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# On the interference of urea with $\text{CO}_2/\text{CO}_3^{2-}$ chemistry of cellulose model solutions in $\text{NaOH(aq)}$

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## ABSTRACT

The  $\text{CO}_2/\text{CO}_3^{2-}$  chemistry of the cellulose/ $\text{NaOH(aq)}$  solutions has been recently reported to comprise a  $\text{CO}_2$  incorporation through formation of a transient cellulose carbonate intermediate along with cellulose –  $\text{CO}_3^{2-}$  interactions. This work explores on molecular interactions arising when this chemistry is brought together with urea, the most common stabiliser of these solutions.  $^1\text{H}$ ,  $^{13}\text{C}$  and steady-state heteronuclear Overhauser effect NMR studies on the cellulose analogues (methyl- $\beta$ -glucopyranoside ( $\beta$ -MeO-Glcp) and microcrystalline cellulose), combined with pH and ATR-FTIR measurements, reveal concurrent interactions of urea with both  $\text{CO}_2$  and  $\text{CO}_3^{2-}$  – leading to increased uptake of  $\text{CO}_2$  and a buffering effect. Yet, regardless of the presence of urea, the route of conversion from  $\text{CO}_2$  to  $\text{CO}_3^{2-}$ , whether going through reaction with the carbohydrate alkoxides or  $\text{OH}^-$ , is likely to determine the chemical environment of the formed  $\text{CO}_3^{2-}$ . These findings shed a new light on rather overlooked, albeit prominent, interactions in these solutions with the readily absorbed air  $\text{CO}_2$ , essential for further development and implementation, whether towards regenerated and modified cellulose or  $\text{CO}_2$ -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  $\text{NaOH(aq)}$ . In spite of the long history of this system (Lilienfeld, 1924), the fundamental interactions governing properties and stability of cellulose solutions in  $\text{NaOH(aq)}$  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 thio-urea, 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/ $\text{NaOH(aq)}$  system, an overlooked dimension was recently found, namely its inherent interaction with  $\text{CO}_2$ . Investigations using MCC and cellulose analogues pointed out an incorporation of  $\text{CO}_2$ , going through the formation of a transient cellulose-carbonate intermediate that readily converts to  $\text{CO}_3^{2-}$  (Gunnarsson, Bernin, Östlund, & Hasani, 2018; Gunnarsson, Theliander, & Hasani, 2017). This route is kinetically favoured over the common alkali mediated conversion of  $\text{CO}_2$  to  $\text{CO}_3^{2-}$  (Chiang, Lee, & Liu, 2017; Faurholt, 1927; Song & Rochelle, 2017) and is responsible for a significant incorporation of  $\text{CO}_2$  in cellulose/alkali systems. In the presence of the cellulose analogues  $\alpha$ -MeO-Glcp and  $\beta$ -MeO-Glcp, more than twice the amount of  $\text{CO}_2$  can be captured compared to pure  $\text{NaOH(aq)}$ . Thus, the properties of the cellulose solutions in cold  $\text{NaOH(aq)}$  are affected by the capturing and conversion of  $\text{CO}_2$ . The  $\text{CO}_3^{2-}(\text{aq})$  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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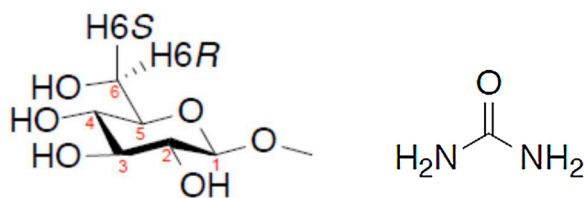


Fig. 1. The molecular structure of  $\beta$ -MeO-Glcp with annotations for the carbons and the protons (left) and urea (right).

(even though in close proximity to the carbohydrate); on the other hand, when formed through addition of  $\text{CO}_2$  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/ $\text{NaOH(aq)}$  systems it becomes highly interesting to investigate the behavior of the observed cellulose carbonate chemistry and cellulose- $\text{CO}_3^{2-}$  association when urea is brought into play. Urea increases the pH of the  $\text{NaOH(aq)}$  solutions (Gunnarsson, Hasani, & Bernin, 2019), exhibits a strong affinity to  $\text{CO}_2$ -species, along with a non-specific association with dissolved cellulose. Given this ability of urea to strongly interact with as well cellulose/ $\text{NaOH(aq)}$  as  $\text{CO}_2$ -species, it is expected to profoundly interfere with the newly discovered  $\text{CO}_2/\text{CO}_3^{2-}$  chemistry of the cellulose/ $\text{NaOH(aq)}$  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/ $\text{NaOH(aq)}$ /urea system with the readily absorbed air  $\text{CO}_2$ . Does the inherent affinity of urea for  $\text{CO}_2$  facilitate the  $\text{CO}_2$  uptake of the cellulose/ $\text{NaOH(aq)}$  solutions? Does it interfere with the established cellulose- $\text{CO}_2$  chemistry of these systems? Does it affect the behavior of the entrapped  $\text{CO}_3^{2-}$  ions? Addressing these fundamental questions is expected to increase a general understanding of the inevitable  $\text{CO}_2$ -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  $\text{NaOH(aq)}$  solutions at low temperature when urea,  $\text{CO}_2$  and cellulose analogues, ( $\beta$ -MeO-Glcp, or microcrystalline cellulose) are brought together.

## 2. Materials and methods

### 2.1. Chemicals

Methyl  $\beta$ -D-glucopyranoside ( $\beta$ -MeO-Glcp) (<99 %) (Fig. 1),  $\text{NaOH}$  (<98 %),  $\text{NaCl}$  (99.5 %),  $\text{D}_2\text{O}$  (99.9 %) and  $\text{Na}_2\text{CO}_3$  (99 atom%  $^{13}\text{C}$ ) 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  $\text{CO}_2$  were prepared by dissolving  $\text{NaOH}$  (2.0 M) and urea (2.5 M) in  $\text{D}_2\text{O}$ . The solutions were cooled down to  $-5^\circ\text{C}$  prior to the addition of  $\beta$ -MeO-Glcp (0.4 M) and  $\text{CO}_2$ . Given the previously observed increased incorporation of  $\text{CO}_3^{2-}$  with prolonged exposure to  $\text{CO}_2(\text{g})$ , a relatively long introduction of  $\text{CO}_2(\text{g})$  was selected for this study (120 s) to ensure easily measurable effects, even though significantly shorter exposure to  $\text{CO}_2(\text{g})$  was shown to render similar interactions.  $\text{CO}_2(\text{g})$  from a  $\text{CO}_2$ -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.  $\beta$ -MeO-Glcp was added prior or after the  $\text{CO}_2(\text{g})$  introduction leading to a  $\beta$ -MeO-Glcp concentration of 0.4 M. The solutions were then stored at  $+5^\circ\text{C}$  prior to the characterisation.

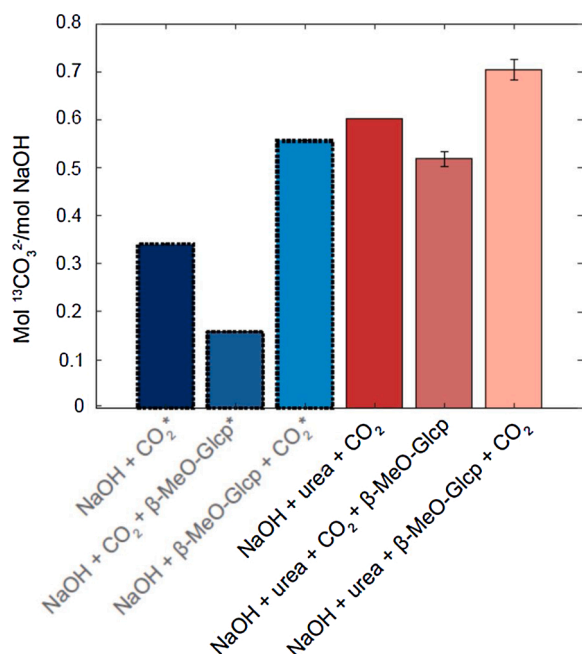
A solution for the steady-state HOE experiment was prepared by dissolving  $\text{NaOH}$  (2.0 M), urea (2.5 M) and  $\text{Na}_2\text{CO}_3$  (1.0 M) in  $\text{D}_2\text{O}$  at room temperature and further added to MCC (0.4 M) in a vial. The suspension was then vigorously shaken to obtain a homogeneous sample, transferred using a pipette to an NMR tube and put in a freezer at  $-20^\circ\text{C}$ . The frozen sample was then placed inside the magnet and thawed at  $+5^\circ\text{C}$ , 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  $\text{NaOH}$  (0.5 M) and urea (2.5 M) in deionised water. The solution was then pre-cooled to  $+10^\circ$  before measuring the pH both before and after the addition of  $\beta$ -MeO-Glcp (0.4 M) and  $\text{CO}_2$  for 120 s, which was added according to method above. Regenerated cellulose samples were prepared by dissolving MCC in  $\text{NaOH(aq)}$  (2.0 M) with urea (2.5 M) at  $-5^\circ\text{C}$  with the addition of  $\text{CO}_2$  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.  $^1\text{H}$  NMR spectra were recorded with the relaxation delay and number of scans set to 5 s and 8, respectively.  $^{13}\text{C}$  NMR spectra were recorded with a low angle radio frequency pulse to minimise relaxation-weighting using a single pulse experiment with  $^1\text{H}$  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  $\text{CO}_2$  while a repetition delay of 5 s was used for the observation of chemical shift differences. A capillary containing  $\text{D}_2\text{O}$  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  $\text{CO}_3^{2-}$  and MCC occurs in the presence of urea when dissolved in  $\text{NaOH(aq)}$ .  $^{13}\text{C}$ -labelled  $\text{Na}_2^{13}\text{CO}_3$  was used to transfer magnetisation from the  $^{13}\text{C}$  to the  $^1\text{H}$  on MCC, which is possible to observe since all bonded H atoms of MCC are visible in a  $^1\text{H}$  NMR spectrum. A low power  $90^\circ$  radio frequency (RF) pulse was applied on  $^{13}\text{C}$  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  $^1\text{H}$  signal was excited with a strong short  $90^\circ$  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  $+5^\circ\text{C}$ .

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  $4\text{ cm}^{-1}$  and 32 scans. All spectra were corrected against air, baseline corrected and normalised against the CH-band around  $2890\text{ cm}^{-1}$ , 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<sub>2</sub> in NaOH(aq) (2.0 M) and NaOH(aq) (2.0 M) + urea (2.5 M) measured as mol CO<sub>3</sub><sup>2-</sup>/mol NaOH obtained from the <sup>13</sup>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<sub>2</sub> in alkaline solution

Deploying on the methods from our previous work where the NaOH (aq) uptake of CO<sub>2</sub> was measured by quantitative <sup>13</sup>C NMR spectroscopy through integration of the CO<sub>3</sub><sup>2-</sup> peak (0.35 mol CO<sub>3</sub><sup>2-</sup>/mol NaOH in 2.5 M NaOH(aq), could be measured), the uptake of CO<sub>2</sub> 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<sub>2</sub> was increased from 0.35 to 0.60 mol CO<sub>3</sub><sup>2-</sup>/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<sub>2</sub> than a pure NaOH(aq) solution. Putting this into the context of cellulose/NaOH(aq) interactions with CO<sub>2</sub>, the question arises whether and how the presence of the cellulose analogue β-MeO-Glcp will influence the CO<sub>2</sub> chemistry of the NaOH(aq)/urea solutions. The addition of the β-MeO-Glcp to an urea-free solution already containing CO<sub>2</sub> converted to CO<sub>3</sub><sup>2-</sup> has, namely, been shown to decrease the measured amount of CO<sub>3</sub><sup>2-</sup> in solution. In other words, our previous study showed that the amount of already captured CO<sub>3</sub><sup>2-</sup> in NaOH(aq) decreased upon the addition β-MeO-Glcp, which could indicate a possible precipitation of the dissolved CO<sub>3</sub><sup>2-</sup> 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<sub>3</sub><sup>2-</sup> signal was significantly less pronounced, indicating a stabilising effect of urea on the CO<sub>3</sub><sup>2-</sup> (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<sub>2</sub> increased the amount of captured CO<sub>2</sub> 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<sub>2</sub> was found to increase from 0.55 to 0.70 mol CO<sub>3</sub><sup>2-</sup>/mol NaOH when β-MeO-Glcp was added to the NaOH(aq)/urea system. The corresponding increase in an urea-free

**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<sub>2</sub> 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 <sub>2</sub>	pH after addition of β-MeO-Glcp	Total decrease in pH
NaOH + urea + CO <sub>2</sub>	14.00	13.85 (-0.15)		-0.15
NaOH + urea + CO <sub>2</sub> + β-MeO-Glcp	14.00	13.85 (-0.15)	13.62 (-0.23)	-0.38
NaOH + urea + β-MeO-Glcp + CO <sub>2</sub>	14.00	13.59 (-0.31)	13.90 (-0.10)	-0.41

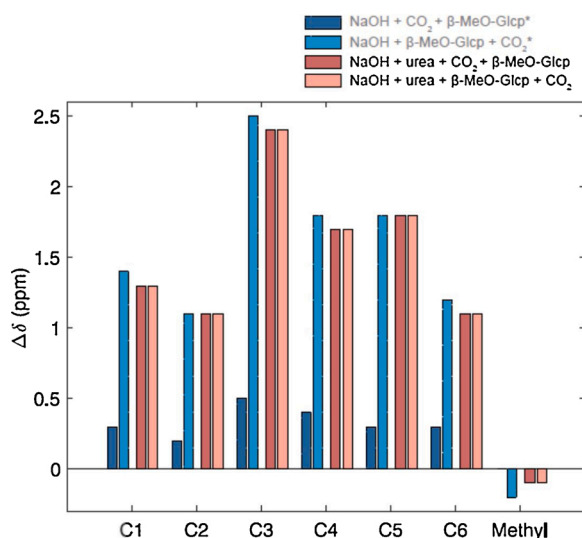
system brought about by the presence of β-MeO-Glcp could be measured to 0.20 mol CO<sub>3</sub><sup>2-</sup>/mol NaOH (Gunnarsson et al., 2020). There is, thus, likely a favored interaction between the CO<sub>2</sub> and urea, even though both the urea and the carbohydrate mediate the CO<sub>2</sub> capture and its conversion to CO<sub>3</sub><sup>2-</sup>.

#### 3.2. pH variations mediated by the presence of urea and the addition of CO<sub>2</sub>

The observed reduction of the amount captured CO<sub>2</sub> in NaOH(aq)/urea when it is added prior to β-MeO-Glcp (pre-carbohydrate addition of CO<sub>2</sub>), 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<sub>2</sub> 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<sub>2</sub> to a carbohydrate-free NaOH(aq)/urea solution lowered the pH (here by 0.15) by consuming OH<sup>-</sup> while converting to CO<sub>3</sub><sup>2-</sup> (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<sub>2</sub> in this case. The higher amount of captured CO<sub>2</sub> in the urea system would be expected to result in a larger pH decrement if the CO<sub>2</sub> to CO<sub>3</sub><sup>2-</sup> conversion would occur through reaction with the OH<sup>-</sup>. Instead, the lower pH decrement suggests a different mechanism for the conversion of CO<sub>2</sub> when urea is present in the NaOH(aq). When also adding β-MeO-Glcp to the NaOH(aq)/urea with CO<sub>3</sub><sup>2-</sup>, the pH decreased further by 0.23, which is due to the β-MeO-Glcp acting as an acid. Without CO<sub>3</sub><sup>2-</sup> present the decrease in pH was lower, indicating poorer deprotonation of the carbohydrate in the absence of CO<sub>3</sub><sup>2-</sup>. The same phenomenon was also observed for the system without urea and implies that the CO<sub>3</sub><sup>2-</sup> acts as a base and promotes deprotonation of the incoming β-MeO-Glcp. An interaction between the dissolved CO<sub>3</sub><sup>2-</sup> and the incoming carbohydrate, possibly promoting precipitation of the CO<sub>3</sub><sup>2-</sup> is also in line with the quantitative





**Fig. 3.** The change in chemical shift for  $\beta$ -MeO-Glcp dissolved in NaOH(aq) with urea and addition of  $\text{CO}_2$  before or after dissolution of the  $\beta$ -MeO-Glcp in comparison to the chemical shift for  $\beta$ -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  $^{13}\text{C}$  NMR  $\text{CO}_3^{2-}$  signal upon addition of the carbohydrate). On the other hand, the post-carbohydrate addition of  $\text{CO}_2$  was associated with a significantly higher incorporation of  $\text{CO}_3^{2-}$  (observed as an increase in the  $\text{CO}_3^{2-}$  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  $\text{CO}_3^{2-}$  when the carbohydrate and  $\text{CO}_2$  are added in different order. This harmonises well with our previous finding on urea-free systems showing significantly higher  $\text{CO}_2$  capture of the post-carbohydrate introduced  $\text{CO}_2$ , without any additional reduction of the final pH compared to the pre-carbohydrate introduced  $\text{CO}_2$ . Interestingly, though, the overall pH reduction accompanying the introduction of  $\text{CO}_2$  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- $\text{CO}_2/\text{CO}_3^{2-}$  interaction possibly associated with a buffering effect. Additionally, even though the final pH was the same, the quantitative NMR measurements showed that more  $\text{CO}_2$  was captured when the NaOH(aq)/urea also contained dissolved  $\beta$ -MeO-Glcp, which once again demonstrates the catalytic effect on the  $\text{CO}_2$  conversion accomplished by the dissolved  $\beta$ -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,  $\text{CO}_3^{2-}$  or freshly introduced  $\text{CO}_2$ ) or due to its buffering effect.

### 3.3. Molecular alterations due to the presence of urea and addition of $\text{CO}_2$

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  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of  $\alpha$ -MeO-Glcp and  $\beta$ -MeO-Glcp are significantly more displaced when  $\text{CO}_2$  is added to a solution already containing a carbohydrate (i.e. post-carbohydrate addition) compared to addition of the same amount of  $\text{CO}_2$  prior to a carbohydrate. An increased incorporation of  $\text{CO}_3^{2-}$  in the case of post-carbohydrate addition was observed presumably going through

**Table 2**

The  $^{13}\text{C}$  NMR chemical shifts in ppm of  $\text{CO}_3^{2-}$  and urea.

Sample	$\text{CO}_3^{2-}$	urea
NaOH + urea + $\text{CO}_2$	171.1	165.6
NaOH + urea + $\text{CO}_2$ + $\beta$ -MeO-Glcp	170.9	165.5
NaOH + urea + $\beta$ -MeO-Glcp + $\text{CO}_2$	169.4	165.5

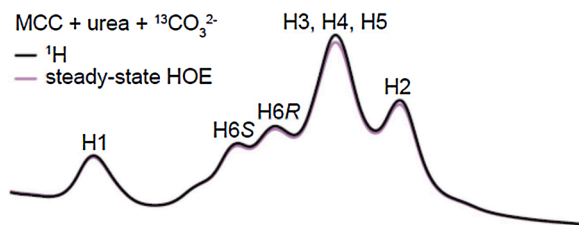
formation of a carbohydrate carbonate intermediate. With urea brought into play, it is of high interest to investigate whether it interferes with this carbohydrate-carbonate chemistry and the (commonly observed) displacement pattern of the chemical shifts.

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  $\text{CO}_2$  could be observed: both the pre and post-carbohydrate addition of  $\text{CO}_2$  displaced equally the  $^{13}\text{C}$  chemical shift of the  $\beta$ -MeO-Glcp (Fig. 3). The same could be observed for the  $^1\text{H}$  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/ $\text{CO}_2$  addition or the presence of  $\text{CO}_3^{2-}$ . Moreover, the  $^{13}\text{C}$  chemical shift values for the urea and  $\text{CO}_3^{2-}$  brought together in a carbohydrate-free NaOH(aq) solution were equal to those observed for urea and  $\text{CO}_3^{2-}$  when dissolved separately in NaOH (aq) (Table 2). Thus, although the addition of urea increased the amount of captured  $\text{CO}_2$  it did not appear to interact with the  $\text{CO}_3^{2-}$  in a way that affects their  $^{13}\text{C}$  chemical shift values. In the presence of a carbohydrate, though, this was changed. Addition of the  $\beta$ -MeO-Glcp to a solution already containing both urea and added  $\text{CO}_2$  (pre-carbohydrate addition of  $\text{CO}_2$ ), displaced the  $^{13}\text{C}$  chemical shift of both the  $\text{CO}_3^{2-}$  and urea towards lower values, albeit very modestly (too small displacement to be considered significant). However, when the addition order was changed and the  $\beta$ -MeO-Glcp was added prior to addition of  $\text{CO}_2$  and urea (post-carbohydrate addition of  $\text{CO}_2$ ), the  $\text{CO}_3^{2-}$  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  $\beta$ -MeO-Glcp in the NaOH(aq)/urea. The same change in the  $\text{CO}_3^{2-}$   $^{13}\text{C}$  chemical shift upon post-carbohydrate addition of  $\text{CO}_2$  was also observed in an urea-free system, suggesting that the change observed is attributed to the presence of  $\beta$ -MeO-Glcp rather than the combination of both urea and  $\beta$ -MeO-Glcp. A comparison of the  $^3J_{\text{HH}}$  couplings between a reference sample ( $\beta$ -MeO-Glcp dissolved in NaCl(aq) with urea) and the  $\beta$ -MeO-Glcp dissolved in NaOH(aq)/urea revealed a significant change in one of the couplings involving the proton in position H6R. 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  $\beta$ -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, & Ryoze, 1983). Interestingly, this change was reverted (the coupling value for the proton on the H6R position changed back by 1 Hz) upon addition of  $\text{CO}_2$ , 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  $\text{CO}_2$ , 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  $\text{CO}_2$ .

### 3.4. Investigation of the interaction between cellulose and $\text{CO}_3^{2-}$ in the presence of urea

The results from the pH measurements and NMR spectroscopy point towards interactions between  $\text{CO}_3^{2-}$  and the cellulose analogue  $\beta$ -MeO-Glcp, and a possible impact of urea on these. To elucidate on the



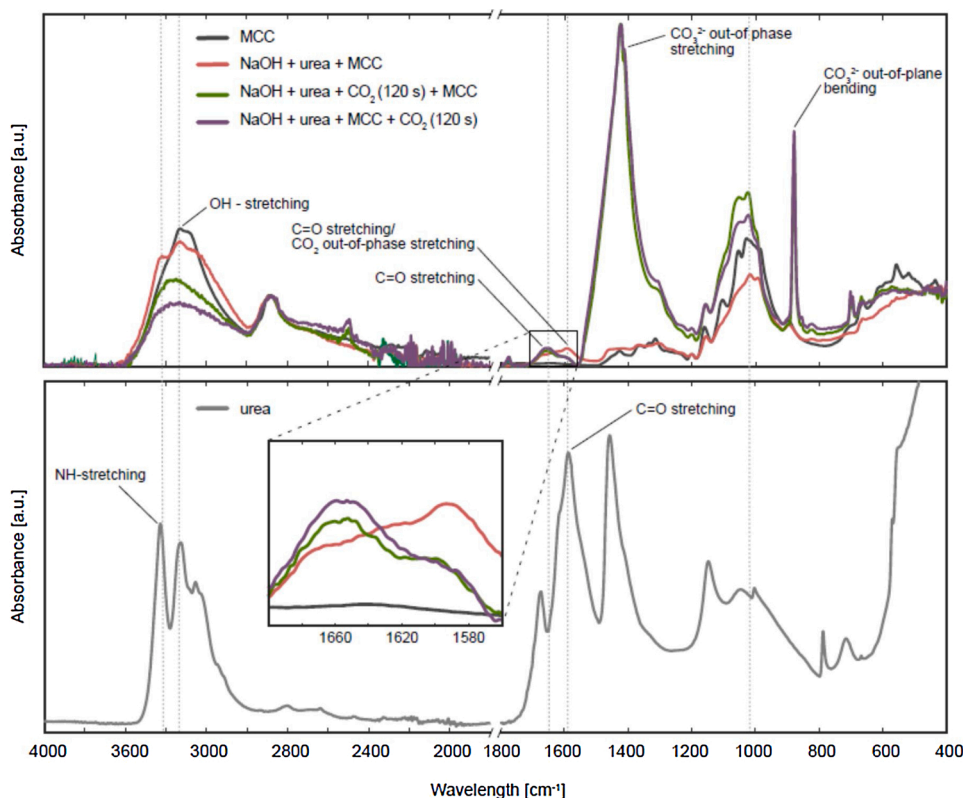
**Fig. 4.** Steady-state HOE measurement of MCC dissolved in NaOH(aq) with  $\text{Na}^{13}\text{CO}_3^{2-}$  (bottom) and MCC dissolved in NaOH(aq) with urea and  $\text{Na}_2^{13}\text{CO}_3$  (top). All measurements were recorded at  $+5^\circ\text{C}$  in  $\text{D}_2\text{O}$ .

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  $^{13}\text{CO}_3^{2-}$ . 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  $^1\text{H}$  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  $^{13}\text{CO}_3^{2-}$  signal was saturated while the  $^1\text{H}$  NMR spectrum of the MCC was recorded (Fig. 4). For an urea-free sample containing MCC dissolved in NaOH(aq) with  $^{13}\text{CO}_3^{2-}$  (Gunnarsson et al., 2020), it could be observed that the signal intensity of the all MCC protons decreased by the saturation of the  $^{13}\text{CO}_3^{2-}$  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  $^{13}\text{CO}_3^{2-}$  (Fig. 4). It appears that in a system containing urea the association between MCC and the  $\text{CO}_3^{2-}$  is counteracted.

As a reminder, with urea present, an equal change in  $\beta\text{-MeO-Glcp } ^{13}\text{C}$

chemical shifts was observed regardless of when the  $\text{CO}_2$  was added (pre or post-carbohydrate). Still, this was not the case for the  $^{13}\text{C}$  chemical shift of the formed  $\text{CO}_3^{2-}$  ions. The chemical shift of the  $\text{CO}_3^{2-}$  formed upon post-carbohydrate addition of  $\text{CO}_2$  to NaOH/urea/  $\beta\text{-MeO-Glcp}$  was, namely, appreciably displaced to lower values compared to the solutions where no interaction between the carbohydrate and freshly added  $\text{CO}_2$  was possible (Table 2). A possible explanation could be that the  $\beta\text{-MeO-Glcp } ^{13}\text{C}$  chemical shift values are primarily sensitive to the presence of urea and/or amount of  $\text{CO}_3^{2-}$  in solutions, both present in high concentrations in the urea containing systems regardless of when  $\text{CO}_2$  is introduced. On the other hand, the chemical shift of  $\text{CO}_3^{2-}$  formed via carbohydrate mediated conversion of  $\text{CO}_2$  (post-carbohydrate addition) reflects this specific formation route (through a carbohydrate carbonate intermediate) leading possibly to a  $\beta\text{-MeO-Glcp} - \text{CO}_3^{2-}$  interaction that affects its chemical shift. Thus, despite the presence of urea, the common  $\text{CO}_2$ -chemistry of the system still seems to be active, with the order of carbohydrate/ $\text{CO}_2$  addition being determinant for the molecular interactions. This chemistry is not observable in the  $\beta\text{-MeO-Glcp } ^{13}\text{C}$  NMR shifts as the presence of urea and the high uptake of  $\text{CO}_2$  in the presence of urea completely mask the differences between the pre and post-carbohydrate addition, but is reflected in the  $\text{CO}_3^{2-}$  chemical shift, as the latter is sensitive to the  $\text{CO}_3^{2-}$  formation route. The order of carbohydrate/ $\text{CO}_2$  addition to the NaOH(aq)/urea system (i.e. the possibility of freshly added  $\text{CO}_2$  interacting with the dissolved carbohydrate), therefore, appears to be determinant for the interactions in the system, which further affects the overall uptake of  $\text{CO}_2$ .

Capturing of  $\text{CO}_2$  by cellulose/NaOH(aq) solutions could be previously observed as a new ATR-FTIR signal ( $1590\text{ cm}^{-1}$ ) of the precipitated samples, originating from the captured cellulose carbonate intermediate formed during post-carbohydrate addition of  $\text{CO}_2$  (Gunnarsson et al., 2017; 2018). The approach of precipitating the MCC samples from the urea/NaOH(aq) with pre- or post-carbohydrate addition of  $\text{CO}_2$  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  $4000\text{--}400\text{ cm}^{-1}$  of untreated MCC (blue) and MCC dissolved in NaOH(aq) + urea (red), MCC dissolved in NaOH(aq) + urea + pre-carbohydrate addition of  $\text{CO}_2$  (green) and MCC dissolved in NaOH(aq) + urea + post-carbohydrate addition of  $\text{CO}_2$  (purple). All solutions were precipitated in ethanol, washed until neutral and dried. At the bottom, ATR-FTIR spectrum from  $4000\text{--}400\text{ cm}^{-1}$  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<sub>2</sub> are shown in Fig. 5. Since neat urea has a significant peak at 1590 cm<sup>-1</sup> corresponding to CO= stretching it is difficult to distinguish it from a cellulose carbonate formed through a CO<sub>2</sub> reaction with cellulose. However, when introducing CO<sub>2</sub> 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<sup>-1</sup> increased in intensity while the peak at 1590 cm<sup>-1</sup> decreased. A similar signature of urea forming a complex with different types of ions, was previously described: the peak at 1677 cm<sup>-1</sup> moves to a lower wavenumber and the peak at 1625 cm<sup>-1</sup> moves to a higher wavenumber (Gangopadhyay et al., 2016; Manivannan & Rajendran, 2011). Drawing parallels to this study, the increasing peak at 1655 cm<sup>-1</sup> could be owing to the peaks at 1590 and 1677 cm<sup>-1</sup> forming an average at 1655 cm<sup>-1</sup> due to formation of a complex between the urea and possibly the CO<sub>3</sub><sup>2-</sup>. The large peaks denoted as CO<sub>3</sub><sup>2-</sup> out-of-phase stretching and out-of-plane bending (Larkin & Larkin, 2011) originate from the precipitated Na<sub>2</sub>CO<sub>3</sub> formed during the precipitation of the samples. The signature peaks for cellulose at 1000 cm<sup>-1</sup> showed no significant changes due to the presence of neither the urea nor the CO<sub>3</sub><sup>2-</sup>, 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<sup>-1</sup>. Interestingly, the incomplete removal of urea in the sample with no CO<sub>2</sub> added (shown as a clear peak at 3420 cm<sup>-1</sup> 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<sub>2</sub>, which could further indicate urea – CO<sub>3</sub><sup>2-</sup> association possibly facilitating washing out of these structures and thus leading to reduction of the peak at 3420 cm<sup>-1</sup>. Conclusively, the affinity between the CO<sub>3</sub><sup>2-</sup> 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<sub>2</sub> interactions threefold: (1) by catalytically increasing the uptake of CO<sub>2</sub> through a parallel urea – CO<sub>2</sub> interaction, visible as an increased CO<sub>3</sub><sup>2-</sup> NMR signal intensity; (2) by moderating the pH changes resulting from addition of both carbohydrate and CO<sub>2</sub>, which points out a buffering effect; (3) by counteracting interactions between a carbohydrate and the CO<sub>3</sub><sup>2-</sup>, possibly by associating to the CO<sub>3</sub><sup>2-</sup> as observed by HOE experiments (pre-carbohydrate addition of CO<sub>2</sub>) 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<sub>2</sub> is changed, i.e. when the carbohydrate interacts with the already present CO<sub>3</sub><sup>2-</sup>, compared to the freshly added CO<sub>2</sub> (forming a carbohydrate-carbonate intermediate). Still, the order of addition of carbohydrate/CO<sub>2</sub> and, thus, the route of the CO<sub>3</sub><sup>2-</sup> formation (whether through reaction with a carbohydrate or OH<sup>-</sup>) is likely to affect the chemical environment of the formed CO<sub>3</sub><sup>2-</sup>. 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<sub>2</sub>/CO<sub>3</sub><sup>2-</sup> 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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