THESIS FOR DEGREE OF LICENTIATE OF ENGINEERING

Investigation of CO_2 interactions with cellulose dissolved in the NaOH(aq) system

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CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2017

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Nr 2017:18

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Cover picture: Partly dissolved and undissolved cellulose fibres.

Printed by Chalmers Reproservice
Gothenburg, 2017

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ABSTRACT

Cellulose derived from wood can be used as raw material for production of textile fibres, making it a renewable alternative to fossil oil. One of the key steps in this process is dissolution of the cellulose. The sustainable solvent NaOH(aq) has shown great potential for dissolution of cellulose, but its narrow dissolution window is still a limiting parameter for large scale implementation. The knowledge about the molecular interactions occurring during dissolution of cellulose in NaOH(aq) plays an important role in order to expand the dissolution window why further research in this field is needed.

In this thesis, the specific interactions that occurs between cellulose and CO_2 (e.g from air) in NaOH(aq) solutions are investigated.

Using ATR-IR and NMR spectroscopy it was shown that CO_2 from air chemisorbs on cellulose when dissolved in 8 wt% NaOH(aq) at -5°C and regenerated with ethanol. The chemisorption of CO_2 was found to be reversible when water was used instead as the regenerating agent. Furthermore, a difference in molecular interactions was discovered for CO_2 added to NaOH(aq) prior or after dissolution of the model substrate methyl α-D-glucopyranoside (MeO-Glcp). The post-dissolution addition of CO_2 was shown to affect the chemical shifts (NMR spectroscopy) of MeO-Glcp more than the pre-dissolution addition of CO_2; the same effect was observed for regenerated materials in ATR-IR spectroscopy. Moreover, in the cellulose solutions aged for two weeks, a gel formation was observed when CO_2 was added after the dissolution of the cellulose substrate, pointing out specific interaction between the dissolved and deprotonated cellulose and freshly added CO_2.

Keywords: cellulose, NaOH(aq), dissolution, CO_2, DBU, ATR-IR spectroscopy, NMR spectroscopy.

List of Publications

This thesis is based on the following papers:

Paper I. **Chemisorption of air CO_2 on cellulose – an overlooked feature of the cellulose/NaOH(aq) dissolution system**

Maria Gunnarsson, Hans Theliander and Merima Hasani

Cellulose, **2017**, *24*, 2427-2436.

Paper II. **The interactions between CO_2 and cellulose in the dissolution system NaOH(aq) at low temperature**

Maria Gunnarsson, Diana Bernin and Merima Hasani

Manuscript for *Green Chemistry*

List of Abbreviations

AGU	anhydroglucosidic unit
AMP	2-amino-2-methyl-1-propanol
ATR-FTIR	attenuated total reflectance Fourier transform infrared spectroscopy
BMIMCl	1-butyl-3-methylimidazolium chloride
DAC	direct air capture
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DP	degree of polymerisation
DEA	diethanolamine
DETA	diethylenetetraamine
DMSO	dimethylsulfoxide
DRIFTS	diffuse reflectance infrared fourier transform spectroscopy
EMIMAc	1-ethyl-3-methylimidazolium acetate
gg	gauche gauche
gt	gauche trans
HSQC	heteronuclear single quantum coherence
HMBC	heteronuclear multiple-bond correlation
IL	ionic liquid
MeO-Glcp	Methyl α-D-glucopyranoside
MCC	microcrystalline cellulose
MEA	monoethanol-amine
NMMO	N-methylmorpholine N-oxide
NMR	nuclear magnetic resonance

tg	trans gauche
PZ	piperamine

Contents

1 Introduction

More than 7 billion people inhabit the Earth at present, and the population continues to grow. The extensive use of clothes will therefore continue to increase worldwide in the foreseeable future, making the production of textile fibres a fast-growing market. The majority of all textile fibres produced today use fossil oil as a raw material. Fossil oil is a finite resource; in combination with its associated environmental issues, an increased need of using renewable resources in the production of textile fibres has been recognised. Cotton, which has been used for textiles fibres for thousands of years, remains the main source of textile fibres obtained from a renewable feedstock (Lenzing AG 2015). Cotton fibres are built up of cellulose, which is an organic polymer that is found naturally in all plants. Despite the fact that cotton is a renewable feedstock, the sustainability of cotton production has been questioned for some time due not only to the arable land and enormous water demand but also the pesticides used during its cultivation (Hämmerle 2011). In an attempt to address this, new light has been shed on cellulose derived from wood as being an alternative feedstock to cotton. Unlike cotton, cellulose fibres derived from wood are very short and must therefore be processed into fibres with a higher length to width ratio. This is typically done through dissolution of the cellulose in a solvent, followed by regeneration into thin and long fibres in an anti-solvent. Only few such processes have been commercialised mainly due difficulties with finding suitable solvents for dissolution of cellulose. Due to the complexity in the cellulose morphology and supramolecular organisation, common solvents are not able to dissolve cellulose why the development of appropriate sustainable dissolution solvent systems continues to be an important issue. One of the unanswered questions, essential for further development, is the mechanism for dissolution of cellulose in different solvents.

1.1 Objective

The objective of this thesis was to provide increased knowledge of the molecular interactions that occurs during and after dissolution of cellulose in NaOH(aq). Emphasis has been applied to evaluating the particular interactions that occur between cellulose and CO_2 that are known to be readily abundant in the NaOH(aq) system and originating from air. In order to elucidate molecular state of the CO_2 (i.e. CO_2, HCO_3^- or CO_3^{2-}) interacting with dissolved cellulose, the effect of CO_2 added prior or after dissolution of cellulose in NaOH(aq) has been evaluated, both in terms of molecular interactions and stability of cellulose solutions.

2 Cellulose

Cellulose is a naturally occurring polymer found in all types of plants. Cellulose, hemicelluloses and lignin form the main components of wood. A pulping process that separates these components from each other allows them to be used more effectively in different types of applications. This is the concept of a wood-based biorefinery, where all the building blocks present in wood may be utilised. The cellulose component can subsequently be re-shaped into a variety of products such as textile fibres, membranes and barriers. This chapter describes the structure and morphology of cellulose, and the challenges that are faced in dissolving cellulose.

2.1 Cellulose morphology and structure

On a molecular level, the cellulose polymer consists of D-glucopyranose units linked together through β-1,4-glycosidic bonds (Figure 1). Each two anhydroglucose units (AGU) in the chain are mutually rotated by 180°, thereby forming the repeating unit called cellobiose. The number of AGU in a cellulose chain is defined as the degree of polymerisation (DP). The DP of cellulose is estimated to be between 9,000 and 10,000 in native wood. During pulping, the DP decreases to 300-1700 depending on the type of pulping process used. The pulp used for the production of textile fibres is called dissolving pulp and generally has a DP of around 250 to 600 (Sixta 2006).

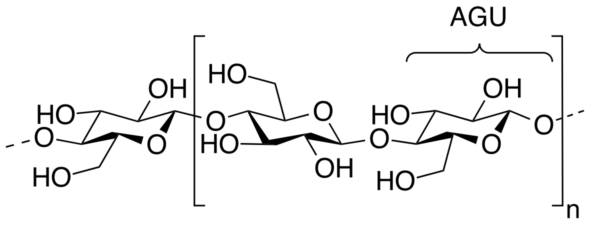

Figure 1. Molecular structure of a cellulose chain.

An AGU has three equatorially positioned hydroxy groups with the ability to hydrogen bond both inter- and intramolecularly to other hydroxy groups. Intramolecular hydrogen bonding stabilizes the flat chain conformation while intermolecular hydrogen bonding leads to alignment of the cellulose chains next to each other, forming a sheet-like structure. The chair conformation of the AGU, and the equatorial position of the hydroxy groups provide for hydrophobic interactions between the sheets, giving cellulose an amphiphilic character (Figure 2). This results in the sheets stacking on top of each other, which stabilizes the crystalline structure of cellulose and packs the cellulose chains into so-called microfibrils. However, the cellulose structure is not fully crystalline but contains less ordered regions caused by a kink every 6-7 AGU why the cellulose microfibrils are regarded as semicrystalline.

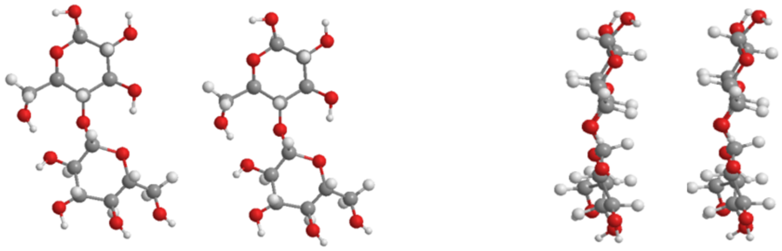

Figure 2. Molecular model of hydrogen bonds between cellulose chains to the left and hydrophobic interactions between sheets built up by cellulose chains to the right, adapted from Olsson et al. (Olsson and Westman 2013).

The semicrystalline microfibrils are aggregated further into macrofibrils which, in turn, are deposited in different layers of the cell walls of fibres. These defined layer structures are a limiting parameter in re-shaping the cellulose, as each layer of the cell wall interacts differently with a solvent. The cellulose fibre is further embedded in a matrix together with lignin and some hemicelluloses where lignin is regarded as being the glue between the fibres and hemicelluloses are proposed to provide interactions between cellulose and lignin (Figure 3).

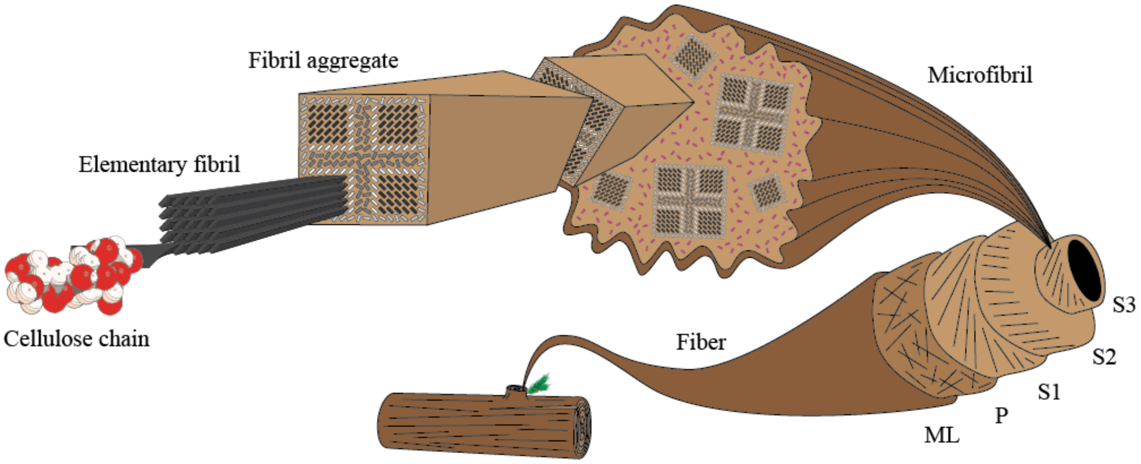

Figure 3. Morphology of cellulose derived from wood. Adapted with the permission of A. Idström.

Cellulose has several crystalline allomorphs, with the most common being called cellulose I, II, III and IV (O'Sullivan 1997). Cellulose I is the native structure where all the chains are arranged parallel to each other. When cellulose I is treated with alkali or dissolved and regenerated, the crystalline structure is rearranged to form cellulose II, which is more thermodynamically stable (Kolpak et al. 1978). The chains are arranged antiparallel in cellulose II, which is an interesting phenomenon still being discussed (Zugenmaier 2008). The crystalline structure is influenced highly by the conformation of the primary alcohol on the cellulose, observed as a change in the hydrogen bonding pattern. Depicted in Figure 4 are the conformations suggested for the primary alcohol: tg is characteristic for the crystal structure of cellulose I and gt for mercerized or regenerated cellulose, i.e. cellulose II, whilst gg is represented in the less ordered regions (Langan et al. 2001).

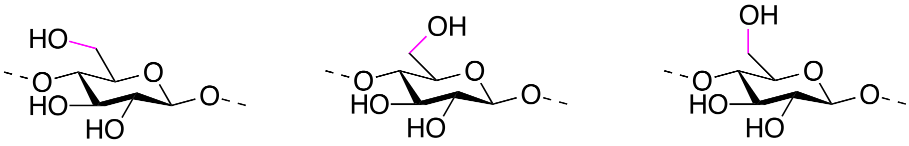

Figure 4. Conformations suggested for the primary alcohol in cellulose. From left to right: tg, gt and gg. t and g denote trans and gauche.

2.2 Cellulose reactivity

The three hydroxy groups on the AGU are reactive handles that enable functionalisation of the cellulose. Functionalisation is feasible via both homogeneous and heterogeneous reactions. In theory, it is possible to perform most reactions involving alcohols on cellulose hydroxy groups, the most important being their esterification, etherification and oxidation, yielding a vast number of derivatives. However, the crystalline structure and morphological organisation of cellulose limit its accessibility when subjected to chemical processing. Homogeneous reactions of cellulose demand complete dissolution of the polymer, which common solvents do not achieve. Heterogeneous reactions also require accessibility, which is why some sort of activation (in form of e.g. swelling) is often performed prior to the actual functionalisation.

Accessibility is very much related to the physical characteristics of the cellulose. The pore structure within the fibres determines the area that is accessible internally, and thereby affects reactivity greatly (El Seoud and Heinze 2005). Adsorption of vapours of for example ethanol or water opens up the pore structure whereas heat treatment usually reduces the pores, so-called hornification (Yasnovsky and MacDonald 1983), and thereby reduces accessibility. Crystallinity is an additional property that affects chemical accessibility. The less ordered regions of the cellulose microfibrils have highly accessible hydroxy groups with a high level of reactivity towards for example derivatising agents. The degree and type of crystallinity depend on the origin of the cellulose and the way it has been treated in, for example, the pulping process. Upon treatment with alkali, cellulose increases its reactivity drastically due to the change in the native morphology and, as a result, increases the amount of amorphous material (Popa and Ciolacu 2010).

Furthermore, the three hydroxy groups on AGU have different reactivities due to their position in the AGU ring. Numbering of the different carbons in the AGU is shown in Figure 5. Position C6 carries a primary alcohol, and is the least sterically hindered and most prone to react in sterically demanding conversions such as substitution reactions with bulky substituents and esterifications. Positions C2 and C3 both carry secondary alcohols, where C2 is the most acidic one and therefore more reactive towards, for example, etherification. After derivatisation of the C2-OH, the hydrogen of the C3-OH becomes more acidic and increases in reactivity.

There are many methods for evaluating reactivity; one approach is to express it as the degree of substitution (DS) associated to a certain chemical derivatization, which basically states the yield of the reaction. The degree of substitution is the average number of hydroxy groups substituted on each AGU. The maximum degree of substitution for cellulose is 3.0. The resulting properties of a functionalised material are highly affected by the DS in terms of solubility, swelling and plasticity (Popa and Ciolacu 2010).

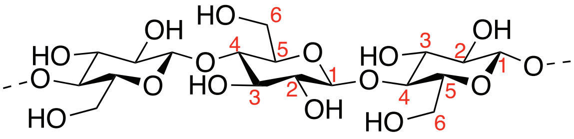

Figure 5. Numbering of the carbons in the AGU.

2.3 Dissolution of cellulose

Cellulosic fibres in wood generally have an aspect ratio (length to width ratio) that is too low for them to be used directly as textile fibres. The native cellulose structure must therefore be dissolved (to form a spin dope) and through spinning into an anti-solvent reshaped into thinner and longer fibres. The complex structure of the cellulose is, however, a limiting parameter in this dissolving process. Both the hydrogen bonds (within and between the cellulose chains) and the hydrophobic interactions, must be overcome to form a completely dissolved polymer solution. Common solvents do not possess the ability to overcome these interactions, which is why the search for cellulose solvents suitable for specific applications has become a relatively large scientific research area (Glasser et al. 2012; Heinze and Koschella 2005; Lindman et al. 2017; Medronho and Lindman 2014; O'Sullivan 1997).

Generally, there is a clear distinction between direct solvents and derivatising cellulose solvents. In the first case, the solvent in itself is able to overcome cellulose-cellulose interactions, whereas in the latter case the cellulose has to be derivatised in order to subsequently dissolve in a certain solvent. From a manufacturing perspective, the direct solvents are preferred because they require one less processing steps.

2.3.1 The viscose process

One of the oldest solvent systems for cellulose is used in the so-called viscose process. The process is based on a derivatising ability of carbon disulphide, which converts alkali treated cellulose into an ester (cellulose xanthate), that is soluble in dilute NaOH(aq). From this, a spinning dope is formed that can be regenerated into new cellulosic fibres, which can be used in textiles. The xanthate is a non-stable ester (Figure 6) and, at a DS as low as 0.5, it dissolves in dilute NaOH(aq) to form a highly viscous solution. During the regeneration step, the viscose solution is spun into an acid solution, hydrolysing the xanthate esters while the pure cellulose is being regenerated into fibres. The viscose process has a large environmental impact, which is why this industry strives to find alternative processes to produce regenerated cellulose fibres.

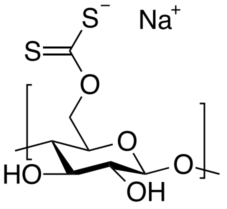

Figure 6. Cellulose xanthate; the sodium salt of the cellulose ester of dithiocarbonate.

2.3.2 The Lyocell process

Although there are a number of direct solvent systems suitable for cellulose, only one is currently employed in a commercialised process, namely the Lyocell process (Medronho and Lindman 2014). This process uses N-methylmorpholine N-oxide (NMMO) as a direct solvent for cellulose, where the NO group has a strong dipole moment that is able to form one or two hydrogen bonds with an AGU of cellulose. The intermolecular hydrogen bonds between cellulose chains are then broken and a stable complex between the hydroxy groups and the NO group is formed (Figure 7). In the following regeneration step, the cellulose solution is subjected to an air gap prior to regeneration in a water in order to align the cellulose chain within the regenerated fibre. This gives the Lyocell fibre its characteristic high strength. One drawback of the Lyocell process, however, is that the solvent is thermally instable but can, nowadays, be controlled in order to avoid explosions. Further, the solvent can be recycled up to 99%, thus improving both the economy and the environmental impact of the process.

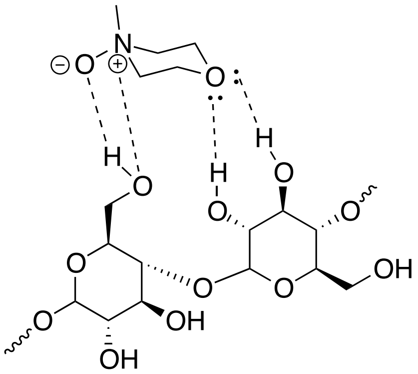

Figure 7. Dissolution mechanism of cellulose in NMMO.

2.3.3 Ionic liquids

In 2002, Swatloski et al. discovered that the ionic liquid (IL) 1-butyl-3-methylimidazolium chloride (BMIMCl) was able to dissolve cellulose, thereby acting as a direct solvent (Swatloski et al. 2002). These types of solvents have been widely explored since this discovery was made, and an increasing number of publications appear each year. An IL is an organic salt liquid below 100°C, where both the cation and the anion can be varied to achieve certain properties. Two of the most common ILs employed in the cellulose research are the aforementioned BMIMCl and 1-ethyl-3-methylimidazolium acetate (EMIMAc) (Figure 8). Like NMMO, ILs are capable of breaking the hydrogen bonds between the cellulose chains, causing cellulose to dissolve. In addition, it has been argued that the interaction with the anion plays the most important role but it has also been shown that the cation needs to fulfil certain structural requirements in order for the cellulose to dissolve in the IL (Zheng et al. 2011). It is therefore of interest to discuss whether the cation is more prone to interfering with the hydrophobic interactions, and the anion to disrupting the hydrogen bonding pattern between the chains.

Figure 8. The chemical structure of BMIMCl (left) and EMIMAc (right).

2.3.4 The NaOH(aq) system

Undoubtedly, from an environmental point of view, an aqueous based system is the most interesting for dissolution of cellulose. New light has therefore been shed on the NaOH(aq) system over the last years.

The first to discover that cellulose could be dissolved in NaOH(aq) was Davidson in the early 1930's (Davidson 1934), who succeeded in dissolving a partly hydrolysed cotton in NaOH(aq), especially at lower temperatures. In 1939, Sobue et al. finalised the phase diagram for cellulose in NaOH(aq) as a function of the concentration and temperature of the NaOH(aq) (Figure 9) (Sobue et al. 1939). From this, it could be elucidated that cellulose dissolves in NaOH(aq) at 7-10 wt% in the temperature range of -5°C to +1°C. In the phase diagram, this region is defined as the Q-state, where Q stands for quellung (the german word for swelling). Moreover, the phase diagram also presents the other types of alkali celluloses, namely Na-Cell I to V, which are formed at varying concentrations of NaOH(aq).

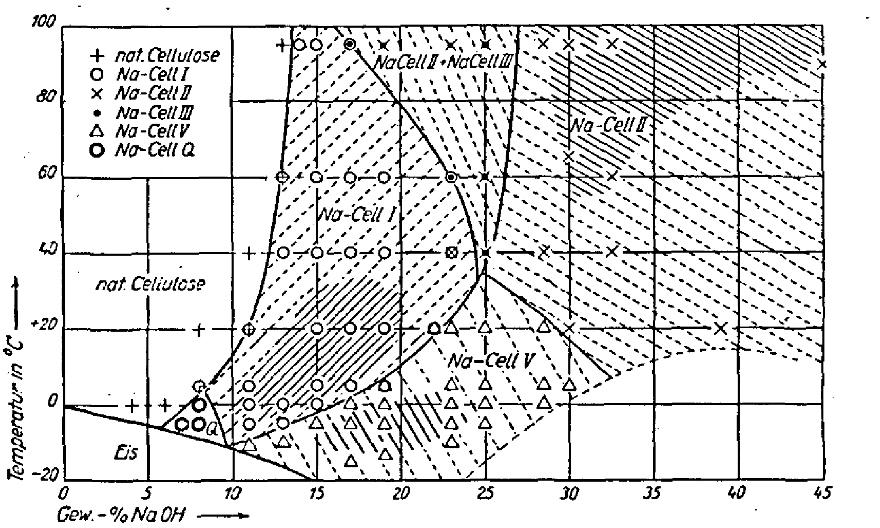

Figure 9. The phase diagram for cellulose in NaOH(aq) as a function of NaOH(aq) concentration and temperature (Sobue et al. 1939).

Clearly, NaOH(aq) is able to dissolve cellulose on its own, but due to the narrow process window, industrial implementation of the system is challenging. Cellulose dissolved in NaOH(aq) must be kept between temperatures of -10 and 10°C to remain in solution. When the solution approaches 10°C, the cellulose chains start to associate to each other and precipitate as regenerated cellulose II. The same process takes place when the solution approaches a temperature below -10°C, which clearly demonstrating that the conformational structure of the cellulose chains between -10 and 10°C is the most beneficial for the dissolution, and must be maintained for the chains to remain in solution. Moreover, a more spontaneous phenomenon occurs in the NaOH(aq) system: the tendency for cellulose to gel, even though the temperature is kept constant at -5°C. The mechanism for this behaviour remains unknown.

As a consequence of these issues, numerous efforts have been made in evaluating different additives in order to widen the process window both in terms of dissolution rate and stability of the solutions (Budtova and Navard 2015). The choice of additive is related closely to the type of interactions that must be overcome to promote the dissolution and stabilize the dissolved polymer. On the molecular level, the dissolution mechanism for cellulose in NaOH(aq) has been a research topic from the very discovery of the system; it has still not reached a final consensus. It has been argued that the dissolution of cellulose in NaOH(aq) requires the hydrogen bonding pattern to be broken, possibly via the action of hydrated Na^+ and OH^- ions, thereby forming new hydrogen bonds with the cellulose(Yamashiki et al. 1988).

Additives such as urea and thiourea (Figure 10), on the other hand, which are known to act as denaturating agents for proteins through breakage of hydrophobic interactions, increase both the dissolution rate and the stability of cellulose in NaOH(aq): hydrophobic interactions are therefore an important force to overcome if efficient dissolution in NaOH(aq) is to be achieved (Rossky 2008). This increase in dissolution rate and stability upon addition of urea/thiourea suggests a specific association between cellulose and urea/thiourea, whereby they act as spacers between the chains. In addition, ZnO has been shown to stabilise cellulose dissolved in NaOH(aq), without enhancing the dissolution rate (Liu et al. 2011). In NaOH(aq), ZnO converts to $Na_2Zn(OH)_4$, (also known as zincate) and has been demonstrated to form stronger hydrogen bonds to cellulose in contrast to hydrates of NaOH (Yang et al. 2011). Thus, it appears that the hydrogen bonding between cellulose chains is an important parameter that must be controlled if the chains are to be prevented from re-associating.

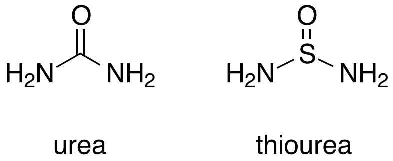

Figure 10. The chemical structures of urea and thiourea, two additives that enhance the dissolution of cellulose in NaOH(aq).

In this context, a somewhat forgotten knowledge is the fact that cellulose is deprotonated to a certain degree in NaOH(aq), which introduces charges on the cellulose chains. In the deprotonated state, cellulose adopts the properties of polyelectrolytes: these are known to dissolve in water due to their charged groups (Bialik et al. 2016). It is therefore plausible to argue that deprotonation of the hydroxy groups and the introduction of charged groups both plays active roles in the dissolution mechanism of cellulose in NaOH(aq): the hydrogen bonding pattern is broken down and repulsion between the charged chains is obtained simultaneously.

3 Absorption of CO_2 in NaOH(aq)

The solvent system NaOH(aq) not only possesses the ability to dissolve cellulose but also readily dissolves CO_2 from air. CO_2 converts to Na_2CO_3 in NaOH(aq) by consuming OH^- which will presumably have an effect on the dissolution of cellulose in the NaOH(aq). In this section, the absorption of CO_2 in NaOH(aq) is discussed vis-à-vis the dissolution of cellulose in NaOH(aq). Furthermore, interactions that are possible between CO_2 and cellulose are discussed in comparison to similar CO_2 capturing systems.

3.1 Direct capture of CO_2 from air

CO_2 capturing has been used for long time as a part of recycling and purifying strategies in the industrial processes (i.e. oil, gas and steel industries). More recently, the need to minimize the global warming as a consequence of man-made CO_2 emissions[1] has intensified efforts on developing new carbon capturing techniques to reduce the atmospheric concentration of CO_2.

Direct air capture (DAC) is a concept implemented by Lackner in 1999, and may be used for the mitigation of climate change (Lackner et al. 1999). Today,

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[1] In 2015 the atmospheric concentration of CO_2 measured 401 ppm, in comparison to the preindustrial value 280 ppm and has already reached the limit for maintaining the global temperature on a level where and the rise of the sea level can be avoided.

the concept is defined more broadly as the direct extraction of CO_2 from ambient air. One of the major benefits of DAC is the potential use of the captured CO_2 as a chemical feedstock for new products. It is therefore of the utmost importance that the CO_2 can be released again from the capturing agent.

One of the oldest approaches for capturing CO_2 is the use of aqueous amine solutions. This method is based on the reaction between an amine and CO_2 in the presence of water, yielding ammonium carbonate or bicarbonate. The mol ratio 1:1 of amine and CO_2 gives the maximum yield of CO_2 captured. Amines used frequently in industrial applications are: monoethanol-amine (MEA), 2-amino-2-methyl-1-propanol (AMP), diethylenetetraamine (DETA), diethanolamine (DEA) and piperamine (PZ) (Jassim et al. 2007; Tan and Chen 2006). A drawback in the use of liquid amines as carbon capturing agents, e.g. in the case of MEA, is that the substances are highly corrosive and demands much energy in the recovery step (Yoo et al. 2013).

Another common way of utilising amines for capturing CO_2 is to use solid-supported materials: surface adsorption takes place here, in contrast to the absorption method discussed earlier (Yu et al. 2012). These materials are classified as (i) amines impregnated into the pores of a support, (ii) amines bonded covalently to the wall of porous materials and (iii) amine monomers polymerised in situ into the walls of a support.

3.2 NaOH(aq) as CO_2 sorbent

Although aqueous hydroxides are, in general, efficient CO_2 capturing agents, it is only recently that they have been studied for the purpose of reducing CO_2 levels (Sanz-Pérez et al. 2016). It is interesting to note that the absorption capacity of CO_2 in NaOH is higher than for the above mentioned MEA. In theory, 0.9 tons NaOH is capable of capturing 1 ton of CO_2, in comparison to 1.39 tons MEA that is required to capture the same amount of CO_2. Reactions (1) to (4) describes the absorption of CO_2 in NaOH and following conversions into HCO_3^- and CO_3^{2-}. In the first step, CO_2 is in its gaseous form and dissolves in NaOH(aq), and is absorbed physically to aqueous CO_2 (1). At high pH (>10), the aqueous CO_2 (l) reacts with an OH^- to form a HCO_3^- which reacts immediately with a new OH^- to generate CO_3^{2-} (3). The overall net reaction of CO_2 absorption in NaOH(aq) at high pH is expressed in (4).

$$CO_2\ (g) \rightarrow CO_2\ (aq) \quad (1)$$

$$CO_2\ (aq) + OH^-\ (aq) \rightleftharpoons HCO_3^-(aq) \quad (2)$$

$$HCO_3^-(aq) + OH^-(aq) \rightleftharpoons H_2O\ (l) + CO_3^{2-}(aq) \quad (3)$$

$$2NaOH\ (aq) + CO_2(g) \rightarrow Na_2CO_3\ (aq) + H_2O\ (l) \quad (4)$$

An increase in the concentration of NaOH(aq) could increase its capacity to capture CO_2, but this will, in turn, result in an increase in viscosity. In order to avoid this, and simultaneously increase the CO_2 capturing ability, the use of an additive in the NaOH(aq) has been suggested: diethylene glycol was proposed by Yu *et al.* and glycerol by (Song et al. 2014; Yu et al. 2013). In fact, an addition of 7 wt% glycerol to a 0.5 M NaOH(aq) solution increases the absorption capacity from 70 to 95% and the diffusion coefficient of CO_2 in NaOH(aq) is doubled (Chiang et al. 2017). This phenomenon could be attributed to the reaction rate being faster between CO_2 and a metal alkoxide than with hydroxide in an aqueous solution (Song and Rochelle 2017). Similar observations had been done earlier by Faurholt in 1927 while investigating the competing reactions between methoxide and hydroxide in the MeOH/NaOH(aq) system at limited access to CO_2. This was later confirmed by Heston et al. in 1943, who repeated and extended the study (Heston et al. 1943). The relative formation of methylcarbonate (through deprotonation of MeOH by NaOH(aq) and subsequent addition of CO_2) vs. CO_3^{2-} (through above mentioned reactions between CO_2 and OH-) could be estimated by precipitating CO_3^{2-} with barium chloride. Similarly, in the studies using glycerol, a glyceroxide has also been proven by Fairbourne et al. to form in strong NaOH(aq) (Fairbourne et al. 1931). In addition to this, it has been shown that the reaction rate constant of CO_2 with glyceroxide is 6-7 times faster than the reaction rate with hydroxide (Song and Rochelle 2017).

Moreover, it has also been discussed if the CO_2 capturing capacity of glycerol and similar structures, such as polysaccharides and poly(ethylene glycol), is due to the ability of the individual polarisable C-O bonds in CO_2 to interact with polar groups (Aschenbrenner and Styring 2010). The CO_2 then acts as a Lewis acid or a Lewis base and is able to participate in hydrogen bonding (Raveendran et al. 2005). The terminal hydroxy groups (e.g. in glycerol or carbohydrates) appears to have a high infinity for CO_2 molecules (Aschenbrenner and Styring 2010). Substances with terminal hydroxy groups can therefore increase the absorptivity of CO_2 compared to molecules containing, for example, only ether groups. Figure 11 shows how the highly polarisable CO_2 may establish a strong electron interaction with a terminal hydroxy group.

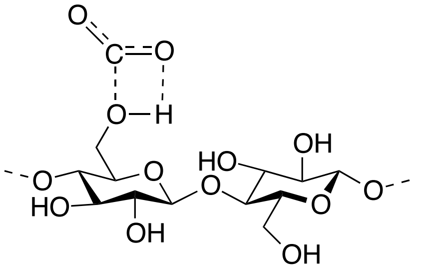

Figure 11. Polar interaction between CO_2 and one of the hydroxy groups on cellulose.

4 Materials and Methods

This section describes briefly the materials and characterisation methods used in the papers appended.

4.1 Cellulose substrates

The focus of this work was to investigate the interactions that take place between CO_2 and cellulose dissolved in the NaOH(aq) system. Due to limited solubility of dissolving pulp in NaOH(aq), two different kinds of cellulose model substrates were chosen (Figure 12). Microcrystalline cellulose (MCC) Avicel PH-101 was used for the dissolution and regeneration experiments in Paper I; the influence of CO_2 upon dissolution and regeneration was investigated using both MCC and methyl α-D-glucopyranoside (MeO-Glcp) in Paper II. Information regarding the purity of the chemicals used for dissolution and regeneration, and the suppliers thereof, can be found in the appended papers.

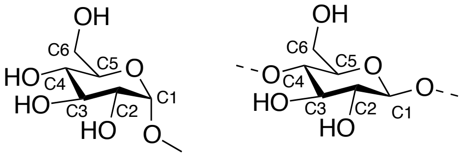

Figure 12. The chemical structures of MeO-Glcp and cellulose, with corresponding annotations used in characterisation.

4.2 Dissolution and regeneration of cellulose

Dissolution of cellulose was carried out by dispersing MCC in deionized water and pre-cooling the suspension to +5°C prior to addition to a -5°C NaOH(aq) solution. The solution was stirred for 1 h in an open atmosphere to reach a transparent appearance. The final concentrations in the solution were 3:8:89 wt% cellulose:NaOH:H_2O.

In order to evaluate the potential of using a superbase as a catalyst for the chemisorption of CO_2 on cellulose, pre-treatment of dispersed MCC with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), was performed. Certain superbases have shown specific interaction with CO_2 (Heldebrant et al. 2005) and have been reported to activate cellulose prior to modification (Zhang et al. 2013). In a typical pre-treatment experiment, MCC was dispersed in deionized water and DBU added at a ratio of 1:3 DBU:MCC and the dispersion was pre-cooled at +5°C, before adding it to NaOH(aq) as described above.

The presence of CO_2, originating from air, during dissolution of cellulose in NaOH(aq) was evaluated in Paper I by regenerating the cellulose solution using water or ethanol. The regenerated sample was subsequently washed, with the regenerating agent, until it was neutral and either freeze dried or dried *in vacuo*.

In Paper II, CO_2 was added by immersing a syringe into the cellulose solution for 30-60 s either before or after dissolution. The syringe was connected to a tube with CO_2 equipped with a flow regulator set to 1 L/min.

4.3 Preparation of MeO-Glcp solutions

The behaviour of the model substrate MeO-Glcp in NaOH/D_2O was compared to the reference solution in NaCl/D_2O to investigate further the dissolution mechanism of cellulose in NaOH(aq) and the influence of CO_2 upon dissolution.

MeO-Glcp was therefore dissolved in D_2O at +5°C and added to a solution of NaOH or NaCl in D_2O, at a temperature of approximately -5°C. The final concentrations of MeO-Glcp and NaOH or NaCl in D_2O were 0.2 and 2.0 M, respectively.

The CO_2 was added to the solutions before or after the dissolution of MeO-Glcp in accordance with the method described in the section above.

4.4 Characterisation

4.4.1 ATR-FTIR spectroscopy

The chemical structures of MCC and the regenerated cellulose samples were examined using Fourier Transform Infrared (FTIR) spectroscopy collected on a PerkinElmer Frontier equipped with an Attenuated Total Reflectance (ATR) sampling accessory, PIKE Technologies GladiATR. Samples were placed on top of the ATR crystal and secured, using a metal clamp, to ensure consistent pressure. The measurements were collected with a resolution of 4 cm^{-1} and 32 scans. Furthermore, all spectra were corrected against air, normalised to the highest band and shown without an absorbance scale.

4.4.2 NMR spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy was used to investigate the interactions of CO_2 during the dissolution of cellulose in NaOH(aq), the effect had by a regenerating agent and the dissolution mechanism of MeO-Glcp in $NaOH/D_2O$ compared to $NaCl/D_2O$.

In Paper I, measurements were recorded for a 30-mg sample in dimethylsulfoxide (DMSO-d_6) with five drops of the ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIMAc) as solvent. EMIMAc was added to achieve complete dissolution and has the benefit of showing no chemical shifts in the region of 60-110 ppm, which is where the cellulose carbon signals appear. In addition, the solvent effect of DMSO on the chemical shifts of EMIMAc has been reported to be minor (Hesse-Ertelt et al. 2010).

1D ^{1}H and ^{13}C NMR experiments were performed in combination with 2D NMR such as heteronuclear single quantum coherence spectroscopy (HSQC). The experimental setup is reported in the appended papers.

5 Results and Discussion

The combined results of the appended papers are presented and discussed here, with no regard being paid to the order in which they are reported therein.

5.1 The influence of superbase pre-treatment of cellulose prior to dissolution in NaOH(aq)

Dissolution of cellulose has been proven to increase upon pre-treatment, such as hydrolysis and alkali extraction (Janzon et al. 2008a; Janzon et al. 2006; Janzon et al. 2008b; Kettenbach and Stein 2002; Roselli et al. 2014), which results in the original structure being disrupted and the reactivity thus being increased. In the present study, dissolving pulp was pre-treated with the super base DBU with this exact intention. DBU has been used previously as one of the components in the synthesis of switchable ionic liquids (Heldebrant *et al.* 2005). Also, DBU is often used as a deprotonating agent in organic synthesis and, bearing this in mind, the hypothesis that DBU deprotonates cellulose prior to dissolution in NaOH(aq), hence activating the cellulose, was outlined. As shown in Fig. 1 in the appended Paper I, cellulose pre-treated with one mol DBU per AGU was shown to increase in swelling and dissolution in NaOH(aq). When the ratio DBU was increased to 3 mol per AGU, it was surprising to find that dissolution was completely absent (Figure 13). Specific interactions between cellulose and DBU exist indeed and need to be optimised in order to, as in this case, achieve increased dissolution in NaOH(aq).

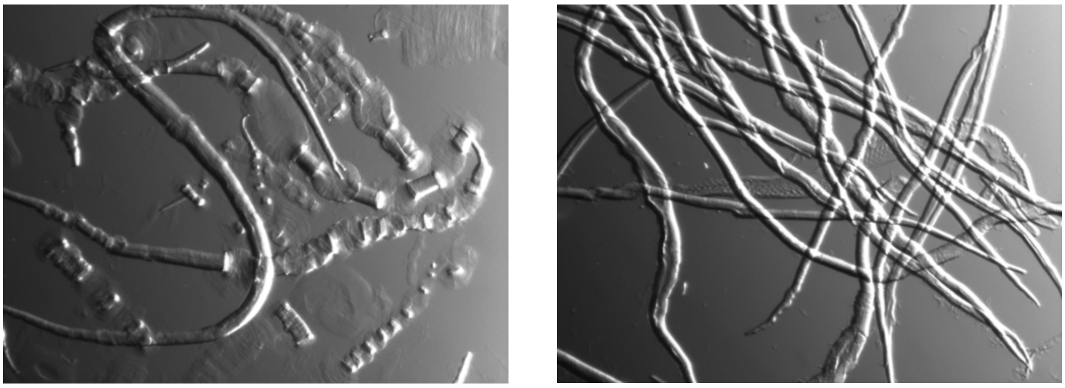

Figure 13. Cellulose dissolved in 8 wt% NaOH(aq) at -5°C. Left: untreated cellulose. Right: DBU pre-treated cellulose at a ratio of 3 mol DBU/AGU.

As dissolving pulps in general are difficult to dissolve fully in NaOH(aq), MCC was chosen as a model substance. The pre-treatment of MCC with different amounts of DBU was expected to increase the dissolution rate. Instead, an increased tendency for MCC to form a gel was observed.

Table 1 shows that the time until gelation occurs is influenced by the concentration of the MCC as well as the ratio of DBU in the pre-treatment.

Table 1. Gelation time for MCC in 8wt% NaOH(aq) at -5°C, with and without pre-treatment with DBU at different ratios.

MCC (wt%)	MCC:DBU	Gelation (time)
3	no DBU added	-
3	3:1	-
3	5:1	-
4	no DBU added	-
4	3:1	1h 30min
6	no DBU added	1h 25min
6	5:1	25min
6	10:1	45min

From these findings, common features of the NaOH(aq) system and DBU was found to be a specific affinity for capturing CO_2. Although NaOH(aq) is known to dissolve CO_2 from ambient air, especially at low temperatures (Lucile *et al.* 2012), the presence and action of CO_2 in NaOH(aq) in terms of cellulose dissolution has not been discussed in the literature. In the case of DBU, Zhang and co-workers have been able to dissolve cellulose in a switchable ionic liquid by reacting DBU with CO_2 at elevated pressure in DMSO (Xie et al. 2014; Zhang et al. 2013). They suggest a hypothesised intermediate where DBU deprotonates cellulose, which then makes a nucleophilic attack on the CO_2 to form a cellulose carbonate ion ($ROCOO^-$) with $DBUH^+$ as the counterion. Moreover, cellulose is activated in the switchable ionic liquid of $DBUH^+$ $ROCOO^-$ and can subsequently be used for the synthesis of cellulose acetate (Yang et al. 2015).

In summary, the specific interactions between both DBU cellulose and DBU CO_2 in combination with the fact that CO_2 absorbs readily in NaOH(aq) suggests that a reaction between the CO_2 and the deprotonated cellulose is plausible, and that it results in a change in the dissolved state and the formation of a gel during the dissolution process.

5.2 Regeneration of cellulose dissolved in NaOH(aq) with and without pre-treatment with DBU

The potential reaction between CO_2 and cellulose dissolved in NaOH(aq) was evaluated in both the presences and absences of DBU by regenerating the cellulose solutions. Organic carbonates synthesised via the reaction of an alkoxide with CO_2 are reported to be hydrolysed during work up in water why instead precipitation with alcohol is used to prevent desorption and preserve the presumably formed carbonate (Franchimont 1910). A similar work up approach was used during the regeneration of the cellulose solutions and the effect of regenerating agent was also evaluated.

Figure 14 shows the ATR-IR spectra of regenerated cellulose and pre-treated regenerated cellulose, both regenerated using ethanol, in comparison to the untreated reference cellulose. As expected, a new waveband at 1592 cm^{-1}, commonly referred to as a carbonate ion (Oh et al. 2005; Zhbankov 1966), could be observed for the pre-treated cellulose regenerated in ethanol. Surprisingly enough, the same waveband appeared for the regenerated cellulose (not pre-treated with DBU), thereby suggesting that the interaction between cellulose and CO_2 occurs without the addition of DBU. Moreover, a change in the intensity of the waveband at 1064 cm^{-1}, corresponding to the primary hydroxy group on cellulose, concurs with the theory that a sterically less-hindered hydroxy group is more reactive towards CO_2 (Aschenbrenner and Styring 2010). The pre-treatment with DBU was shown not to have any dramatic effect on the chemical structure when compared to the untreated cellulose: this suggests that DBU works as a catalyst and increases the rate of reaction of the chemisorption of CO_2 on cellulose during dissolution in NaOH(aq).

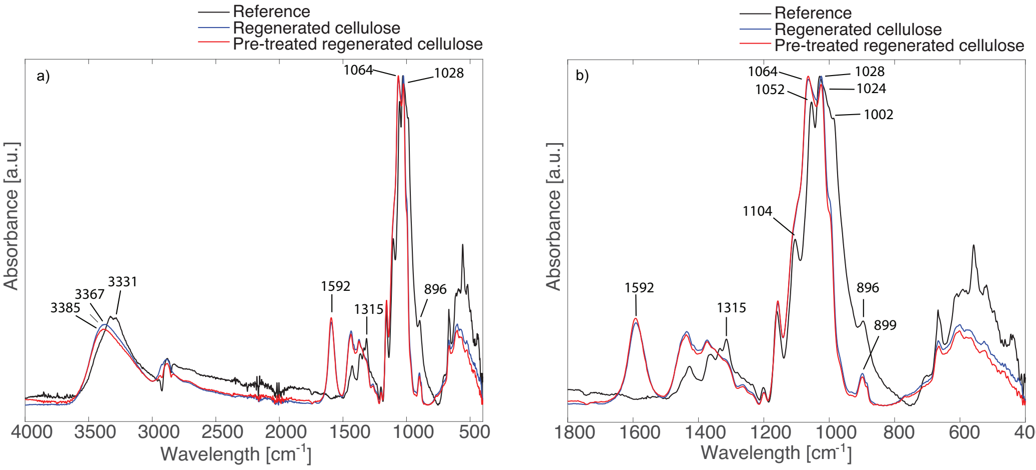

Figure 14. ATR-IR spectra of the reference cellulose, regenerated cellulose and pre-treated regenerated cellulose (both regenerated in ethanol) from a) 400-4000 cm^{-1} and b) magnified in the zone of 500-1800 cm^{-1}.

In addition, the reported reversible nature of the CO_2 incorporation as a carbonate was confirmed by varying the regenerating agent (Figure 15). The waveband at 1592 cm^{-1} disappeared indeed upon regeneration in water: as mentioned previously, this is a common behaviour of organic carbonate salts.

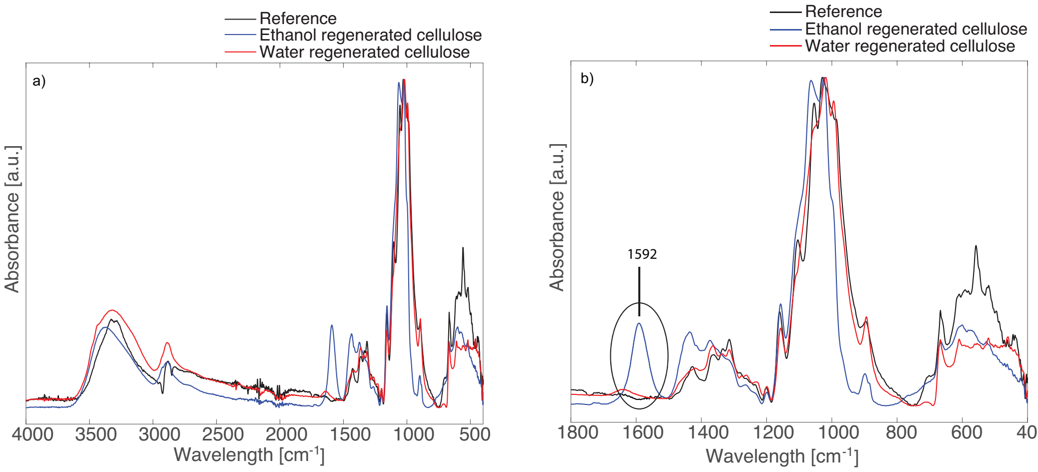

Figure 15. ATR-IR spectra of the reference cellulose, the ethanol regenerated cellulose and the water regenerated cellulose a) 400-4000 cm^{-1} and b) magnified in the zone of 400-1800 cm^{-1}.

The regenerated cellulose materials were characterised further using ^{13}C 1D and ^{1}H-^{13}C 2D NMR spectroscopy. In all the recorded spectra typical signals of cellulose carbons C1, C2, C3, C4, C5 and C6 could be observed at 102.7, 73.5, 74.8, 78.9, 75.5 and 60.0 ppm, respectively. In accordance with the results obtained from ATR-IR spectroscopy, both the untreated and the DBU pre-treated ethanol regenerated materials displayed a new signal at 154 ppm in the ^{13}C NMR (Figure 16), corresponding to the carbonyl moiety in an organic carbonate (Elschner and Heinze 2015).

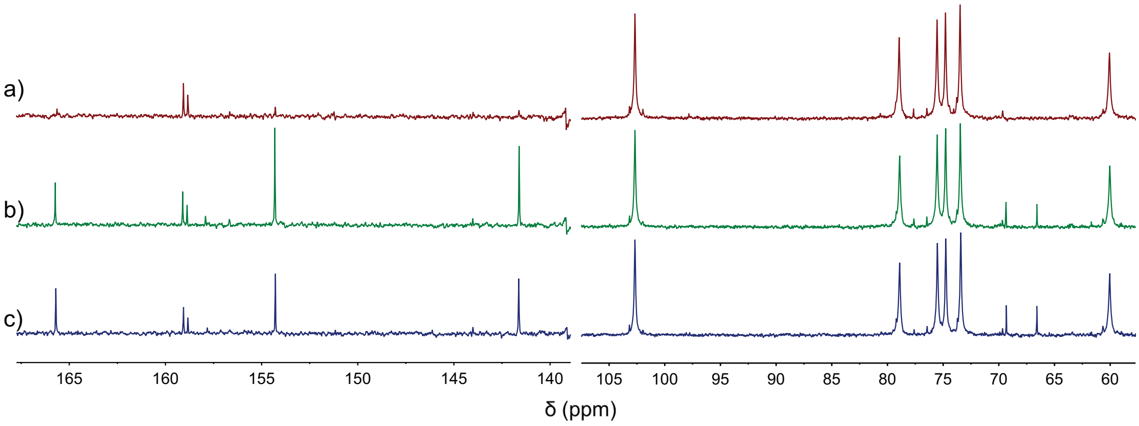

Figure 16. ^{13}C NMR spectra of a) reference cellulose b) untreated cellulose dissolved in NaOH(aq) and regenerated in ethanol and c) pre-treated cellulose dissolved in NaOH(aq) and regenerated in ethanol. All measurements were recorded at room temperature in DMSO d$_6$/EMIMAc.

In addition to this, two new signals were observed at 66.6 and 69.4 ppm in the cellulose area for the ethanol regenerated materials. In line with the previously reported changes in chemical shift upon substitution of cellulose with an electron withdrawing group, it is most likely that the signal at 66.6 ppm corresponds to a substituted C6 position on cellulose. Since substitution of the hydroxy group in position C6 results in a change in the hydrogen bonding pattern, which intermolecularly affects the C2 position, the signal at 69.4 ppm could be the result of a new chemical shift for the C2 position. The C2 position then moves upfield as it becomes more shielded. The 2D ^{1}H-^{13}C HSQC NMR spectrum of an ethanol regenerated material shown in Figure 17 reveals that the signal at 66.6 ppm belongs to a CH_2-group, i.e. potentially the C6 position. The signal at 69.4 ppm was shown to originate from either a CH_3-group or a CH-group, implying that it may correspond to a new C2 signal on the cellulose.

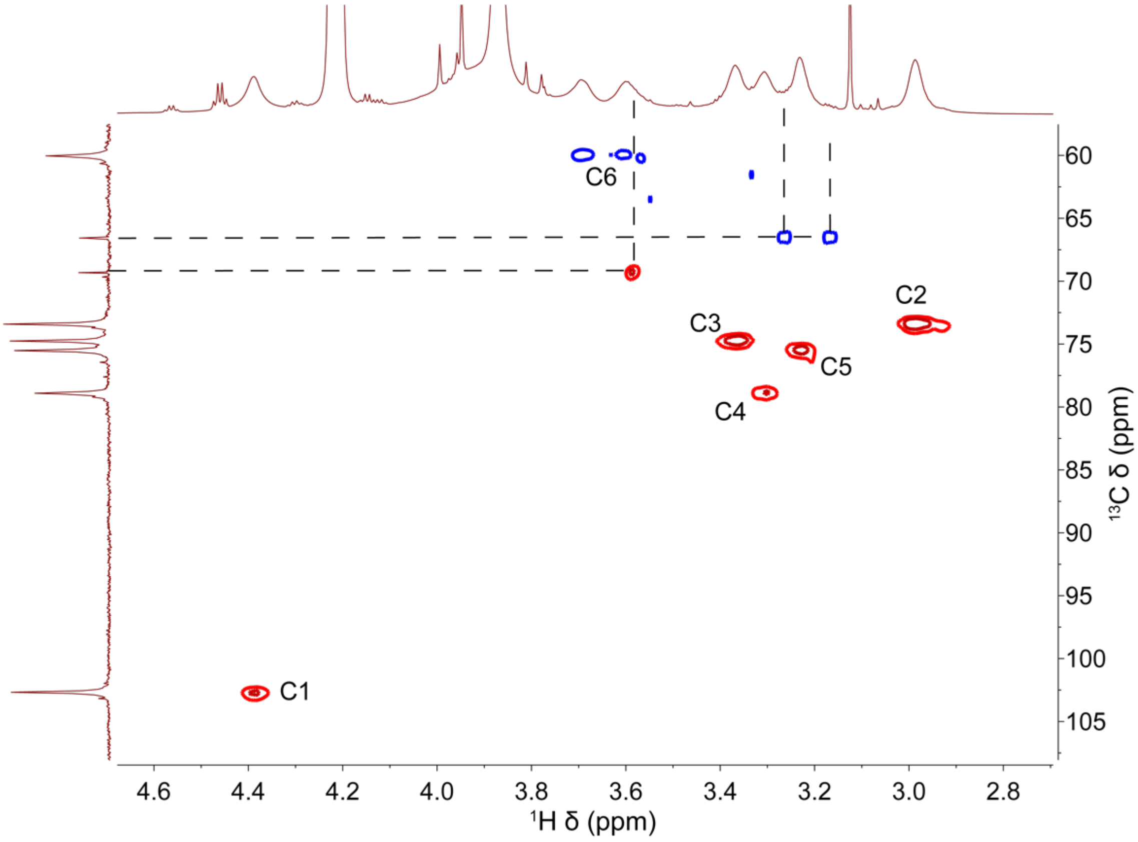

Figure 17. ^{1}H-^{13}C HSQC NMR spectroscopy of cellulose dissolved in 8wt% NaOH(aq) at -5°C and regenerated in ethanol. All measurements were recorded in DMSO d_6/EMIMAc at room temperature.

The materials regenerated with water showed neither the carbonate nor the new cellulose signals in ^{13}C NMR (Figure 18). This confirms the results observed with ATR-IR spectroscopy and further suggests that the chemisorption of CO_2 on cellulose is reversible upon regeneration in water.

Moreover, the cellulose materials regenerated with ethanol showed, in addition to the new cellulose signals, an interesting appearance of a new resonance structure of the cation ($EMIM^+$) of the EMIMAc. This has been found to be the result of a carboxylation reaction between CO_2 captured by cellulose and EMIM+ (Besnard et al. 2012; Kortunov et al. 2015), once again confirming that CO_2 chemisorbs on cellulose during dissolution in NaOH(aq). The chemical shifts of the new resonance structure are shown in Table 1 in the appended Paper I.

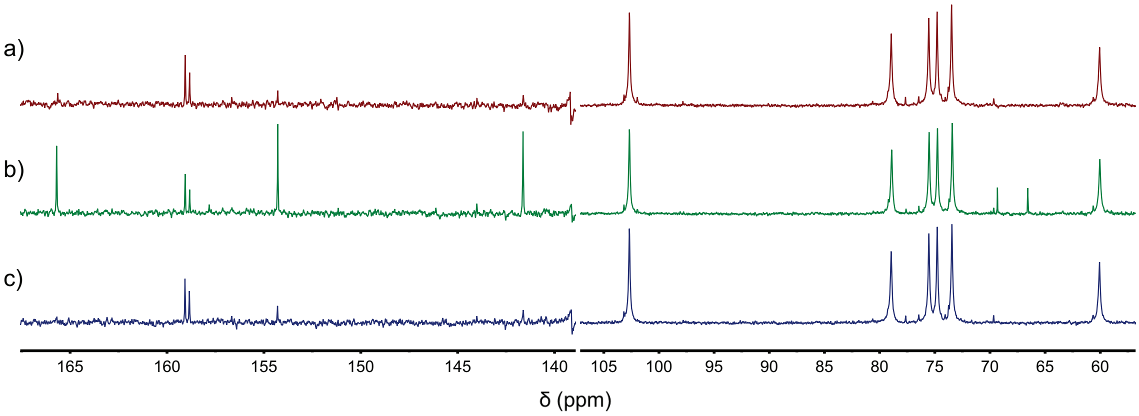

Figure 18. ^{13}C NMR spectra of a) reference cellulose, b) pre-treated cellulose dissolved in NaOH(aq) and regenerated with ethanol and c) pre-treated cellulose dissolved in NaOH and regenerated with water. All measurements were recorded at room temperature in DMSO d_6/EMIMAc.

Finally, a technique called diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to substantiate further the fact that CO_2 is chemisorbed onto regenerated cellulose materials. DRIFTS involves subjecting a sample to an inert atmosphere while the temperature is regulated. The desorbing gases from the material are then characterised using IR and mass spectroscopy. Indeed, when the temperature in the reaction cell was increased, CO_2 (and water) was shown to desorb from a regenerated cellulose material (Figure 19). Interestingly enough, varying amounts of CO_2 were observed to desorb at different temperatures whilst the temperature was being ramped up:

this indicates that CO_2 chemisorbs with different strengths at different positions on the cellulose.

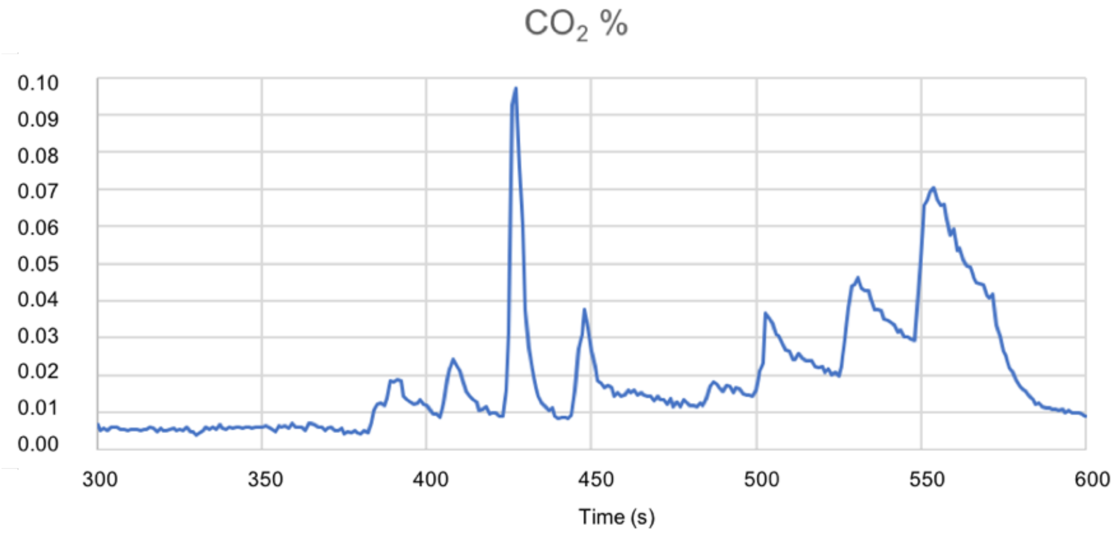

Figure 19. DRIFTS graph of cellulose pre-treated with DBU, dissolved in NaOH(aq) and regenerated in ethanol and run under argon with linear temperature ramping from 60 to 200°C.

5.3 The effect of pre- or post-dissolution addition of CO_2 to the cellulose/NaOH(aq) system

The model substrate MeO-Glcp was used in NMR studies to elucidate how CO_2 interacts with cellulose in NaOH(aq): its solubility in pure water makes MeO-Glcp preferable to using cellulose. The chemical changes that occur during dissolution in NaOH(aq) in comparison to a reference system of NaCl(aq) are therefore easily monitored. Additionally, the effect of CO_2 addition pre- and post-dissolution of the MeO-Glcp in both solvent systems can be evaluated representatively. Furthermore, dissolution of MCC with an addition of CO_2 pre- or post-dissolution was performed in order to investigate the stability of the solutions as well as the chemical structures upon regeneration.

5.3.1 Molecular investigation using NMR spectroscopy

Figure 20 shows the ^{13}C NMR spectra of MeO-Glcp dissolved in NaCl(aq) and NaOH(aq). Dissolution in NaOH(aq) clearly has an effect on the chemical shifts of MeO-Glcp, as all the carbons are shifted downfield. This phenomenon was discussed earlier by Isogai, who described it as dissociation of the hydroxy groups and carbons undergoing an electron-deshielding effect caused by NaOH(aq) (Isogai 1997). A similar explanation is given by Bialik et al., although the phenomenon in this case is referred to as deprotonation of the hydroxy groups, giving the cellulose the properties of a polyelectrolyte (Bialik et al. 2016). Here, the positions C1 and C3 are observed to be the most affected, suggesting that position C2 is the most prone to deprotonatation: this concurs the results found by Bialik et al. The change in the chemical shift for C1 and C3 would then be due to the β-effect from deprotonation on the neighbouring C2. The change in chemical shift of all the carbons in MeO-Glcp make it likely that the three hydroxy groups on MeO-Glcp are deprotonated to some degree.

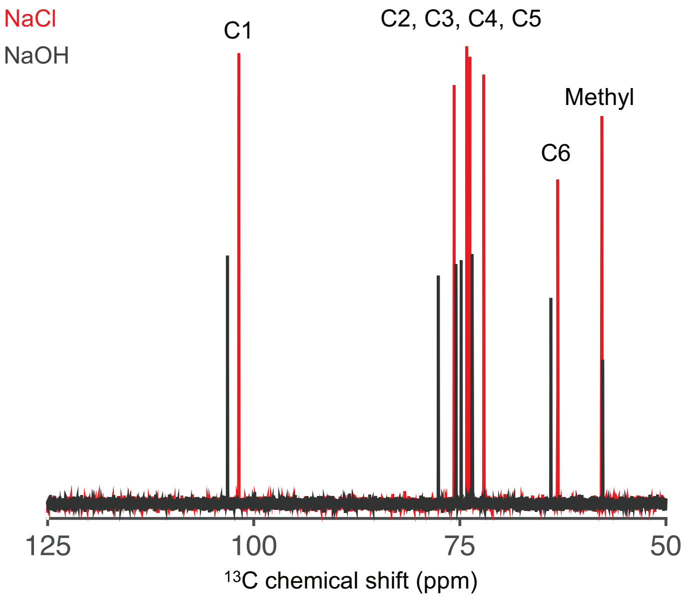

Figure 20. ^{13}C NMR spectra of MeO-Glcp dissolved in NaCl(aq) (red) and NaOH(aq) (black) recorded at +5°C.

All of the carbon moved consistently upfield in the chemical shift again upon the addition of CO_2, both pre- and post-dissolution of the MeO-Glcp. This shift upfield is due to the change in pH, as CO_2 converts to CO_2^{3-} by consuming hydroxide ions. However, the change in the chemical shift is not equal when CO_2 is added post-dissolution compared to pre-dissolution. When CO_2 is added pre-dissolution, it is expected to convert fully into CO_3^{2-} and thereby decrease the pH prior to the addition of MeO-Glcp. This will, in turn, affect the deprotonating ability of the solvent when MeO-Glcp is subsequently added and thus lower the electron-deshielding effect. In the case of the addition of CO_2

post-dissolution, the change in the chemical shift is observed as being even larger, suggesting other interactions occur between the CO_2 and MeO-Glcp already in the deprotonated state. The same effect was observed for the protons in the ^1H NMR measurements (Figure 21). It should be mentioned that addition of CO_2 to MeO-Glcp in NaCl(aq), both prior and after the dissolution of MeO-Glcp, was observed to not have an effect on neither the chemical shifts nor the integrals.

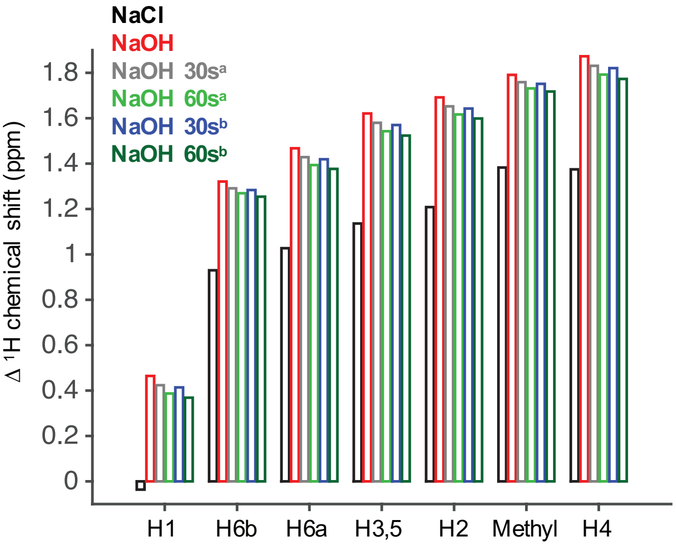

Figure 21. The changes in the chemical shifts for all proton in MeO-Glcp. All spectra were recorded at +5°C. 30s or 60s indicates the duration of the CO_2 addition in seconds. [a] CO_2 addition prior to the dissolution of MeO-Glcp, [b] CO_2 addition after the dissolution of MeO-Glcp.

Interestingly enough, the intensity of the ^{13}C integrals for MeO-Glcp dissolved in NaOH(aq) was observed to be reduced by more than 30% when compared to integrals for MeO-Glcp dissolved in NaCl(aq), even though the salt content was the same in all samples. Surprisingly, when CO_2 was added, both prior and after dissolution, the intensity increased again and especially in the case of post-dissolution addition of CO_2 (Figure 22). These findings may be indicative of distinct interactions in the carbohydrate/NaOH(aq)/CO_2 system, in particular those involving interactions of CO_2 with deprotonated cellulose, contributing to the intensified NMR signals and are to be further investigated.

It should be also mentioned that the CO_3^{2-} signal originating from the pure CO_2/NaOH(aq) system appears at 168.0 ppm, while in presence of MeO-Glcp (both in the case of pre- and post-dissolution, addition of CO_2) the signal shifts to 168.5 ppm, which indicates an interaction between CO_3^{2-} and MeO-Glcp.

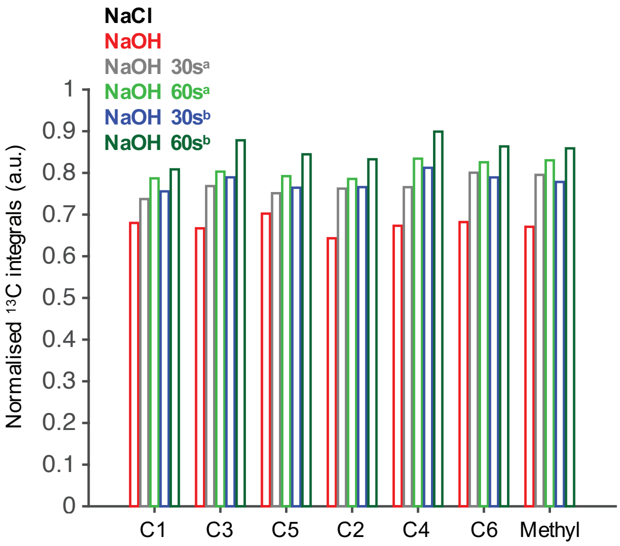

Figure 22. Intensity of the ^{13}C integrals of MeO-Glcp dissolved in NaOH(aq) at -5°C. The integrals are normalised to those of MeO-Glcp dissolved in NaCl(aq). All spectra were recorded at +5°C. 30s or 60s indicates the duration of the CO_2 addition in seconds. ^{a} CO_2 addition prior to the dissolution of MeO-Glcp, ^{b} CO_2 addition after the dissolution of MeO-Glcp.

5.3.2 Stability and regeneration of cellulose solutions in the case of pre- and post-dissolution addition of CO_2

Cellulose dissolved in NaOH(aq) at low temperatures is known to precipitate when approaching room temperature. During precipitation, the cellulose chains re-associate and the solution turns turbid and increases in viscosity. In order to investigate the stability of MCC dissolved in NaOH(aq) with addition of CO_2 both pre- and post-dissolution, solutions were left to age at room temperature for a period of two weeks. All solutions were transparent in appearance directly after dissolution.

After ageing for two weeks, the difference in the stability of the solutions with CO_2 added was profound (Figure 23). The solution without an addition of CO_2 turned a little turbid but remained as a liquid. The solution with an addition of CO_2 pre-dissolution also remained as a liquid even though it turned much more turbid than that without a CO_2 addition. The exciting result was the solution with an addition of CO_2 post-dissolution: this which turned completely opaque and formed a highly viscous gel. In combination with the results from the NMR investigation, ocular observations point towards a specific interaction taking place between CO_2 and cellulose: for the latter, when already in the deprotonated state.

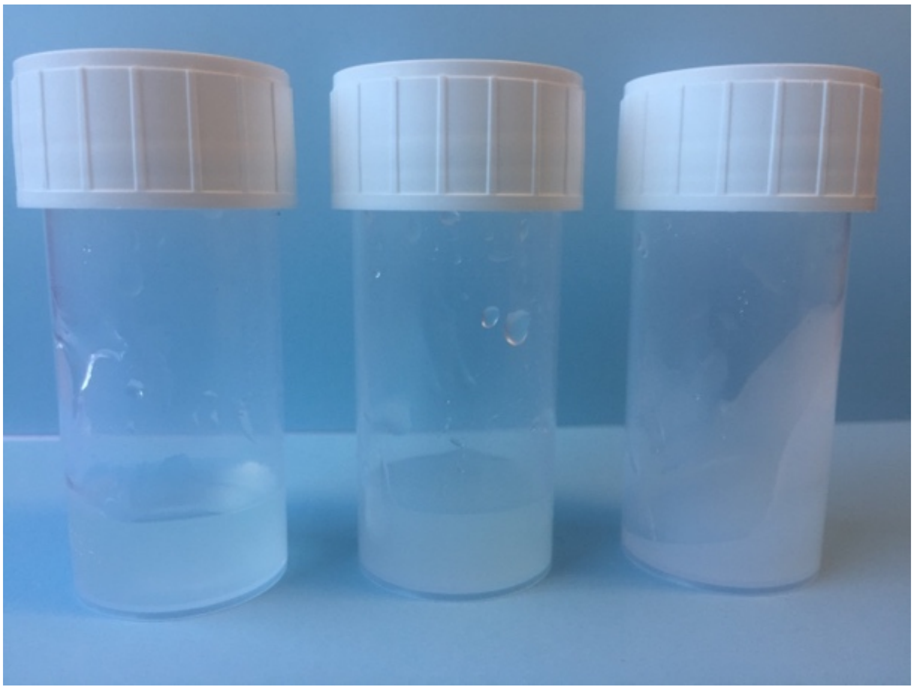

Figure 23. MCC dissolved in 8 wt% NaOH (aq) at -5°C without CO_2 addition, with pre-dissolution addition of CO_2 and with post-dissolution addition of CO_2, from left to right, after two weeks.

Based on the above described observations, it is plausible to argue for the formation of cellulose carbonate by addition of CO_2 to a solution of dissolved and deprotonated cellulose in NaOH(aq). Suggested mechanisms found in the literature for MeOH and glycerol reactions with CO_2 (Faurholt 1927; Song and Rochelle 2017) involves deprotonation of the alcohol and a subsequent kinetically favoured nucleophilic attack of the alkoxide on CO_2 to afford an alkyl carbonate over OH^- converting CO_2 to CO_3^{2-}.

The ability of cellulose carbonate to form hydrogen bonds with neighbouring chains will then lead to formation of a crosslinked network, observed as a gel in the sample where CO_2 was added after the dissolution of cellulose in NaOH(aq) (Figure 24).

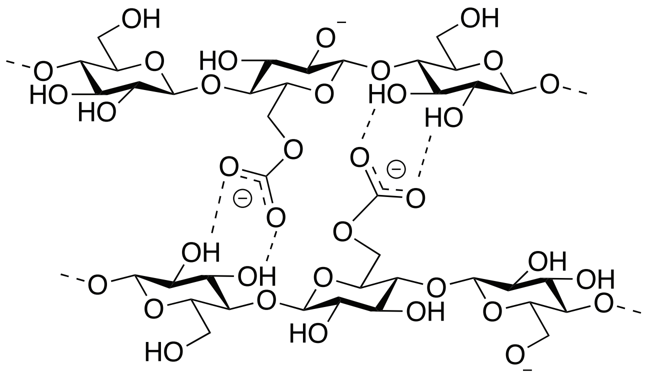

Figure 24. Mechanism suggested for hydrogen bonding between two chains of cellulose carbonate.

Furthermore, the aged cellulose solutions (both with pre- and post-dissolution addition of CO_2), were regenerated with ethanol, to preserve the chemisorbed CO_2 (Franchimont 1910) and analysed using ATR-IR spectroscopy to obtain structural information on the aged samples. The addition of CO_2, both pre- and post-dissolution, clearly has an effect on the chemical structure of regenerated materials (Figure 25). The most pronounced change, compared to untreated MCC, is a strong waveband at 1427 cm^{-1}. This is commonly assigned to CH_2-deformation (Larkin 2011) which, in this case, would refer to a change at the primary alcohol at position C6 on the cellulose. In addition to this, the decrease in intensity of the OH-stretching at 3300 cm^{-1} indicates a change in the crystalline structure due to disruptions in the hydrogen bonding pattern and possibly also due to partial carbonate substitution of the cellulose hydroxy groups. In line with the above discussed observations and implications, the change seems to be more profound for the materials with a post-dissolution addition of CO_2. Concurring with the previous ATR-IR spectroscopy results, all of the regenerated materials show a small waveband at 1592 cm^{-1}, corresponding to out-of-phase stretching of CO_2 (Zhbankov 1966) Moreover, the strong waveband at 880 cm^{-1} for the generated materials is due to the formation of Na_2CO_3 in NaOH(aq), which is still present in the materials.

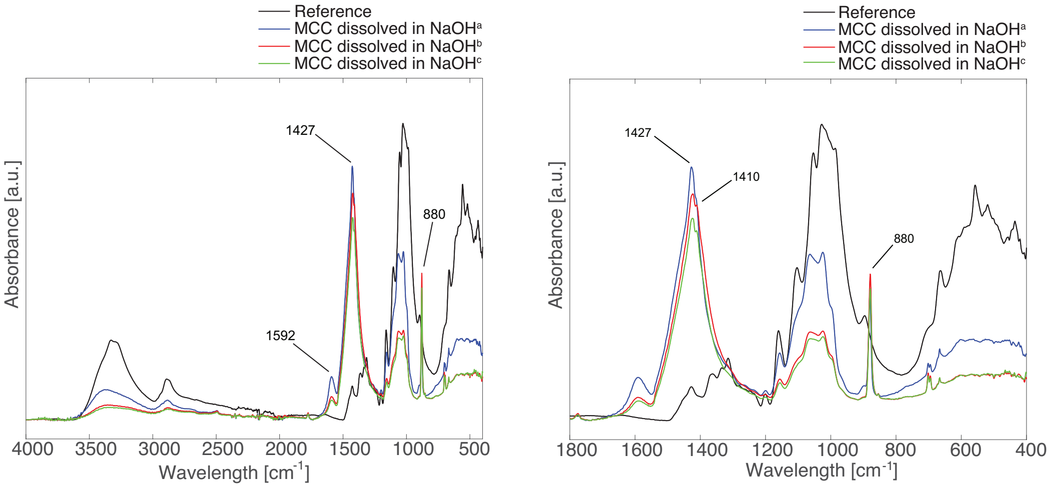

Figure 25. ATR-IR spectra of the reference cellulose, [a] MCC dissolved in NaOH with pre-dissolution addition of CO_2 during 60 s, [b] MCC dissolved in NaOH with post-dissolution addition of CO_2 during 60 s, [c] MCC dissolved in NaOH with post-dissolution addition of CO_2 during 120 s. All dissolved MCC solutions were regenerated in ethanol.

In the case of CO_2 additions made post-dissolution, a small shoulder appears at 1410 cm^{-1}, which is attributed to the in-phase stretching of CO_2 (Larkin 2011). It suggests again that specific interactions occur between the cellulose dissolved in NaOH(aq) and the CO_2 added post-dissolution.

6 Concluding remarks and Future work

The interactions between CO_2 and cellulose during its dissolution in NaOH(aq) have been examined. The results obtained from each study are now summarised and discussed in relation to each other. Suggestions for future work are also presented.

This thesis has shown that cellulose dissolved in NaOH(aq) interacts with CO_2. Early investigations in this project used a pre-treatment with a superbase, namely DBU, with the intention of activating cellulose prior to dissolution and thus increasing the rate of dissolution. It was surprising to discover that this pre-treatment did just the opposite and, instead, increased the tendency of cellulose to gel in NaOH(aq). From this it was concluded that a common feature of both DBU and NaOH(aq) is their ability to capture CO_2. The hypothesis that DBU catalyses a carbonation reaction between cellulose and CO_2 in NaOH(aq) was then formulated.

Bearing this in mind, untreated and DBU pre-treated cellulose was dissolved in NaOH(aq) and regenerated further with ethanol to avoid the hydrolysis of presumed cellulose-CO_2 adducts. Characterisation of the regenerated materials using ATR-IR spectroscopy showed that CO_2 indeed chemisorbs onto pre-treated cellulose when dissolved in NaOH(aq) because a new waveband appeared at 1592 cm^{-1}. CO_2 was also observed to chemisorb onto cellulose without being subjected to the pre-treatment, which was remarkable. Additional characterisation using NMR spectroscopy of the regenerated material confirmed the results of the ATR-IR spectroscopy: a signal appeared at 154 ppm, which is commonly assigned to a carbonate, for both untreated and pre-treated materials regenerated with ethanol. Later, the signal at 154 ppm was found to originate from a subsequent reaction between CO_2 and EMIMAc, which was used as a solvent for the NMR measurement: this proves CO_2 was introduced on the regenerated cellulose material via chemisorption. Moreover, NMR spectroscopy revealed two new signals in the cellulose area, which are interpreted as new chemical shifts for C6 and C2: it is possible they are due to substitution of cellulose with CO_2. One additional technique, DRIFTS, was used to prove that CO_2 was chemisorbed onto cellulose: it did indeed show that CO_2 and water desorb from ethanol-regenerated materials upon heating.

Further, the effect of CO_2 added pre- and post-dissolution of cellulose in NaOH(aq) was investigated in NMR spectroscopy studies using the model substrate MeO-Glcp. Firstly, MeO-Glcp dissolved in NaOH(aq) showed a clear change in chemical shifts of both ^1H and ^{13}C when compared to MeO-Glcp dissolved in NaCl(aq). This is interpreted as one or several of the hydroxy groups on MeO-Glcp being deprotonated in NaOH(aq). The ^{13}C chemical shifts moved downfield, whereas the ^1H chemical shift moved upfield, in the MeO-Glcp dissolved in NaOH(aq) compared to MeO-Glcp dissolved in NaCl(aq). Upon the addition of CO_2, both pre- and post-dissolution of MeO-Glcp in NaOH(aq), the ^{13}C chemical shifts moved upfield again, partly because of a change in pH. It is interesting that the change upfield was larger when CO_2 was added post-dissolution of MeO-Glcp in NaOH(aq), suggesting that other interactions take place between the CO_2 and the cellulose when the latter is in its highest deprotonated state. Moreover, the integral intensity of ^{13}C increased consistently as the amount of CO_2 added increased. A larger increase was, however, observed when CO_2 was added post-dissolution of MeO-Glcp in NaOH(aq), once again indicating other interactions compared, in this case, to when CO_2 is added post-dissolution of MeO-Glcp in NaOH(aq).

The effect of CO_2 was considered further in terms of the stability of MCC dissolved in NaOH(aq) with the addition of CO_2 pre- or post-dissolution. Solutions were aged at room temperature for two weeks. A clear difference in stability could be observed, since the solution with the addition of CO_2 post-dissolution had turned into a viscous, turbid gel. This was in direct contrast to solutions with no addition of CO_2 or a CO_2 addition pre-dissolution, both of which remained as liquids. A possible explanation for this gel phenomenon could be that it is the result of formation of a cellulose carbonate with the ability to create a crosslink between two chains through hydrogen bonding.

In combination with these results, ATR-IR spectroscopy of the corresponding regenerated materials revealed a difference in their chemical structure. The materials regenerated from solutions with CO_2 added post-dissolution showed an additional waveband commonly assigned to the in-phase stretching of CO_2 and the materials regenerated from solutions with an addition of CO_2 pre-dissolution did not.

Summarising, the results presented in the thesis imply that the interaction mechanisms differ, and depend on whether the CO_2 is added pre- or post-dissolution of cellulose in NaOH(aq), pointing out a decisive reaction between deprotonated cellulose and CO_2 in its molecular form (i.e. not in its carbonate form, CO_3^{2-}).

In future work, the low abundance of $^{13}CO_2$ is a limiting factor in NMR spectroscopy measurements should be taken into consideration. ^{13}C labelled CO_2 should be used in investigations of whether or not CO_2 interacts differently with cellulose when added post-dissolution versus pre-dissolution. If it does, then additional signals in the ^{13}C NMR of the different CO_2 species are to be expected.

Other studies regarding the interactions between cellulose and zincate have shown that an obvious change in the chemical shift is not to be expected even though zincate interacts with cellulose. This could also be true for cellulose and CO_2, which is why diffusion NMR spectroscopy could be an alternative technique for measuring if different diffusion rates exist for CO_2 in the NaOH(aq) system.

In addition, the gel formed during the dissolution of cellulose in NaOH(aq) should be analysed with, for example, solid-state NMR spectroscopy to elucidate its chemical structure.

Acknowledgements

This thesis and the associated work are part of the research network **Avancell – Centre for Fiber Engineering**, a collaboration between Södra Innovation, Chalmers University of Technology, Lund University, University of Coimbra, Swerea IVF AB and RISE Research Institutes of Sweden AB. The project is financed by the research foundation **Södra Skogsägarnas stiftelse för forskning, utveckling och utbildning.**

Furthermore, a number of people are greatly acknowledged for making this thesis achievable:

- My main supervisor and examiner, Hans Theliander, for encouragement and fruitful discussion, both scientific and in my personal development.

- My co-supervisor, Merima Hasani, for your never-ending enthusiasm and support regarding organic chemistry and cellulose.

- My co-supervisor, Gunnar Westman. Thank you for always having time for me!

- The Swedish NMR Centre. A special thanks to Diana, Cecilia and Maxim for great support and expertise.

- All my colleges and friends on Floor 3, for nice "fika" during Fridays and your diversity in scientific skills. A special thanks to Eva and Malin, for keeping SIKT in shape with your drive and helpfulness.

- All the lovely people on Floor 9, for being excellent in organic chemistry and guiding me in reactions and techniques. Most of all, to PhD Anna Said Stålsmeden!

- My friends, both inside and outside of Chalmers, especially when bringing me happiness on the dance floor.

- My mum and dad, for always believing in me and for your ability to give the best advices through both joy and difficulties.

- And lastly, my endless love to Pontus and Frank. You keep me steady on the ground ♥

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