COTTON FIBER AND MOISTURE – SOME OF THE BASICS

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Abstract

The possible locations of water molecules in cotton fibers are explored based on fiber size, crystallite size, known crystal structures of cellulose hydrates, and cross-sections of swollen cotton fibers. A 5% moisture content, a normal value for room conditions, corresponds to roughly 760 monolayers of water if it all goes on the external fiber surface, or about 0.3 monolayers if it were able to access all surfaces of the crystallites that are indicated by x-ray diffraction studies. Additional information on hydrogen bonding, the major mechanism for the interaction of water and cotton, is provided by studies of water clusters with quantum mechanics. These theoretical studies show variation on the order of 10% in the length of hydrogen bonds, depending on the position of the water relative to other water molecules. These poorly understood fine distinctions are not found with studies based on available empirical force fields, the only method fast enough to be used for production studies on large molecules such as cellulose, so the empirical methods must be modified appropriately.

Introduction

It would be difficult to overstate the importance of moisture in the testing and processing of cotton. Backe (2001) recently reviewed these relationships. The relationship between cotton and moisture is also important to such diverse characteristics as the comfort of cotton and the costs of garment care. Many of the physical aspects of these relationships are well known. For instance, it is known that higher levels of moisture in cotton fiber cause the fiber to break at higher levels of force, while lower moisture allows trash to be removed more easily at the gin. The effect of moisture on strength is particularly interesting because that observation is contrary to the behavior of most other carbohydrate materials that weaken or dissolve with increasing moisture. One of the big complications in understanding the role of water is the phenomenon of hysteresis, the lag in the internal moisture compared to the change in environment. It is possible that the controversial practice of addition of moisture at the gin may well take advantage of hysteresis by providing higher internal moisture during grading by the Agricultural Marketing Service, even though they test under tightly controlled conditions.

A more thorough understanding of the relationship between water and cotton is desirable for additional reasons. Some varieties may take better advantage of water, and new cottons could be bred that dry more quickly or that otherwise mimic the effect of high moisture despite low actual moisture. In our initial steps towards improving this understanding, it is necessary to understand where the water goes and what its interaction with the cotton cellulose is. A number of studies have referred to the pores in cotton fibers that take up dyes or other solutes as well as water molecules, but we have yet to observe anything that might be described as a pore. Instead, we have framed the discussion in this work in the context of accessible surfaces for which there is fairly direct (e.g. microscopic or crystallographic) evidence. On the other hand, the actual interaction of individual water molecules with cotton is quite difficult to image experimentally. Therefore, computerized molecular modeling is the tool of necessity if not choice, and we review some of our as yet unpublished calculations on water clusters, a simple model for interactions between the hydroxyls of cellulose and neighboring water molecules.

Methods

The cotton fiber was assumed to be a solid cylinder of cellulose with a central lumen, with a length of 28 mm and a diameter of 15 μm (microns, micrometers or 10^{-6} meters). Its weight was 5 μg (5 x 10^{-6} g). A crystallite of the cellulose was assumed to correspond to a 6 x 6 array of cellulose chains with a square cross section, 4 nm on each side, and a given length of 28 mm. The density of the crystallites was taken as 1.63 g/cm^3, consistent with recent crystal structure determinations of cellulose I (Nishiyama et al., 2002, 2003). A monolayer of water was assumed to have a thickness of 0.25 nm. This corresponds to ordered water; the thickness of a monolayer of ordinary liquid water is about 0.31nm.

A transmission electron micrograph (Figure 1a, Rollins et al., 1965) shows the cross section of a cotton fiber that had been swollen with water and infused with methylacrylate monomer that had subsequently been polymerized. It resulted in a round cross section with numerous pockets. The formation of these pockets was attributed to expansion during polymerization of the monomer that had accessed the accessible surfaces during swelling. Thus, the surfaces were pre-existing and the pockets merely made these surfaces visible. The perimeters of each of these pockets in a digitized image of that cross section were assessed with image analysis (Image Pro Plus). A surface area was calculated based on the assumption that the pockets ran the length of the fiber. Although that was not likely, it was expected that there would be similar pockets along the length of the fiber. The result is referred to as the Rollins surface area.

Growth rings were found in swollen fibers that had grown under conditions with very cold nights by Haigler et al. (1991). These rings were much smoother than the irregular pockets found by Rollins et al. Their fiber cross-section was considered to have 20 of these rings, spaced at intervals of 0.5µm starting with perimeter at 15 µm diameter and ending with the lumen diameter at 5 µm as shown in Figure 1. Each ring shown in Figure 1b was assumed to correspond to two accessible surfaces, one on the interior side and one on the exterior side. Again, the accessible surfaces were assumed to run the length of a cylindrical fiber. We call the result the Haigler area.

Electronic structure theory (quantum mechanics) calculations were carried out with PQS software from Parallel Quantum Solutions, Fayetteville, AK. Two to eight water molecules were constrained to make linear arrays by additional dummy atoms (B. Jursic, A. D. French, G. P. Johnson, unpublished) and otherwise full optimizations were carried out at the stated levels of theory to the default convergence criteria. Other levels of theory have also been tried, with the same software and with other software. A wide range of energy values was found. Most examples selected showed an increasing stabilization per additional water molecule but in some cases the results were erratic. The use of diffuse functions (indicated by the + sign or aug) for levels of theory that incorporate initial approximations to electron correlation energy (such as MP2 and B3LYP) is considered necessary to avoid basis set superposition errors (Lii et al., 1999). Such errors over-estimate the energy of interaction, but the geometries are not significantly affected.

Results and Discussion

Table 1 shows the various specific surface areas calculated as described in Methods. Also tabulated are average values of surface areas from the Methylene Blue dye absorption experiments of Kaewprasit et al. (1998), X-ray scattering (Fink and Walenta, 1994) and the classical nitrogen absorption experiments of Blair and McElroy (1976). This is a wide range of surface areas. If the moisture level of the fiber is 5%, that weight of water could provide something like 760 monolayers of water on the outer surface, as also indicated in Table 1. Such a coating of water would be about 190 nm (= 0.19 µm) thick, compared to the 15 µm fiber diameter. This is one rough estimate; another would be to consider the wall thickness to be 3 µm, and 5% water (by weight) would correspond to a thickness of about 0.24 µm. But, nobody expects all of the water to be on the outer surface. At the other extreme, if all hydroxyl groups were available for hydrogen bonding to the water, 5% water would only be enough for 0.45 water molecules per anhydroglucose unit, or about one water per cellobiose unit. Also shown in Table 1, even at the level of the crystallite, 5% water does not provide complete coverage with a monolayer, being able to cover only about 30% of the surface. With the assumed full-length crystallites, the fiber could be considered to be divided into about 6.85 million crystallites. Division of a large particle into many small ones increases the surface area by approximately the square root of the number of particles. The ratio of the area of the crystallites to the area of the simple fiber cylinder is 2350, quite similar to the square root of 6.85 million (2617), an independent check on these calculations.

The degree of penetration of cellulose crystallites by water is a current controversy. Two fiber crystal structure studies are in the literature: cellulose II hydrate (Lee and Blackwell, 1976) and soda cellulose IV (Nishimura and Sarko, 1991). The latter structure is part of a series of structures induced by action of sodium hydroxide on cellulose but is found after all of the base is rinsed out; no sodium is present. It has one water per cellobiose unit, and the II hydrate structure has two water molecules per cellobiose unit. Figure 3 shows the packing of the cellulose chains in both of these structures. Only in the case of soda cellulose IV were the water oxygen atoms located. Both of these structures are unstable at humidities less than 93% and revert to cellulose II. The II hydrate was also prepared by the action of a powerful agent, ethylene diamine, that gave an intermediate crystal structure. Both of these extreme examples of the interaction of cellulose and water preserve the basic molecular shape found in native cellulose. Some may find it interesting that the cellulose chains in both structures are still in contact with each other on their hydrophobic surfaces. Although hydrogen bonding is often described as the"glue" of cellulose, this hydrophobic association appears to be equally or more important.

The primary evidence for some penetration of the crystallites comes from complex Nuclear Magnetic Resonance (NMR) studies (Hediger et al., 2002). On the other hand the diffraction patterns of cellulosic fibers are little changed by the presence of water, indicating that the crystal structures are not affected by water – the crystal structures are determined with no precautions against water absorption from the atmosphere. At a relatively low level of moisture such as 5%, gross effects would not be expected.

Figure 4 shows our octameric water cluster that was produced by B3LYP/6-31G** quantum mechanics calculations. Whereas the water dimer (two water molecules connected by a hydrogen bond) has a hydrogen bond length of about 0.193 nm at this level of theory, the H··O distance is reduced by about 10% when the molecule is in the center of the octameric cluster. This is a result of "cooperativity" in the structure. The correct energy of stabilization of a water dimer, vs. two isolated water molecules, is about 5 kcal/mol, but as shown in Figure 5, there is substantial dependence of the calculated value on which of the four levels of theory is used in the calculation, even with these relatively standard methods. As the length of the cluster is increased, the stabilization energy increases asymptotically to where the stabilization by addition of the eighth water molecule is about 50% greater than for the joining of the simple water dimer. These aspects of cooperativity are not reproduced with available empirical models that would typically be used to study large systems such as hydrated cellulose chains so more development is needed on this point.

Summary

There are several possible surfaces that water might find in a cotton fiber. We have considered several, none of which correspond very well with the nitrogen or Methylene Blue adsorption experiments (which are very different from each other). The action of water on fiber properties would perhaps be most obvious if it functioned as a lubricant. In this case the water would provide a means to satisfy hydrogen bonding requirements without inducing the strain that is otherwise inevitable from formation of hydrogen bonds directly among the crystallites. Hydrogen bonding structures could be easily destroyed and rebuilt under layers of water. That would require several layers of water around the affected entities, such as the level of the Methylene Blue sorption. However, it is likely that water could penetrate areas that could not be penetrated by the dye, and so fewer layers of water would result from 5% moisture than are indicated by that measure. Specific interactions have not been addressed at this point, and the most unknown factor in all of this is the role of the non-crystalline cellulose. Perhaps these non-crystalline regions correspond to the level of structure indicated by the Methylene Blue sorption experiments. Another unknown is how the water enters the fiber structure.

Acknowledgements

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Table 1. Specific Surface Areas for Cotton Fiber (x 10^{-3} km^2/kg) and number of monolayers from 5% moisture.

Surface model or experiment	Specific Surface Area	Number of Monolayers
Solid cylinder model of fiber	0.26	760
Nitrogen Sorption (Blair and McElroy, 1976)	0.80	250
Small Angle X-Ray Scattering (Fink and Walenta, 1994)	3.75	53
Rollins surface (Rollins et al., 1965)	5.8	34
Haigler layers (Haigler et al., 1998)	7.3	27
Methylene Blue (Kaewprasit et al., 1998)	40.0	5
Crystallites 4 nm x 4 nm	613	0.3
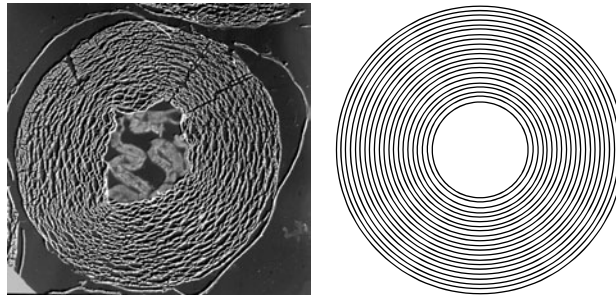
Figure 1. Cross sections of swollen fibers. 1a) (left) photograph from Rollins et al. (1965). 1b) (right) Model of the growth rings in a swollen cotton fiber (after Haigler et al., 1998).
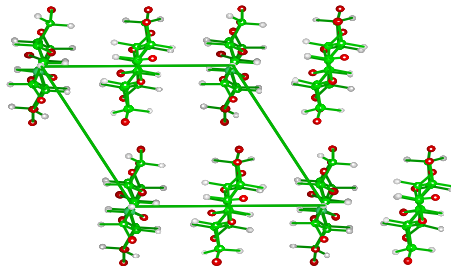

Figure 2. Cellulose II hydrate crystal structure, perpendicular to the chain axis. Water positions were not determined. From Lee and Blackwell, 1981.
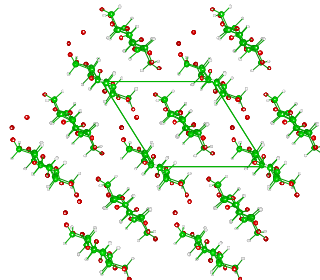

Figure 3. Soda Cellulose IV. Water positions indicated by lone oxygen atoms. This is one water per cellobiose unit but no sodium. See text. Based on Nishimura and Sarko, 1991.
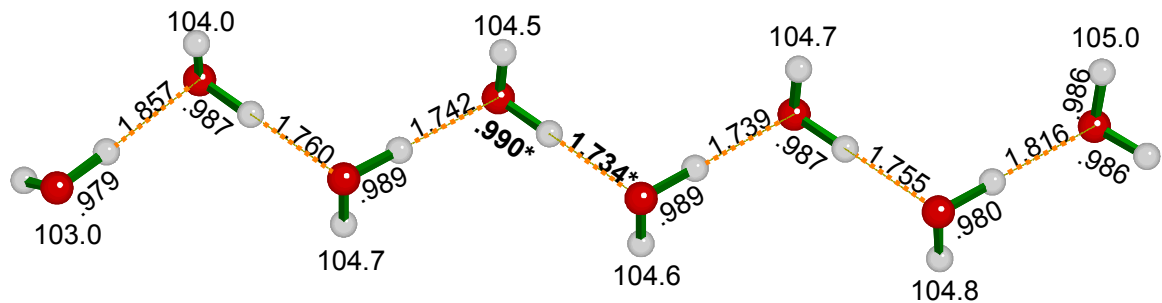
Figure 4. Constrained linear water cluster with eight water molecules optimized with B3LYP/6-31G** quantum mechanics. Distances are in Ångstroms (1 Å= 0.1 nm). From unpublished work by Jursic, French and Johnson.
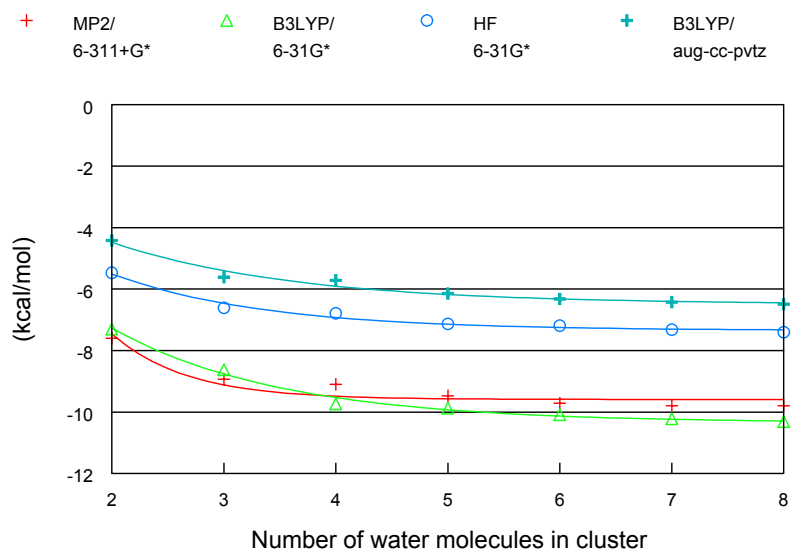

Figure 5. Quantum mechanics energy of stabilization for each additional water in cluster.