Sodium chloride interaction with solvated and crystalline cellulose: sodium ion affects the cellotetraose molecule and the cellulose fibril in aqueous solution

Giovanni Bellesia · S. Gnanakaran

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Abstract Inorganic salts are a natural component of biomass which have a significant effect on the product yields from a variety of biomass conversion processes. Understanding their effect on biomass at the microscopic level can help discover their mechanistic role. We present a study of the effect of aqueous sodium chloride on the largest component of biomass, cellulose, focused on the thermodynamic and structural effect of a sodium ion on the cellotetraose molecule and the cellulose fibril. Replica exchange molecular dynamics simulations of a cellotetraose molecule reveal a number of preferred cellulose-Na contacts and bridging positions. Large scale MD simulations on a model cellulose fibril find that Na⁺ perturbs the hydroxymethyl rotational state population and consequently disrupts the ‘native’ hydrogen bonding network.

Keywords Biomass · Sodium chloride · Molecular dynamics · Conformations

Introduction

Inorganic salts are an integral part of any biomass material. Indeed, plant biomass naturally contains alkali and alkaline earth metals, including potassium, sodium, phosphorus, calcium, and magnesium (Mohanty et al. 2006; Patwardhan et al. 2009; Patwardhan et al. 2011). While the total mineral content is less than 1 %, the effect, either adverse or favorable, on biomass degradation and product distribution is significant. Removal of these cations would add cost (Scott et al. 2001) to biofuel production, which is already more costly than conventional petroleum-based fuels. Thus, it is preferable to understand how the inorganic material interacts with the biomass to better steer conversion toward more valuable products. In particular, a detailed understanding of the interactions between inorganic salts and biomass is of central importance for devising efficient biomass degradation protocols for bioenergy production.

In fast pyrolysis, the presence of inorganic salts has been shown to increase the yield of lower-value low-molecular weight species and adversely affects the
formation of levoglucosan (the main pyrolysis product of pure cellulose) (Patwardhan et al. 2010). Conversely, in steam gasification of biomass-derived charcoal, Li, Na and K chlorides have been used as catalysts to increase gas yield and to reduce the operational temperature (Encinar et al. 2001). The beneficial effect of inorganic salts has also been outlined in recent studies showing that the presence of NaCl increases the yield of levulinic acid in acid-catalyzed depolymerization of cellulose in water (vom Stein et al. 2010; Potvin et al. 2011). Those studies are especially relevant as they combine low-price NaCl with relatively mild reaction conditions and low temperatures \((T = 373–473 \text{ K})\). In those acid catalysis experiments the NaCl concentration varies in the range of \(5 – 50 \text{ wt\%}\). The peak in the sugars’ yield has been obtained with NaCl concentrations in the range of \(20–30 \text{ wt\%}\). It is speculated that NaCl contributes to the destabilization of the highly-structured hydrogen bond network in cellulose, thereby increasing the efficiency of the cellulose hydrolysis process. In terms of enzymatic hydrolysis, the NaCl destabilization effects on crystalline cellulose could be exploited in combination with recently discovered cellobiohydrolases from the marine wood borer Limnoria quadripunctata that exhibit unchanged or increased levels of activity at high salt concentration (Kern et al. 2013).

In our study we employ classical computational methods to study the atomistic details of the interactions of NaCl oligomeric and crystalline fibrillar cellulose. Oligomeric and crystalline fibrillar cellulose were studied via replica exchange molecular dynamics and via single temperature molecular dynamics (MD) simulations respectively. The use of classical simulation methods and enhanced sampling algorithms is mostly motivated by the need of obtaining sufficient statistics (conformational sampling) for both the oligomeric and fibrillar cellulose systems. Overcoordination of ions, a significant problem linked to the use of classical MD with NaCl-water systems, has been avoided using relatively low NaCl concentrations (Wang et al. 2000; Chen and Pappu 2007) (see Computational methods section). Our results show that there are multiple positions for Na\(^{+}\) to associate with hydroxyl groups of a pyranose ring within thermal energy \((k_B T)\) at temperatures relevant to biomass conversion. It is expected that these ions could affect many different reactions and thus have wide-ranging effects on decomposition of biomass.

### Computational methods

We performed replica exchange Langevin dynamics (LD) and single temperature NPT–LD simulations to analyze the equilibrium dynamics of a cellotetraose molecule and of a model fibril of crystalline cellulose in NaCl aqueous solution, respectively. Replica Exchange LD simulations (Swensen and Wang 1986; Sugita and Okamoto 1999) were carried out in a simulation box of dimensions \(L_x = 38.8 \text{ Å} \quad L_y = 43.1 \text{ Å} \quad L_z = 34.4 \text{ Å}\) containing 1839 water molecules and 5 NaCl pairs. The cellulose-NaCl ratio in the cellotetraose system corresponds to a 40 wt% concentration (or \(\sim 0.1 \text{ M}\)), which is within the range of the experimental wt% concentrations used in salt-assisted acid catalysis experiments of cellulose decomposition (vom Stein et al. 2010; Potvin et al. 2011). Forty-eight replicas were used corresponding to 48 temperatures in the interval \([298–550] \text{ K}\). The total simulation time per replica was 100 ns with replica swaps performed every 40 ps and a swap acceptance ratio varying between 0.1 and 0.3. The last 50 ns were considered for data analysis. The cellotetraose molecule was capped with reducing and non–reducing ends (Kirschner et al. 2008; Shen et al. 2009). The cellotetraose molecule and the ion pairs were spatially constrained within a sphere of radius \(r_s = 15 \text{ Å}\) centered in the water box center (Bellesia and Shea 2009). In more detail, spherical harmonic boundary conditions were enforced on the cellotetraose molecule and the ion pairs by means of a single potential function,

\[
E_s = \begin{cases} 
  k_s(\left|\mathbf{r}_i - \mathbf{r}_c\right| - r_s)^2 & \text{if } \left|\mathbf{r}_i - \mathbf{r}_c\right| > r_s, \\
  0 & \text{otherwise}
\end{cases}
\]

where \(k_s = 10 \text{ kcal/mol}\), \(\mathbf{r}_i\) is the current position of atom \(i\) and \(\mathbf{r}_c\) is the center of the sphere. The potential \(E_s\) was used to increase the NaCl concentration (\(\approx 0.6 \text{ M}\)) without increasing the size of the system and, therefore, the computational cost of the simulations. Additional Replica Exchange LD simulations were carried out for a cellotetraose molecule in aqueous solution without NaCl under the same simulation conditions used in the NaCl simulations.
For these calculations, the total simulation time per replica was 40 ns and the last 20 ns were considered for data analysis. Two single temperature NPT–LD simulations on a crystalline Iβ cellulose fibril composed of 30 octameric glucan chains were performed at $T = 298$ K and $T = 400$ K. For the initial fibril conformation we considered an equilibrated structure from previous LD simulations (Chundawat et al. 2011). Each octameric cellulose chain was covalently connected to its periodic image along its main axis in order to mimic an infinitely long cellulose fibril (Chundawat et al. 2011). The fibril was solvated in a rectangular box containing 6,660 water molecules and 15 NaCl pairs. The cellulose-NaCl ratio in the cellulose fibril system corresponds to 2 wt%, which is within the concentration range present in real biomass feedstock (0.5–5%) and relevant to fast pyrolysis experiments (Patwardhan et al. 2010). The 2 wt% concentration used in our simulations is close to the lowest concentration used in acid cataysis experiments (5 wt%) (vom Stein et al. 2010; Potvin et al. 2011). The use of this relatively low NaCl concentration is justified by the fact that for higher concentrations (both in terms of weight percent and molarity), ions tend to form small unphysical clusters that strongly limit the NaCl reactivity and negatively affect the statistical sampling of the NaCl-cellulose interactions. This is a well known problem that arises when classical force fields are used (Wang et al. 2000; Chen and Pappu 2007).

The solvated cellulose fibril underwent first a local optimization, followed by a short (0.5 ns) NPT–MD simulation, where the temperature was gradually increased from 100 to 298 K. This initial optimization-thermalization simulation was followed by two separate 100 ns long NPT–MD simulations at $T = 298$ K and $T = 400$ K, respectively. The pressure $P$ was 1.01325 bar. The first 10 ns of the 100 ns run were considered as the initial equilibration time and the remaining 90 ns as the production time. During the 100 ns simulation runs we applied a cylindrical boundary potential (oriented along the cellulose fibril main axis) analogous to the one shown in Eq. 1 using a radius $r_{cyl} = 35$ Å and an infinite length. We found that the magnitude of both the spherical and the cylindrical potential is negligible when compared to the total potential energy of our systems (<0.01% of the total potential energy). Hence, we do not expect the presence of the boundary potentials to affect our results and conclusions. In addition, we used the same protocol to run a 50 ns simulation on a fibril in pure water at $T = 400$ K. In all simulations, the time step was fixed at 2.0 fs. The covalent bonds involving hydrogen atoms were constrained by means of the SHAKE algorithm (Ryckaert et al. 1977). We used the NAMD software package (Phillips et al. 2005) with the GLYCAM06 (Kirschner et al. 2008) force field and the TIP3P explicit water model (Jorgensen et al. 1983). The reliability of the GLYCAM force field for solvated and crystalline cellulose systems has been assessed in a number of recent publications (Shen et al. 2009; Chundawat et al. 2011; Bellesia et al. 2011; Matthews et al. 2012). A Langevin thermostat and Nose–Hoover Langevin barostat with a stochastic component were used to control the temperature and the pressure, respectively (Feller et al. 1995; Martyna et al. 1994). The damping coefficient for the Langevin integrator was set to 1.0 ps$^{-1}$, while for the Nose–Hoover Langevin barostat we applied an oscillation period of 200 fs and a damping period of 100 fs. The cutoff for the non-bonded interactions in the coordinate space was fixed at 10.0 Å. All the simulations were performed under periodic boundary conditions, and the long-range electrostatic interactions were calculated by using the Ewald summation method with the particle mesh Ewald algorithm (Darden et al. 1993). The particle mesh Ewald accuracy was fixed at $10^{-6}$, the order of the interpolation functions on the grid was set to 4 and the grid spacing was $\approx 1.0$ Å.

Results and discussion

Cellotetraose conformations

Conformations of a cellotetraose molecule have been analyzed considering a set of relevant dihedral degrees of freedom (Shen et al. 2009): the hydroxymethyl rotational state (Shen et al. 2009; Chundawat et al. 2011) and the three puckering angles defining the conformation of the glucose ring ($C2C3C4C5$, $C4C5O5C1$, $O5C1C2C3$). In Fig. 1a we plot the percentage for the three hydroxymethyl rotational states ($tg$, $gt$ and $gg$) as a function of temperature. At 298 K, the rotational population is mostly dominated by the $gg$ state with the $gt$ state contributing as well. The statistical weight of the $tg$ state (dominant in native crystalline cellulose) is quite small at
room temperature. Not surprisingly, the statistical weight of \( t_g \) increases with temperature as the thermal energy “flattens” the energy barriers between the three hydroxymethyl states. In Fig. S1(A,B,C) in the Supporting Information we show the residuals between \( t_g \), \( g_t \) and \( g_g \) data, respectively, calculated as the difference between the percentages collected in \( \text{NaCl} \) aqueous solution (Fig. 1a) and the analogous data collected from the simulations of the cellotetraose molecule in pure water. The normalized sums of the residuals are 0.27, 1.20 and \(-1.47\%\), for \( t_g \), \( g_t \) and \( g_g \), respectively. These data show that when \( \text{NaCl} \) is present, the statistical weight of the \( g_g \) state diminishes mostly at the expense of the \( g_t \) state that becomes moderately more favorable than in pure water.

In Fig. 1b we plot the percentage of distorted, non-\(^4\text{C}_1\) conformations (black triangles) defined by negative values of at least one of the dihedrals \( \text{C}_2\text{C}_3\text{C}_4\text{C}_5, \text{C}_4\text{C}_5\text{O}_5\text{C}_1 \) and \( \text{O}_5\text{C}_1\text{C}_2\text{C}_3 \) (Shen et al. 2009). We also show the partial percentages for each of the three angles defining the ring conformation. The percentage of distorted, non-chair-like conformations appears to increase linearly with temperature. Comparison with simulations in pure water (Figure S1(D) in the Supporting Information) shows that the statistical weight of the non-\(^4\text{C}_1\) conformations is negligible when \( \text{NaCl} \) is present (normalized residual = 1.15 \%).

**Cellotetraose–Na\(^+\) interaction**

To analyze the interaction of solvated cellulose with \( \text{NaCl} \), and in particular with \( \text{Na}^+ \), we first considered a set of radial distribution functions (RDFs) related to ion–cellulose heavy atom interactions. The limited number of ions in our system together with the lack of radial symmetry make the use of RDFs problematic, especially when it comes to normalization at large distances. Nevertheless, we make preliminary use of ion-cellulose RDFs to obtain information about the location of the first minimum which defines the cutoff distance for the ion–cellulose interactions (Fig. S2 in the Supporting Information). A systematic analysis of the RDFs reveals that the most relevant ion–cellulose interactions involve \( \text{Na}^+ \) and the hydroxyl oxygen atoms. The sharp peaks near 2.5 \( \text{Å} \) indicate that \( \text{Na}^+ \) forms a well-defined coordination with hydroxyl groups. The peak is stronger in the \( \text{O}_3–\text{Na}^+ \) case indicating that the coordination is stronger in this case. With increasing temperature, the peaks lose intensity and become slightly broader.

The first minimum in those critical RDFs is typically well–defined and located at a distance \( r_c = 3.2 \text{ Å} \). That distance represents an accurate cutoff measure for the first coordination cell and for defining “contacts” between \( \text{Na}^+ \) and oxygen atoms in cellulose. In Table 1, we report the relative probabilities for the “contacts” between \( \text{Na}^+ \) ions and the relevant oxygen atoms \( \text{O}_2, \text{O}_3 \) and \( \text{O}_6 \) (hydroxymethyl oxygen) in cellulose at \( T = 298 \text{ K} \), \( T = 402 \text{ K} \) and \( T = 502 \text{ K} \). Oxygen that belong to the non-reducing end of the cellotetraose molecule are included in the calculations. Our results show that \( \text{O}_3 \) is slightly more prone to form contacts with \( \text{Na}^+ \) than \( \text{O}_6 \) and \( \text{O}_2 \). The full temperature dependence for the relative probabilities of the \( \text{O}_2–\text{Na}^+, \text{O}_3–\text{Na}^+ \) and \( \text{O}_6–\text{Na}^+ \) contacts is shown in Fig. 2. The rotational flexibility of the hydroxymethyl group allows the
relative probability for the $O_6$–Na$^+$ contacts to increase with temperature and to become the largest at temperatures $\sim 410$ K. In the bottom part of Table 1 we show the results for the relative three–body contacts (joint probabilities) involving Na$^+$, $O_x$ and $O_y$ ($x, y = 2, 3, 6, x \neq y$) at $T = 298$, $T = 402$ and $T = 502$ K. Full temperature dependence data show that the Na$^+$ coordination involving $O_2$ and $O_3$ atoms has, by far, the highest statistical weight across the temperature interval considered in our simulations.

In terms of intramolecular cellulose hydrogen bonding in both the NaCl and pure water simulations of the solvated cellotetraose molecule, we observe a dominant $O_3$–$O_5$ bond and marginal contributions from $O_6$–$O_3$, $O_3$–$O_6$, $O_6$–$O_2$ and $O_2$–$O_6$ hydrogen bonds. These results are in good quantitative agreement with Recent NDIS and NMR spectroscopy experiments on cellubiose in aqueous solution (O’Dell et al. 2012). The percentage contribution of the $O_3$–$O_5$ hydrogen bond decreases linearly from $\sim 80$–90 to $\sim 57$ % with temperature increasing from 298 to 400 K. Conversely, the same temperature increase is associated with an increase in the percentage contribution of $O_6$–$O_3$, $O_3$–$O_6$, $O_6$–$O_2$ and $O_2$–$O_6$ hydrogen bonds together from 7–9% to 23–25% (data not shown).

### Cellulose I$_b$ fibril

The comparison between the hydroxymethyl population in a model cellulose fibril in NaCl aqueous solution (at 298 and 400 K) and an identical fibril in pure water (Chundawat et al. 2011) (at 298 and 400 K) is reported in Table 2. The results show that

| Table 1 Cellotetraose in NaCl aqueous solution |
|------------------|--------|--------|--------|
| T(K)  | $O_2$ | $O_3$ | $O_6$ |
| 298   | 0.32  | 0.37  | 0.30  |
| 402   | **0.34** | 0.33  | 0.32  |
| 502   | 0.32  | 0.32  | **0.35** |

| T(K)  | $O_2$–$O_3$ | $O_2$–$O_6$ | $O_3$–$O_6$ |
|-------|-------------|-------------|-------------|
| 298   | 0.22        | 0.02        | 0.10        |
| 402   | **0.17**    | 0.02        | 0.07        |
| 502   | 0.15        | 0.02        | 0.07        |

Two and three-body relative contact probabilities between Na$^+$ and cellulose oxygens $O_x$ where $x = 2, 3, 6$. For example, the two–body relative contact probability between Na$^+$ ions and $O_6$ oxygens is calculated as $P(\text{Na}–O_6) = \frac{\text{Na}–O_6—\text{contacts}}{(\text{Na}–O_2—\text{contacts} + \text{Na}–O_3—\text{contacts} + \text{Na}–O_6—\text{contacts})}$ while the three–body contact probability between Na$^+$ ions, $O_3$ and $O_6$ is calculated as $P(\text{Na}–O_3–O_6) = \frac{\text{Na}–O_3–O_6—\text{contacts}}{(\text{Na}–O_3—\text{contacts} + \text{Na}–O_6—\text{contacts})}$. The largest value for each relative contact probability is indicated in bold font.

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Fig. 2 Cellotetraose in NaCl aqueous solution. Full temperature dependence of the relative probabilities of $O_2$–Na$^+$, $O_3$–Na$^+$, $O_6$–Na$^+$ contacts are shown in panels (a), (b) and (c), respectively. $O_6$ increases its contact probability to Na$^+$ at higher temperatures. At $\sim 410$ K, $O_6$ contact probability to Na$^+$ becomes the largest.
Table 2  Rotational state occupancy for the hydroxymethyl group in the fibril crystalline core and on the surface cellulose chains in cellulose Iβ fibrils in pure water at 298 K (Fib-298) (Chundawat et al. 2011), in NaCl aqueous solution at 298 K (Fib-298-NaCl) and at 400 K (Fib-400-NaCl)

|                | Fib-298(Chundawat et al. 2011) | Fib-298-NaCl | Fib-400-NaCl |
|----------------|--------------------------------|--------------|--------------|
|                | Crystalline core | Surface chains | Crystalline core | Surface chains | Crystalline core | Surface chains |
| tg             | 92.8% | 25.8% | 59.9% | 15.7% | 9.3% | 11.4% |
| gt             | 4.6   | 28.1  | 25.2 | 37.1 | 43.7 | 35.1 |
| gg             | 2.6   | 46.1  | 14.9 | 47.2 | 47.0 | 53.5 |

the presence of NaCl perturbs the hydroxymethyl rotational state occupancy favoring the gt and gg conformations over tg in both the fibril crystalline core and its surface at both temperatures. At 400 K, the gg rotational state becomes the dominant one both on the fibril surface and in its crystalline core. Despite the change in the hydroxymethyl rotational state occupancy, due to the presence of NaCl, the fibril maintains Iβ symmetry in its crystalline core at both 298 and 400 K (data not shown). We did not observe any non-chair–like conformation in our simulations of the cellulose fibrils (neither at 298 nor at 400 K).

Cellulose Iβ fibril–Na+ interaction

In Table 3 we report the results for the relevant two and three-body relative contact probabilities involving Na+ and the cellulose oxygens Ox (x = 2, 3, 6) in a model cellulose fibril. The cellulose-Na+ contacts analyzed in our study apply to the cellulose chains on the fibril surface and exposed directly to the solvent. We did not observe any substantial penetration of the Na+ ions within the cellulose fibril. Single contacts are highly favored over bridging positions, and among those single contacts, O6 has the highest probability of contact to Na+ at both T = 298 and T = 400 K. The contacts between the cellulose oxygens O2, O3, O6 and Na+ account for over 70 % of the total contacts between cellulose heavy atoms and Na+ Cl− pairs. Specifically, the ratio between Cl− and Na+ contacts with the cellulose heavy atoms is 0.29 at 298 K and 0.27 at 400 K. O2 shows the highest probability of contact to Cl− at 298 and 400 K. We did not observe any simultaneous contact between Cl− and cellulose oxygen pairs (bridging positions).

The internal hydrogen bond for the cellulose fibril in the presence of NaCl shows some differences when compared with the results from simulations in pure water (Chundawat et al. 2011). When the hydroxymethyl group deviates from the tg conformation (typical of native crystalline cellulose) we expect the weakening (or the disappearance) of the native intramolecular hydrogen bonds involving the hydroxymethyl oxygen O6 and the appearance of new hydrogen bonds connecting neighboring layers within the crystal (Nishiyama et al. 2002; Wada et al. 2004). Indeed, a comparison with previous simulations in pure water (Chundawat et al. 2011) shows that the presence of NaCl leads to a lower number of intramolecular hydrogen bonds (Fig. S3 and S4, top row in the Supporting Information) with the number decreasing with increasing temperature from 298 to 400 K, and a higher number of intersheet hydrogen bonds (Fig. S3 and S4, bottom row in the Supporting Information) with the number increasing with increasing temperature from 298 to 400 K. The intermolecular/intrasheet hydrogen bond network (Fig. S3 and S4, center row in the Supporting Information) does not seem to be perturbed by the presence of NaCl at 298 K. Conversely, at 400 K the presence of NaCl results in a lower number of intermolecular/intrasheet hydrogen bonds.

In Table 4 we show the relative contributions to the cellulose-water hydrogen bond network at 298 K of oxygens O2, O3, O6 for a model cellulose fibril with NaCl (Fib-NaCl) and without NaCl (Fib) (Chundawat et al. 2011). Our data reveal that the presence of NaCl (even at relatively low concentrations—see Computational methods Section) results in a decrease of the relative contribution of the hydroxymethyl oxygen O6 possibly due to its high relative affinity to Na+. Typically, the water coordination to O3 is the lowest...
Table 3  Cellulose Iβ fibril in NaCl aqueous solution

| T(K) | O2  | O3  | O6  |
|------|-----|-----|-----|
| 298  | 0.24| 0.33| 0.41|
| 400  | 0.18| 0.35| 0.46|

Table 4  Relative contribution to the cellulose–water hydrogen bond network at 298 K of oxygens O2, O3, and O6. Comparison between fibril with NaCl (Fib-NaCl) and fibril without NaCl (Fib). (Chundawat et al. 2011). The largest values for each measurement are indicated in bold font.

| System  | O2  | O3  | O6  |
|---------|-----|-----|-----|
| Fib-NaCl| 0.29| 0.32| 0.27|
| Fib     | 0.31| 0.24| 0.35|

due to presence of persistent O3–O5 intrachain hydrogen bond. Interestingly, a slight increase is seen in O3 hydrogen bonding to water in the presence of NaCl. The cellulose-water hydrogen bonding maintains these same general trends also at 400 K in the crystalline cellulose simulations. Interestingly, for the solvated cellotetraose molecule neither the presence of NaCl nor a change in temperature (in the interval 298–550 K) alters the relative contributions of the oxygens O2, O3 and O6 to the cellulose–water hydrogen bond network.

Conclusion

Inorganic salts, in general and NaCl in particular, are known to adversely affect biomass fast pyrolysis and to increase the efficiency of catalytic cellulose degradation in the aqueous environment. The purpose of this computational study was to resolve the atomistic details of the interactions of oligomeric and fibrillar forms of solvated cellulose with Na⁺.

Our classical MD simulations show that the dominant interaction is the one between the Na⁺ and the hydroxyl oxygen atoms in cellulose.

In more detail, we observe that, in cellulose, the two backbone oxygens O2, O3 and the sidechain oxygen O6 account for most of the interactions with Na⁺, with the hydroxymethyl oxygen O6 dominating at high temperatures (>410 K) in solvated cellulose and at both 298 and 400 K in crystalline cellulose. In solvated cellulose, we also noticed a high affinity for Na⁺ to be in a “bridging” position between the O2 and O3 backbone oxygens.

Our simulations also show only minor structural changes in the pyranose ring due to the presence of NaCl. The chair conformation was the dominant ring structure for both oligomeric and crystalline cellulose in the classical MD simulations. In crystalline cellulose, the presence of NaCl perturbs the rotational state population of the hydroxymethyl group. As a consequence of the perturbation of the hydroxymethyl rotational state population, the hydrogen bonding network in crystalline cellulose is also perturbed by the presence of NaCl.

In particular we observed the disappearance of a number of intramolecular hydrogen bonds and a consequential emergence of intersheet hydrogen bonds as seen previously in the high temperature MD simulations of native cellulose and cellulose IIIβ (Chundawat et al. 2011; Matthews et al. 2011). The enhanced understanding of the interactions of sodium chloride with cellulose gained from this computational study will provide valuable information for the design of cost-effective thermochemical degradation protocols for cellulolic biomass.

The Supporting Information contains 4 figures: (1) Residuals between cellotetraose tg, gt and gg data. (2) Radial distribution functions for Na⁺ and O2, O3, and O6. (3) Data for the hydrogen bond network in cellulose Iβ in pure water and in NaCl solution at 298 K. (4) Data for the hydrogen bond network in cellulose Iβ in pure water and in NaCl solution at 400 K.

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