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On the interference of urea with CO_2/CO_3^{2-} chemistry of cellulose model solutions in NaOH(aq)

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ABSTRACT

The CO_2/CO_3^{2-} chemistry of the cellulose/NaOH(aq) solutions has been recently reported to comprise a CO_2 incorporation through formation of a transient cellulose carbonate intermediate along with cellulose – CO_3^{2-} interactions. This work explores on molecular interactions arising when this chemistry is brought together with urea, the most common stabiliser of these solutions. ^1H, ^{13}C and steady-state heteronuclear Overhauser effect NMR studies on the cellulose analogues (methyl-β-glucopyranoside (β-MeO-Glcp) and microcrystalline cellulose), combined with pH and ATR-FTIR measurements, reveal concurrent interactions of urea with both CO_2 and CO_3^{2-} – leading to increased uptake of CO_2 and a buffering effect. Yet, regardless of the presence of urea, the route of conversion from CO_2 to CO_3^{2-}, whether going through reaction with the carbohydrate alkoxides or OH^-, is likely to determine the chemical environment of the formed CO_3^{2-}. These findings shed a new light on rather overlooked, albeit prominent, interactions in these solutions with the readily absorbed air CO_2, essential for further development and implementation, whether towards regenerated and modified cellulose or CO_2-capturing concepts.

1. Introduction

In a world facing a necessary transition to a bio-based economy, there is an urge to develop new dissolution systems for cellulose that would enable new processing technologies, not the least those relevant for cellulose-based textiles. Given the complex organisation of cellulose, including both intra- and intermolecular hydrogen bonding and stacking interactions (Lindman, Karlström, & Stigsson, 2010), there are only few solvents capable of dissolving cellulose and, thereby, allowing sustainable large-scale processing. One of the oldest and most attractive solvent systems is undoubtedly cold NaOH(aq). In spite of the long history of this system (Lilienfeld, 1924), the fundamental interactions governing properties and stability of cellulose solutions in NaOH(aq) are still not fully understood (Budtova & Navard, 2016). One of the main challenges for commercial implementation is the instability of these solutions, manifested as a spontaneous re-association of cellulose chains. In efforts to address this issue, numerous additives capable of improving solution stability have been investigated. Urea, along with zinc oxide and thiourea, has emerged as one of the most promising additives increasing both dissolution capacity and stability of obtained solutions (Cai & Zhang, 2005; Davidson, 1937; Egal, Budtova, & Navard, 2008; Jin, Zha, & Gu, 2007; Jiang et al., 2017; Liu, Budtova, & Navard, 2011; Qin, Lu, Cai, & Zhang, 2013; Yang et al., 2011). However, mechanistic understanding of the action of these additives is still scarce. In the search for comprehensive understanding of the molecular interactions of the cellulose/NaOH(aq) system, an overlooked dimension was recently found, namely its inherent interaction with CO_2. Investigations using MCC and cellulose analogues pointed out an incorporation of CO_2, going through the formation of a transient cellulose-carbonate intermediate that readily converts to CO_3^{2-} (Gunnarsson, Bernin, Östlund, & Hasani, 2018; Gunnarsson, Theliander, & Hasani, 2017). This route is kinetically favoured over the common alkali mediated conversion of CO_2 to CO_3^{2-} (Chiang, Lee, & Liu, 2017; Faurholt, 1927; Song & Rochelle, 2017) and is responsible for a significant incorporation of CO_2 in cellulose/alkali systems. In the presence of the cellulose analogues α-MeO-Glcp and β-MeO-Glcp, more than twice the amount of CO_2 can be captured compared to pure NaOH(aq). Thus, the properties of the cellulose solutions in cold NaOH(aq) are affected by the capturing and conversion of CO_2. The CO_3^{2-}(aq) formed shows different interactions with the carbohydrate depending on when (relative to the carbohydrate) it is introduced: when present in the solution prior to addition of the carbohydrate it was found to be poorly stabilised and prone to precipitate

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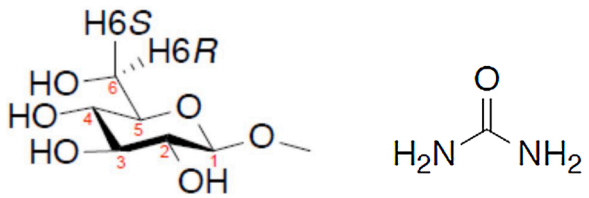

Fig. 1. The molecular structure of β-MeO-Glcp with annotations for the carbons and the protons (left) and urea (right).

(even though in close proximity to the carbohydrate); on the other hand, when formed through addition of CO_2 to a solution already containing a carbohydrate it seems to be stabilised by the very presence of carbohydrate (likely promoted by a specific formation route going through a carbohydrate-carbonate intermediate) (Gunnarsson, Bernin, & Hasani, 2020). In light of the increasing importance of the urea stabilised cellulose/NaOH(aq) systems it becomes highly interesting to investigate the behavior of the observed cellulose carbonate chemistry and cellulose – CO_3^{2-} association when urea is brought into play. Urea increases the pH of the NaOH(aq) solutions (Gunnarsson, Hasani, & Bernin, 2019), exhibits a strong affinity to CO_2-species, along with a non-specific association with dissolved cellulose. Given this ability of urea to strongly interact with as well cellulose/NaOH(aq) as CO_2-species, it is expected to profoundly interfere with the newly discovered CO_2/CO_3^{2-} – chemistry of the cellulose/NaOH(aq) solutions. Aiming at a comprehensive molecular understanding as a prerequisite for implementation and a broader development of these important solutions, this work sets out to elucidate molecular interplay of the cellulose/NaOH(aq)/urea system with the readily absorbed air CO_2. Does the inherent affinity of urea for CO_2 facilitate the CO_2 uptake of the cellulose/NaOH(aq) solutions? Does it interfere with the established cellulose-CO_2 chemistry of these systems? Does it affect the behavior of the entrapped CO_3^{2-} ions? Addressing these fundamental questions is expected to increase a general understanding of the inevitable CO_2-chemistry of these solutions and open up for further work on resolving their instability (not the least the role of urea as a common additive) and, in a broader perspective, developing new modification approaches. Complementary spectroscopic methods, as well as pH measurements were employed in order to investigate the molecular interactions of the NaOH(aq) solutions at low temperature when urea, CO_2 and cellulose analogues, (β-MeO-Glcp, or microcrystalline cellulose) are brought together.

2. Materials and methods

2.1. Chemicals

Methyl β-D-glucopyranoside (β -MeO-Glcp) (<99 %) (Fig. 1), NaOH (<98 %), NaCl (99.5 %), D_2O (99.9 %) and Na_2CO_3 (99 atom% ^{13}C) were purchased from Sigma Aldrich and used as received. Urea (99–100.5 %) (Fig. 1) was purchased from VWR and used as received. Microcrystalline cellulose (MCC) Avicel PH-101, with a degree of polymerisation of 260, was purchased from FMC BioPolymer and used without further treatment.

2.2. Sample preparation

Solutions for the evaluation of chemical shift values and quantification of captured CO_2 were prepared by dissolving NaOH (2.0 M) and urea (2.5 M) in D_2O. The solutions were cooled down to -5 °C prior to the addition of β-MeO-Glcp (0.4 M) and CO_2. Given the previously observed increased incorporation of CO_3^{2-} with prolonged exposure to CO_2(g), a relatively long introduction of CO_2(g) was selected for this study (120 s) to ensure easily measurable effects, even though significantly shorter exposure to CO_2(g) was shown to render similar interactions. CO_2(g) from a CO_2-tube was introduced to the solutions through a syringe connected to a flow regulator set to 4 ml/min. The syringe was immersed into the solutions for 120 s. β-MeO-Glcp was added prior or after the CO_2(g) introduction leading to a β-MeO-Glcp concentration of 0.4 M. The solutions were then stored at +5 °C prior to the characterisation.

A solution for the steady-state HOE experiment was prepared by dissolving NaOH (2.0 M), urea (2.5 M) and Na_2CO_3 (1.0 M) in D_2O at room temperature and further added to MCC (0.4 M) in a vial. The suspension was then vigorously shaken to obtain a homogeneous sample, transferred using a pipette to an NMR tube and put in a freezer at −20 °C. The frozen sample was then placed inside the magnet and thawed at +5 °C, which dissolves the cellulose and gives a stable solution to perform measurements on.

The pH was measured using a HACH HQD Multimeter with an Intellical PHC705 A1 pH probe and carried out by dissolving NaOH (0.5 M) and urea (2.5 M) in deionised water. The solution was then precooled to +10° before measuring the pH both before and after the addition of β-MeO-Glcp (0.4 M) and CO_2 for 120 s, which was added according to method above. Regenerated cellulose samples were prepared by dissolving MCC in NaOH(aq) (2.0 M) with urea (2.5 M) at −5 °C with the addition of CO_2 for 120 s, according to the method above, before or after dissolution of the MCC. The MCC was let to dissolve under stirring for 60 min before precipitated and regenerated with the addition of ethanol (98 %) and further washed with ethanol until neutral pH. The regenerated MCC samples were then dried *in vacuo* before characterisation.

2.3. Characterisation

All NMR experiments were run on an 800 MHz magnet equipped with a Bruker Avance HDIII console and a TXO cryoprobe. ^1H NMR spectra were recorded with the relaxation delay and number of scans set to 5 s and 8, respectively. ^{13}C NMR spectra were recorded with a low angle radio frequency pulse to minimise relaxation-weighting using a single pulse experiment with ^1H decoupling during acquisition. Hence, the repetition delay and number of scans was set to 33.0 s and 64, respectively, for monitoring the amount of dissolved CO_2 while a repetition delay of 5 s was used for the observation of chemical shift differences. A capillary containing D_2O with 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) was placed inside the tube as internal reference. 1D steady-state heteronuclear Overhauser effect (HOE) experiments were recorded to observe if any specific interactions between the CO_3^{2-} and MCC occurs in the presence of urea when dissolved in NaOH(aq). ^{13}C-labelled $Na_2^{13}CO_3$ was used to transfer magnetisation from the ^{13}C to the ^1H on MCC, which is possible to observe since all bonded H atoms of MCC are visible in a ^1H NMR spectrum. A low power 90° radio frequency (RF) pulse was applied on ^{13}C resonance of the carbonate peak 100 times with a delay of 10 ms in between to saturate the carbonate signal. After a delay of 13 s, the ^1H signal was excited with a strong short 90° RF pulse and recorded. The difference between two experiments, one with and one without saturation, indicates which sites interact with the carbonate. 1600 accumulations of the signal were recorded for both experiments at +5 °C.

FT-IR (Fourier Transform Infrared) spectra were recorded 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; they were measured with a resolution of 4 cm^{-1} and 32 scans. All spectra were corrected against air, baseline corrected and normalised against the CH-band around 2890 cm^{-1}, which was shown not to be affected by the different treatments in the sample preparation. All spectra are shown without an absorbance scale.

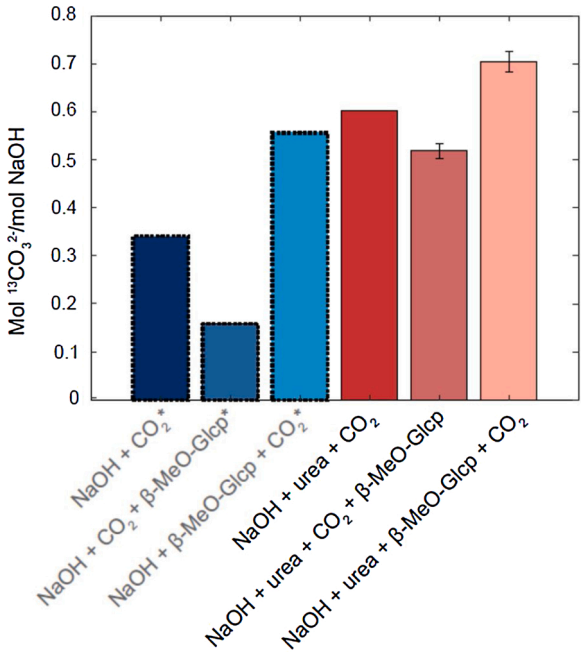

Fig. 2. The uptake of CO_2 in NaOH(aq) (2.0 M) and NaOH(aq) (2.0 M) + urea (2.5 M) measured as mol CO_3^{2-}/mol NaOH obtained from the ^{13}C NMR integrals before or after dissolution of β-MeO-Glcp. The order of the components in the labels reflect the addition order. Data marked with * is reprinted from Gunnarsson et al. (2020) for comparison.

3. Results and discussion

3.1. Urea increases the uptake of CO_2 in alkaline solution

Deploying on the methods from our previous work where the NaOH (aq) uptake of CO_2 was measured by quantitative ^{13}C NMR spectroscopy through integration of the CO_3^{2-} peak (0.35 mol CO_3^{2-}/mol NaOH in 2.5 M NaOH(aq), could be measured), the uptake of CO_2 in the presence of urea was studied (Fig. 2). By the addition of 2.5 M urea to the NaOH(aq), the uptake of CO_2 was increased from 0.35 to 0.60 mol CO_3^{2-}/mol NaOH. In other words, a NaOH(aq) solution containing urea that is let to stand in contact with the surrounding air will capture more CO_2 than a pure NaOH(aq) solution. Putting this into the context of cellulose/NaOH(aq) interactions with CO_2, the question arises whether and how the presence of the cellulose analogue β-MeO-Glcp will influence the CO_2 chemistry of the NaOH(aq)/urea solutions. The addition of the β-MeO-Glcp to an urea-free solution already containing CO_2 converted to CO_3^{2-} has, namely, been shown to decrease the measured amount of CO_3^{2-} in solution. In other words, our previous study showed that the amount of already captured CO_3^{2-} in NaOH(aq) decreased upon the addition β-MeO-Glcp, which could indicate a possible precipitation of the dissolved CO_3^{2-} mediated by addition of the carbohydrate (Gunnarsson et al., 2020). Interestingly, in the system containing urea, the same phenomenon was observed, although the decrease of the CO_3^{2-} signal was significantly less pronounced, indicating a stabilising effect of urea on the CO_3^{2-}(aq). It is possible that the rather amphiphilic carbonate ion, indeed, is stabilised by urea, which is known to promote solubilisation of amphiphilic and hydrophobic structures by affecting the surrounding water structure (Yadav & Chandra, 2018).

Conversely, dissolution of the β-MeO-Glcp in the NaOH(aq)/urea system prior to the addition of the CO_2 increased the amount of captured CO_2 even more compared to the carbohydrate-free NaOH(aq)/urea, which is in line with the previously observed capturing ability of the urea-free systems. The amount of captured CO_2 was found to increase from 0.55 to 0.70 mol CO_3^{2-}/mol NaOH when β-MeO-Glcp was added to the NaOH(aq)/urea system. The corresponding increase in an urea-free system brought about by the presence of β-MeO-Glcp could be measured to 0.20 mol CO_3^{2-}/mol NaOH (Gunnarsson et al., 2020). There is, thus, likely a favored interaction between the CO_2 and urea, even though both the urea and the carbohydrate mediate the CO_2 capture and its conversion to CO_3^{2-}.

Table 1
The pH of NaOH(aq) with urea, 0.5 M and 2.5 M, respectively at +10 °C and with addition of CO_2 and β-MeO-Glcp. The decrease in pH after each addition is shown within parenthesis while the total decrease in pH is shown in the last column.

Sample	Starting pH	pH after addition of CO_2	pH after addition of β-MeO-Glcp	Total decrease in pH
NaOH + urea + CO_2	14.00	13.85 (-0.15)		−0.15
NaOH + urea + CO_2 + β-MeO-Glcp	14.00	13.85 (-0.15)	13.62 (-0.23)	−0.38
NaOH + urea + β-MeO-Glcp + CO_2	14.00	13.59 (-0.31)	13.90 (-0.10)	−0.41

3.2. pH variations mediated by the presence of urea and the addition of CO_2

The observed reduction of the amount captured CO_2 in NaOH(aq)/urea when it is added prior to β-MeO-Glcp (pre-carbohydrate addition of CO_2), compared to the enhanced capture when adding it to a solution containing already dissolved carbohydrate (post-carbohydrate addition) suggests a difference in dynamics when solutes are added in different order. To further elucidate this observation, the pH variations accompanying addition of CO_2 and β-MeO-Glcp in varying order to the NaOH (aq)/urea were measured. Firstly, it was observed that the addition of urea to NaOH(aq) resulted in a pH increase (from 13.90 to 14.00 upon addition of 2.5 M urea to the 0.5 M NaOH(aq) solution). Since the concentration of NaOH in the solution was kept constant, this points out a change in the water activity and apparently a decrease in the proton activity mediated by urea. The increase in pH due to the addition of urea in aqueous solutions has already been observed and attributed to the ability of urea to perturb the activity coefficients of protons and ionisation of water (Bull, Breese, Ferguson, & Swenson, 1964). Schäfer reported, for instance, that urea interferes with neutralisation of acetic acid due to complexation of protons (Schäfer, 1976), while Gupta and Moulik suggested this complexation to occur through the carbonyl oxygen of urea, leading to a decreased proton activity as an exponential function of urea concentration (Das Gupta & Moulik, 1987).

Yet, applicability of these results to high pH solutions needs to be further investigated. It is, however, evident that the addition of urea has an impact on the NaOH(aq) system. As expected, addition of CO_2 to a carbohydrate-free NaOH(aq)/urea solution lowered the pH (here by 0.15) by consuming OH^- while converting to CO_3^{2-} (Table 1). Notably, the corresponding pH decrement was considerably larger in the urea-free solution (0.44), which is surprising considering the comparably lower amount of captured CO_2 in this case. The higher amount of captured CO_2 in the urea system would be expected to result in a larger pH decrement if the CO_2 to CO_3^{2-} conversion would occur through reaction with the OH^-. Instead, the lower pH decrement suggests a different mechanism for the conversion of CO_2 when urea is present in the NaOH(aq). When also adding β-MeO-Glcp to the NaOH(aq)/urea with CO_3^{2-}, the pH decreased further by 0.23, which is due to the β-MeO-Glcp acting as an acid. Without CO_3^{2-} present the decrease in pH was lower, indicating poorer deprotonation of the carbohydrate in the absence of CO_3^{2-}. The same phenomenon was also observed for the system without urea and implies that the CO_3^{2-} acts as a base and promotes deprotonation of the incoming β-MeO-Glcp. An interaction between the dissolved CO_3^{2-} and the incoming carbohydrate, possibly promoting precipitation of the CO_3^{2-} is also in line with the quantitative

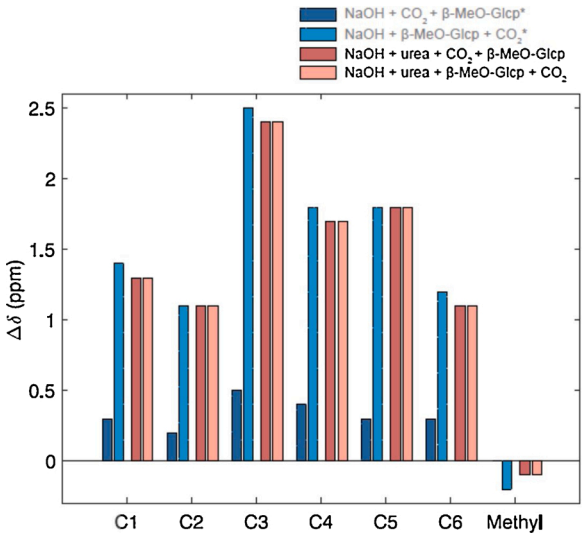

Fig. 3. The change in chemical shift for β-MeO-Glcp dissolved in NaOH(aq) with urea and addition of CO_2 before or after dissolution of the β-MeO-Glcp in comparison to the chemical shift for β-MeO-Glcp dissolved in NaOH(aq) with urea. All measurements were recorded at +5 °C. Data marked with * is reprinted from Gunnarsson et al. (2020) for comparison.

NMR measurements as discussed above (showing decrease in the ^{13}C NMR CO_3^{2-} signal upon addition of the carbohydrate). On the other hand, the post-carbohydrate addition of CO_2 was associated with a significantly higher incorporation of CO_3^{2-} (observed as an increase in the CO_3^{2-} NMR signal) but, in spite of that, reduced the pH to the approximately same final level. Once again, this points out a difference in reaction pathways leading to CO_3^{2-} when the carbohydrate and CO_2 are added in different order. This harmonises well with our previous finding on urea-free systems showing significantly higher CO_2 capture of the post-carbohydrate introduced CO_2, without any additional reduction of the final pH compared to the pre-carbohydrate introduced CO_2. Interestingly, though, the overall pH reduction accompanying the introduction of CO_2 was lower for the system containing urea. With urea present, the pH decreased from 14.00 to 13.59 and 13.62 upon pre and post-carbohydrate addition, respectively (Table 1), while the corresponding decrease in the absence of urea was 13.90 to 13.15 and 13.25 (Gunnarsson et al., 2020). This implies an urea-CO_2/CO_3^{2-} interaction possibly associated with a buffering effect. Additionally, even though the final pH was the same, the quantitative NMR measurements showed that more CO_2 was captured when the NaOH(aq)/urea also contained dissolved β-MeO-Glcp, which once again demonstrates the catalytical effect on the CO_2 conversion accomplished by the dissolved β-MeO-Glcp. In summary, all the pH variations, although following the same general trends as observed in an urea-free system, were suppressed by the presence of urea, which raises the question whether this is due to specific interactions of urea with other solutes (carbohydrate, CO_3^{2-} or freshly introduced CO_2) or due to its buffering effect.

3.3. Molecular alterations due to the presence of urea and addition of CO_2

The quantitative NMR and pH measurements showed that the order of the addition of the studied solutes appears to affect the dynamics of the system and results in different chemical environments. This concurs with our previous findings showing that both ^1H and ^{13}C chemical shifts of α-MeO-Glcp and β-MeO-Glcp are significantly more displaced when CO_2 is added to a solution already containing a carbohydrate (i.e. post-carbohydrate addition) compared to addition of the same amount of CO_2 prior to a carbohydrate. An increased incorporation of CO_3^{2-} in the case of post-carbohydrate addition was observed presumably going through formation of a carbohydrate carbonate intermediate. With urea brought into play, it is of high interest to investigate whether it interferes with this carbohydrate-carbonate chemistry and the (commonly observed) displacement pattern of the chemical shifts.

Table 2
The ^{13}C NMR chemical shifts in ppm of CO_3^{2-} and urea.

Sample	CO_3^{2-}	urea
NaOH + urea + CO_2	171.1	165.6
NaOH + urea + CO_2 + β-MeO-Glcp	170.9	165.5
NaOH + urea + β-MeO-Glcp + CO_2	169.4	165.5

Interestingly, contrary to previous observations on the urea-free system, with urea present in the NaOH(aq) no difference in pre and post-carbohydrate addition of CO_2 could be observed: both the pre and post-carbohydrate addition of CO_2 displaced equally the ^{13}C chemical shift of the β-MeO-Glcp (Fig. 3). The same could be observed for the ^1H NMR shifts. In other words, it appears that the presence of urea has a larger impact on the chemical shifts (i.e. the chemical environment) than the order of the carbohydrate/CO_2 addition or the presence of CO_3^{2-}. Moreover, the ^{13}C chemical shift values for the urea and CO_3^{2-} brought together in a carbohydrate-free NaOH(aq) solution were equal to those observed for urea and CO_3^{2-} when dissolved separately in NaOH (aq) (Table 2). Thus, although the addition of urea increased the amount of captured CO_2 it did not appear to interact with the CO_3^{2-} in a way that affects their ^{13}C chemical shift values. In the presence of a carbohydrate, though, this was changed. Addition of the β-MeO-Glcp to a solution already containing both urea and added CO_2 (pre-carbohydrate addition of CO_2), displaced the ^{13}C chemical shift of both the CO_3^{2-} and urea towards lower values, albeit very modestly (too small displacement to be considered significant). However, when the addition order was changed and the β-MeO-Glcp was added prior to addition of CO_2 and urea (post-carbohydrate addition of CO_2), the CO_3^{2-} peak was significantly more shifted (by 1.7 ppm), which indicates a different chemical environment experienced by this specie when formed in the presence of β-MeO-Glcp in the NaOH(aq)/urea. The same change in the CO_3^{2-} ^{13}C chemical shift upon post-carbohydrate addition of CO_2 was also observed in an urea-free systems, suggesting that the change observed is attributed to the presence of β-MeO-Glcp rather than the combination of both urea and β-MeO-Glcp. A comparison of the ^3J HH couplings between a reference sample (β-MeO-Glcp dissolved in NaCl(aq) with urea) and the β-MeO-Glcp dissolved in NaOH(aq)/urea revealed a significant change in one of the couplings involving the proton in position H6*R*. This coupling value decreased about 1 Hz going from the NaCl(aq)/urea to the NaOH(aq)/urea (data not shown).

The same change was observed in the urea-free systems (Gunnarsson et al., 2020) and is likely to arise from the conformational changes due to pH variation rather than from a β-MeO-Glcp – urea interaction. This phenomenon has previously been attributed to an alteration in orientation of the primary hydroxyl going from *tg* (*trans-gauche*) to *gt* (*gauche-trans*) (Bergenstråhle-Wohlert, Angles d'Ortoli, Sjöberg, Widmalm, & Wohlert, 2016; Horii, Hirai, & Ryozo, 1983). Interestingly, this change was reverted (the coupling value for the proton on the H6*R* position changed back by 1 Hz) upon addition of CO_2, whether added prior or after the carbohydrate. However, without urea in the system, this reversion occurred only in the case of post-carbohydrate addition of CO_2, which once again confirms that the presence of urea in the system seems to mask the spectral differences between the pre and post-carbohydrate addition of CO_2.

3.4. Investigation of the interaction between cellulose and CO_3^{2-} in the presence of urea

The results from the pH measurements and NMR spectroscopy point towards interactions between CO_3^{2-} and the cellulose analogue β-MeO-Glcp, and a possible impact of urea on these. To elucidate on the

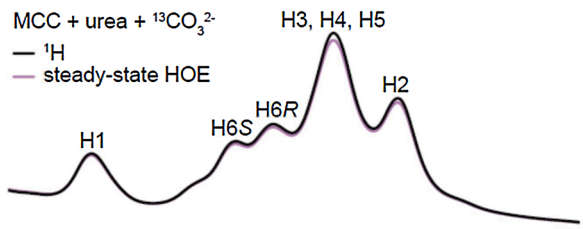

Fig. 4. Steady-state HOE measurement of MCC dissolved in NaOH(aq) with $Na^{13}CO_3^{2-}$ (bottom) and MCC dissolved in NaOH(aq) with urea and $Na_2^{13}CO_3$ (top). All measurements were recorded at +5 °C in D_2O.

indicated interactions, NMR experiments relying on the Heteronuclear Overhauser Effect (HOE) in combination with ATR-IR spectroscopy were performed using MCC as a cellulose substrate of satisfactory solubility in NaOH(aq). Samples for the steady-state HOE experiments were, therefore, prepared by dissolving MCC in either NaOH(aq) or NaOH(aq)/urea with $^{13}CO_3^{2-}$. The concept of a steady-state HOE measurement is to saturate the signal of a specific molecule and analyse how it affects other molecules in the system. The measurement is compared to a ^{1}H NMR spectrum without saturation and the effect is observed as an increase or decrease of the intensity of the studied molecules indicative of their proximity to the saturated signal molecule. In this case, the $^{13}CO_3^{2-}$ signal was saturated while the ^{1}H NMR spectrum of the MCC was recorded (Fig. 4). For an urea-free sample containing MCC dissolved in NaOH(aq) with $^{13}CO_3^{2-}$ (Gunnarsson et al., 2020)), it could be observed that the signal intensity of the all MCC protons decreased by the saturation of the $^{13}CO_3^{2-}$ signal, indicating that although the dynamics are fast, the two structures are close to each other for a short time. On the contrary, the corresponding measurement on the urea containing system showed that the intensity of the MCC protons was almost unaffected by the saturation of the $^{13}CO_3^{2-}$ (Fig. 4). It appears that in a system containing urea the association between MCC and the CO_3^{2-} is counteracted.

As a reminder, with urea present, an equal change in β-MeO-Glcp ^{13}C chemical shifts was observed regardless of when the CO_2 was added (pre or post-carbohydrate). Still, this was not the case for the ^{13}C chemical shift of the formed CO_3^{2-} ions. The chemical shift of the CO_3^{2-} formed upon post-carbohydrate addition of CO_2 to NaOH/urea/ β-MeO-Glcp was, namely, appreciably displaced to lower values compared to the solutions where no interaction between the carbohydrate and freshly added CO_2 was possible (Table 2). A possible explanation could be that the β-MeO-Glcp ^{13}C chemical shift values are primarily sensitive to the presence of urea and/or amount of CO_3^{2-} in solutions, both present in high concentrations in the urea containing systems regardless of when CO_2 is introduced. On the other hand, the chemical shift of CO_3^{2-} formed via carbohydrate mediated conversion of CO_2 (post-carbohydrate addition) reflects this specific formation route (through a carbohydrate carbonate intermediate) leading possibly to a β-MeO-Glcp - CO_3^{2-} interaction that affects its chemical shift. Thus, despite the presence of urea, the common CO_2-chemistry of the system still seems to be active, with the order of carbohydrate/CO_2 addition being determinant for the molecular interactions. This chemistry is not observable in the β-MeO-Glcp ^{13}C NMR shifts as the presence of urea and the high uptake of CO_2 in the presence of urea completely mask the differences between the pre and post-carbohydrate addition, but is reflected in the CO_3^{2-} chemical shift, as the latter is sensitive to the CO_3^{2-} formation route. The order of carbohydrate/CO_2 addition to the NaOH(aq)/urea system (i.e. the possibility of freshly added CO_2 interacting with the dissolved carbohydrate), therefore, appears to be determinant for the interactions in the system, which further affects the overall uptake of CO_2.

Capturing of CO_2 by cellulose/NaOH(aq) solutions could be previously observed as a new ATR-FTIR signal (1590 cm^{-1}) of the precipitated samples, originating from the captured cellulose carbonate intermediate formed during post-carbohydrate addition of CO_2 (Gunnarsson et al., 2017; 2018). The approach of precipitating the MCC samples from the urea/NaOH(aq) with pre- or post-carbohydrate addition of CO_2 was therefore used also here to investigate a possible interference of urea with this signature (Fig. 5). The ATR-FTIR spectra of MCC precipitated from NaOH(aq)/urea neat and from NaOH(aq)/urea

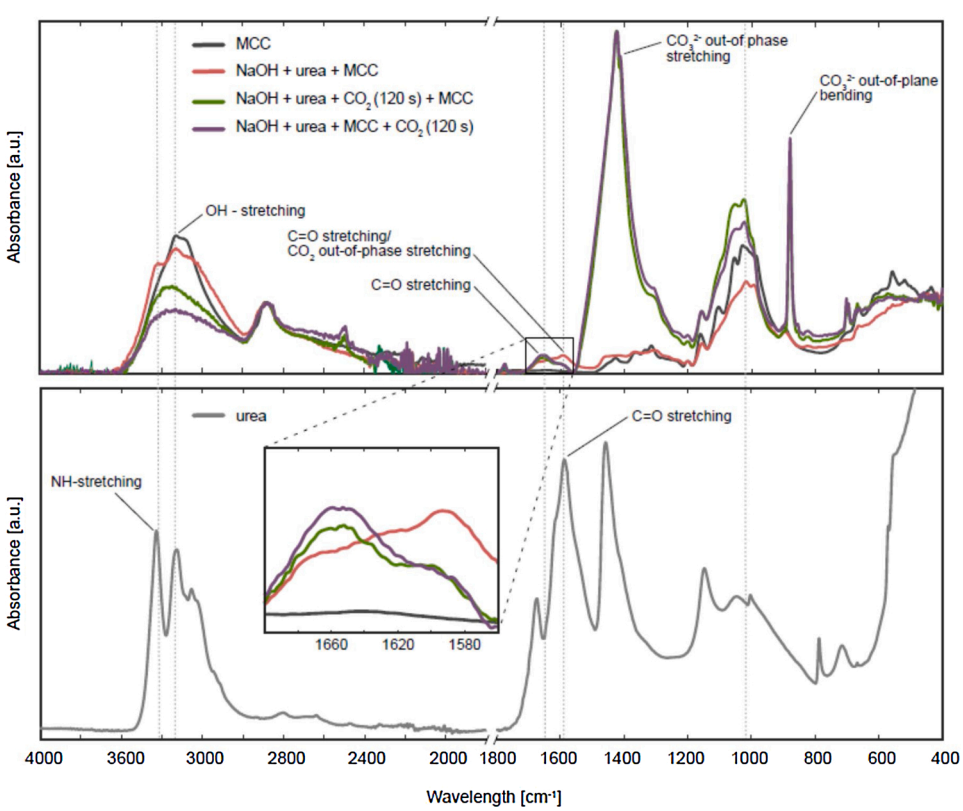

Fig. 5. At the top, ATR-FTIR spectra from 4000-400 cm^{-1} of untreated MCC (blue) and MCC dissolved in NaOH(aq) + urea (red), MCC dissolved in NaOH(aq) + urea + pre-carbohydrate addition of CO_2 (green) and MCC dissolved in NaOH(aq) + urea + post-carbohydrate addition of CO_2 (purple). All solutions were precipitated in ethanol, washed until neutral and dried. At the bottom, ATR-FTIR spectrum from 4000-400 cm^{-1} of neat urea (brown) for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

with pre or post-carbohydrate addition of CO_2 are shown in Fig. 5. Since neat urea has a significant peak at 1590 cm^{-1} corresponding to CO═ stretching it is difficult to distinguish it from a cellulose carbonate formed through a CO_2 reaction with cellulose. However, when introducing CO_2 to the system, whether through pre or post-carbohydrate addition (green and purple sample, respectively, at the top in Fig. 5), an interesting feature could be observed. A new peak at 1655 cm^{-1} increased in intensity while the peak at 1590 cm^{-1} decreased. A similar signature of urea forming a complex with different types of ions, was previously described: the peak at 1677 cm^{-1} moves to a lower wavenumber and the peak at 1625 cm^{-1} moves to a higher wavenumber (Gangopadhyay et al., 2016; Manivannan & Rajendran, 2011). Drawing parallels to this study, the increasing peak at 1655 cm^{-1} could be owing to the peaks at 1590 and 1677 cm^{-1} forming an average at 1655 cm^{-1} due to formation of a complex between the urea and possibly the CO_3^{2-}. The large peaks denoted as CO_3^{2-} out-of-phase stretching and out of-plane bending (Larkin & Larkin, 2011) originate from the precipitated Na_2CO_3 formed during the precipitation of the samples. The signature peaks for cellulose at 1000 cm^{-1} showed no significant changes due to the presence of neither the urea nor the CO_3^{2-}, but only the expected conversion from its native crystal structure (cellulose I) to the crystal structure of regenerated cellulose (cellulose II) e.g. loss in intensity of the peak at 1100 cm^{-1}. Interestingly, the incomplete removal of urea in the sample with no CO_2 added (shown as a clear peak at 3420 cm^{-1} corresponding to the N—H stretching of urea in the red sample at the top in Fig. 5) was largely absent in the samples with introduced CO_2, which could further indicate urea $-CO_3^{2-}$ association possibly facilitating washing out of these structures and thus leading to reduction of the peak at 3420 cm^{-1}. Conclusively, the affinity between the CO_3^{2-} and the urea observed in the HOE experiments was also evident in the ATR-FTIR spectra of the precipitated samples.

4. Conclusions

The presence of urea in the NaOH(aq) seems to affect the carbohydrate-CO_2 interactions threefold: (1) by catalytically increasing the uptake of CO_2 through a parallel urea – CO_2 interaction, visible as an increased CO_3^{2-} NMR signal intensity; (2) by moderating the pH changes resulting from addition of both carbohydrate and CO_2, which points out a buffering effect; (3) by counteracting interactions between a carbohydrate and the CO_3^{2-}, possibly by associating to the CO_3^{2-} as observed by HOE experiments (pre-carbohydrate addition of CO_2) and the ATR-FTIR studies of the precipitated samples. These factors in combination are likely to suppress the otherwise prominent changes in the chemical environment of the carbohydrate (NMR chemical shifts) when the order of addition of carbohydrate/CO_2 is changed, i.e. when the carbohydrate interacts with the already present CO_3^{2-}, compared to the freshly added CO_2 (forming a carbohydrate-carbonate intermediate). Still, the order of addition of carbohydrate/CO_2 and, thus, the route of the CO_3^{2-} formation (whether through reaction with a carbohydrate or OH^-) is likely to affect the chemical environment of the formed CO_3^{2-}. These findings shed a new light on the behavior and interplay of the two poorly understood, albeit very common, components of the cellulose/NaOH(aq) solutions – CO_2/CO_3^{2-} and urea – opening up for an improved understanding of their (in)stability and implementation possibilities.

CRediT authorship contribution statement

Maria Gunnarsson: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Diana Bernin:** Methodology, Supervision, Writing - review & editing. **Merima Hasani:** Conceptualization, Supervision, Writing - review & editing.

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