THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Cellulose solutions in aqueous hydroxide bases

Combining bases as a means towards improving and understanding dissolution and solution properties

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Department of Chemistry and Chemical Engineering
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Gothenburg, Sweden 2020

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Cover: Image of samples where cellulose has been added to six different solvents. In the three first samples, starting from the left, the cellulose is dissolved. In the three subsequent samples the cellulose is not dissolved, and has sedimented at the bottom.

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Abstract

Cellulose is a renewable and widely available carbohydrate polymer whose utility for mankind only increases as we move towards a circular bioeconomy. Unlike most plastics or metals, it cannot be melted, and therefore, solution processing is important. The dissolution of cellulose is, however, not trivial, and traditional industrial methods must derivatize it in order to dissolve it adequately. Today, a number of direct solvents have been developed with considerable variation in both the structure of the solvent and the mechanism through which dissolution occurs. Despite this, one solvent that was reported as early as the 1920s still holds interest: cold aqueous NaOH solutions. Since the main processes in the pulp and paper industry are water-based, and NaOH is one of the main chemicals used, it is easy to see the attraction behind this solvent. The dissolution capacity and solution properties are however poor and must be improved. In order to design a solvent, the interactions between cellulose and the solvent as well as the interactions between cellulose molecules needs to be understood.

Therefore, the purpose of this thesis has been to improve understanding for interactions governing cellulose dissolution and behaviour in NaOH(aq) and other aqueous solutions of hydroxide bases. In order to achieve this, cellulose dissolution at low temperatures in an aqueous solution of NaOH, combined with selected quatenary ammonium hydroxide bases, tetramethylammonium hydroxide (TMAH) and benzyltrimethylammonium hydroxide (Triton B), as well as urea, have been investigated. The impact of different solvent combinations on the maximum dissolution capacity of cellulose and the rheology of the solutions were also investigated. The structure of the solvents was studied using spectroscopic and calorimetric methods. It was found that by combining hydroxide bases in an aqueous solution, the dissolution capacity and stability of the solution was improved and the effect was comparable to the addition of urea. The resulting solution properties depended on the base pair employed, probably due to a difference in contribution of hydrogen bonding versus van der Waals interactions, which in turn determines such properties as the temperature stability of the solution.

Keywords: cellulose; dissolution; solvent; aqueous; NaOH; quatenary ammonium hydroxide

List of Publications and presentations

This thesis is based on the following papers:

Paper I: **Dissolution of cellulose using a combination of hydroxide bases in aqueous solution**
Beatrice Swensson, Anette Larsson, Merima Hasani
Cellulose, 2020, 27, 101-112.

Paper II: **Probing interactions in combined hydroxide base solvents for improving dissolution of cellulose**
Beatrice Swensson, Anette Larsson, Merima Hasani
Manuscript.

Part of the work has been presented by Beatrice Swensson at:

The Treesearch Progess conference (oral presentation)
Norrköping, Sweden, 8-9 May 2019

The 6th EPNOE International Polysaccharides Conference (oral presentation)
Aveiro, Portugal, 21-25 October, 2019

Contribution report

Beatrice Swensson's contribution to the papers presented in this thesis is as follows:

Paper I: Designed and carried out all of the experimental work with the exception of the NMR-experiment, which was performed with the help of the Swedish NMR-centre and interpreted by the main supervisor, Merima Hasani. Interpreted the results and wrote the article with support from Merima Hasani and co-supervisor Anette Larsson.

Paper II: Designed and carried out all of the experimental work. Interpreted the results and wrote the article with support from main-supervisor Merima Hasani and co-supervisor Anette Larsson.

Contents

1 Introduction to the thesis

Cellulose is one of nature's building blocks that provide strength to the cell wall of plants and it is therefore an abundant resource. It is also renewable and strong, while still being light, and it is therefore an excellent raw material if we utilise it properly and source it responsibly. In Sweden, 70 % of the country is covered with forest, and the Swedish forest industry is one of the world's largest exporters of pulp and paper [1]. The traditional products from pulp are different types of paper, cardboard, and textile fibers. While some products will continue to be relevant in the future, because of online sales increasing the need for packaging and an increasing world population that increases our textile consumption, other products, such as newspaper have already declined significantly. New research has come up with new products and applications, such as hydro- and aerogels, barrier films, or new types of textile fibers. There is a desire to re-shape or derivatize cellulose for many of these applications, but since it degrades before it melts, it can not be processed in the same way as traditional plastics or metals. The dissolution of cellulose, can instead, be utilised to process and re-shape it or to derivatize it under homogeneous reaction conditions. The dissolution of cellulose can also be important for certain analytical methods, such as size exclusion chromatography or intrinsic viscosity for determination of molecular sizes, or for solution NMR spectroscopy for investigating chemical structures and interactions.

There is a need for a range of solvents for cellulose to meet these demands; some must produce stable solutions without degrading the cellulose, while a high dissolution capacity might be important in industrial processes. It is, however, not trivial to understand the mechanism and driving force behind cellulose dissolution, but it is important in order to consciously develop and improve dissolution-based processing and applications. This thesis deals with water-based solvents for cellulose where the objective is to further understand what limits and what drives dissolution of cellulose in basic aqueous solutions, and to use this knowledge to develop and improve such water-based solvents, with a special focus on the cold NaOH(aq) system. In order to elucidate the role of the cation and additives in these systems, a broad comparison of several hydroxide bases, such as tetramethylammonium hydroxide, as components in NaOH(aq) have been made. The most interesting candidates were further investigated in terms of molecular interactions, flow properties, and dissolution capacity. Urea, as the most common additive, was included in order to investigate the action of urea in comparison to a base with hydrophobic properties.

2 Cellulose

Cellulose is a linear and unbranched polymer consisting of repeating units of β-1,4-linked D-glucopyranose units. Each cellulose chain has two odd ends: one non-reducing end(*in Figure 2.1) and one reducing end that can ring-open to form an aldehyde(** in Figure 2.1). Cellulose is mainly found in the cell wall of plants and although there are other sources of cellulose, such as bacteria, the main sources are cotton seed hair and wood. Cellulose co-exists in wood with lignin and hemicellulose, and the liberation of cellulose from the wooden matrix has certain consequences for its structure, such as reduced chain length and the introduction of oxidised groups. The cellulose chains in the native form can reach up to ca 10 000 repeating units, but this number is typically closer to 2000 units after pulping. Along the chains there are intramolecular hydrogen bonds between the hydroxyl group on the C6 and the C2' and between the oxygen in the ring and the hydroxyl on the C3'. These bonds contribute to the stiffness of the chain, where the elastic modulus has been reported to be as high as 138 GPa [2].

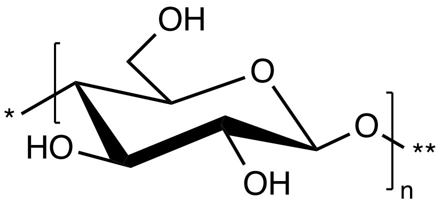

Figure 2.1: The structure of the repeating unit of cellulose, the anhydroglucose unit

2.1 The hierarchical structure of cellulose

All of the hydroxyl groups in the cellulose glucose unit are arranged in an equatorial position, which also allows them to create an intermolecular network of hydrogen bonds. The cellulose chains in the native structure of cellulose are arranged parallel to each other, with an intermolecular bond between the hydroxyl on C6 and that of C3" on an adjacent chain, as illustrated in Figure 2.2 [3]. There is no such possibility for hydrogen bonding in the axial direction of the pyranose ring, and instead, the cellulose chains interact via van der Waals forces. This allows the chains to stack into a crystalline structure called cellulose I, with the less polar regions of the pyranose rings on top of each other. The cellulose chains in these sheets pack into elementary fibrils with a diameter of 3-4 nm that are not entirely crystalline, there are regions which are more disordered, and these regions have a higher reactivity and accessibility. These fibrils then bundle into macrofibrils with a diameter of 10-25 nm and exist in the wooden matrix [4].

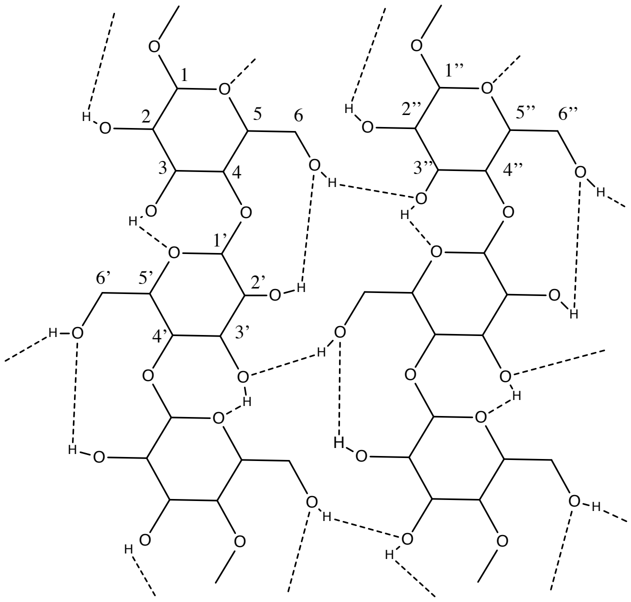

Figure 2.2: Illustration of the hydrogen bonding in and between native cellulose chains

There are several other crystal structures which cellulose can adapt besides Cellulose I, the most common being the cellulose II crystal structure, where the chains are arranged anti-parallel to each other. Cellulose can be converted from cellulose I into cellulose II through several different treatments, e.g. by dissolving and regenerating it in certain solvents, subjecting it to alkaline conditions without dissolving it (mercerisation) [5], through acid hydrolysis [6], or through ball milling it when wet [7]. The transformation from cellulose I to cellulose II is irreversible, and has been attributed to the cellulose II crystalline form being thermodynamically more stable. In cellulose II, the intramolecular hydrogen bond between the oxygen in the ring and the C3’ hydroxyl remains, but that between the C6 and the C2’ hydroxyl groups has not been formed, leading to a significant reduction in elastic modulus compared to cellulose I [8]. There are, however, several possibilities for intermolecular bonding in cellulose II. A simplified description of these hydrogen bonds is that the main ones occur between the hydroxyl groups on: the C2 and C6’, the C6 and C6’, and the C2 and C2’ of adjacent chains [9].

2.2 Solubility of cellulose

The solubility of cellulose in a given solvent depends on both the entropic and enthalpic contributions that favour the dissolved state. One example of a parameter which will effect the entropy gain of dissolution is the chain length. With decreasing chain length the entropy gain will increase and therefore it is easier to dissolve shorter cellulose chains. The enthalpy contribution is mainly determined by the bonds and interactions between cellulose and the solvent, which need to overcome the attractive interactions between cellulose chains. It is however not easy to determine if dissolution is hampered by entropic or enthalpic means. Cellulose is for example insoluble in water and other common organic solvents. It has been suggested that it is the amphiphilicity of cellulose which is the cause of the insolubility of cellulose in water, due to the so-called hydrophobic effect [10]: there is a strong network of hydrogen bonds between water molecules in bulk, and this is broken around the less polar (more hydrophobic) pyranose ring as it can not participate in hydrogen bonding. The water molecules situated in this area might suffer both from fewer hydrogen bonds (enthalpic punishment) and be more restricted in their mobility (entropic punishment), leading to favourable interactions if the cellulose chains stack and exclude water from the hydrophobic surface. If the hydrophobic (assembly) effect is driven mainly by a change in enthalpy or entropy is debated and might be dependent on the size of the hydrophobic solute [11].

In general, dissolution of cellulose is often achieved in two ways: using direct solvents or through derivatization of cellulose. The latter is sometimes referred to as "indirect solvents" but it is more of a method than a solvent category. It refers to the method of derivatizing cellulose into a more easily soluble cellulose derivative which, after dissolution, is regenerated into cellulose by cleaving off the attached side groups. The derivatization approach often requires more process steps than direct dissolution. The interest for utilizing solvents for cellulose has grown a lot over the last two decades , as can be seen by the number of articles published on the subject (see Figure 2.3). There are a number of cellulose solvents known today, such as ionic liquids (ergo BMIMCl [12]) [13], DMAc/LiCl[14], DMSO/TBAF[15] and NaOH/urea(aq)[16] to name a few. The focus of this thesis is on investigating cellulose solutions in water-based solvents, and they will be described in more detail in the following chapter.

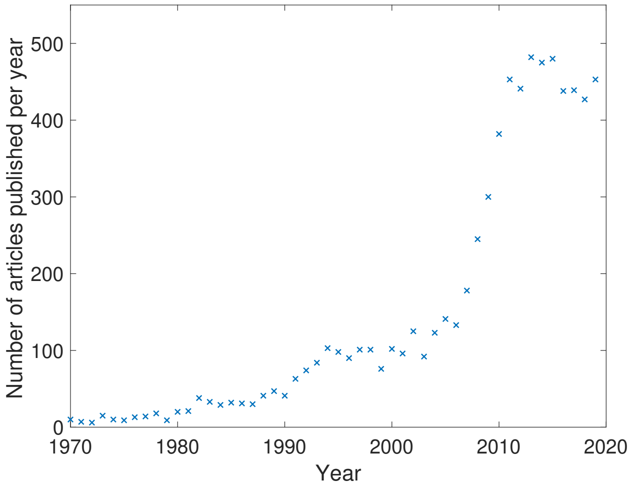

Figure 2.3: Number of articles published per year, indexed in Scopus related to dissolution of cellulose (when searching for "cellulose and dissolution")

3 Water-based solvents for cellulose

3.1 Derivatizing solvents

Due to the challenging solubility and accessibility of the cellulose structure, the oldest industrial processes have relied on derivatising approaches and these are still the dominating ones. The main industrial process where cellulose is dissolved is the Viscose process, and it has been in operation since the start of the 20th century. The main bulk application is textile fibres but specialty qualities used for example for tire-cord are also produced. This is a derivatizing approach, involving several steps where the main ones are: alkalization of the pulp in NaOH(aq) solution, followed by pressing, shredding and ageing of the slurry before the Na-cellulose is reacted with carbon disulfide into cellulose xanthate which dissolves in NaOH(aq) and forms a dope. This dope is then ripened and filtered before being spun in an acid bath containing sulphuric acid. This illustrates the many steps required to ensure a homogeneous solution. While modern processes recover the carbon disulfide, NaOH and sulphuric acid are spent and large amounts of Na_2SO_4 are produced as a by-product [17].

$$C_6H_{10}O_5 + NaOH \rightleftharpoons C_6H_9O_4 - O^-Na^+ + H_2O$$

$$C_6H_9O_4 - O^-Na^+ + CS_2 \rightleftharpoons C_6H_9O_4 - O - CS_2^-Na^+$$

$$2C_6H_9O_4 - O - CS_2^-Na^+ + H_2SO_4 \rightleftharpoons C_6H_{10}O_5 + Na_2SO_4$$

The carbamate process is another derivatizing process, similar to the traditional Viscose process, where cellulose is reacted with urea at elevated temperatures and pressure, but there are not any major industrial applications for this process so far [18].

3.2 Non-derivatizing direct solvents

There is a bright future for direct solvents, where the Lyocell process is one that has been commercialized since the late 1980s. In this process, cellulose is dissolved at elevated temperatures and pressure in a melt of the monohydrate of N-methylmorpholine-N-oxid(NMMO). There are two stable hydrates of NMMO, the monohydrate and the NMMO·2.5 H_2O hydrate, but the latter can not dissolve cellulose. This might be because the positions available for hydrogen bonding are already taken up by water [19]. The role of water in this solvent seems only to be to decrease the melting point of the hydrate, which is probably why this is not always classified as a water-based solvent. A considerable advantage of this solvent is that it is fully recyclable, whereas a disadvantage is that there is a risk for runaway side reactions. This risk can be counteracted through the addition of a stabilizer.

Another class of water-containing and direct solvents are sometimes called the aqueous inorganic complexes, these all consist of a transition metal hydroxide salt dissolved in aqueous solutions of amines. Interestingly, although the deprotonation of cellulose in alkaline solutions is debated, it is believed that cellulose is deprotonated in these types of complexating solvents (to different extents depending on the solvent in question). Fuchs *et al.* studied cyclodextrins in aqueous solutions of copper hydroxide and lithium hydroxide, and found that the carbohydrate was deprotonated and formed a chelate complex with the copper(II) ion [20]. This was later investigated by Burchard *et al.* through other model substances of cellulose (anhydroerythriol and methyl-4-O-methyl-β-D-glucopyranoside) dissolved in Cuoxam(copper(II) hydroxide in aqueous ammonia) and Cuen (copper(II) hydroxide in aqueous ethylenediamine). Using spectral photometry, they found that both model substances formed doubly deprotonated complexes at elevated pH. Consequently, they suggested that cellulose in Cuoxam forms polymeric metal complexes where the hydroxyls on C2 and C3 on cellulose are deprotonated as in Figure 3.1.

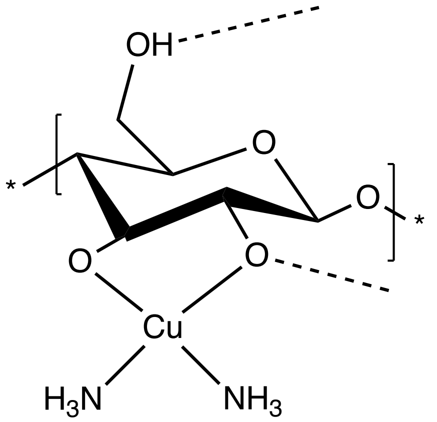

Figure 3.1: The complex formation between cellulose and the copper complex in Cuam, based on a figure in [21]

In the same study, it was also suggested that the hydrogen bond between the hydroxyl on the C6 and the oxygen on C2' is stronger due to that the acceptor (the hydroxyl group on the C2) is deprotonated. They concluded that this type of complexation would increase the chain stiffness of the cellulose, and this was confirmed through light scattering methods [21].

Another solvent class that has mainly been used for lab purposes is molten hydrates of inorganic salts (e.g. $ZnCl_2$) that do not allow for a lot of water and where the degradation of cellulose has been reported to occur in solution [22].

Aqueous solutions of hydroxide bases

The class that allows for most water of the water-based solvents for cellulose is probably the aqueous solutions of hydroxide bases. In most cases, this class contains an excess of bulk water. There are several hydroxide bases that can dissolve cellulose: the alkali bases sodium hydroxide (NaOH) and lithium hydroxide (LiOH), several quaternary ammonium and phosphonium hydroxides and mixtures thereof. The hydroxide anion is the strongest base that exists in water, and therefore has the most potential for interaction with the hydroxyl groups on cellulose. If the cation is paired with another suitable anion, it can also be used to dissolve cellulose in other solvents than water. For example, tetrabutylammonium hydroxide(TBAH) can dissolve cellulose in water [23], while tetrabutylammonium fluoride (TBAF) [15] and tetrabutylammonium acetate (TBAAc) can dissolve cellulose in DMSO [24].

The alkali bases

The discovery that aqueous solutions of sodium hydroxide at low temperatures (usually below zero) can dissolve certain pre-treated celluloses was made as early as in the 1920s, and a patent related to this was filed by Lilienfeld in 1928 [25]. Further research on the subject was conducted in the 1930s. It was suggested by Davidson that cellulose acts as a very weak acid, and forms a salt with the NaOH, 'sodium cellulosate', which is soluble in alkali [26]. The deprotonation of cellulose and the relevance of this for dissolution of cellulose in NaOH(aq) and other solutions of hydroxide bases are still under investigation. Some authors assert that mainly hydrogen bonding occuring between the hydroxyl anion and the hydroxyl groups of cellulose, while others assert that deprotonation occurs [27]. Bialik *et al.* have performed electrophoretic NMR on cellobiose and molecular dynamics simulations on cellodecaose and found that the OH group on the C2 carbon is, to a large extent, deprotonated in aqueous alkali [28].

LiOH can also dissolve cellulose under conditions similar to NaOH (temperatures below zero, ca 2 M concentration) and has been reported to show slightly better solution properties and dissolution capacity than NaOH(aq) [16]. LiOH has not recieved as much attention as the NaOH(aq) system, probably because the use of NaOH is more attractive to industry.

The dissolution of cellulose in NaOH(aq) is, however, poor and has been suggested by Roy *et al.* to yield suspensions and not true solutions [29]. Hagman *et al.* have used Static Light Scattering (SLS) combined with Small Angle X-ray Scattering (SAXS) and found that cellulose aggregates in NaOH(aq) solutions in clusters of ca 100 nm sizes in rather dilute solutions [30]. Another issue with solutions of cellulose in NaOH(aq) or LiOH(aq) is that they are not stable over time. It has been shown that they gel or become turbid suspensions with increasing time and temperature [29]. In a recent study, cellulose solutions where gelation had been induced thermally were analysed using WAXS, and aggregation of solutions was monitored using rheology and turbidity measurements. It was demonstrated that aggregation induced by an increase in temperature is not reversible by lowering the temperature, and WAXS confirmed that the aggregates formed were crystalline. It was suggested that the gel-like properties originates from crystal domains where cellulose chains participate in more than one domain, creating a network of physically linked chains [31].

Quaternary ammonium hydroxides(aq)

As early as 1924, the use of quaternary ammonium hydroxides (QAHs) was patented for cellulose dissolution by Leon Lilienfeld [32]. He found that aqueous solutions of 20-50 wt.% of tetraethyl-, tetramethyl- and phenyltrimethyl-ammoniumhydroxide could dissolve cellulose at room temperature or temperatures below zero, depending on the cellulose to be dissolved. In this work it was also mentioned that addition of alkali hydroxides to these solutions enhanced dissolution but without giving further details.

Powers *et al.* have patented the use of benzyl substituted ammonium hydroxide solutions and found that these bases created even better solvents for cellulose than the alkalis or for example tetramethylammonium hydroxide. Those authors have concluded that these benzyl substituted quaternary ammonium hydroxides must be soluble in water in order to give strong basic solutions, but that the solvent action of the bases are not solely dependent on their basicity. Two of the bases mentioned in this patent are trimethylbenzylammonium hydroxide and dimethylbenzylphenylammonium, and they required a minimum concentration of 2.1 M (35 wt.%) and 1.8 M (42 wt.%), respectively, to dissolve cellulose [33].

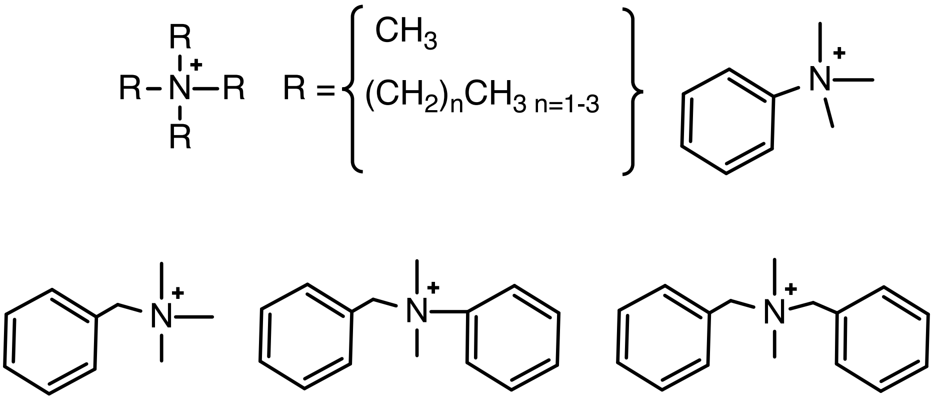

Figure 3.2: Starting from the upper left, structure of the cations in: tetramethyl/ethyl/propyl/butyl ammonium hydroxide, trimethylphenyl-, trimethylbenzyl-, dimethylbenzylphenyl- and dimethyldibenzyl ammonium hydroxide

The solvent action of trimethylbenzyl- and dimethyldibenzyl ammonium hydroxide(aq) (commercialised under the names Triton B and Triton F, see Figure 3.2 for their structures) was further investigated by Brownsett and Clibbens [34]. The study found that the maximum solubility at 20 °C had two maximas: the first at a concentration of 2.15 M base and the second at ca 3.5 M. The dissolution capacity of these solvents increased with decreasing temperature, and the concentration of base where maximum dissolution occurred decreased with decreasing dissolution temperature. Another finding was that with increasing molecular weight of the base, the solvent power and the viscosity of the aqueous solutions of the bases at a given molar concentration increased, and was explained by the introduction of a large molecule between the cellulose chains. This has been investigated through the use of x-ray diffraction, and it was found that when cellulose is subjected to these bases to form so-called alkali-cellulose, it is accompanied by an extension of the crystalline lattice. No significant difference was, however, found in the extension when bases with small or large molecular volumes were compared.

A recent investigation of the dissolution of cellulose in QAHs suggests that the reason for the improved dissolution of cellulose in benzyl-substituted ammonium hydroxide bases can be attributed to increasing hydrophobicity of the bases with increasing molecular weight. Due to the amphiphilicity of cellulose, this increase in hydrophobicity helps to stabilize the more hydrophobic regions of the pyranose ring and prevent the aggregation of cellulose caused by hydrophobic stacking [35].

Tetrabutylammonium hydroxide is another QAH that has been utilised as a solvent, with reported efficiency being optimum between ca 2.0 - 2.3 M (50-60 wt.%) of TBAH [23]. Zhong *et al.* have investigated the dissolution of cellulose in more concentrated QAHs and found that as much as 25 wt.% of microcrystalline cellulose could be dissolved in a solution of 60 wt.% TBAH(aq), the dissolution limit was however only determined through visual inspection of the solutions. Those authors also measured the Kamlet-Taft parameters of the solvents (indicative of hydrogen bonding and van der Waals interactions), and found that increasing β-value (indicative of the hydrogen bond acceptor ability) gave increasing cellulose solubility and that β slightly increased with increasing length of the side chains on the cation, ergo with increasing hydrophobicity [36].

Quaternary phosphonium hydroxides(QPHs) have also been reported to dissolve cellulose. Tetrabutylphosphonium hydroxide solutions of 60 wt.% in water has been reported to dissolve 20 wt.% of microcrystalline cellulose within 5 minutes at 25 °C. Ethanol regenerated cellulose from these solutions has been studied by X-ray diffraction and was found to be mainly amorphous, while the results from FTIR showed that after dissolution the crystal structure remained as cellulose I [37].

Additives

Because of the poor dissolution capacity of NaOH(aq) and the stability issues of the cellulosic solutions, different additives such as urea [16], thiourea [38], ZnO [39], [40] or PEG [41], have been used to improve dissolution. The ones that have received the most attention are ZnO and urea, and their action on cellulose dissolution will be described in this section.

ZnO

As early as 1937, Davidson reported that concentrated, stable solutions of modified cotton could be prepared in NaOH(aq) solutions containing zinc oxide. Davidson found that a NaOH concentration of 2.5 M, a ZnO/NaOH ratio of ca 0.1 and a dissolution temperature of – 5 °C were optimum for dissolution. The addition of ZnO to a KOH(aq) solution was also found to increase dissolution, although NaOH(aq) solutions were still superior in dissolution capacity. KOH(aq) could most likely only dissolve the shortest of chains. Besides ZnO, beryllium oxide and aluminium oxide was also added to NaOH(aq) solutions. Beryllium oxide was found to increase dissolution but not to the level of zinc oxide, while aluminium oxide on the contrary impeded dissolution [39]. More recent investigations into NaOH/ZnO(aq) solutions have reported that the addition of ZnO delays the gelation of the solutions, and suggested that ZnO acts as a water binder [42]. In another study it was found that ZnO exists as $[Zn(OH)_4^{2-}][Na^+]_2$ in these strongly alkaline solutions, and that the $Zn(OH)_4^{2-}$ formed hydrogen bonds with cellulose. It was also suggested that the hydrogen bonds between $Zn(OH)_4^{2-}$ and cellulose are stronger than those between NaOH and cellulose [40].

Urea and urea derivatives

The additive that has gained the most attention is urea, where most of the work has been performed at the Wuhan University in China. Cai and Zhang have reported that cellulose with a viscosity average molecular weight corresponding to a DP of 1389 could be dissolved in 7 wt.% NaOH/12 wt.%

urea (0.175 mol NaOH/0.2 mol urea) in solutions pre-cooled to – 10 °C within 5 minutes. When the cellulose was precipitated from the solutions in acetic acid the resulting cellulose had a cellulose II-type crystal structure [16]. Addition of urea has also been shown by Cai and Zhang to delay but not prevent gelation [43]. Thiourea has also been used as an additive to NaOH(aq) solutions and gelation of cellulose dissolved in NaOH/urea/thiourea was investigated by Zhang *et al.* They found that below 3.5 wt.% cellulose the solutions did not gel when subjected to temperatures up to 90 °C. At cellulose concentrations above 3.5 wt.% the solutions gelled at decreasing temperatures with increasing cellulose concentration, from 81 °C to 38 °C [44]. The choice of additive has also been shown to have an effect on the temperature at which dissolution occurs. Jiang *et al.* found that with thiourea dissolution occurred at 8 °C instead of at - 5 °C, as with urea. Inspection of dilute solutions of cellulose in NaOH/thiourea(aq) using DLS however revealed the presence of aggregates and showed that not all of the cellulose was molecularly dissolved [38]. Urea and ZnO has also been used together as additives to NaOH solutions, and was found to increase the dissolution capacity of cellulose in the solvent[40].

As for the NaOH- and LiOH(aq) solutions, urea and derivatives of urea have been used as an additive to improve dissolution in both QAH- and QPH(aq) solutions. Sirviö and Heiskanen have reported that not only urea, but also N-methylurea, N-ethylurea, 1,3-dimethylurea, and imidazolidone were found to improve dissolution of cellulose when dissolved in tetraethylammonium hydroxide(aq) solution [45].

4 Materials and methods to investigate the dissolution of cellulose and the properties of the solutions

The material and methods used throughout this thesis will be briefly explained in this section, but the reader is referred to the appended articles for more detailed descriptions.

4.1 Materials

A microcrystalline cellulose (MCC) was used throughout this work, except for the NMR measurements. MCC is a purified and depolymerized cellulose made by the partial acid hydrolysis of specialty wood pulp, with a degree of polymerization of ca 180 and high crystallinity. This was chosen because it is soluble in most solvents for cellulose and widely employed when studying dissolution of cellulose, which allows for a comparison between the investigated solvents. The other chemicals used were purchased from large suppliers and used as received, and the details of these chemicals can be found in the appended papers.

4.2 Methods

4.2.1 Characterisation of the solvent structure and interactions

Differential Scanning Calorimetry (DSC) was employed to identify the melting temperature of possible hydrates in solution and correlate them to their structure. The enthalpy was obtained from the peak area in the obtained thermoscans and correlates to the amount of the hydrate in solution. Nuclear Magnetic Resonance(NMR) spectroscopy was employed in order to investigate how the bases interacted with a glucose model of cellulose in solution. Solvatochromic dyes, which change their absorption in the UV-Visible range depending on the interactions with the solvent, were used to estimate the possible hydrogen bonds and van der Waals interactions between cellulose and the solvents.

4.2.2 Dissolution of cellulose

In order to dissolve cellulose in the solvent systems investigated here, the temperature must be brought below ca zero degrees Celsius. The exact temperature dependency of the dissolution process was not under investigationin this work, so the procedure was chosen because it was practical and fairly quick. The procedure was as follows: The solvent was prepared by dissolving the desired amount of base in deionized water so that the final concentration without urea amounted to 4 mol% base (2.3 mol base per litre of water) and with urea 3.8 mol% base and 4.4 mol% urea (2.3 mol base and 2.6 mol urea per litre of water). The cellulose was added under stirring while the solution was cooled in an ice bath and left to stir for 5-15 minutes until the cellulose was immersed in the solvent. The solution was then stored in a freezer at -20 °C for 20 minutes before being stirred in an ice bath for ca 5 minutes to remove any ice crystals that might have formed, and to ensure a more homogeneous sample.

4.2.3 Maximum dissolution capacity

Determining the dissolution limit of cellulose is not as easy as one would think, and the result depends on the method used. Due to the heterogeneity of the cellulose structure with variations in chain length, these solutions often do not have a clear saturation point where addition of more cellulose would lead to precipitation. The first sign of dissolution is that the solutions turn transparent, but there can still be significant aggregates just below micrometers in size in solution. Methods such as small angle x-ray scattering or different types of light scattering are required to determine if the cellulose has been molecularly dissolved. Molecular dissolution might not, however, be required for most applications and, consequently, we chose two methods that do not require as advanced instruments but still allow for a comparison of the dissolution properties of the different solvents. The first method was the inspection of solutions with increasing amounts of cellulose using a light microscope in order to observe the occurence of undissolved particles (Paper I). The second method was to prepare solutions of increasing amounts of cellulose and centrifuge them in order to separate the undissolved particles from solution and weigh them (Paper II).

4.2.4 Methods to measure the stability of the solutions

Different types of rheological measurements were performed in order to investigate the rheology of the solutions as it is indicative of polymer solvent interactions and important for applications. Oscillatory dynamic rheology measurements, where the evolution of the elastic- and loss modulus of the solutions was measured over time, was used to measure the stability of the solutions over time. Rotational rheological measurements, where the viscosity was measured as a function of shear rate, were used to investigate the flow behaviour of the solutions, to determine if they behaved as Newtonian solutions or exhibited shear thinning. Intrinsic viscosity was measured to investigate if the observed solution properties were reflected in the expansion of the cellulose chains in the solvent.

5 Results and Discussion

5.1 Dissolution capacity of aqueous solutions of combined hydroxide bases

While the aforementioned additives (urea and several urea derivatives, ZnO, PEG) have positive effects on the dissolution of cellulose in the NaOH(aq) solvent system, the addition of others have negative effects on the stability of the solutions. These additives are not limited to but include Al_2O_3[39], DBU[1](unpublished results) or ethanol (used as a coagulant). In this study, the idea that another hydroxide base can be used as an additive was explored. However, previous studies dealing with the combination of bases are scarce, so at first it had to be determined if it would be possible to combine bases without disturbing the dissolution capacity of the individual bases. An initial investigation was performed that combined NaOH with KOH, TMAH, or TBAH to a total concentration of 4 mol% base in water (see Figure 5.1). Upon visual inspection of the solutions, it was apparent that only the combination of NaOH with TMAH in an aqueous solution was successful. Based on this finding, it appeared that the two bases had to be able to dissolve cellulose on their own and within the same temperature interval for the combinations to dissolve cellulose. The dissolution of cellulose in 2 mol% solutions of NaOH respectively TMAH were also tested and it was confirmed that at these concentrations they cannot dissolve MCC and therefor they must be cooperating in the combined solution. Based on this, additional combinations, using NaOH and a few commercially available and selected quaternary ammonium/phosphonium hydroxide bases, were tested for dissolution of cellulose through simple visual inspection of the solutions (see Table [5.1]). These bases have earlier been shown to dissolve cellulose.

Table 5.1: The combination of bases or individual bases which could dissolve cellulose at low temperatures

Base	NaOH	TMAH	Triton B	TBPH	TBAH
NaOH	Yes	Yes	Yes	No	No
TMAH	-	Yes	Yes	Yes	No
Triton B	-	-	Yes	Yes	No
TBPH	-	-	-	Yes	No
TBAH	-	-	-	-	No

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[1] 1,8-Diazabicyclo[5.4.0]undec-7-ene

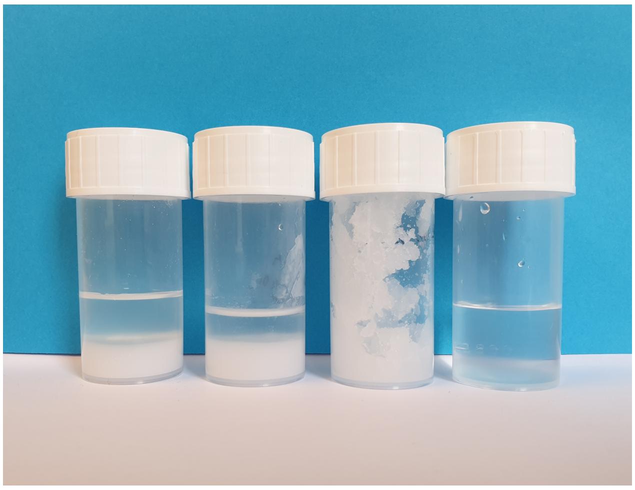


Figure 5.1: From left to right: 3 wt.% MCC in 4 mol%(aq) solution of 50/50 KOH/TMAH, 50/50 KOH/NaOH, 50/50 NaOH/TBAH and 50/50 NaOH/TMAH

Noteworthy is the fact that tetrabutylammonium hydroxide (TBAH) could not dissolve the MCC on its own under the conditions applied or at room temperature. Perhaps, higher concentrations than 4 mol% (37.5 wt.%) are required, as reported by Zhong *et al.* who used a 55 wt.% TBAH(aq) solution [23], or the presence of other salts (such as KBr from the production process) disturbed dissolution as reported by Ema *et al.* [46]. Because NaOH is nontoxic, cheap, and readily available, the continued investigation focused on the combinations with NaOH while also comparing the dissolution power of the combinations to the effect of adding urea. The results on the maximum dissolution capacity as measured through the dissolution and subsequent centrifugation of the solutions can be seen in Table [5.2].

The dissolution limit for 4 mol% NaOH(aq), TMAH(aq) and 50/50 NaOH+TMAH(aq) had previously been estimated by assessing the occurence of undissolved particles with a microscope. For the NaOH(aq) and 50/50 NaOH/TMAH(aq) solutions, the results were consistent with that obtained through centrifugation (3 respectively 5 wt.%). However, the dissolution limit for the TMAH(aq) solutions was higher (5 wt.%) when determined with microscopy. This indicates that there are aggregates in the TMAH(aq) solutions that were not visible through a microscope, but large enough to be separated through centrifugation. This highlights the fact that, depending on the method chosen, the dissolution limit will be different. However, applying the same method to a series of samples allows for internal comparison. The dissolution capacity of the individual bases was found to increase with an increase in hydrophobicity of the cation (NaOH<TMAH<Triton B) as has been reported by Wang *et al.* [35]. Combining NaOH with TMAH had a synergistic effect on dissolution and increased the dissolution capacity beyond that of NaOH(aq) or TMAH(aq) when measured with the centrifugation method. Combining NaOH with Triton B increased the dissolution capacity beyond that of NaOH(aq) but the result is significantly below the dissolution capacity limit of Triton B. Adding urea significantly increased the dissolution capacity of solvents containing NaOH or TMAH, but had no significant effect on solutions of Triton B. The increased dissolution capacity of the 50/50 NaOH+Triton B(aq) solvent upon the addition of urea can likely be attributed to the effect of urea on NaOH.

Table 5.2: The maximum dissolution capacity of MCC in the specified solvent, in weight% and molar concentration

Solvent(aq)	Max wt.% MCC	Max mol MCC per L solvent	Mol base per mol AGU at the dissolution limit
4 mol% NaOH	2.0	0.12	16.6
4 mol% TMAH	2.7	0.17	11.0
4 mol% NaOH/Triton B (50/50)	3.1	0.20	9.3
4 mol% NaOH + urea	3.5	0.24	8.3
4 mol% NaOH/TMAH (50/50)	4.2	0.27	7.4
4 mol% NaOH/Triton B (50/50) + urea	4.2	0.28	6.1
4 mol% TMAH + urea	4.9	0.32	5.3
4 mol% NaOH/TMAH (50/50) + urea	6.1	0.41	4.4
4 mol% Triton B	6.8	0.44	3.7
4 mol% Triton B + urea	6.8	0.46	3.3

5.2 Stability of the solutions

Because NaOH(aq) solutions have been reported to be unstable over time, the effect of combining NaOH with TMAH on the stability of the solutions was measured by monitoring the evolution of the loss and storage modulus over time. When the loss modulus is lower than the storage modulus the solution is more liquid-like, but as the storage modulus increases and becomes greater than the loss modulus, this is a sign that the solution may have gelled or precipitated. As can be seen in Figures 5.2, 5.3 and 5.4, the solution with NaOH and TMAH combined was more stable over time at all of the investigated temperatures (15, 25 and 35 °C). This shows that combining these bases delays the gelation of the solution. However, gelation eventually occurred for all the solutions, and faster with increasing temperature. The same trends were also found for more dilute cellulose solutions, containing less cellulose (3 wt% MCC, see Figures 9.9 and 9.10 in the appendix). In order to further investigate the temperature dependencies of these solutions and to gain additional information of the state of cellulose in solution, flow sweeps were conducted that included the combination of NaOH with the more hydrophobic base Triton B.

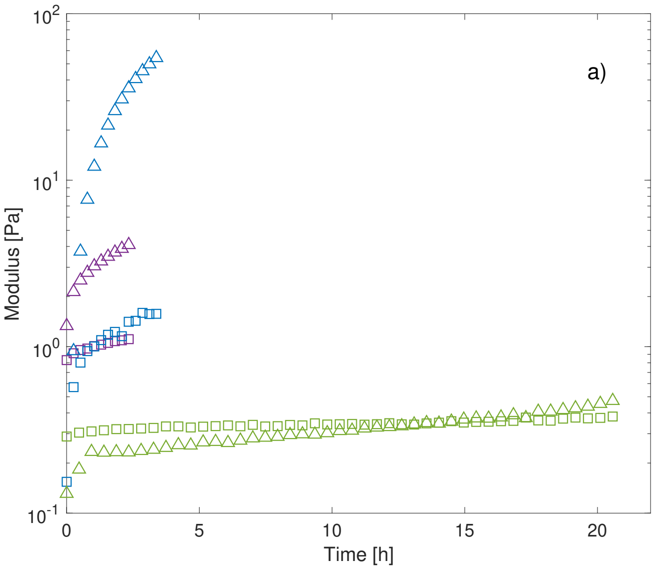


Figure 5.2: Storage modulus G'(triangles) and loss modulus G"(squares) of 5 wt% MCC in 2.3 M NaOH(aq) (purple), 2.3 M TMAH(aq) (blue) and 2.3 M 50/50 mol% NaOH/TMAH(aq) (green) as a function of time at 15 °C

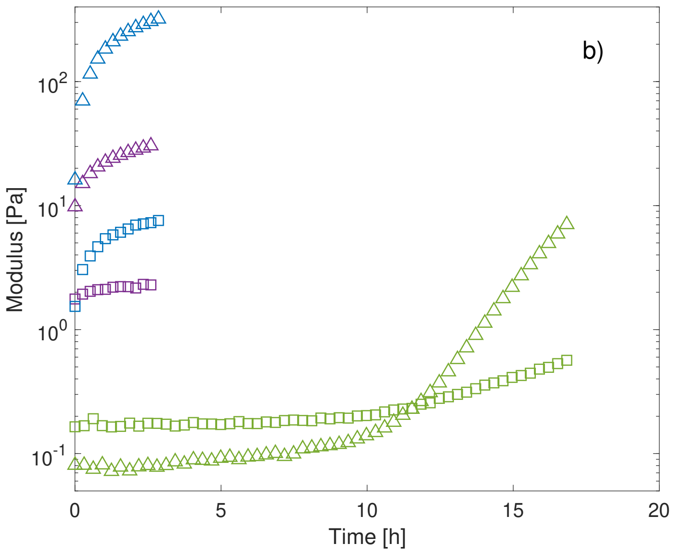


Figure 5.3: Storage modulus G'(triangles) and loss modulus G"(squares) of 5 wt% MCC in 2.3 M NaOH(aq) (purple), 2.3 M TMAH(aq) (blue) and 2.3 M 50/50 mol% NaOH/TMAH(aq) (green) as a function of time at 25 °C

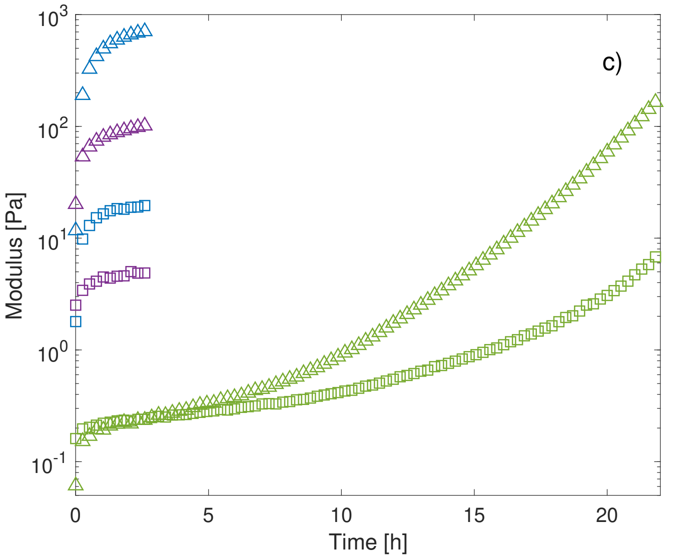


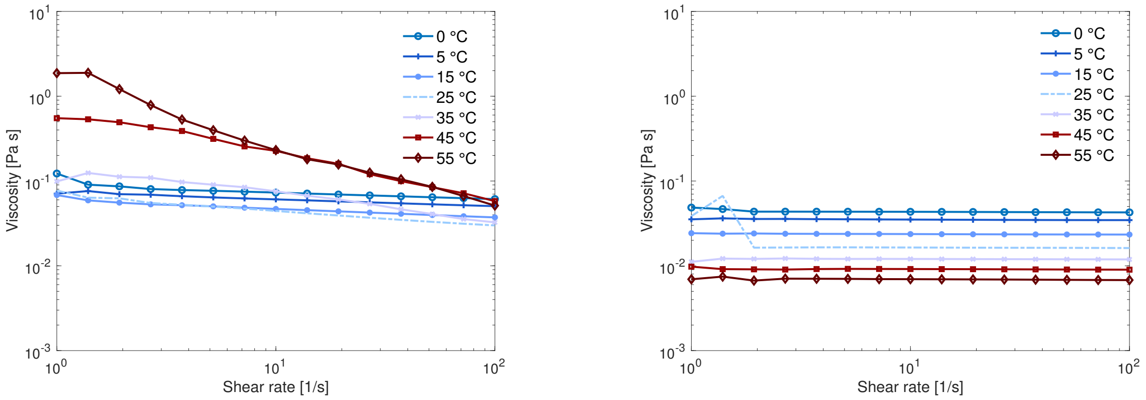
Figure 5.4: Storage modulus G'(triangles) and loss modulus G" (squares) of 5 wt% MCC in 2.3 M NaOH(aq) (purple), 2.3 M TMAH(aq) (blue) and 2.3 M 50/50 mol% NaOH/TMAH(aq) (green) as a function of time at 35 °C

Flow sweeps of solutions without urea

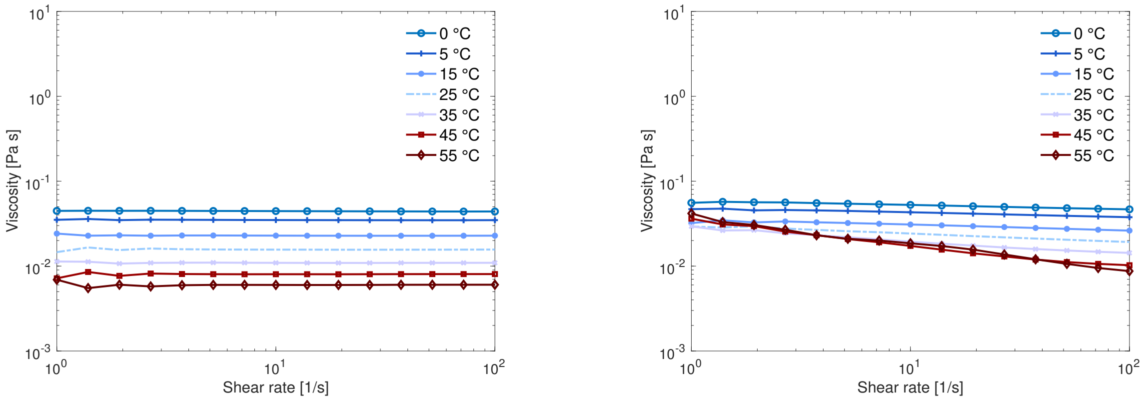
The flow sweeps showed that at the investigated cellulose concentration, the NaOH(aq) solution was never fully Newtonian (see Figure 5.5a), indicating that there are entanglements in the solution. These may consist of aggregates of cellulose acting as junction points [31], while at 45 °C the viscosity at low shear rates increased substantially, which could be due to further aggregation and partial precipitation of cellulose. For the TMAH(aq) solution, two samples of the same composition were tested and while one exhibited Newtonian behaviour over the investigated temperature interval(Figure 5.5b), the other was shear thinning at lower temperatures (see Figure 9.11 in the appendix). This indicates that cellulose in TMAH(aq) has greater temperature stability than cellulose in NaOH(aq) solution, but also that in TMAH(aq) aggregation of cellulose can occur even at low cellulose concentrations.

Combining NaOH and TMAH resulted in a solution that became shear thinning with increasing temperature (Figure 5.5d). Shear thinning commonly indicates the formation of a transient polymer network and could, in this case, indicate that the overlap concentration had decreased with an increase in temperature because the chains became more rigid or had started to aggregate. This temperature behaviour is, however, in line with the findings from the oscillatory rheology measurements, that showed that the solutions gelled faster with increasing temperature.

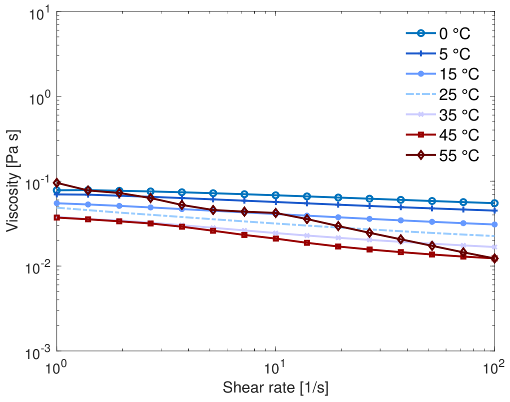
The Triton B(aq) solution displayed completely Newtonian behaviour regardless of the applied temperature, indicating that it effectively dissolves and stabilizes cellulose better than the other bases (Figure 5.5c). When combining NaOH with Triton B (Figure 5.5e), the flow properties deteriorated with increasing temperature as shear thinning could be observed. The flow behaviour was still better than what was found for NaOH(aq) alone but worse than that of the NaOH/TMAH combination. This aligns with the findings for dissolution capacity and points out a lack of synergy between Triton B and NaOH in these solutions.



(a) NaOH (b) TMAH



(c) Triton (d) 50/50 NaOH+TMAH



(e) 50/50 NaOH+Triton

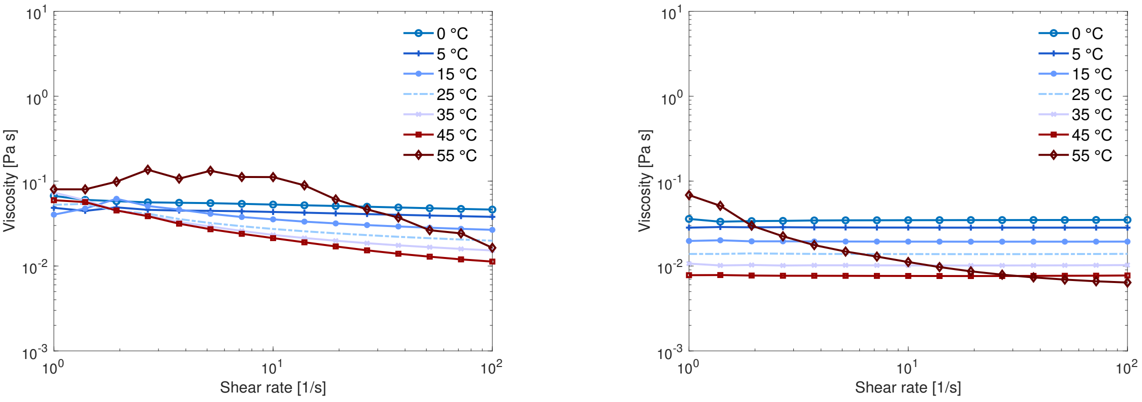
Figure 5.5: Flow sweeps of 0.36 mol% MCC in 4 mol% base (11:1:266 molar ratio of base:AGU:H2O)

Flow sweeps of solutions with urea

The results from the flow sweeps for the solutions that also contain urea show similar trends as the results from the dissolution capacity measurements: the addition of urea enhances the Newtonian behaviour of solutions containing NaOH and/or TMAH (Figure 5.6a,5.6d and 5.6b) but does not have the same effect on solutions with Triton B (Figure 5.6c), much like the effect urea had on the dissolution capacities of the solvents. This was evident in that the NaOH/TMAH/urea solution (Figure 5.6d) displayed Newtonian behaviour over the entire temperature range in contrast to the same solution without urea (Figure 5.5d).

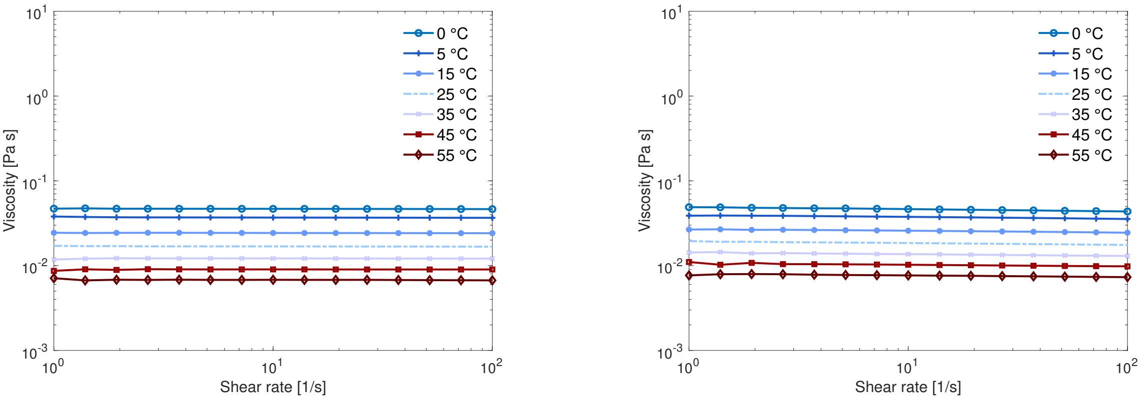
The addition of urea to Triton B(aq)(Figure 5.6c) had no impact on the flow sweeps of the solution, but it is difficult to draw any conclusions based solely on this since the Triton B solution was fully Newtonian even without urea. The NaOH/Triton B/urea solution(Figure 5.6e) was however less shear thinning than the corresponding solution without urea, but not fully Newtonian like the Triton B solutions. This is in line with the results from the dissolution capacity tests and indicates that the addition of urea probably improves the dissolution capacity and dissolution properties of NaOH(aq), but not Triton B(aq).

The oscillatory and rotational rheology measurements highlight that combining NaOH with a suitable QAH can delay gelation as well as improve the temperature stability of a solution. At the investigated cellulose concentration, Newtonian solutions are achieved if cellulose is dissolved in solutions of Triton B or 50/50 NaOH+TMAH with addition of urea. Newtonian behaviour is indicative of dilute solutions without entanglements. Entanglements in these types of solutions have been shown by Pereira *et al.* to be due to crystalline aggregates acting as junction points [31]. Therefore, it appears that in solutions of Triton B, or upon addition of urea to a 50/50 NaOH+TMAH solution, aggregation of cellulose is suppressed.



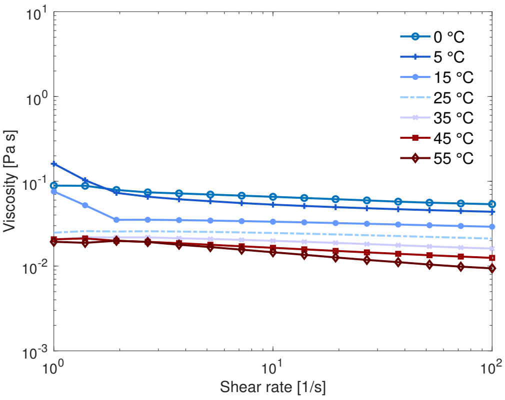
(a) NaOH+urea

(b) TMAH+urea



(c) Triton+urea

(d) 50/50 NaOH+TMAH+urea



(e) 50/50 NaOH+Triton+urea

Figure 5.6: Flow sweeps of 0.34 mol% MCC in 3.8 mol% base and 4.4 mol% urea (11:1:266:13 molar ratio of base:AGU:H2O:urea)

5.3 The state of cellulose in solution

Intrinsic viscosity is a measure of how extended a polymer is in a solvent, and thereby the quality of the solvent since a better solvent would cause the polymer to extend more, because the polymer would favour interaction with the solvent, over interacting with itself. Due to the finding that combining NaOH and TMAH can have a positive effect on the dissolution capacity and gelation of the solution, intrinsic viscosity was measured to investigate if this is due to cellulose interacting more with this solvent combination. The combination of NaOH/TMAH(aq) showed a slightly higher intrinsic viscosity of 1.14 dL/g than that of TMAH(aq) at 0.92 dL/g which, in turn, is slightly higher than that of NaOH(aq) at 0.88 dL/g, as seen in Figure 5.7. The difference between the intrinsic viscosities measured for pure TMAH(aq) and pure NaOH(aq) is not significant when taking into consideration that there is an error margin of 2% when determining the relative viscosities, and a linear regression is made using these values. Compared to NaOH, TMAH is more hydrophobic, but despite this, it does not improve the solvent's quality significantly, at least when measured by intrinsic viscosity. It is however in line with the results on maximum dissolution capacity, where the dissolution capacity of pure NaOH(aq) and pure TMAH(aq) were similar. It is then reasonable to assume that dissolution in NaOH(aq) and TMAH(aq) occurs through similar mechanisms and that the effects on the conformation and subsequent entanglement of the cellulose will be similar.

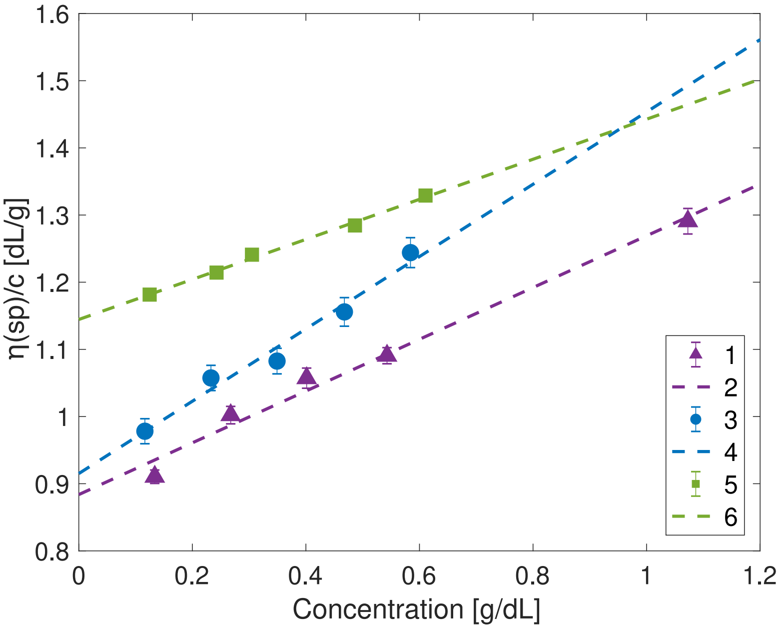


Figure 5.7: Specific viscosity divided by concentration (η_{sp}/c) as a function of cellulose concentration, used to extrapolate(see trendlines 2, 4 and 6) values of intrinsic viscosity at 25 °C for MCC dissolved in 4 mol%: NaOH(aq) (1), TMAH(aq) (3), and 50/50 NaOH/TMAH(aq) (5)

However, the intrinsic viscosity of cellulose in the combined NaOH+TMAH solution was slightly higher than for cellulose in NaOH(aq) or TMAH(aq). This finding indicates that the observed solution properties might be related to favourable interactions between cellulose and the bases when they are combined. In order to further investigate if this might be due to the bases influencing each other, Differential Scanning Calorimetry (DSC) and Nuclear Magnetic Resonance (NMR) were employed to investigate the structure of the solvents.

5.4 Structure of the solvents and intermolecular interactions between the solvent and cellulose

Thermoscans of solutions without cellulose

Thermoscans were performed using DSC to identify melting temperatures and enthalpies of different hydrates in the solutions in order to investigate the structure of the hydrated bases and to study their interactions with cellulose. NaOH forms different hydrates depending on the concentration when dissolved in water. For NaOH concentrations around 4 mol%, Roy *et al.* have reported that a eutectic hydrate salt with a reported composition of $NaOH{\cdot}9\ H_2O$ (melting temperature of - 34 °C) and free water are present in solution [47]. The same could be identified here (solvent ratio of 100/0 NaOH/TMAH in Table 5.3). Thermoscans of 4 mol% TMAH(aq) solution showed that it contained a eutectic hydrate salt with a melting point of -26.3 °C and unbound water, as given in Table 5.3. This is in agreement with a previously reported investigation of TMAH hydrates: from the published phase diagram by Mootz and Siedel the structure of the eutectic hydrate salt can be calculated to $TMAH{\cdot}16\ H_2O$ and the melting temperature read from a diagram as -28 °C [48]. The ratio of the bases was then varied in order to observe how the hydrates of NaOH and TMAH would be affected by each other. In a solution of 75/25 mol% NaOH/TMAH(aq), hydrates of NaOH and TMAH are formed with the same structures as in the reference solutions of 100 mol% NaOH(aq) and 100 mol% TMAH(aq), based on the fact that there was no significant shift in their melting temperatures. The enthalpy of the NaOH hydrate, however, decreased significantly, indicating only a modest formation of the previously observed NaOH hydrates. When the concentration of TMAH was increased further to 50/50 mol% NaOH/TMAH(aq), two hydrate salts were again observed: the melting temperature of the NaOH hydrate had however shifted to $-\ 27.8$ °C, which is closer to the melting point reported for $NaOH{\cdot}7\ H_2O$ than for $NaOH{\cdot}9\ H_2O$ (Pickering 1893). When the concentration of TMAH was increased even further to 25/75 mol% NaOH/TMAH(aq), only one peak (besides that of ice) was observed, with a melting temperature and enthalpy consistent with a TMAH salt. It is reasonable to assume that NaOH was still hydrated by water and present in the solutions even when there was no identifiable peak in the DSC trace. However, these measurements show that the presence of TMAH can prevent the NaOH hydrate from crystallising. The TMAH hydrate probably retains its structure, with its melting temperature affected only slightly by a change in solution composition.

Table 5.3: Melting temperature Tm [°C] and enthalpy ΔH [J/g sample] of peaks in 4 mol%(aq) base solutions

Solvent ratio	Tm °C NaOH	ΔH [J/g] NaOH	Tm °C TMAH	ΔH [J/g] TMAH	Tm °C Ice	ΔH [J/g] Ice
100/0 NaOH/TMAH	-33.7	95.0	-	-	-9.7	170.6
75/25 NaOH/TMAH	-34.4	16.1	-25.3	41.5	-13.2	30.6
50/50 NaOH/TMAH	-27.8	15.3	-25.1	72.2	-14.7	42.1
25/75 NaOH/TMAH	-	-	-27.3	69.4	-16.0	41.9
0/100 NaOH/TMAH	-	-	-26.3	68.0	-17.3	27.8

Thermoscans of solutions with cellulose

Measurements were made for solutions of 3 wt% MCC in 4 mol%: NaOH(aq), TMAH(aq) and 50/50 NaOH+TMAH(aq). It was observed that when cellulose was dissolved in the NaOH(aq) solution, the melting temperature of the NaOH hydrate decreased slightly and the enthalpy decreased significantly compared to NaOH(aq) without cellulose, as can be seen in Table 5.4. The same behaviour had previously been observed by Egal *et al.* upon dissolution of MCC in NaOH(aq) [49]. This indicates that whilst the structure of the NaOH·9 H_2O salt remains the same, only a small amount was crystallized in the presence of cellulose, which is the same behaviour that was observed without cellulose but when NaOH and TMAH were combined. The drastic decrease in the amount of crystalline NaOH hydrate cannot only be explained by the addition of cellulose: there is about 11 NaOH per anhydroglucose unit (AGU) at 3 wt% MCC in 4 mol% NaOH(aq) solution (and it is more likely to be $1-3$ NaOH molecules interacting with one AGU), which should be sufficient to form the NaOH·9 H_2O salt even with cellulose present. One plausible explanation, previously proposed by Egal *et al.* (2007), is that interaction of NaOH hydrates with cellulose affects the surrounding network of the hydrates preventing them from crystallizing in the eutectic salt. Upon dissolution of cellulose in 4 mol% TMAH(aq) or 4 mol% 50/50 NaOH/TMAH(aq), the same hydrate structures were formed as in cellulose-free solutions but only the enthalpy of the TMAH hydrate decreased, possibly indicating a preferred cellulose interaction with the TMAH hydrate.

Table 5.4: Melting temperature Tm [°C] and enthalpy ΔH [J/g sample] of peaks in 3 wt.% MCC solutions dissolved in 4 mol%(aq) base solutions

Solvent ratio	Tm °C NaOH	ΔH [J/g] NaOH	Tm °C TMAH	ΔH [J/g] TMAH	Tm °C Ice	ΔH [J/g] Ice
100/0 NaOH/TMAH	-34.5	13.7	-	-	-9.0	68.7
0/100 NaOH/TMAH	-	-	-26.4	63.2	-15.6	34.3
50/50 NaOH/TMAH	-28.16	15.3	-25.4	57.7	-12.7	50.6

A series with increasing concentrations of MCC in 4 mol% 50/50 NaOH/TMAH(aq) was therefore measured in order to further investigate whether cellulose favours one base over another. Only minor shifts in the melting temperatures of the hydrates were observed when the concentration of MCC was increased, indicating that no essential changes in their structures took place. The enthalpy of the hydrate salt of TMAH decreased linearly with increased concentration of MCC, whereas the enthalpy of the hydrate salt of NaOH slightly increased, as can be seen in Fig. 5.8. The implication here is that TMAH interacts with the cellulose instead of forming a crystalline hydrate salt in the solution; the slight increase in the enthalpy of the NaOH hydrate salt could be due to less TMAH salt crystallizing in solution and interfering with the NaOH structure.

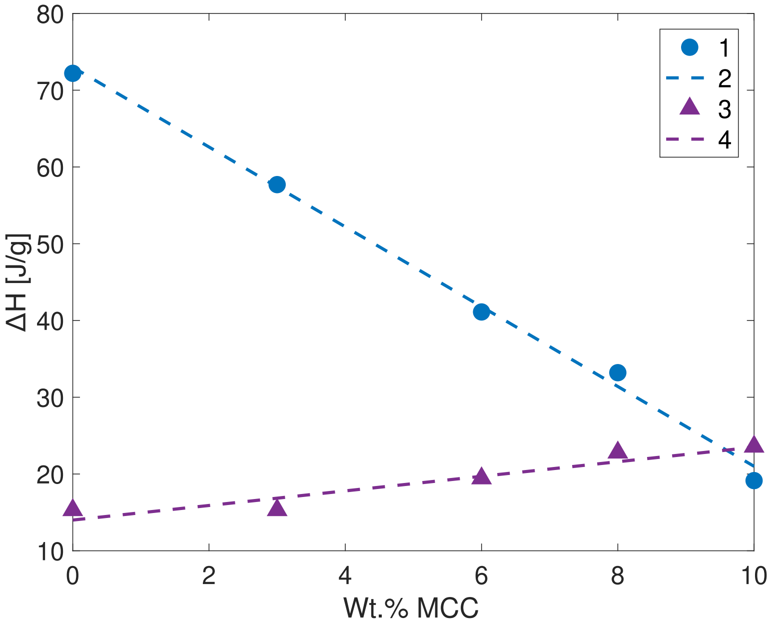


Figure 5.8: Enthalpy of TMAH-hydrate (1) with linear trendline (2) and NaOH-hydrate (3) with linear trendline (4) as a function of cellulose concentration in solutions of 4 mol% 50/50 mol% NaOH/TMAH(aq)

It is interesting to note that although both bases are required for dissolution, the DSC results indicate that only TMAH seemed to be interacting with the cellulose. Another significant feature is that, at the observed dissolution limit of 5 wt% MCC, the levels of the eutectic salts did not reach zero (5 wt% MCC corresponds to ca 3 TMAH/AGU). If the linear trend of decreasing TMAH-hydrate would continue, it would reach zero at 14 wt% MCC, corresponding to ca 1 TMAH/AGU.

Thermoscans were also performed of solutions of 4 mol% Triton B(aq) and 4 mol% 50/50 NaOH/Triton B(aq). Interestingly, there was no formation of the otherwise observed NaOH crystalline hydrate (see Table 9.1). Only one peak could be observed, and although it is difficult to identify the structure that this originates from, this indicates that combining the two bases NaOH and Triton B disrupts the structure of the respective bases, compared to the single base solutions.

Nuclear Magnetic Resonance spectroscopy

NMR analysis was performed in order to shed light on molecular interactions in the solutions. Replacing NaOH(aq) with TMAH(aq) led to a downfield displacement of all the ^{1}H chemical shifts observed. For the signal originating from water, a displacement in the chemical shifts corresponding to 0.15 ppm downfield could be observed upon replacement of 50% NaOH and, finally, displacement corresponding to additional 0.1 ppm when dissolved in TMAH only, as can be seen in Figure 5.9. It is in agreement with the effect observed previously of dissolving relatively hydrophobic cations in water solutions and is commonly interpreted as being evidence of the formation of stronger H-bonding. It is, in fact, rather an effect of the perturbation of the water structure in close proximity to TMAH, causing the water structure to have lower mobility. ^{1}H chemical shifts of the model glucose compound are also displaced downfield: this is indicative of the displacement of electron density away from the glucose C–H protons and is possibly due to the proximity of the TMAH cation.

Furthermore, changes in ^{13}C chemical shifts (see Figure 5.10), albeit modest, additionally witness of perturbation of electron density experienced by the glucose ring upon addition of TMAH in the NaOH(aq) system. Carbon atoms in positions 2, 4 and 6 show deshielding effects when the amount of TMAH is increased (displacement of the chemical shift downfield corresponding to 0.2 ppm when going from NaOH(aq) to TMAH(aq)), while those in positions 1, 3 and 5 seem to experience a very poor shielding effect (a modest chemical shift displacement upfield).

Interestingly enough, this does not comply with the deprotonation signature commonly observed: an upfield displacement of 1H chemical shifts together with a downfield displacement of the 13C signals originating from the C atoms carrying deprotonable OH-groups. Consequently, the presence of TMAH is probably not associated with enhanced deprotonation of the carbohydrate, it is more likely involved in other interactions responsible for deshielding of the glucose C–H moieties.

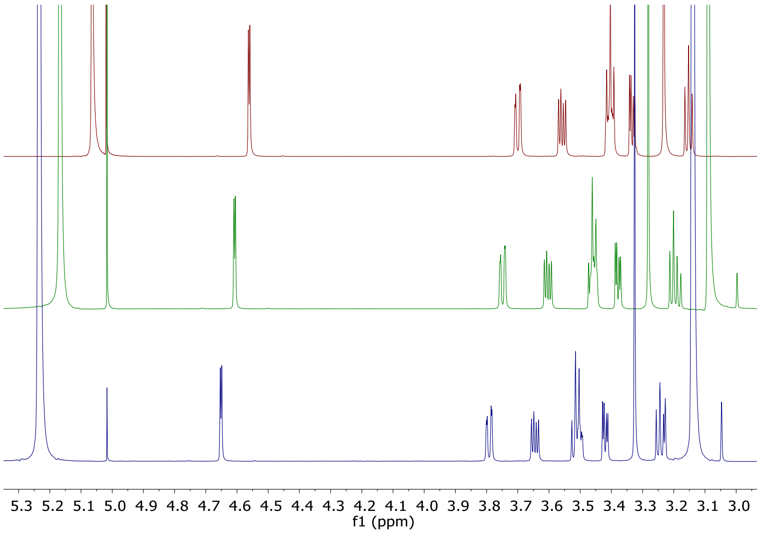


Figure 5.9: H-NMR spectra of methyl-α-D-glucopyranoside dissolved in 4 mol% NaOH (red spectra), 4 mol% 50/50 mol% NaOH/TMAH (green spectra) and 4 mol% TMAH (blue spectra), all in D_2O

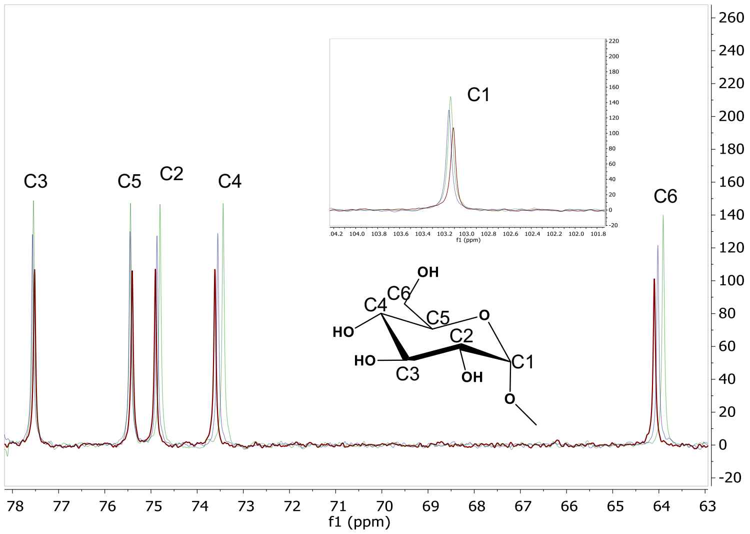


Figure 5.10: ^{13}C-NMR spectra of methyl-α-D-glucopyranoside dissolved in 4 mol% NaOH (green spectra), 4 mol% 50/50 mol% NaOH/TMAH (blue spectra) and 4 mol% TMAH (red spectra), all in D_2O

Solvatochromic parameters

To further investigate possibilities for cellulose-solvent interactions in the studied solutions, the solvatochromic parameters π^*, β, and α, the so-called Kamlet-Taft parameters, were determined in order to elucidate the solvent properties in terms of polarity/polarizability and hydrogen bonding capacity. These parameters are based on the interaction between a dye and the solvent and could give indication on possible interactions between cellulose and the solvents. Many dyes can be used to determine these interactions, but one should not compare the absolute values obtained from different dyes and should rather compare trends, as demonstrated by Rani *et al.* [50].

The π^* parameter

The π^* parameter measures the polarity and polarizability of the solvent, increasing with increasing polarizability and polarity with $\pi^*=0$ for cyclohexane and $\pi^*=1$ for dimethyl sulfoxide. According to the original method by Kamlet, Abboud, and Taft at least seven different probes were used to measure π^* in order to minimize any specific interaction which could occur between a probe and a solvent. The average value of these seven π^* values was then considered reliable enough to be used [51]. In most studies today, a single π^* probe is used but we have used two different π^* probes, and as can be seen in Figure 5.11, the absolute values obtained differ but the trends were in general the same for the two probes 4-Nitroanisole and N,N-diethyl-4-nitroaniline.

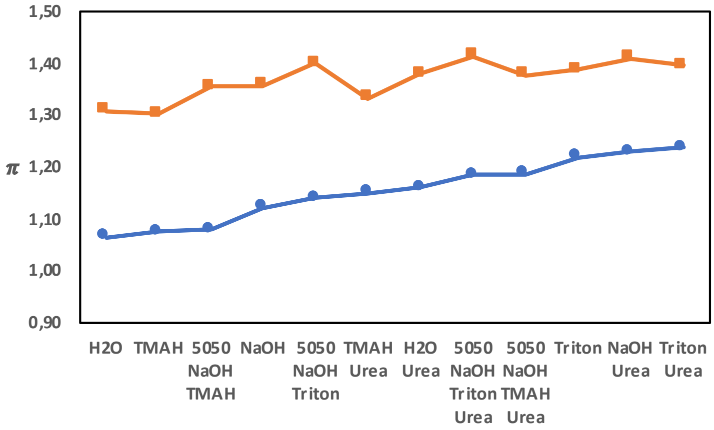


Figure 5.11: The pi-values obtained with two different probes, 4-nitroanisole(blue, circles) and N,Ndiethyl-4-nitroaniline(orange, squares) for the different solvents

It has been shown that the solvent quality improves if it can match the amphiphilic nature of cellulose [10]. It is, however, difficult to use π^* as a measure of the solvent's amphiphilic character since π^* is influenced both by polarity and polarizability. The obtained π^* values are listed in Table 5.5. When comparing the solutions of TMAH and Triton B, Triton B is more hydrophobic, but still has a higher π^*, which can probably be attributed to that it is more polarizable due to its benzyl group with delocalized electrons. Compared to pure water, all solutions have slightly higher π^*-values which could be due to that the hydroxide ions are quite polarizable since they have an excess of electrons. For both probes, addition of urea generally increases π^* which could be explained by urea being more polarizable than water, with the exception of the Triton B solution which appear to be unaffected. This could be indicative of a relatively strong interaction between Triton B and the π^* probe, excluding urea from also interacting with the probe. The effect on the NaOH(aq) solution is in line with the findings by Wang *et al.* who found that addition of urea to LiOH(aq) solution increased π^* [52].

Table 5.5: The π^* parameters for the specified solvent and the difference in π^* for the same solvent with urea, obtained at room temperature

4 mol% solvent at RT	π_1^*	π_2^*	$\Delta\pi_1^*$	$\Delta\pi_2^*$
H_2O	1.06	1.31	0.10	0.07
NaOH	1.12	1.36	0.11	0.05
TMAH	1.08	1.30	0.07	0.03
Triton B	1.22	1.39	0.02	0.01
50/50 NaOH+TMAH	1.08	1.35	0.11	0.02
50/50 NaOH+Triton B	1.14	1.40	0.04	0.01

The β parameter

The β parameter measures the hydrogen bond acceptor ability of the solvent, with the reference point being the value of hexamethylphosphoramide set to 1 [53]. Both water and urea are hydrogen bond acceptors as well as hydrogen bond donors. The hydroxide ion is however a stronger hydrogen bond acceptor than water or urea and should thus dominate the β parameter. Despite the fact that all the bases have the same hydroxide anion and concentration, we found differences in the β-values for the different single-base solvents(Table 5.6). This could originate from differences in hydration due to different hydrophobicities of the cations. Even though the exact hydration behaviour of the hydroxide ion has not been resolved, it should be affected by the presence of the counterion and local polarity. The highest β values obtained are for solutions of Triton B and might be favorable in hydrogen bonding with the hydroxyl groups on cellulose. The combined solvents have a β value corresponding to an average of the two single-base solvents, which is also shown in Figures 9.3 and 9.7 in the appendix, where the β values did not deviate much from that of an ideal solution. This indicates that the observed solution properties of the combined solvents (such as delayed gelation and improved dissolution capacities) does not stem from an effect on the hydroxides ability to hydrogen bond.

The addition of urea to water slightly increased β. This means that compared to water, urea was a slightly better hydrogen bond acceptor. When both urea and base were present in an aqueous solution, there was no effect on β, owing to the fact that urea cannot compete with the hydroxide ion as a hydrogen bond acceptor.

Table 5.6: The β parameter for the specified solvent and the difference in β for the same solvent with urea, obtained at room temperature

4 mol%(aq) solvent at RT	β	$\Delta\beta$
H_2O	0.13	0.04
NaOH	0.20	0.01
TMAH	0.31	-0.02
Triton B	0.38	-0.01
50/50 NaOH+TMAH	0.24	0.00
50/50 NaOH+Triton B	0.31	-0.01

The α parameter

The α parameter measures the hydrogen bond donor ability of the solvent where the value for methanol has been set to 1 [54]. As previously mentioned, water and urea can act as hydrogen bond donors as evidenced by their high α values (Table 5.7). When NaOH is dissolved in water, α is reduced due to that water forms hydrogen bonds with the hydroxide ions instead of with the α probe, showing that the anion has an indirect effect on α. None of the cations investigated here have hydrogens capable of conventional hydrogen bonding, despite this, α increased in the order of $Na^+ < TMA^+ < TritonB^+$ at 4 mol% base. Water has a high hydrogen bond donor ability and if the cation does not contribute to the α value, then increasing the concentration of the base should lower α. To investigate this, the Kamlet-Taft parameters were also determined for an additional solvent series with two concentrations of base. The results in Table 5.8 show that as the concentration of base is increased, α decreased for NaOH and TMAH but not for Triton B. A possible reason for this, is that the more hydrophobic bases, such as Triton B, are less hydrated which increases the possibility for Lewis acid activity since the positive charge is not as shielded. Another contribution might come from the water around the hydrophobic base Triton B, containing so-called dangling water, with fewer hydrogen bonds as commonly observed in the hydration shell of hydrophobic solutes [55]. This water might possibly be more prone to hydrogen bond to the alkoxide of the dye, unless its mobility is too restricted.

The addition of urea to water decreased α, indicating that compared to water, urea is a weaker hydrogen bond donor. The presence of base and urea still lowers α, due to the fact that the bases offer no competition as hydrogen bond donors. The solutions of Triton B are an exception, where addition of urea has no significant effect on α, which was also observed for the π values. This could mean that owing to Triton B's already strong interactions, attributed to lower hydration and more possibilities for van der Waals interactions, urea was excluded from interacting with the probe completely. This is in correlation with the observation that the addition of urea barely increased the dissolution capacity of Triton B.

Table 5.7: The α parameter for the specified solvent and the difference in α for the same solvent with urea, the values are an average of values obtained at 15 and 35 °C

4 mol%(aq) solvent	α	$\Delta\alpha$
H_2O	1.05	-0.10
NaOH	0.24	-0.11
TMAH	0.28	-0.08
Triton B	0.55	0.03
50/50 NaOH+TMAH	0.26	-0.05
50/50 NaOH+Triton B	0.69	-0.04

Table 5.8: The Kamlet-Taft parameters for increasing concentrations of base, obtained at room temperature (*average of values obtained at 15 and 35 °C)

Solvent(aq)	π_1^*	π_2^*	β	α
4 mol% NaOH	1.12	1.36	0.20	0.24*
8 mol% NaOH	1.22	1.29	0.39	0.04
4 mol% TMAH	1.08	1.30	0.31	0.28*
6.2 mol% TMAH	1.06	1.29	0.40	0.17
4 mol% Triton B	1.22	1.39	0.38	0.55*
6.7 mol% Triton B	1.24	1.37	0.47	0.57
4 mol% 50/50 NaOH+TMAH	1.08	1.35	0.24	0.26*
8 mol% 50/50 NaOH+TMAH	1.09	1.30	0.40	0.09
4 mol% 50/50 NaOH+TritonB	1.14	1.40	0.31	0.69*
8 mol% 50/50 NaOH+TritonB	1.23	1.37	0.47	0.61

Summarizing this into possible interactions between cellulose and the bases; in these very basic solutions (pH ca 14) one can expect a portion of the cellulose hydroxyl groups to be deprotonated by the bases which would certainly have a positive effect on dissolution. Considering the polyelectrolyte effect, we might however consider a large part of the hydroxyl groups to still be in their protonated state. The electrostatic interaction between the cation and hydroxyl groups on the cellulose would not be as strong as that observed between the cation and the zwitterionic α dye. This does however indicate that the superior dissolution power that Triton B has over NaOH or TMAH might not only be due to the hydrophobicity of the cation but also due to electrostatic interactions between the cation and cellulose.

A comparison of the combination of NaOH and TMAH in an aqueous solution to the individual base solutions showed small differences in the measured Kamlet-Taft parameters, but overall, they were on the same levels despite clear differences in dissolution properties. From this it seems that the improved dissolution properties do not primarily stem from an impact on polarity/polarizability or hydrogen bonding. When the ratio of NaOH-to-TMAH is varied, the values did not deviate much from the behaviour of an ideal solution(see Figures 9.1-9.4 in the appendix) even though the observed solution properties show synergistic effects. When NaOH is combined with Triton B the behavior is quite different, where the solvatochromic parameters seemed to be dominated by the properties of Triton B. This was especially evident in the high α-value obtained, and shows that Triton B probably enriches in the shell around the dye, and therefor the dye does not reflect the properties of the bulk solvent. To confirm this, we varied the ratio of NaOH/Triton B (see Figures 9.5-9.8 in the appendix) and the measured Kamlet-Taft parameters did not reflect an ideal solution behaviour. The structure of the dyes and cellulose are very different but still cellulose could also be expected to show a preference for the more hydrophobic base.

6 Conclusions

This work has shown that it is possible to combine two hydroxide bases in an aqueous solution to dissolve cellulose, and that this can be used to have the same effect on cellulose dissolution as an additive such as urea. This can be done at concentrations where the individual base can not dissolve cellulose, as long as the total concentration of base reaches a certain level. The exact minimum concentration of base required has not been determined but probably depends on the base pair employed. There appears to be some requirements on the hydroxide bases that can be combined: they both must have the ability to dissolve cellulose on their own at a sufficiently high concentration (for example KOH can not be used as part of the base pair), and they must have an overlapping temperature interval where they can dissolve cellulose.

Combining NaOH and TMAH in a 50/50 mol ratio had a positive effect on the solvents dissoluton capacity of cellulose, and delayed gelation of the solution compared to dissolving cellulose in NaOH(aq) or TMAH(aq) at the same concentration. If NaOH was combined with Triton B, instead, there were no synergistic effects on dissolution despite the fact that Triton B(aq) is a better solvent for cellulose than NaOH(aq) or TMAH(aq) when employed alone. A tentative explanation is that in order for a combination of hydroxide bases to have synergistic effects on cellulose dissolution, the presence of another base must still allow for the other to form the hydrates relevant for cellulose dissolution.

From results on differential scanning calorimetry and solvatochromic parameters it appears that in the presence of two bases with different hydrophobicities, cellulose preferably interacts with the more hydrophobic base. This is believed to be because a more hydrophobic base can interact with the pyranose ring through van der Waals interaction and exclude water from the pyranose ring, and thereby weaken the hydrophobic assembly effect. This can both give rise to delayed gelation of the solution and increased temperature stability. Moreover, more hydrophobic bases are stronger hydrogen bond acceptors, and this contributes to improved cellulose-solvent interactions favourable for dissolution.

Adding urea to solutions of NaOH and/or TMAH further improved dissolution of cellulose. On the other hand, addition of urea to Triton B(aq) did not have a significant effect on cellulose dissolution or solution properties. The results from the measurements using solvatochromic probes indicated that urea might be excluded from interacting with cellulose in the presence of Triton B. The reason why the presence of urea or a more hydrophobic base provides higher dissolution capacity and increased temperature stability compared to NaOH(aq) solutions is believed to be because of the same interaction mechanism, they weaken the hydrophobic effect by replacing water in the hydration shell of the pyranose ring and have a larger contribution of less temperature sensitive van der Waals interactions.

7 Future Work

For the continuation of this PhD, efforts to understand the molecular interactions and their effect on dissolution of cellulose will continue. The mechanism behind the observed synergistic effect of combining NaOH with TMAH compared to the rather mild effect of combining NaOH with Triton B needs further investigation. This probably requires further method development, for example the question whether or not cellulose is molecularly dissolved in the combined solutions has not been answered and it would be interesting to utilize scattering methods to determine the size and shape of cellulose in solution.

Furthermore, investigating if regenerated cellulose from the combined solvent solution yields the Cellulose II crystal structure might give indirect information of what the state of cellulose was in solution. For future possible applications it might be relevant to establish the concentrations and temperatures at which cellulose can be dissolved and analyze the interactions govern this.

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9 Appendix

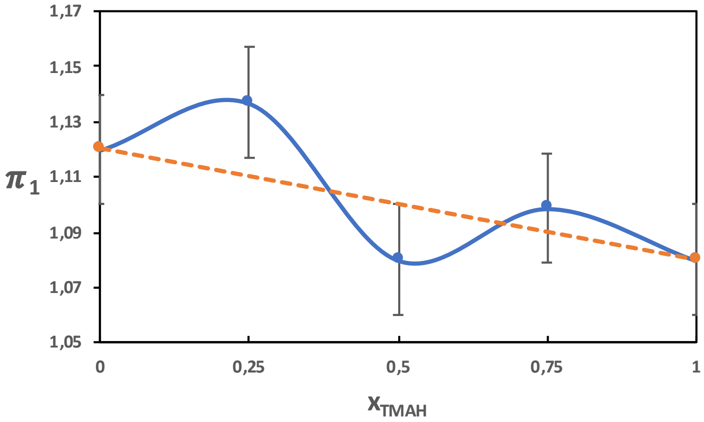

Figure 9.1: The $\pi(1)$ parameter as a function of the molar fraction of TMAH in solutions of 4 mol% NaOH/TMAH

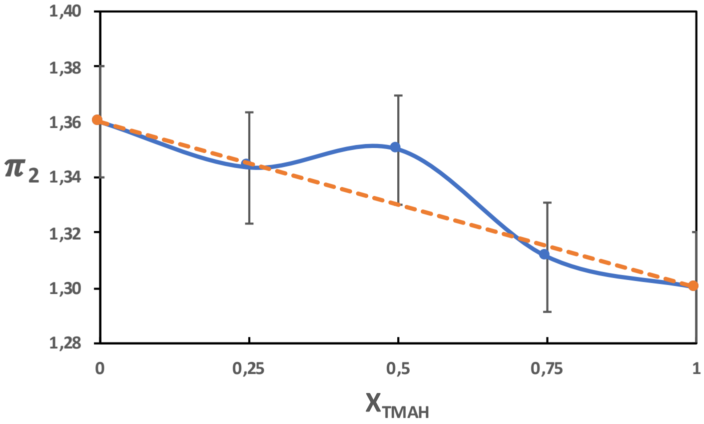

Figure 9.2: The $\pi(2)$ parameter as a function of the molar fraction of TMAH in solutions of 4 mol% NaOH/TMAH

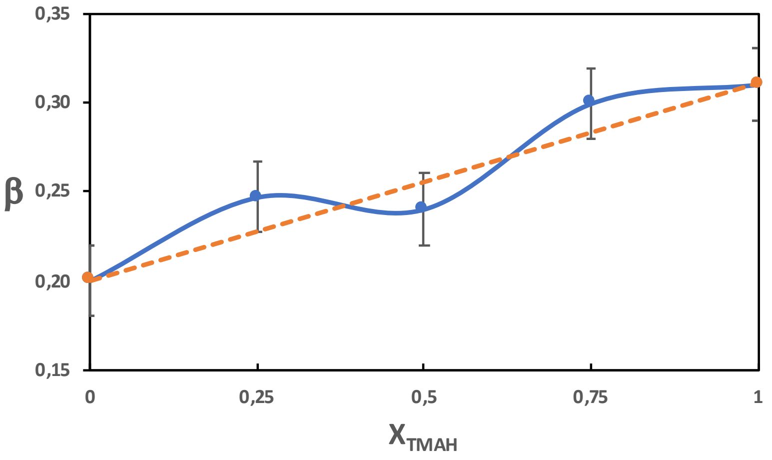

Figure 9.3: The β parameter as a function of the molar fraction of TMAH in solutions of 4 mol% NaOH/TMAH

Table 9.1: Melting temperature Tm [°C] and enthalphy ΔH [J/g sample] of peaks in 4 mol%(aq) base solutions

Solvent ratio	Tm °C NaOH	ΔH [J/g] NaOH	Tm °C Triton B	ΔH [J/g] Triton B	Tm °C Ice	ΔH [J/g] Ice	Tm °C	ΔH [J/g]
100/0 NaOH/Triton B	-33.7	95.0	-	-	-9.7	170.6	-	-
0/100 NaOH/Triton B	-	-	-21.2	88.5	-	-	-	-
50/50 NaOH/Triton B	-	-	-	-	-	-	-16.3	38.5

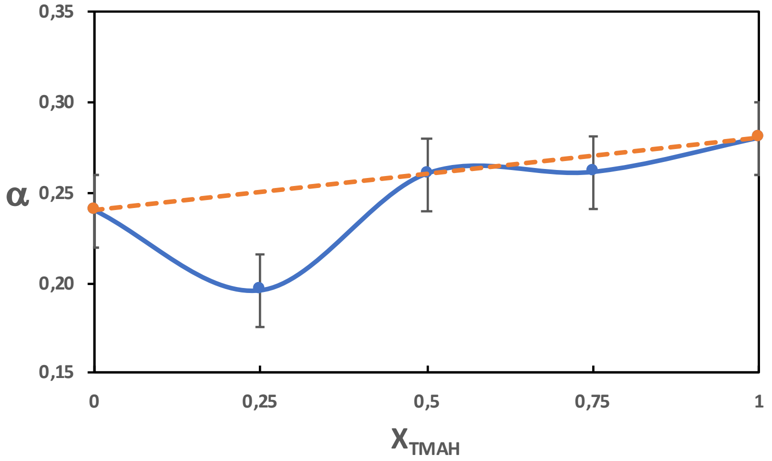

Figure 9.4: The α parameter as a function of the molar fraction of TMAH in solutions of 4 mol% NaOH/TMAH

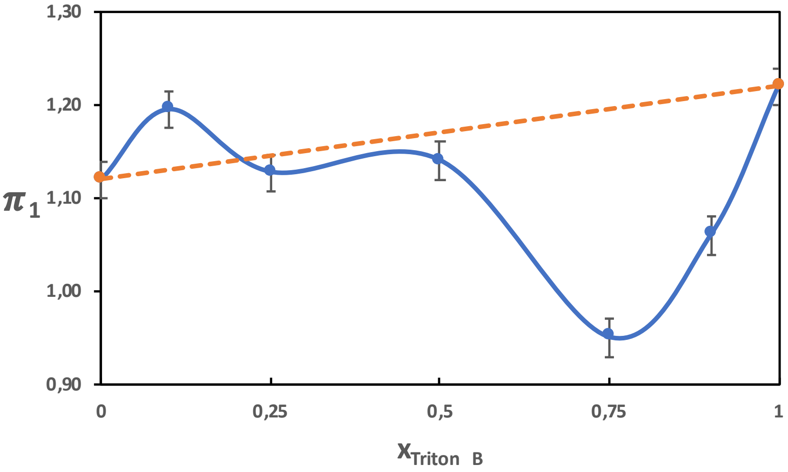

Figure 9.5: The $\pi(1)$ parameter as a function of the molar fraction of Triton in solutions of 4 mol% NaOH/Triton

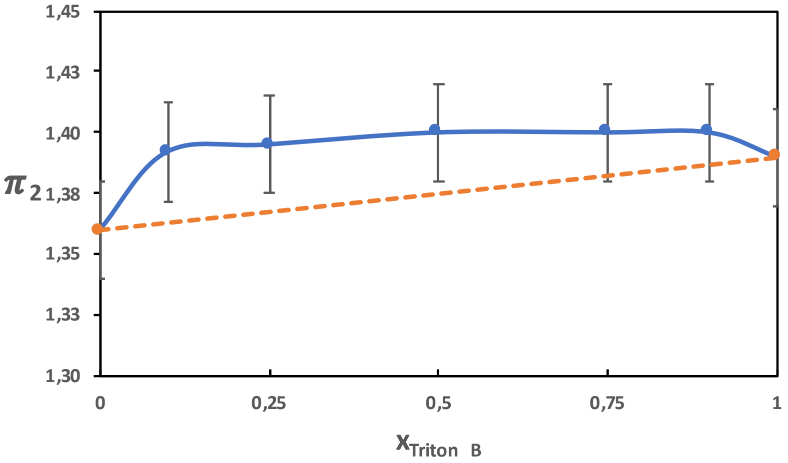

Figure 9.6: The $\pi(2)$ parameter as a function of the molar fraction of Triton in solutions of 4 mol% NaOH/Triton

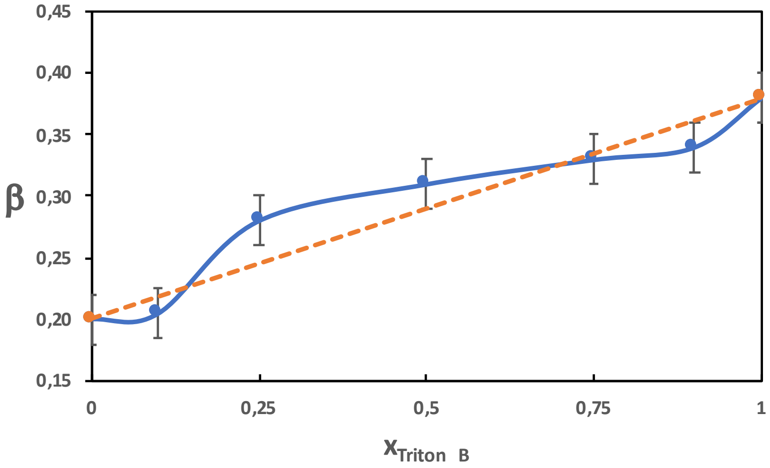

Figure 9.7: The β parameter as a function of the molar fraction of Triton in solutions of 4 mol% NaOH/Triton

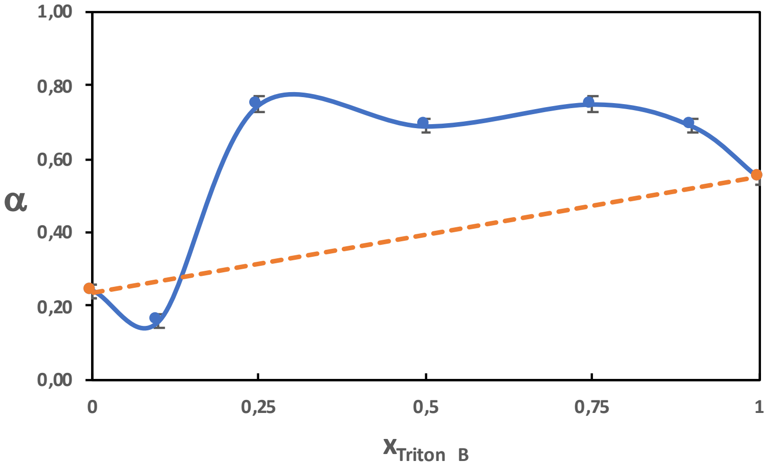

Figure 9.8: The α parameter as a function of the molar fraction of Triton in solutions of 4 mol% NaOH/Triton

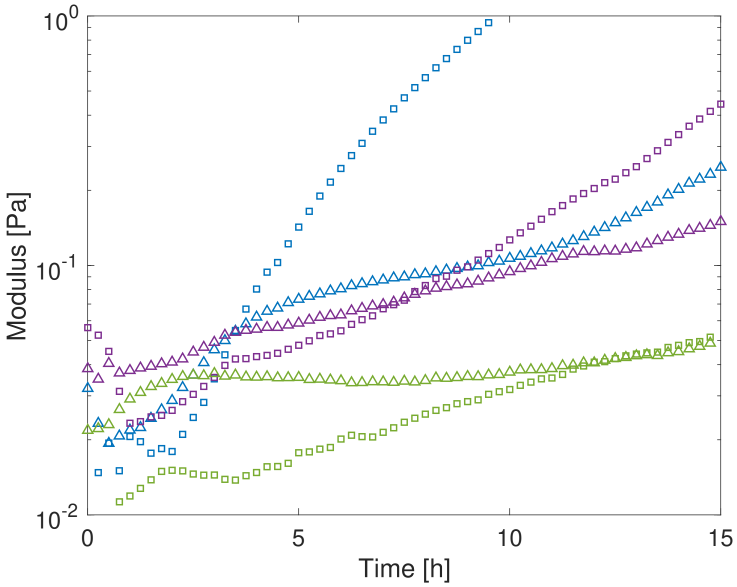

Figure 9.9: Time sweeps(G'(squares), G"(triangles)) of 3 wt.% MCC solutions in 4 mol% base solutions at 25 °C. TMAH(aq) in blue, NaOH(aq) in purple and 50/50 NaOH/TMAH(aq) (green)

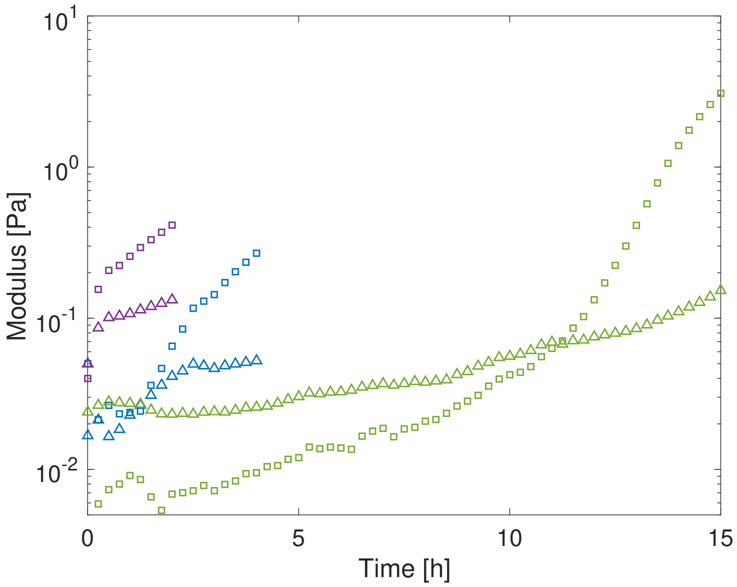

Figure 9.10: Time sweeps(G'(squares), G"(triangles)) of 3 wt.% MCC solutions in 4 mol% base solutions at 35 °C. TMAH(aq) in blue, NaOH(aq) in purple and 50/50 NaOH/TMAH(aq) (green)

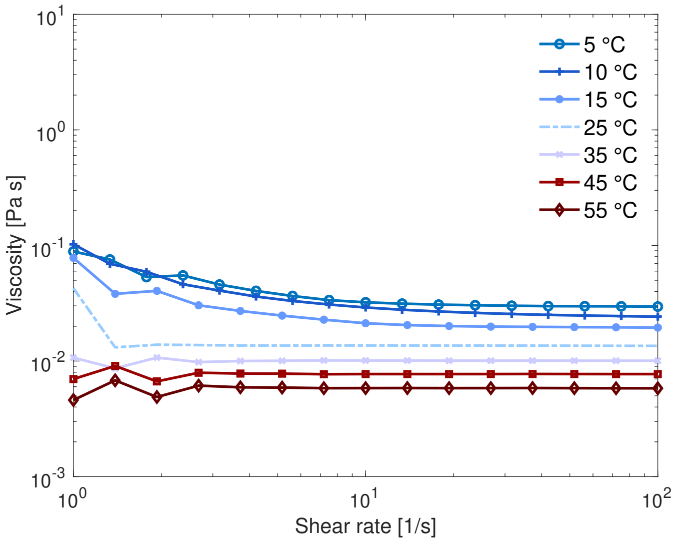

Figure 9.11: Flow sweeps of 0.36 mol% MCC in 4 mol% TMAH (11:1:266 molar ratio of base:AGU:H2O)