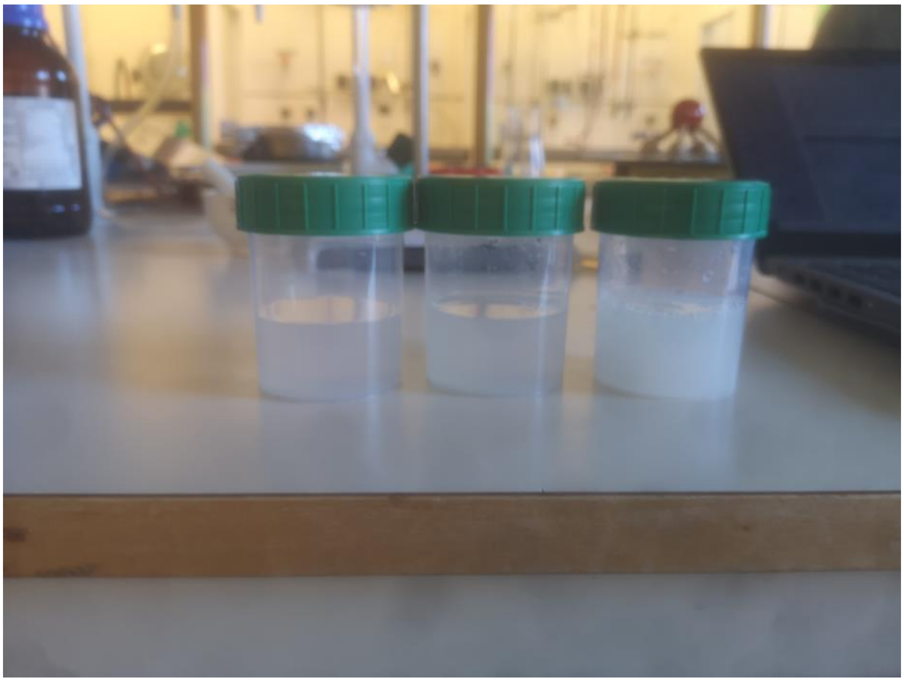
Critical aggregation concentration

of CNC

Bachelor's thesis in engineering program Chemical Engineering



Nora Linnér

DEPARTMENT OF ORGANIC CHEMISTRY

CHEMISTRY AND CHEMICAL ENGINEERING

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2021

www.chalmers.se

Determined of CAC in CNC NORA LINNÈR

Supervisor: Gunnar Westman and Amit Kumar Sonker Chemistry and Chemical Engineering

Examiner: Gunnar Westman Chemistry and Chemical Engineering

Department of Chemical and Biological Engineering

Division of Organic Chemistry

Chalmers University of Technology

SE-412 96 Göteborg

Sweden

Telephone: +46(0)31-772 1000

Göteborg, Sweden2012

Cover: Determined of critical aggregation concentration in nanocrystallin cellulose

Abstract

The main point in this report is the manufacture of CNC cellulose nanocrystal and the measurement of conductivity and aggregation effect from different compounds when added to the cellulose nanocrystal. Both high sulfate group CNC and low sulfate group CNC are manufactured. For the high sulfate group CNC is coordinated with different hydroxide, different organic compounds and different molar ratio of sodium hydroxide compared. For the low sulfate CNC only the different hydroxide and different organic compounds are compared.

Nanocellulose is available in, among other things, in three different forms which are cellulose nanocrystal (CNC), cellulose nanofibers (CNF) and bacterial nano-cellulose (BNC). Where the difference between them is the size of the molecule. In this report the main focus is on the cellulose nanocrystal because it was the one that was manufactured. The manufacture of cellulose nanocrystal is made with sulfuric acid and microcrystalline cellulose.

In the result the comparison between the different compound and the two different amounts of sulfate groups in the CNC also the critical aggregation was calculated. It can be seen the size of the additive plays a role for the conductivity but not for the critical aggregation concentration. For the conductivity it can be seen that the smaller molecule gets a larger conductivity compared to a molecule that is larger when the high sulfate CNC is used. But for the low sulfate group CNC was the opposite trend observed. But the size has no impact on the critical aggregation concentration.

And for the different molar ratio it goes up in conductivity when lower amounts of sodium hydroxide are added to the high sulfate CNC. Also for the organic compounds in the high sulfate CNC the conductivity is affected by size but for the low sulfate CNC the size has not as much of an impact on the conductivity. Also for these two experiments the critical aggregation is not depended upon the size of the organic compound nor the amount of sodium hydroxide that show no impact.

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1. Introduction

The main question for this work was to determine the critical aggregation concentration in cellulose nanocrystalline when there is a high amount of sulfate groups and low amounts of sulfate groups. So under this a comparison between different hydroxide, different organic compounds and different molar ratio between sulfate groups and sodium hydroxide was done. Also a comparison between high sulfate content groups on CNC and low sulfate content groups on CNC.

So for this we need to know more about how the critical aggregation concentration is and how to calculate it. Firstly cellulose nanocrystalline was produced and that it can come from different types of materials. But also we need to know where cellulose come from and that there are several different variants of nanocellulose. But also to know how critical aggregation works we need to know how critical micelle concentration works.

With known critical micelle concentration we need to know how surfactants work and that four different surfactants are available and that they have different characteristics. But also how micelle will be formed and how it works. But also what kind of things it is used in.

So in this report you can read about cellulose in general and how that works. About nanocellulose and little about the different types that are available. A brief information about the different types and most about cellulose nanocrystalline. How to manufacture cellulose nanocrystalline. More about how surfactants and micelle works. But also the difference between critical micelle concentration and critical aggregation concentration. There are results and differences when having various amounts of sulfate groups in the CNC and what the difference in the experiment is. And if the molecule size has an impact on the critical aggregation concentration and what the conductivity on different compounds gets when the weight percent gets lower.

1.1 Background

1.1.1 Cellulose

Cellulose is one of the most important components in biomass[1]. It will be up to 40 to 45 percent of the total weight that the wood has, but of course it depends on which wood source that are used. There is a difference depending on the necessary varieties. Cellulose is the most natural polymer on this planet. Every year about 75 to 100 billion ton of cellulose are produced on a global level. Year 1938 was the first time that humans succeeded in producing and discovered that cellulose existed on the earth. How did humans discover it? It was when the wood variety was treated with nitric acid that the human for the first time found out about cellulose see figure (2.2 for the molecule structure).The structure of cellulose (see figure 2.1 for cellulose molecule) is a long chain with thousands of glucan molecules that are bound together using the bonding known as beta-1,4. Glucan is a polysaccharide and cellulose is glucan that is called β-1,4 glucan.

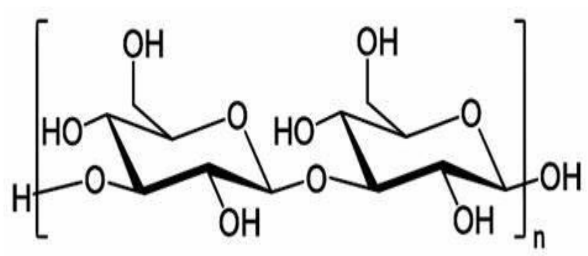

Figure 1.1 Structure of cellulose[1]

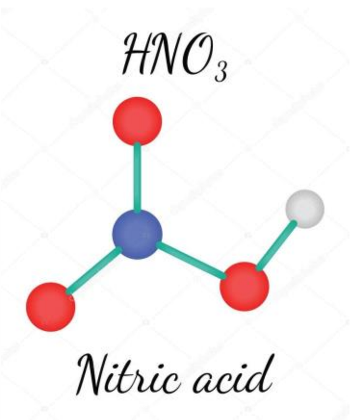

Figure 1.2 Nitric acid[2]

As mentioned earlier cellulose is the most common compound on the earth. Cellulose can be found in dietary fiber food, construction and fireproofing materials[2]. For more than 150 years cellulose has been considered to be a polymer that is good for the environment and renewable and it can also be used as an energy source[3].

1.1.2 Nanocellulose

Something that is very unique with nanocellulose is that it is a natural compound that is produced from cellulose that comes from nature[3].Nanocellulose is very friendly for the environment. It is produced using different manufacturing methods. The characteristics of nanocellulose are very fascinating. Characteristics such as surface chemistry, exceptional physical and chemical strength and rich hydroxyl groups for modification are common for nanocellulose.There are many advantages with nanocellulose characteristics because they have many biological characteristics and it is good for the environment. The biological characteristics are among other things biodegradability, biocompatibility and non toxicity.

As mentioned earlier, nanocellulose is one of the compounds that has low negative impact on for the environment[3]. There are three different variants on nanocellulose. Cellulose nanocrystal (CNC), cellulose nanofibers (CNF) and bacterial nano-cellulose (BNC).

1.1.3 Microcrystalline cellulose (MCC)

Microcrystalline cellulose is mostly used in industries like food, medicine and cosmetics[4]. Manufactured microcrystalline cellulose comes from wood or cotton cellulose and hydrolysis with a mineral acid is what the industries use when producing microcrystalline cellulose. Since cellulose can come from different sources the property will be different. The property will be based on the property the cellulose has. Cellulose can come from other sources than wood and cotton, but these two are the main sources that are most used in the industry. For example coconut shell and sugarcane bagasse has been used to manufacture microcrystalline cellulose.

The molecule formula for microcrystalline cellulose is (6CH10O5)n and it is a white powder that comes from refined wood pulp[5]. This polymer is a subject that can not decompose during digestion. Microcrystalline cellulose can be used in the pharmaceutical industry as an excipient. Since microcrystalline cellulose is an excellent characteristic in the form of compressibility it can be used as a solid form of pills. These pills can be formed to be hard and dissolve very quickly. Cellulose and microcrystalline cellulose are the same except the USP standard.

1.1.4 Cellulose nanocrystal (CNC)

The term CNC is a type of cellulose nanomaterial that has a length that mostly is between 50 to 500 nanometer long[1]. The diameter can be between 3 to 10 nanometer. It also has a partial degree of crystallinity. If we want to define CNC you can say that it is very good and has a high crystallinity. But we cannot by science define what CNC for real is. In some studies it is defined nanocellulose as a material that is produced from a hydrolysis that is made from enzymes or from oxidation which determines cellulose. These are called crystalline cellulose. Most studies that have rapport about CNC produced says that the cellulose material must go through a chemical process. Just crystalline cellulose exists in natural form and is used in natural form.

Definition of CNC may be very vague but at some time in the late 1940s to early 1950s they started to produce CNC[1]. Manufacturing of CNC is mainly done through the use of a cellulose material and acid hydrolysis that is mixed together. In these studies the manufacturing of CNC comes from cotton cellulose as cellulose material and sulfuric acid as acid hydrolysis. See chapter 2 to read more about the step in CNC manufacturing.

In many studies manufacturing of CNC is mostly defined by the use of mineral acid[1]. For manufacturing of CNC sulfuric acid and phosphoric acid are used. Sulfuric acid that has weight% of 64 is the most used of the two compounds. But what makes sulfuric acid the best acid hydrolysis for manufacturing of CNC depends on the sulfate group that is attached to the cellulose molecule. It is when sulfate groups attached to cellulose that are making it more stable and make it easier when the aqueous processing is going on.

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One disadvantage when using mineral acid when manufacturing CNC is the final recovery[1]. It is because we need to have an extreme amount of acid when manufacturing CNC. Therefore, the process needs to be developed into a more friendly for the environment and cheaper manufacturing technology for CNC. Lately it has been using organic acid like dicarboxylic acid to manufacture CNC. But unfortunately organic acid will be much weaker, which means that the exchange of CNC will be lower. It is because cellulose depolymerization does not form as much.
Manufacturing of CNC when cellulose is produced from acid hydrolysis the cellulose comes from cotton or wood is extracted[6].

1.1.5 Cellulose fiber (CNF)

CNF is referred to the type of cellulose that has a diameter around 100 nanometer or lower and with a length around 500 nanometer or higher[1]. The only thing that can define CNF is the physical dimension. When CNF first was manufactured was it through mechanical partial fibrillation and is called microfibrillar cellulose. CNF is produced from beginning through mechanical fibrillar. But this manufacture is very energy-intensive. Despite the structure of CNF, it is good to do clean and strong CNF-fiber. But it can also be troublesome to manufacture products with high quality.

Chemical pretreatment is commonly used to reduce energy consumption in the factory that manufactured much of chemical or thermochemical pulp and mass industry[1]. It can also be used to manufacture substrates that are fine and can be used to improve the cell membrane. Enzymatoc or chemical pretreatment can be done so the energy consumption is reduced upon cellulose fiber production.

1.1.6 Bacterial nano-cellulose (BNC)

Bacterial nano-cellulose is a polymer with a structure that is three dimensional [7]. Formed by pure cellulose and is of nanofibers. It is also synthesized by bacteria and it is organized in a network that is contact with each other. Their mechanical properties and biocompatibility are used in scientific studies in biomedical, electrical applications by other things. Furthermore, nanosized material can be introduced to form 3D network structure.

Bacterial nano-cellulose it's a material has low negative impact on the environment[8]. It's most known because of the structure that is a network and for the physical properties. Some of the good physical properties it has is the good surface area, water holding capacity, chemical stability and being very friendly to the environment. With these properties it does so bacterial nano-cellulose is a good candidate when manufactured as a three-dimensional carbon nano-material or flexible material for architecture. Some other things the studies have shown is the impact of bacterial nano-cellulose as energy storage in for example lithium batteries or the energy conversion in for example oxygen reduction reactions.

1.1.7 Micelle

For almost all molecules that are dissolved/dispersed in water the molecules will start to aggregate to some extent, organizing their polar and are non polar structural segments[9]. The polar side will become a head that will be in contact with the water. The non polar will be a tail that will contact each other in the middle. The core will be with the nonpolar tails. The form of the micelle can be changed if some of molecular segments or external parameters are changed. The parameters are for example the temperature and acidity of the solution.

What is micelle most used for?[9] They are most used for the ability to dissolve particles that are nonpolar and transfer them into the water or carry drugs which do not dissolve in water. Micelle is most used in biological and industrial fields. With carrying drug micelle is a very good carrier molecule and it can also change the sizes of the micelle molecule.

When a certain concentration reaches for the amphiphilic molecules it is called critical micelle concentration or in short form CMC.[9] Micelle form can not only be formed in water it can also be formed in a nonpolar organic solvent. In the cases with organic solvent it will be called inverse micelles and it is because of the situation that it will be in the opposite way from the cases with water.

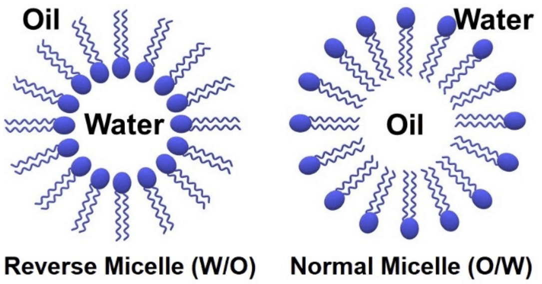


Figure 1.3 Micelle form.[3]

1.1.8 Surfactants

Everything on this planet is in some way implicated by chemistry and chemicals[10]. Chemistry is something that is important for the existence of humans and the existence of the material in the world. Today around 120 million organic and non organic compounds exist on this planet. So the more we know about chemistry, the more we know about our world. A couple of the 120 million compounds have a meaning for humans and can simplify our life. One of the things is surfactants. Surfactants is a compound that has a hydrophobic “tail” and a hydrophilic “head”[11]. Many of the products that we are using every day have surfactants in themselves. For example shampoo, detergent and oils.

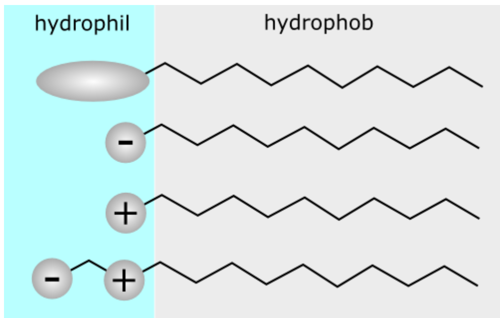


Figure 1.4 How a surfactant look like[4]

Surfactant is a substance that has two parts[10]. A hydrophobic and hydrophilic part, see figure 1.4 to see how it looks. The hydrophobic part consists of a carbon chain, which contains 8 to 18 carbon atoms. The chain can be strengthened or branched and every carbon atom has a hydrogen (H) or flour (F) bound to it. The hydrophilic group consists mostly of a substance that is an ionic or polar group. With a high effect the surfactant can be related to CMC which is lower and has a lower surface tension. CMC stands for critical micelle concentration. Read more about CMC in capital 1.1.9.

The surfactactants can be classified as four different types of surfactants[12]. Anion activity surfactants there the hydrophilic “head” will have a negative charge with sulphates, sulfonates or carboxylates. Cation activity surfactants there the hydrophilic “head” will have a positive charge with quaternary ammonium salts or ammonium salts. Non ionic surfactants are when the hydrophilic “head” has a neutral activity like alcohol or polyethylene glycols. Zwitterion surfactants have both a positive and negative charge that take out each other and will be neutral[12]. This type of surfactant is best paired up with a non ionic surfactant or an anion for best result. Gemini is also a type of surfactant. This type has two hydrophilic ”heads” and hydrophobic “tails” with a spacer between the two heads. If the hydrophilic part has the same molecule and is identical and the hydrophobic part is the same this gemini surfactant will be identical[10]. One example of anion is SDS and one example of cation is CTAB.

1.1.9 CMC- Critical micelle concentration

When a concentration reaches a specific level of micelle (read more about micelle in chapter 1.1.8) starts to form[13]. This is called critical micelle concentration (CMC). When the point has been shown and when adding more surfactant it will no longer have an effect on the surface tension. Critical micelle concentration is defined by surface tension as a function of the surfactant concentration.

So the value of critical micelle concentration can be determined by the physicochemical properties of a solution with surfactant change and as concentration increases of the surfactant [14]. When added electrolytes the critical micelle concentration will decrease. The effect of the decrease will be density on the counterion.

1.1.10 CAC- Critical aggregation concentration

A charge system is a strong attraction between a group that is charged[15]. The attraction between them is electrostatic and with this attraction it will lead to a concentration of surfactant over a bulk complex. This is called critical aggregation concentration. How critical aggregation concentration is determined is usually the surface tension or by surfactant-specific electrode. The surfactant-specific electrode can not go together with a surfactant molecule that is nonassociated.

An interaction between polymers and surfactants in a solution is something that is really important for the science field of colloidal studies[16]. When the critical micelle concentration gets lower than the original critical micelle concentration (surfactants alone) the system should be. This is called critical aggregation concentration.

The critical aggregation concentration is defined when the concentration in the bulk of polymer mixed with a surfactant complex starts to form[16]. Critical aggregation that has an opposite charge in systems with polyelectrolyte and surfactant mostly get surface tension isotherms. This type can get up to three steps lower in magnitude than what the critical micelle concentration has.

2.Experimental

2.1 Manufacture of nanocellulose (CNC) from MCC

Two days before starting with the manufacture of nanocellulose ensure that you have 64 weight% sulfuric acid. Manufacture of 64 weight% by mixing 350 ml of 99 weight% of sulfuric acid with 360 ml non ionic water. Added sulfuric acid portion-wise with about 5 to 10 minutes intervals for every addition (10 to 30 ml for every addition) to non ionic water. When added sulfuric acid to water it will be an exoterm reaction, which means that it will be a big heat development.

When 64 weight% sulfuric acid is manufactured, warm it up to 45 degrees celsius in a water bath see picture 1 for set where sulfuric acid warms up and mixes with MCC (cotton) cellulose. Mix MCC cellulose slowly to the sulfuric acid. 1050 ml sulfuric acid mixed with 120 grams MCC. When done, stir it for 2 hour. Start time 08:42 and it took 15 minutes to put in the MCC to the sulfuric acid. When 2 hour have gone pour 7 liters of non ionic water to the solution.

Machine were the CNC was manufacture

When the solution has mixed with the water it is time for centrifugation. Pour the solution into the centrifugation bottle and weigh the bottle. All four bottles and the solution should weigh approximately the same. If they don't weigh the same it will be an imbalance in the machine. First start weight will be a total of 750 gram..

Centrifugation at 4300 rpm and takes around 15 minutes plus 3 minutes of cool down.

Table for all centrifugation made.

1	750,12	750,00	750,00	750,04
2	750,5	750,43	750,41	750,75
3	801,81	801,8	801,8	801,8
4	666,0	666,0	666,0	666.6
5	401,9	402	401,99	401,8
6	407	407	407	407
7	500,03	500,1	500,0	500,12
8	500,71	500,5	500,87	500,82
9	506	506,1	506	506
10	502	502	502	502

Picture on a centrifugation that was used.

When the centrifugation step is clear and all solutions are done it is time for the next step which is dialysis. Dialysis takes away the sulfuric acid that is still in the CNC. At dialysis we are using a dialysis membrane, which you can see on the picture down below.

What dialysis looks like.

Unit on conductivity that is measured in is s which is microsiemens. When the conductivity of the water change is under 5 s so much so for 3 whole days for the CNC to be done to use.

Table over conductivity in the water

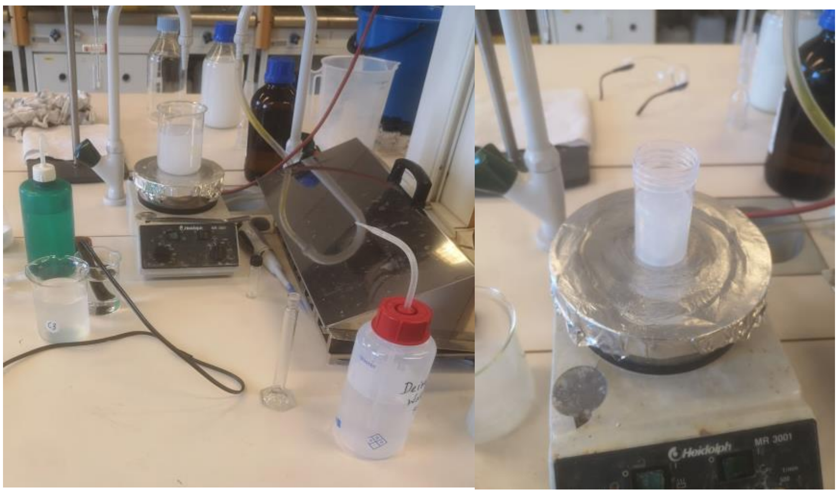
Time and date for water change	The big box	The small box
Friday den 26 March 2021 O'clock 16.12	740 s	672 s
Monday den 29 March 2021 O'clock 09.16	1107 s	2,4 ms
Monday den 29 March 2021 O'clock 15.31	140.7 s	42.0 s
Tuesday den 30 March 2021 O'clock 09.13	277 s	66.4s
Wednesday den 31 March 2021 O'clock 09.22	199.9 s	46.2 s
Wednesday den 31 March 2021 O'clock 12.10	26.2 s	6.5 s
Wednesday den 31 March 2021 O'clock 15.55	33.3 s	7.8 s
Friday den 2 April 2021 O'clock 11:40	96.5 s	16 s
Tuesday den 6 April 2021 O'clock 09:21	145.3 s	28.4 s
Tuesday den 6 April 2021 O'clock 12:06	1.5 s	1.2 s
Tuesday den 6 April 2021 O'clock 15:06	1.6 s	1.1 s
Friday den 9 April 2021 O'clock 08:29	25.4 s	7.8 s
Friday den 9 April 2021 O'clock 12:26	1.4 s	1.0 s
Monday den 12 April 2021 O'clock 09:30	18.3 s	5.1 s
Tuesday den 13 April 2021 O'clock 09.17	1.9 s	1.3 s

As we can see on the morning of 13 April both the CNC dialysis was below 5 s which means that we now has to stay for 3 days so it stays under 5 s. There is no changing of the water. After three days the CNC is done. When the CNC is done the moved to a container and the dry content was measured to 2.8.

To get low sulfate CNC from high sulfate CNC is to boil the high sulfate CNC for 4 hour at a temperature of 90 degrees. After 4 hour let it cool down and put it in a dialysis. Change water of the dialysis to ensure that the conductivity is under 5 S.

2.2 Measurement of conductivity with different compound

Now it’s time for the main part of this work. Measurement of conductivity when using different compounds. Look in the capital materials where all the compound that was used is with and little information about them. Below is a picture of the set so the experiment was able to perform. In the cup on the heat plate is the one used for the CNC and the compound that will be used for the time. No heat was used, only the rotation. The rotation that I used for this experiment was between 150 to 250. To the left are two cups and the machine part that can be seen is from the conductivity machine which is used for the measurement of the conductivity in the CNC mixture. You don’t need a big cup like the one on the picture to the left. The one that is on the right was what we were using under this experiment.



How the experiment set up looks like

So what was done under this part of the experiment? So the thing that now was to do was to measure conductivity of the CNC with different compounds and different concentrations. Why different weight percent? It was because every minute was 1 milliliter distilled water added to the CNC solution. Från the start weight percent 3.33 wt% of the CNC to 0.5 wt% in some cases and some it is 0.4 wt% in other cases. More of the weight percent and how it looks in the capital result 3.

Under this experiment a comparison is between three different hydroxide compounds, three different organic compounds and between sodium hydroxide at different concentrations are compared to CNC. Sodium hydroxide with 5 different molar ratios against the CNC. It has more CNC molecules than what's added to the sodium hydroxide. The wt% of CNC that was used had a concentration of 4.475 and was 275 mol/g. Among CNC that was measured up to every experiment was 4.6 g CNC and then 1.54 g water added so the weight percent gets to 3.33 wt%.
So 2.2 milligram of sodium hydroxide will be added when the molar ratio between CNC and sodium hydroxide is 1:1. When ratio 1:0.75 is 1.65 milligram added, ratio 1:0.5 is 1,1 milligram added, ratio 1:0.25 is 0.55 milligram added and ratio 1:0.15 is 0.33 milligram added. In volume it will be in order 44 microliter, 33 microliter, 22 microliter, 11 microliter and 7 microliter. How much in volume it will be depends on how much weight water and sodium hydroxide pellets that mixed together. 99 milligram sodium hydroxide was mixed with 2 milliliter water.

For the experiment part when comparing different hydroxide in this experiment was lithium hydroxide, sodium hydroxide and potassium hydroxide used. This one was only done for solutions wherein the molar ratio between CNC and the hydroxide was 1:1. For the lithium hydroxide was 168.4 milligram powder mixed with 2.69 milliliter water. With that 35 microliter of lithium hydroxide was added to the CNC. For the potassium hydroxide was 70.6 milligram pellets mixed with 2.52 milliliter water. With that 78 microliter of potassium hydroxide was added to the CNC. Sodium hydroxide 90 milligram pellets mixed with 2.09 milliliter water and 51 microliter added to the CNC.

For the low sulfate CNC the comparison between different hydroxide and the organic compound was just done, more specific lithium hydroxide, sodium hydroxide, potassium hydroxide, diethylamine, dihexylamine and dioctylamine where used. For for the different compound the adding of the compound was as follows. Dioctylamine was 3.98 microliter, dihexylamine 3 microliter, diethylamine 1.4 microliter, potassium hydroxide 22 microliter, sodium hydroxide 15 microliter and for lithium hydroxide 10.2 microliter was added to the CNC.

2.3 Materials

The different compounds that will be used for the main part of the experiment.

Sodium Hydroxide-NaOH[17]: Sodium hydroxide is also known as caustic soda. When at room temperature sodium hydroxide is a white solid crystalline. When mixed with water it becomes very warm and it will be a exoterm reaction. If sodium hydroxide appears as a liquid as a solution it is colorless. If you come in contact with the body it can severely irritate the skin, eyes and mucous membrane. If you “eat it” it will be toxic. It corrodes when it comes in contact with metals.

Lithium Hydroxide-LiOH[18]: Lithium hydroxide is used to make a few other chemicals. When it is a solution it looks like a clear to water-white liquid and it can smell a pungent odor. If you come in contact with the body it can severely irritate the skin, eyes and mucous membrane. If you “eat it”, inhalation and absorption on the skin it will be toxic.

Potassium Hydroxide-KOH[19]: Potassium hydroxide is also known as lye. Potassium hydroxide can be in three different solid forms: pellets, flakes and powders. As a solution it will be a clear aqueous solution. It corrodes when it comes in contact with metals and tissues together with noncombustibility.

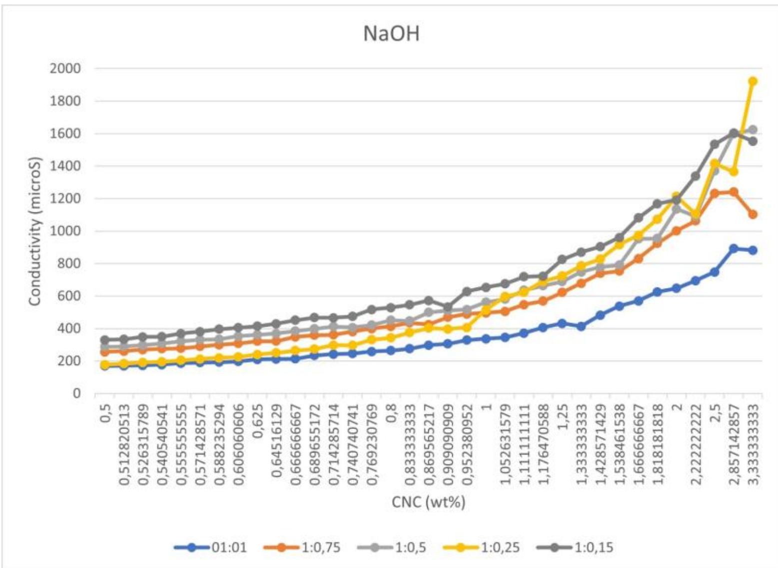
Diethylamine-C4H11N[20]: It’s a liquid that is colorless and smells like ammonia odor. When inhaling it is irritant. Corrosive when contact with skin and eyes. Vapories on this compound heavier the air we breathe. When it heats up toxic oxides will be produced.

Dihexylamine-C12H27N[21]: This compound is a colorless liquid.

Dioctylamine-C16H35N[22]: This compound is irritant to skin and eyes. Is in a liquid that is colorless.

3.Discussion & Result

When the experiment was done and all the graph was plotted so the conclusion can be seen by the different experimentally parts. For the part when comparing sodium hydroxide when using different molar ratios. Comparing ratio 1:1 where both the sulfate group and sodium hydroxide amount are the same down to 1:0.15. There sodium hydroxide will be the part where the molar ratio is the different one that always is changing. One thing that can be seen from graph 1 is that the conductivity is higher as long as the molar ratios change. The conductivity goes up when the amount of sodium hydroxide is changing. But why is it going up? Because when is the same amount of sulfate group as sodium hydroxide. All of the sulfate groups get a sodium molecule on itself because the amount of molecule is the same. For the 1:0.15 is only 6.7 percent of the sulfate groups has a sodium bound to it. This one is for high sulfate CNC.



Graph 1 The conductivity NaOH with different molar ratio. For high sulfate CNC.

So when the molar ratio is changing the amount of free sulfate group that is not bound to a sodium molecule will be more. So the amount of sodium hydroxide that is used compared to the amount of sulfate group will decrease the conductivity. So when a lower amount of sodium hydroxide is used the higher the conductivity will be and the opposite when a high amount of sodium hydroxide is used the lower the conductivity will be.

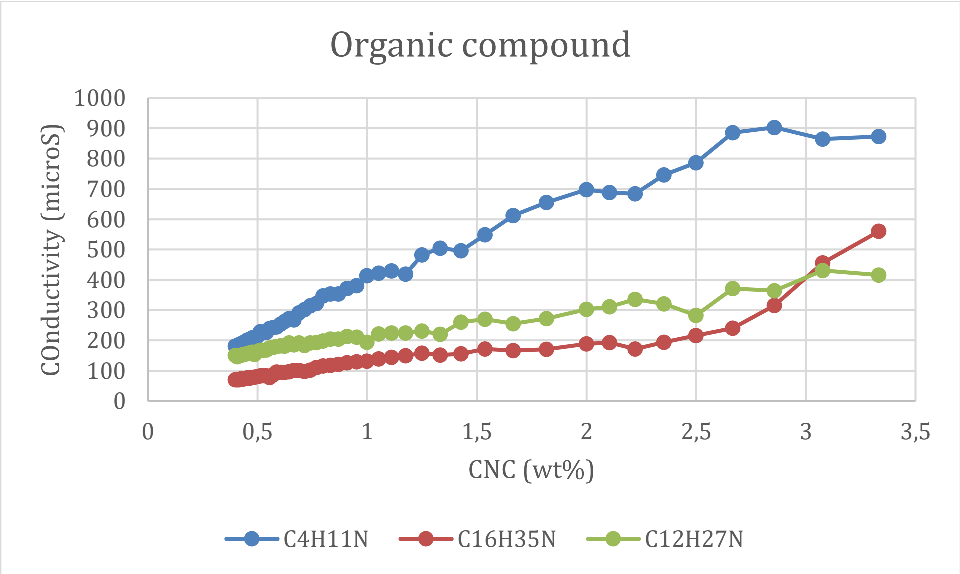
When we look at the CAC you can see the value in the table below. More than this one with different molar ratios we can not find a pattern between them as we can see with the conductivity. After the refraction of the conductivity curve we can see when the CAC will be formed.

So from my experiment you can see that the molar ratio and CAC is not going on the same trend as the conductivity. When 1:1 is not the highest and it is not going down in the same way.

1:1	Around 1.33
1:0.75	Around 1.25
1:0.5	Around 1.45
1:0.25	Around 1.5
1:0.15	Around 1.15

For the organic compound we can see the conductivity is highest for diethylamine which is the compound with least amount of carbon out of the three compounds. The lowest conductivity is for dioctylamine which is the compound that has the most amount of carbon. Why is it higher conductivity when we use a compound like diethylamine that only has four carbons compared to the dioctylamine that has sixteen carbons? One reason that the conductivity gets higher is that diethylamine with four carbon is not as big as dioctylamine. Dioctylamine is so long that it can "screen off" more than the sulfate group there is bound to. They do so because not all the sulfate groups on the CNC surface can coordinate with dioctylamine. But for diethylamine that has four carbon there is no screening effect. So these particles only take up only one sulfate group and not "screen off" some else of the sulfate group only the one they are bound to.

A trend that also can be seen between diethylamine, dihexylamine and dioctylamine. Is the one between dihexylamine (twelve carbon) and dioctylamine (sixteen carbon).
As can be seen in the graph 2 is that dihexylamine and dioctylamine are in line with each other for the most of the time under this experiment. But on the other hand the diethylamine has a larger slope compared to dihexylamine and dioctylamine where the slopes are very flat.



Graph 2 The conductivity between three different organic compounds. For high sulfate CNC.

First time when using the organic compound by name dioctylamine the start conductivity was much higher then the diethylamine and dihexylamine. For that one a smaller magnet was used but when a bigger magnet was used we get the graph that is above. So too see the "bad" one look in the appendices. So graph 2 gets a much better and more accurate value. So using a bigger magnet gets a better result for the dioctylamine. One other problem that I got under this part of the experiment was also when using dioctylamine. It was when I poured in the amount of dioctylamine I needed. The rotation on was too high so the CNC got very foamy and the start conductivity was low and the conductivity was jumping very much in between higher and lower. So the rotation should not be so high. So instead start on a low rotation speed and raise as longer the experiment goes on. This is for the CNC with high sulfate.

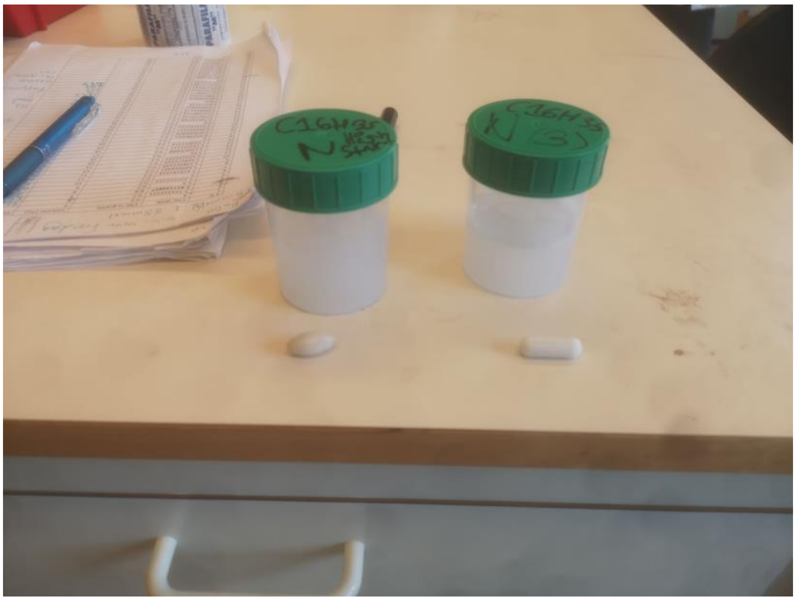
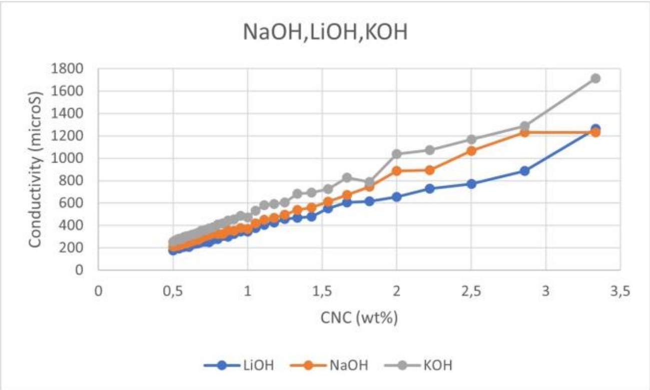


Figure: The difference is simple with a magnet. Small magnet to left and bigger to right

Below here you can see the CAC for the three different organic compounds.

Diethylamine	2.25
Dihexylamine	1.8
Dioctylamine	2.35

The last part of this experiment was to compare three different hydroxide. Lithium, sodium and potassium. As we can see in graph 3 the three hydroxide is going in the order of potassium, sodium and lithium. The one that has the highest conductivity is the one that is the lowest in the periodic table. Potassium is the biggest molecule out of the three. So by looking at the periodic tables we can see that the “bigger” molecule gets the higher conductivity. So the bigger molecules the higher conductivity.



Graph 3. Different hydroxide compared with each other. For high sulfate CNC.

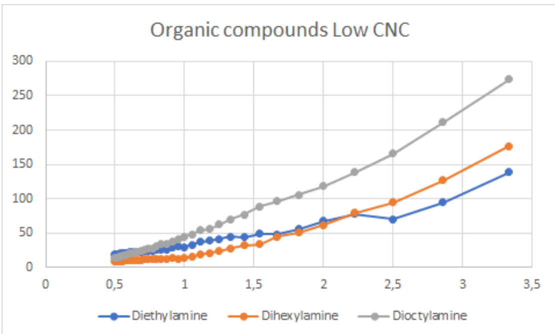
One other thing that also can be seen is all of these three compounds are on the same side and row in the periodic tables. All of them have an electron over so they would not have a full electron shell. So the conductivity decreases with the particle size. It is not the properties of the compound that play a role here. Something that can be seen is that all of the three hydroxide are located close to each other. That's not so much room in between each other compared to the organic compound for example. Lithium, sodium and potassium are all three basically in a straight line. The point that stands out for the three is the starting point. But beside that they are going in the lines as they are in the periodic tables. They are pretty much going the same way and have the same gap for every milliliter of water that is adding to it. For this is high sulfate CNC.

Below here you can see the CAC for the three different hydroxide compounds.

LiOH	1.8
NaOH	2.25
KOH	2

After the experiment with the high sulfate CNC it is now time for the result of the low sulfate CNC. For the low sulfate CNC the experiment part is only with the three organic compounds and lithium hydroxide, sodium hydroxide and potassium hydroxide that were used in the high sulfate CNC experiment.

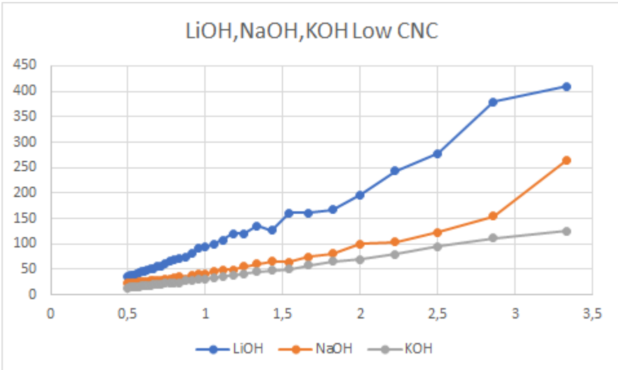
When looking at graph 4 below we can see that our organic compounds that we used were diethylamine, dihexylamine and dioctylamine. As we can see compared to the high sulfate CNC is that the low sulfate CNC is the opposite. For the low sulfate, the biggest carbon chain in dioctylamine has the biggest starting conductivity compared to the high sulfate where the smaller carbon chain in diethylamine has the higher starting conductivity. Something that can also be seen is that for the low sulfate CNC the start conductivity begins where the last conductivity of the high sulfate CNC.



When having a lower amount of sulfate group the group is not “sitting” as tight as it does in the CNC with high amount of sulfate group. This allows the biggest organic compound dioctylamine to not “screen off” as many sulfate groups as it does for the high sulfate CNC. It cannot with their long carbon chains “screen off” when the amount of sulfate group is not as many as in the high sulfate CNC. So when all of them have the same terms “to play with” in other words the different organic compounds can be bound to the same amount of sulfate group compared to in the high sulfate CNC. So therefore we can see that having an organic compound with a long carbon chain gets higher conductivity because the ion exchange is better.

Diethylamine	around 2
Dihexylamine	around 1.8
Dioctylamine	around 2.25

By looking on graph 5 below we can see for our hydroxide that it is the opposite from the high sulfate CNC. Here we can see that lithium hydroxide is the higher one compared to potassium hydroxide that is the higher one for the high sulfate CNC. For the low CNC the different hydroxide goes from biggest to the smallest molecules. There lithium hydroxide is the smallest and potassium is the biggest when we look at the periodic table. One thing that can also be seen is that the initial conductivity is must lower than for the high sulfate CNC samples. since the amount of sulfate group on the CNC is much lower than for the high sulfate CNC.



For the CNC with lower amount of sulfate group on the surface the distance between them is much larger than for the high sulfate group CNC. As a consequence the size of the added molecule has an effect on the conductivity. Now, the smaller the molecule gets the higher conductivity than the before for the high sulfate CNC. So for the lower sulfate CNC when it comes to the different hydroxide is that the larger the anion are the lower the conductivity gets. So if we have another one that is in the same group as lithium, sodium and potassium we will probably get a lower conductivity for that because it is much bigger than the other three compounds.

LiOH	around 1.6
NaOH	around 2
KOH	around 1.8

4.Conclusion

When using different hydroxide for the high sulfate CNC it goes in order from the largest molecule size to the smallest size. From potassium to lithium. So for the conductivity we can see that the size of the molecule gets them in order. That the bigger molecule the higher the conductivity is. For the low sulfate CNC is it the opposite for the high sulfate CNC. It goes from smallest to biggest molecules. From lithium to potassium. But for the critical aggregation concentration can it be seen that the size of the molecule doesn't go in order. Thus, that size of the molecule doesn’t do so the critical aggregation concentration goes in the same order that the conductivity does. Together with that we can also see that the critical aggregation concentration for the low sulfate CNC is a little bit lower than the high sulfate CNC.

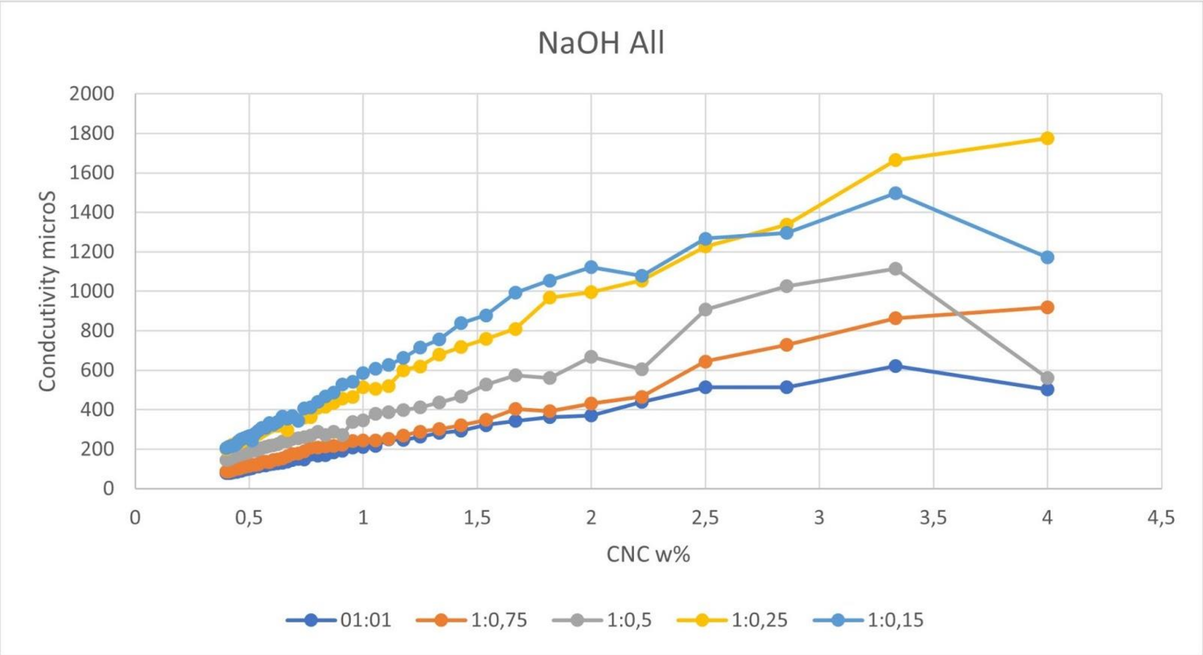
For the different organic compounds in the high sulfate CNC the molecule goes in order of their size. From smaller to biggest whereas for the low sulfate CNC it almost goes from biggest to smaller. There is a larger difference in the conductivity for the high sulfate CNC then it is for the low sulfate CNC where the different compounds are more “together” in the graph. There is a bigger gap between the compounds in the high CNC. The critical aggregation is the same for the different hydroxide where there is not so big difference between the compounds. Also it is not as big a difference for the critical aggregation concentration in the different amounts of sulfate groups it is in the CNC.

So when using different hydroxide in high sulfate CNC is going from biggest to smallest and in the low sulfate CNC it goes from smallest to biggest. But the critical aggregation is not going in the order but it is the same order for both low and high sulfate CNC.

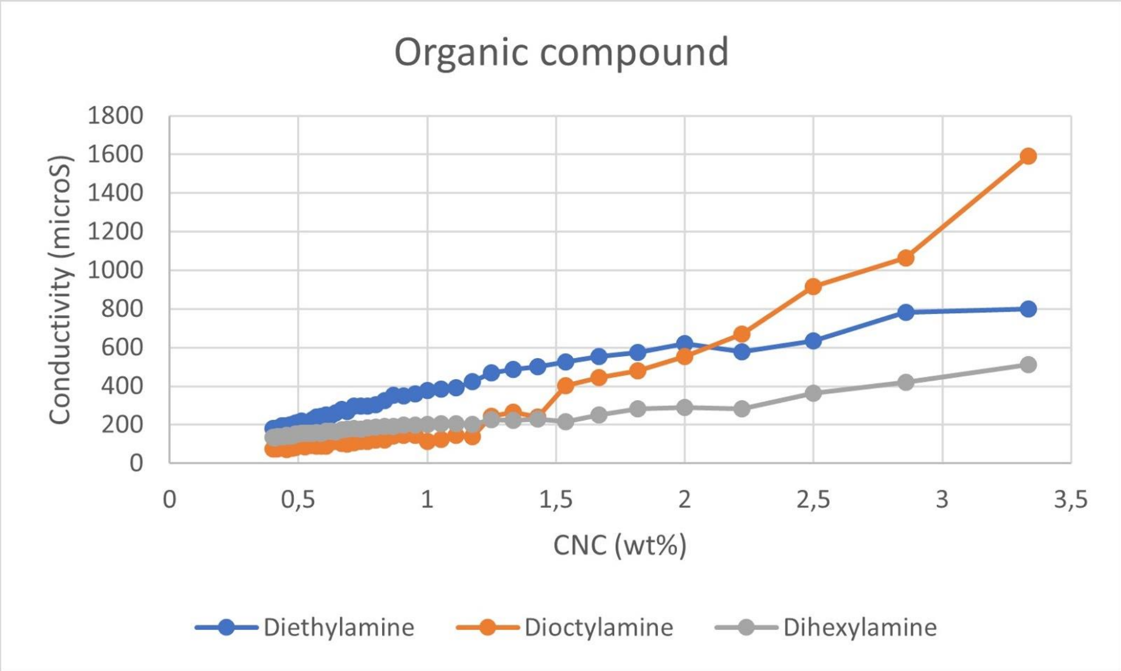
For the organic compounds in the high sulfate CNC is going in order from smaller to biggest and for the low sulfate CNC is not a special order they are just closer to each other compared to the high sulfate CNC.

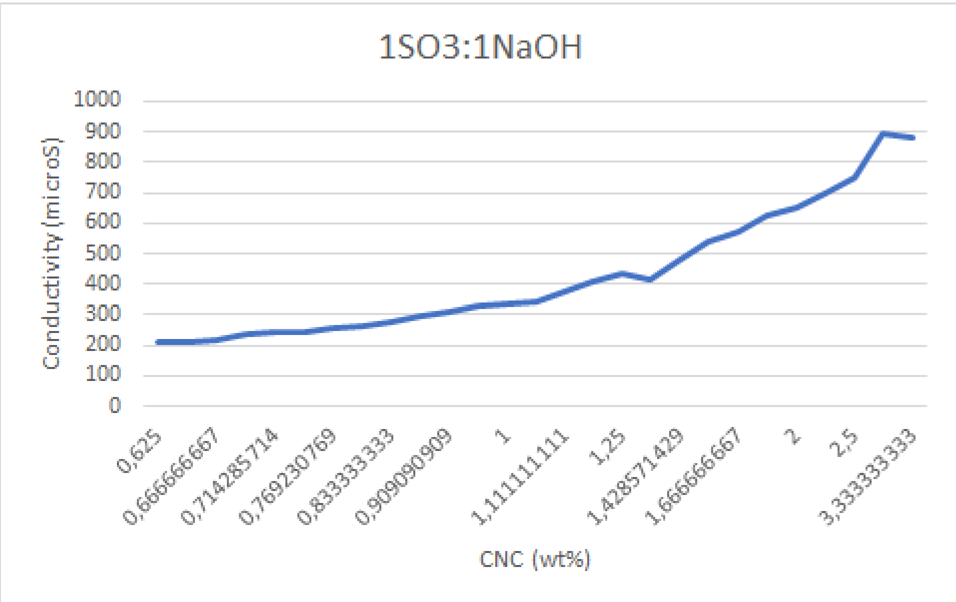
5.Appendices

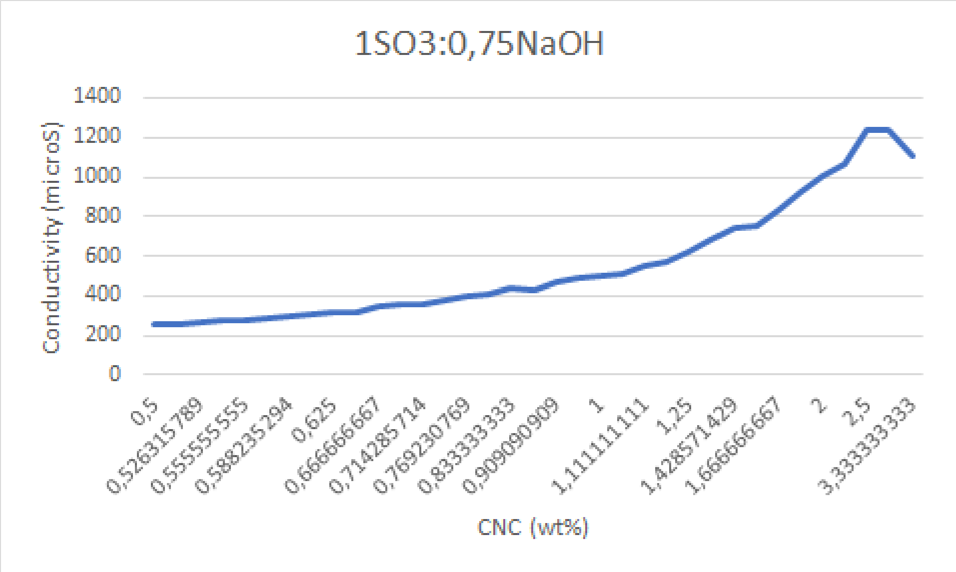
Below you can see a diagram of NaOH with different molar ratios against CNC. Here is how it looks when you forgot to add water to the CNC in the beginning.

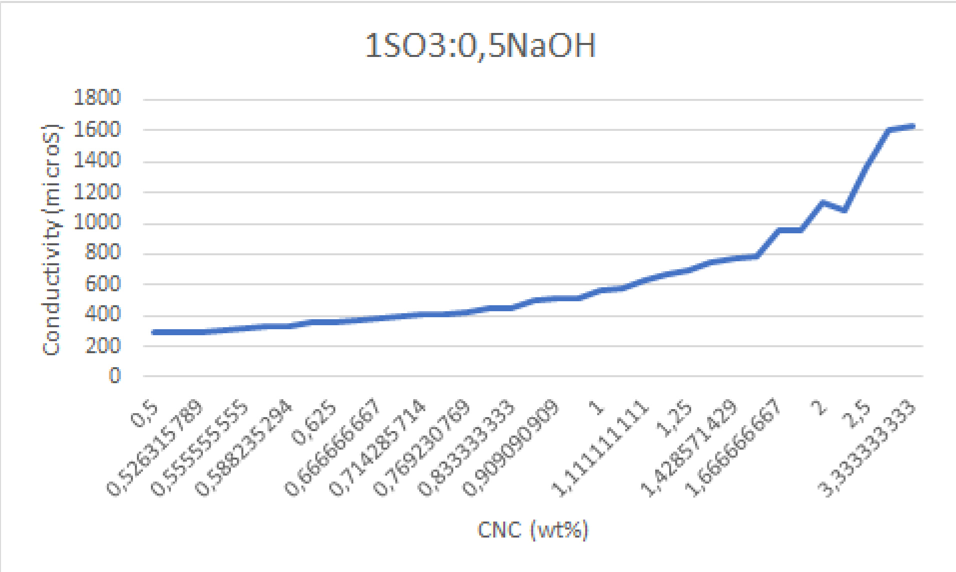


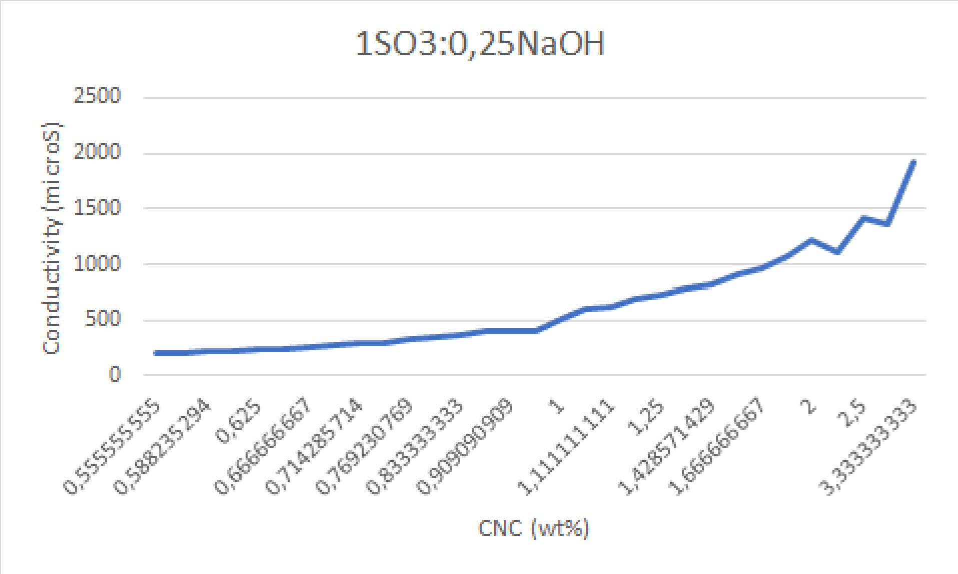
Below you can see organic compounds with little magnet and where the start conductivity for dioctylamine is very high.

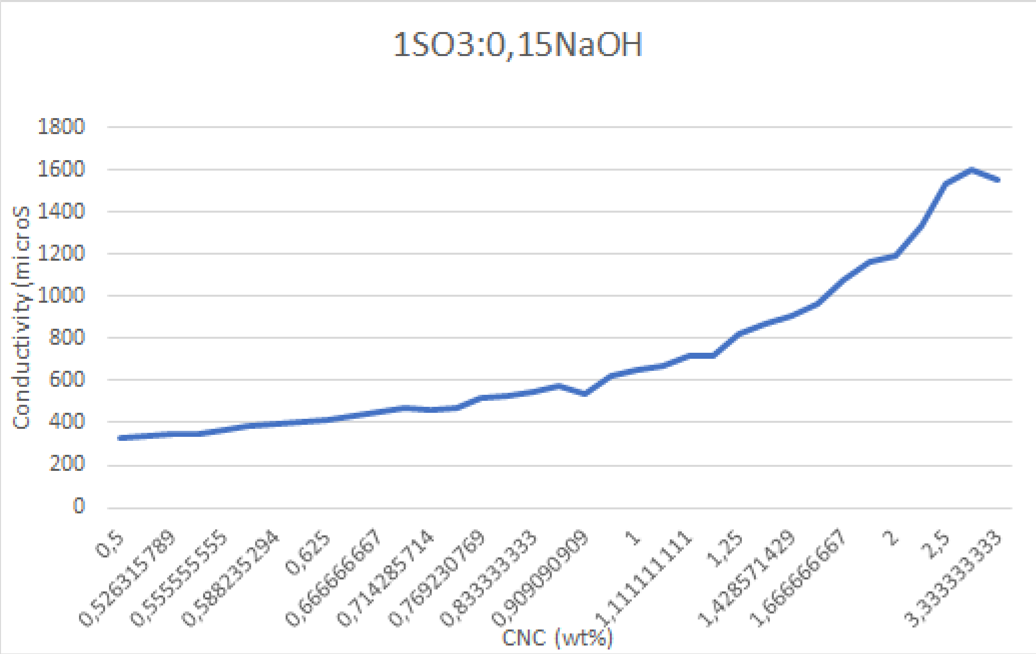


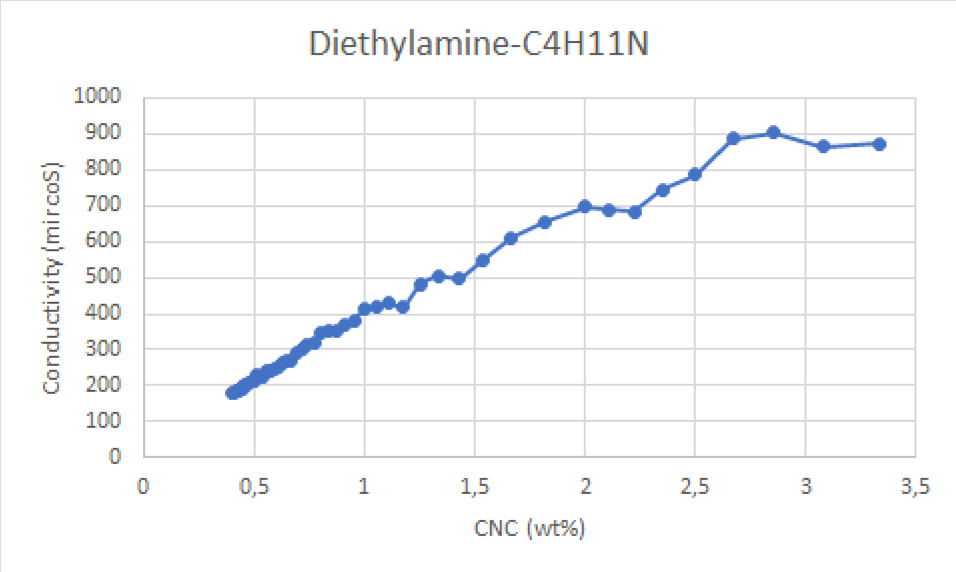



1SO3:0,75NaOH
Conductivity (microS)
1400
1200
1000
800
600
400
200
0
0,5
0,526315789
0,555555555
0,588235294
0,625
0,666666667
0,714285714
0,769230769
0,833333333
0,909090909
1
1,111111111
1,25
1,428571429
1,666666667
2
2,5
3,333333333
CNC (wt%)

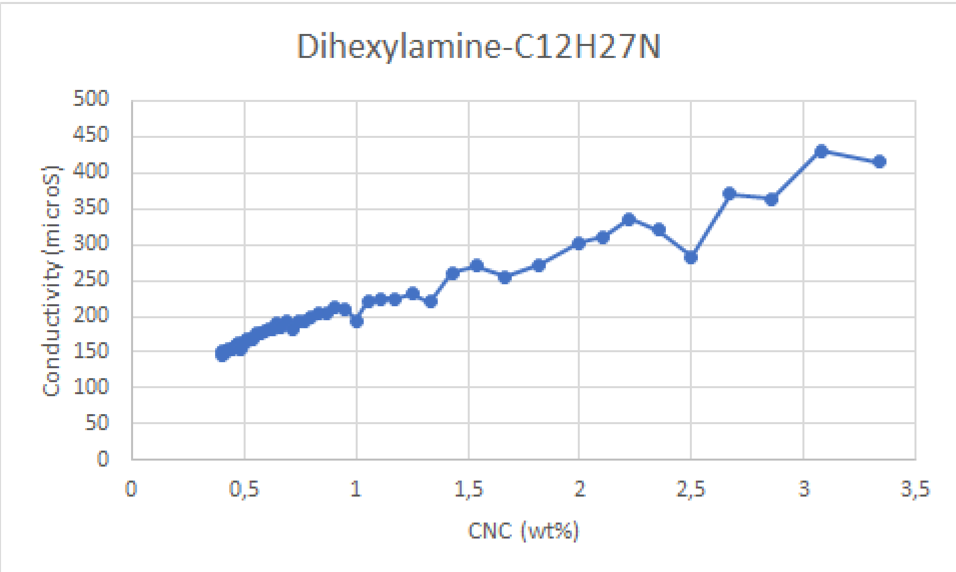

1SO3:0,5NaOH
Conductivity (microS)
1800
1600
1400
1200
1000
800
600
400
200
0
0,5
0,526315789
0,555555555
0,588235294
0,625
0,666666667
0,714285714
0,769230769
0,833333333
0,909090909
1
1,111111111
1,25
1,428571429
1,666666667
2
2,5
3,333333333
CNC (wt%)


1SO3:0,25NaOH
Conductivity (microS)
2500
2000
1500
1000
500
0
0,555555555
0,588235294
0,625
0,666666667
0,714285714
0,769230769
0,833333333
0,909090909
1
1,111111111
1,25
1,428571429
1,666666667
2
2,5
3,333333333
CNC (wt%)

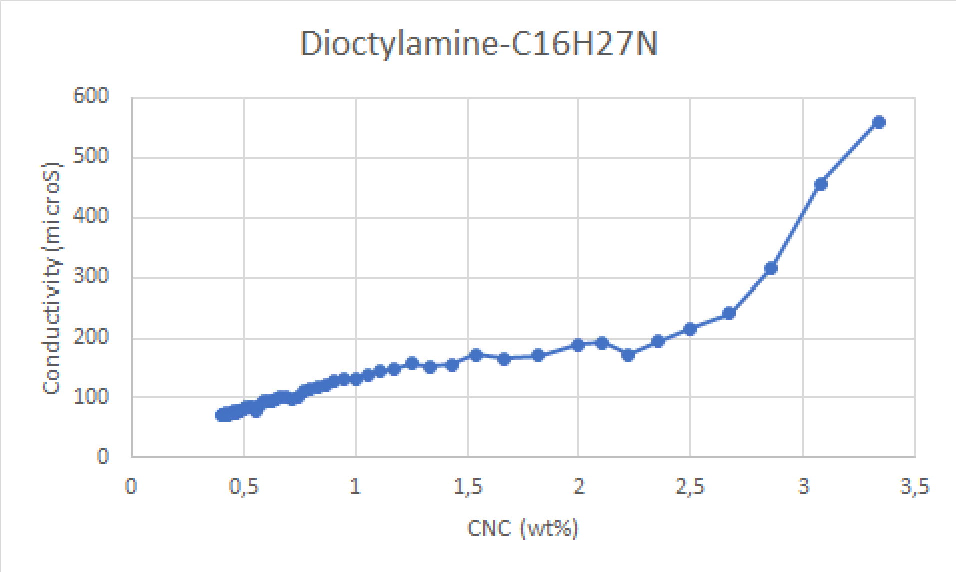

1SO3:0,15NaOH
Conductivity (microS
1800
1600
1400
1200
1000
800
600
400
200
0
0,5
0,526315789
0,555555555
0,588235294
0,625
0,666666667
0,714285714
0,769230769
0,833333333
0,909090909
1
1,111111111
1,25
1,428571429
1,666666667
2
2,5
3,333333333
CNC (wt%)

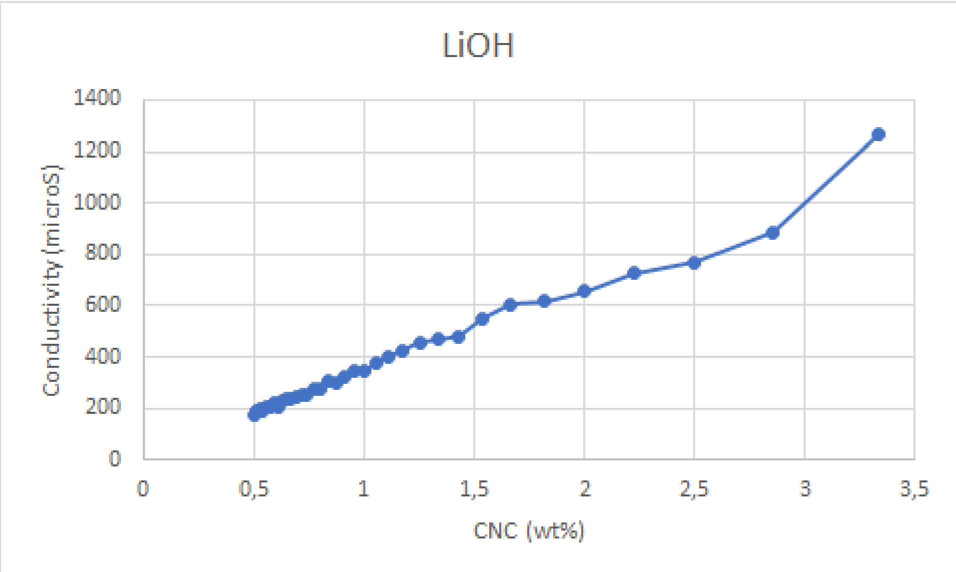


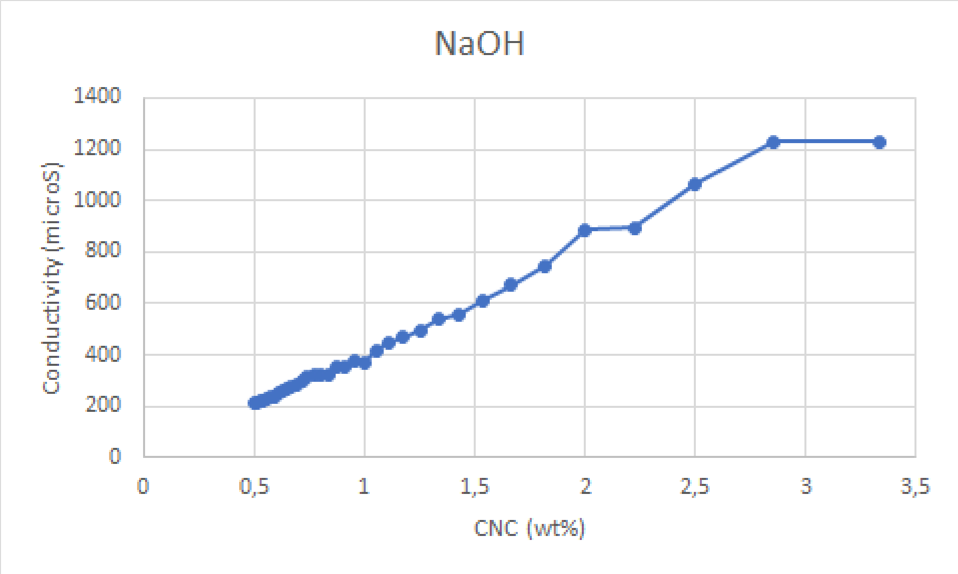
Diethylamine-C4H11N
Conductivity (mircoS)
CNC (wt%)

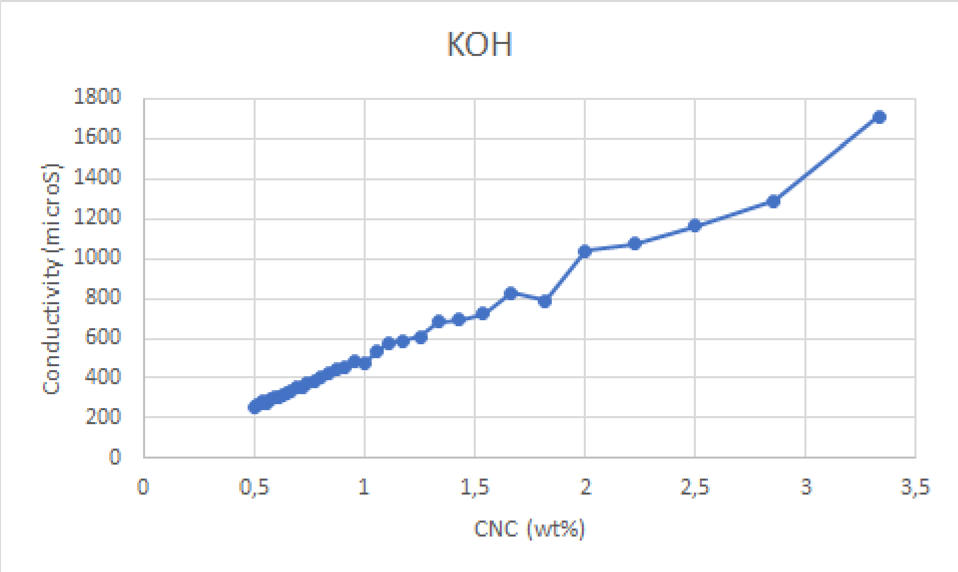


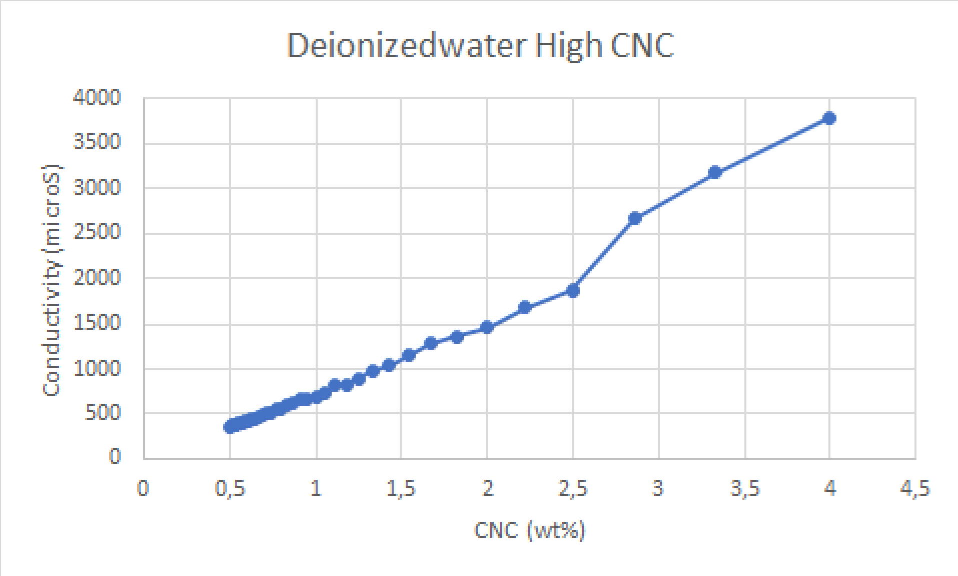
Dihexylamine-C12H27N
Conductivity (microS)
CNC (wt%)


Dioctylamine-C16H27N
Conductivity (microS)
CNC (wt%)
0
100
200
300
400
500
600
0
0,5
1
1,5
2
2,5
3
3,5


LiOH
Conductivity (microS)
CNC (wt%)
0
200
400
600
800
1000
1200
1400
0
0,5
1
1,5
2
2,5
3
3,5


NaOH
Conductivity (microS)
CNC (wt%)
0
200
400
600
800
1000
1200
1400
0
0,5
1
1,5
2
2,5
3
3,5


KOH
Conductivity (microS)
CNC (wt%)
0
200
400
600
800
1000
1200
1400
1600
1800
0
0,5
1
1,5
2
2,5
3
3,5



Deionizedwater High CNC
Conductivity (microS)
4000
3500
3000
2500
2000
1500
1000
500
0
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
CNC (wt%)

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