# Binding Strength of Sodium Ions in Cellulose for Different Water Contents

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The interaction strength of sodium ions (Na$^+$) with cellulose is investigated from *first principles* for varying degrees of water content. We find that the interaction of water molecules and Na$^+$ can be studied independently at the various OH groups in cellulose which we categorize as two different types. In the absence of water, Na$^+$ forms strong ionic bonds with the OH groups of cellulose. When water molecules are anchored to the OH groups via hydrogen bonds, Na$^+$ can eventually no longer bind to the OH groups, but will instead interact with the oxygen atoms of the water molecules. Due to the rather weak attachment of the latter to the OH groups, Na$^+$ becomes effectively more mobile in the fully hydrated cellulose framework. The present study thus represents a significant step toward a *first-principles* understanding of the experimentally observed dependence of ionic conductivity on the level of hydration in cellulose network.

## Introduction

Cellulose plays a very important role in many industrial processes, predominantly in the production of cardboard or paper but also of cotton-based textiles. In its microcrystalline form, cellulose is commonly used as a drug delivery vehicle in tablets. After ingestion by a patient, the hydrophilic nature of cellulose assists in the release of the medicine upon contact by the tablets with water. This process is initiated by an ionization of the polar drug molecules and subsequent formation of a hydration shell around the ionic components of the drug.[1] Hence, the speed of the drug release depends on the strength of the interaction between the drug molecules and the water molecules as well as the hydroxyl groups present in the cellulose framework.[2] Despite extensive studies of the properties of cellulose, there is still much left to be understood about the details of the interactions between cellulose and various solids and liquids. It is therefore important to analyze and understand these interactions also with respect to identifying possible ways to alter the nanostructure of cellulose in order to achieve better control over the drug release process. Recently, a series of experimental studies[1–6] investigated the mechanisms at work in the drug release process. In these studies, NaCl was commonly used as a stand-in model for the polar drug components. Here, we present results from our complementary theoretical study, where we have concentrated on the interaction of the Na$^+$ ion with cellulose having different levels of water concentration in the network.

It is well-known[4,7–9] that the ionic conductivity in cellulose rises with increasing water content, following a power function with a high exponent of nine. To explain this observation, one model considers water forming a pathway in cellulose on which alkali ions could move.[7] Another model takes into account the contribution of dissociated water molecules to the charge transport process.[8,9] More recently, it was argued that the high-exponent power-law increase in the conductivity[7] has its cause in either a tunneling transport mechanism or in the strong anisotropy of the cellulose fibers.[4] It was furthermore shown that the observed behavior of the conductivity could be due to both a rapid increase in the number of charge carrier ions participating in the conduction process and a moderate decrease in their mobility with increasing cellulose moisture content.[4]

The motivation for our work was therefore to understand the interaction of sodium ions with cellulose for differing levels of hydration from *first principles*. Such an insight is likely to prove very helpful in the analysis of behavior of the ionic conductivity of cellulose with increasing water content. With that aim, we carried out a systematic study of the binding strength of sodium ion to cellulose and considered the effects that the presence of water molecules can have on the interaction of sodium with the OH groups in cellulose. The remainder of the paper is organized as follows. First, we will explain the computational details of our work and how we modeled the system in our theoretical study. This section will be followed by the presentation and discussion of the results we obtained in the three broad scenarios considered, namely (i) cellulose interacting with water, (ii) cellulose interacting with sodium in the absence of water, and (iii) cellulose interacting with sodium in the presence of water. Finally, we provide a summary of our work together with the conclusions that can be drawn from our study.

## Computational Methods

The electronic structure calculations were performed in the framework of density functional theory (DFT)[10,11] in which we used ultrasoft pseudopotentials within the generalized gradient approximation (GGA)[12] as given by Perdew−Wang 91, implemented in the Vienna ab initio simulation package (VASP).[13]

The monolayer cellulose structure corresponds to a polymer of $\beta$-D-glucose where two six-membered rings are connected

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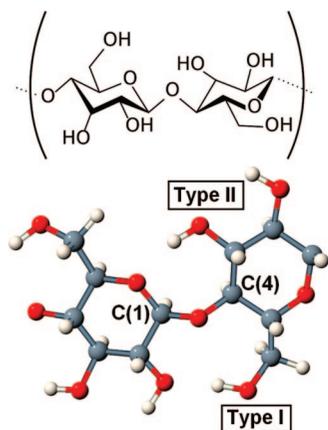
**Figure 1.** Basic unit of cellulose in skeletal representation (top) and in ball-and-stick representation (bottom). Carbon atoms are represented as gray spheres, oxygen atoms in red, and hydrogen atoms in white. The labels "Type I" and "Type II" indicate the two types of OH sites that we refer to in the text.

via one oxygen atom, linking alternately to C(1) and C(4) in the sugar ring (Figure 1).[14] We therefore constructed the supercell by placing a basic unit of the cellulose[14] in the *xy*-plane inside a rectangular grid with surface-to-surface separation of 15 Å. This approach ensures a negligible interaction between the cellulose chain and its repeated images in calculations. The dimension of the supercell along the *x*-axis was 10.54 Å, which leads to an uninterrupted infinite 1-D chain of linked cellulose units. Our model system can be regarded as artificial insofar as it ignores interstrand interactions between parallel cellulose chains. However, the advantage of this approach is that it allowed us to concentrate on studying the interaction of water and Na$^+$ ions with a *single* cellulose chain. The cutoff energy for the plane-wave basis set we used was 500 eV. Gaussian smearing was employed with a smearing width $\sigma = 0.1$ eV. The resulting entropy, i.e., the difference between the free energy and the total energy was found to be negligible. The calculations for the determination of the equilibrium geometry used the quasi-Newton algorithm implemented in VASP and were considered to be converged when the force on each ion was less than 0.03 eV/Å with a convergence in the total energy between $10^{-4}$ and $10^{-5}$ eV.

The binding energy $E_b$ of water molecules to cellulose was determined using the following formula

$$E_b = E[\text{cellulose}] + nE[\text{H}_2\text{O}] - E[\text{cellulose} + (\text{H}_2\text{O})_n]$$

where $E[X]$ refers to the total energy of any given system X (here: cellulose, water molecules, and the combination thereof). The interaction energy $E_{int}$ of Na$^+$ ions in the two-, three-, or four-body complexes composed of the ion, cellulose, and up to two water molecules, was calculated as follows:

$$E_{int} = E[\text{cellulose} + (\text{H}_2\text{O})_n] + E[\text{Na}^+] + E[\text{Cl}^-] -$$
$$E[\text{cellulose} + (\text{H}_2\text{O})_n + \text{Na}^+ + \text{Cl}^-]$$

Here $n$ can take values 0, 1, and 2. (While this formula appears to include the interaction energy of the Cl$^-$ ion as well, we show below that due to the particular setup in our simulations, its actual contribution to the interaction energy can be neglected in all cases considered here.) For the determination of the respective total energies, all structures were fully relaxed. In those cases where more than one possible configuration exist (due to the presence of multiple docking sites), the binding/interaction energies provided by us refer to averaged quantities

from separate calculations. The reference total energies for the isolated constituents that appear in the above equations have the following values: $E[\text{cellulose}] = -6498.86$ eV, $E[\text{H}_2\text{O}] = -464.31$ eV, $E[\text{Na}^+] = -12.51$ eV, and $E[\text{Cl}^-] = -414.23$ eV.

## Results and Discussion

**i. Cellulose with Water.** We start by presenting our results for the interaction of cellulose with water molecules exclusively. In our study, we placed H$_2$O near the cellulose network in such a manner that the hydrogen atoms of water can easily form a hydrogen bond with the oxygen atom of the OH groups of cellulose. The atomic coordinates were then relaxed to obtain the equilibrium geometry. These steps were carried out for all possible OH binding sites on cellulose and for different degrees of hydration in the cellulose structure.

In the following, we distinguish two different types of OH binding sites in cellulose: type I possesses a single OH group protruding from the six-membered ring, while type II has two such OH groups protruding from the same side of the ring. Figure 1 shows such a cellulose structure consisting of one OH group of each type at every ring. When water is bound at a type I site (Figure 2a), only one hydrogen bond can be formed, and we find a binding energy of about 0.30 eV (Table 1). On the other hand, when water binds at a type II site (Figure 2b), two hydrogen bonds can be formed: one with each OH group, and the corresponding binding energy is found to be approximately twice as large, i.e., about 0.63 eV (Table 1). We note that the somewhat higher values for the hydrogen bond energies than the typical 5 kcal/mol per O···H—O bond are most likely due to the lack of zero-point vibration energy corrections in the present work. This systematic offset does however not affect the conclusions drawn in our comparative study.

We furthermore note that the water molecules are essentially interacting with cellulose independently from each other. This manifests itself in the additive nature of the binding energies (Table 1). Thus, we find that the binding energy of two water molecules bound to different OH groups at cellulose, e. g., at a type II site (Figure 2c), is with 0.9 eV almost exactly the sum of the individual binding energies of about 0.6 eV (from the formation of two H-bonds by one water molecule) and about 0.3 eV (from the formation of one H-bond by the other water molecule). Similar results have been predicted by us for other combinations of water-trapping sites, including up to four water molecules binding simultaneously to the various sites on the cellulose structure.

This finding had important consequences for the further study suggesting that investigation of the different binding sites on cellulose can be performed independently from each other. Therefore, in the following, we will only consider one binding site at a time for further calculations.

**ii. Cellulose with Sodium.** We now turn to the results obtained for the interaction of the sodium ion with cellulose in the absence of water. All of the OH-groups on cellulose have been investigated, with the sodium ion being placed closely toward the OH group and a geometry optimization was carried out to determine the equilibrium configuration of the system. The interaction between the positively charged sodium ion and the partially negatively charged OH group is found to be purely ionic.

It is important to mention that in calculations involving Na$^+$, we have also placed a single chloride ion (Cl$^-$) in the supercell to maintain charge neutrality of the system. As we are employing

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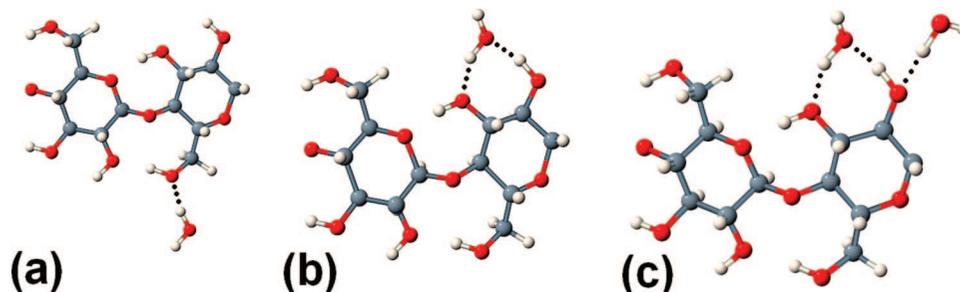


**Figure 2.** (a) One water molecule at a type I site forming a single H-bond (represented by black dotted lines); (b) one water molecule at a type II site forming two H-bonds; (c) two water molecules at a type II site, with the left forming two H-bonds and the right forming one H-bond.

**TABLE 1: Total Energy and Binding Energy ($E_b$) of Water Molecules at the Various Sites of the Cellulose Structure**

| number of water molecules and site | total energy (eV) | $E_b$ (eV) |
|---|---|---|
| 1 $H_2O$ @ type I | −6963.47 | 0.30 |
| 1 $H_2O$ @ type II | −6963.80 | 0.63 |
| 2 $H_2O$ @ type II | −7428.38 | 0.90 |
| 2 $H_2O$ @ type II and 2 $H_2O$ @ type I | −8357.89 | 1.79 |



**Figure 3.** (a) $Na^+$ ion (blue larger sphere at the bottom) at a type I site in the absence of water. The $Cl^-$ ion (green smaller sphere at the top) is always kept far away from the structure (not in the same plane as the cellulose chain). (b) $Na^+$ ion at a type II site in the absence of water. Ionic bonds involving the $Na^+$ ion are shown as colored dotted lines.

**TABLE 2: Total Energy and Interaction Energy ($E_{int}$) of $Na^+$ Ion and Separation to Oxygen Atoms**

| amount of water and site | total energy (eV) | $E_{int}$ (eV) | $R_{Na^+}-O$ (cellulose) (Å) | $R_{Na^+}-O$ (water) (Å) |
|---|---|---|---|---|
| no water molecule | | | | |
| type I | −6928.96 | 3.36 | 2.26 | |
| type II | −6928.96 | 2.66 | 2.43 | |
| one water molecule | | | | |
| type I | −7393.73 | 3.52 | 2.57 | 2.20 |
| type II | −7393.28 | 2.74 | 2.35 | 3.24 |
| two water molecules | | | | |
| type II | −7858.65 | 3.16 | 3.49 | 2.16 |

is of course highly relevant for the separation-dependent Coulomb interaction taking place between $Na^+$ and the partial negative charge of the oxygen atom of OH in the network. The cause for the larger separation at the type II site can be found in the particular orientation of the O−H bond (Figure 3b) which cause the partially positively charged H atom to be closer to the $Na^+$ ion, thus slightly repelling it. At the type I site, the O−H bond is oriented in a slightly different manner (Figure 3a), so that the repulsion by the H atom is less strong, allowing the $Na^+$ ion to approach the oxygen atom of the OH group somewhat more closely.

**iii. Cellulose with both Water and Sodium.** We finally come to the most interesting results for the interaction of sodium in cellulose when water is present. Here, we have considered the presence of the water molecules at the previously identified binding sites which are targeted by the sodium ions in the network. Clearly, the presence of water molecules will lead to a steric obstruction of the sodium ion, hindering it from reaching a close proximity to the OH groups. Initially, one might be led to think that this would result in a reduction of the interaction strength of sodium. However, as we will show in the following, the interaction strength of sodium is actually enhanced in the presence of water (Table 2). This seemingly counter-intuitive result can nevertheless be brought in reconciliation with the experimental results which show a rise in ionic conductivity with increasing water content.[4,7–9]

We now focus on the interaction of $Na^+$ with two OH groups at the water trapping type I and type II sites in the cellulose structure. First, let us consider the case when $Na^+$ is interacting with the OH group at type I site where a water molecule has already been trapped (Figure 4a). Here, we find that the interaction energy of $Na^+$ in the three-body complex is 3.52 eV. This should be compared to the value of 3.36 eV obtained for the case when no water molecule is present in the network. We thus conclude that the presence of water has, in fact, resulted in a slight but significant increase in the interaction energy.

the supercell approach, any excess charge would lead to an infinite Coulomb potential. Thus, the presence of any ion requires either a constant charge background to neutralize it, or a counterion with the opposite charge. We employed the latter approach, since it appears to be closer to the actual scenario in the system where both cations and anions are present. In calculations, the $Cl^-$ ion was kept sufficiently far away from both cellulose and $Na^+$ ions, so that except for its intended purpose to provide charge neutrality, any other direct interactions can be neglected.

For interaction of $Na^+$ with a type I site (Figure 3a), we find an interaction energy of 3.36 eV while the interaction with a type II site (Figure 3b) leads to an interaction energy of 2.66 eV. It may, at first, be surprising that the interaction strength of $Na^+$ with cellulose is lower when two OH groups are present in the network. However, one needs to consider the particular relative positioning of $Na^+$ which shows that its interaction takes place only with one of the two available OH groups (Figure 3b). The strength of the interaction is then determined mainly by the proximity of $Na^+$ to the OH group of the cellulose structure. Here we find that, for the type I site (with higher interaction energy), the bond distance $R_{Na^+}-O$ is 2.26 Å, while for the type II site (with lower interaction energy), $R_{Na^+}-O$ is 2.43 Å. The difference in the interaction energy between type I and type II sites is thus due to the difference in $R_{Na^+}-O$, which

**Figure 4.** (a) Na$^+$ ion at a type I site in the presence of one water molecule at the same site; (b) Na$^+$ ion at a type II site in the presence of one water molecule at the same site; (c) Na$^+$ ion at a type II site in the presence of two water molecules at the same site. Ionic bonds involving the Na$^+$ ion and H-bonds are shown as dotted lines.

Figure 4a shows that Na$^+$ interacts electrostatically with the OH group while simultaneously drawing additional interaction strength of a smaller degree from the nearby oxygen atom of the water molecule, resulting in the predicted increase in its interaction energy in the cellulose structure.

For the case of sodium interacting with the OH groups at the type II site with one water molecule being present (Figure 4b), the interaction energy of Na$^+$ in the three-body complex comes out to be 2.74 eV. This can be compared with the value of 2.66 eV when no water molecule was present at the site. Thus, we find that the addition of water leads again to an increase in the interaction energy. However, the magnitude of the increase in interaction energy is smaller since the oxygen atom of the water molecule is further away from the Na$^+$ as compared to the case at the type I site. Furthermore, the larger separation of Na$^+$ to the oxygen from OH at the type II site should be taken into account (Table 2). This is again due to the partially positively charged H atom of OH which in closer proximity to the Na$^+$ ion slightly repels the latter (Figure 4b). At the type I site, on the other hand, the O−H bond is again oriented in such a way (Figure 4a) that the repulsion by the H atom is weaker, enabling the Na$^+$ ion to get closer to the oxygen atom of the OH group.

Finally, we come to the case of two water molecules at the type II site with sodium attempting to bind to either one of the OH groups (Figure 4c). We predict the interaction strength of sodium in this four-body complex to be 3.16 eV. Interestingly, this is even larger than the 2.74 eV found previously when only one water molecule was present at the type II site. The large increase of about 0.4 eV in the interaction strength can be understood from the very close proximity of Na$^+$ to the O atom of the second water molecule, with a separation of 2.16 Å. On the other hand, the interaction of Na$^+$ with OH group is greatly diminished, as the distance between Na$^+$ and the O atom of the nearest OH group of cellulose is 3.49 Å. Therefore, the interaction energy of sodium is mainly determined by the interaction with the water molecules surrounding the cellulose rather than with the OH group of cellulose itself.

Although sodium is predicted to be bound more strongly when water molecules are present in cellulose, the result is nevertheless in agreement with the experimentally observed rise in ionic mobility (and hence conductivity) in cellulose as the hydration level increases. The key point is that the binding partner of sodium is, in the case of absence of water, an OH group which is covalently bound to cellulose, while in the case of the presence of water, the "anchoring point" of sodium is shifted to one or more water molecules which are only bound through comparatively weaker hydrogen bonds (about 0.3 eV per hydrogen bond) to the OH group of cellulose. Thus, our results support the suggestion[2] that for small ions, the interaction between the OH

groups of cellulose and the water molecules in the hydration shell of the ion essentially determines how fast the ions can move within the cellulose framework.

When the electric field is applied to the system, the force acting on the Na$^+$ ion may not be large enough to remove it from its strong bond with an OH group, but it could unlock the relatively weakly coupled complex system formed by a Na$^+$ ion and nearby water molecules. Indeed, sodium is shown to prefer binding to the water molecule as compared to the OH group of cellulose, as the calculated interaction strength is about 0.5 eV larger in the former case. Therefore, our results also demonstrate that a sodium ion trapped at an OH site of cellulose could even be moved to the available competitive binding site with nearby water molecules in the network.

**Summary and Conclusions**

We have presented here the results of a systematic *first-principles* study of the interaction of water and sodium with cellulose. Our results show that the interaction of water molecules with the various OH groups of cellulose is independent from each other, and can thus be analyzed separately for each site. Most importantly, we find that the interaction strength of sodium increases with the number of water molecules added to a site. This behavior has its root in the electrostatic interaction of sodium with the oxygen atoms of the water molecules. When two water molecules are hydrogen-bonded to both OH groups at a type II site, sodium is hindered in its approach to the cellulose chain, and will instead interact strongly with the two water molecules. It is important to understand that sodium is therefore not bound to the OH groups which are fixed to the cellulose chain, but rather to the mobile water molecules. Thus, the overall effect of a high-level water content in cellulose is an enhancement of the mobility of sodium as it can then move along more easily with the less-tightly bound water clusters, since the interaction between OH groups of cellulose and water molecules in the hydration shell of the ion essentially determines how fast the ions can move within the cellulose framework. This interpretation of our results can thus provide a *first-principles* explanation of the experimental results[1–4] which demonstrate a rise in ionic conductivity with increasing water content. However, it was observed[4] as well that initially the ionic mobility decreases as the water content is raised from zero. This behavior can also be understood from our results, since in the low-level water content regime, represented in our simulations by a single water molecule occupying the OH groups, Na$^+$ is able to interact with both the OH groups of cellulose and the oxygen atom of the trapped water molecule (Figure 4a), and is thus bound to the framework much more strongly (Table 2).

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Additionally, the mobility of $Na^+$ is also reduced due to its hopping sites being occupied by water molecules.

As it is common for theoretical studies such as the present one, we had to make a number of approximations in our investigation. For example, we excluded adjacent parallel strands of cellulose in order to keep the model system simple and to purposefully concentrate on the interaction of water and $Na^+$ with a single cellulose chain. In future theoretical work, we aim to include the direct effect from the interstrand interactions to test its influence on the properties discussed in the present work. Likewise, one could argue that we adapted a rather coarse model for the water content here with zero, one, or two water molecules considered per OH binding site (Type I and type II). However, as we have shown, the interactions at spatially separated OH binding sites of cellulose can be treated independently and the three different water concentrations should therefore correspond to an apt representation of the actual situation in cellulose as the hydration level is changed. Thus, our main conclusion regarding the qualitative change in the interaction strength and mobility of sodium for different water content regimes is considered sound by us.

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