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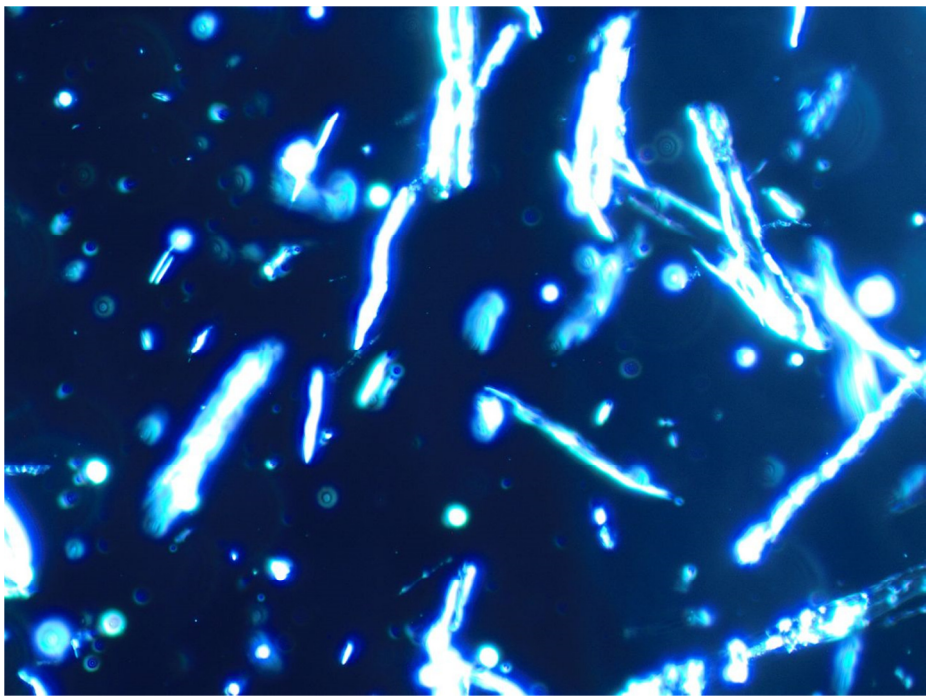

Dissolution of pulp using acidic solutions

Master of Science Thesis

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The cover image represents a light microscopy picture of cellulose suspended in a solvent system consisting of sulphuric acid, glycerol, and water.

ABSTRACT

There is an increasing demand on finding novel environmentally friendly materials for usage in the textile industry since today the largest fibre fraction of resources employed need extensive fresh water irrigation and pesticide spraying during culturing. A promising alternative may be wood based cellulose fibres; however there are many challenges and barriers that need to be overcome for it to be used as intended. These difficulties mainly derive from the strong intra- and inter-molecular interactions present within the cellulose structure that need to be broken for fibre reshaping and regeneration into textile. The cellulose structure can first be opened up using for example different grinding techniques that allow easier access for solvents to penetrate into the cellulose network, and finally dissolves it.

During this project, the solvent system of mainly sulphuric acid and glycerol was employed to dissolve Buckeye V67 (batch 5959A) pulp, with the aim of textile fibre regeneration. Sometimes distilled water was added additionally into the system to aid the hydrolysis of the pulp exerted by the acid. The objective of the study was to establish the percentages of acid, glycerol, and water that would result in adequate cellulose dissolution. Before dissolution started, the pulp had been dry milled to increase the accessibility for the reactants. The dissolution of pulp was performed at different temperatures and using different temperature controls, which gave information about the great temperature sensitivity of the system. The obtained solutions were evaluated based on visual parameters such as colour, stability, viscosity, and transparency. The most promising and optimized system was made up by 4.6 % cellulose, 66 % sulphuric acid, 26 % glycerol, and 3.4 % water. Rheology measurements were thereafter performed to give insight to the flow behaviour of the optimized dissolution. Based on these measurements the dissolution was promising for further reshaping. However, the cellulose could not be regenerated. Diffusion nuclear magnetic resonance spectroscopy was employed to provide knowledge about the mechanisms of the dissolution process. From these trials it could be suspected that the acid, explaining the challenges of regeneration, had degraded the cellulose too aggressively; also there was maybe an undesirable reaction occurring between the acid and the glycerol. Based on the difficulties trying to dissolve the cellulose, this particular solvent system was evaluated to be too sensitive and could therefore not be used as intended for industrial applications.

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First and foremost, I would like to thank my supervisor Alberta Mok for all help and assistance she has provided during my diploma work. The project would have been more challenging without her enlightening introduction and explanations to the science behind cellulose and cellulose dissolution. I would also like to thank Åsa Östlund at SP Sveriges Tekniska Forskningsinstitut for helping me performing diffusion NMR measurements and for providing knowledge and advice throughout the project, as well as Lars Nordstierna and Krister Holmberg within the division of Applied Chemistry for giving appreciated guidance and support.

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1. INTRODUCTION

In the current textile industry, there is an increasing demand on finding novel materials that can be used to create an environmentally friendly and sustainable production. Two of the negative effects that accompany the employment of the materials used today, *e.g.* cotton, are the need of fresh water irrigation (a scarce commodity in the areas where the cotton plants are grown) and the high frequency of pesticides and herbicides utilized during culturing (World Wildlife Fund, 2013).

A promising compound and material that may be employed for such purposes is cellulose pulp, a natural polymer with excellent biocompatibility. In addition to the environmental benefits of cellulose, the material is also considered to be relatively cheap and has the intended functionality. Unfortunately, the intra- and intermolecular interactions across the cellulose network make dissolving the cellulose difficult.

During this thesis work, the primary purpose was to study and evaluate the dissolution of cellulose in an acidic solvent system consisting of sulphuric acid, glycerol, and water. In such a system, the acid functions by hydrolysing the pulp, *i.e.* it breaks the strong interactions within the cellulose structure. The breakage needs to occur to a certain extent; too much degradation would result in too short chains, which are difficult to regenerate as textile fibres due to high solubility. Glycerol functions as a stabilizer and thereby prevents the hydrolysis somewhat and makes the reaction less aggressive. It is thought not to react with the cellulose and remain inert; a hypothesis that was tested during the project by diffusion NMR. Water is naturally present in the pulp as well as in the acid and glycerol to different extent depending on purity. It is sometimes added additionally to the system to assist the acid hydrolysis.

1.1 Purpose

The most effective and perhaps well-known solvent used for cellulose dissolution is ionic liquid for example 1-ethyl-3-methylimidazolium acetate. However due the high cost of ionic liquid other solvents are studied and in this project the bulk chemicals sulphuric acid, glycerol, and water were the ones chosen as solvent system components. This system has previously been established to possess promising dissolution properties.

Various reaction parameters influencing the result were intended to be optimized, including:

- Preparation of pulp prior to the dissolution trial
- Composition of solvents (*i.e.* ratio between acid, glycerol, and water)
- Reaction time
- Reaction temperature
- Cellulose concentration

The obtained dissolution was evaluated by investigating solubility, stability, and fibre regeneration. It was also intended to characterize the degree of polymerization (DP) of the regenerated fibre. The strategy was to understand the chemistry and the behaviour of this potential solvent system by optimizing the dissolution conditions followed by fundamental studies of the dissolution.

1.2 Methods and boundaries

The initial work started with an experimental design of the experiments planned to be performed to reach the goals and purpose listed previously. A determination of the appropriate approach to prepare the cellulose to have an adequate accessibility was made primarily since this would be a fundamental parameter. The two approaches tested were based on dry and wet milling respectively of the cellulose. Following, the ratio of solvent components was determined and the dissolution was evaluated. Light microscopy was employed to give insight to the solubility of the cellulose fibres. The flow behaviour of the dissolution was determined by rheological measurements in order to evaluate if there was a significant amount of un-dissolved cellulose present in the solution. NMR spectroscopy was utilized to provide a better understanding of the chemistry of the system. The NMR measurements were also performed to study the degree of polymerization by establishing the diffusion coefficient of the dissolved cellulose that correlates to the size of the polymer.

The optimization of solvent ratio was proven to be challenging and time consuming, therefore no other acidic solvent system was tested. The difficulties of finding a system that fulfilled all requirements adequately also affected the intended purpose to test the spinnability of spin dopes.

2. THEORIES

In this section, a theoretical introduction to the various parts of the project will be presented. The chapter will include a description of cellulose, its occurrence and structure, how it may be dissolved and the challenges related to the dissolving process. Also, the techniques and methods used for performance and analysis of the laboratory work will be described.

2.1 Cellulose occurrence in nature and purification

Cellulose is the most abundant polymer worldwide making it a highly attractable raw material for processes involved in several different industries and productions. It is found to various extents in the cell wall of lignocellulosic plants in which the percentage of cellulose depends on several factors, for example plant specie and maturity as well as the region and environment where the plant is grown. The cell wall gives the plant protection and mechanical strength, and besides cellulose it consists of lignins, hemicelluloses and other carbohydrates. In order for the cellulose fibres to be utilized for industrial applications in the correct and intended way, it needs to be isolated and purified from the matrix (Liu, C-F. et al., 2010).

There are different methods of purifying the cellulose, either through a mechanical or chemical process known as pulping. When using the mechanical approach, the wood is treated with steam followed by grinding and refinement to achieve cellulose separation. The chemical method involves thermodynamic treatment regimes and reactant utilization as well as mechanical refinement to achieve desired separation. These different procedures result in the production of pulp. To obtain cellulose suitable for further reshaping; requirements of a high content of cellulose and bleaching of the pulp chemically must be fulfilled.

2.2 Cellulose fibre structure

As stated previously, a challenge for utilization of cellulose is breaking the strong interactions within the molecule with the purpose of ultimate dissolving and reshaping. In this section, the molecular, the supramolecular and the morphological structure of cellulose will be concerned to describe these bonds and forces.

2.2.1 Molecular structure

At a molecular level, the cellulose molecule can be illustrated as in Figure 2.1 consisting of repeating units of *β*-(1,4)-D-glucopyranose making up the linear homopolysaccharide. The hydrogen bonding at this intramolecular level is believed to occur between O(3)H and cyclic (O) and between O(6)H and O(2)H (Dupont, A., 2003).

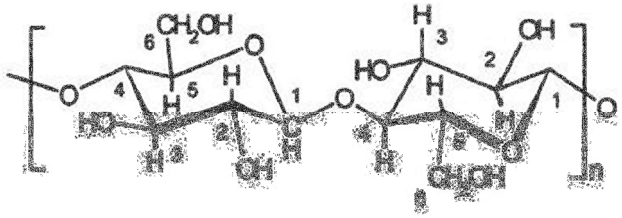

Figure 2.1: The repeating units of β-(1,4)-D-glucopyranose making up the cellulose molecule and holding it strongly together through hydrogen bonding (Dupont, A., 2003).

The molecular formula of one cellulose unit, or the anhydroglucose unit as it is also abbreviated, may be written as $C_6H_{10}O_5$ (Wang, Y., 2008). The number of units or the degree of polymerization of natural cellulose is approximately 10 000 and once processed and pulped, a mixture of chains having different lengths and polymerization is obtained. This phenomenon is known as polydispersity and depends both on the source of cellulose and the degradation mechanisms (Dupont, A., 2003).

A continuous chain of 20-30 cellulose units is sufficient to give the polymer its characteristics and special properties. One of the two chain ends of the cellulose molecule is the reducing end consisting of O(4)H, while the other end (the non-reducing) is made up by O(1)H. The native molecular structure may chemically be altered; during such process other functional groups might for example be introduced into the structure giving the cellulose altered properties (Rohrling, J. et al., 2002)

2.2.2 Supramolecular structure

At the supramolecular level, the intermolecular hydrogen bonds arise between hydroxyl groups of different cellulose molecules. These groups are oriented in a radial direction; the aliphatic hydrogen atoms of cellulose are on the contrary oriented in an axial manner. This structural orientation aid and ease the hydrogen bonding between chains, which tend to pack into parallel strands because of such bonds and additional van der Waals and dipole interactions. The cellulose strands together form ordered crystallites and between them there are disordered, non-crystalline polymer molecules linking the crystallites together giving rise to internal cohesion (Hearle, J.W.S., 1958, Dupont, A., 2003, Wang, Y., 2008). This attractive force helps to build up the cellulose network and can be seen in Figure 2.2.

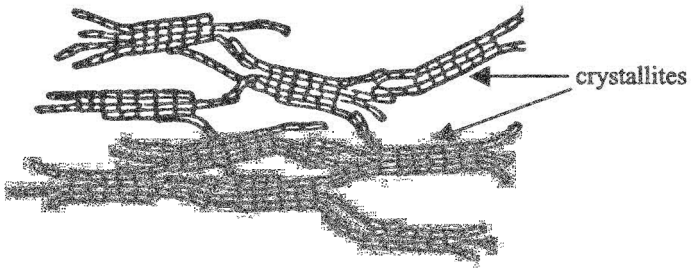

Figure 2.2: The supramolecular structure of cellulose consisting of ordered crystalline regions linked together by polymer molecules (Gardner, K.H. et al., 1974).

The crystal regions of cellulose is thus not continuous throughout the cellulose structure, there are also amorphous areas spread in between within the elementary fibre. However, these areas are not as great as the crystals when considering how many units the make up in longitudinal fibre course (Nishiyama, Y. et al. 2003, Wang, Y., 2008).

The crystal lattice of cellulose varies depending on if the cellulose has been modified or if it is in its native state. The native or natural form is referred to as cellulose I, which has a densely packed structure due to the hydrogen bonds formed by hydroxyl groups located within the lattice. Cellulose I can exist in two different crystalline states or phases called I_α and I_β; bacteria and other lower organisms most often produce I_α while the I_β phase is common among higher plants. The cellulose that is regenerated through industrial processes is named cellulose II (Meyer, K.H. et al., 1937, Fengel, D. et al., 1984, VanderHart, D.L. et al., 1984). This form is the most stable since its crystal lattice has the lowest energy. Other cellulose forms are III and IV, which may be produced from the two other variants using chemical treatments (Wang, Y., 2008).

2.2.3 Morphological structure

The elementary fibrils of cellulose I are aggregated into micro fibrils, which in turn are packed into macro fibrils. The cellulose fibres may have different morphologies depending on the source in which they are found. As stated in preceding sections, in lignocellulosic plants cellulose is one of the constituents in the cell wall and associated with among others lignin and hemicellulose that aid the micro fibrillar aggregation (Dupont, A., 2003).

The wood fibre cell wall is built up by a number of layers; the innermost being the lumen (W) surrounded by the tertiary wall (T), the secondary wall (S2), the winding (S1), the primary wall (P), and the outermost layer of the middle lamella (ML) as illustrated in Figure 2.3. The largest amount of cellulose may be found in the walls of the main body and the winding. The shape of the wood fibres varies among different plants due to growth factors and other reasons stated in previous sections; the fibres might be long as for softwood or they can be shorter as is the case for hardwood giving the material their different properties (Krässig, H.A., 1993).

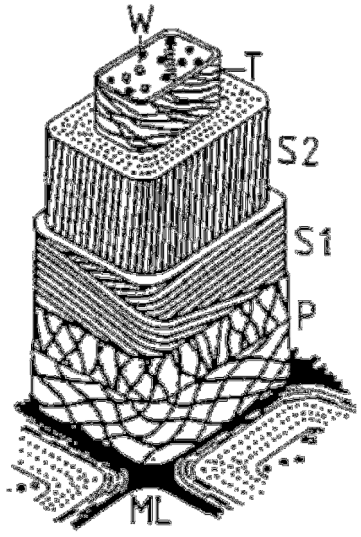

Figure 2.3: The layers making up the cell wall of wood fibres: the lumen (W), the tertiary wall (T), the secondary wall (S2), the winding (S1), the primary wall (P), and the middle lamella (ML) (Krässig, H.A., 1993).

2.3 Dissolving cellulose and related challenges

To dissolve cellulose, beside the use of an effective solvent, increasing the accessibility of cellulose is equally important. To promote better accessibility, penetration of the packed structure through pores and gaps with *e.g.* water or other ionic solutions, followed by swelling of the cellulose may be implemented. Another possible route by which the structure and cellulose molecules can be made accessible to reactants is by mechanical separation. During such, dry or wet milling may be employed, although wet milling might cause unwanted degradation of the cellulose if not performed properly. Structural opening is thus a stage required before processing the cellulose (Dupont, A., 2003).

In order for any form of dissolution to occur, the free energy of the mixed state needs to be lower than the energy of the two separate solutions. Even if this condition might be fulfilled for two phases, dissolution is still not guaranteed since it might be a very slow process. In order to drive the reaction forward by increasing contacts between solute and solvent, stirring and/or heating may be required. The free energy is also affected by the size of the molecule, as the entropic contribution is generally much smaller for molecules with high molecular weight such as cellulose. The flexibility of the polymer is an additional consideration since stiffer molecules are not able to increase their conformational freedom during dissolution to an adequate extent. For cellulose, the β-linked glucopyranose residues are the main components contributing to its stiffness.

The rigidity of cellulose furthermore makes the molecule unable to minimize the contact between its hydrophobic parts and water when subjected to that particular solvent. The inability of dissolving cellulose in water is believed to be due to the combination of the hydrophobic effect and the hydrogen bonding formed both intra and inter molecularly within the polymer structure. This is perhaps contradictory since a generally applied concept is that solutes unable of forming such bonds would have low solubility in water. Other interactions must therefore also be considered, such as for example van der Waals forces and hydrogen bonds between water-water, water-cellulose, and cellulose-cellulose.

Some researchers within the field are of the opinion that the water insolubility in addition derives from the crystal structures of the cellulose molecule; these regions have lower energy because of their increased stability compared to the amorphous arrangements. It should be noted that this contribution to the insolubility is not a generally accepted statement as there are reports also stating that the two states are equivalent.

The presence of hydroxyl groups in the cellulose structure makes the polymer extensively polar, and thereby insoluble in nonpolar substances. However, there are also hydrophobic regions within the molecule making it amphiphilic and consequently amphiphilic solvents would perhaps aid dissolution. When dissolving cellulose, it is highly attractive to employ non-derivatizing solvents that do not decrease the degree of polymerization nor participate in any reaction with the polymer. The usage of some acids as solvents is due to their ability to protonate cellulose and thereby increases the solubility by providing additional charges (Lindman, B. et al., 2010).

2.4 Acidic solvent systems

As mentioned previously, there are several challenges when dissolving cellulose and thus different approaches and reaction mechanisms are implicated as cellulose is interacting with the solvent of choice. When utilizing acid as solvent, the cellulose in such a system is acting as a base. Cellulose may be behaving as an acid when a base is used as solvent, as a ligand when the solvent is a complexing agent, or a reactive compound for systems in which the cellulose is transformed into an intermediate or other soluble temporary derivative. This categorisation is based upon the interactions between the solvents and cellulose; another way of classifying different solvents used might be accordingly: aqueous, non-aqueous, derivatizing or non-derivatizing (Liebert, T., 2010).

In this master thesis, sulphuric acid was used in combination with glycerol and water to achieve adequate dissolution of cellulose. The literature has stated that this particular acid function by affecting the amorphous areas within the cellulose structure (De Souza Lima, M.M. et al., 2002). When using acid as the solvent of choice, there is a risk of degradation of the cellulose instead of dissolution. During this undesirable process, the cellulose molecule is turned into either cellulose of low molecular weight or a sulphuric bi-product like cellobiose. One of the main differences when comparing the two outcomes of acid treatment is that dissolution results in breakage of the hydrogen bonds within the cellulose structure and alters the solid crystal to form a molecular solution. This solution can be used to regenerate into fibre. If hydrolysis would occur instead, the low weight molecules would bring about a great loss of cellulose mass; the small molecules would not be able to be reshaped into fibres. An additional difference is that during hydrolysis, the solvent is used to drive the chemical reaction forward while this is not the case for dissolution (Wang, Y., 2008).

A major cause to the occurrence of hydrolysis when cellulose is subjected to acid is the great sensitivity of the β-1,4-glycosidic bond within the cellulose molecular structure, for which breakage result in depolymerisation. Also contributing to hydrolysis is the existence of hydroxyl groups within the structure, as well as the concentration and strength of the acid employed in the solvent system. The time and temperature during which the reaction takes place also influences the outcome and can thus be altered to affect if hydrolysis is to occur or not. The extent of hydrolysis affects several qualities of the final regenerated fibres. For example, if the hydrolysis is dominant the chains will be short and thereby is their strength influenced. A scheme describing the general process during hydrolysis can be viewed in

Figure 2.4. The reaction takes place through three distinct processes involving for example protonation, charge transfer, and water addition. Ultimately, a free saccharide residue is formed (Nevell, T.P. et al., 1985).

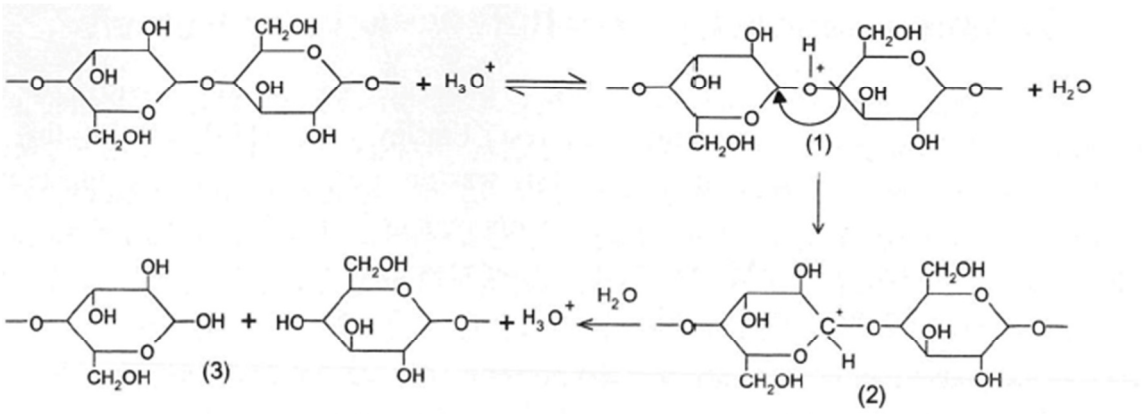

Figure 2.4: Schematic illustration of the hydrolysis reaction occurring between cellulose and acid. The reaction can be divided into three processes involving protonation, charge transfer, and water addition (Nevell, T.P. et al., 1985).

As stated, glycerol might act only as a stabilizer in the system and not participate in any reaction. However, the reaction of glycerolysis could possibly occur instead during which the glycerol may be involved in dissolving and degrading the cellulose. To evaluate if such a process takes place diffusion NMR was performed; a technique described in more detail in latter sections.

2.5 Coagulation of cellulose solution

Once the cellulose has been adequately dissolved in the solvent system, it can be regenerated if the dissolution has occurred to a desired extent. Too much degradation and hydrolysis would result in too short fibres that cannot be used for further reshaping as described earlier.

The fibres are regenerated in a so-called coagulation bath. Such a bath is made up by anti-solvents; liquids that function as precipitants for the cellulose dissolved. When anti-solvents are present in the swollen cellulose film a gel-like substance is formed. The solvents can be evaporated and a solid substance is generated. This process may occur through different mechanisms that involve physical and/or chemical interchange (Zhang, S. et al., 2011). The role of the anti-solvent is to neutralize the solvent, in this case the sulphuric acid. The amount of cellulose that could be regenerated can be determined gravimetrically, and thus also the efficiency of the process since a high regeneration amount is wanted to avoid unnecessary losses.

2.6 Rheological measurements

Rheology is a science that considers the deformation properties of materials that cannot be characterized as ideal (Malkin, A.Y. et al., 2012). The cellulose polymer solutions obtained during this project has been classified as such a material, and therefore the study of the solutions obtained will include rheological measurements of properties as viscosity.

2.6.1 Rheological properties of polymers

When cellulose is dissolved in the acidic solvent system, the fibres are degraded. However, often the extent of degradation is not uniform within the sample and cellulose chains of different lengths are present. This phenomenon is called polydispersity and has been mentioned previously. This non-uniformity will ultimately result in rheological measures that are based on sample diversities, the average properties of the molecular mass distribution. Viscosity is one rheological characteristic that is strongly correlated to the polymer molecular mass (Malkin, A.Y. et al., 2012).

The viscosity of a fluid may be defined as its tenacity towards changes in shape and its resistance to flow. It can also be described as an internal friction within the sample of interest, which derives from the molecules moving relative to each other. Some liquids and gases are denoted Newtonian fluids; these possess a characteristic known as dynamic viscosity meaning that the shear stress resulting in flow is proportional to the rate of deformation or rate of shear strain. Fluids not displaying this relationship are known as non-Newtonian; for which the viscosity varies with time or with shear rate simultaneously as the shear rate is kept constant (Encyclopedia Britannica Online). The cellulose dissolutions of this project are believed to belong to the first category of Newtonian fluids.

Not only do the lengths and masses of the polymer chains influence rheological measurements, also the structures are important to be considered. Although such experiments will only give qualitative results and values, for example the comparative study of branched and linear polymers. The composition of the structure, *e.g.* side groups, similarly influences the polymers rheological characteristics (Malkin, A.Y. et al., 2012).

2.6.2 Correlating intrinsic viscosity and DP

The ability to coagulate the dissolution and regenerate the cellulose will depend strongly on the degree of polymerization of the dissolved cellulose fibres. To determine DP, a technique measuring the intrinsic viscosity η of the dissolution may be utilized since there is an established relationship between the two parameters described accordingly (Wang, Y., 2008):

$$DP^{0.905} = 0.75[\eta] \quad (1)$$

The viscosity of a solution can be measured using a variety of techniques and apparatuses. The instrument utilized during this project to determine plate/rotational viscosity was a cone-and-plate viscometer or rheometer; a device classified as a rotational viscometer. This class of viscometers evaluate the rotational rate of a solid in a viscous solution as a torque of a certain size is applied. The size of the torque depends on how much force is required to rotate the solid at a definite angular speed. The cone-and-plate viscometers are utilized most frequently when non-Newtonian liquids are being studied but they can also be implemented for Newtonian fluids (Viswanath, D.S. et al., 2007). A simple schematic picture of this device can be seen in Figure 2.5.

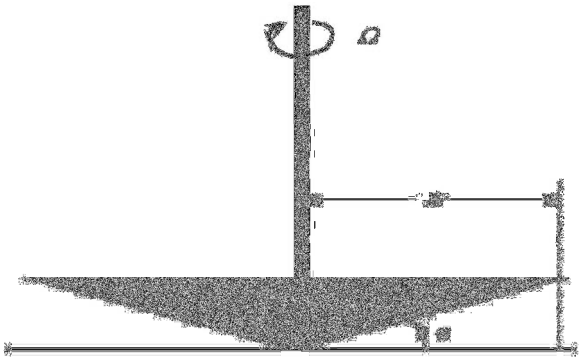

Figure 2.5: Schematic picture of the cone-and-plate viscometer (Viswanath, D.S. et al., 2007).

The fluid of interest is placed in the gap between the horizontally placed plate and the cone having a wide vertical angle. The angle α between the two components is made small, generally no large than a couple of degrees. Only one component is moving during the measurement while the other one is stationary; in the following sections the equations stated is based upon the assumption that the cone is the element in motion (Oka, S. et al., 1966).

The rate of shear D at a certain distance R from the cone axis may be described as the ratio between the relative angular velocity Ω and the angle α between the plate and the cone. The

shear rate is thus independent of *R*, making the shearing stress independent as well of the distance from the axis. The torque *T* may be written as:

$$T = \int_0^R FR(2\pi R)dR = \frac{2\pi R^3 F}{3} \quad (2)$$

For a Newtonian liquid, the viscosity is thereafter calculated by using the following formulas:

$$\eta D = F \quad (3)$$

$$\eta = \frac{3T\alpha}{2\pi R^3 \Omega} = \frac{CT}{\Omega} \quad (4)$$

C is the so-called instrument constant and is usually stated by the producer of the particular viscometer used.

The cone-and-plate viscometer was the instrument of choice because of the advantages it brings during study and evaluation of liquids. Some of these are inter alia the ability to perform continual measurements of solutions having characteristics that is temperature dependent, the capability to perform such at steady state conditions, and the consistency and stability of the shear rate within the solution of interest. Nevertheless, when using such a viscometer some errors are introduced, especially for instruments that are not calibrate or constructed adequately. Examples of such errors might be the additional torque derived from secondary flow that arises from inertia forces dragging the plate and cone closer to each other, edge effects, and non-linear flow etc. (Viswanath, D.S. et al., 2007).

By performing rheological measurements, it would be possible to determine the state of the dissolution; if it can be described as a liquid or a solid. A liquid behaviour would indicate a low amount of un-dissolved cellulose. The flow properties depending on the viscosity could also be established; such characteristics would additionally provide insight to the extent of dissolution that would affect spin dope production.

2.7 NMR spectroscopy

During the experimental performance, nuclear magnetic resonance (NMR) measurements were performed. First in this section, an introduction is given to the basics of NMR followed by a more detailed description of diffusion NMR (NMRd) that was a type of NMR used.

2.7.1 Introduction to NMR spectroscopy

NMR spectroscopy utilizes the intrinsic spin characteristic of certain NMR active nuclei; a property making them sensitive to static magnetic fields and radio frequency (r.f) pulses that may be applied to induce atomic electron transitions between energy states. These transitions result in a detectable signal recorded by the NMR instrument. Transitions occur when the resonance condition is fulfilled; meaning when the field or pulse applied has a frequency (Larmor frequency) equal to the energy separation between the states.

As the r.f pulse is applied and state transitions occur, radiation is subsequently transmitted at the resonance frequency. The nuclear resonance frequency depends both on the strength of the magnetic field present and on the molecular position of the nucleus since electrons from atoms surrounding the nucleus shields it from the field. The shielding effect is distinctive for each nucleus as their surrounding environment differs due to structural differences in the molecule. The frequency and ultimately the detected signal are unique as well, making elucidation of molecular structure achievable.

After application of an r.f pulse, the spins of the system studied returns to its original state through a process known as relaxation and are dependent on the spin´s environment and surroundings. Two constants are normally used to describe relaxation: the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2. Slow molecular motions that give rise to changes in local magnetic fields particularly affect T_2. For cellulose, T_2 is typically short due to the size and rigidity of the molecule provided by the strong interactions within the molecule described previously. Correspondingly, a flexible molecule would display a long T_2 as is also the case for small molecules as they move more rapidly. These constants affect the NMR signal; the signal becomes narrow for shorter molecules, and wider for larger ones. For cellulose and other polymers in solution, T_2 is additionally affected by the strength of the rigidity of the chains generating a shorter T_2 and differences in recording the signals arise (Canet, D., 1996, Hore, J.P., 1994, Östlund, Å., 2009).

2.7.2 Diffusion NMR spectroscopy

The degree of polymerization and its distribution may be evaluated by using NMRd. If the hydrolysis during dissolution is too advanced, then there will be an issue with coagulating the cellulose. Difficulties with coagulation may although depend on other factors, such as choice of coagulant or too low cellulose content, therefore diffusion NMR was used in this project to follow chain degradation of cellulose. The obtained information would thereafter be used to evaluate the success of the dissolution process and the associated formula of acidic solvent system components. NMR would furthermore be useful when evaluating if the glycerol in the system is inert as intended or if it reacts with the cellulose; a possible reaction (glycerolysis) that would be needed to be considered during interpretation of results.

Diffusion NMR is a technique that can be employed to calculate the diffusion coefficient of a sample to the NMR data obtained during measurement. The detected self-diffusion is taking place along an NMR tube in which the sample of interest is contained. Separation is obtained as a result of mass variations of the sample molecules as smaller ones diffuse faster than larger molecules. Different molecules will give rise to dissimilar resonance. Hence, diffusion coefficient will vary for different molecules; and thus it is possible to distinguish and identify substances (Kagan, G.L., 2011).

As cellulose is dissolved in the acidic solvent system it gets diluted. A characteristic of polymers diluted is their random translational movement also known as Brownian diffusion, D_0. The rate of this diffusion depends on several factors including the friction that occurs between the solvent and the polymer chain as well as the temperature. D_0 may be calculated by using the Stokes-Einstein equation:

$$D_0 = \frac{k_B T}{6\pi\eta R_H} \qquad (5)$$

where k_B denotes the Boltzmann constant, T the temperature, and R_H the hydrodynamic radii of the polymer in solvent system. The friction, previously described, is incorporated in the viscosity term η, which notably is the viscosity of the solvent, and additionally in the R_H term correlating to the size of the polymer. Equation 5 can be rewritten to include the molecular weight M_w of the polymer studied:

$$D_0 = \frac{T}{\eta a n m_w^{-\upsilon}} M_w^{-\upsilon} g(MWD, \upsilon) \quad (6)$$

In which the additional terms a is the length and m_w describes the molecular weight of the specific monomer. The polymer chain rigidity is denoted by n. g(MWD, υ) scales the molecular weight distribution MWD to the power of υ depending on the MWD appearance. υ is affected by the interaction between solvent and polymer molecules; a poor solvent affecting D_0 by increasing it for example reduces υ (Bernard, D.A. et al., 1983).

In the NMRd experiment a normal stimulated echo was used, but between the radio frequency pulses gradient pulses is applied to encode and decode the spins of the nuclei. The time duration between the primary and secondary gradient pulse is kept short (~75 ms) to minimize the relaxation effects. If the encoded spins have changed position by self-diffusion during this time, there will be a loss in macroscopic magnetization; hence also be a damping of the NMR signal will occur. An array of experiments is performed with increasing gradient strength, which will generate a continuous decrease in signal intensity. These intensity values are thereafter normalized, and the following Stejskal-Tanner equation is employed to derive the diffusion coefficient for the specie of interest:

$$\frac{I}{I_0} = \frac{1}{2}\exp(-kD) \quad (7)$$

Where I/I_0 is the normalized signal, D is the diffusion coefficient, and k describes the dependence on the gyromagnetic ratio of each nucleus and the gradient pulses length, strength, and diffusion time. k values are plotted versus the normalized intensity I/I_0 and subsequently the diffusion coefficient can be determined using Equation 7 (Stejskal, E.O. et al 1965).

Diffusion NMR has advantages contributing to it being the technique of choice for substance identification. Such studies could possibly have been performed using X-ray crystallography instead, but this technique is more appropriate for observing solids than solutions. Mass spectrometry would also have been a technique used for identification; however, during analysis the compounds within the dissolution may react further and thereby provide an improper or incorrect result (Kagan, G.L., 2011). The broad spectrum of molecules possible to study using diffusion NMR contributes to its attractiveness as well.

3. MATERIALS AND METHODOLOGIES

In this section, a presentation of the layout and the intent behind the laboratory working methods and materials used during the project is stated. A list of chemicals and substances employed is listed initially.

3.1 Materials

The following materials were utilized during the laboratory performance:

- Buckeye V67 pulp
    - Batch 032012
    - Batch 5959A
- Glycerol (99.5 % Sigma-Aldrich)
- Sulphuric acid
    - 99.999 % (Sigma-Aldrich)
    - 95-98 % (Sigma-Aldrich)
    - 95-97 % (MERCK)
- Distilled water
- Acetone (99.5 % Sigma-Aldrich)
- Ethanol (96 % Solveco)
- Sodium hydroxide (NaOH) pellets (≥ 98 % Sigma-Aldrich)
- Avicel PH-101 (batch P11823018 FMC BioPolymer)
- 1-ethyl-3-methylimidazolium acetate (EMIMAc) (≥ 90 % Sigma-Aldrich)
- Cellobiose (batch BCBK5377V ≥ 99 % Sigma-Aldrich)
- Glucose (CAS no. 50-99-7 Sigma-Aldrich)

3.2 Conductance of dry and wet milling of pulp to increase accessibility of cellulose prior to dissolution

As stated, the intention was to start with the investigation of the appropriate approach to prepare the cellulose prior to dissolution in acid system to have a fair accessibility and thus give the best dissolution. What must be noted is that two different batches of pulp were used during this part of the project. Batch 032012 was employed for the wet milling approach while batch 5959A was utilized when evaluating the dry milling approach. Batch 032012 had been used in previous projects and was therefore available initially. Batch 5959A was the pulp otherwise used in the project.

3.2.1 The wet milling approach

The wet milling approach could be an efficient way to swell the cellulose and has from previous studies been proven to give adequate dissolution of pulp in the system consisting of polyphosphoric acid (PPA), ethanesulfonic acid (ESA), and distilled water. Therefore, the wet milling approach was preliminary chose in this project. This dissolution was valued by noting viscosity, transparency, and colour of the solution and thereafter used as a comparison and reference when relating with the dissolution of cellulose obtained when employing dry milling.

For the wet milling approach, dried pulp sheets were shredded and milled. The milled pulp was dried at 50 °C for two hours. Distilled water was added to the container filled with the desired amount of cellulose to adjust the moisture. As mentioned, this approach had formerly been employed and a recipe of the ratios of pulp, PPA, ESA, and water that resulted in adequate dissolution had been established and was known. The container was sealed, and then shaken vigorously to spread the water homogenously into the pulp (unpublished method). The cellulose and water mixture was put into an incubator (Incubator SI60D, Stuart) at 37 °C for 40 min. Since movement of the water molecules in the pulp bulk must occur to make water spread evenly in the structure; the temperature of 37 °C was assumed to be appropriate. After incubation, the wetted pulp was introduced into the acidic solvent system.

3.2.2 The dry milling approach

As described, this was another possible approach by which the cellulose can be made accessible to reactants easier and more straightforward. The obtained dissolution after utilizing this approach and dissolving the pulp in PPA, ESA, and water was evaluated by noting the same visible parameters as for the wet milling approach (viscosity, transparency, and colour). For this method, the grinder of choice used for milling was a smoothie blender (BL-1200/MIXER, Wilfa) selected because of its high capacity (1200 W).

When grinding, pulp from batch 5959A was cut into smaller pieces and placed into the blender. Repeated blending processes were required to transform the pulp into a fluffy structure. Between these processes, pressure was placed on the cellulose in order to push it closer to the knifes. The milled pulp was put into plastic bags and sealed. The dry content between bag batches differed slightly (94.54 % ± 1.16 %). The appliance used for such measurement was a Mettler Toledo MJ33 Infrared Moisture Analyzer.

3.3 Dissolving cellulose in acidic solvent system

Hereafter, a description of the general procedure employed when the pulp was dissolved in the solvent system is stated. There were some deviations from this method with the purpose to test the effects of different parameters (*e.g.* acid purity and reaction temperature) on the acquired dissolution, which also is described in this section.

3.3.1 General procedure when performing the dissolution process

First, pulp preparation prior to introduction of the pulp into the acid system was performed to increase the accessibility. The calculated amount of cellulose and solvent system components (sulphuric acid, glycerol, and occasionally added water) were weighted on a Sartorius BP221S balance. For the solvent systems without water added, the acid and the glycerol were collected into one common container before the rest of the experimental procedure was conducted. When water was added, it was mixed with glycerol in the plastic container and the acid was weighted separately to avoid the risk of a vigorous reaction outside the fume hood. Once weighted, the acid was carefully added to the glycerol and water mixture. The pulp was temporarily stored after weighting in a lid sealed plastic container to prevent the dry content from changing.

Under fume hood, a stirring device consisting of a motor (Janke & Kunkel RW-20) placed on a stand using clamps was mounted. Driven by and connected to the motor, a stainless steel stirrer was set which was soaked into the sulphuric acid and glycerol mixture. The speed of the stirrer was determined by the motor; and set to 450 rpm ± 20 rpm. The motor was after set-up started and the system was stirred by the impeller. Thereafter, by using stainless steel tweezers, the pulp was transferred from its container into the acid and stabilizer solvent system. This was done fast in order to quickly achieve a single system in which the pulp could dissolve simultaneously and under the same conditions. A stainless steel spatula was frequently used to push pulp pieces from the container walls down into the solution. Due to the low density of the mechanically grinded pulp, this procedure was more often used for that approach compared to the wet milling approach. A timer was employed for monitoring the progress of the process; normally the experiments were conducted during circa 20-30 min. This time frame would allow the cellulose to dissolve properly and also give information about the dissolution stability. In industrial applications, it would be desirable to have a short production time (often 30 min was more than enough to dissolve the pulp).

3.3.2 Variations from the general procedure

For all laboratory work conducted, 99.5 % glycerol was used as a component of the solvent system. On the contrary, the acid employed was of different origin and purity during the project due to pricing and availability. The dissolution employing the acidic solvent system was tested at different reaction temperatures: fixed at 20 °C throughout the experiment, at 30 °C when starting the stirring process and thereafter semi-controlled, and at an uncontrolled temperature where no cooling or heating of the system was conducted during the experiment.

When cooling the system to 20 °C, an icebox was employed as well as a thermometer to ensure that the desired temperature level had been reached. For these experiments, the acidic system was contained in a stainless steel beaker into which the pulp was transferred. When lowering the temperature, an even temperature distribution within the solution of interest is desired and thus stainless steel beaker was believed to be more suitable than plastic. The wall material of the beaker used was unfortunately thought to be reacting with the acidic system since bubbles appeared and there was a distinct metallic smell noticeable. The explanation to the unwanted reaction might be that there was some other material present besides steel.

For the semi-controlled experiments starting at 30 °C, a similar approach was used. The solvents were mixed in a plastic container and were thereafter left to cool down to 30°C in the fume hood without the use of an icebox. The container was then mounted on the stands and the stirrer was placed accordingly and started. As pulp was added into the system, there was a raise in temperature. For some experiments, the temperature was uncontrolled while for others an icebox was once again used to keep the temperature lowered and also to decrease the time during which the system would be subjected to a high temperature. When the system had cooled down to the starting temperature of 30 °C, the icebox was removed and no longer used. For the experiments without temperature control, the set-up was the same as for the semi-controlled ones except the use of the icebox.

By using the methods stated above in this section, a variety of solvent systems were tested in order to derive the one recipe best suitable for dissolving cellulose. The percentages of the different components (acid, glycerol, and water) were greatly varied and tested. The pulp amount and content was also varied, ranging from ~5 % to 15 %. In Table A1 in Appendix, all experiments performed using the different percentages are listed. In Table A2, the temperature profile for each trial is displayed using the different methods described.

3.4 Evaluation of the obtained cellulose solution

After obtaining a dissolution that had the desired properties in terms of the viscosity, transparency, and colour; an evaluation of the dissolved cellulose was needed to be carried out using methods that would validate the visible observations.

3.4.1 Stability

When performing the experiments, the stability of the solution could to some extent be determine by studying the change in colour. It was preferred to have a stable solution colour during the dissolution process, but also afterwards since there might be time gap before the solution is spun into fibre. Therefore, samples were stored at room temperature (about 20 °C) and at 4 °C in fridge to determine the chance in stability during a couple of hours after the dissolving process.

3.4.2 Solubility

Besides the stability, the degree of polymerization (DP) also needed to be determined in order to evaluate the success of the experiment and the recipe of solvents used. The solution was preferred to consist of cellulose with a DP high enough to allow cellulose regeneration, and one approach utilized for this evaluation was performing coagulation tests by forming films of the cellulose. During such, a small amount of the solution was spread evenly on the bottom of a glass beaker that was sunken into a coagulation bath of anti-solvent. The particular anti-solvents used were distilled water, acetone, and ethanol. The coagulation tests were performed using them separately and in the same order as recently stated. The coagulation desired to be observed was a transparent, gel-like film forming on the bottom of the beaker, which after some time in the bath could be peeled off, dried, and weighted to determine the cellulose content of the regenerated material.

During the later stages of the laboratory work concerning the optimization of solvent ratios and appropriate temperature control, NaOH was employed as anti-solvent for the obtained dissolution using one particular solvent system composition. For these trials, a different approach for spreading the solution on the surface, which was sunken into the bath, was used. The solution was put onto a petri dish, thereafter an identical second dish was used on top of the first and the two dishes with solution between them was pressed towards each other. This

would result in a more evenly spread solution compared to the method using the beaker bottom (not entirely planar) and would intentionally aid film formation.

Coagulation was once tested using the so-called “syringe approach”. Employing this method, the obtained solution was transferred into a syringe. The content was weighted before the dissolution was let out from the syringe into a beaker of anti-solvents stirred by a magnetic stirrer. The intent was to hopefully observe some coagulation, thereafter filter the solution and collect the gel-like material. No coagulation could however be collected. The filter paper was left in an oven (ElektroHelios) at 105 °C for approximately 30 min to dry. Unfortunately no dried material was obtained and the amount of coagulated cellulose could not be compared to the weight of the dissolution which otherwise would have indicated regeneration efficacy.

For the initial laboratory work, the only approach to evaluate the solubility was by using the coagulation bath method. A polarizing light microscopy (System microscope BX53, Olympus) was used later in the project. This was a great tool that could be used as an efficient complement to the coagulation study to observe the dissolution. Polarized light filters off everything not crystalline, making the un-dissolved crystallites visible. Using the software cellSense version 1.6 that accompanied the microscope, photos were taken of the fibres in solution/suspension.

Before the dissolution trials were observed in the light microscope, they were centrifuged in order to remove air bubbles. The settings of the centrifuge (4233 ECT, ALC) were accordingly: 15-20 °C operating temperature, 2520 rpm speed for 10-12 min duration. After centrifugation, photos of the solutions/suspensions were taken for documentation using a digital camera.

In order to evaluate the results for the system consisting of ~5 % cellulose, a ternary phase diagram was made. This would hopefully provide some indications of which solvent ratios that was appropriate to use, and also how to proceed with systems at higher cellulose amounts. The axes of the diagram stated the weight percentages of solvents, and the different regions of it described a solution that was either not adequately dissolved/turbid, stable, too advanced hydrolysis, or transparent.

3.5 Rheological measurements

When performing the rheology measurements, only one solvent system was tested. The sample for this study was prepared using the optimized conditions found in this project. When starting the rheometer (MCR 300, Anton Paar), the temperature of the water bath used for cooling was set to 16 °C and the operating temperature to 20 °C. The pressure was set at 45 bar. For this instrument, 0.6 ml was required of the viscous solution sample to cover the 5 cm diameter stainless steel CP50-1 (indicating the 1 ° α angle) top plate that was placed on top of the bottom plate having the sample in between. The temperature was controlled by the cone (TEK bottom plate), which was coated with plasma that would prevent corrosion exerted by the samples tested.

The rheometer was connected to a computer and the software RHEOPLUS/32 V3.40 was used for analysis. Two types of experiments were performed: oscillation test and flow curve assessment. The oscillation test was performed to study the effect of frequency application (network formation or gelatination vs. temperature). From these measurements, two values abbreviated G' and G'' could be obtained. G' describes how solid the sample is and G'' describes how liquid it is. 21 data points were collected and the time interval between them was set to 1 s.

The flow curve would give knowledge about the flowing behavior of the sample, *i.e.* shearing behavior measurement and shearing thinning or thickening property determination. Two flow curves were produced using different settings. For the first trial, three intervals were employed. The first interval was set to give 0 data points during 30 s; during the second no shear was applied to allow the sample to recovery and thus 0 data points was obtained; the third resulted in 29 data points during a 5 s measurement. For the second trial there was only one time interval of 36 s during which 50 data points was collected. There was also a difference between shear rates applied; for the first trial the rate was set from 0 to 100 s^{-1} while the second trial interval was set from 0 to 200 s^{-1}.

3.6 Preparations and NMR measurements

Nuclear Magnetic Resonance (NMR) was used to possibly follow degradation or reactions occurring during the dissolution trials. For this both one-dimensional NMR spectra and diffusion NMR (NMRd) were evaluated. More inert samples could be prepared in advance while the acidic trials had to be freshly made. The NMR equipment used was situated at the Swedish NMR Centre at the University of Gothenburg, situated at Sahlgrenska Science Park.

Solutions containing 5 % Avicel and 5 % Buckeye 5959A were dissolved in EMIMAc as two separate samples. Avicel is a microcrystalline cellulose source having an established DP of ~100, while Buckeye V67 has a DP of ~600. The solvent EMIMAc is a polar ionic liquid used to efficiently dissolve cellulose (Pinkert, A. et al., 2009). Results from the NMR analysis of these two samples respectively would be compared to the measurement obtained for the optimized acidic solvent system; thus a reduction in DP of the cellulose in the solution would be possible to detect.

1 % and 5 % stock solutions of cellobiose and glucose dissolved in D_2O respectively were also made in advance, inter alia for later instrument optimization. D_2O was employed instead of H_2O since H_2O would interfere with the ^1H sample signal. In Table 3.1, the samples studied are listed.

Table 3.1: Listing all samples studied in the diffusion NMR measurements of which samples containing sulphuric acid were prepared at site to avoid degradation.

Sample no.	Content
1	1 % cellobiose in D2O
2	5 % cellobiose in D2O
3	8.55 % glycerol in D2O
4	52.5 % sulphuric acid in D2O
5	Cellobiose + 8.55 % glycerol in D2O
6	Cellobiose + 52.5 % sulphuric acid in D2O
7	8.55 % glycerol + 52.5 % sulphuric acid in D2O
8	Cellobiose + 8.55 % glycerol + 52.5 % sulphuric acid in D_2O
9	Buckeye + 8.55 % glycerol + 52.5 % sulphuric acid in D_2O
10	Avicel in EMIMAc
11	Buckeye in EMIMAc
12	EMIMAc

Samples containing 8.55 % glycerol (no. 3, 5, 7-9, in Table 3.1) were made with the purpose to establish if the glycerol reacted with the other(s) sample component(s). The concentrations chosen were based on previous trials of which this was the lowest amount employed. The hypothesis was that if a low amount reacted, higher percentages would presumably do so as well. The amount utilized for the 52.5 % acid samples (4, 6-9, in Table 3.1) was chosen based on similar reasoning. The acid and glycerol was tested with cellobiose instead of Buckeye cellulose as a model system since cellobiose would result in better NMR detection due to different relaxation mechanisms. The scheme presented in Table 3.2 describes the experimental design for the glycerolysis trials.

Table 3.2: Showing the experimental design employed when investigating if glycerol reacted with any of the other component in the acidic solvent system; the study of possible glycerolysis reaction occur.

H_2SO_4 (%) ➔	0	52.5
Glycerol (%) ⬇		
0	0 % cellobiose	0 % cellobiose
	1 % cellobiose	1 % cellobiose
8.55	0 % cellobiose	0 % cellobiose
	1 % cellobiose	1 % cellobiose

NMR measurements were also performed to evaluate the optimized solvent system (no. 9); *i.e.* if the pulp had degraded too aggressively by the acid and thus no coagulation could be observed. This sample was run three times to study the degradation as a function of time: the first run was started right after sample preparation and run during 9 hours, the second was t10 hours old at the start of the measurement, and at the beginning of the third run the same sample was circa 20 hours old. Samples no. 10-12 were made for comparison of diffusion coefficients in ionic liquid of pulps with different DP, if a change in D is possible to observe. All samples prepared at the Swedish NMR Centre were weighted on a Sartorius CP124S balance. The NMR-tubes used were 5 mm wide and 178 mm long of type 5TA (ARMAR Chemicals). The measurements were performed at 30 (±0.1) °C except for ionic liquid samples at 48 °C on a Bruker 600 MHz Avance spectrometer equipped with a Diff30 diffusion probe with a ^{1}H radio frequency coil. The parameters were δ adjusted between 0.5-1ms, Δ adjusted between 50-100 ms, and the gradient amplitude, g, was increased linearly from 0.1 to 1000 T/m (adapted to the molecules studied) in 16 gradient steps. In order obtain sufficient signal-to-noise ratio, at least 16 numbers of transients were accumulated for each gradient step.

4. RESULTS AND DISCUSSIONS

In this section, a presentation of the results obtained during the laboratory work of the project will be given as well as associated discussions. First, an evaluation of the pulp preparation approach will be submitted. Secondly, the results obtained from the trials performed to determine the appropriate solvent system composition are stated and concerned. At last, the results from the rheological and NMR measurements will be considered.

4.1 The dry and wet milling approach of pulp preparation to increase accessibility

An initial evaluation was performed to determine if the dry milling approach would result in dissolution of cellulose that was comparable to the one obtained after using the wet milling approach. There were no differences observed for the viscosity, the transparency, or the colour, which were the parameters employed for comparison of the two approaches. Based on these results, the dry milling approach was identified as the most suitable for further use in the project when evaluating solvent ratio and other relevant parameters. This approach would induce higher experimental time efficiency, less and simpler equipment need, and was considered easier to implement in real situations and working environments.

4.2 Optimization of the solvent composition

The main part of the project was devoted to finding the composition of solvents, *i.e.* sulphuric acid, glycerol, and water that would result in adequate cellulose dissolution and possible regeneration of cellulose. This turned out to be challenging, as the system was proven to be very sensitive with respect to both solvent ratios and reaction temperature. The main difficulty was to find the correct amounts of sulphuric acid and glycerol, since more acid in the system simultaneously influenced the solubility and stability in a counteractive manner. If more acid was present, better was the transparency, viscosity, and solubility. However, the stability of the dissolution was affected negatively and the hydrolysis risked being too aggressive and advanced. The reaction time was therefore not as prominent as expected and therefore not evaluated in great depth.

4.2.1 Optimizing solvent ratios for ~5 % cellulose system

At first, experiments employing the lowest amount of cellulose were conducted. The results from these trials were intended to be implemented for higher cellulose content as a starting point. Numerous experiments were performed varying the solvent content, all of which are listed in Table A1 in Appendix. In Table 4.1, the different ranges of the respective components are listed.

Table 4.1: The different ranges of concentrations of sulphuric acid, glycerol, and water used in the ~5 % cellulose system. For the experiments, their respective content varied diversely between the values listed.

	Min (wt-%)	Max (wt-%)
Sulphuric acid	41.03	86.18
Glycerol	11.03	53.40
Water	0.31	14.98

The solvent system recipe that resulted in adequate dissolution in terms of transparency, viscosity, colour, and stability consisted of:

- 4.6 % cellulose
- 66 % sulphuric acid
- 26 % glycerol
- 3.4 % water

When this recipe was tested at first, the solution was too unstable and the hydrolysis too severe and was therefore evaluated using the semi-controlled temperature approach with the intention to make the reaction less aggressive. Using this methodology, a good solution was obtained with respect to the stated criteria (transparency, viscosity, stability, and solubility).

Not only did the result of this recipe depend on if it was temperature controlled, it was also affected by how the temperature control was performed. In order to evaluate the repeatability of the experiment, the same optimized recipe was tested three times. There was a slight difference in solution colour, which can be seen in Figure 4.1.

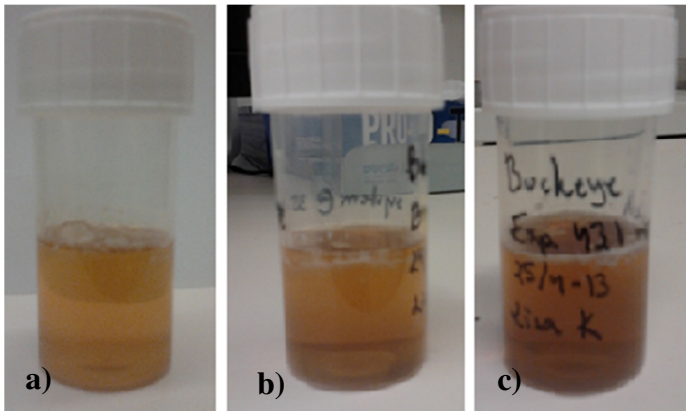

Figure 4.1: The dissolutions obtained after centrifugation for the recipe of 4.6 % cellulose, 66 % sulphuric acid, 26 % glycerol, and 3.4 % water. There is a slight difference in colour depending on different temperature control.

The performance of the resulting solution depends on how fast the temperature dropped. As pulp was added into the stirred system, the reaction temperature raised from 30 °C to about 50 °C. If the reaction was put on ice quickly and the temperature could be lowered to 30 °C hastily, the resulting solution got a more yellow colour. For a) in Figure 4.1, the total time required for the system to once again reach a temperature of 30 °C was the shortest (5.5 min) and the solution was the clearest yellow. Dissolution c) in Figure 4.1 required the longest time (8 min) to reach the original temperature, and the corresponding colour was orange/brown. b) in Figure 4.1 was in between the other two with respect to time requirements and colour. The temperature profile of dissolution a), b), and c) in Figure 4.1 is presented in Table 4.2. The associated column for each dissolution presents the time required for the temperature to drop within the interval stated in the far left column.

Table 4.2: The obtained temperature profile for dissolution a), b), and c) shown in Figure 4.1. a) displayed the shortest time requirements to reach the starting temperature of 30 °C, while c) displayed the longest. The temperature profile of b) was in between the two others.

Temperature (°C)	a) (min)	b) (min)	c) (min)
50 → 35	1.5 → 3.5	1.0 → 5.2	1.0 → 5.0
35 → 30	3.5 → 5.5	5.2 → 7.0	5.0 → 8.0

As stated earlier, the stability was determined by the colour and the change in colour of the dissolution while the solubility was determined by evaluating coagulation and observing the dissolution in light microscopy. For this recipe, the coagulation tests performed were unsuccessful with respect to obtaining a film that could be collected. When something was forming in the bath, it was not retainable and it disappeared relatively fast; thus textile fibres

could not be regenerated and no documentation was possible. Light microscopy pictures of solution b) and c) was obtained using polarized light and can be viewed in Figure 4.2.

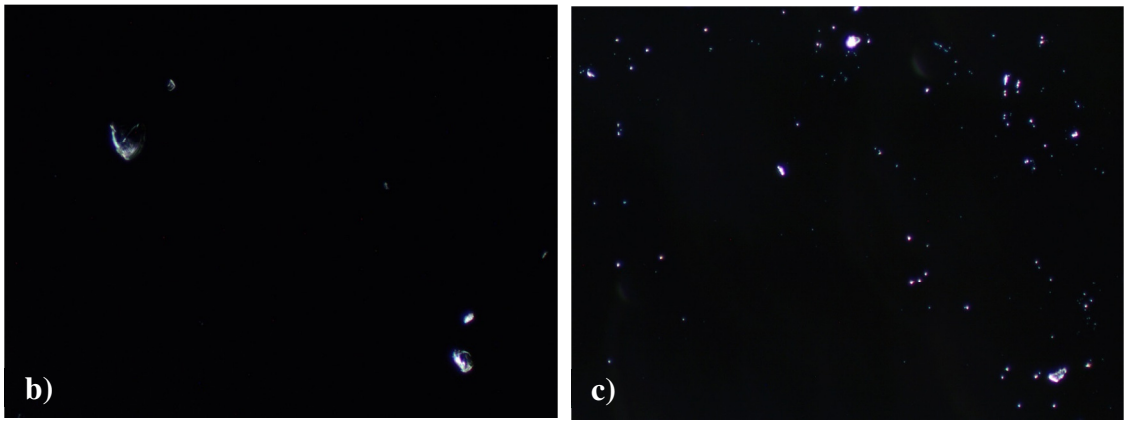

Figure 4.2: Light microscopy pictures of solution b) and c), which are based on the same solvent system formula. More fibres are visible for c); however the length is somewhat similar for the two solutions (the fibres in b had approximately a length of 20 µm). For solutions that were unsuccessful with respect to the stated criteria, the fibres would appear as a dense pad and the fibre length would be significantly greater.

Because of computer issues no pictures were attained for solution a), however the fibres could be described to have an appearance similar to solution b), *i.e.* short and relatively scarce. The appearance in light microscopy for solutions that were termed unsuccessful with respect to the stated criteria was quite different from the fibres visible in Figure 4.2. For those, a dense pad could be observed consisting of remaining fibres of greater length. The fibres in b) is circa 20 µm; much shorter than the pad fibres which could stretch more than the length of the picture frame. A picture taken of dissolved cellulose utilizing non-polarized light can be seen in Appendix Figure A3, having only a few remaining fibre fragments. A possible explanation to why no coagulation occurred could therefore be that the acid had degraded the fibres too much, providing them with a too low degree of polymerization. If so, the anti-solvents would not be able to bring the existing chains together and create the desired solid film.

Beside the solvent composition and the established temperature sensitivity, which was studied by employing all of the stated performances with varying temperature control, additional results and knowledge were obtained from the ~5 % cellulose system experiments:

- More water in the system turns the system more exothermal. For experiments with similar acid:glycerol ratio, an increase in water content by merely 3 % results in a temperature increase of almost 20 °C.

- A higher content of acid in the solvent system
    - improves solubility
    - lowers stability

  As more acid is present, the hydrolysis is more advanced, fast, and aggressive. As a result, the fibres were degraded extensively.
- If the dissolution occurs at a constant temperature of 20 °C, it will not transpire despite a very high acid content. It was interesting to test if the process would be successful at room temperature because of the efficiency and simplicity it would bring into industrial application.

4.2.2 Optimizing solvent ratios for ≥ 7 % cellulose system

When the optimized conditions with respect to transparency, viscosity, and colour, of the cellulose solutions had been determined for the ~5 % cellulose system, they were used to dissolve cellulose with higher content. Solution trials made up of ≥ 10 % cellulose could be used to produce spin dopes and spinnability could subsequently be tested, as described in previous sections.

The ~5 % optimized conditions were tested for 7 % cellulose systems but failed to reach the criteria, therefore other solvent compositions were evaluated as well. Table 4.3 lists the ranges of the amounts of the included components; unfortunately no recipe resulted in a successful dissolution of the cellulose fibres. The same dilemma as before was encountered; more acid resulted in good dissolution, transparency, and viscosity but simultaneously the stability got worse. All these tests were performed using the semi-controlled temperature approach.

Table 4.3: The ranges of concentrations of sulphuric acid, glycerol, and water used in the 7 % cellulose system. For the experiments, their respective content varied between the limits listed below and can be viewed in Appendix Table A1.

	Min (wt-%)	Max (wt-%)
Sulphuric acid	53.68	65.19
Glycerol	25.17	37.17
Water	2.11	3.36

Systems made up of 10 % cellulose were also tested. Table 4.4 lists the ranges of the amounts of the solvents included in the system:

Table 4.4: The ranges of different concentration of sulphuric acid, glycerol, and water used in the 10 % cellulose system. For the experiments, their respective content varied diversely between the limits listed below and can be viewed in Appendix Table A1.

	Min (wt-%)	Max (wt-%)
Sulphuric acid	47.48	64.02
Glycerol	25.42	40.90
Water	0.63	7.04

The dissolution trials for 10 % were unsuccessful to reach the criteria for further industrial implementation. During these experiments, there was no temperature control. This was due to the fact that the temperature sensitivity of the system had not been established at the time when these experiments were conducted. The 7 % trials were performed following the ~5 % optimization, however the 10 % tests were done parallel to the ~5 % and prior to the suitable solvent composition and temperature control had been found. Although, since the 7 % dissolution trials were not adequate, it was assumed pointless to redo the trials using 10 % cellulose in the system.

Despite the undesired results obtained for the systems of higher cellulose content, some knowledge about the solvent system could be made:

- A higher content of acid in the solvent system
    - improves solubility
    - lowers stability
- Less glycerol and more water in the solvent system increase the temperature.
- A lower solvent system temperature when pulp is added improves stability.

A few trials were done with 15 % cellulose using the same experimental procedure as for 10 % cellulose. These were very few and are therefore not listed but can be found in Appendix. For systems with such high cellulose amount, there was an issue with the equipment. The stirrer used seemed to be unable to rotate adequately fast to agitate the solution properly. The operating speed of the motor could not be adjusted. A magnetic stirrer as well as a more advanced and powerful stirrer were tested but failed to achieve proper stirring.

4.2.3 Combined evaluation of all tested systems

Some of the results obtained for systems with higher cellulose content were equivalent to the system consisting of less pulp. The starting temperature needed to be lowered before the cellulose was added otherwise the solution was too unstable. More acid and less glycerol promote hydrolysis and lowers stability simultaneously, making it challenging to find the correct ratio. In Figure 4.3, three dissolutions (~5 % cellulose) obtained by employing the same experimental procedure but alternating the solvent composition slightly are presented. As can be seen, the appearance of the dissolution varies significantly. In Figure 4.3 a) consists of 66 % acid, 26 % glycerol, and 3 % water; b) of 60 % acid, 32 % glycerol, and 3 % water; c) of 58 % acid, 34 % glycerol, and 3 % water. Fibres viewed in light microscopy was very dense and long for solutions having the appearance of c), while fibres of a) were short and dispersed as can be seen in Figure 4.2. Fibres in b) were an average of the two others.

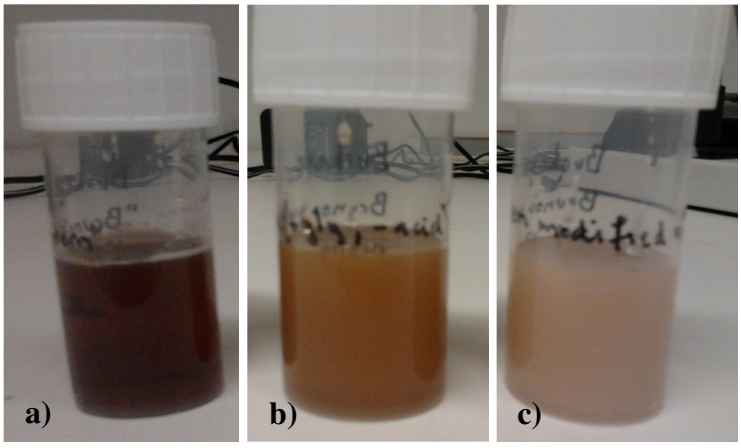

Figure 4.3: Three dissolutions obtained for ~5 % cellulose system by using the same experimental procedure; the difference is the ratio sulphuric acid:glycerol. a) consists of 66 % acid, 26 % glycerol, and 3 % water; b) of 60 % acid, 32 % glycerol, and 3 % water; c) of 58 % acid, 34 % glycerol, and 3 % water. The sensitivity of the system can be established since only a small change in acid and glycerol content affect the appearance so prominently.

Other parameters did not change the stability and solubility as much as the ratio of these two solvents; although the temperature throughout the process of dissolving the pulp was an important factor influencing the result. As stated and illustrated in Figure 4.1, the temperature at which the reaction happened and how the temperature control was implemented easily affected the dissolution. Also observed was the fact that more glycerol seems to be required in the system when more pulp is used in order to achieve stability.

Not only was the acidic solvent system sensitive, the employment of it did not result in any dissolution able to coagulate properly in any of the coagulating baths made up by four different anti-solvents respectively. It was thought that despite the appropriate appearance of the solution, the hydrolysis might still have degraded the fibres too extensively. Another theory was that ~5 % cellulose in samples was not an adequate amount to obtain a coagulation film and therefore coagulation tests were performed for dissolutions of higher cellulose content. However, the results of these trials were the same as for ~5 % cellulose dissolution; for most of the solutions nothing could be observed. Hereafter are some deductions listed; the term coagulation refers to substance re-dissolving:

- More acid and less glycerol result in less coagulation, indicating that the hydrolysis and degradation of the fibres is too extensive or that the acid is making the cellulose charged by mechanisms of its sulphuric groups.
- Based on the ~5 % systems, the limit for coagulation to occur is sensitive. For a system consisting of 58 % acid and 34 % glycerol there was coagulation but for 60 % acid and 32 % glycerol consisting system there was no coagulation. It is difficult to compare this result with the optimized conditions since the temperature control varied.
- More pulp resulted in a generally more prominent coagulation, however it should be noted that this conclusion is only based on visual inspection.

For systems of similar acid:glycerol ratio, there was an increase in temperature as more water was added. As sulphuric acid and water is mixed, the following reactions may occur:

$$2H_2SO_4 + H_2O \leftrightarrow SO_3 + H_3O^+ + HSO_4^- \quad \text{a)}$$

$$SO_3 + H_2O \leftrightarrow H_2SO_4 \quad \text{b)}$$

Reaction b) is exothermic during which 88 kJ heat is produced (Prevor, nd). If more water is present in the system, a higher frequency of molecules react and thus more heat is produced.

A ternary phase diagram with axes describing the solvent content was created to give insight to if there could be some correlation with respect to the resulting dissolution. Due to the temperature sensitivity such relationship was difficult to derive. Even though the trials for higher cellulose content was unsuccessful, they was thought to give some insight to if there might be any linear association between results obtained for dissolutions having different cellulose content and forecast the formula needed to produce the spin dopes required for spinnability testing. Unfortunately, no information could be derived.

4.3 Rheology profile of the optimized cellulose solution

For the oscillation test performed during rheology measurements, the obtained graph for the optimized dissolution is presented in Appendix Figure A4. The G values give knowledge about how solid or liquid the sample is, and from the graph displaying how they vary depending on the frequency it is possible to determine their state. As can be observed, the two curves representing the solid and liquid state respectively are not dependent on one another. The G' curve representing the solid state is approximately parallel to the x-axis at a viscosity value close to 0 Hz while the liquid curve of G'' is linearly increasing, indicating a liquid behavior rather than a solid for the solution. At frequency values close to 0 Hz there is an intercept of the two lines. This would imply that the sample simultaneously displays a liquid and a solid behavior. However, this is implausible and the signal is most likely due to noise.

The graphs representing the first flow curve trial can be viewed in Appendix Figure A5 and A6. As described, this trial consisted of three intervals when shear stress was applied in the first and third; the latter being the only one from which data points were collected. The viscosity stays at a constant value throughout the measurement regardless of how much shear stress is applied. The dissolution can be concluded not to have a thickening or thinning property and its shearing behavior is similar to that of water implying that the cellulose has dissolved extensively. If there were un-dissolved cellulose present in the sample, intermolecular interactions would have been promoted. When applying a stress these interactions would be disrupted and a shear thinning property of the sample would have been observed. As the sample gets thinner throughout the experiment as more shear stress is applied, the viscosity would decrease continuously. The second trial was performed using only one interval, however the resulting graphs presented in Appendix Figure A7 and A8 has an appearance similar to the third interval of the first trial. Thus, the flow behavior of the dissolution can be confirmed.

Based on these measurements, it would seem as if the sample would be appropriate to use for spin dope production to generate textile fibres. Because of the extensive dissolution there would be a high spin dope yield after filtration, which is desirable. On the contrary, if a lot of un-dissolved cellulose would be present in the sample, a low yield would be obtained due to the low cellulose content after filtration.

4.4 NMRd measurements

The main purpose of the NMRd measurements were to conclude if the cellulose had been degraded to extensively (which might explain the absence of coagulation) and if the glycerol was inert in the system as intended or if it reacted with any of the other components. In this section, the results from these measurements are presented and discussed.

4.4.1 Evaluation of solution quality by NMR

In Figure 4.4 the NMRd measurements derived from the investigation of DP of the dissolved cellulose is displayed. As can be seen in Figure 4.4, the diffusion coefficient, *D*, presented on the y-axis becomes smaller for the 10-hour-old Buckeye sample compared to the fresh one, possibly due to gelation. Also, *D* for dissolved cellobiose is similar to the correlating one of Buckeye thereby demonstrating comparable DP. The two are generally smaller than *D* of cellobiose in D_2O but however relatively similar. The diffusion coefficient of the solvent system only (shown at the chemical shift of 8.5 ppm) is very similar to *D* of dissolved cellobiose and Buckeye respectively. This may indicate that the NMRd signal mainly is dependent on and dominated by the solvent system and not so much on the dissolved cellulose; this possibly due to the extensive degradation of cellulose, in combination of gelation or high rigidity of the cellulose chains not degraded.

From Figure 4.4, it can be concluded that the cellulose detected in the optimized solvent system has been degraded to a molecule of approximately similar size as cellobiose. Cellobiose has a DP of 2, implying the dissolved Buckeye pulp to have a DP close to this value. The diffusion coefficient of freshly dissolved Buckeye sample is higher than for the 10-hour-old sample. A higher *D* would denote a smaller molecule, thus the cellulose chain in the old sample would be longer than in the fresh one and degradation would have been reversed. This is probably not the case. The explanation to this observation may be that the dissolution changed drastically, *e.g.* it became less viscous and darker in color, which would affect its properties and the interaction between cellulose and the solvent system. If a high value of *D* is detected, it may also be due to the fact that only a fraction of the sample has given rise to the signal, *i.e.* the fraction representing shorter cellulose fragments that have been degraded by the acid to oligomeric cellulose. Longer cellulose chains may have been gelled instead.

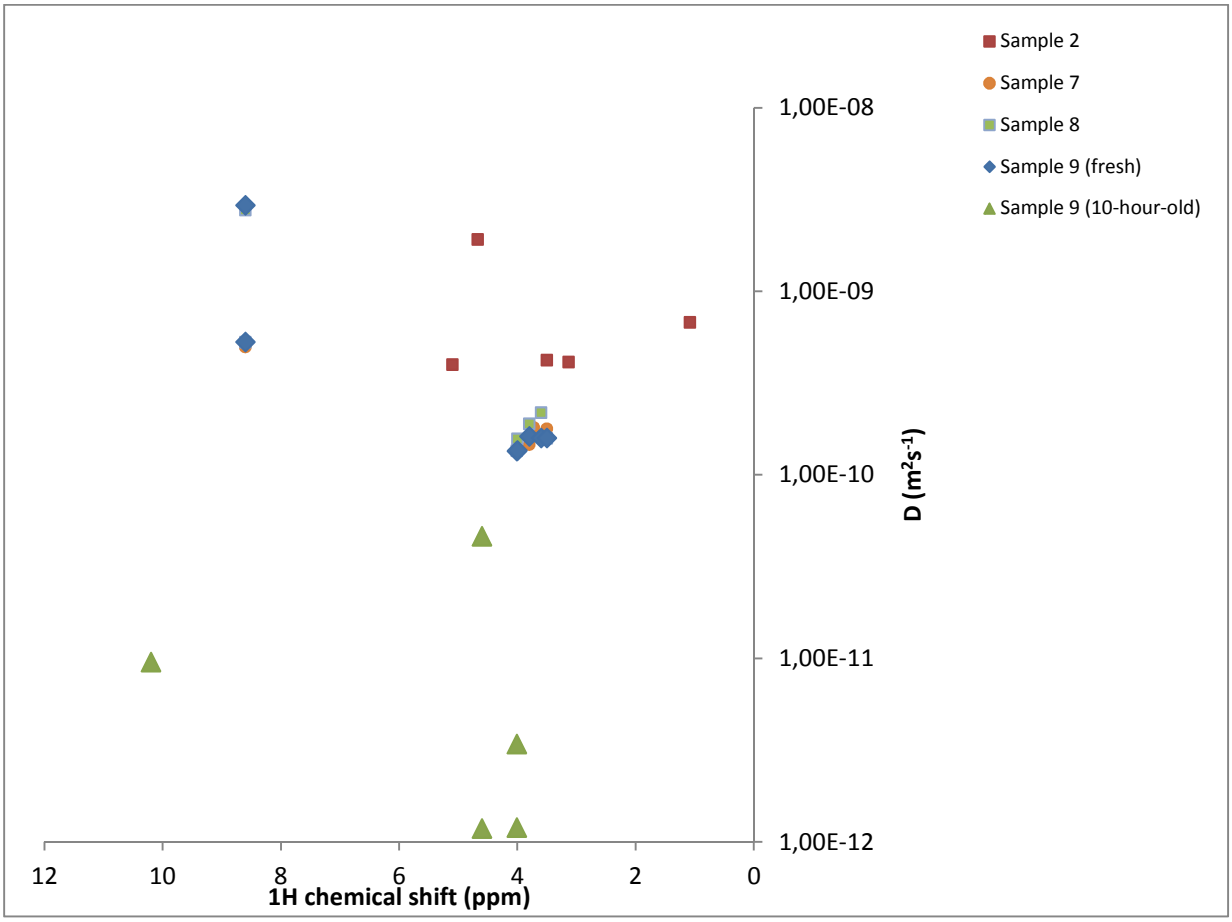

Figure 4.4: A plot of self-diffusion coefficients obtained from the NMRd measurements for the samples consisting of: 5 % cellobiose in D_2O (sample 2), the solvent system only (sample 7), cellobiose dissolved in the solvent system (sample 8), and Buckeye dissolved in the optimized solvent system (sample 9). As can be seen, the old Buckeye sample has a smaller coefficient than the fresh.

To study the difference in *D* of cellulose from different sources and thereby cellulose of different DP, Avicel and Buckeye was dissolved in EMIMAc and investigated by NMRd (see Figure 4.5). As EMIMAc is a good solvent for cellulose, it was expected to show a difference in the *D* although these values cannot be compared with the *D* of cellulose dissolved in the sulphuric acid, due to different viscosity of the solvent and also the experiment for EMIMAc samples were run at 40 ℃, compared to 30 ℃. From these measurements, Buckeye can be concluded to have dissolved to a smaller molecule than Avicel in this particular solvent. This is most likely not related to DP, but rather due to contamination in the Buckeye pulp or the shorter cellulose chains remaining from the pulp cook.

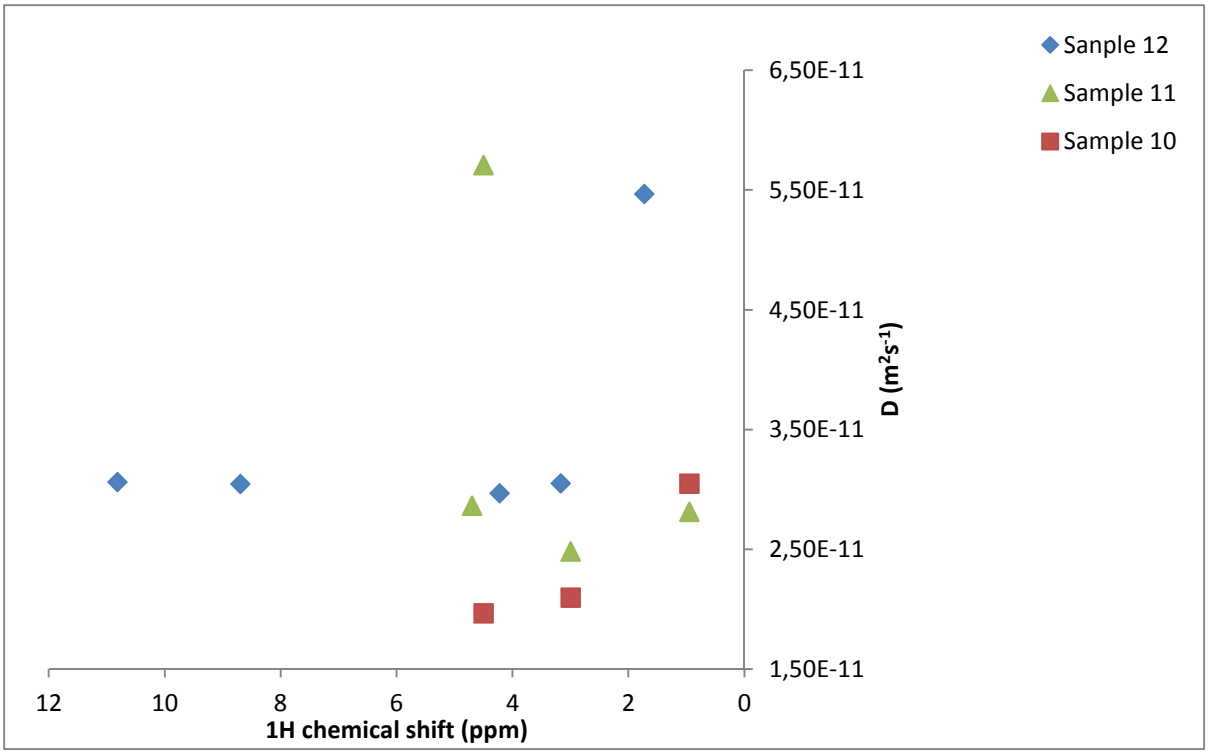

Figure 4.5: Plot of the results obtained from the NMRd measurements at 40 °C describing the diffusion coefficients for the samples consisting of: EMIMAc (sample 12), Buckeye and Avicel dissolved in EMIMAc respectively (sample 11 and 10). The diffusion coefficient is commonly smaller for Avicel than Buckeye, thus Buckeye has been dissolved to a smaller molecule.

Both temperature and viscosity of solvent influences the *D* as can be seen in the Stokes-Einstein relationship (Equation 5). The diffusion coefficients of the two cellulose sources are approximately similar, indicating comparable signal contribution in ionic liquid, *i.e.* longer cellulose chains give shorter T_2 relaxation which is more difficult to record signal from and leads to loss in signal from longer cellulose chains. As expected, when coagulation was tested in a coagulation bath made up by the anti-solvent of water, something gel-like and collectable was forming and thus the cellulose was regenerated.

The diffusion coefficient detected of Buckeye was $2.5*10^{-11}$ m^2/s when dissolved in EMIMAc and correspondingly slight smaller than $5.0*10^{-10}$ m^2/s when dissolved in the optimized acid solvent system. These values cannot be compared without compensating for the temperature difference and the viscosity of the solvents. The lack of coagulation for Buckeye dissolved in sulphuric acid, glycerol, and water may though be due to the too extensive degradation exerted by the acid based on the results. Unfortunately NMR cannot show this in this rather short diffusion study.

4.4.2 Establishment of glycerolysis occurrence

In Figure 4.6, the 1D NMR spectrum of glycerol in D_2O at 30 °C is presented.

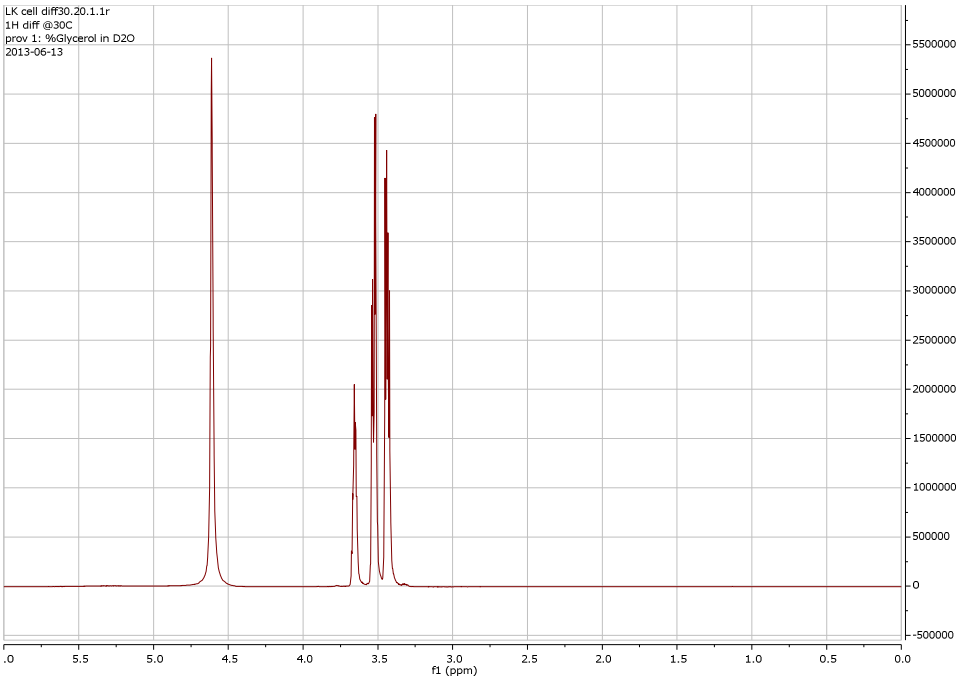

Figure 4.6: 1D ^1H NMR spectrum of glycerol in D_2O.

In Figure 4.7, the correlating spectrum of sulphuric acid in D2O at 25 °C is displayed.

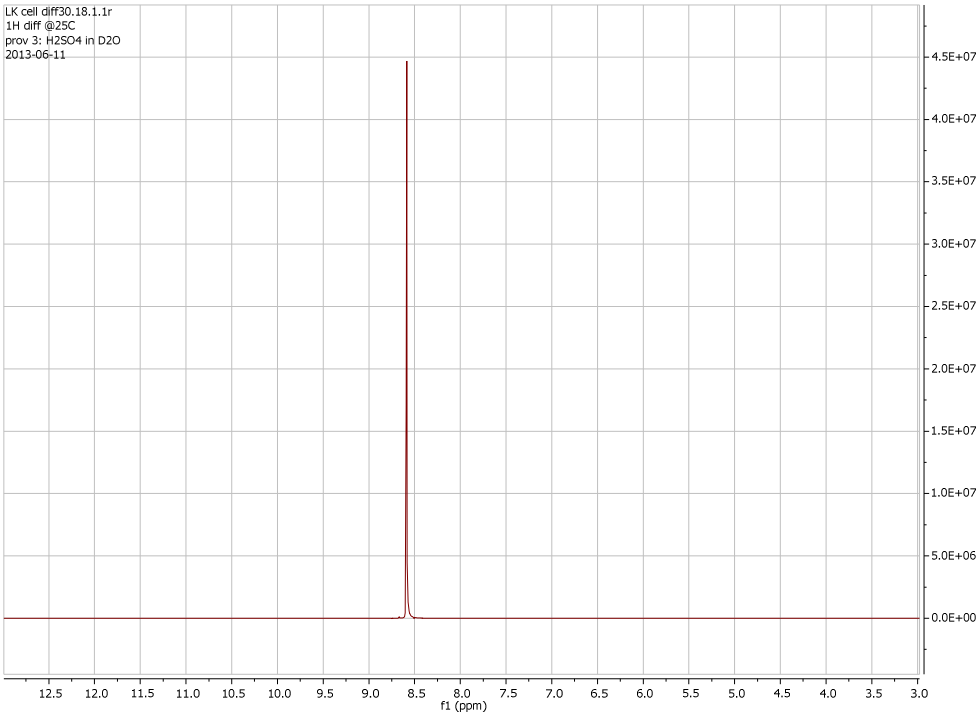

Figure 4.7: 1D^1H NMR spectrum of sulphuric acid in D_2O.

The two components of the solvent system were mixed and studied correspondingly by NMR at 30°C and presented in Figure 4.8.

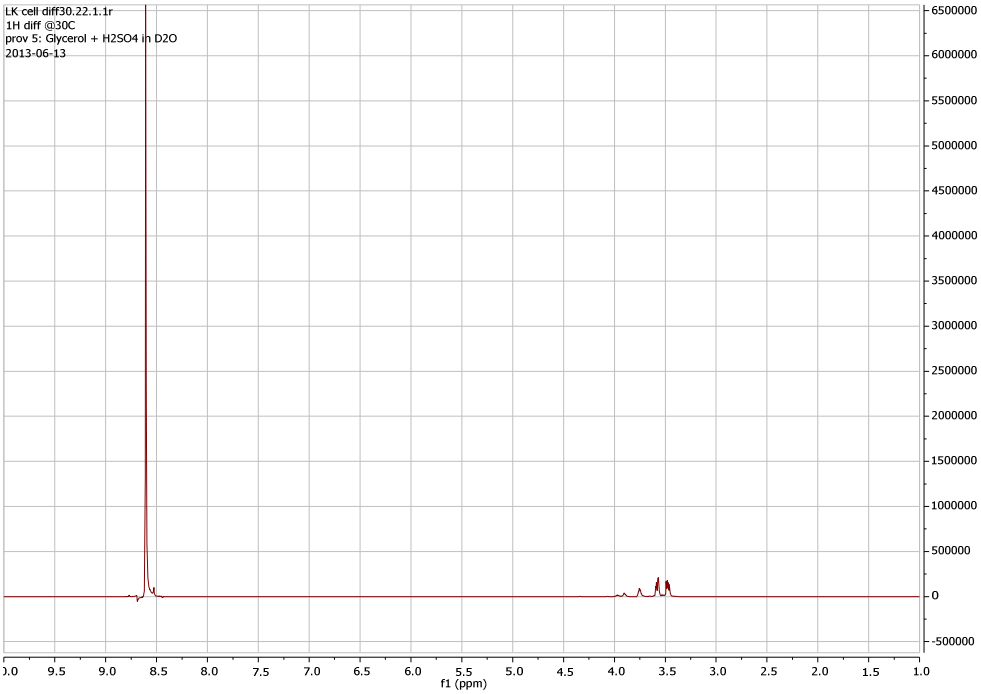

Figure 4.8: 1D ^{1}H NMR spectrum of glycerol and sulphuric acid in D_2O.

The peaks observable at circa 4.0-3.5 ppm was investigated further and a close up is presented in Figure 4.9.

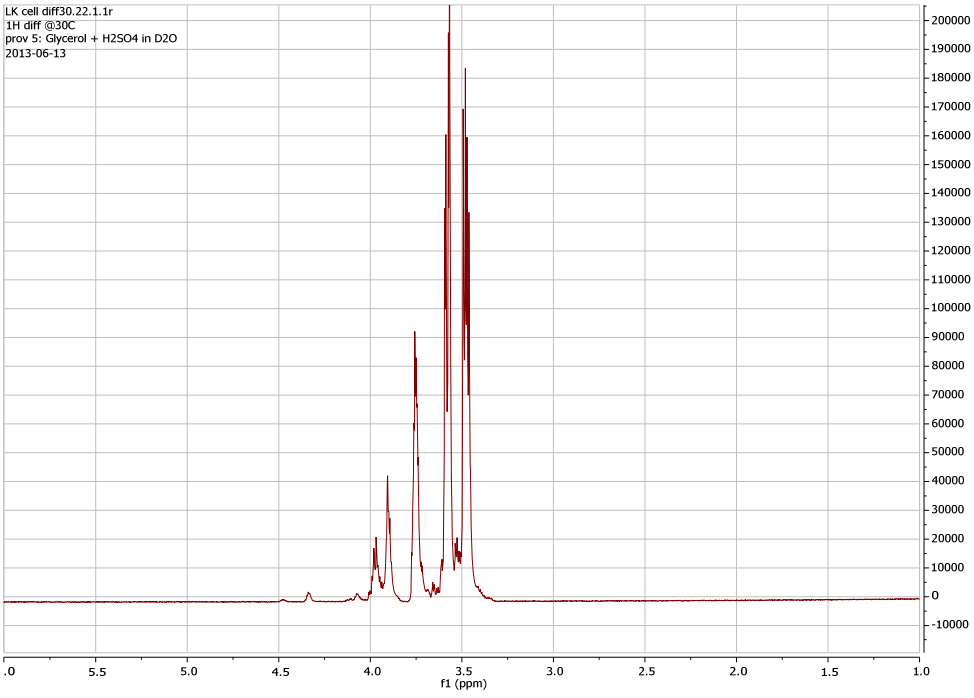

Figure 4.9: 1D^{1}H NMR spectrum of glycerol and sulphuric acid in D_2O, a close up of the region 6.0-1.0 ppm in Figure 4.8.

As stated, the glycerol is intended to function as an inert stabilizer and should not participate in any reaction. However, this may have occurred and could thereby have affected the result of the dissolving process. For the sulphuric acid, when comparing Figure 4.7 and Figure 4.9 the corresponding peak is situated at about 8.5 ppm in both spectra. The temperature difference of 5 °C was considered to be negligible based on comparisons made of glycerol spectra at 25 °C and 30 °C for which no difference in NMR signal appearance could be observed. For glycerol, comparison between Figure 4.6 and Figure 4.9 make a spectral difference derivable. The three peaks close to 3.5 ppm have changed in appearance and additional peaks have emerged and others have disappeared.

A spectrum displaying cellobiose dissolved in the solvent system was also collected and is presented in Appendix Figure A9. As in Figure 4.9, it displays a close up of the region ranging from 6.0-1.0 ppm. The acid as before gave rise to a peak at 8.5 ppm. Figure A9 is comparable to Figure 4.9, confirming the hypothesis that the cellulose present in the system becomes degraded to such a high extent that the NMR signal is dominated by the solvent system. The diffusion coefficient of glucose and sulphuric acid was measured both respectively and mixed, the obtained data is displayed in Appendix Figure A10. The diffusion coefficients differ especially for the glycerol in sulphuric acid, which most likely is due to a change in viscosity of the highly acidic solvent.

As stated, glycerolysis happens if glycerol reacts with the cellulose and the acid present function as a catalyst. However, for the samples studied the most obvious reaction taking place is between the acid and the glycerol preliminary. When cellobiose is present, the NMR spectrum is approximately identical to the corresponding spectrum without cellobiose. The signal thus derives mostly from the solvent system and not from the cellulose source of cellobiose. Thus, the establishment of glycerolysis occurrence could not be fully conducted since the reaction taking place was not characterized as the expected change in chemical of the substituted cellulose would appear around 3.6 ppm, which is a region in the spectrum covered with signals both from un-substituted cellulose and pure glycerol.

5. CONCLUSIONS AND FURTHER WORKS

Referring to the purpose; the aim of this project was to find and optimize the reaction parameters influencing the result of the cellulose dissolution in a solvent system consisting of sulphuric acid, glycerol, and water. The following was ought to be determined:

- Preparation of pulp prior to solvent system introduction – the method established to be most suitable was the dry milling approach.
- Composition of solvents – the solvent system successful (4.6 % cellulose) was 66 % acid, 26 % glycerol, and 3.4 % water.
- Reaction time – the dissolving trials was conducted during 20-30 min for most experiments and evaluated thereafter. By visual inspection, the optimized conditions required approximately 15 min to dissolve the pulp sufficiently.
- Reaction temperature – the reaction temperature needed to be lowered to 30 °C for the optimized system. The reaction needed to be temperature controlled by the use of a cooling system in order for the temperature to return to its original level. This was desired to be achieved fast to improve the stability.
- Cellulose concentration – the only cellulose concentration that could be dissolved efficiently was ~5 %. Adequate dissolution was not obtainable for system having higher cellulose content.

Since not high enough cellulose content in systems could be dissolved, it was not possible to produce the spin dopes (≥ 10 % cellulose) intended to be used for spin ability evaluation. It was neither achievable to coagulate the optimized system properly in a coagulation bath using any of the anti-solvents tested. However, the rheology measurements indicated that the dissolution would be appropriate for spin dope production based on the flow behaviour of the dissolution containing ~5 % cellulose. From the NMRd results, it was suggested that Buckeye cellulose becomes degraded in the acidic solvent system compared to a system consisting of ionic liquid. This may be the explanation to why coagulating the dissolution is not possible. The glycerol present in the system is most likely not inert and reacts with sulphuric acid by unknown mechanism that could be further studied to elucidate the reaction when mixing the two components. Based on all the facts known about the acidic system and its behavior, it was concluded too sensitive to progress with as a candidate for cellulose dissolution and textile fibre regeneration.

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APPENDIX

*Table A1: All trials performed for solvent system optimization. The trials denoted with * were trials performed using a percentage interval, with the number to the left being the starting composition and the number to the right the composition obtained at termination of the dissolution. The trials are listed according to the order in which they were performed.*

Trial no.	Cellulose (%)	H_2SO_4 (%)	Glycerol (%)	Water (%)
1	4.79	41.31	53.40	0.51
2	4.76	47.46	47.30	0.47
3	4.77	57.01	37.39	0.43
4*	4.97-4.51	58.24-62.07	36.36-33.03	0.43-0.39
5*	4.98-23.44	94.78-75.40	-	0.25-1.16
6	4.98	86.18	8.55	0.29
7	4.97	67.70	26.95	0.38
8	4.97	63.22	31.40	0.40
9	9.92	64.02	25.42	0.64
10	9.51	62.08	27.78	0.63
11*	4.98-3.96	86.21-68.42	8.53-27.29	0.29-0.33
12*	4.98-3.30	67.72-78.56	26.93-17.88	0.38-0.25
13	4.97	77.05	17.63	0.35
14	4.97	81.35	13.35	0.33
15	4.97	83.68	11.03	0.31
16	14.85	56.26	28.00	0.88
17*	15.28-6.76	45.39-20.08	38.38-16.98	0.95-76.26
18	14.29	50.13	33.67	1.90
19	14.85	52.12	31.07	1.96
20	12.04	51.14	35.07	1.76
21	11.92	52.31	33.99	1.77
22	9.94	60.57	27.67	1.82
23	9.92	47.48	40.90	1.71
24	9.93	53.19	35.09	1.79
25	10.21	49.64	36.09	4.07
26	10.20	48.70	36.07	5.03
27	10.21	46.74	36.09	6.97
28	9.99	49.99	32.98	7.03
29	9.99	53.98	29.00	7.04
30	4.98	63.43	29.25	2.35
31	4.98	52.53	40.42	2.07
32	4.98	55.71	37.16	2.15
33	4.98	51.07	38.99	5.03
34	5.00	57.98	31.99	5.03
35	5.00	55.00	31.99	8.01
36	5.00	41.03	39.00	14.98

37	4.60	66.03	25.98	3.39
38	4.58	61.87	29.93	3.61
39	4.60	57.97	33.98	3.45
40	7.00	57.15	33.18	2.67
41	5.00	59.88	31.98	3.14
42	4.60	57.95	33.99	3.46
43	4.60	65.97	25.98	3.45
44	4.60	66.00	25.98	3.43
45	7.00	65.19	25.17	2.64
46	7.00	59.99	30.02	2.99
47	7.00	60.00	30.00	3.00
48	7.03	53.68	37.17	2.11
49	7.02	56.86	33.60	2.53
50	4.60	66.03	26.01	3.36

Table A2: The temperature profiles for all experiments. The temperatures have been rounded to the nearest integer, and the correlating time values state the point at which that temperature was reached. If there were no change in temperature during the rest of the experiment, then it is not listed again (e.g. for experiment 50, the last temperature is 29 °C at 8min. The experiment lasted in total 30 min, however the temperature remained at 29 °C).

Trial no.	Temperature (°C)	Time (min)
1	-	-
2	-	-
3	-	-
4	-	-
5	-	-
6	-	-
7	-	-
8	-	-
9	49→42→38→37→35	0→6→11→15→20
10	79→35	0→20
11	20	0→20
12	20→23→20	0→32→45
13	20	0→20
14	20	0→13
15	20	0→20
16	34	0
17	51	0
18	56	0
19	63	0
20	54	0
21	56	0
22	61	0
23	52	0
24	-	-
25	65	0
26	70	0
27	70	0
28	78	0
29	72	0
30	54	0
31	53	0
32	57	0
33	70	0
34	69	0
35	70→35	0→15
36	70→31	0→15

37	30→32	0→15
38	30→51→32	0→2→15
39	30→52→33	0→3→15
40	30→55→32	0→3→30
41	30→57→31	0→2→30
42	-	-
43	30→43→35→30→29	0→1→5→8→11
44	30→50→53→30→29	0→1→5→7→25
45	30→55→35→30	0→1→7→10
46	23→45→35→30→31	0→4→7→11→22
47	30→50→35→30→31	0→2→8→12→20
48	30→47→35→30→31	0→6→12→15→26
49	30→53→35→30→31→33	0→4→12→19→25→30
50	30→47→35→30→29	0→2→4→6→8

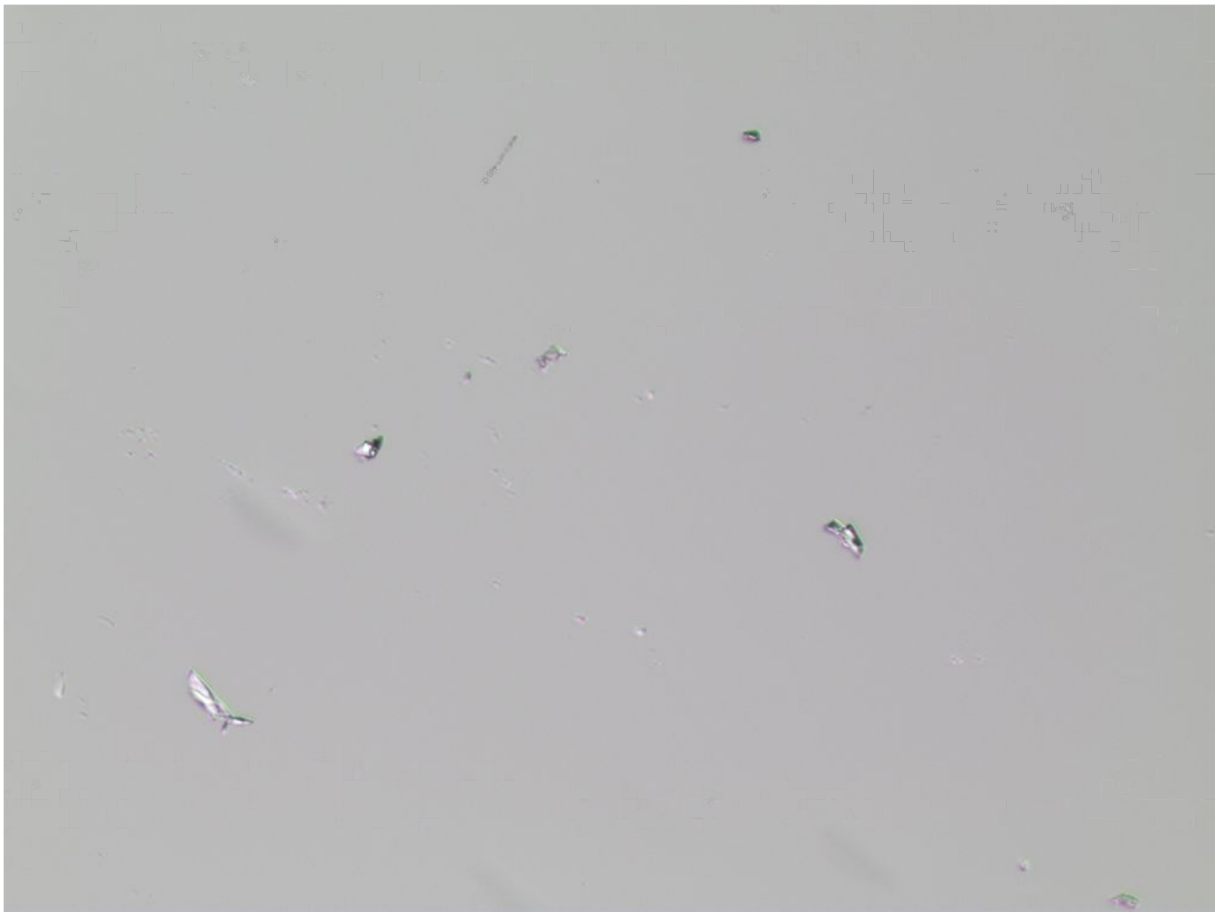

Figure A3: A picture of the dissolved cellulose taken by light microscopy not utilizing polarized light. The solvent system used to dissolve the cellulose was the optimized one, and the temperature control was exerted. The scale is the same as for the other pictures taken, i.e. one cellulose fibre measures approximately 10-20 μm.

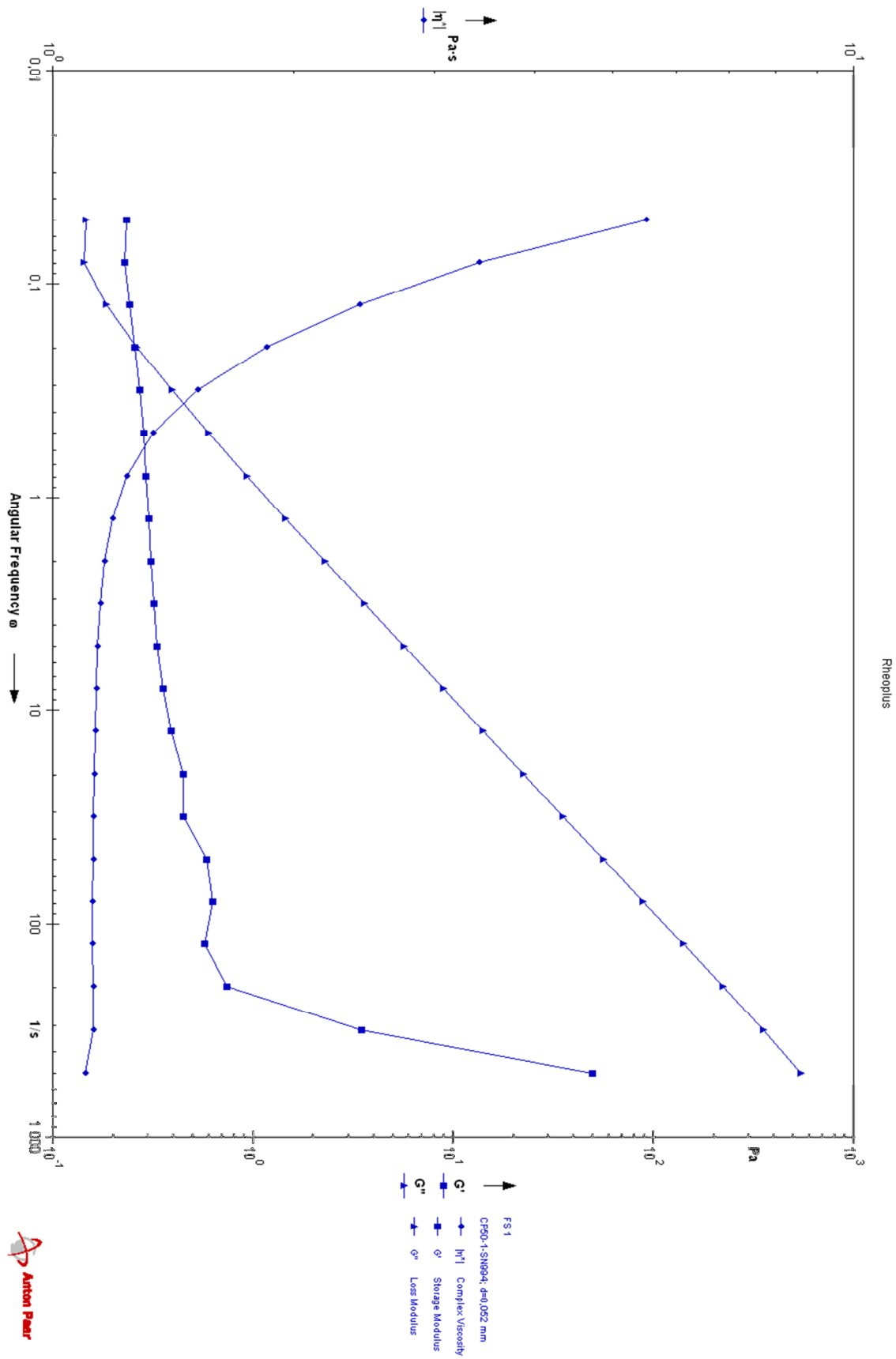

Figure A4: The graph obtained from the oscillation test. The G' curve is approximately parallel to the x-axis at a viscosity value close to 0 Hz while G'' is linearly increasing, indicating a liquid behavior rather than a solid for the dissolution.

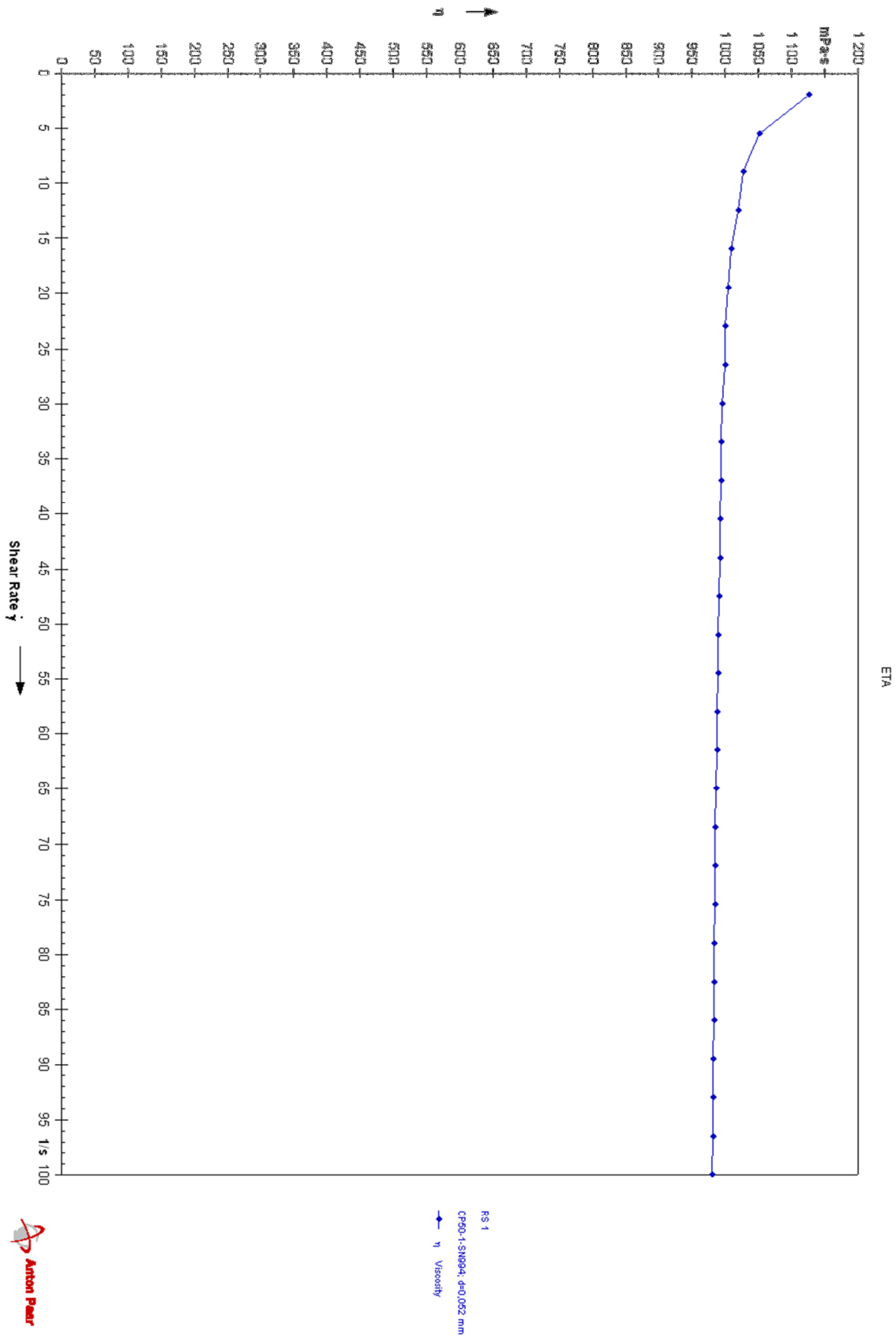

Figure A5: Flow curve from the first trial using interval settings. The curve describes the change in viscosity throughout the experiment; as can be seen there is very little variation.

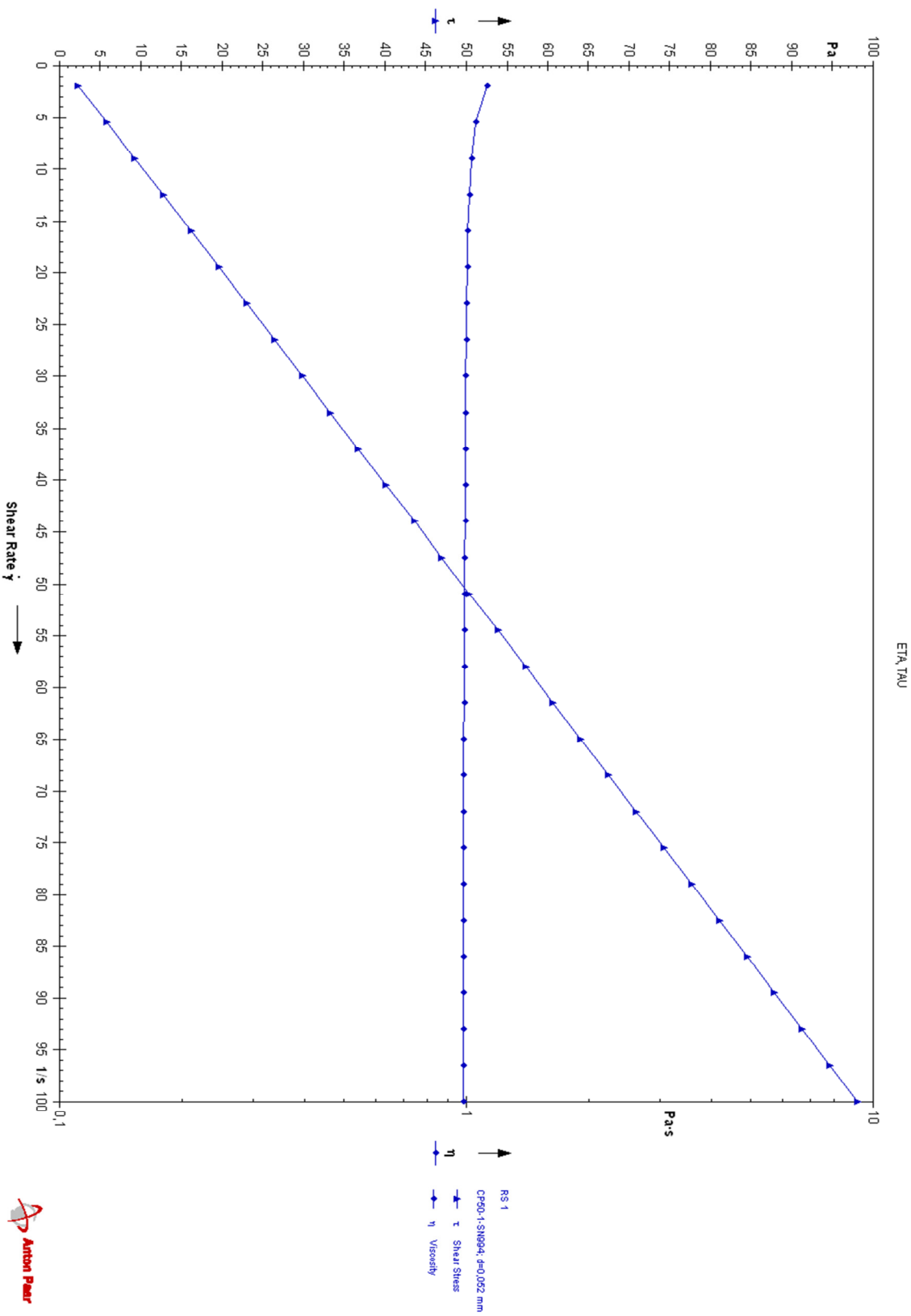

Figure A6: Flow curve from the first trial using interval settings. The curve describes the change in viscosity as a function of the shear stress applied. No dependence between the two parameters can be elucidated.

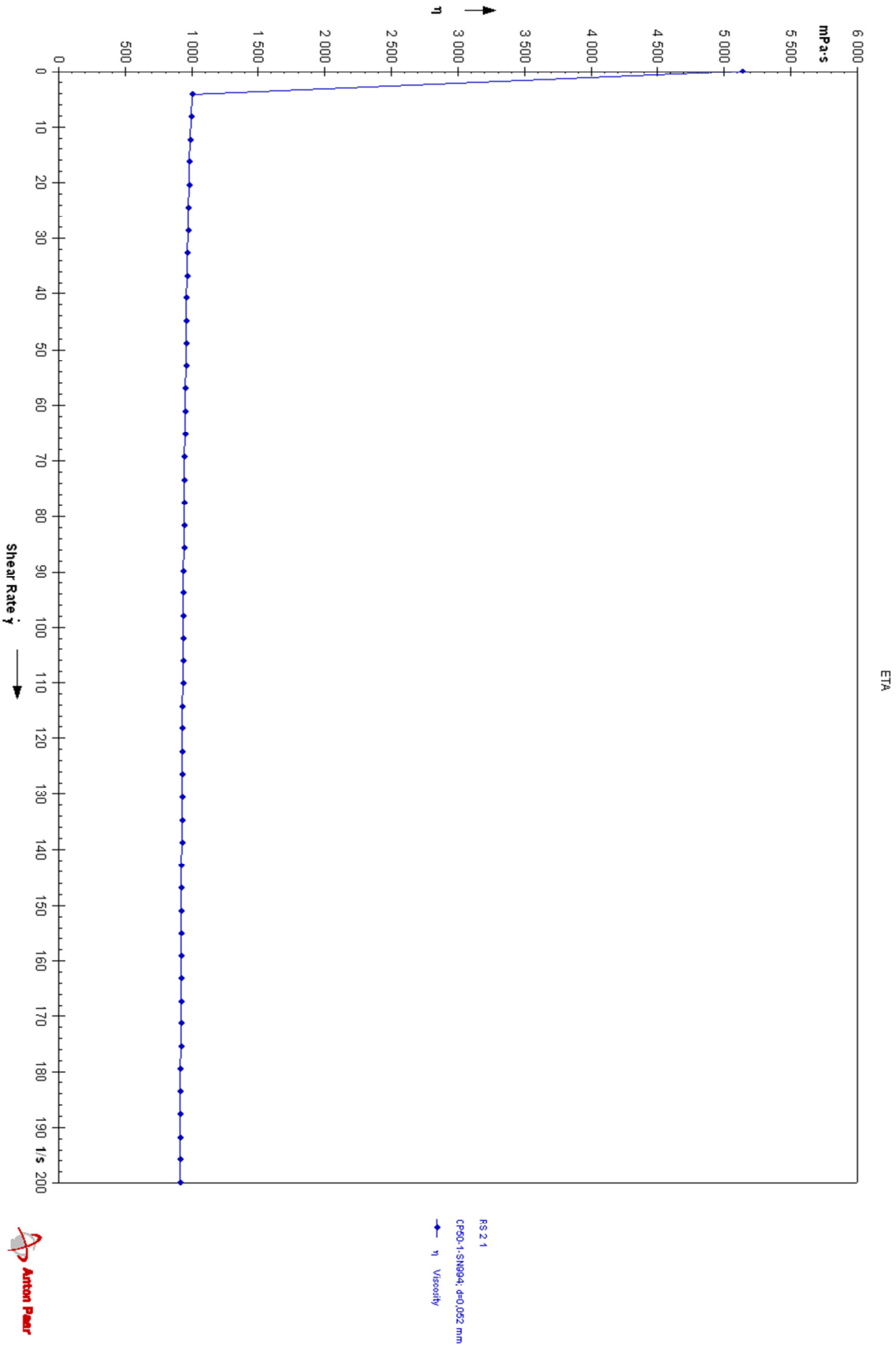

Figure A7: Flow curve from the second trial. The curve describes the change in viscosity throughout the experiment; as can be seen there is very little variation and the appearance is similar to that of the first trial.

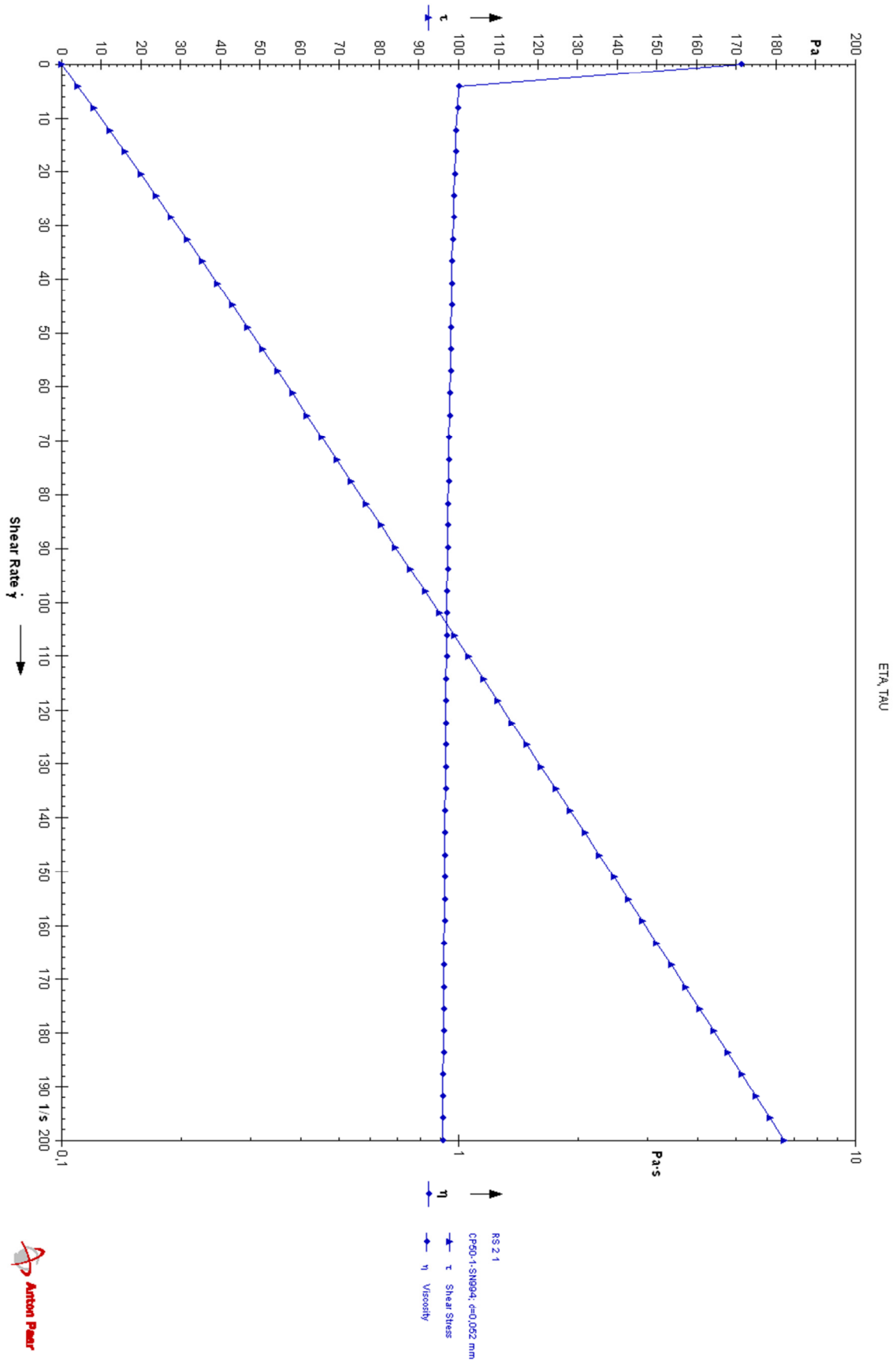

Figure A8: Flow curve from the second trial. The curve describes the change in viscosity as a function of the shear stress applied. No dependence between the two parameters can be elucidated, which correlates to the graph obtained from the first trial.

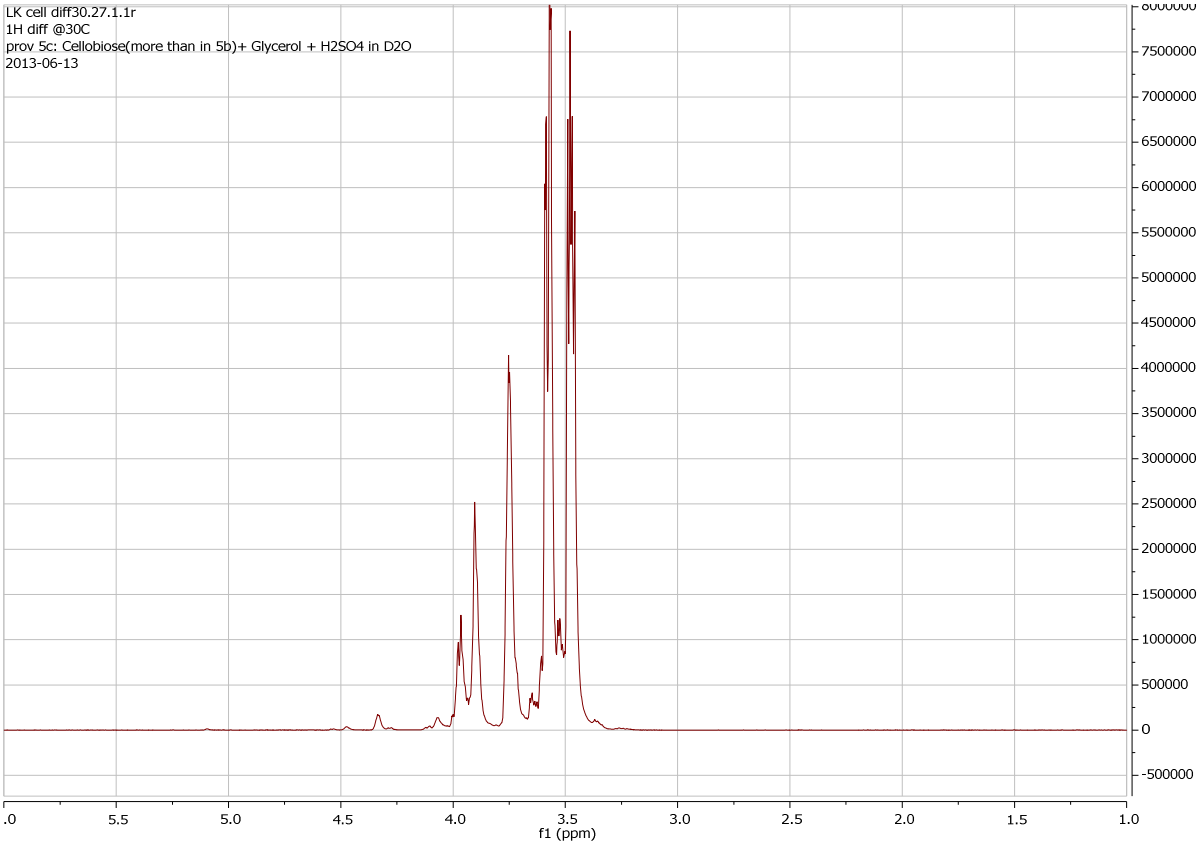

Figure A9: The 1D NMR spectrum of cellobiose dissolved in sulphuric acid and glycerol in D_2O. This is a close up from a spectrum presenting 10.0-1.0 ppm. As in Figure 4.6 and Figure 4.7, a peak derived from the acid was for this sample present around 8.5 ppm.

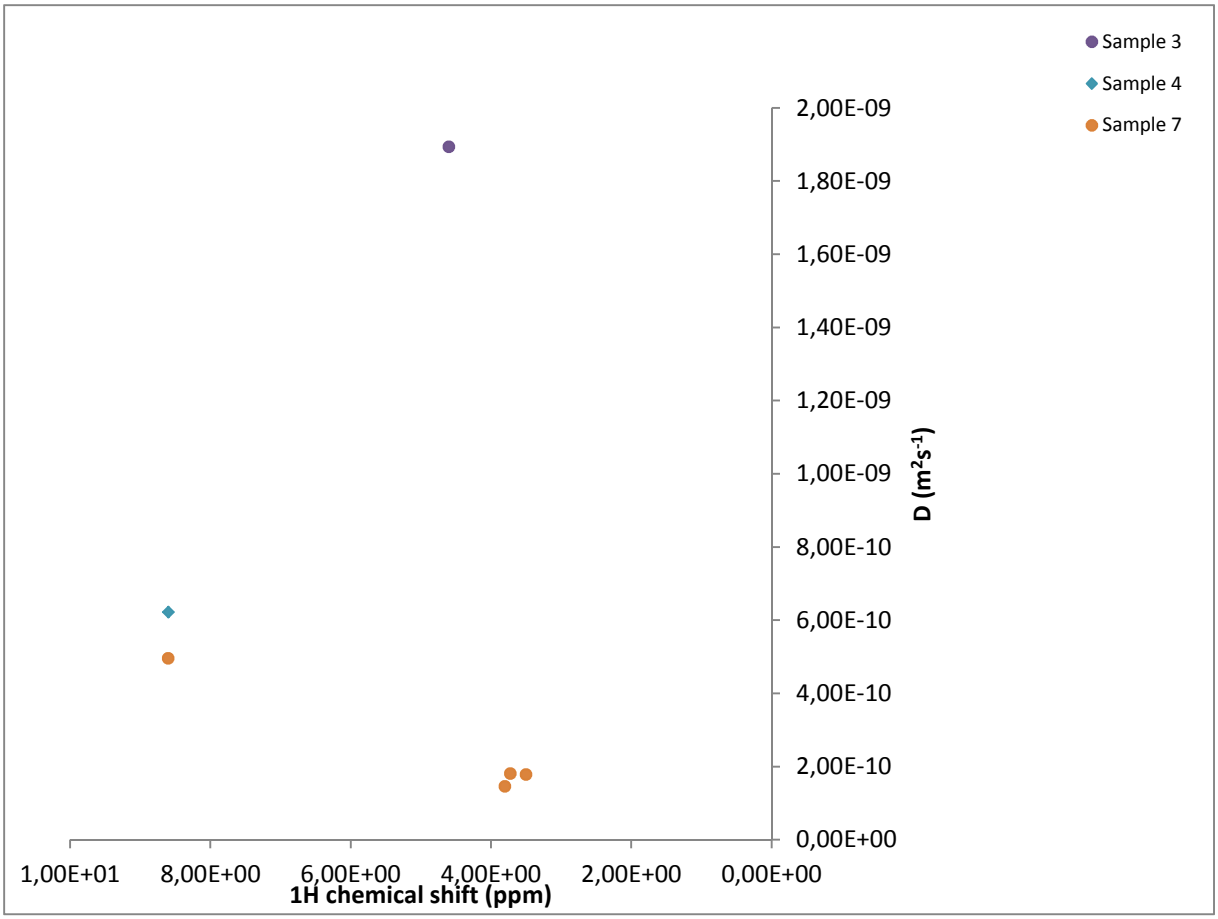

Figure A10: The results obtained from the NMRd measurements describing the diffusion coefficients for the samples consisting of both glycerol and sulphuric acid in D_2O respectively and mixed. The coefficient for both components mixed differs from their respective ones, especially for the glycerol.