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Gunnarsson, M., Bernin, D., Hasani, M. (2020). The CO₂/CO₃²⁻ chemistry of the NaOH(aq) model system applicable to cellulose solutions. *Cellulose*, 27(2): 621-628. <http://dx.doi.org/10.1007/s10570-019-02782-6>

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The $\text{CO}_2/\text{CO}_3^{2-}$ chemistry of the $\text{NaOH}(\text{aq})$ model system applicable to cellulose solutions

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Received: 31 July 2019 / Accepted: 9 October 2019 / Published online: 4 November 2019
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Abstract Molecular interactions governing the recently reported $\text{CO}_2/\text{CO}_3^{2-}$ chemistry of cellulose/ $\text{NaOH}(\text{aq})$ solutions are investigated using a cellulose analogue methyl- β -D-glucopyranoside in $\text{NaOH}(\text{aq})$ solutions under conditions feasible with cellulose dissolution. ^1H , ^{13}C and steady-state heteronuclear Overhauser effect NMR spectroscopy complemented by pH measurements reveal carbohydrate- CO_3^{2-} interactions as an important component of this chemistry. However, depending on in which order carbohydrate and CO_3^{2-} are brought together in $\text{NaOH}(\text{aq})$ this interaction is different with different implications on stability of the CO_3^{2-} in the solution.

Keywords Methyl β -D-glucopyranoside · CO_2 · CO_3^{2-} · Cellulose dissolution · $\text{NaOH}(\text{aq})$ · NMR · pH

Introduction

Elucidating fundamental interactions of the attractive cellulose/ $\text{NaOH}(\text{aq})$ solutions is a pre-requisite for rational development of these systems towards a new sustainable processing technology. Yet, after more than a century of scientific and industrial interest, cellulose/ $\text{NaOH}(\text{aq})$ interactions still pose challenges on mechanistic comprehension, particularly intriguing being the still unresolved instability of the solutions manifested as a remarkably strong tendency for cellulose–cellulose associations. Over the years repeated efforts have been made to elucidate the stabilising interactions and structure of this system pointing out eutectic sodium hydroxide hydrates as the key solubilising species (Roy et al. 2001; Egal et al. 2007), along with deprotonation of dissolved cellulose (Bialik et al. 2016). Interestingly, despite the inherent affinity of alkaline solutions for $\text{CO}_2(\text{g})$ (due to low temperature and high alkalinity) influence of $\text{CO}_2(\text{g})$ on the molecular interactions in this system has never been considered. Recently our group investigated an overlooked incorporation of $\text{CO}_2(\text{g})$ in these solutions going through a reaction with cellulose alkoxides and the formation of a transient cellulose carbonate readily hydrolysed to CO_3^{2-} (Gunnarsson et al. 2017). Similar chemistry had previously been observed in alkaline alcohol solutions (Faurholt 1927; Song and Rochelle 2017). Studies of a model compound methyl- α -D-glucopyranoside (α -MeO-Glcp)

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10570-019-02782-6>) contains supplementary material, which is available to authorized users.

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enabling investigation by NMR spectroscopy, established a significant incorporation of CO_3^{2-} through this route as it is kinetically favored over the well-known conversion of CO_2 to CO_3^{2-} by OH^- due to a higher affinity of CO_2 for carbohydrate alkoxides (Chiang et al. 2017; Song and Rochelle 2017). The conversion of $\text{CO}_2(\text{g})$ to $\text{CO}_3^{2-}(\text{aq})$ in $\text{NaOH}(\text{aq})$ was more than doubled in the presence of a α -MeO-Glcp (Gunnarsson et al. 2018). Surprisingly, this excess incorporation of CO_3^{2-} was not accompanied with any additional pH decrement and indicated a strong impact on the tendency of cellulose chains to re-associate. Applied to cellulose solutions, this new knowledge will add to comprehensive understanding of the delicate cellulose– $\text{NaOH}(\text{aq})$ interplay along with the prospect of developing new means of functionalising and assembling cellulose structures from aqueous alkaline solutions. As such, this newly found dimension calls for further investigations of the CO_2 –cellulose/ $\text{NaOH}(\text{aq})$ chemistry in terms of structural requirements on the carbohydrate, dissolution conditions, etc., where conditions relevant for cellulose dissolution are of particular interest. With the narrow range of conditions favouring dissolution of cellulose in mind, we here turn our attention to a model system feasible with these very conditions, including the use of a more relevant low molecular analogue, β -MeO-Glcp (Fig. 1). Relying on a detailed NMR analysis of chemical shifts, coupling constants and interactions via the heteronuclear Overhauser effect (HOE), we further investigate the fundamentals of the $\text{CO}_2(\text{g})$ capturing chemistry under conditions applicable to cellulose solutions (in terms of temperature and $\text{NaOH}(\text{aq})$ concentration). A complementary analysis of accompanying pH changes provides additional insight in interactions affecting the NMR signature. While aiming at general understanding of this chemistry, the formation and fate of the main reaction product, $\text{CO}_3^{2-}(\text{aq})$, is in focus.

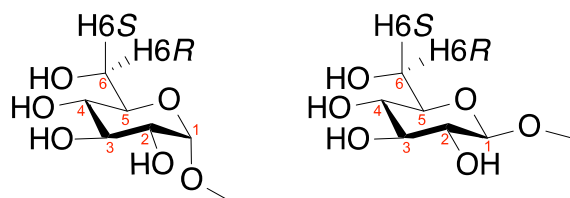


Fig. 1 The molecular structure of α -MeO-Glcp (left) and β -MeO-Glcp (right)

Experimental

Materials and sample preparation

β -MeO-Glcp (< 99%), NaOH (< 98%), NaCl (99.5%), D_2O (99.9%) and $\text{Na}_2^{13}\text{CO}_2$ (99 atom% ^{13}C) were purchased from Sigma Aldrich 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.

Solutions for characterisation of the chemical shift values and quantification of captured CO_2 were prepared by dissolving NaCl (2.0 or 3.0 M) or NaOH (2.0 or 3.0 M) in D_2O . The solutions were then cooled down to -5°C . The cool solutions were then added to pre-weighed β -MeO-Glcp (0.4 M), let to dissolve and stored at $+5^\circ\text{C}$. $\text{CO}_2(\text{g})$ was added for 120 s to the solutions, pre or post-dissolution of β -MeO-Glcp, by immersing a syringe into the solutions. The syringe was connected to a tube containing $\text{CO}_2(\text{g})$, mounted with a regulator set to approximately 4 ml/min. A solution for the steady-state HOE experiment was prepared by dissolving NaOH (2.0 M) and $\text{Na}_2^{13}\text{CO}_2$ (1.0 M) in D_2O at room temperature and added to pre-weighed 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 $+5^\circ\text{C}$, which dissolves cellulose and gives a stable solution to perform measurements on.

The pH measurements were carried out by pre-cooling $\text{NaOH}(\text{aq})$ with a concentration of 0.5 M at $+10^\circ\text{C}$. The pH was then measured pre or post-dissolution of β -MeO-Glcp (0.4 M) with addition of $\text{CO}_2(\text{g})$ for 120 s pre or post-dissolution of the β -MeO-Glcp according to the method above. The pH was measured using a HACH HQ430D Multimeter with an Intellical PHC705A1 pH probe.

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.

A steady-state heteronuclear Overhauser effect (HOE) measurement was performed to observe if there is any specific interaction between the CO_3^{2-} and MCC. A 1D HOE experiment was recorded using ^{13}C labelled $\text{Na}_2^{13}\text{CO}_3$ to transfer the magnetisation between the ^{13}C to the ^1H , which can be observed 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 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 $+5^\circ\text{C}$.

Results and discussion

β -MeO-Glcp mediated uptake of $\text{CO}_2(\text{g})$

As expected β -MeO-Glcp (3.0 M samples) showed a significant difference in chemical shifts compared to the previously investigated α -anomer, proving the difference in orientation of the methyl group at position C1 to largely influence the chemical environment of the surrounding carbons in the ring (see Supplementary Information Fig. 1a) (Lemieux 1971) and probably also the interaction with $\text{CO}_2(\text{g})$. Moreover, the alkali concentration appeared to change the NMR signature of the carbohydrate, as comparison between the 2.0 and 3.0 M systems showed that only some of the carbons of the β -MeOH-Glcp experienced a change in chemical shift upon increase in the alkali concentration (see Supplementary Information Fig. 1b). This was probably due to a difference in the hydroxyl exchange rate owing to the difference in pH, which consequently could affect the

$\text{CO}_2(\text{g})$ uptake of the system. With this in mind, further exploration of the $\text{CO}_2(\text{g})$ uptake was performed on the 2.0 M $\text{NaOH}(\text{aq})$ solutions (comparable to cellulose solution conditions) and in the presence of the β -MeO-Glcp substrate. The uptake of $\text{CO}_2(\text{g})$ by 2.0 M β -MeO-Glcp/ $\text{NaOH}(\text{aq})$ estimated from the CO_3^{2-} integral by quantitative ^{13}C NMR is shown in Fig. 2.

In our previous study the presence of α -MeO-Glcp in 3.0 M $\text{NaOH}(\text{aq})$ was found to increase the uptake of $\text{CO}_2(\text{g})$ regardless of whether it was added prior or after addition of the carbohydrate (Gunnarsson et al. 2018), i.e. whether by stabilising the already dissolved $\text{CO}_3^{2-}(\text{aq})$ or by mediating incorporation of $\text{CO}_2(\text{g})$ through organic carbonate and facilitate stabilisation of the subsequently formed CO_3^{2-} . Interestingly, the β -anomer in 2.0 M, studied here, showed this effect only when dissolved in the $\text{NaOH}(\text{aq})$ prior to addition of $\text{CO}_2(\text{g})$. When added to the solution already containing $\text{CO}_3^{2-}(\text{aq})$, the stabilisation effect seemed to be reversed and a reduced $\text{CO}_3^{2-}(\text{aq})$ peak could be measured (Fig. 2). This intriguing reduction of the $\text{CO}_3^{2-}(\text{aq})$ peak cannot be attributed to a

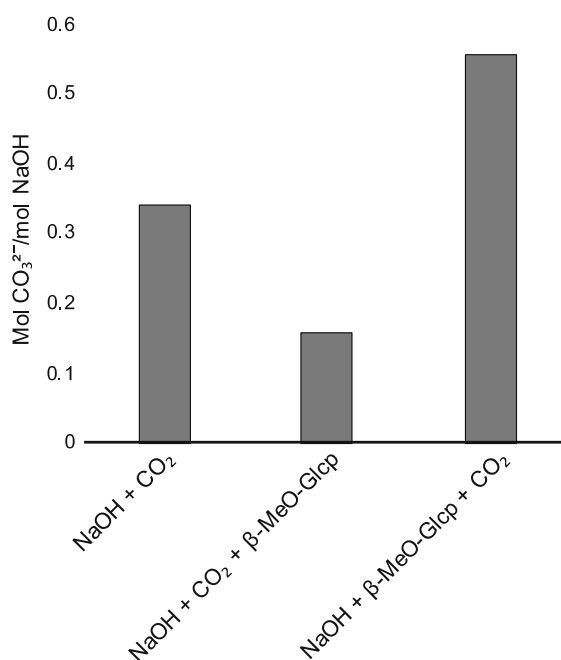


Fig. 2 Mol $^{13}\text{CO}_3^{2-}$ / mol NaOH obtained from the CO_3^{2-} integrals in ^{13}C NMR spectra for $\text{NaOH}(\text{aq}) + \text{CO}_2(\text{g})$ (120 s), $\text{NaOH}(\text{aq}) + \text{CO}_2(\text{g})$ (120 s) added before dissolution of β -MeO-Glcp and $\text{NaOH}(\text{aq}) + \text{CO}_2(\text{g})$ added after dissolution of β -MeO-Glcp. All measurements were recorded at $+5^\circ\text{C}$ in D_2O

conversion of $\text{CO}_3^{2-}(\text{aq})$ to $\text{CO}_2(\text{g})$ at this high alkalinity, but could possibly indicate precipitation of the CO_3^{2-} from the solution. In support to the precipitation possibility, the overall uptake of CO_2 (g) measured in this study (2.0 M NaOH(aq)) was higher compared to the previously studied 3.0 M NaOH(aq) (0.35 mol CO_3^{2-} compared to 0.08 mol CO_3^{2-} per mol carbohydrate-free NaOH(aq)), possibly due to a difference in viscosity reducing the reaction rate in the 3.0 M NaOH(aq). Attempts were made to confirm precipitation of $\text{Na}_2\text{CO}_3(\text{s})$ by light scattering, but no conclusive results could be obtained. Nevertheless, adding the carbohydrate to a solution containing already dissolved $\text{CO}_3^{2-}(\text{aq})$ contributes poorly to stabilisation of this ion, unless present in low concentrations.

On the other hand, incorporation of $\text{CO}_3^{2-}(\text{aq})$ introduced to a NaOH(aq) solution already containing dissolved carbohydrate (post-carbohydrate addition of $\text{CO}_2(\text{g})$) is remarkably facilitated by the presence of β -MeO-Glcp, just as in the case of the α -anomer (Gunnarsson et al. 2018). The uptake of $\text{CO}_2(\text{g})$ increased, namely, from 0.35 mol $\text{CO}_3^{2-}/\text{mol}$ NaOH to 0.55 mol $\text{CO}_3^{2-}/\text{mol}$ NaOH when β -MeO-Glcp was present before the addition of $\text{CO}_2(\text{g})$. The significantly higher content of $\text{CO}_3^{2-}(\text{aq})$ in the solution does not, in this case, lead to precipitation but seems to be remarkably stabilised by the β -MeO-Glcp present in the solution prior to formation of $\text{CO}_3^{2-}(\text{aq})$.

Notably, the total increase in the $\text{CO}_2(\text{g})$ uptake due to presence of carbohydrate was equal in both the 3.0 M and 2.0 M system (0.2 mol/mol NaOH) which points out the critical role of the carbohydrate for the $\text{CO}_2(\text{g})$ uptake.

The intriguing question is why stabilisation of the dissolved CO_3^{2-} ions is more efficient when $\text{CO}_2(\text{g})$ is introduced to the solution containing already dissolved carbohydrate (whether α or β anomer)? Are there CO_3^{2-} ions experiencing two different chemical surroundings: the CO_3^{2-} ions hydrated prior to the addition of carbohydrate and those (significantly more abundant), formed and solvatised in the presence of carbohydrate? Here, the amphiphilic nature of the CO_3^{2-} ion and its ability to form strong structures with water should be considered (Winkworth-Smith et al. 2016; Yadav and Chandra 2018).

In an effort to address these questions, changes in chemical shifts and coupling constants of the

carbohydrate and chemical shifts of CO_3^{2-} when added to the NaOH(aq) solution in different order were studied.

NMR signature of the $\text{CO}_2(\text{g})$ uptake

In line with previous observations, the ^{13}C chemical shifts for the β -MeO-Glcp in NaOH(aq) moved towards higher values compared to the reference solution in NaCl(aq). Given the high pH of these solutions (theoretical pH at 25 °C is 14.3), this change indicates deprotonation of one or several of the hydroxyl groups on the β -MeO-Glcp since the carbons exhibit an electron-desielding effect (Isogai et al. 1987). The change observed in ^1H NMR chemical shifts (i.e. move towards lower chemical shift values due to the shielding effect) also concurs with the previously observed deprotonation signature. The largest change in chemical shift, in both the ^{13}C and ^1H NMR measurements, was observed for the C3 and H3 position in the β -MeO-Glcp (see Supplementary information). Given a relatively low acidity of the hydroxyl in position 3, it is not likely that the large change can be attributed to deprotonation at this position but rather to a change in the surrounding environment induced by the deprotonation of one of the neighboring hydroxyl groups in position 2 and 4, a hypothesis not yet thoroughly investigated.

Addition of $\text{CO}_2(\text{g})$ to the NaOH(aq) system prior or after the dissolution of β -MeO-Glcp, displaced the ^{13}C NMR peaks to lower chemical shifts, with the accomplished displacement being significantly larger when adding $\text{CO}_2(\text{g})$ after the dissolution of the carbohydrate (post-carbohydrate addition). In the case of post-carbohydrate addition of $\text{CO}_2(\text{g})$, a significantly higher amount of $\text{CO}_3^{2-}(\text{aq})$ is produced, which probably is partly responsible for the observed larger change in chemical shift. However, it should be kept in mind that $\text{CO}_3^{2-}(\text{aq})$ incorporation in this case (post-carbohydrate addition) occurs through a different route—a reaction between the deprotonated carbohydrate and $\text{CO}_2(\text{aq})$ via formation of a carbohydrate carbonate intermediate and might, as such, result in CO_3^{2-} with different solvatisation and interactions additionally affecting the chemical shifts of the carbohydrate (Fig. 3) (Gunnarsson et al. 2018). This assumption is consistent with the change in chemical shifts between the pre- or post-carbohydrate addition of $\text{CO}_2(\text{g})$ being different for different C atoms. This

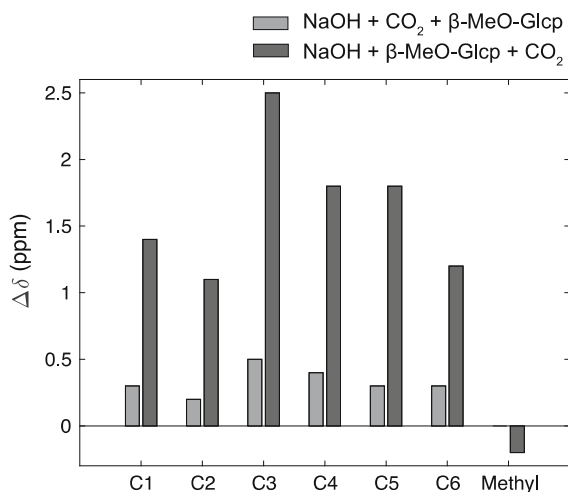


Fig. 3 The change in chemical shift for β -MeO-Glcp upon addition of CO_2 (120 s) before or after dissolution in $\text{NaOH}(\text{aq})$ when compared to β -MeO-Glcp dissolved in $\text{NaOH}(\text{aq})$ without addition of CO_2 . All measurements were recorded at $+5^\circ\text{C}$ in D_2O and the spectral resolution was 0.55 Hz (0.00069 ppm)

indicates different carbohydrate– CO_3^{2-} interactions in the two cases, whether due to changed actual carbohydrate– CO_3^{2-} association or changed structuring of the solvating water around these. The largest difference could be observed for position C3 and C5.

The estimated spin–spin couplings (see Supplementary information) agreed well with the other reports in the literature (Stenutz et al. 2002). Analysis of the spin–spin couplings informs on molecular orientation between the adjacent protons and, thus, conformational changes in these two cases concurred with this observation: a change in the $^3J_{\text{HH}}$ couplings of the β -MeO-Glcp could only be observed upon addition of $\text{CO}_2(\text{g})$ to the $\text{NaOH}(\text{aq})$ after dissolution of carbohydrate. A difference by 1 Hz could be observed for one of the couplings on the H6R proton, which by applying the Karplus equation indicates a change to a larger population with the hydroxymethyl group adopting the *gauche*–*trans* (*gt*) orientation (Stenutz et al. 2002; Angles d’Ortoli et al. 2015). In native cellulose crystals, the hydroxymethyl group is, namely, predominantly oriented away from the ring oxygen (a 180° torsional angle O5–C5–C6–O6, *trans*) and close to the C4 (a 60° torsional angle C4–C5–C6–O6, *gauche*), referred to as a *trans*–*gauche* (*tg*) conformation. Upon dissolution, the other two available populations (*gauche*–*gauche* (*gg*) with the both torsional angles of 60° and *gauche*–*trans* with the

torsional angle O5–C5–C6–O6 being 60° and C4–C5–C6–O6 adapting 180°) will significantly increase. This proton couples both to another proton (H6S) on the same carbon (C6) and to the proton (H5) on the neighboring carbon (C5). The change for only one of the protons on the C6 carbon makes it reasonable to argue that it is the coupling to H5 that is affected by the post-carbohydrate addition of $\text{CO}_2(\text{g})$. Unfortunately, the equal change for H5 could not be observed due to overlap with H3. Interestingly, the same proton is affected upon dissolution of the β -MeO-Glcp in $\text{NaOH}(\text{aq})$ (the only $^3J_{\text{HH}}$ changes observed when going from $\text{NaCl}(\text{aq})$ to $\text{NaOH}(\text{aq})$ solvent) due to the well-known conformation change of the primary hydroxyl from *tg* to *gt* in aqueous solutions (Horii et al. 1983; Bergenstrahle-Wohlert et al. 2016). Addition of $\text{CO}_2(\text{g})$ prior to carbohydrate did not affect the $^3J_{\text{HH}}$ couplings. These findings further strengthen the indication of different carbohydrate– $\text{CO}_3^{2-}(\text{aq})$ interactions in the case of $\text{CO}_2(\text{g})$ introduction prior and after the carbohydrate.

Evaluation of the chemical shift of $\text{CO}_3^{2-}(\text{aq})$ in the studied solutions harmonise to large extent with these findings (Table 1). The chemical shift of the $\text{CO}_3^{2-}(\text{aq})$ in a carbohydrate-free $\text{NaOH}(\text{aq})$ and in the solutions where $\text{CO}_2(\text{g})$ was added prior to carbohydrate were equal, namely 171.1 ppm. On the other hand, when $\text{CO}_2(\text{g})$ was added after dissolution of carbohydrate, the chemical shift of the $\text{CO}_3^{2-}(\text{aq})$ decreased to 169.2 ppm. As formation of $\text{HCO}_3^-(\text{aq})$ (and a fast exchange between the $\text{CO}_3^{2-}(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$ resulting in a peak at the average of the two species) can be excluded at this high pH, the reduction of the chemical shift of the $\text{CO}_3^{2-}(\text{aq})$ implies formation of this ion in a different chemical environment. Possibly, the reaction between the deprotonated β -MeO-Glcp and the added $\text{CO}_2(\text{g})$ going through formation of a transient carbohydrate carbonate (although not observed as a new

Table 1 The ^{13}C chemical shifts of CO_3^{2-}

Sample	$^{13}\text{C}\text{CO}_3^{2-}$ (ppm)
$\text{NaOH} + \text{CO}_2$	171.1
$\text{NaOH} + \text{CO}_2 + \beta\text{-MeO-Glcp}$	171.1
$\text{NaOH} + \beta\text{-MeO-Glcp} + \text{CO}_2$	169.2

The spectral resolution was 1.66 Hz (0.0082 ppm)

intermediate peak) leads to β -MeO-Glcp- CO_3^{2-} associations different from those established when $\text{CO}_3^{2-}(\text{aq})$ is formed in a carbohydrate free NaOH (aq) prior to the carbohydrate addition.

Of course, having in mind the significantly larger $\text{CO}_2(\text{g})$ uptake when added after the dissolution of the carbohydrate (Fig. 2), the observed alterations of the NMR signature of β -MeO-Glcp (chemical shifts and $^3J_{\text{HH}}$) and $\text{CO}_3^{2-}(\text{aq})$ (chemical shifts) could be partly attributed to a larger amount $\text{CO}_3^{2-}(\text{aq})$ present in the system creating different surroundings. Still, as the change in chemical shift between the pre- and post-carbohydrate addition of $\text{CO}_2(\text{g})$ varies for different C-atoms, there are likely other interaction differences than those originating merely from variations in the $\text{CO}_3^{2-}(\text{aq})$ concentration. Our previous attempts on elucidating chemical shift variations as a function of increasing $\text{CO}_3^{2-}(\text{aq})$ concentration indicated indeed different variation patterns for pre- and post-carbohydrate addition (Gunnarsson et al. 2018).

The obvious possibility of pH variations affecting deprotonation and, thus, giving rise to variations in $\Delta\delta$ among the C-atoms could be excluded by establishing approximately equal final pH values for both cases (as will be seen further down).

An effort was made to distinguish between the different $\text{CO}_3^{2-}(\text{aq})$ in the system by lowering the temperature in the NMR experiment since the chemical shift value is an average of the different chemical structures of a molecule in solution and a decrease in temperature will slow down the kinetics of the system and allow several species to be observed. Unfortunately, this approach could not be applied due to the

fact that $\text{CO}_3^{2-}(\text{aq})$ precipitates below 0 °C, which would affect the dynamics and change the properties of the system.

Comparison to changes in pH

Interactions of the system with CO_2 should be closely related to pH, why pH changes—carrying additional information of the dynamics of the system—were monitored. Incorporation of $\text{CO}_3^{2-}(\text{aq})$ is supposedly accompanied by a reduction of pH, even though the route going through formation of a carbohydrate carbonate was observed to consume relatively low amount of OH^- leading to a comparably modest pH lowering (Table 2). The pH values measured for reference solutions and NaOH(aq) solutions with CO_2 and β -MeO-Glcp added in different order are shown in Table 2, while the overall decrease in pH is shown in Table 3.

Deprotonation of β -MeO-Glcp could be observed as a reduction of pH upon dissolution in NaOH(aq). Interestingly, when $\text{CO}_3^{2-}(\text{aq})$ is present in the system prior to carbohydrate dissolution (i.e. when CO_2 is added prior to the dissolution of the β -MeO-Glcp) the deprotonation effect is even more pronounced, indicating that $\text{CO}_3^{2-}(\text{aq})$ facilitates deprotonation of the β -MeO-Glcp (Fig. 4).

Just as shown in our previous study, in spite of higher incorporation of CO_3^{2-} in the case of post-carbohydrate addition of $\text{CO}_2(\text{g})$ almost equal final pH of the solutions (whether $\text{CO}_2(\text{g})$ was added prior or after the carbohydrate) could be measured. This excludes the possibility of pH variations being responsible for the observed changes of the NMR

Table 2 pH of NaOH(aq) at 0.5 M with addition of CO_2 and β -MeO-Glcp. All measurements were made at +10 °C

Sample	Starting pH	pH after addition of CO_2	pH after addition of β -MeO-Glcp
NaOH + CO_2	13.90	13.46	–
NaOH + β -MeO-Glcp + CO_2	13.90	13.46	13.15
NaOH + CO_2 + β -MeO-Glcp	13.95	13.25	13.77

Table 3 The difference in pH compared to the pH before addition of CO_2 and β -MeO-Glcp

Sample	Difference in pH after addition of CO_2	Difference in pH after addition of β -MeO-Glcp	Total difference in pH
NaOH + CO_2	– 0.44	–	– 0.44
NaOH + β -MeO-Glcp + CO_2	– 0.44	– 0.31	– 0.75
NaOH + CO_2 + β -MeO-Glcp	– 0.52	– 0.18	– 0.80

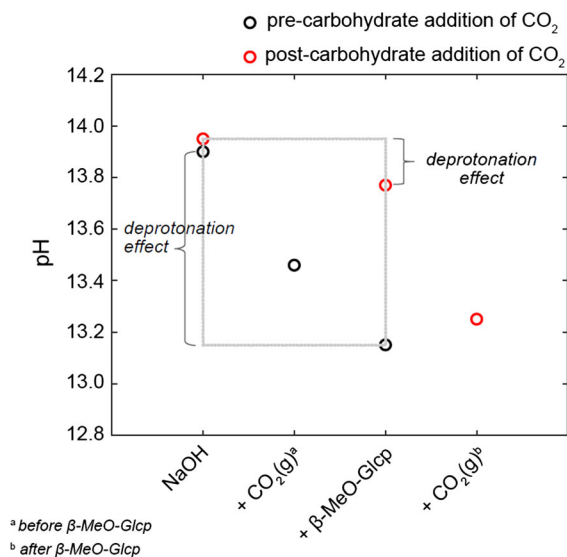


Fig. 4 The change in pH of NaOH(aq) upon addition of CO₂(g) and β-MeO-Glcp in different order

peaks and once again points out displacement of chemical shifts as a strong indication of carbohydrate–CO₃²⁻ interactions in the case of post-carbohydrate addition of CO₂(g).

Taken together, our results strongly suggest a specific interaction between the CO₃²⁻ formed through the carbohydrate carbonate chemistry upon post-carbohydrate addition, observed as changed NMR-signature of the carbohydrate ($\Delta\delta$, $^3J_{\text{HH}}$) and CO₃²⁻(aq) (decreased chemical shift), along with modest changes in pH accompanying this significant incorporation of CO₃²⁻. On the other hand, the CO₃²⁻(aq) present in the solution prior to carbohydrate addition seems to promote deprotonation of the added carbohydrate, while showing tendency itself to possibly precipitate upon carbohydrate addition. The question is whether this type of the CO₃²⁻ also associates to carbohydrate. To address this question steady-state HOE experiments were employed.

Is there association between CO₃²⁻ and cellulose?

The results obtained from both NMR and pH measurements all point towards an interaction between CO₃²⁻ and β-MeO-Glcp when dissolved in NaOH(aq), particularly in the case of post-carbohydrate addition of CO₂(g). Therefore, an attempt was made to probe whether there actually is an association between the

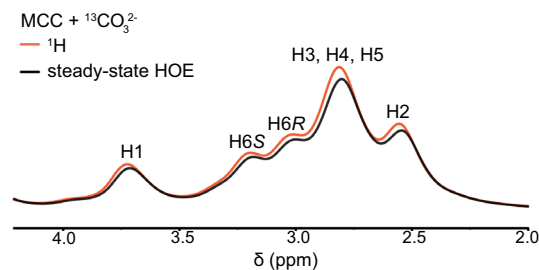


Fig. 5 Steady-state HOE spectra of MCC dissolved in NaOH(aq) with ¹³CO₃²⁻. All measurements were recorded at +5 °C in D₂O

CO₃²⁻(aq) introduced to the system prior to addition of carbohydrate (in this case microcrystalline cellulose, MCC) by measuring steady-state HOE on MCC dissolved in NaOH(aq) in the presence of ¹³CO₃²⁻. The concept of a steady-state HOE measurement is to saturate a specific site of a molecule and, use the magnetisation transfer via the Overhauser effect, to other nuclei to probe their proximity. Here, the ¹³CO₃²⁻ was saturated while a ¹H spectrum of dissolved MCC was recorded. Conventional 1D HOESY experiments that require strong heteronuclear dipolar couplings were also tested without success. If the ¹³CO₃²⁻ is located sufficiently close to the MCC to allow for magnetisation transfer, it will be observed as a change in intensity of the measured proton peaks. Indeed, the intensity for all the MCC protons decreased by the saturation of the ¹³CO₃²⁻ signal, which thereby proves an association between the ¹³CO₃²⁻ and the MCC (Fig. 5). However, the decrease in intensity observed for all the protons indicates a non-specific association and a fast exchange between the ¹³CO₃²⁻ and the MCC, which motivates further studies of this interaction.

Conclusions

The CO₃²⁻(aq) formed in NaOH(aq) solutions of a cellulose analogue β-MeO-Glcp, through incorporation of CO₂(g) 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 seems to be capable of facilitating deprotonation of the incoming carbohydrate. Even though HOESY measurements confirm a non-specific association between cellulose and CO₃²⁻(aq), this CO₃²⁻(aq) is likely poorly stabilised by the carbohydrate and prone to

precipitate at higher concentrations. On the other hand, CO_3^{2-} formed through addition of $\text{CO}_2(\text{g})$ to a system containing already dissolved carbohydrate seems to be stabilised by the very presence of carbohydrate most likely promoted by a specific reaction with carbohydrate alkoxides accompanied by a conformational change of the primary hydroxyl group. In this case a significantly higher amount of CO_3^{2-} is incorporated in the solutions through the previously described carbohydrate carbonate route responsible for modest OH^- consumption and, thus, comparably modest pH change. The high amount of introduced CO_3^{2-} along with its anticipated stabilising interaction with the carbohydrate is likely one of the main reasons behind the significant decrease of the chemical shifts (of both carbohydrate and CO_3^{2-}) in the case of post-carbohydrate addition of CO_2 .

Still, one of the most intriguing questions remains to be further elucidated: why is the $\text{CO}_3^{2-}(\text{aq})$ formed through the post-carbohydrate addition of CO_2 stabilised in the $\beta\text{-MeO-Glcp/NaOH}(\text{aq})$ solution, while the $\text{CO}_3^{2-}(\text{aq})$ formed by OH^- reaction with CO_2 prior to dissolution of $\beta\text{-MeO-Glcp}$ is not?

Acknowledgments Open access funding provided by Chalmers University of Technology. This work has been carried out as a part of the framework of Avancell—Center for Fiber Engineering, which is a research collaboration between Södra Innovation and Chalmers University of Technology. The author thanks the Södra Skogsägarnas Foundation for Research, Development and Education for their financial support. The Swedish NMR Center is acknowledged for spectrometer time.

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