Production of nanomaterial through ionic self-assembly and spin casting

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Through application of X-ray scattering, differential scanning calorimetry, elementary analysis, light absorption- and mass spectrometry, various microscopy methods and a synthesized dye-surfactant complex has been examined to investigate structural and thermal properties. The goal was to examine thermal influence on the phase structure of the nanomaterial, and create a spin casted thin film lamellar structure. Thermal analysis showed that the material remained crystallized even after surfactant melting. Microscopy revealed traces of lamellar structure in the thin film samples.

Introduction

The recent years study [1-2] of molecular structures and mesoscopic order have presented exciting new possibilities for the theoretical production of new materials with desired qualities. One method of producing larger amounts of nanomaterials is by reproducing nature through the process of ionic self-assembly (ISA). Experiments have proved that it is possible to create such materials with very specific molecular structures [2], and that in solution and as solids this has been achieved using reproducible methods. It is desirable to be able to process the nanomaterials into ordered structures such as thin films so that their properties can be determined. Attempts have been made to achieve a predictable method of producing a thin film with lamellar order, but the process is still not completely understood. Our aim was to reproduce the works of M. Santella[1] with slightly different materials, and to test the effect of temperature on our nanomaterial
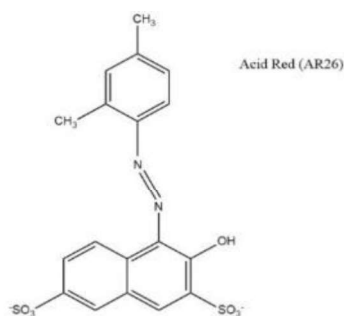
Figure 1. Acid red (AR26), the azo-dye used in the experiment. There are two negative charges localized at the sulphonic acid groups.
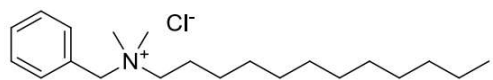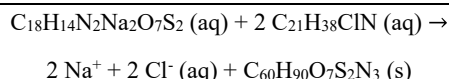

Figure 2. Benzyldimethyldodecylammoniumchloride, or BC12, the surfactant used in the experiment. There is one positive charge found at the nitrogen.

We expected to create a nanomaterial with high mesoscopic order and a clear lamellar structure through the process of ionic self-assembly. The goal was to create a thin film using a mixture of BC12 surfactant and AR26 dye (commercially available products) in a dichloromethane solvent. The dye, having a negative charge, combined with the positive charge of the surfactant head (see figure 1 and 2), should, with the interaction between the two, in theory create an energetically favorable lamellar structure of densely packed molecules. This would happen by electrostatic interactions between the cationic surfactant head (+) and the polyanionic dye (-), causing ionic self-assembly

During the analyzing process, it was determined that we had achieved an ordered (possibly lamellar) thin film and a crystallization in the product that was not spin casted.

Method and Experiment

The nanomaterial was produced by dissolving 1 gram of Acid Red dye (AR26) and 1.42 gram of surfactant (BC12) in 100ml of demineralized water giving a ratio of two surfactants per one dye. These two solutions were then mixed together to create the combination of dye and surfactant.

$$C_{18}H_{14}N_2Na_2O_7S_2 \text{ (aq)} + 2\ C_{21}H_{38}ClN \text{ (aq)} \rightarrow$$

$$2\ Na^+ + 2\ Cl^- \text{ (aq)} + C_{60}H_{90}O_7S_2N_3 \text{ (s)}$$

To separate the new material from the water and charged ions, the solution was filtered. The process of suction filtering requires access of water to create pressure under the filter, which then separates the liquid from the combined compounds that lie above the filter. To clean the dye and surfactant complex, 30ml of demineralized water was poured into the suction filter. Some of the dried dye compound was dissolved in two different solutions, one with 100mg of dye and 100ml of DCM (1:1) and the other one with 100mg of dye and 20ml of DCM (5:1).

To make the nanomaterial lie in order and spread equally, the dye and surfactant solutions had to be spin casted. The two

Table 1. Elementary composition of material as calculated beforehand and when measured using Elementary Analysis.

	Dye (atoms)	Surfactant (atoms)	Weight calculated (%)	Weight from EA (%)	Deviation (%)
Carbon	18	21	69.06	69.01	0.05
Hydrogen	14	38	8.69	9.12	0.43
Nitrogen	2	1	5.37	5.33	0.04

solutions (1:1 and 5:1) were spin casted on to two separate sheets of glass substrates.

For the absorbance tests, 50 microliters of solution of 100mg dye and 100ml DCM (1:1) were dissolved with 3ml of DCM. This solution was poured into a cuvette and placed in the sample cell. In the reference cell there was placed a cuvette with only DCM. With thin films there was first placed a blank sample as reference data. Then the thin film of 1:1 solution was placed and examined several times by rotating the thin film in steps of 10 degrees (beginning with 0 degrees and ending with 60 degrees).

For the DSC (Differential Scanning Calorimetre) tests, exactly 3.13mg of the dried dye was placed in a small standard aluminum capsule and closed using a stamp. An empty capsule was prepared in the same way to be used as a reference. Both capsules were placed in the DSC device.

The spin casted samples (of solution 1:1 and 5:1) were examined using an AFM microscope, to look at the surface of the thin film. An AC240 tip was used, set to tapping mode.

When looking at the spin casted samples using optical microscopy, both the solutions were examined.

Small circular copper grids were covered in a thin layer of solution by placing a small drop of 1:1 solution on the grids and storing them in an air tight container. These were used for the TEM.

Results and discussion

The nanomaterial was made using the dye AC26 and the surfactant BC12. AC26 has two negative charges and would be expected to make ionic bonds with two surfactants that have one positive charge each. Elemental analysis[13] showed that our product's elementary composition was within a 0.5 +/- percentage of the expected theoretical values (see table 1), meaning that our two compounds reacted with each other as expected. Mass spectrometry[15] analysis supported this conclusion.

Figure 3 shows absorbance as a function of wavelength. This data is obtained through absorption spectroscopy[16] of the dye solution. The x-axis is wavelength lambda λ (nm), which shows the visible light spectrum from 300nm to 700nm[10].

The y-axis is the absorbance A of light, which shows which part of the spectrum is absorbed and eliminated by the solution. The graph at 300nm is increasing progressively to approximately 525nm, which indicates that the solution has absorbed the light from 300nm till 525nm. Whether there is a low or high absorbance at a wavelength depends on the

Table 2. Factor K_f and angle α for wavelength λ 500nm, 550nm and 600nm.

| Wavelength λ	c(λ)	a(λ)	b(λ)	Factor K_f	Angle α
500 nm	0.037444	-0.0514	0.09	0.27	58.78
550 nm	0.037058	-0.0496	0.06	0.20	63.32
600 nm	0.037199	-0.0474	0.05	0.10	71.32

material. This solution has the most absorbance at 525nm,

which is green light. The graph hereafter decreases exponentially to 0 absorbance at 600nm and continues at 0 absorbance. This indicates that the solution has eliminated the part of spectrum between 600nm and 700nm.

Figure 4 shows absorption of thin films as a function of wavelengths from 300nm to. It is the same thin film of dye that has been rotated 10 degrees after each spectroscopy examination (from 0 degrees to 60 degrees). Figure 3 and Figure 4 differ as to their highest absorbance within the visible light spectrum. The thin film has its peak absorbance at approximately 490nm, which is the spectrum of blue light. The different angles of the thin film shows that higher angles correspond to lower light absorbance in the material. As an example, at a wavelength of 500 nm, evidently higher absorbance is measured at an angle of 0 degrees, than at an angle of 60 degrees, at an identical wavelength. The difference between testing the solution and the thin film, is that the molecules in the solution flow in all directions and they are not ordered, while the molecules in the thin film have a thin layer of the dye which is more in order and has a more structural form. Therefore molecules in the thin film can be used to determine at which angle the dye molecules lie in the thin film, and with that make a conclusion regarding the unit cell structure.
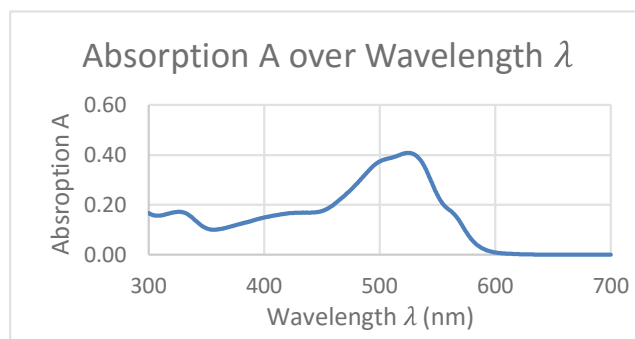
Figure 3. UV/VIS data, showing absorption over wavelength for the compound in solution. Absorbance is highest around a wavelength of 520 nm (green light).
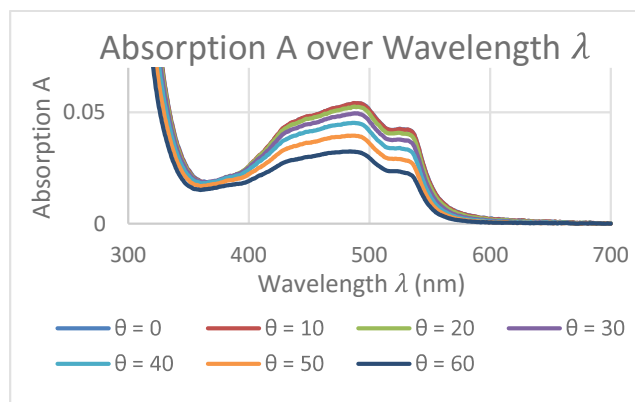
Figure 4. UV/VIS data, showing absorption for the different angles of the thin film. The readings can be used to determine the angle of the molecule on the surface of the glass substrate.

For that, an α angle has to be determined by the following formula

$$K_f = \frac{\dfrac{a+b}{b-c}}{2 + \dfrac{a+b}{b-c}}$$

$$\alpha = \arccos(\sqrt{K_f})$$

Molecules in the thin film have, at a wavelength of 500 nm, an α-angle of 58.78°. At a wavelength of 550, the α angle is 63.32° and at 600 nm the α angle is 71.32° (see table 2). Deviations for a(λ) and b(λ) values is approximately 0.01-0.08. From the results, it can be concluded that there are two transition dipole moments where the dye molecules lie orderly with the given angles at a specific wavelength; that can also explain the difference between solution and film spectra. Assuming crystalline supramolecular composition of the dianionic compound, structural constitution was studied through powder X-ray diffraction (XRD)[14]. Analysis of the resulting XRD scattering data (see Figure 5) confirms crystalline structure of the ayo-dye complex, as well as providing insight regarding the volumetric configuration of the unit cell[12]. By looking at lattice spacing in relation to peak diffraction intensities in Figure 5, spatial proportions of the corresponding unit cell, can be determined. These calculations are examined with regard to the proposed proportions of the dye and surfactant molecules, which were calculated using a Van der Wall's radius[11] based molecular model (see Figure 6). For the width of the model, the depth of a carbon atom as seen as a sphere with a shell with Van der Wall's radius, was chosen.

With acquisition of the voluminous outline of the unit cell through XRD, the feasible supramolecular arrangement of the unit cell can be estimated by comparing these numbers with the spatial properties of the calculated possible dye-surfactant configurations (see table 3). Experimentation with said data reveals a two-complex containing unit cell (see Figure 7). The proposed molecular arrangement in the unit cell, allows for a lamellar structure (see Figure 8). Several methods of microscopy were used to study the structure of the spin casted samples of the compound.

The atomic force microscopy (AFM)[7-8] pictures gave a picture of the surface of the film, showing height variations. By looking closely at certain sections of the picture, and analyzing the pixel intensity, it was determined that a lamellar structure was present in the material. Two neighbor peaks were found to have a spacing distance of around 3.5 nm (see Table 4), which corresponds to one of the lengths found in XRD and also to the calculated length of our molecule. The pictures showed a surface that has a 60 nm variation in height for the 1:1 solution and a 4 nm variation for the 5:1 solution (See figure 9, 10 and 11). Which means, that the molecules of the higher concentration has more densely packed molecules. Transmission electron microscopy (TEM)[9] was applied to examine the structural character of the dye-surfactant complex, revealing trace amounts of material arranged in filmic structures (See figure 12). However, upon investigation, both samples proved deficient for conclusive visual analysis. Optical microscopy was also used on the spin casted samples, and the data supported the existence of a thin film that could potentially have a lamellar structure (See figure 13 and 14).
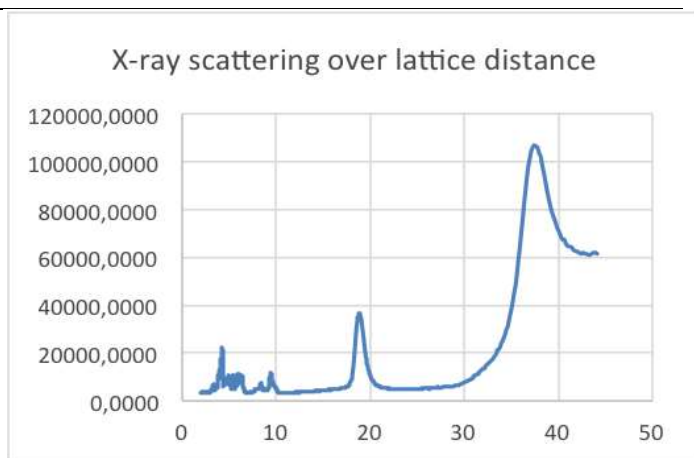
Figure 5. XRD data showing the peaks corresponding to the dimensions og the unit cell.

Table 3. Dimensions of a two complex containing unit cell as calculated using the VdW models compared to the XRD readings.

	Length	Height	Width
VdW model (Å)	20.82	34.84	3.4
XRD readings (Å)	18.86	37.43	4.26
Difference (Å)	-2.04	+2.59	+0.86
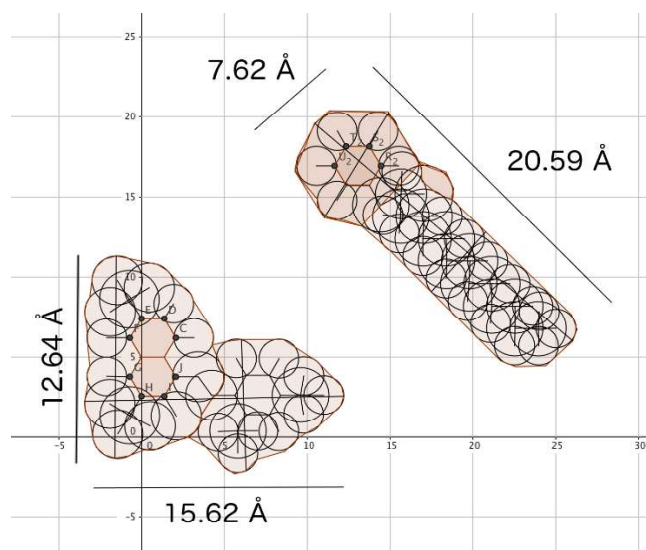
Figure 6. Models of the molecules that were used in the experiment created in Geogebra. The atoms are represented by circles with the corresponding Van der Wall's radius. The dimensions were then measured

A differential scanning calorimeter (DSC)[4] test was conducted to examine the effect of temperature on the nanomaterial. The data (see table 5) derived from the plotting of heat flow over temperature (see figure 15) showed that the compound had a melting point of 189 degrees Celsius with the latent heat chemical bonds. The energy added during the melting process was 657.31 kJ/mole, which corresponds to the energy needed to break the two ionic bonds. There is a small dip around 55 degrees, which might have been a glass transformation state, but because it is very small this is not regarded

as probable. There is a small dip around 55 degrees, which might be the melting of the surfactant, as Benzyldimethyldodecylammoniumchloride[3] has a melting point of 60 degrees Celsius. It might also indicate the glass transformation state of the polymer, as there is observed no definite peak but an incline of the graph.
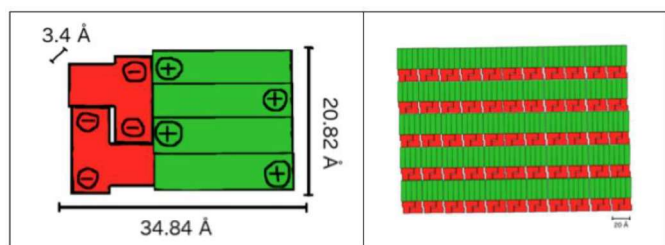

Figure 7 & 8. Proposed unit cell and packing model of the spin casted thin film. Each unit cell is composed of two dye-surfactant complexes. The complexes arrange themselves in a lamellar structure as seen in figure 8.

Table 4. AFM-peak spacing found using the 3-D analyzis program Gwyddion.

| X (nm)	Y (μm^{-1})	Width (nm)
-32.95	65.5	3.43
-17.14	56.1	15.87
-13.84	52.9	3.55
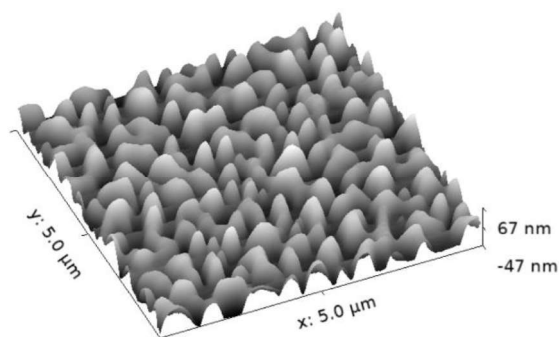
Figure 9. AFM picture showing height difference in the surface of the material, stretching from -47 nm to 67 nm. For the 1:1 solution.
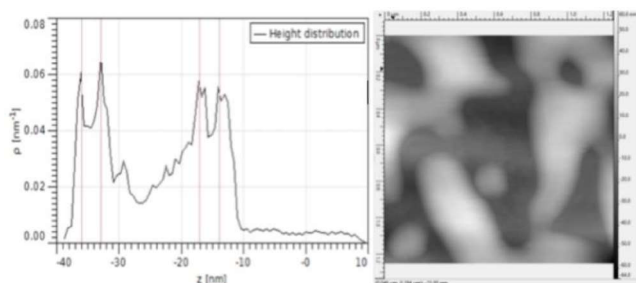

Figure 10 and 11. AFM pixel intensity showing two layers with the same height as our unit cell as supported by XRD readings. For the 5:1 solution
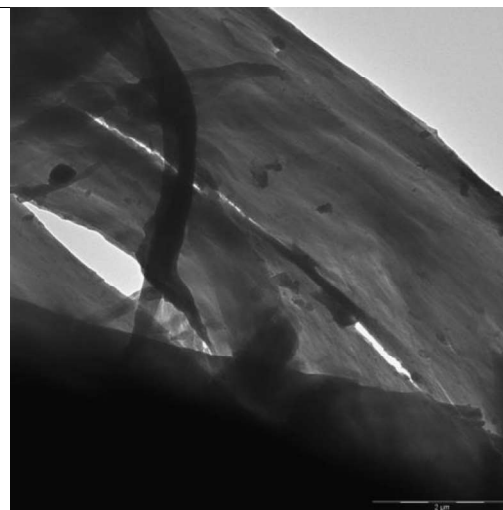
Figure 12. TEM picture showing filmic structure. There was not a lot of material on the copper grid, making it hard to see the material.
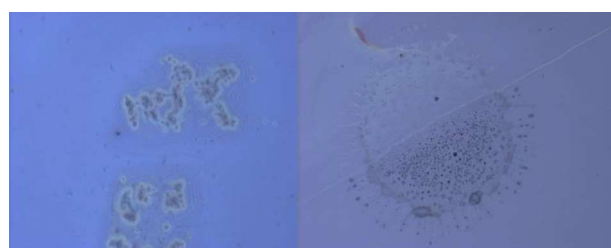
Figure 13 and 14. Pictures taken using optical microscopy with 50x and 10x magnification. We can see that the sample is contaminated, but has a flat structure.
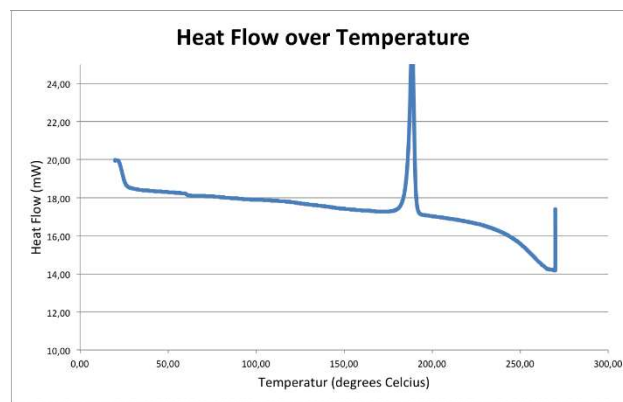
Table 5. Data derived from the Differential Scanning Calorimeter test.

Start peak (°C)	184
End peak (°C)	191
Area of peak (mW)	26.65
Time of melting (s)	78
Energy of melting (mJ)	2078.7
Weight (mg)	3.3
Latent heat of melting (J/g)	629.9

Figure 15. DSC readings showing the heat flow over time. There are two interesting deviations at 55 and 191 degrees, signifying a charge in the compound.

Conclusions

The results of our experiment have shown that the ionic self-assembly between AR-26 and BC12 did indeed result in a successful synthesis and the desired thin film structure with lamellar order. A crystalline structure has been confirmed through XRD, with unit cell dimensions that corresponded to the calculated lengths of a proposed unit cell. Relating to temperature changes, we have revealed that the surfactants in the material can melt while retaining supramolecular interactions in the complex.

Acknowledgements

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