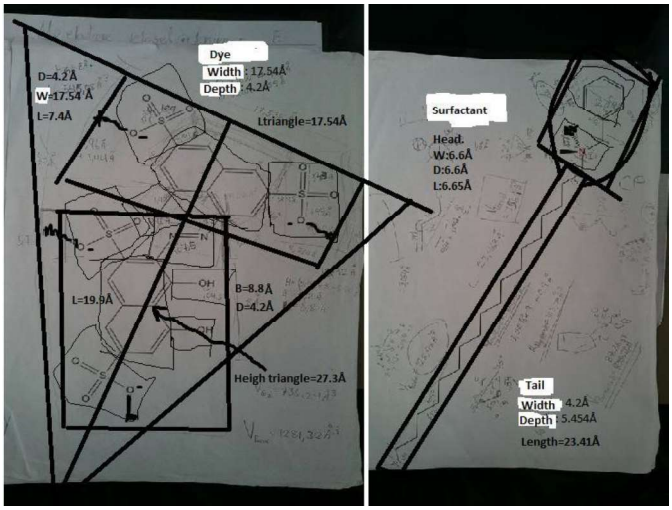


Figure [5]: Our surfactant and dye with measurements written on.

The way the volume of the molecules were measured, was to find the length, width, and depth for each groups, separate. For example, the dimensions for the tail of the surfactant were measured isolated, and the OH-groups were measured for themselves. Trigonometry was used to find the length of each dimension, by knowing the bond lengths, angles1, and Van der Wahl values2. Last of all the small boxes were put into bigger boxes and the widest length in each dimension of the bigger boxes was used. Notice figure [5] to see the different measurements.

2.3 – XRD

This part will get around the packing of the thin film layers. Also our test results from XRD and DSC, and data processing.
Our packing solution would be 4 surfactant-molecules for every dye-molecule. This is caused by the 4 negative charges on every dye-molecule, also the sizes fit (surfactant against dye).

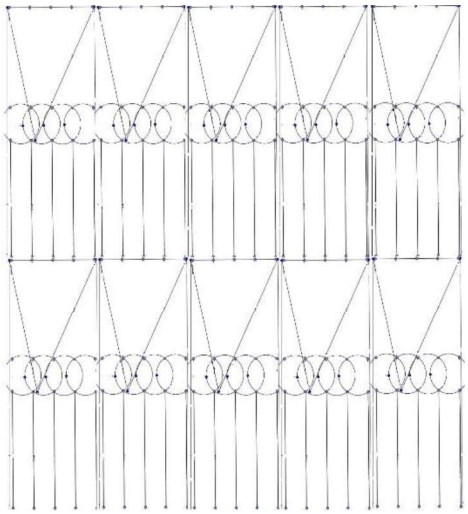


Figure [6]: Shows our solution to the packing of the dye and surfactant.

On the figure above each grid part got a volume on 3839.8 Å^3. Our packing solution which are showed on figure [6], are formed from the data given by table [2] and [3]. Since table [2] shows the size of our dye + surfactant, and table [3] which shows the angles and length, which are used to form the unit cell. Therefor by combining these data, we were able to form the packing solution.

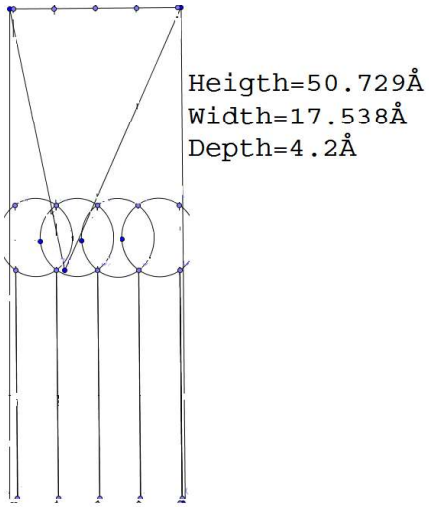


Figure [7]: Shows the measurements of the unit cell.

The picture above is showing the measurements of the unit cell from the packing solution.

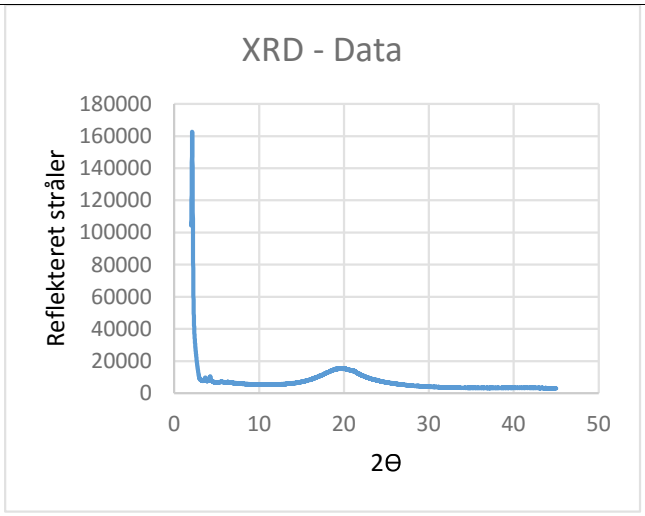


Figure [8]: XRD test results (X symbolize the angle)

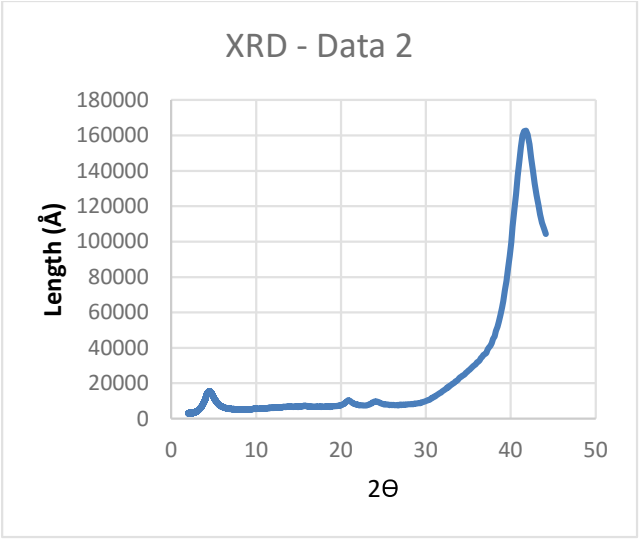


Figure [9]: XRD test results showing the length of a unit cell

Figure [8] and [9] show the results found through the XRD test. The results in Figure [8] show the angle, while Figure [9] shows the length of the unit cell.

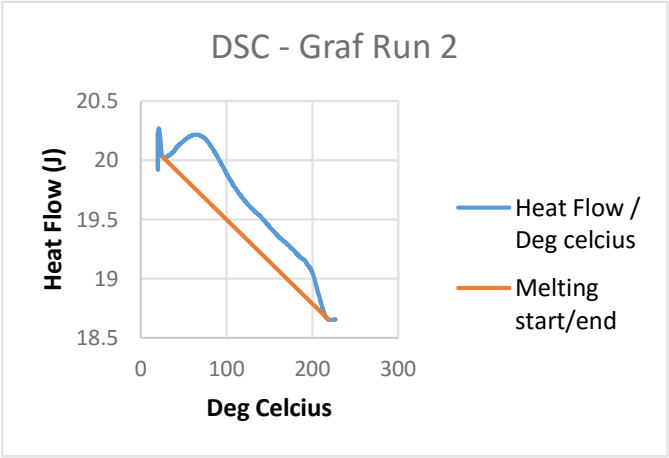


Figure [10]: DSC test results (run 2)

(Now that the nanomaterial consists of different compounds, it can be

interesting to make look into the phase-shifts that are made when it got heated up, to do so a sample of the not pulverized (if possible) nanomaterial was needed. The reason that we wanted it not to be pulverized was that it would be a lot easier to find a phase-shift when the material wasn't completely pulverized. The empty capsule was for the machine, so that it can subtract the melting points (or other disturbing things), that the aluminium capsules make from the sample of nanomaterial.)

On figure [10] are our test results from the DSC shown, the blue line was from the original run, while the orange line indicates the area from where we predict the melting started and ended. This area are used to find out the total amount of energy the melting or phase-shift required.

Table [3]: Data aligned from the top points in the two XRD figures.

XRD 2	x	y	z
2Θ	2,1228	4,2715	19,7113
d [Å]	41,98964454	21,12491043	3,954743202
Theoretical [Å]	Length 17.538 Å	Height 50.729 Å	Depth 4.2 Å

In the table above the data from both XRD figures, top-points are listed. This data will now be used to form a unit cell, by doing this we can find the density of our product. First, we find the volume of the unit cell, that is given by the x, y and z value, which gives us the result: 3.507 $Å^3$, compared to our known value from the packing solution. This match with an around 300$Å^3$ difference. This was a known factor, since our self-measured molecule had a lot of free space. We have now confirmed that our packing solution matches our unit cell. From here we can calculate the density of our unit cell, which is 1.042g/c<m^3. To relate with the density of water, it makes sense, that our nanomaterial has a higher value. This can be explained by the Sulfate atoms contained in the molecule.

2.4 – TEM and Microscopy

On this part we will describe the following figures from the tests: TEM, and Optical Microscopy.
At the TEM test we needed to have cobber-grids, with our 1mg/mL solution dripped on.

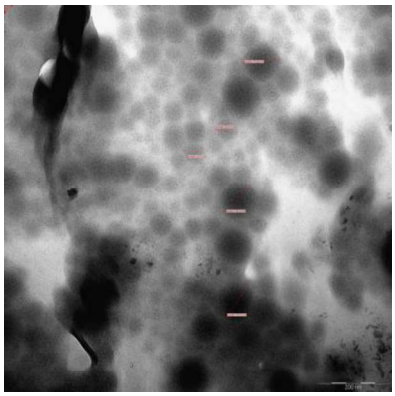


Figure [11]: TEM 1, test C

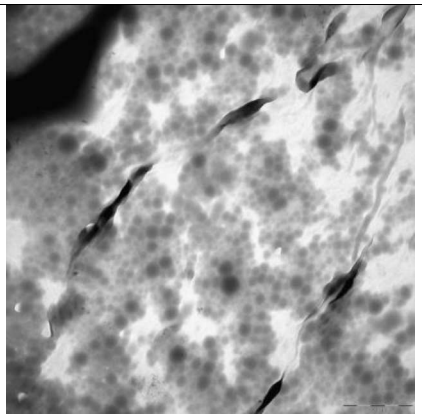


Figure [12]: TEM 2, test C

On figure [12] it is possible to see layers in the material which forms the film, these layers are important to notice since we are interested in the way that the material are build. There are further to very contrast folds where the material have contracted, which shows that the material are able to form different structures, and not just flat layers of film.

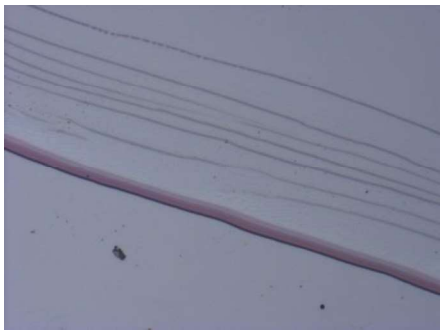


Figure [13]: Optical microscopy test showing an edge in the mid of our spin casting film. 10x zoom

These next figures, from the optical microscope test, shows that we have a consistent structure. Also that we have edged in the middle of the sample. This is because it holds two drops of material, instead of one.

Figure [14]: Optical microscopy test showing the mid of our spin casting film. 10x zoom

Figure [14] are almost completely white, this are because the film have some areas where it are uniform.

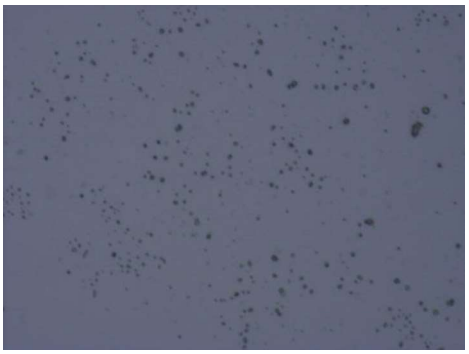


Figure [15]: Optical microscopy test showing the mid of our spin casting film. 20x zoom

Figure [15] got a lot of discolors dots, this are places on the film where there are small areas that are not completely covered with both layers of the film.

Figure [16]: Optical microscopy test showing these fish-like edges in the mid of our spin casting film. 10x zoom

Because of the two drops, these fish-like marks are formed at the edge in the middle of the sample.

2.5 – Thin Film

In this part the thin film is presented, referring to previous data and assumptions.

To find out, whether the material has formed itself to thin film, notice the figures showed earlier. At first, taking a close look at figure [11] from the TEM test, it is possible to see that the film is forming layers, which is showed by the different attitudes (that you can see). This is again possible to see in figure [13] from the micros-copy, because of the edges on the surface. The predicted thin film can be seen on figure [6]. Due to high differences in height measurements, see next section with AFM results, the packing solution is not a good enough solution.

2.6 – AFM and Structure of Thin Film

This section involves comments on the structure of the surface of the spin-casted nanomaterial; and a presentation of the AFM data.

The AFM results gave the measured structure of the surface, as shown on the figures below. The surface had some few tips, which were not too high. It was overall a flat surface, probably caused by having too little material on the spin casting sample with the 5mg/mL solution.

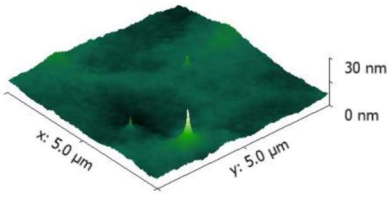


Figure [17]: AFM test in 3D showing the surface of the spin-casting film, with measured heights

These figures are showing the hights and deapths in 3D and 2D of the layered film.

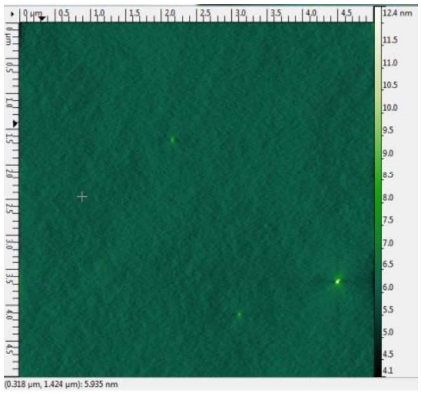


Figure [18]: AFM test in 2D showing the surface of our spin-casting film

On the figure underneath, the high peaks are impurities of the thin film, and the smaller peaks resemble the lamellar structure of the film. Basically it is showing the roughness of the surface structure. skal ind ved afm til sidst i afsnittet med "On the fuígure underneat are the high peaks.

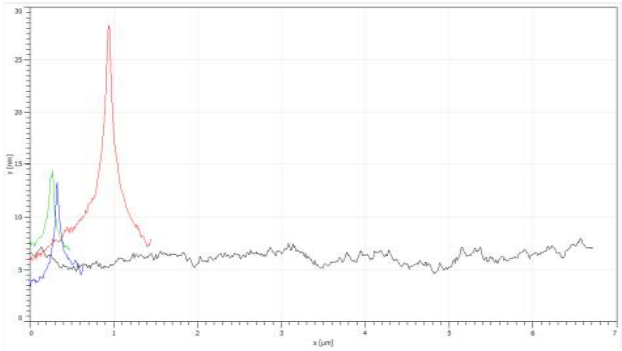


Figure [19]: AFM test in 2D showing the surface of our spin-casting film, with measured heights

The layer of the thin film is divided in levels, by different height distributions. The height difference of the two layers equals the height of the thin film, for the chosen area. The next picture is showing the height distribution for a chosen area on the thin film. Since the layer was very thin, it did not matter, where the thin film was examined with the Atomic Force Microscope.

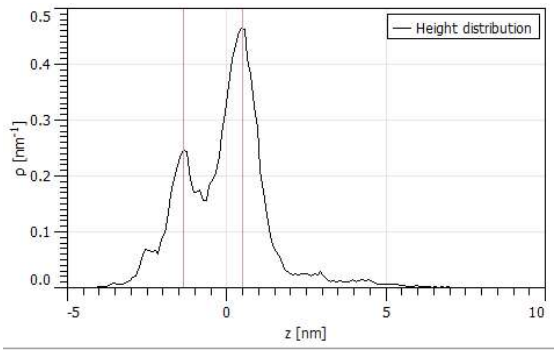


Figure [20]: Height distribution of the two levels of the thin film

The following table was made from the height distributions of multiple areas on the thin film.

Table [4]; AFM test showing the extracted data of the measured heights.

Layer 1(nm)	0.167	-3.25	-1.17	-1.36	-1.553	-1.
Layer 2(nm)	-1.265	-0.81	2.38	0.50	0.937	0.
Height (nm)	1.432	2.44	3.45	1.86	2.490	2.
Measurement	1	2	3	4	5	6
Average height(nm)	2.265					

These layers are not making a huge difference in height; thereby the surface structure can be determined to be fairly flat, caused by too little material. The height from the self-made package solution, 50.73Å, is way above the height extracted from AFM, 2.265nm (22.65Å), and does thereby not match. But compared to the height value of the unit cell from the XRD-results, 21.12Å, the values are much alike, with only 6.75% in difference.

2.7 – Optical Spectroscopy

In figure [22] it's to be seen, which colours were being absorbed by the 1mg/mL sample, when the light went straight on; at □=0.

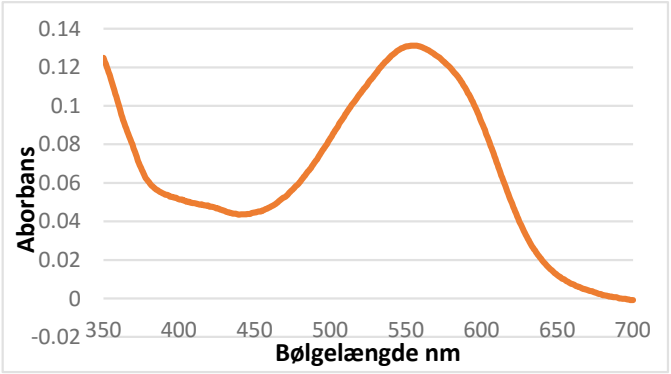


Figure [21]: Shows the Uv/vis test for the solution on 0,032 mg / mL

This test was used to compare with the glass-sample, where the approach of light, was set to different angles. This was done to investigate, how the thin-film was structured. But because of the glass plate sample was too little concentrated, the film was very thin; so the wavelengths was absorbed almost equally at the differ-ent angles. This is to be shown in the figure below.

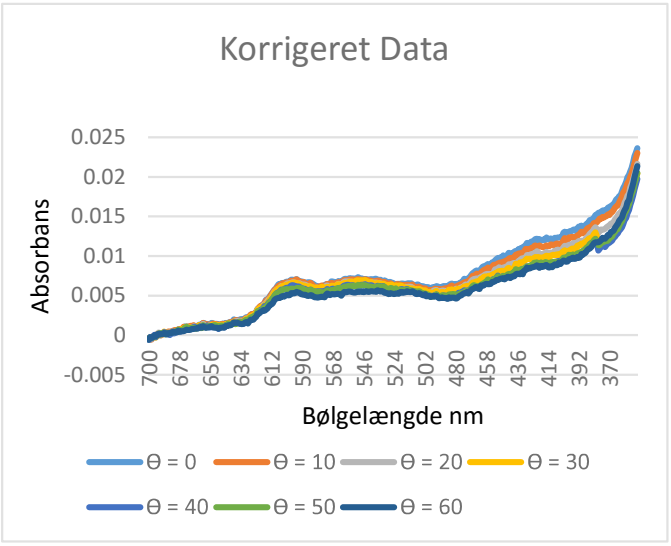


Figure [22]: Shows the data from Uv/vis with the glass plates 5mg/mL containing our film.

From this, what the structure looks like, cannot be concluded; related to angle between the dye and the glass plate.

3. Experimental; Procedure

Synthesis: The materials that were used for this synthesis were the surfactant, BC18 and the dye, Beryllon ll(90%), and demineralised water.

First 1g(1.354*10-3mol) dye and 2.55g(6.006*10-3mol) surfactant was weighted and put in each of its own 500mL flask. Then 100mL of water was added to the dye and 255mL was added to the flask with surfactant. NB: The surfactant was added after the water, to prevent too much foam. Both solutions were being stirred - the surfactant solution was stirred under heat, due to faster dissolution. The surfactant solution was then titrated into the dye solution, while stirred. Then the whole solution was filtrated by use of sub-pressure, and the sub-pressure was created by running water. The powder/crystals were cleansed with demineralised water, and sat to dry, then put in a container.

Solutions: There were used two different solutions in the experiments; the first one was made with 100 mg / 100 ml and the second was made with 500 mg / 100 ml. The solutions were made very simply, by putting nanomaterial (100 mg), so that it matched the amount of dichloromethane.

EA: A small sample was taken from the nanomaterial (about 15mg) and sat up for Elementary Analysis. This is a procedure of determining the weight percentage of the atoms from the sample.

MS: Even less nanomaterial was taken and sat up for Mass Spectrometry. This test was made to examine whether the theoretical components is to be found in the sample.

XRD: The analysis was used to gather information about the crystalline size, by making an x-ray beam, at a specific angle, deflect or

diffract in different ways, depending on the crystal-structure of the nano-material. Here to get a better result, it was recommended to use pulverized powder instead of large pieces of the nanomaterial. Therefor to start with, the material that should be tested were pulverized and moved to a container, where it was put until use.

TEM: The concentration (1mg / 1ml) was dripped unto a copper grid. The copper grid was thereafter exposed to accelerated electrons. By doing that, it was possible to get a picture of the nanomaterial, this by a transmission electron microscopy.

Microscopy: The 5mg/mL spin casting sample was used for this investigation. First, the whole sample was looked through, to see if there were good observation spots. Then pictures were taken of the edges and different areas in the mid, to study variations in the structure.

Spin Casting: Two small glass plates were cleansed with methanol and acetone. The one glass plate was taped to a rotating plate (spin-casting machine). The machine was being turned on, started spinning, and one drop of the 100mg/100mL solution was dripped to the centre of the glass plate. The same goes, for the 500mg/100mL solution. Two drops was dripped at the 5mg/mL though.

AFM: The glass-plate with the 5mg/mL spin casting was used for the AFM-machine to analyse the structure of the surface of the film.

UV/VIS: 100µL of the 1mg/mL and 3mL dichloromethane was put together in a 1cmx1cm squared plastic-sample, which was used for the Uv/Vis test. This solvent was used for measurement of the absorbance to compare with. The 5mg/mL spincasting sample was taken, and was exposed to tests of absorbance at different angles to match the solvent, first measured.

DSC: To make the test, there were made two aluminium capsules; one with the nanomaterial and one with nothing, these two were put into a machine, which thereafter melted the sample at a setting, which was wanted. In the two tests a 10 C increase every minute up to 260 C and 270 C, was used.

4. Conclusion

The prior motive was to synthetize dye and surfactant, and create an ionic self-assembling film. It can be concluded that the theoretical values, match the results from EA and MS analyses. Though the height does not match the AFM or XRD data, the theoretical volume of the unit cell was close to the experimentally determined volume. The spin casting and the dissolved nanomaterial, tensioned over the cobber-grid, showed in the tests that the nanomaterial was able to form layered film. From Uv/Vis, the angle between dye and glass plate was not easy to determine because of the thin solution. But in the AFM-, TEM- and Optical Microscopy tests, our examined film, was thin and uniform all over. It was therefore possible to create an ionic self-assembling thin film with BC12 and Bell.

5. Acknowledgements

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6. Notes and References

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1) Bond lengths and bond angles were known values, found in "Es-sential Organic Chemistry", by Paula Yurkanis Bruice, Pearson Edu-cation Limited 2016, third edition 1988. Chapter 1, pages 29-64. ISBN 13: 978-1-292-08903-4. 9-24-2015 17.00

2) Van der Wahl values found on website 9-24-2015 17.00
http://periodictable.com/Properties/A/VanDerWaalsRadius.v.html

3) Article describing the previous nano-students' work, found on website 10-07-2015
https://absalon.itslearning.com/ContentArea/ContentArea.aspx?FolderID=3084069&LocationID=63035&LocationType=1

4) Future ideas for nano-films, found on website 10-07-2015 http://aktuelnaturvidenskab.dk/fileadmin/Aktuel_Naturvidenskab/nr-4/AN4-2015bags.pdf