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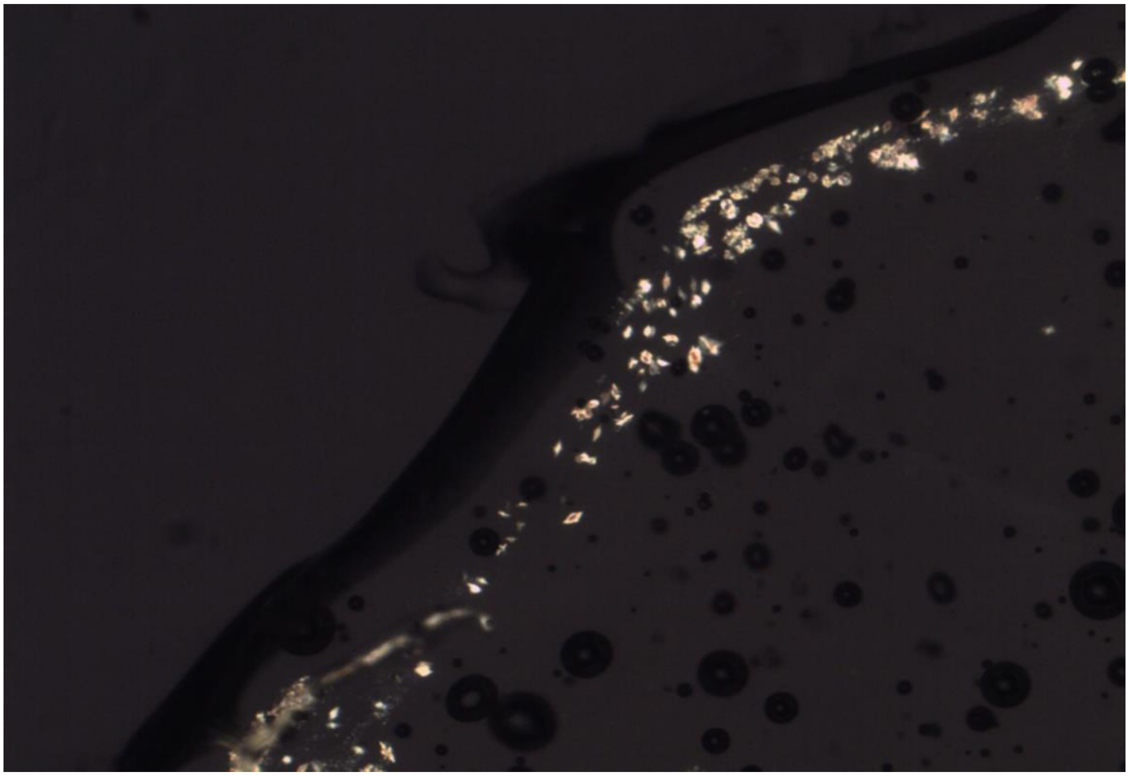

Investigating coagulation of cellulose solutions

Master's thesis in Materials Chemistry

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Summary:

As the need to replace cotton as a resource in textile production increases alternative materials with the same properties as cotton becomes very interesting. One of the most interesting raw materials is the most abundant biomaterial on earth, cellulose from lignocellulosic material. The most sustainable process for producing fabrics out of cellulose from wood fibres is the lyocell process in which the cellulose is dissolved in N-methylmorpholine N-oxide (NMMO) and regenerated as filaments. The regeneration is done by rearranging the cellulose molecules in its dissolved state and then coagulating it using a non-solvent. The lyocell solvent NMMO has worked well but have some problems as it is thermally unstable. A family of relatively new solvents are ionic liquids, molten salts with very low vapor pressures. Ionic liquids have shown different abilities as cellulose solvents but some have also shown great potential. In this project the coagulation of three different ionic liquids was researched, the previously studied 1-ethyl-3-methyl imidazolium acetate (EmimAc) and 1-butyl-3-methyl imidazolium chloride (BmimCl), and the less studied tetra-methyl guanidine acetate (TMGHOAc), the later has the unique property of being a distillable ionic liquid. Two different non-solvents were analyzed; water and isopropanol. Three different analyzing methods was used; the coagulation value method in which the required weight fraction of non-solvent that has to be added before the dissolved cellulose starts to coagulate is measured, the mass-transport rate method in which the rate of the total diffusion of non-solvent into and of solvent out of a cellulose solution as it is submerged in non-solvent, and a visual coagulation front propagation measurement in which the thickness of the coagulated layer is measured as it is submerged in non-solvent.

The dissolution of cellulose in the tetra-methyl guanidine acetate proved to be more complex than the other ionic liquids. It was shown that the TMGHOAcs dissolution ability is highly dependent on the pH of the solution and that a pH below the equivalence point of the tetra-methyl guanidine and acetate ions makes dissolution impossible. Another problem was caused by the fact that the ionic liquid phase changed from a liquid into a solid structure even after cellulose had seemingly been dissolved in it. This could be hindered by using increased amounts of DMSO which prevented the phase transition of the solution. The difficulty to avoid the liquid to solid phase transition that seem to occur regularly might be the reason why poor properties of fibers spun from TMGHOAc solutions have been observed. It was also found that the latter stage of the diffusion in TMGHOAc is substantially slower than for EmimAc and BmimCl. This resulted in very thick coagulated layers with large swelling even after long submersion times.

The coagulation mechanism was investigated for all three ionic liquids and it was found that the mechanism varied heavily between the solvents. The BmimCl solutions showed almost no change in turbidity as it coagulated while the EmimAc and TMGHOAc showed a sharp increase in turbidity. The diffusion rate experiments showed that the diffusion process is very different for water and isopropanol for EmimAc and BmimCl which is possibly caused by the isopropanol interacting much more with the ionic liquid than the water. The same could not be seen in the TMGHOAc where the isopropanol and water diffusion curves looked very similar. The coagulation depth method showed that the growth of the coagulation layer is the fastest in BmimCl while the EmimAc and TMGHOAC have similar growth rates.

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Contents

1 Introduction:

The production of cotton textiles is as of today a very unsustainable process. Cotton requires huge amounts of water to grow and process. Additionally the cotton industry is today responsible for 16% of the world's total pesticide use [1]. As the population grows and the number of people with the monetary requirements to afford mass produced clothes and textiles increases, a new alternative to cotton becomes more and more relevant. Cellulose, the polymer building material of all plants, exists all over the globe and has some very good properties for textile production. To be able to harness the potential of cellulose it first has to be isolated from the wood material and reshaped into fibers. Unlike plastic polymers cellulose cannot be melted and reshaped as it decomposes at elevated temperatures. The process of manufacturing fabric out of cellulose instead requires the cellulose to be dissolved and regenerated by coagulation. This process is called wet spinning and it frees the cellulose molecules which then may be rearranged into filaments.

The two most common methods for producing cellulose fibers are the viscose process, in which the cellulose is derivatized into cellulose xanthate and dissolved in sodium hydroxide, and the lyocell process, where the cellulose is directly dissolved [2]. The solvent used in the lyocell process is NMMO (N-methylmorpholine N-oxide). The process is much more environmentally sustainable than either cotton textile manufacturing or the viscose method. Furthermore, NMMO is low in toxicity and biodegradable [2] however the usage of NMMO as a solvent is not without any drawbacks. It has poor thermal stability which means that it can react violently exothermically [3] [4] if it is heated excessively. It will gradually decompose [3] and it may discolor the solution and the spun fibers by forming chromophores which will also degrade the pulp [3] and large amounts of stabilizers are required. These drawbacks have led to prominent research in alternate solvent which may circumvent the problems associated with the usage of NMMO.

The most investigated and prominent alternative solvents to NMMO have been ionic liquids, salts with relatively low melting points consisting of an anion with a corresponding cation. Ionic liquids are thermally stable with a minimal release of volatile substances [5] and have good miscibility with common anti solvents such as water and different alcohols. Most ionic liquids irreversibly decompose at temperatures above 175 C [6] and have very low vapor pressures, around 0.1-0.05 mbar, but there are ionic liquids that have higher vapor pressures and therefore can be separated from decay products and residual glucose at higher temperatures using distillation. A distillable ionic liquid would be highly beneficiary as it would allow for a higher rate of recyclability and a cleaner recycled ionic liquid. An ionic liquid that is recyclable by distillation can be produced by mixing 1,1,3,3-tetramethylguanidine (TMG) with acids such as formic(CO_2H_2), acetic(HOAc) and propionic(HCO_2Et) acids. The TMGH ionic liquids have been shown to meet the required hydrogen bond basicity to break up the intra molecular hydrogen bonding and overcome the hydrophobic interactions caused by the celluloses structure, in order to dissolve the cellulose [7]. The TMG ionic liquids have been shown to be able to effectively dissolve high cellulose contents but the spun fibers have shown very poor properties which might be related to the coagulation step. In this project the coagulation mechanism and dissolution properties of TMGHOAc will be investigated and compared to 1-ethyl-3-methyl imidazolium acetate and 1-butyl-3-methyl imidazolium chloride, two widely researched ionic solvents that have been used to varying degrees of success in wet-spinning.

2 Theory:

2.1 The cellulose polymer:

Cellulose is a polysaccharide consisting of linked glucose units and is the key building block in the cell walls of plants and is also the most abundant biomaterial on earth [1]. The glucose units are linked through 1-4 beta glycosidic bonds with an ether bond consisting of a single oxygen group. The monomers are referred to as anhydrous glucose units. Each of the anhydrous glucose units have three hydroxyl groups that can hydrogen bond and this hydrogen bonding causes the cellulose to be more ordered and crystalline which makes it a very hard substance to dissolve. It is also believed that the amphiphilic (both polar and apolar) structure of the cellulose structure contribute to the insolubility. The hydrophobic parts are drawn to each other and holds the cellulose together making it harder to dissolve [8].

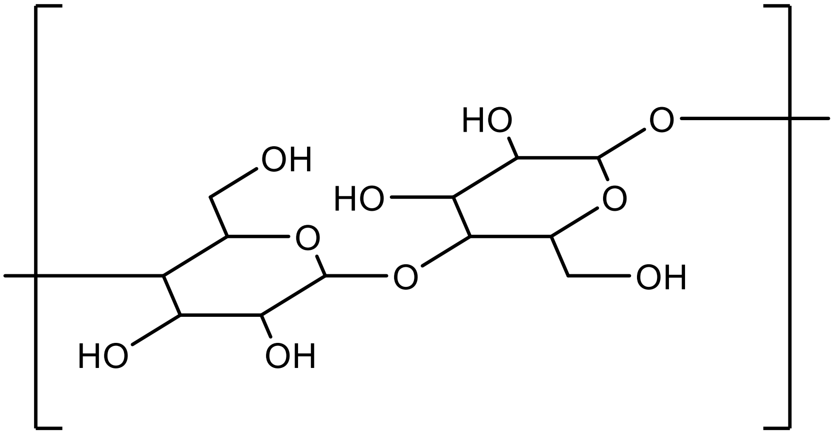


Figure 1: The general structure of the repeating unit of the cellulose chain consisting of linked glucose units.

The length of the cellulose chain is measured by the degree of polymerization which is defined as the number of linked glucose units and has been shown to greatly affect the tenacity and stiffness of drawn fiber from air gap spun cellulose [9]. The typical degree of polymerization is approximately 8000 for native wood cellulose but is reduced by approximately 10 times in the pulping process [10]. The degree of polymerization can be decreased by two different reactions; alkaline hydrolysis where the glucose chain is cut under basic conditions by hydroxide ions that splits the polymer chain, and end group removal where glucose units are removed from the end of the glucose chains by radical reactions that is propagated by elevated temperatures.

Cellulose chains are linear and unbranched but the cellulose material varies in crystalline forms. There are four major distinct cellulose allomorphs called cellulose I, II, III and IV. Cellulose type I is the untreated cellulose found in nature such as cotton and wood and is by far the most common of the four types. Type I cellulose has parallel chains bonded by hydrogen bonds creating sheets which are stacked and held together by van der Waals bonding [10]. Cellulose of type II is formed when cellulose of type I is mercerized or in the wet spinning process when the cellulose is dissolved and precipitated. In Cellulose II the hydrogen bonding occurs both in the sheets plane direction, as in cellulose I, and between the different sheets. Cellulose III can be prepared by treatment of cellulose I or cellulose II with liquid ammonia [11]. The cellulose is inflated by the ammonia molecules and forms crystalline complexes with the cellulose and as the ammonia is evaporated the complex bonding is replaced by hydrogen bonding between the sheets [12]. Cellulose IV is obtained by heating cellulose III in glycerol and the cellulose is transformed into a hydrated form of cellulose II [13].

The cellulose that is being used in this project is not normal dissolving pulp but instead micro crystalline cellulose. Microcrystalline cellulose is refined cellulose that can be produced by acid hydrolysis of cellulosic fibers which disintegrates and remove the amorphous domains between the crystalline domains [14][15].

2.3 Dissolution and coagulation of cellulose

The solvent dissolve the cellulose by breaking the celluloses hydrogen bonds and disrupting the hydrophobic interactions, instead forming new hydrogen bonds between the solvent molecules and the celluloses hydroxyl groups [16]. This means that the strength of the solvent hydrogen bond must be stronger than the hydroxyl-hydroxyl hydrogen bonds of the original cellulose allomorph in order for the ionic liquid to dissolve the cellulose. A critical property for the dissolution is the Kamlet Taft parameters α, β and $^{*}\pi$ where α describes the solvents hydrogen bond donating acidity, β describes the solvents hydrogen bond accepting basicity and $^{*}\pi$ describes the dipolarity/polarizability ratio [17]. In a study from 2012 the Kamlet Taft parameters for the ionic liquid tetramethyl guanidinium propionate was researched. It was found that the hydrogen bond basicity and the net basicity, β-α, were the critical parameters for the dissolution of cellulose and it was determined that when $\beta<0.8$ and when $\beta-\alpha<0.35$ the dissolution of cellulose is no longer possible in this specific solvent [18] and the cellulose start to coagulate.

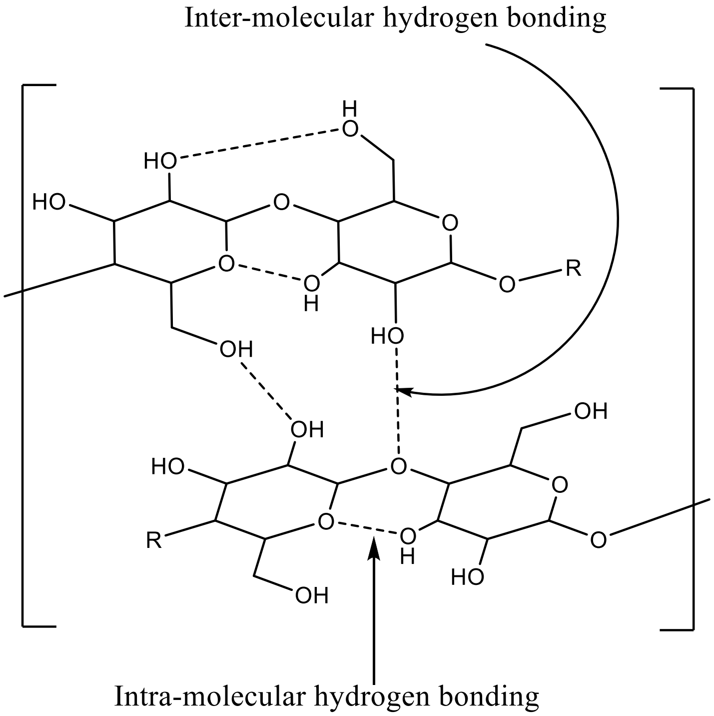


Figure 2 The inter-molecular hydrogen-bonding between the different cellulose chains and the intra-molecular hydrogen-bonding within the cellulose chains.

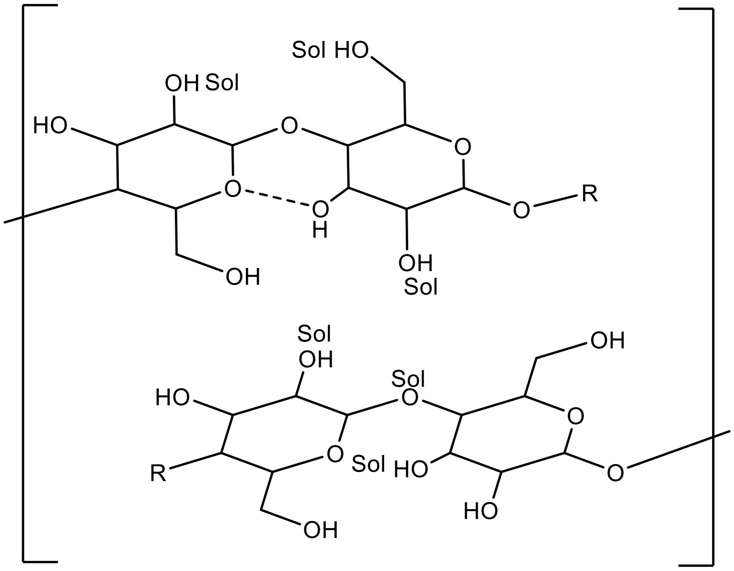


Figure 3 In order to dissolve the cellulose a solvent (sol) that is able to break the hydrogen bonds of the cellulose is required. R denotes the continuation of the polymer chain

Coagulation of cellulose in a cellulose solution happens when the solvent is removed from the cellulose. In order to coagulate the cellulose the hydrogen bonds need to be reestablished. This is achieved by using a non-solvent that can remove the solvent from the cellulose thereby reestablishing the hydrogen bonds and van der Waals forces between the cellulose sheets. Addition of an anti-solvent will decrease the hydrogen bond basicity β and as the basicity gets low enough the cellulose will start to precipitate and coagulation will set in. The regeneration process can be divided into four stages: Gelation, particle formation, regenerated cellulose with water/IL absorbed and removal of residual IL via washing [18].

One of the most important parts in the mechanism for cellulose coagulation is the diffusion of non-solvent into the cellulose solution and the diffusion of cellulose solvent out from the solution. In a study from 2006 [19] the diffusion of NMMO, the most commonly used solvent in the lyocell process, was investigated and the diffusion of ionic liquids are believed to occur in a similar way. It was determined that there are two different diffusion regimes for NMMO as it diffuses from the cellulose. The first regime is fast and happens as hydrogen bonds form between the water and the NMMO and the second regime is much slower. It has been shown that NMMO due to its hygroscopic nature, its ability to hold water, has a diffusion coefficient that is 10 times smaller than the diffusion of water into the solution [20] in the second region. It has also been shown that the diffusion rate is not related to the molecular weight of the cellulose molecule which has lead to the assumption that the diffusion is predicated upon the number of hydrogen bonds between the NMMO and the cellulose hydroxyl groups. According to one study the difference in diffusion between the non-solvent and the solvent will influence how solid the coagulated layer becomes [21]. According to this study, if the solvent is removed at a higher rate than the non-solvent can diffuse into the coagulated layer, the layer will become more solid and if the opposite is true the coagulated layer will be thicker and more gel like.

The coagulation bath in wet spinning generally contains water which is the most common non-solvent [22] but it can also contain other forms of non-solvents such as alcohols, which interact with the ionic liquid similar to water. The value of coagulation is defined as the amount of non-solvent divided by the amount of solution and gives a ratio that determines at which weight percentage of the original solvent the cellulose will start to coagulate. The coagulation value is a useful tool when comparing different solvents or anti-solvents.

2.4 Ionic liquids as solvents:

Ionic liquids are as described earlier, molten salts consisting of corresponding anions and cations. An ionic liquid is by definition in its liquid state at 373K [23] and usually consists of a large asymmetrical organic cation with a smaller inorganic or organic anion [23]. The dissolving capabilities for ionic liquid is linked to the anions ability to form strong hydrogen bonds to the celluloses hydroxyl groups.

The three ionic liquids that are investigated in this project are ethyl-methyl imidazolium acetate, butyl-methyl imidazolium chloride and tetra-methyl guanidine. Ethyl-methyl imidazolium acetate is made up of two corresponding ions, ethyl-methyl imidazolium being the cation and acetate being the anion while butyl-methyl imidazolium chloride consists of butyl-methyl imidazolium as the cation and chloride as the anion. These ionic liquids are both imidazolium derivatives which together with pyridinium derivatives are the most common ionic liquids [23]. Ethyl-methyl imidazolium acetate is liquid at room temperature which makes it easy to handle while butyl-methyl imidazolium chloride has a melting point around 70 degrees Celsius which means that the ionic liquid has to be either dissolved in a solvent such as water or that it must be heated before it can be used to dissolve cellulose.

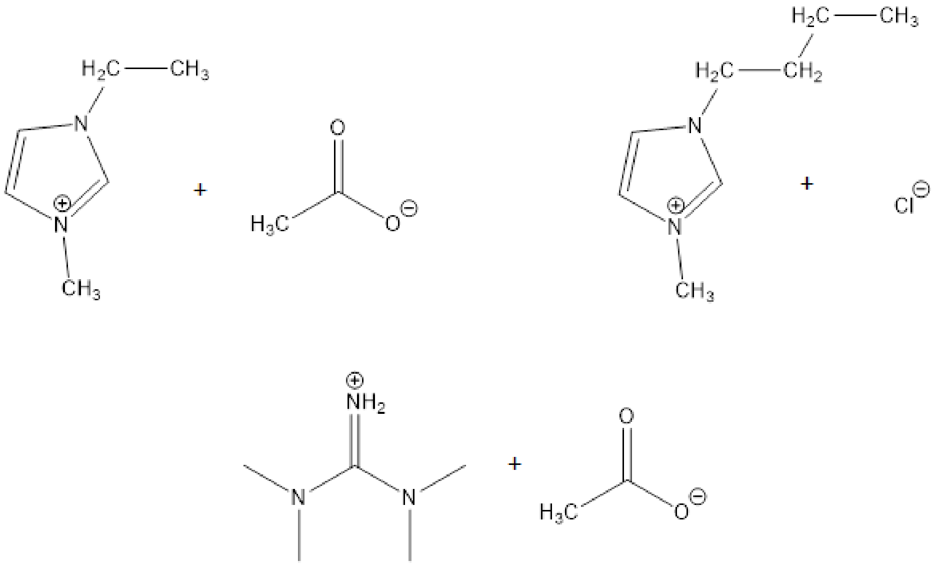


Figure 4 The ethyl-methyl imidazolium acetate ion pair on the top left, the butyl-methyl imidazolium chloride ion pair on the top right and the tetra-methyl guanidine acetate ion pair on the bottom

The cellulose dissolution abilities of different ionic liquids have been found to differ greatly and in a study from 2008 [24] butyl-methyl-imidazolium chloride (BmimCl), ethyl-methyl-imidazolium chloride (EmimCl), butyl-methyl-imidazolium acetate (BmimAc), ethyl-methyl-imidazolium acetate (EmimAc) and NMMO were compared. It was shown that BmimCl dissolves cellulose similarly to NMMO by studying the tourque moment during dissolution and seeing how closely it resembles that of NMMO. The cation affects the zero shear viscosity of the solution as it was shown in the same study that a 13.5% cellulose EmimAc solution had a zero shear viscosity of 2281 Pas compared to a 13.2% cellulose BmimAc solution which had a zero shear viscosity of 9690 Pas. The authors suggest that this might be due to the smaller ethyl-methyl imidazolium cation being able to interact more with the cellulose chain compared to the bulkier butyl-methyl imidazolium cation. The exchange in anions from chloride to acetate was shown to have much greater effect on the properties of the solution than the exchange in cations. The BmimAc solutions had a zero shear viscosity of 9690 Pas compared to the previously mentioned BmimCls zero shear viscosity of 47540 Pas. The chloride IL spun fibers also showed greater tenacity and loop tenacity values than those spun in the acetate ILs. The acetate ILs were able to dissolve a higher amount of cellulose which according to the authors might be related to the difference in solution states between the acetate and chloride ILs. Anisotropic behavior has been found in BmimCl with 20 w% cellulose at 100 degrees Celsius while an anisotropic behavior for EmimAc was not detected until the elevated cellulose concentration of 25 w% [25]. All of the anisotropic effects increase as the cellulose concentration increases for all ILs but the authors also made clear that the change from an isotropic to anisotropic state happens very slowly and can take up to several days.

The cation of the ionic liquid also affect the dissolution process although not as obviously as for the case of the anion. In a study by Kosan (2014) it was found that the acidic protons on the anion greatly affect the dissolution process. The authors suggest that the acidic protons form hydrogen bonds with the glucose hydroxyl groups or the ether bonds between the glucose units [26]. In a study from 2012 the authors speculate that the length of the alkyl chain in a methyl-alkyl imidazolium ionic liquid affects the distribution of the chloride ions with a longer chain obstructing the chloride ions from interacting with the cellulose decreasing the maximum amount of cellulose that could potentially be dissolved. [27]

The ionic liquid TMGHOAc consisting of the tetra-methyl guanidine cation and the acetate anion has been shown to have a melting point between 90-97 degrees Celsius and a vaporization point between 100 and 250 degree Celsius at atmospheric conditions [7]. The vaporization of these ionic liquids is greatly dependent on the basicity of the anion. According to a study [7] the basicity of the anion will determine the volatility of the ionic liquid. A more basic anion results in a more volatile ionic liquid. The vaporization process of these ionic liquids is based on the fact that the ion pair goes back to the neutral species which have their own distinct vapor pressures [28]. This fact also means that the corresponding base and acid of the ionic liquid will vaporize one by one with the TMG having a boiling point at 52-54 degrees Celsius and HOAc having a boiling point at 117-118 according to Sigma Aldrich. The dissolution of cellulose have already been proven for these ILs but the wet spinning of these solutions have proved to have unfavorable spinning conditions. In a study by L. Hauru [28] the [TMGH][OAc] spun fibers were shown to be collectable but the spun filament only had a tenacity of 10.9 cN/tex at a draw ratio of 2.0 compared to the NMMO spun filaments which showed a tenacity of 31.2 cN/tex at a draw ratio of 6.2.

The [TMGH][OAc] gel has been shown to have good resilience and strength which suggests that this is not the reason why the spinning does not work. In the previously mentioned study [28] it was found that the diffusion rate of ionic liquid was constant during the regeneration phase for [TMGH][OAc] while it decreased significantly for NMMO. The authors suggest that the changes in diffusion rate is caused by the realignment, and regeneration should be accompanied by a significant decrease in the diffusion rate. The authors suggest that the reason for the poor spinnability may be due to a gel like structure which does not allow the fibers to realign and reorient themselves to gain sufficient strength for spinning [28]. Furthermore to achieve good filament strength during spinning the polymer chains must be allowed to align and then form intermolecular bonds during drying [28]: a gelatinous structure would prevent both of these steps and is the reason behind the poor properties of the spun fibers.

In 2014 a patent for the use of a diazabicyclonene (DBN) based ionic liquid for the use in a process concerning different spinning methods of lignocellulosic cellulose material was filed [29]. The authors found that the cellulose DBN solution had the same viscoelastic properties as NMMO but at lower temperature and that the filament could be drawn to draw ratios exceeding 10.

Dimethyl sulfoxide (DMSO) has been used in many studies as a co-solvent to the ionic liquid in cellulose dissolution. DMSO can act both as a soft base in its sulfoxide sulfur form and as a hard base in its sulfoxide oxygen form, which allows the DMSO to dissolve a number of different substances. DMSO cannot dissolve cellulose by itself but it can swell the cellulose making it easier for the actual solvent to penetrate the cellulose structure [30]. The main purpose of the DMSO is to disassociate the anion and cation in the ionic liquid. The enhanced dissociation of the ions makes the ions more readily available for hydrogen bonding to the cellulose and the cellulose dissolution becomes easier [31][32]. DMSO has also been found to decrease the viscosity of the cellulose/ionic liquid solution making it easier to work with [33] and it is also inert to the ionic liquid.

3 Purpose

The purpose of the project is to further improve the understanding of the cellulose coagulation phenomena and how it relates to the mechanical properties of the wet spun fibers. The reasons behind the difficulties when using [TMGH][OAc] will be investigated thoroughly and it will also be investigated if the coagulation in these solution can shed some light on its poor performance in fiber spinning. The dissolution of cellulose in [TMGH][OAc] will also to be examined and the factors that affect the dissolution process will be investigated.

3.1 Scope

The following limitations have been set for this project: Only micro crystalline cellulose will be analyzed. The solvents has been limited to ethyl-methyl imidazolium acetate, butyl-methyl imidazolium chloride and tetramethyl guanidinium acetate. The non-solvents have been limited to water and isopropanol.

4 Method:

4.1 Preparation of cellulose solutions

The dissolution of the cellulose is done by mixing the cellulose in the solvent during stirring and heating. The heating should not be excessive and should be kept below 80 degrees during the entire process. The ionic liquid will in some cases be diluted with DMSO in order to lower the viscosity and decrease the amount of ionic liquid used.

4.2 Preparation of TMGHOAc ionic liquid

The preparation of TMGHOAc ionic liquid have been described in a study by Gao (2003) [34]. The ionic liquid was prepared by neutralizing TMG in ethanol by adding a molar equivalent amount of acetic acid. 20mmol TMG was solved in 100ml ethanol in a 250 ml flask and kept in a water bath with a temperature of 25 degree Celsius. 20 mmol of acetic acid was solved in 35 ml ethanol and gradually added to the TMG solution. The reaction took up to 2 hours and after the reaction was completed the reaction mixture was evaporated under reduced pressure and the remaining residue was then dissolved in 100 ml ethanol and treated with active carbon. The product was then filtered and evaporated under vacuum which resulted in the finished ionic liquid.

In another study [35] the preparation of the TMG ionic liquid was done in a similar way, using dichloromethane instead of ethanol. The ratio between TMG and dichloromethane were 50 mmol TMG to 40 ml dichloromethane and 50 mmol acetic acid to 30 ml dichloromethane. In this study the ionic liquid was simply washed with hexane in a vacuum after the evaporation of the dichloromethane.

TMGHOAc has also been prepared in larger volumes and it has been reported that a volumetric ratio of 1:3 between the IL and the co-solvent was used [6].

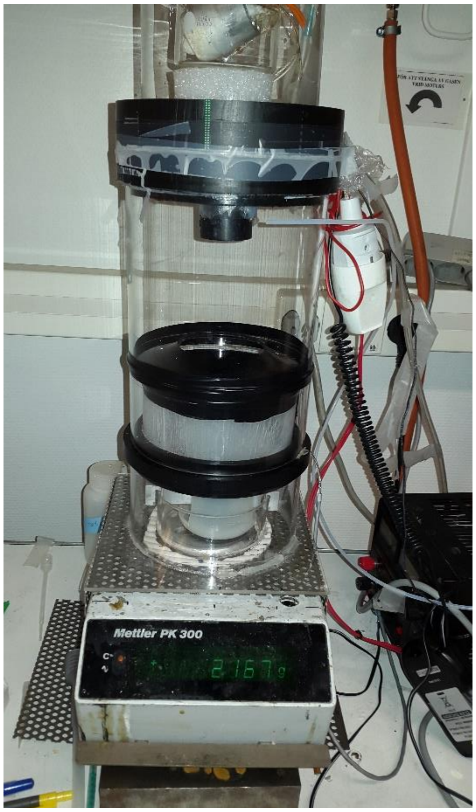


Figure 5: Picture of the CV-measurement setup.

4.3 Coagulation value measurements

Measuring of the coagulation values (CV) was done using a method where in the light absorbance of the cellulose is measured [36]. First roughly 0.75 grams of the dissolved cellulose solution was weighed up on a glass plate. Another glass plate was added on top and by adding pressure a thin layer of cellulose solution was created. The two plates were separated resulting in two different cellulose films. One of the samples were placed within the analyzing apparatus while the other was placed in a sealed container with nitrogen to avoid exposure to moisture in the air. In the apparatus the cellulose film was placed on a HDPE pipe on a scale with a light source underneath it. Above the light source a light meter measured the intensity of the light that passes through the cellulose film. Above the light source a bath containing the non-solvent with a heater was located. The whole system was closed to the surrounding atmosphere so the heated water bath will locally increase the moisture of the air in the same space as the cellulose film. By continuously measuring the weight and light intensity the absorbed mass of water at which the cellulose start to coagulate (the coagulation value) could be found.

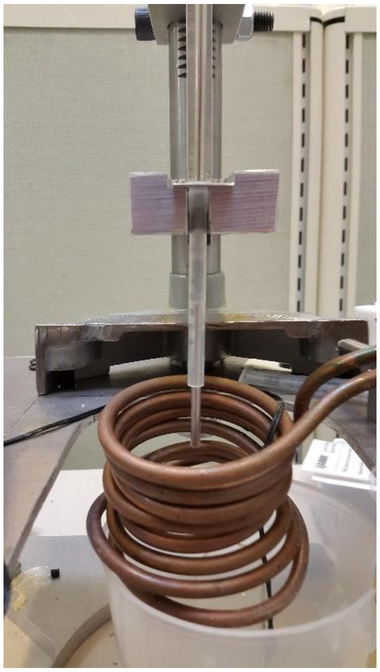


Figure 6: Picture showing the Coagulation rate measurement setup.

4.2 Mass-transport rate measurements

The coagulation rate was measured with an apparatus with the following setup. A small metal rod was inserted into a plastic syringe that has been filled with cellulose solution. As the rod was inserted into the syringe it became covered in cellulose solution. The rod and syringe was placed above a bath filled with anti-solvent (water, isopropanol) and the rod was pushed out of the syringe into the bath and kept there under a controlled amount of time. The total mass of the rod, the syringe and the solution was weighed before and after immersion which yields the net mass transport of the solution. The dimension of the cellulose solution that covers the rod was in a cylindrical shape with the length of 5.8 cm, the diameter of 4.6mm with a thickness of 0.35 mm. The conductivity in the non-solvent bath was measured which determined the amount of the ionic liquid diffused out from the cellulose which in combination with the net mass transport yields the non-solvents apparent diffusion into the solution. The mass transfer of the non-solvent can be calculated using the following equation: $Q_{net} = Q_{NS} - Q_{IL}$. The conductivity was correlated to the concentration of ionic liquid by making a conductivity to concentration series for the different ionic liquids in water and isopropanol (see Appendix A figures 26-30). The conductivity to concentration correlation between water and EmimAc could be deduced by a previously existing reference curve. The diffusion coefficient has been described in previous studies to have Fickian characteristics meaning that it follows Ficks second law of diffusion [35] and is independent of the concentration of the solution (Ficks second law: $\frac{dC}{dt} = D\frac{d^2C}{dx^2}$). The diffusion coefficient of the initial mass transfer can be calculated by the following equation: $\frac{m}{m_0} = 2(\frac{Dt}{l^2})^{0.5} * \pi^{-0.5}$[37], where $\frac{m}{m_0}$ is a function of the root of time, D is the diffusion coefficient, t is the submersion time and l is the thickness of the cellulose solution layer.

4.3 Coagulation depth measurements

The rate of the expansion of the coagulation layer is measured using a microscope and laser combined with a program that allows you to measure the thickness graphically. The cellulose solution is inserted into a glass pipe and a glass rod is inserted into the pipe. The construction is mounted into a support frame of the microscope with a laser beneath it pointed upwards into the glass pipe. The laser allows one to better distinguish the cellulose layer and the microscope with its built in camera is used to see and analyze the growth of the layer. The method was also used without a laser, using a normal light instead.

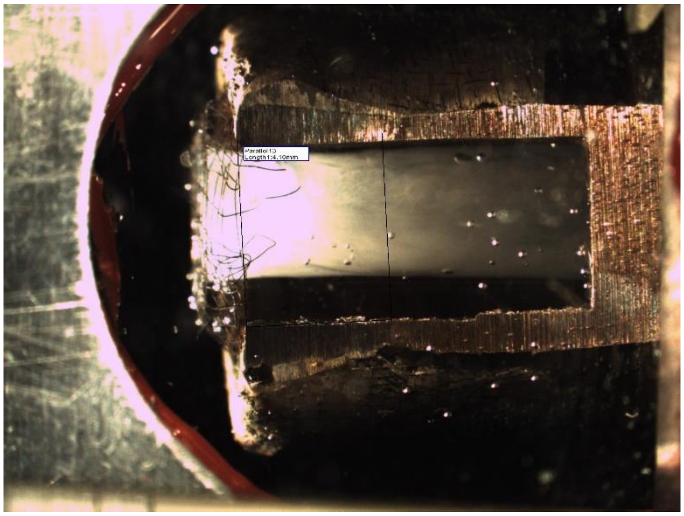


Figure 7: Picture showing the microscope image of the cellulose layer as it coagulates

4.4 Solution preparation

The cellulose dissolution sometimes requires certain procedure. Some of the ionic liquids are solid at room temperature and thus have to be dissolved before being mixed with the cellulose. The ionic liquid solvents that has been used to dissolve the solid ionic liquids in this study has been water and isopropanol. Water and isopropanol are as previously mentioned non-solvents and will hinder the dissolution in the mixture. The additive solvent must be vaporized before dissolution can be achieved. After the additive solvent has been evaporated the ionic liquid/cellulose solution stays in its liquid phase at room temperature.

4.5 Preparation of EmimAc cellulose solution:

The preparation of the ethyl-methyl imidazolium acetate cellulose solution was done by mixing the components and then stirring the solution in an open top syringe using a drill. The syringe is mounted into a structure that holds the syringe in place and minimizes air supply. The mixing takes place during two hours after which the solution is centrifuged to remove air bubbles. The two solutions that were prepared contained 13% and 8% cellulose respectively, both containing a 99:1 weight ratio between the ionic liquid and the DMSO.

Table 1: EmimAc solution compositions

Solution	IL	MCC	DMSO
13%	17.33	2.75	0.18
8%	18.39	1.67	0.19

4.6 Preparation of BmimCl cellulose solution:

The butyl-methyl imidazolium chloride cellulose solution was prepared by first dissolving the ionic liquid in a NaOH water solution with pH 10 as it is a solid at room temperature. The pH of the water solution is important in order to avoid the acidic degradation that will occur if the pH is not kept at a high value. The ionic liquid has 5w% water after having been dissolved in the NaOH water solution. The components of the different solutions were then mixed in the same way as with the EmimAc solution. After the mixing stage the solution was spread onto a sheet and placed in a vacuum oven until the water has been evaporated. The dissolution is observed by using a microscope where undissolved cellulose can easily be spotted. The 75:25 IL:DMSO solution contained enough DMSO to dissolve the ionic liquid without the use of water.

Table 2 BmimCl solution compositions

Solution	m_{BmimCl}(g)	m_{mcc}(g)	m_{DMSO}(g)
13%C 99:1	20.88 (5% water)	3.17	0.22
8%C 99:1	22.25 (5% water)	1.92	0.24
13%C 75:25	16.66	3.26	5.52
8%C 85:15	19.22 (5% water)	1.63	0.19

4.7 Synthesis of TMGHOAc ionic liquid

The synthesis of the tetra-methyl guanidine ionic liquid was performed by neutralizing the tetra-methyl guanidine base with acetic acid. The acetic acid was put in an e-flask and placed in an ice bath while the TMG was added carefully using a syringe. The acetic acid was originally dissolved in acetone in order to further prevent the sharp temperature rise that occurs as the reaction is very exothermic and the TMG vaporizes at 52-54 degrees Celsius. The acetone was later avoided as it was hard to distinguish the separation of acetone and TMG and the temperature increase could be managed with the ice bath and using an excess of TMG to. For detailed description of the synthesis of the different TMGHOAc solutions see appendix B.

4.8 Investigation of the TMGHOAC ionic liquid

The TMGHOAc ionic liquids composition and dissolution capabilities had to be investigated before using it as a cellulose solvent. In order to determine the composition of the produced ionic liquid a series of conductivity test were performed in which the ionic liquid was dried at 65 degrees Celsius for several hours and the conductivity was measured before and after the drying step in which it was determined that 4% of the original sample had evaporated. The conductivity was measured by putting the IL in a water bath at different concentrations and using a conductivity meter to determine the conductivity. The conductivity was measured at 3 different concentrations as can be seen in the table below.

Table 3: Conductivity test results showing the difference between dried and undried TMGHOAc related to the concentration

Sample	Concentration (W%)	Conductivity (S)	Cond/Conc	$(Cond_{Undried}/Conc_{Undried})/(Cond_{Dried}/Conc_{Dried})$

Dried 1	0.9992	3210	3212.6	0.956
Undried 1	0.9963	3060	3071.4	
Dried 2	0.7756	2550	3287.8	0.961
Undried 2	0.7757	2450	3158.4	
Dried 3	0.5540	1843	3326.7	0.961
Undried 3	0.5482	1752	3195.9	

The results which proved that the conductivity was roughly 4 % higher for the dried IL than for the undried IL.

The conductivity to concentration relationship of the TMGHOAc, the TMG and the HOAc was investigated in order to find how the composition of the ionic liquid affects its conductivity. The substances were diluted in water at different concentrations and the conductivity at these concentration were measured, the result can be seen in the figure below.

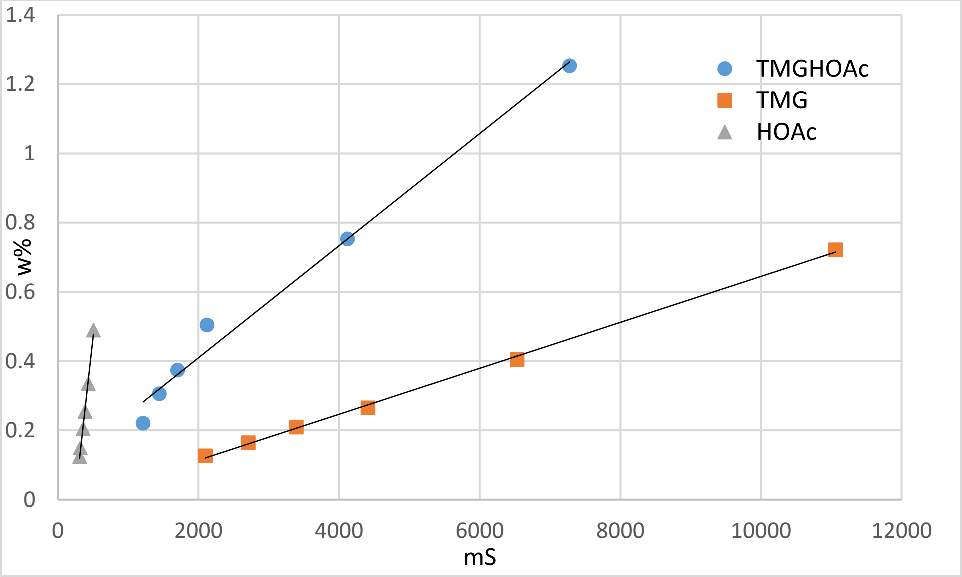


Figure 8: The conductivity to correlation relationship for TMGHOAc, TMG and HOAc

The result showed that an excess of TMG base will lead to a higher conductivity to concentration correlation while the opposite is true for the HOAc acid. This result shows that the vaporized component in the first conductivity test was residual acetone as this would increase the conductivity.

Another experiment measuring the pH instead of the conductivity was performed. In this experiment the sample was dried in a vacuum oven and it was determined that 12% of the original sample had evaporated. The pH was measured by dissolving the IL in water at different concentrations and using a pH-meter.

Table 4: pH tests comparing the dried and undried TMGHOAc related to the concentration of TMGHOAc

Sample	Concentration (w%)	pH	(pH1/Conc1)/(pH2/Conc2)
Dried1	0.6298	5.58	0.887
Undried1	0.6297	6.29	
Dried2	0.3277	5.56	0.843
Undried2	0.3136	6.31	

The results of the pH measurements showed that the pH decreases as the samples are dried which suggested that the evaporated fraction was the TMG base.

In order to correlate the pH of the solution to the composition of the IL a pH titration series was performed in which a 500 ml 0.1 M acetic acid solution was titrated with 0.5M TMG solution. The equivalence point was found to be 8.8 (see figure 9).

An experiment to investigate how the pH of the IL affects the cellulose dissolution was performed. The original IL had a pH of 5.89. The pH was once again measured by dissolving the IL in water and using a pH-meter

Table 5: pH dissolution series sample compositions and dissolution ability

Sample	Solution (g)	TMG (g)	pH	Dissolution
1	0.6466	0.0320	6.80	No
2	0.7824	0.0570	9.21	Partial
3	1.0689	0.2343	10.78	Yes
4	0.7190	0.2895	10.89	Yes
5	0.5041	0.3449	11.03	Yes
6	0.6348	0.6993	11.50	Yes

A clear correlation between the pH and the dissolution capabilities of the IL could be observed and an increase in the pH value was shown to promote the dissolution of the cellulose with dissolution being impossible below the equivalence point. This can be seen in the figure 9 below.

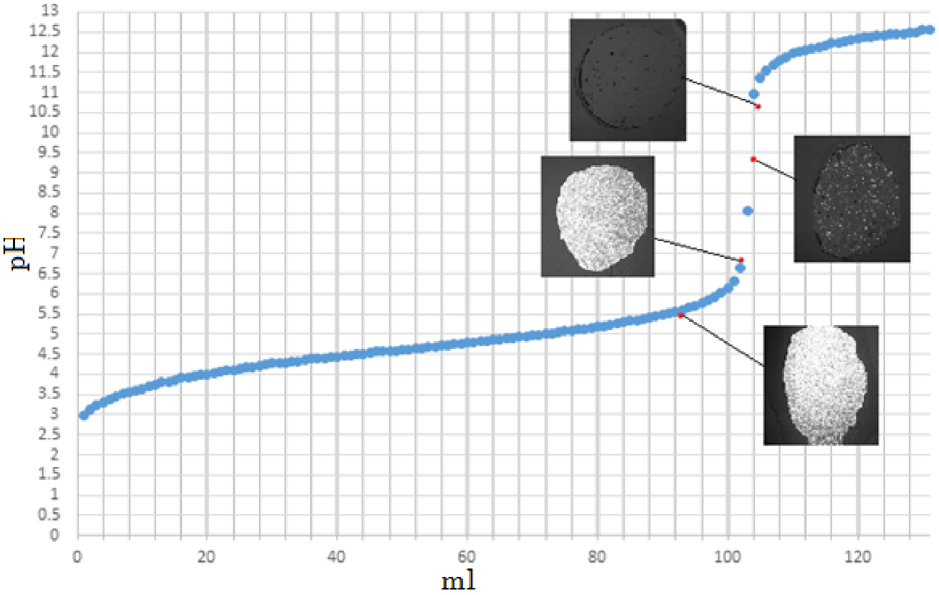


Figure 9: The pH-titration curve with added images showing the cellulose dissolution at pH: 5.89, 6.80, 9.21 and 10.78.

A test to evaluate DMSO as a co-solvent was administered. A 50:50 IL:DMSO solution was compared to a solution without any cellulose. The results showed that the 50:50 DMSO:IL mixture shows much greater dissolution capabilities than the 0:100 DMSO:IL solution. The result can be seen in the figure 10 below.

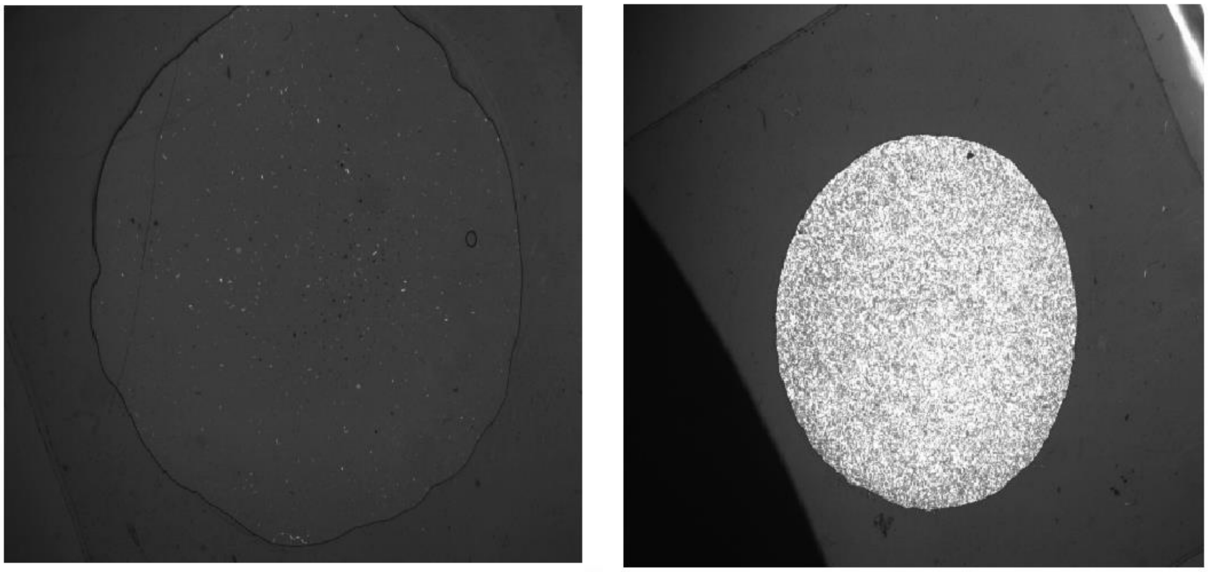


Figure 10: The 50:50 IL:DMSO solution on the left side and the 100:0 IL:DMSO solution on the right side

4.9 Large scale cellulose dissolution in TMGHOAc

The dissolution of larger volumes of cellulose solution were initially performed using a metal container with a surrounding heating band and a stationary drill was used as a stirrer. The container was enclosed preventing air contact. The IL was first adjusted to a lower pH before dissolution with the intention of increasing the pH, by adding additional TMG after the mixing as this method to achieve dissolution had been shown to be successful in the pH titration test. This was done to minimize the evaporation of the volatile TMG so that the contents of the solution would be known with some accuracy.

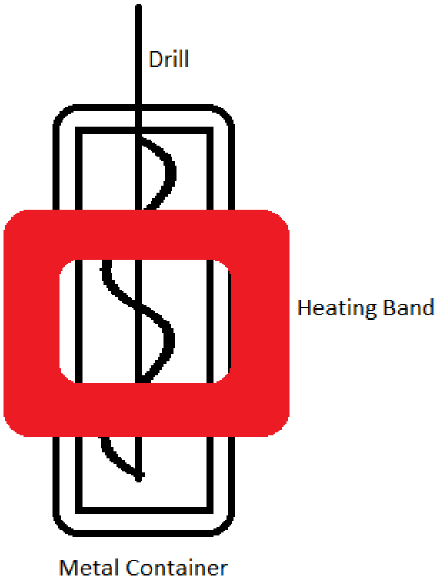


Figure11: Schematic figure of the heating chamber set-up

The method proved to be problematic as the metal container was too large for the drill, preventing sufficient mixing.

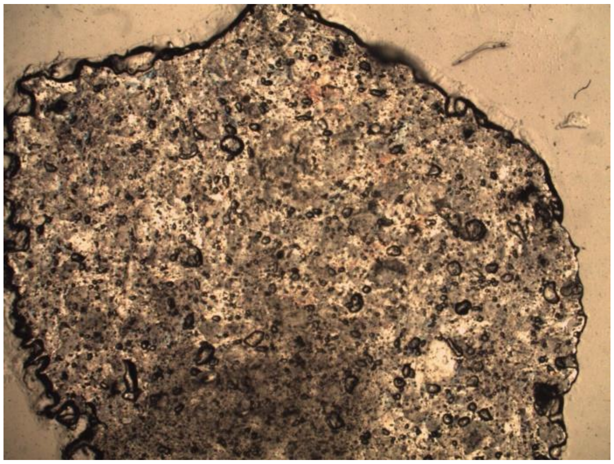


Figure 12: The unsuccessful attempt at cellulose dissolution in TMGHOAc

A new method was used in which the components were premixed in an open syringe and subsequently heated. The results for the dissolution attempts resulted in a hard gel like solid material even after the extra TMG had been added. After several attempts it was determined that adding the TMG after the heating was a problem as. The IL with the higher pH can be used directly and the composition of the IL can be determined after the fact using the titration curve and measuring the pH.

Dissolution of 8w% cellulose in a 99:1 IL:DMSO solution is attempted with the following composition:

Table 6: Components of the first TMGHOAc solution with 8w% cellulose and 99:1 IL:DMSO ratio.

Component	Amount(g)
IL	9.122
MCC	0.802
DMSO	0.093

The components were premixed and then heated at 120 degrees Celsius. The dissolution seemed to be successful as it remained in its liquid form without the sample solidifying. The solution had a dark red color which suggested that there had been degradation of the cellulose.

Dissolution tests were performed on solutions with the following compositions:

Table 7: Compositions of failed TMGHOAc solutions

Composition	IL(g)	MCC(g)	DMSO(g)
8%C, 99:1 IL:DMSO	9.122	0.802	0.093
13%C, 97:3 IL:DMSO	8.441	1.299	0.281
13%C, 96:4 IL:DMSO	12.694	1.953	0.557
8%C, 95:5 IL:DMSO	5.130	0.302	0.472

All of the tests resulted in the samples solidifying. The phase change in the 8% cellulose 95:5 IL:DMSO took several hours even as it was refrigerated at a low temperature.

The DMSO to IL ratio was increased to 10:90 and a new solution was produced. The pH of the IL was 12.64 during this dissolution attempt.

Table 8: Components of the first TMGHOAc solution with 8w% cellulose and 90:10 IL:DMSO ratio.

Component	Amount(g)
IL	12.437
MCC	1.205
DMSO	1.387

The solution remained in its liquid state and the solution could be analyzed.

Table 9: Components of the first TMGHOAc solution with 8w% cellulose and 85:15 IL:DMSO ratio.

Component	Amount(g)
IL	5.189
MCC	0.533
DMSO	1.387

Table 10: Components of the first TMGHOAc solution with 13w% cellulose and 85:15 IL:DMSO ratio.

Component	Amount(g)
IL	11.100
MCC	1.948
DMSO	1.966

5 Results:

5.1 Coagulation value results:

The CV test performed on the ethyl-methyl imidazolium acetate solutions resulted in solid films with a clear change in turbidity and it could generally be observed that the coagulation happened at a lower weight percentage for water compared to isopropanol. The coagulation was easy to measure as the intensity signal was large and the change happened quickly at a specific amount of mass uptake of the non-solvent. The mass uptake denotes the weight difference between when the plates are weighed together immediately after the solutions has been added to the plates and the weight of the plates as they are weighed individually as the test is being performed and represents the additional water that has been absorbed from the moisture in the air.

Table 11: The CV results for the EmimAc solutions.

Sample	First	second	Mass uptake	Average
13w% Cellulose 99:1 IL:DMSO				
Water 1	16.30	15.31	0.58%	16.095
Water 2	17.24	16.28	0.65%	17.085
IPA 1	20.77	16.45	2.5%	19.86
IPA 2	23.8	25.50	1%	25.15
IPA 3	19.24	-		
8w% Cellulose 99:1 IL:DMSO				
Water 1	19.65	20.02	0.38%	20.025
Water 2	19.55	22.77	0.49%	21.405
IPA 1	19.82	24.65	2.85%	23.66
IPA 2	25.63	31.8	2.99%	29.21

The butyl-methyl imidazolium chloride CV results were much harder to interpret than the EmimAc results as the coagulation process happened over a longer period of time resulting in a less clear signal and for the fact that the signal was much lower in magnitude. This led to the BmimCl CV results being inconclusive as can be seen in the figure below (see Appendix A: Figures 3, 4, 5 for further examples).

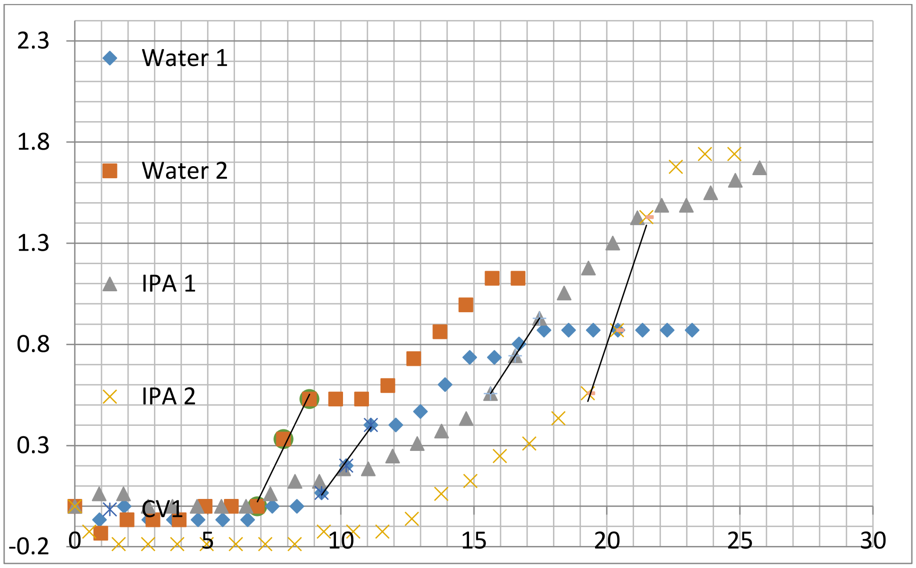


Figure 13: the cv results for the 8% cellulose 99:1 IL:DMSO, BmimCl solution

The CV results for the TMGHOAc solutions showed a coagulation similar to EmimAc with clear changes in turbidity (see appendix A figure 6).

Table 12: CV results for the TMGHOAc solutions.

Sample	CV1	CV2	Losses (%)	Average CV
8w% Cellulose 90:10 IL:DMSO				
Water 1	18.04	18.31	1.33	18.840
Water 2	18.24	16.55	1.30	18.045
IPA 1	20.16	20.89	1.73	21.390
IPA 2	28.85	28.62	2.18	29.825

5.2 Mass-transport rate results

The mass-transport tests resulted in information about the net mass-transport in and out of the cellulose solution and the apparent diffusion of IL out of the solution by relating the conductivity of the solution to the concentration of IL. The conductivity/concentration correlation was made by doing a conductivity series with different IL concentrations in both water and ipa. The series shows that there is a linear relation between the concentration of IL and the conductivity (see Appendix A figures 20, 21, 22, 23). The concentration was compared to a long time sample where it is assumed that all of the IL has diffused from the solution in order to find the amount of ionic liquid that has diffused into the non-solvent compared to the total amount of ionic liquid in the cellulose solution. The apparent diffusion of the non-solvent as well as the apparent diffusion coefficients are calculated as described in chapter 4.2. Note that the non-solvents apparent diffusion rate and diffusion coefficient could not be accurately calculated in the solutions with a high DMSO concentration as the DMSO diffusion was not measured. The results for the 8w% 99:1 DMSO solutions proved to be unreliable.

The diffusion rate experiments for the EmimAc were performed on the 13w% cellulose 99:1 IL:DMSO.

Table 13: Mass-transport rate results for the EmimAc solutions

	Water	IPA
13w% Cellulose 99:1 IL:DMSO		
Initial rate of net mass transport $((\Delta m/m_0)/\sqrt{t})$	0.0166	0.0155
Rate of IL diffusion$((\Delta m_{IL}/m_0)/\sqrt{t})$	0.0520	0.0295
Rate of Non-solvent diffusion$((\Delta m_{NS}/m_0)/\sqrt{t})$	0.0706	0.0450
$D_{IL}(m^2/s)$	1.929E-10	6.208E-11
$D_{NS}(m^2/s)$	4.793E-10	1.947E-10

The diffusion rate experiments for the BmimCl were performed on the 8w% cellulose 99:1 IL:DMSO, 13w% cellulose 99:1 IL:DMSO and the 13w% cellulose 25:75 IL:DMSO.

Table 14: Mass-transport rate results for the BmimCl solutions.

	Water	IPA
13w% Cellulose 99:1 IL:DMSO		
Initial rate of net mass transport $((\Delta m/m_0)/\sqrt{t})$	0.0223	0.0139
Rate of IL diffusion$((\Delta m_{IL}/m_0)/\sqrt{t})$	0.0332	0.0233
Rate of Non-solvent diffusion$((\Delta m_{NS}/m_0)/\sqrt{t})$	0.0555	0.0372
$D_{IL}(m^2/s)$	7.863E-11	3.873E-11
$D_{NS}(m^2/s)$	2.962E-10	1.331E-10
8w% Cellulose 99:1 IL:DMSO		
Initial rate of net mass transport $((\Delta m/m_0)/\sqrt{t})$	0.0178	0.0131
Rate of IL diffusion $((\Delta m_{IL}/m_0)/\sqrt{t})$	0.0459	0.0226
Rate of Non-solvent diffusion$((\Delta m_{NS}/m_0)/\sqrt{t})$	0.0637	0.0357
$D_{IL}(m^2/s)$	1.681E-10	4.074E-11
$D_{NS}(m^2/s)$	3.902E-10	1.226E-10
13w% Cellulose 75:25 IL:DMSO		
Initial rate of net mass transport $((\Delta m/m_0)/\sqrt{t})$	0.0114	0.0100
Rate of IL diffusion$((\Delta m_{IL}/m_0)/\sqrt{t})$	0.0599	0.0323
$D_{IL}(m^2/s)$	1.469E-10	4.271E-11

The diffusion rate experiments for the TMGHOAc were performed on the 8w% cellulose 90:10 IL:DMSO solution and on 8w%.and 13w% cellulose 85:15 IL:DMSO.

Table 15: Mass-transport rate results for the TMGHOAc solutions

	Water	IPA
8w% Cellulose 90:10 IL:DMSO		
Initial rate of net mass transport (($\Delta m/m_0$)/$\sqrt{t}$)	0.0229	0.0171
Rate of IL diffusion(($\Delta m_{IL}/m_0$)/$\sqrt{t}$)	0.0436	0.0231
D_{IL}(m^2/s)	1.253E-10	3.518E-11
13w% Cellulose 85:15 IL:DMSO		
Initial rate of net mass transport (($\Delta m/m_0$)/$\sqrt{t}$)	0.0156	0.0121
Rate of IL diffusion(($\Delta m_{IL}/m_0$)/$\sqrt{t}$)	0.0412	0.0251
D_{IL}(m^2/s)	8.926E-11	3.287E-11
8w% Cellulose 85:15 IL:DMSO		
Initial rate of net mass transport (($\Delta m/m_0$)/$\sqrt{t}$)	0.0176	0.0172
Rate of IL diffusion(($\Delta m_{IL}/m_0$)/$\sqrt{t}$)	0.0376	0.0200
D_{IL}(m^2/s)	8.317E-11	2.352E-11

5.3 Coagulation depth results

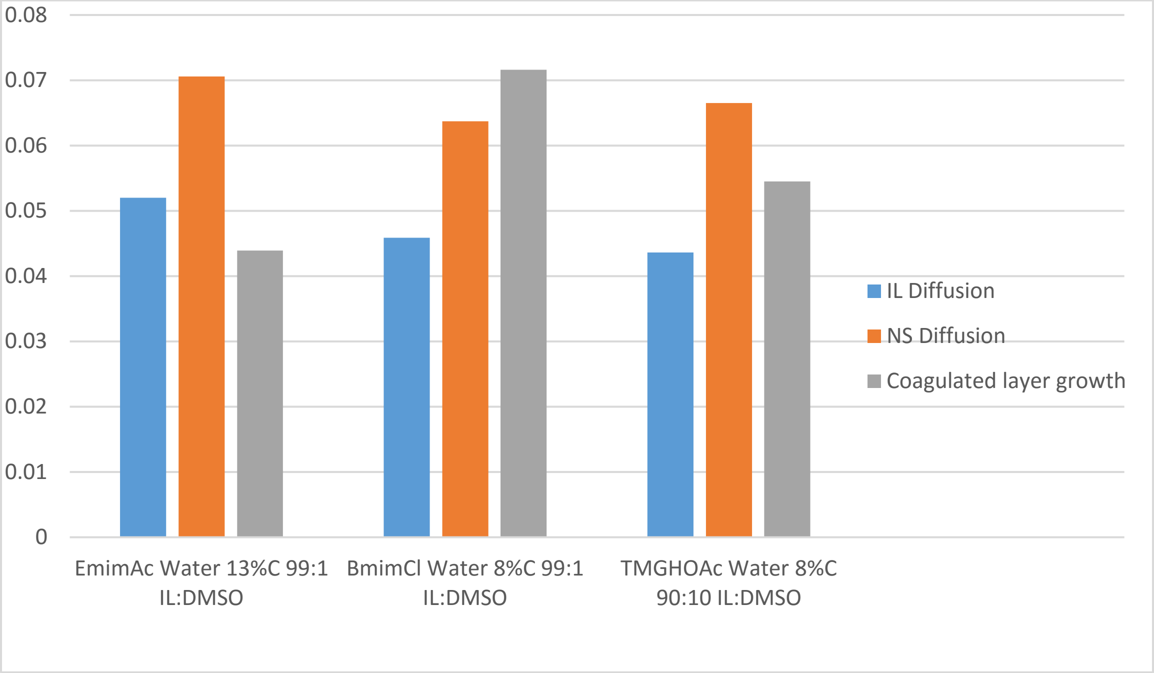
The microscope method was performed on the 8w% cellulose EmimAc, BmimCl solutions and with TMGHOAc 8w% cellulose 10:90 DMSO:IL, 8w% cellulose 15:85 DMSO:IL and 13w% cellulose 15:85 DMSO:IL with water being the used non-solvent. The growth rate is defined as the change in thickness of the coagulated front divided by the square root of the time submerged in non-solvent.

Table 16: Microscope results for the EmimAc, BmimCl and TMGHOAc 8w% cellulose solutions with water as non-solvent.

Ionic liquid	Growth rate (mm/√s)
EmimAc	0.0439
BmimCl	0.0716
TMGHOAc 8w% 10:90	0.0545
TMGHOAc 8w% 15:85	0.0195
TMGHOAc 13w% 15:85	0.044

The apparent diffusion rates of the ionic liquids and non-solvents can be compared to the growth rate of the different cellulose solutions as they are all proportional to the square root of time. This comparison can be seen in the figure below.

Table 17: Comparison of the IL and non-solvents apparent diffusion and the growth rate of the coagulated layer.



6 Discussion:

The coagulation value analyzing method proved to be somewhat problematic for some of the solutions being analyzed. The method worked well for the EmimAc and TMGHOAc solutions as these solutions showed a clear change in light transmittance between the liquid solution and the coagulated layer with a transmitted intensity change in the range of 7-17% for the EmimAc solutions and 14-18.5% for the TMGHOAc (see appendix figures 1,2 for EmimAc and 6 for TMGHOAc). This was expected for the EmimAc as the solvent has been studied previously and shown to work well with this methods and the TMGHOAc fortunately also showed very clear results. The results showed that the coagulation occurred at a lower non-solvent fraction for TMGHOAc cellulose solutions than for the EmimAc solutions although the difference in DMSO concentration makes the results not fully comparable.

The BmimCl was much harder to analyze and the CV tests with this ionic liquid are less conclusive due to the very small signal that was shown as the cellulose coagulated with a transmitted intensity decrease of 0.5-2.5% (see appendix figures 3 and 4). Combining the low intensity change with a very slow gradual coagulation and the results become very hard to interpret. The low opacity change might be a result from the cellulose being less crystalline in this solution since a more crystalline polymer tends to be more opaque than an amorphous polymer. The low signal can also be caused by the pore size of the cellulose being too small to observe in the BmimCl solution. If the pore size is smaller than 200 nm the pore will not be able to reflect visible light since it is smaller than half of the smallest wavelength in visible light. The CV technique seems to not be the ideal analyzing method for ionic liquids where the coagulated cellulose produces a transparent films. This type of weak signal has been observed previously with solutions with cellulose concentrations above 25% showing similarly weak signals [36].

The diffusion rate shows what was previously discussed in the theory segment, that the apparent diffusion of non-solvent into the cellulose solution is much faster than the apparent diffusion of solvent out of the solution. This shows that the rate determining step is the apparent diffusion of solvent out of the solution and it was determined that the apparent diffusion rate of IL in the initial stage of coagulation is in descending order: EmimAc, BmimCl, TMGHOAc. It can be observed that water diffuses through the ionic liquids slightly faster than isopropanol. The apparent diffusion of IL out from the solution is much faster when water is used. This seems to suggest that the structure of the IPA allows it to interact both with the cellulose and the ionic liquids whereas the water preferably interacts with the cellulose. A good example of this can be seen in the IL diffusion result for BmimCl with 8w% cellulose where it is apparent that that the apparent diffusion of ionic liquid has reached completion after 225 seconds when water was used as a non-solvent whereas the apparent diffusion in isopropanol is much slower (see Appendix A figure 10).

The diffusion rate experiments performed on the TMGHOAc solutions shows that the apparent diffusion pattern for water and isopropanol is more similar than they were for the EmimAc and BmimCl samples (see Appendix A figure 14). It could also be seen that the swelling of the coagulated layer was much greater in the TMGHOAc and that the apparent diffusion of ionic liquid out of the cellulose solution is much slower than it has been in the previously examined solvents. The slow apparent diffusion leads to a very thick coagulated layer with substantially larger swelling than the EmimAc and BmimCl solutions.

The microscope measurements were only performed with water as the non-solvent. The results showed that the rate at which the coagulated layer grows is the fastest in the BmimCl solutions followed by the TMGHOAc solutions and the slowest being the EmimAc solutions (see appendix figures 15, 16 and 17). A potential reason that makes the microscope method slightly unreliable is that the angle between the top of the coagulating cellulose layer and the mirror might not be exactly the same for all of the samples resulting in a slight error. In the comparisons between IL and non-solvents apparent diffusion and the growth of the coagulated layer it can be seen that faster mass transfer through the solution result in a quicker growth of the coagulated layer.

The dissolution of cellulose in the tetra-methyl guanidine ionic liquid was found to be very difficult to perform as the solution easily reverted back to a solid structure at room temperature. The high dependence on pH on the dissolution might explain this as it seems as if an abundance in acid promotes the phase change. The unreacted acid might be able to hydrogen bond to the IL anions thereby preventing them from interacting with the cellulose and stopping the cellulose solution from initiating. The fact that the TMGH ionic liquid is distillable and that the TMG base in its nonionic form is very volatile also makes handling of the ionic liquid much more complicated than the more stable ionic liquids.

It was also determined that the easiest way to achieve dissolution is to simply use heat to liquefy the tetra-methyl guanidine ionic liquid and to use DMSO as a co-solvent. Because of the TMGs high vapor pressure and volatility the evaporation stage of an eventual solvent such as an alcohol becomes problematic. The easiest way to be sure of what components are present in the final solution is to only use heat and measure the pH to determine the composition of the solution.

The DMSO is able to facilitate the dissolution in the TMGHOAc solutions, preventing the phase change of the solution. The reason behind this phenomena might be that the ion pair does not separate well enough to effectively dissolve the cellulose before returning to the solid state. The DMSO is known to enhance dissociation of the ion pair of ionic liquids allowing the ionic liquid to remain in its liquid state. A gel like structure during regeneration of cellulose was observed in a previous study [33] and was believed to be a reason for why the spun fibers showed poor mechanical properties. In that study the authors produced a cellulose solution with a concentration of 13% cellulose without any DMSO. Such a high cellulose concentration without any DMSO could not be produced in this study as the solidification occurred once the temperature was decreased.

7 Conclusion:

The aim of this study was to investigate the coagulation process of the three ionic liquid solvents. It was shown that the three solvents coagulate in different ways. EmimAc and TMGHOAc shows clear changes in turbidity and opacity while BmimCl coagulates while showing only a minimal change in turbidity making the CV value very hard to determine. The diffusion rate experiments also showed widely different results with the EmimAc and BmimCl showing similar $\Delta m/\Delta m_0$ curves with the water giving a more rapid apparent diffusion into the solution and an ability to rapidly wash out solvent from the solution compared to isopropanol. The TMGHOAc instead had much more similar $\Delta m/\Delta m_0$ curves for water and isopropanol. These results suggests that the different ways that water and isopropanol interact with the imidazolium based cations is not present in the tetra-methyl guanidine ionic liquid where the difference in mass-transfer in and out from the IPA and water non-solvents only differ slightly.

The dissolution of cellulose in TMGHOAc solvent was shown to be highly dependent on the pH value of the system and a pH lower than the equivalence point will prevent the cellulose from dissolving. It was shown that the easiest way to achieve dissolution was to use heat and stirring without dissolving the ionic liquid in water or IPA. The higher vapor pressure of the ionic liquid which is its most interesting property also proved to be somewhat of a disadvantage as the heating required for dissolving the cellulose will vaporize parts of the solvent affecting its composition and changing the dissolution properties of the solvent. In this study it was found that the TMGHOAc solutions that were able to successfully dissolve the cellulose had an excess of TMG which evaporates at a low temperature. The evaporation of the TMG base will change the composition of the solution. The change can be kept under control by keeping the solution in a sealed container during heating and it can be monitored by measuring the pH before and after the heating. It was shown that the phase change of the solution can be avoided by using greater amounts of DMSO in the solution.

8 Future work:

Potential future works may include investigating the coagulation of NMMO based cellulose solutions to compare the mechanism to the standard cellulose solvent. It would be interesting to compare the coagulation of ionic liquid solvents to NMMO to investigate if there is any noticeable difference between the two or if the process is close to identical. Further investigation of the TMGHOAc would also be interesting such as increasing the cellulose concentration without changing the IL:DMSO ratio to find if the gel formation which makes the solvents so difficult to work with is caused solely by the ionic liquid or if the cellulose promotes the gel formation. Spinning trials of TMGHOAc solutions with higher amounts of DMSO would also be an interesting future study to find if the TMGHOAc truly have insufficient spinning properties or if they can be circumvented by the use of DMSO as a co-solvent.

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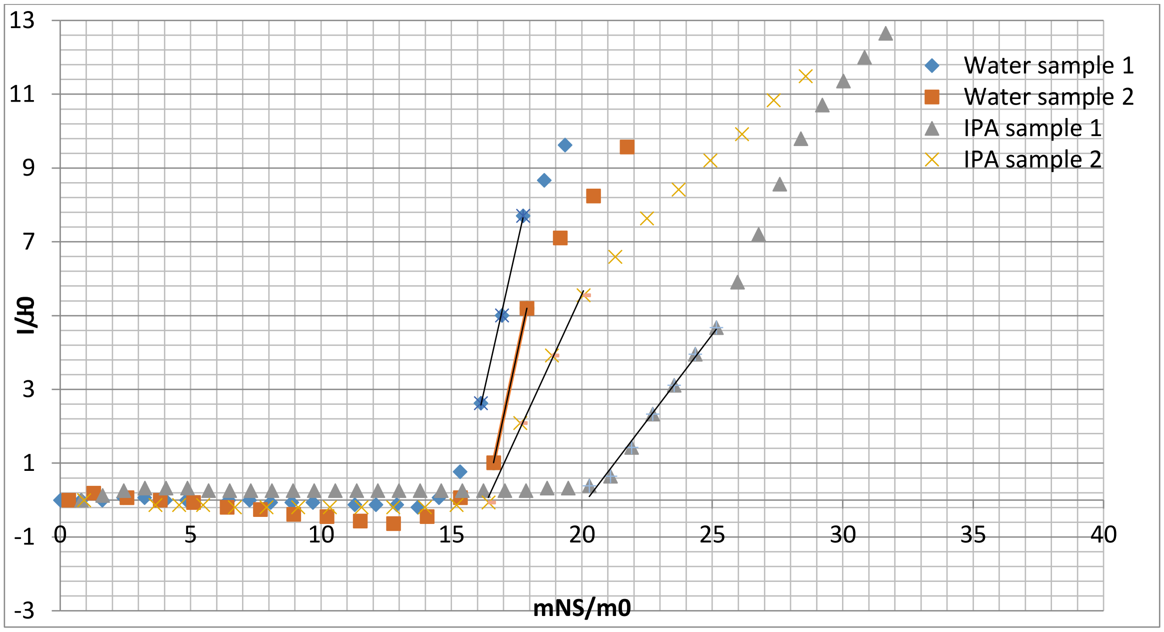
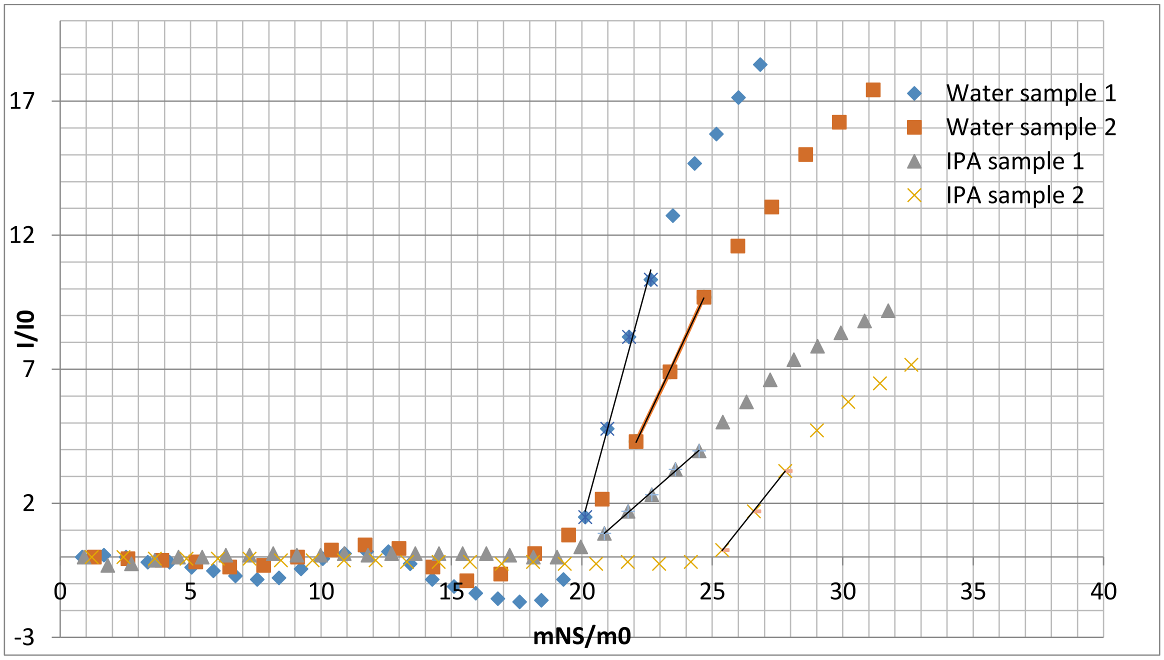
Appendix A: Results and measurements

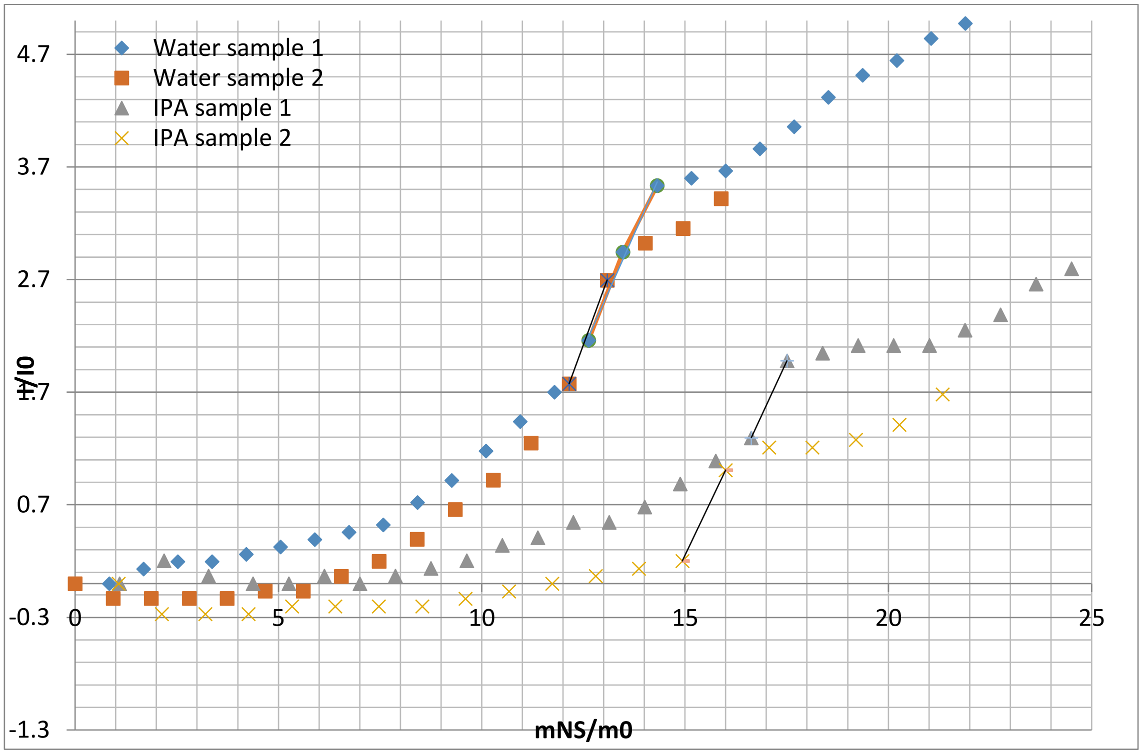
Appendix A figure 1: Example of the CV measurements for 13% cellulose EmimAc solutions with a 1:99 weight fraction between DMSO and IL



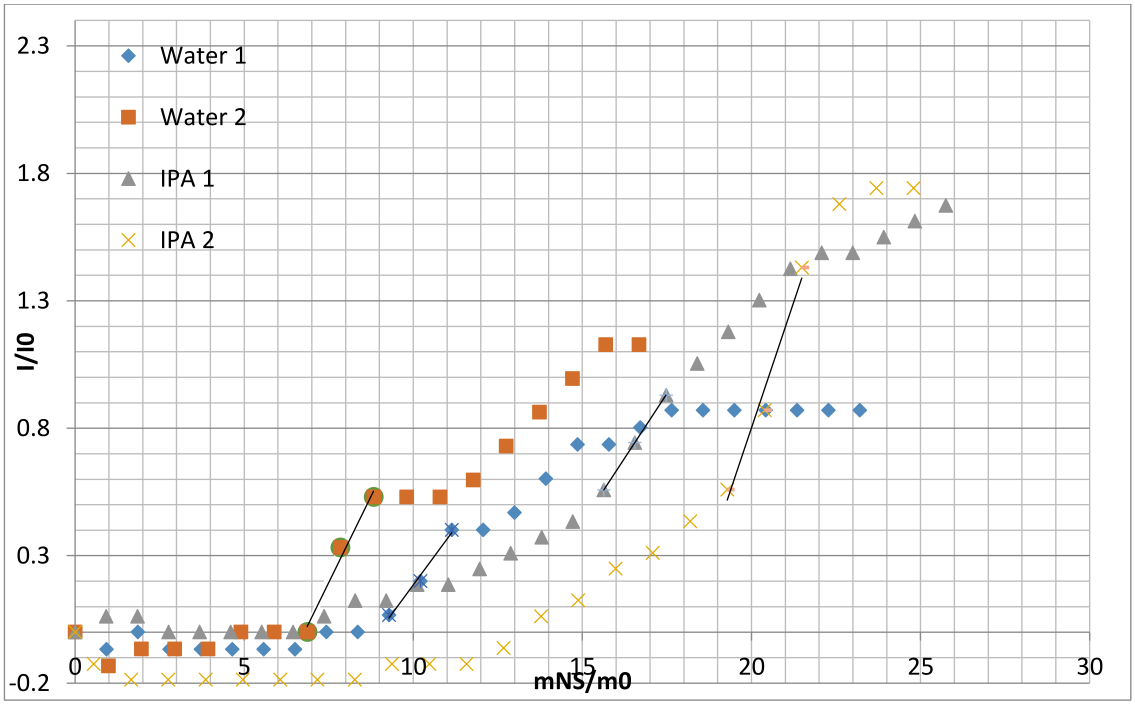
Appendix A figure 2: Example of the CV measurements for 8%cellulose EmimAc solutions with a 1:99 weight fraction between DMSO and IL



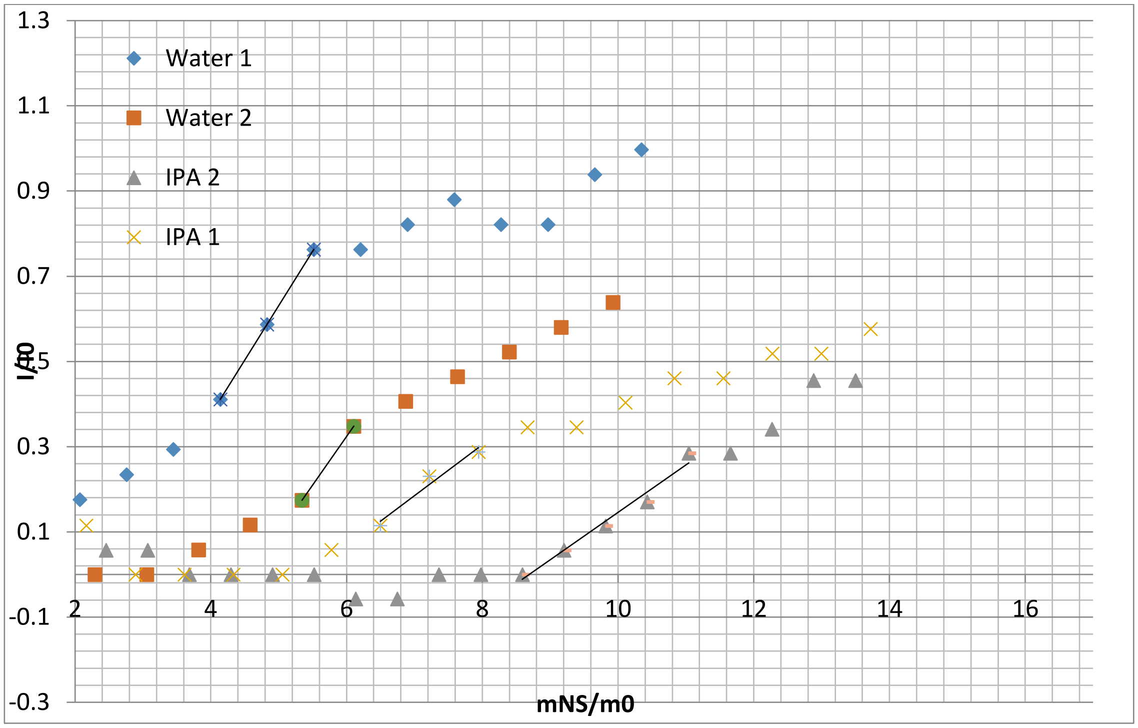
Appendix A figure 3: Example of the CV measurements for 13%cellulose BmimCl solutions with a 1:99 weight fraction between DMSO and IL



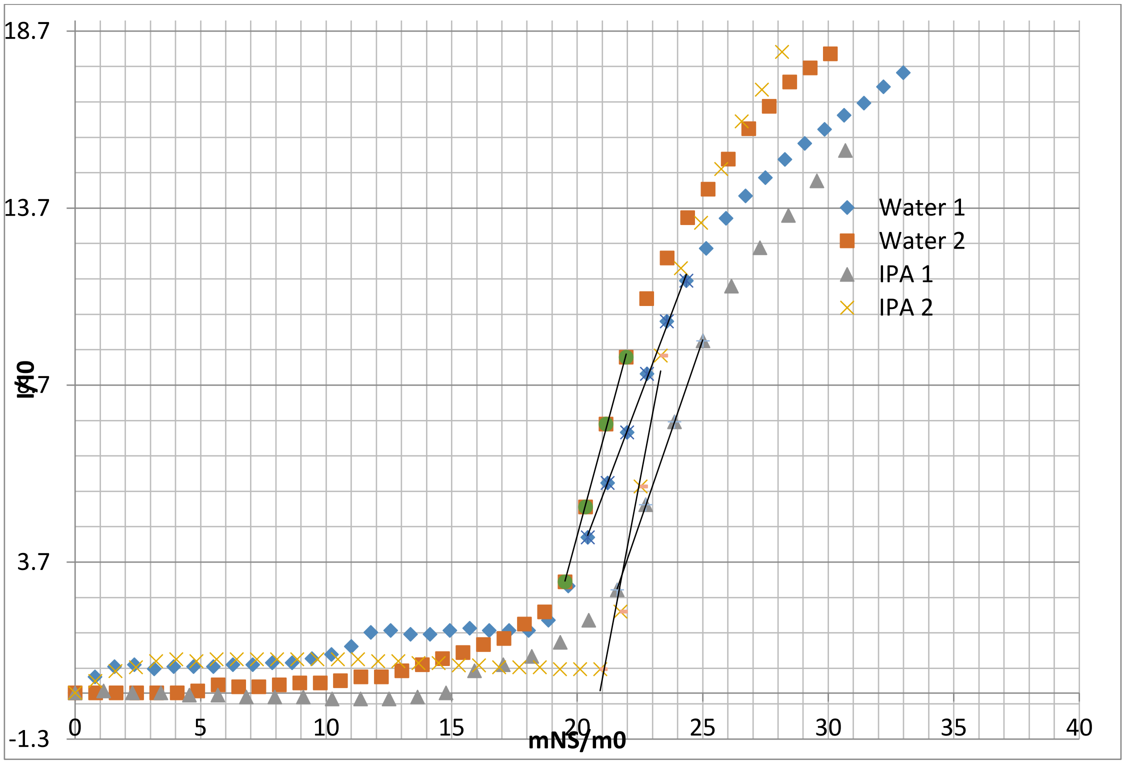
Appendix A figure 4: Example of the CV measurements for 8%cellulose BmimCl solutions with a 1:99 weight fraction between DMSO and IL.



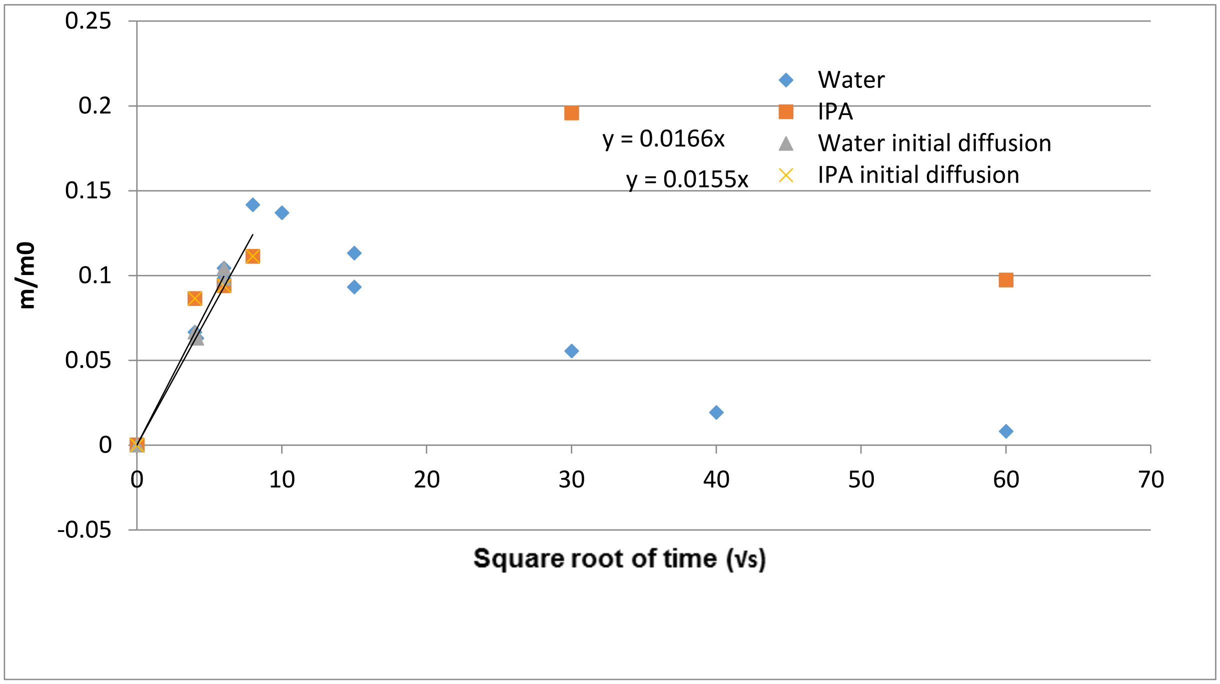
Appendix A figure 5: Example of CV measurements for 13% Cellulose in BmimCl solution with a 25:75 weight fraction between DMSO and IL



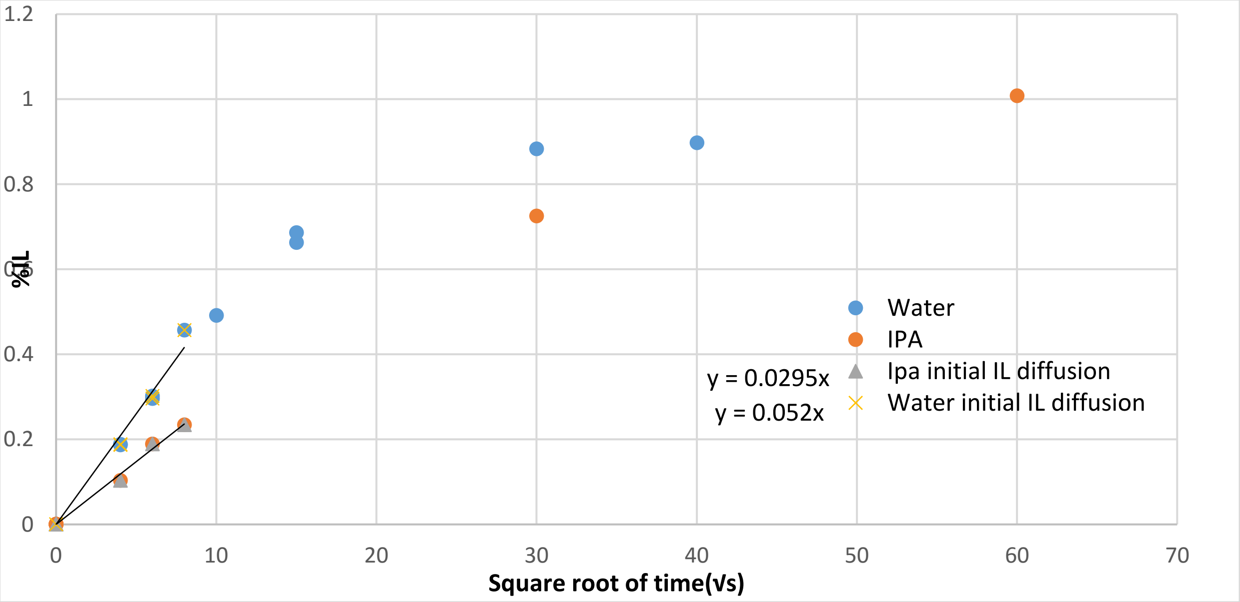
Appendix A figure 6: Example of CV measurements for 8% Cellulose in TMGHOAc with a 10:90 weight fraction between DMSO and IL



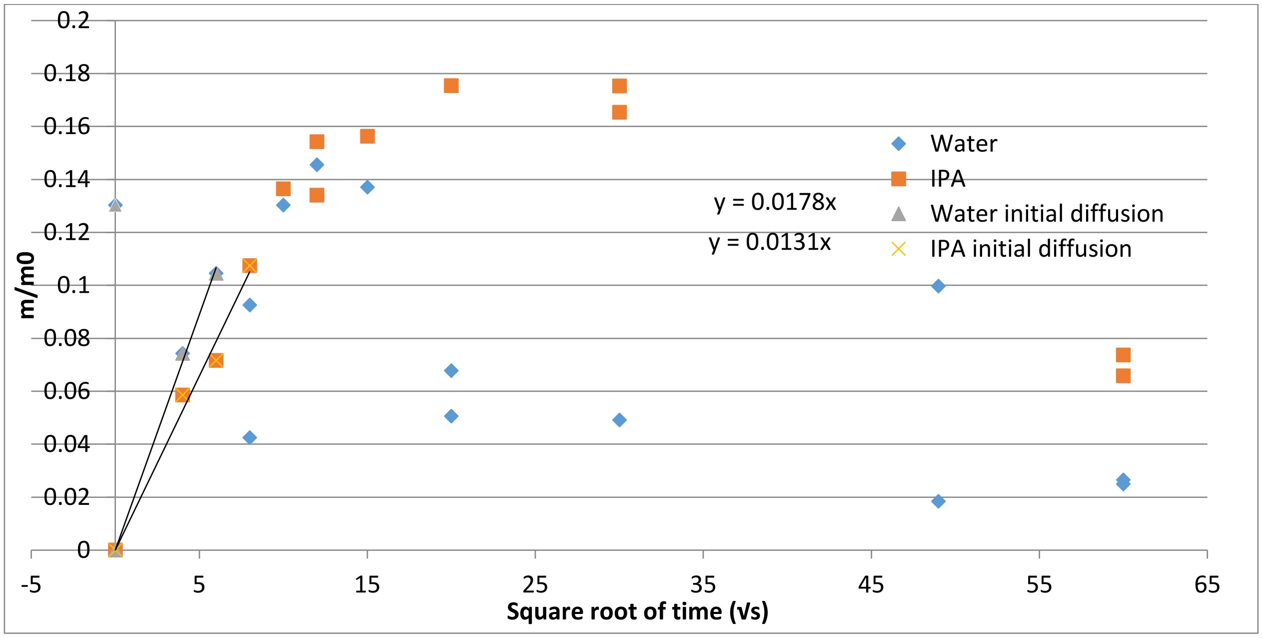
Appendix A figure 7: Diffusion rate results for EmimAc 13% cellulose



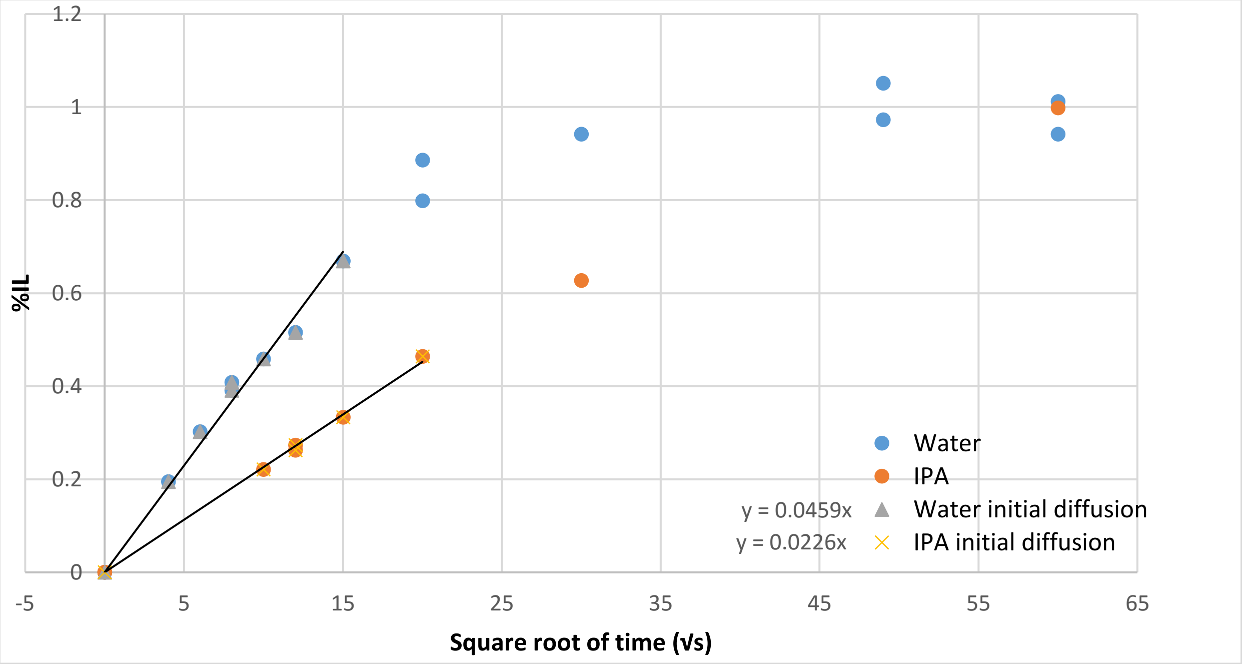
Appendix A figure 8: Diffusion rate results for EmimAc 13% Cellulose IL diffusion



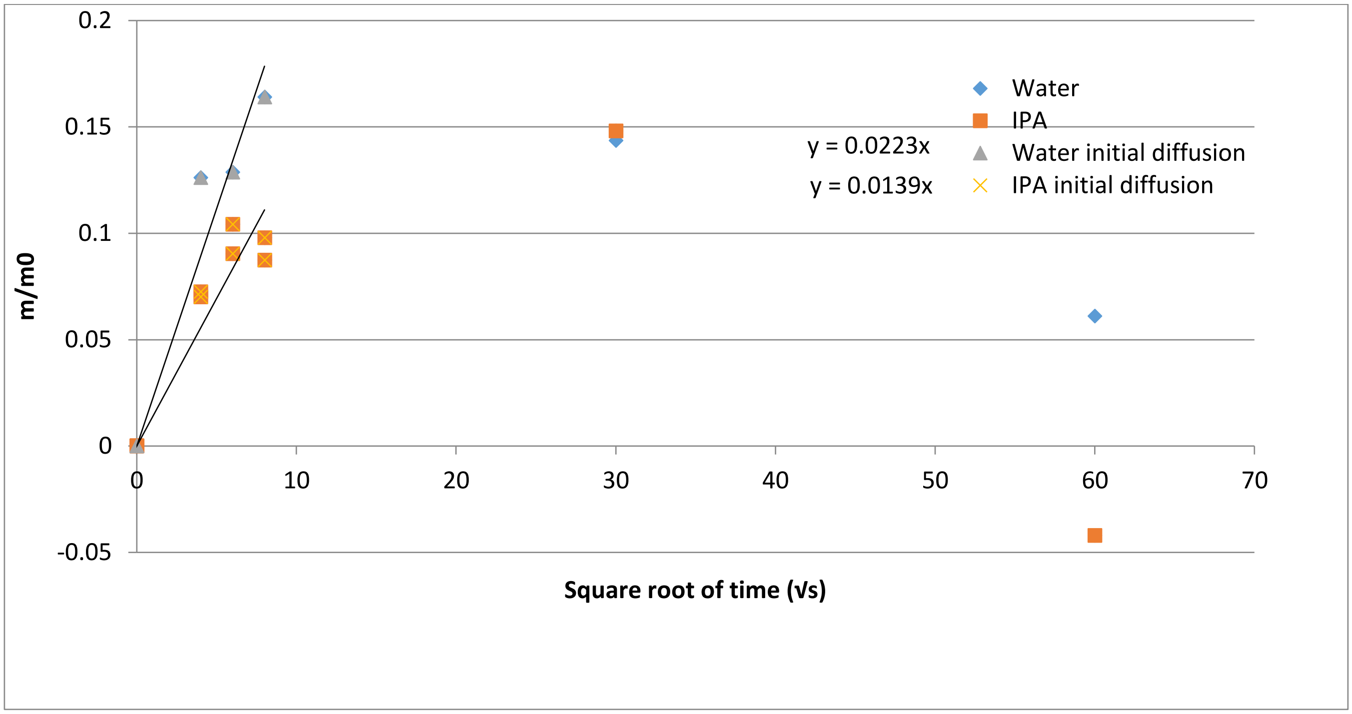
Appendix A figure 9: Diffusion rate results for BmimCl 8% Cellulose



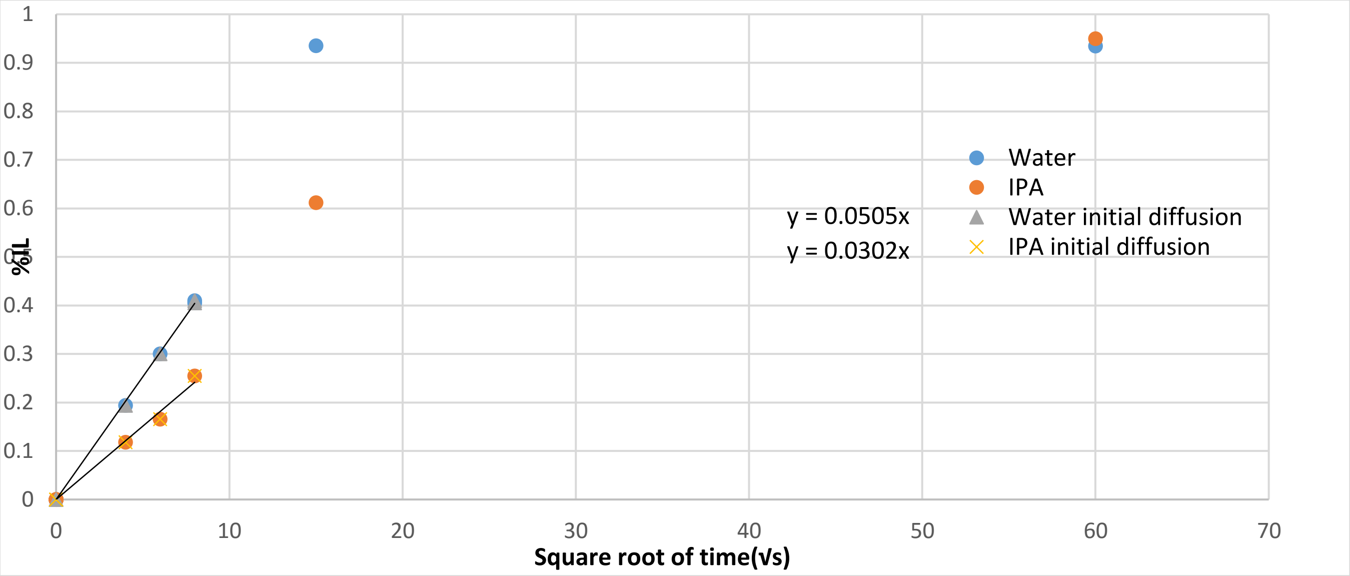
Appendix A figure 10: Diffusion rate results for BmimCl 8% Cellulose IL diffusion



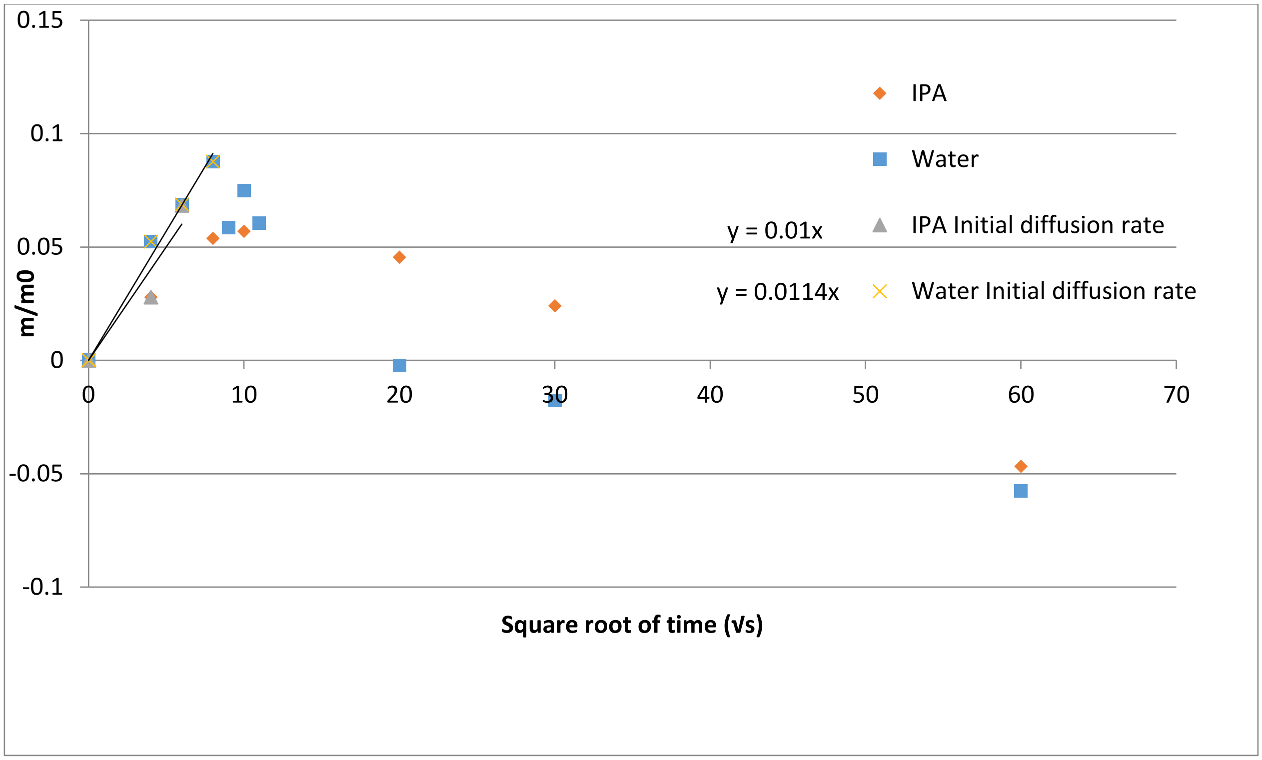
Appendix A Figure 11: Diffusion rate results for BmimCl 13% Cellulose



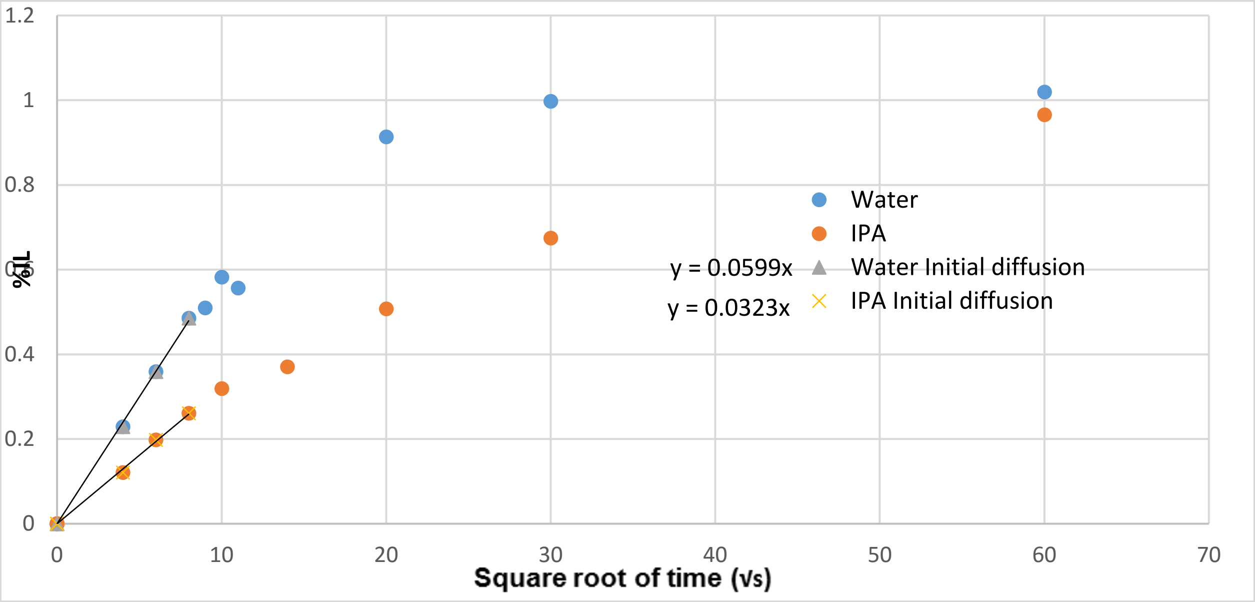
Appendix A Figure 12: Diffusion rate results for BmimCl 13% Cellulose IL diffusion



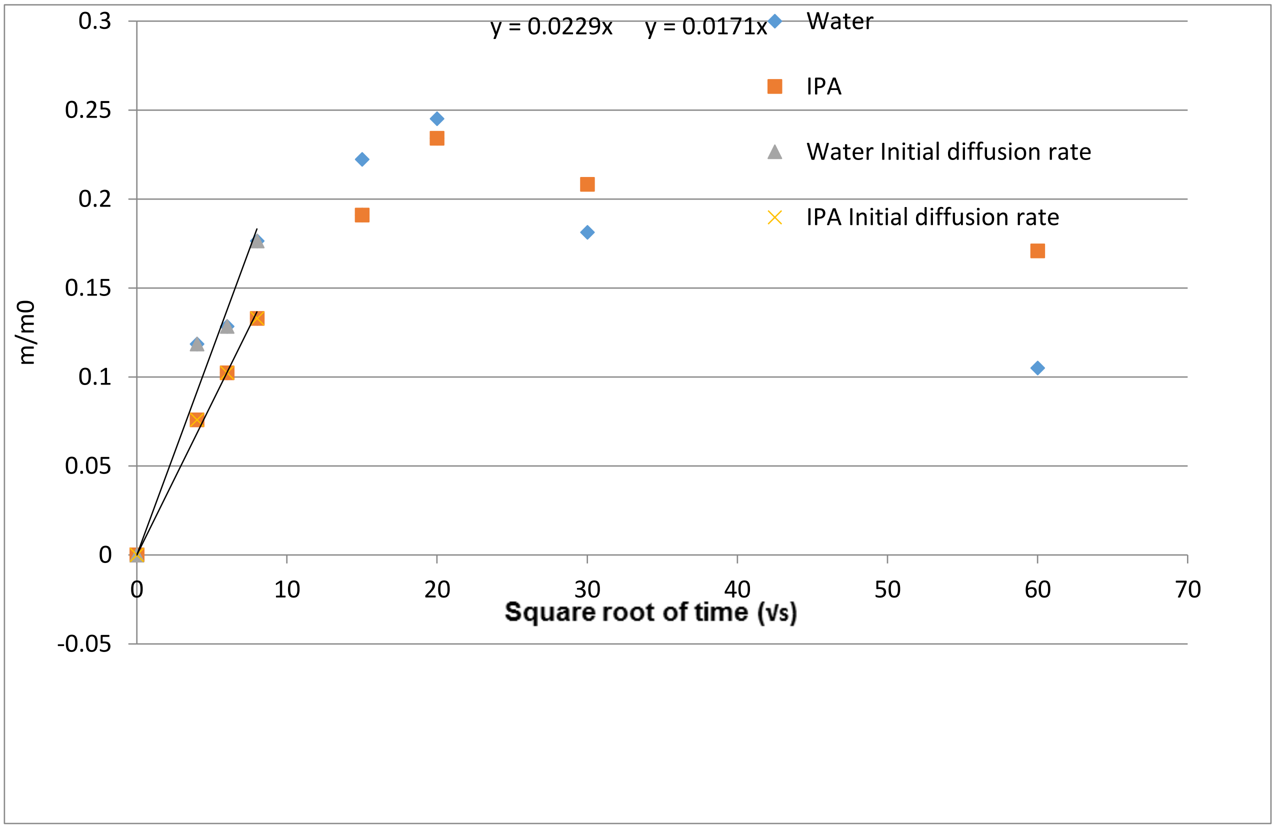
Appendix A figure 13: Diffusion rate BmimCl 13% Cellulose 25:75 DMSO:IL



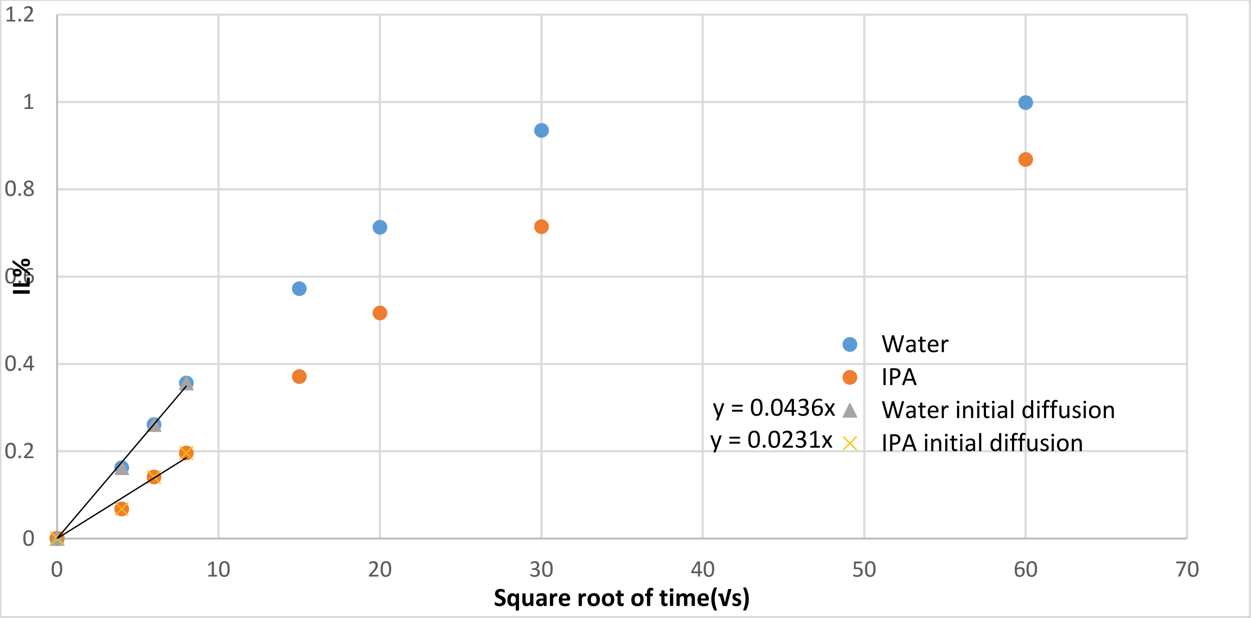
Appendix A Figure 14: Diffusion rate for BmimCl 13% Cellulose 25:75 DMSO:IL



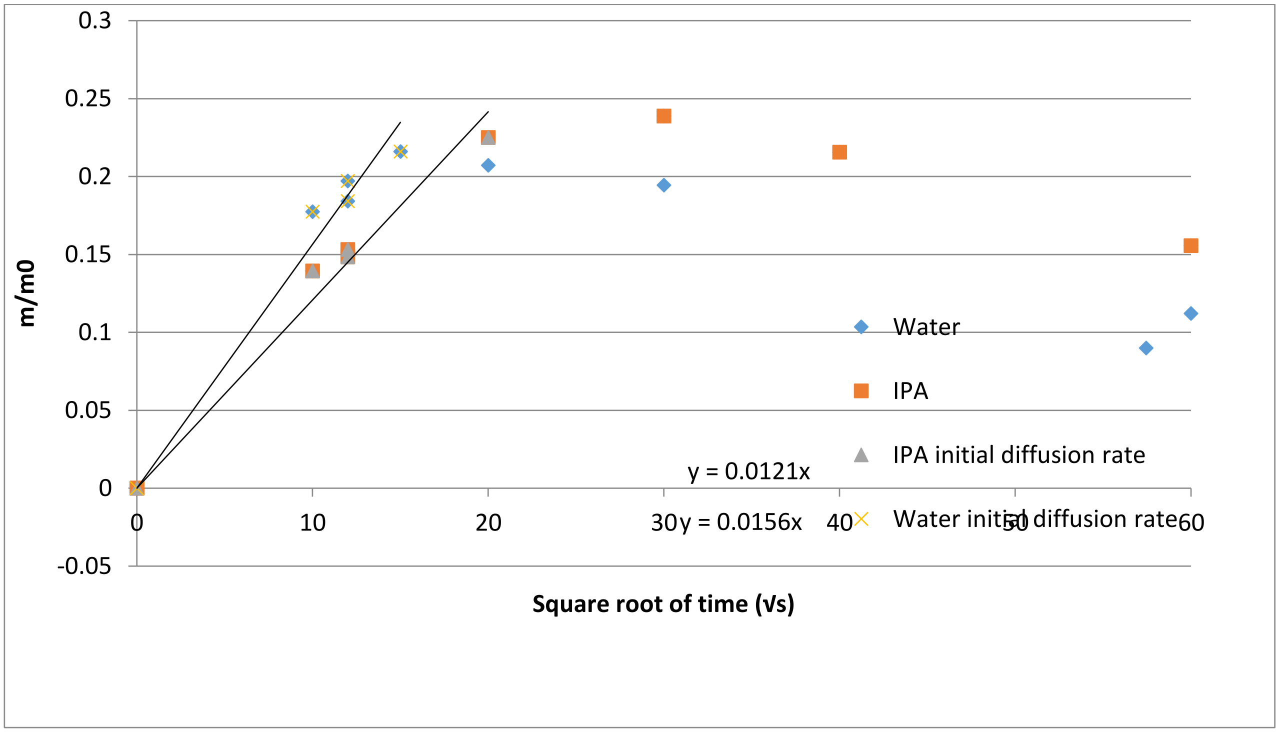
Appendix A figure 15: Diffusion rate results for TMGHOAc 8% Cellulose 10:90 DMSO:IL



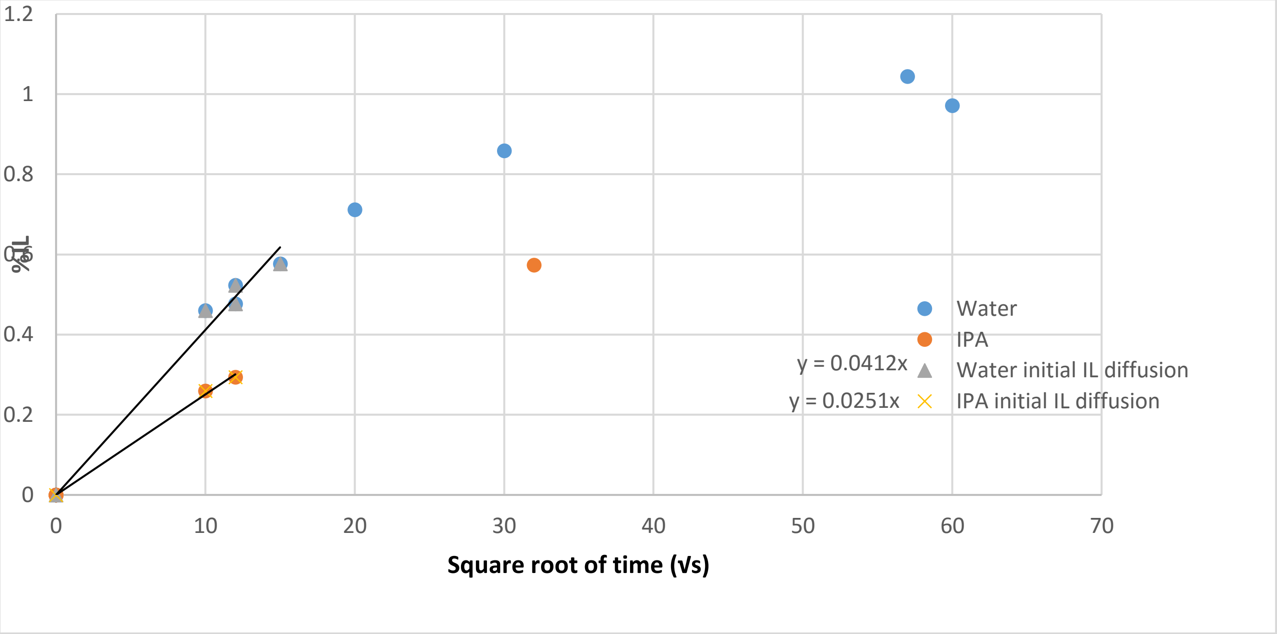
Appendix A figure 16: Diffusion rate results for TMGHOAc 8% cellulose 10:90 DMSO:IL IL diffusion



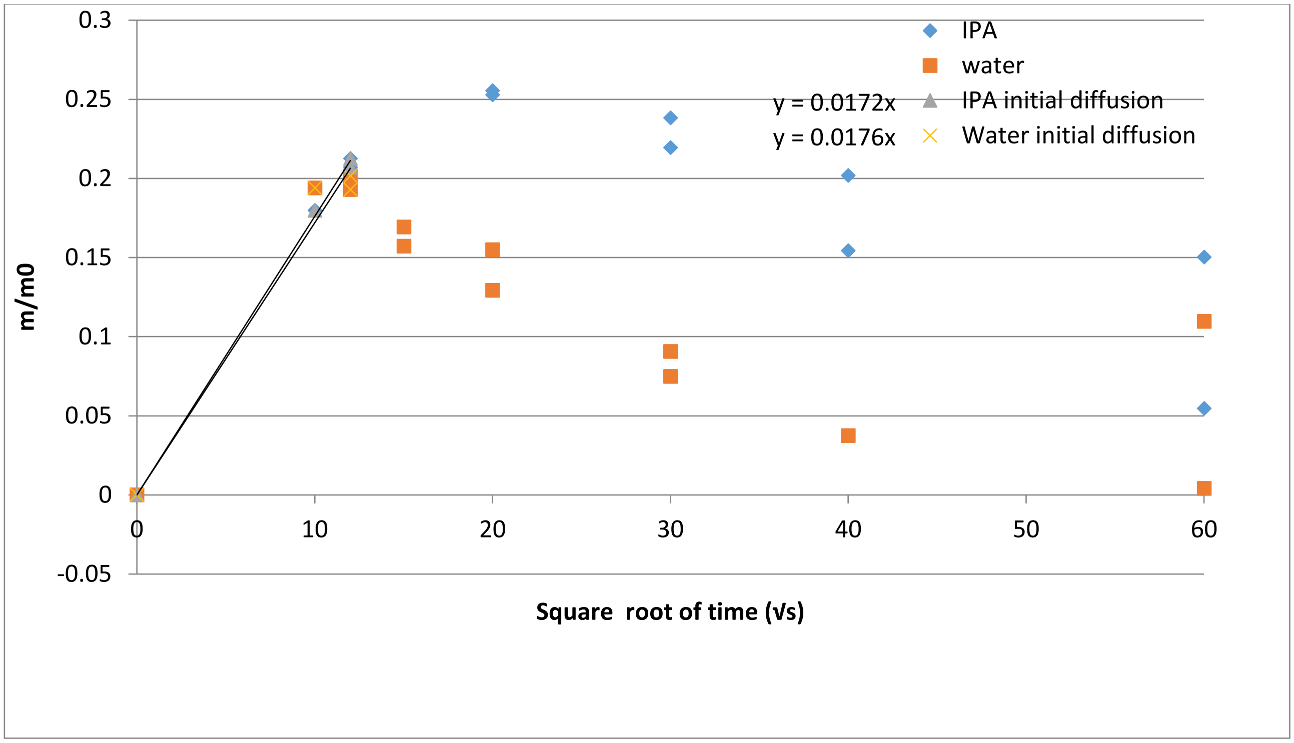
Appendix A figure 17: Diffusion rate results for TMGHOAc 13% cellulose 15:85 DMSO:IL



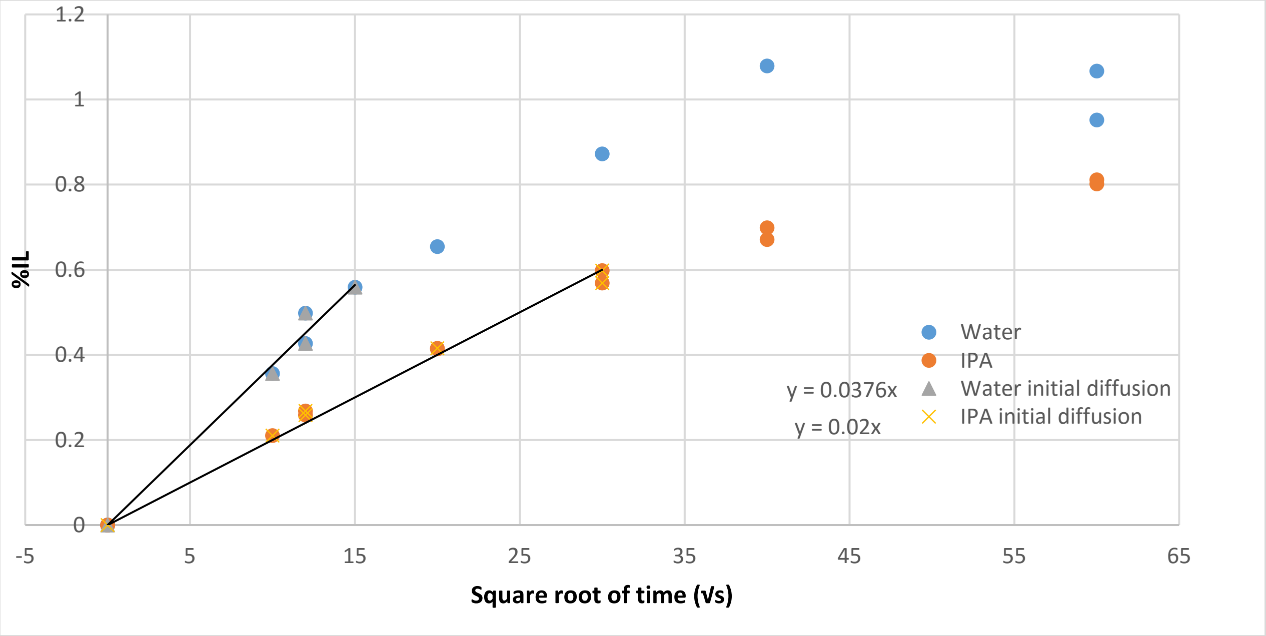
Appendix A figure 18 Diffusion rate results TMGHOAc 13% cellulose 15:85 DMSO:IL



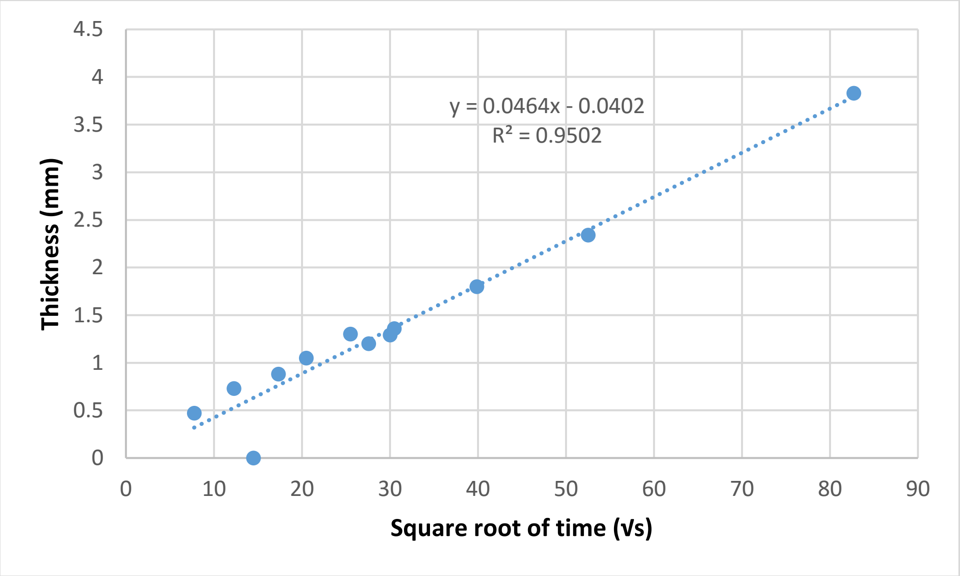
Appendix A figure 19: Diffusion rate results TMGHOAc 8% cellulose 15:85 DMSO:IL



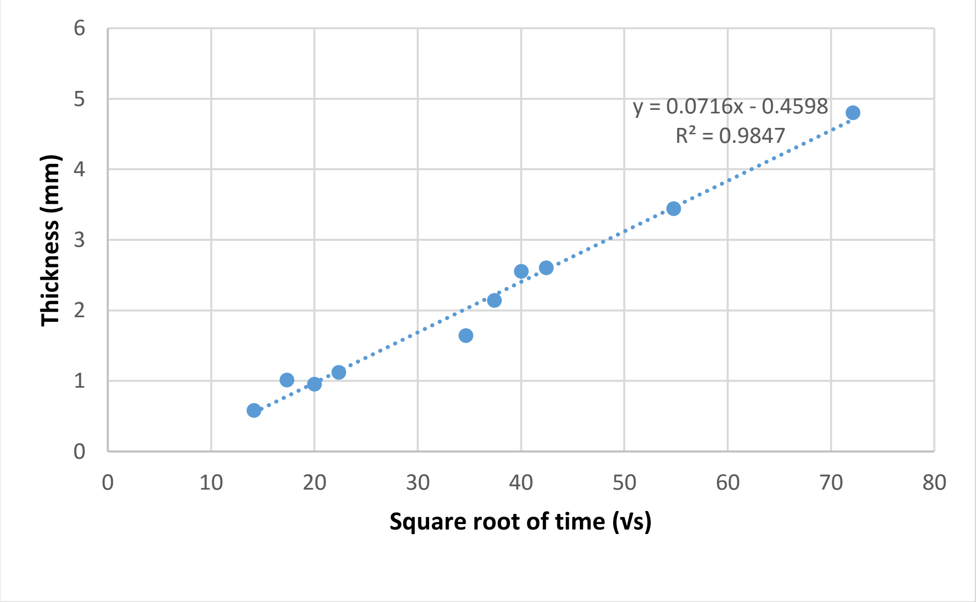
Appendix A figure 20: Diffusion rate results TMGHOAc 8% cellulose 15:85 DMSO:IL



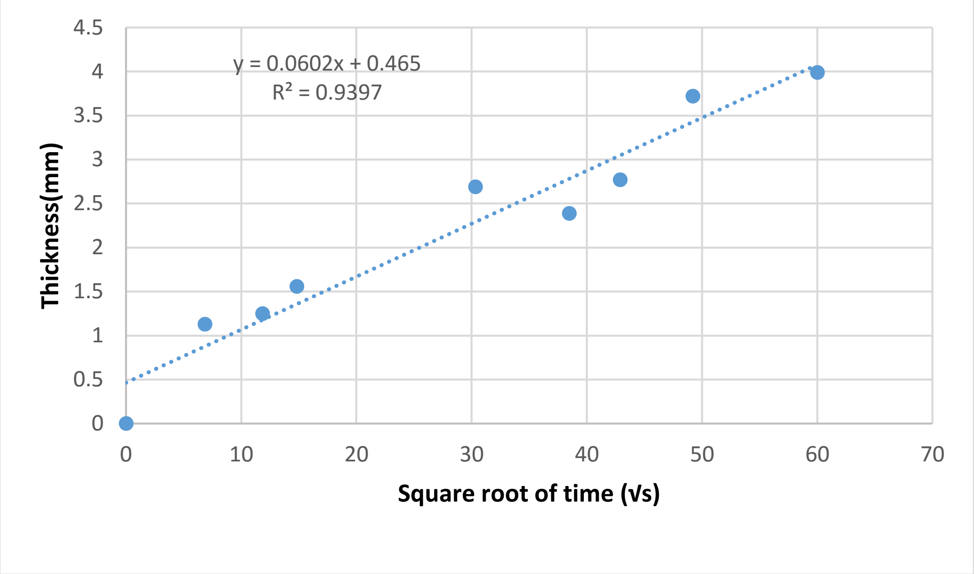
Appendix A figure 21: Coagulation depth results for EmimAc 8% Cellulose solution



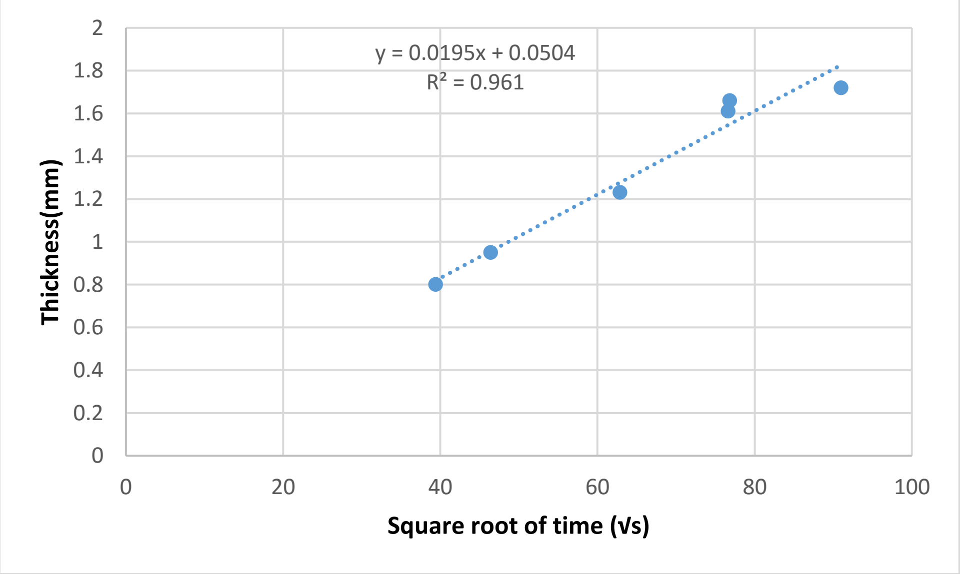
Appendix A figure 22: Coagulation depth results for BmimCl 8% Cellulose solution



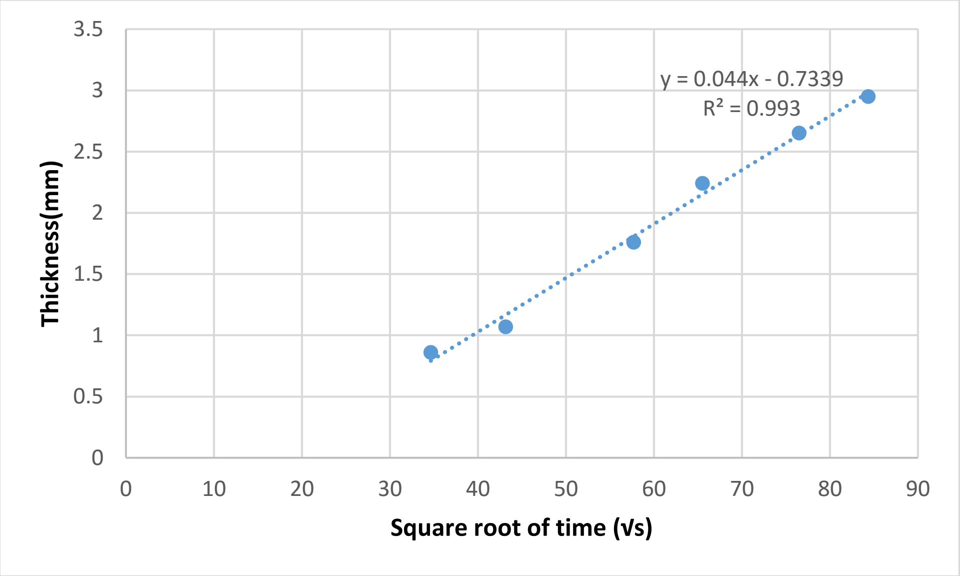
Appendix A figure 23: Coagulation depth results for TMGHOAc 8% Cellulose 90:10 IL:DMSO



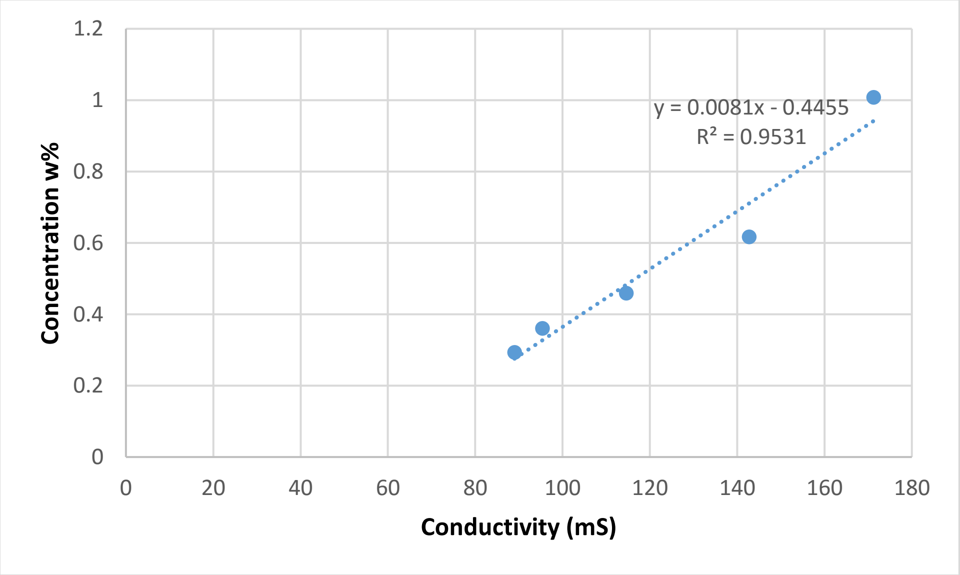
Appendix A figure 24: Coagulation depth results for TMGHOAc 8% Cellulose 85:15 IL:DMSO



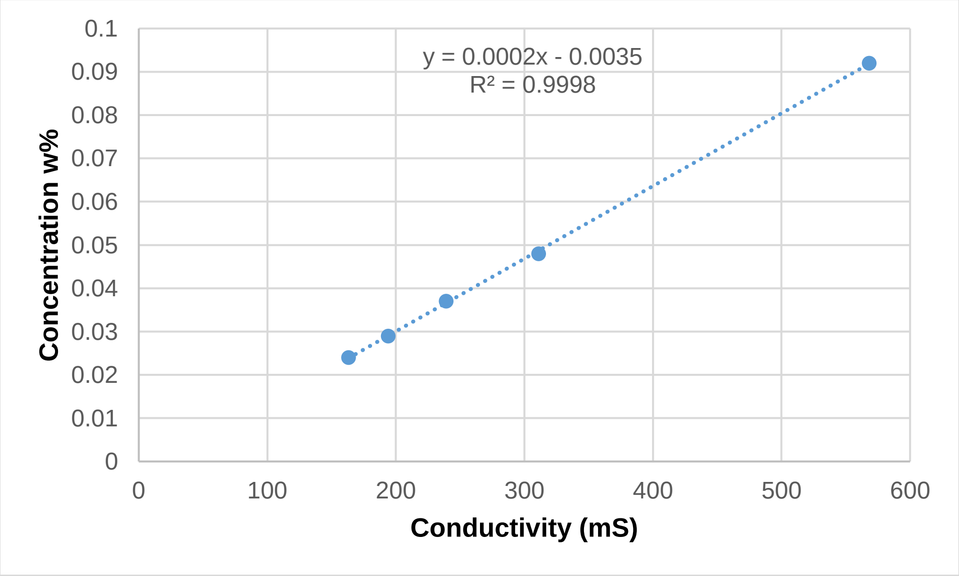
Appendix A figure 25: Coagulation depth results TMGHOAc 13% Cellulose 85:15 IL:DMSO



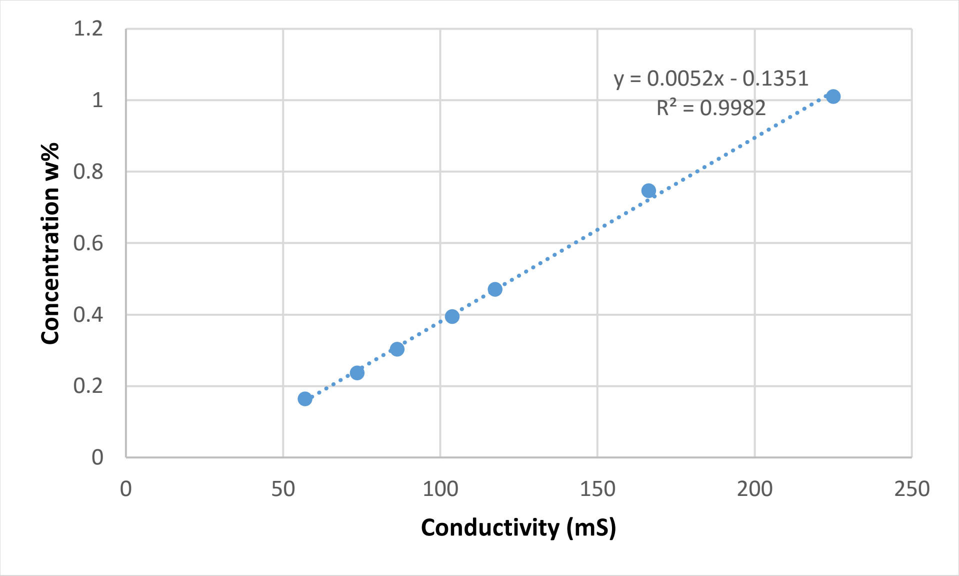
Appendix A figure 26: EmimAc concentration-conductivity relationship for EmimAc in isopropanol



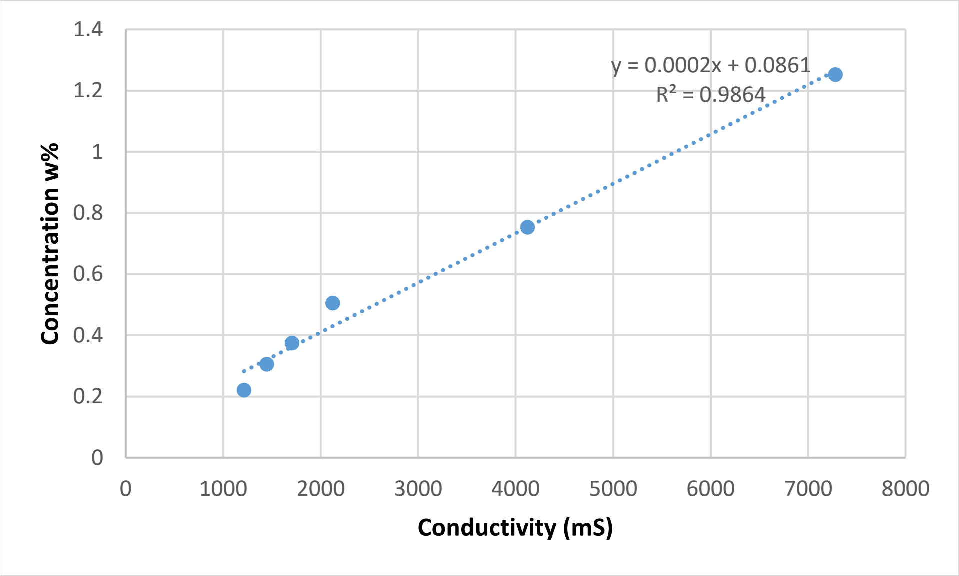
Appendix A figure 27: BmimCl concentration-conductivity relationship for BmimCl in water



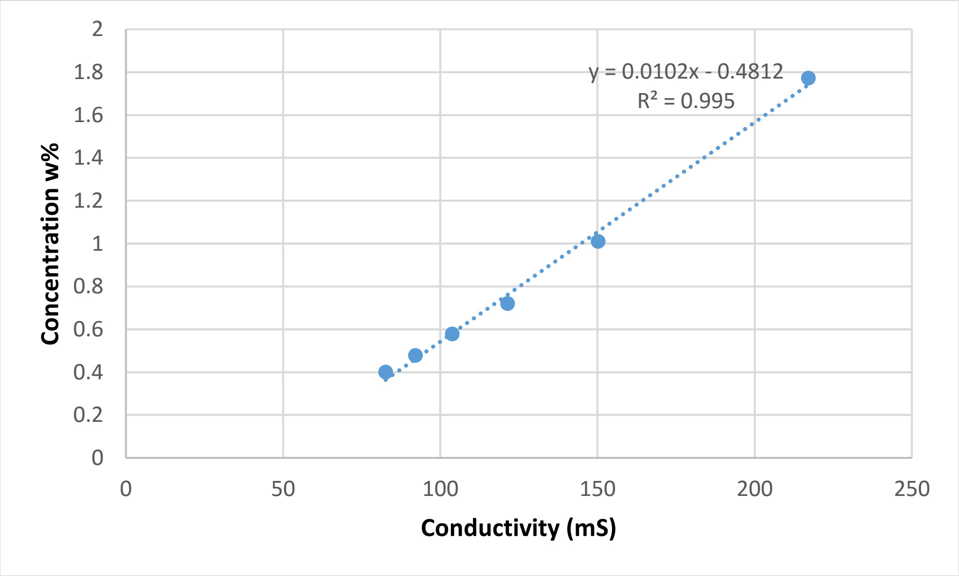
Appendix A figure 28: BmimCl concentration-conductivity relationship for BmimCl in Isopropanol



Appendix A figure 29: TMGHOAc concentration-conductivity relationship for TMGHOAc in water



Appendix A figure 30: TMGHOAC concentration-conductivity relationship for TMGHOAc in Isopropanol



Appendix B: Extended experimental section

Preparation of EmimAc cellulose solution:

The preparation of the ethyl-methyl imidazolium acetate cellulose solution was done by mixing the components and then stirring the solution in an open top syringe using a drill. The syringe is mounted into a structure that holds the syringe in place and minimizes air supply. The mixing takes place during two hours after which the solution is centrifuged to remove air bubbles. The two solutions that are prepared contain 13% and 8% cellulose respectively, both containing a 99:1 weight ratio between the ionic liquid and the DMSO.

Appendix B Table 1: EmimAc solution compositions

Solution	IL	MCC	DMSO
13%	17.325	2.745	0.175
8%	18.388	1.670	0.186

Preparation of BmimCl cellulose solution:

The butyl-methyl imidazolium chloride cellulose solution was prepared by first dissolving the ionic liquid in a NaOH water solution with pH 10 as it is a solid at room temperature. The Ionic liquid has 5w% water after being dissolved. The components of the different solutions were then mixed in the same way as with the EmimAc solution. After the mixing state the solution is spread onto a sheet and placed in a vacuum oven until the water has been evaporated. The evaporation of the water is observed by using a microscope to find if the cellulose has been completely dissolved as even low water concentrations would hinder dissolution of the cellulose. The 75:25 IL:DMSO solution contained enough DMSO to dissolve the ionic liquid without the use of water.

Appendix B Table 2: BmimCl solution compositions

Solution	m_{BmimCl}(g)	m_{mcc}(g)	m_{DMSO}(g)
13%C 99:1	20.877 (5% water)	3.166	0.2167
8%C 99:1	22.254 (5% water)	1.919	0.2446
13%C 75:25	16.657	3.258	5.517

Preparation of [TMGH][OAc] ionic liquid:

Appendix B Table 3: Molar mass and density for the components used in the TMGHOAc synthesis

Compound	**Molar mass[g/mol]**	**Density[g/l]**
TMG	**115.18**	**918**
HOAc	**60.05**	**1050**
Acetone	**58.08**	**791**

In the synthesis of the tetra-methyl guanidine aceteate ionic liquid the tetra-methyl guanidine was titrated with the acetic acid using an E-flask and a syringe. The TMG which is a super base, i.e. an extremely strong base, is placed in the syringe while the weak acetic acid is placed in the E flask. The first trial is done at a small scale and the HOAc is diluted in acetone with a 1:1 volume ratio to reduce the temperature increase of the reaction by vaporization. The TMG is kept undiluted.

An initial test in order to evaluate the setup was performed using 2.611g, 2.8 ml, Acetic acid diluted in acetone, 2.767g. The E-flask with the acetic acid and acetone solution is placed in an ice bath. The TMG is weighed up to some excess at 6.623 g (0.057 moles) and is slowly added to the acetic acid/acetone solution. There is a relatively sharp temperature increase but it is manageable with the ice bath and the acetone and never exceeds 70 degrees Celsius. The TMG is slowly added and then the reaction is allowed to take place, there is no specific time taken during the addition but it is done so that the temperature increase is kept relatively low. When all the TMG has been added and the temperature goes back to normal the E-flask is placed on the heating plate in order to vaporize the excessive TMG base and the remaining acetone.

Appendix B Table 4: Composition of the first TMGHOAc synthesis.

Component	Amount(g)	Volume(ml)
TMG	6.623	7.2147
HOAc	2.611	2.8
Acetone	2.767	3.5

As the flask is being heated a rubber with a needle for the gasses to escape through is placed on the top of the E-flask. Unfortunately the acetone managed to erode the rubber lid and contaminate the sample. After the heating the sample remained as a solid with what appeared to be fairly large crystals. The sample was placed in a vacuum oven where it was melted and further cleaned from remaining acetone and TMG. The TMG IL seems to have a high melting point and also seems to revert back to its solid state fairly quickly after it has been removed from the oven.

Second synthesis of [TMGH][OAc] IL

The second synthesis of the [TMGH][OAc] ionic liquid was performed in the same manner as the first time but at a larger scale as 50 g of the liquid was the aim. The volume ratio between HOAc and Acetone was around 1:1 as in the first attempt but ended up being slightly higher for the acetone. The temperature increase is much lower than it was during the first attempt and the product is not a solid as was the case in the first synthesis. The solution is heated on the heating plate to remove acetone and excess TMG. The pH is tested to 8.36 immediately after the reaction and 8.06 after the solution has been heated on the heating plate. The heating plate does not seem to be a very effective way of distilling the unwanted components from the solution as there seems to be a lot of condensation at the top of the E-flask where the distilled fraction seem to return to the solution. The solution is put inside of the vacuum oven set at a temperature of 100 degrees Celsius. The remaining liquid is hard to drive off and after several hours the solution is still a liquid.

Appendix B Table 5: Composition of the second TMGHOAc synthesis

Component	Mass (g)	Volume (ml)
TMG	33.857	39
Acetic acid	17.384	17

Acetone	14.6	19

Heating test

By heating the sample it can be determined that the solution is 95% dry material. The test is done fairly quickly and without liquefying the sample. Upon cooling the rest of the IL also solidified to a structure similar to the first synthesis test and when two more samples are heated it can be determined that the solid content after one day standing in a sealed E-flask to be 75% after 1.5 hours and 63% after 2 hours suggesting that the IL might have vaporized and both of the samples had completely liquefied.

Conductivity test

A new test with lower temperature around 65 degrees Celsius is being administered for several hours. The IL stays in its solid form so it can be assumed that none of the IL has been evaporated. The solid content of this sample was determined to be 90%. Comparing the conductivities of the dry and undried IL it was found that the dried ionic liquid had a higher conductivity than the undried one. The difference in conductivity between the dried and undried ionic liquid was shown to be roughly 4%, which is unexpected since it would have been suspected that the undried IL could possibly contain some remaining TMG base or acetic acid that might increase the conductivity but that was not the case. This suggests that there is some remaining acetone left in the undried IL. A pH test is performed in order to further try to understand the properties of the ionic liquid and how to determine its contents.

Appendix B Table 6: Conductivity test results showing the difference between dried and undried TMGHOAc related to the concentration

Sample	Concentration (W%)	Conductivity (S)	(CondUndried/ConcUndried)/(CondDried/ConcDried)
Dried 1	0.9992	3210	0.956
Undried 1	0.9963	3060	
Dried 2	0.7756	2550	0.961
Undried 2	0.7757	2450	
Dried 3	0.5540	1843	0.961
Undried 3	0.5482	1752	

A pH test is performed in order to further try to understand the properties of the ionic liquid and how to determine its contents. A new sample is dried and roughly 88% of the original IL remains. The pH for the dried samples are found to be significantly lower in pH than the undried sample suggesting that their might be some residual TMG left in the sample. The pH is measured by dissolving the IL in water and using a pH-meter.

Appendix B Table 7: pH tests comparing the dried and undried TMGHOAc related to the concentration of TMGHOAc

Sample	Concentration (w%)	pH	(pH1/Conc1)/(pH2/Conc2)
Dried1	0.6298	5.58	0.887
Undried1	0.6297	6.29	
Dried2	0.3277	5.56	0.843

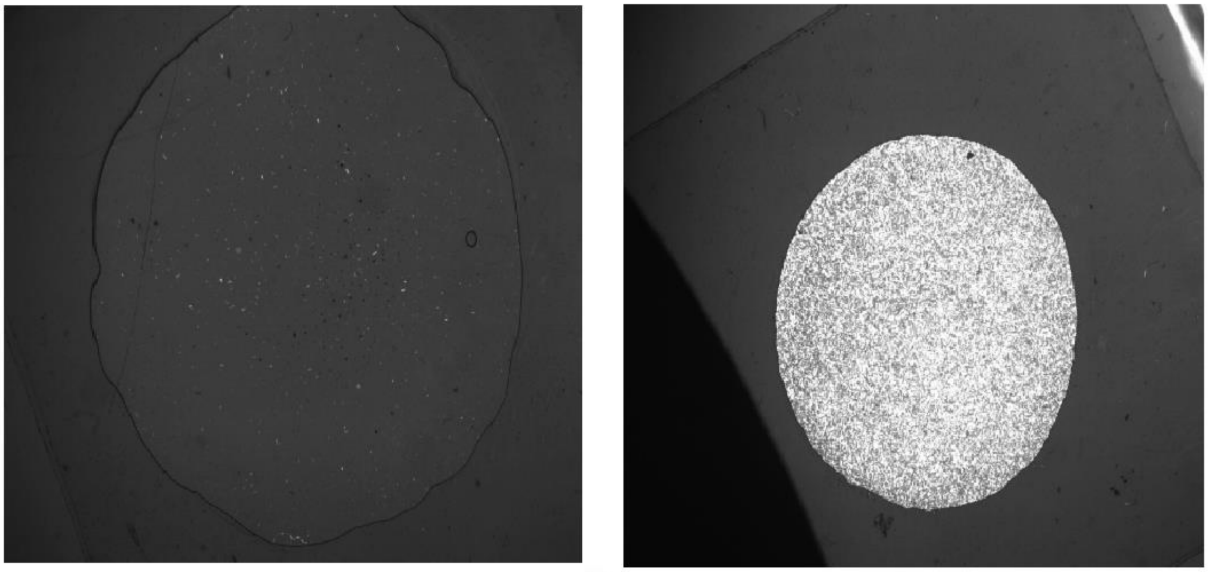
Undried2	0.3136	6.31	

These results seem to contradict each other since the conductivity test seem to suggest that only acetone has evaporated while the pH test seems to suggest that TMG has evaporated.

pH titration test:

A titration is being performed with the acetic acid and TMG in order to determine the pH at the equilibrium of the ionic liquid. A volume of 500 ml 0.1 M acetic acid solution is being titrated with a 0.5M TMG solution. It can be determined that the equivalence point is at a pH of 8.795. This result points to the fact that the vaporized fraction in the dried samples are part of the ionic liquid. The TMG base has a higher vapor pressure than the acetic acid which would lead to it being the first component to vaporize. The undried ionic liquid has a pH around 6.3 which is still too low when compared to the titration curve. This suggests that there is still some un-reacted acid left in the sample. It can be determined that it is important to react all of the acid in the sample and to have the TMG in excess to minimize the residual acid since it would seem that the residual acid is not easily removed by vaporization. A pH test on the first batch of [TMGH][OAc] ionic liquid reveals that this one had a pH of 5. 46, much lower than the pH of the equivalence point revealed in the titration test.

In order to try to correct the pH dissolution tests were done where extra TMG base was added to the solution. A test with ethanol as the co-solvent was performed where 1.8827g IL, 0.5304g EtOH, 0.1028g TMG and 0.250g Cellulose. The pH of this solution, when dissolved in water was determined to be 10.16 giving a pH value that is within the interval for the equivalence point. The solution was mixed and heated in order for the ethanol to dissolve and to create a cellulose IL solution. The solutions greatly resemble the previous cellulose solutions but when examined under the microscope it can be seen that the cellulose has not been dissolved. Tests were performed on an IPA solution and a 50:50 DMSO solution neither of which were able to dissolve the cellulose completely, although the DMSO solution showed much more promise than the IPA solution and had almost fully dissolved the cellulose.

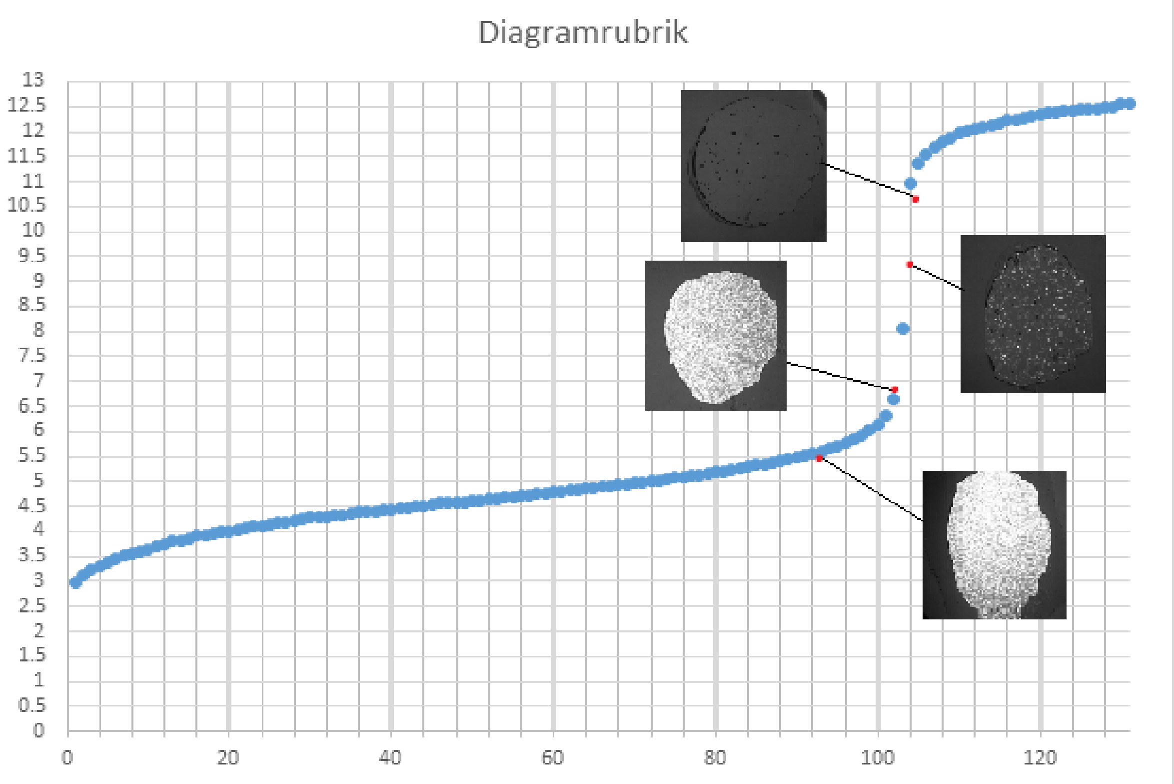


Appendix B Figure 1: The 50:50 IL:DMSO solution on the left side and the IPA solution on the right side.

In order to determine if and how the pH affect the dissolution of the cellulose a test were set up where the pH of the solution was altered. A base cellulose solution with 9 w% cellulose and pH 5.89 was prepared. The cellulose solution was separated into different samples and different amounts of TMG was added to the respective samples (see table 9). As can be seen in the picture below it was discovered that the pH of the solution determines if the cellulose can be dissolved or not and it was shown that while a low pH meaning an excess in acid cannot dissolve the cellulose, an excess in base is capable of dissolving the cellulose. The pH is measured by dissolving the IL in water and using a pH-meter.

Appendix B Table 8: pH dissolution series sample compositions and dissolution ability

Sample	Solution (g)	TMG (g)	pH	Dissolution
1	0.6466	0.0320	6.80	No
2	0.7824	0.0570	9.21	Partial
3	1.0689	0.2343	10.78	Yes
4	0.7190	0.2895	10.89	Yes
5	0.5041	0.3449	11.03	Yes
6	0.6348	0.6993	11.50	Yes



Appendix B Figure 2: The pH-titration curve with added images showing the cellulose dissolution at pH: 5.89, 6.80, 9.21 and 10.78.

Synthesis 3:

The next synthesis is done once again trying to produce 50 g of IL. This time a greater excess of TMG is being used, 1:1.5 molar equivalence between the HOAc and TMG. Using excessive amount of TMG and letting the reaction be carried out over a longer time should hopefully create a better ionic liquid without evaporating enough reactant base to leave unreacted acid in the solution than during previous synthesizes.

Appendix B Table 9: Composition of the third TMGHOAc synthesis

Component	Mass(g)	Moles
TMG	51.275	0.445
HOAc	17.152	0.286
Acetone	12.699	0.219

Dissolution test

A dissolution test with only heat as a dissolution medium was performed. First the IL was weighed to 1.2114g, it was then heated until it was completely liquefied and weighed again to 1.0523g. This means that 0.1519 g of the original solution has evaporated. Afterwards 0.114g of cellulose was added to the solution. The solution solidifies quickly after it has been removed from the heating but the cellulose can be added to the solid anyway. Once the cellulose has been added the solution is heated once again under stirring. The dissolution of the cellulose happens relatively quickly and takes place in a matter of minutes. This seems to be the easiest way to achieve effective dissolution of the cellulose.

Cellulose dissolution at a larger scale:

The dissolution of solutions in the 20g range needs a different approach than the small scale test solution that has been made up to this point. In this larger scale preparation the components of the solution are first weighed up in a syringe. The mixture is then placed in a metal container with a heating band around it. The drill that was previously used in the other IL is stuck into the mixture and the top is sealed off with a plastic lid to prevent uptake of moisture from the atmosphere. The pH of the ionic liquid is adjusted to a level beneath the equivalence point (5-6) in order to make all of the solutions equivalent since a higher pH would mean that there is a higher amount of unreacted base in the solution. The unreacted base is very volatile and might vaporize during the heating of the sample leading to there being different amounts of ionic liquid in the samples, making the later tests inconsistent. The lower pH will lead to the ionic liquid not being completely dissolved but as has been shown earlier, the pH can be adjusted subsequently to achieve a good dissolution. The amount of base needed to adjust the pH to the desired level is calculated using the titration curve and this additional base is taken into account when preparing the solution and is considered as part of the IL.

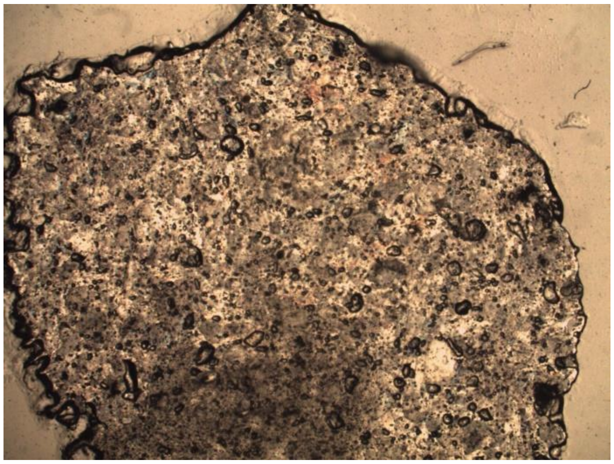
In the first attempt at large scale dissolution the following amounts of the different components are used:

Appendix B Table 10: Components of the first TMGHOAc solution with 13w% cellulose and 99:1 IL:DMSO ratio

Component	Amount (g)
IL	15.917

MCC	2.606
DMSO	0.182
TMG	1.308

The first attempt is a failure and the cellulose seems to be burned to a crisp. This result might be due to poor mixing and too rapid heating of the solution. The IL is solid when they are placed in the metal container and the cellulose and IL is because of this very segregated until the IL starts to liquefy. Another problem is that the container is too large for the drill leading to some dead space where the solution is not affected by the mixing. A solution to this might be to premix the components using the drill directly into the syringe and to try to press the mixture down into the container minimizing the amount that might get stuck on the walls of the container.



Appendix B Figure 11: The unsuccessful attempt at cellulose dissolution in [TMGH][OAc]

The second attempt is started by first putting the IL in the vacuum oven at 70 degrees Celsius to remove any remaining acetone and some of the excess base. The IL is then treated to reduce the pH which was 12.93 at the start and it is then treated with 2.58g HOAc which reduces the pH to 5.66. The following components are mixed:

Appendix B Table 11: Components of the second TMGHOAc solution with 13w% cellulose and 99:1 IL:DMSO ratio.

Component	Amount (g)
IL	14.515
MCC	2.598
DMSO	0.184
TMG	2.749

All of the components with the exception of TMG are premixed before being put into the metal container and the mix is then heated during stirring. The heating does not exceed 75 degrees Celsius and samples for the video microscope is being taken in conjuncture with the mixing. All of the sample shows that the cellulose has not been dissolved and that the mixture appears more as a sludge than as a regular cellulose solution. This is not unexpected since the cellulose were not supposed to dissolve at this low a pH and speaks for the previous result that pH greatly affects the ILs dissolution capabilities. 7 weight percent of losses are calculated leading to the amount of TMG being reduced from 2.749g to 2.562g. The TMG is added but there seem to be no real dissolution this time either when the sample is examined in the microscope.

Two new tests are performed, one where the IL, DMSO and cellulose is homogenized using the drill and then placed inside of the oven to melt the IL and create a cellulose solution. In the other method the IL is melted in the oven alone and the cellulose is added to the melted IL along with the DMSO and subsequently the solution is mixed using the drill.

Appendix B Table 12: Components of the third TMGHOAc solution with 13w% cellulose and 99:1 IL:DMSO ratio

Component	Amount (g)
IL	7.853
MCC	1.306
DMSO	0.091
TMG	1.139

Appendix B Table 13: Components of the third TMGHOAc solution with 13w% cellulose and 99:1 IL:DMSO ratio without added TMG.

Component	Amount (g)
IL	7.846
MCC	1.302
DMSO	0.087
TMG	-

The tests result in the same way as previously with a hard sludge like material. The two samples are heated at 120 degrees until they appear liquefied and a clear distinction can be seen between the sample with the added TMG and the sample without the added TMG. The sample with the added TMG appears as one of the previous successful cellulose solutions while the one without the added base quickly reverts to its gel like state. The pH for the samples are measured to 9.9 for the one with the added base and 6.6 for the one without the added base. However as the samples are kept overnight the sample with the added base also reverts back to its gel like state. The samples are heated once again at 120 degrees Celsius and once again return to their liquid states. The solution state seem to be highly temperature dependent and goes back to its solid state quickly after the temperature is lowered

A new batch of [TMGH][OAc] is prepared this time with the following components:

Appendix B Table 14: Components of the fourth TMGHOAc synthesis

Component	Amount(g)
TMG	38.51
HOAc	17.14

The base is added in excess to the acetic acid by 1:1.7 molar equivalence. The acetone is neglected this time since the evaporation of acetone seems to be a bigger problem than the initial temperature increase caused by the reaction.

Because of the difficulty to create a solution that is usable in the tests a DMSO test is performed.

Appendix B Table 15: DMSO solubility test

Sample	IL(g)	DMSO(g)	DMSO(%)	Dissolution
1	1.9642	0.064	3.15	No
2	2.1676	0.084	3.73	Yes
3	2.0074	0.106	5.01	Yes

The test shows that the 3.73w% and the 5.01w% DMSO solutions remain as liquids after cooling.

A new dissolution is done, this time with 8w% cellulose and without lowering the pH of the ionic liquid. The following components are used:

Appendix B Table 16: Components of the first TMGHOAc solution with 8w% cellulose and 99:1 IL:DMSO ratio.

Component	Amount(g)
IL	9.122
MCC	0.802
DMSO	0.093

The components are placed in the open syringe and then the mixture is mixed using the drill. After the mixture has been homogenized the mixture is put in the oven at 120 degrees Celsius. The dissolution seem to have worked but there seems to be damage on the cellulose in the solution due to the high temperature of the heating stage as the solution is darker and has a more red color which is believed to be caused by saccharification of the cellulose chain.

A dissolution with 13% cellulose and 3% DMSO is performed as the DMSO helps the IL remain a liquid without reverting back to its solid state. The dissolution is successful but the high temperature once again causes sacharification of the cellulose which is evident by its reddish color.

Appendix B Table 17: Components of the first TMGHOAc solution with 13w% cellulose and 97:3 IL:DMSO ratio.

Component	Amount(g)
IL	8.441
Cellulose	1.299
DMSO	0.281

A new dissolution is prepared this time with a larger volume and the solution is heated to 80 degrees Celsius. 4w% DMSO is used.

Appendix B Table 18: Components of the first TMGHOAc solution with 13w% cellulose and 96:4 IL:DMSO ratio.

Component	Amount(g)
IL	12.694
Cellulose	1.953
DMSO	0.557

The gel formation is once again a big problem and the dissolution does not work. Another dissolution with only 8 w% cellulose is carried out with 5w% DMSO. But gel formation sets in once again.

Appendix B Table 19: Components of the first TMGHOAc solution with 8w% cellulose and 95:5 IL:DMSO ratio.

Component	Amount(g)
IL	5.130
DMSO	0.302
MCC	0.472

The gel formation in the samples with higher DMSO and lower cellulose is slow and takes several hours even if they are refrigerated.

A new solution with 10 w% DMSO is prepared with 8w% cellulose. This solution remains a liquid without going back to its gel state and has a seemingly low viscosity. But again once the solution is moved from the centrifuge tube the solution is turned into a gel. This is believed to be caused by poor mixing as the equipment necessary was not available at the time.

Appendix B Table 20: Components of the first TMGHOAc solution with 8w% cellulose and 90:10 IL:DMSO ratio.

Component	Amount(g)
IL	6.696g
DMSO	0.808g
MCC	0.658g

A bigger batch of 10 w% DMSO must be produced and for this more ionic liquid is required. 60g of [TMGH][OAc] is synthesized. The pH of the ionic liquid is measured to be 12.64.

Appendix B Table 21: Components of the fifth TMGHOAc synthesis.

Component	Amount(g)
TMG	46.154
HOAc	20.571

The new IL is used in a new dissolution of cellulose with 8w% cellulose with 10:90 ratio between the DMSO and the IL. The solution remains a liquid and can be analyzed.

Appendix B Table 22: Components of the first TMGHOAc solution with 8w% cellulose and 90:10 IL:DMSO ratio.

Component	Amount(g)
IL	12.437
MCC	1.205
DMSO	1.387